

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1936.

General, Physical, and Inorganic Chemistry.

Width of stellar hydrogen lines. P. ROSSIER (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 85—86).—Widths are approx. const. and independent of the brightness of the star and of its temp. over 7000—14,000°. N. M. B.

Spectroscopic determination of [atomic] mass of deuterium from the Balmer series. A. HAGENBACH and H. GÄRTNER (Helv. phys. Acta, 1935, 8, 314—315; Chem. Zentr., 1935, ii, 3885).—The Balmer lines excited in the vapour of 58% heavy H₂O have satellites of shorter λ which are due to D. From their Rydberg const., $M_D/M_H=1.996$. J. S. A.

Extension of the absorption spectrum of the hydrogen molecule. J. J. HOPFIELD (Physical Rev., 1935, [ii], 47, 788—789).—Discrete absorption lines have been observed as far as 738 Å. in H₂ at low pressures. L. S. T.

Stark effect with the helium line λ 4686. B. KULLENBERG (Z. Physik, 1936, 102, 423—427).—The Stark effect for the He line λ 4686 Å. has been investigated for fields up to 40 kv. per cm. A. J. M.

Spectra of helium by high-frequency excitation. M. PETERSEN and H. CARL (Physical Rev., 1935, [ii], 47, 803).—Conditions of enhancement of certain singlet lines have been ascertained. L. S. T.

Spreading in the first positive bands of nitrogen. E. T. S. APPELYARD (Proc. Physical Soc., 1936, 48, 763—771).—An experiment is described to distinguish between the theories of Maxwell (cf. A., 1932, 1185) and of Skinner (cf. A., 1933, 893) for the secondary excitation responsible for the production of spreading. The resonance radiation of N emitted from an electron beam is passed through a thin celluloid window which holds back metastable atoms; results show that part, or possibly the whole, of the secondary excitation of the first positive bands is due to collisions of the second kind with mols. in the $\alpha^1\Pi$ state, supporting Skinner's theory. N. M. B.

Energy of metastable nitrogen molecules. H. HAMADA (Sci. Rep. Tôhoku, 1936, 25, 217—226).—From the intensity distribution in bands attributed to the metastable $A^3\Sigma N_2$ mol., the energy of metallic spectra excited by this mol., and the intensity distribution in bands in the afterglow of active N, it is deduced that the concn. of mols. in low vibrational states among the metastable mols. is small. It is suggested that the high concn. of mols. in states $v''=7-8$ can be deduced from the Franck-Condon principle. O. D. S.

Origin of the afterglow in active nitrogen. G. CARIO and U. STILLE (Z. Physik, 1936, 102, 317—330).—An apparatus for photography of the band systems of the N afterglow under various conditions of pressure and discharge is described. Effects of wall activation and pressure are discussed with reference to the Cario-Kaplan theory. L. G. G.

Nuclear magnetic moment of ²³Na. L. A. WILLS and G. BREIT (Physical Rev., 1935, [ii], 47, 704—705).—A discussion. L. S. T.

Magnetic moment of the ²³Na nucleus. W. E. SHOUPP, J. H. BARTLETT, jun., and C. G. DUNN (Physical Rev., 1935, [ii], 47, 705—706).—A discussion. This moment is probably about 2.5—3.1 nuclear magnetons. L. S. T.

Alkali-metal films transparent in the Schumann region. W. H. WATSON and D. G. HURST (Canad. J. Res., 1936, 14, A, 153—157; cf. this vol., 1039).—Na films on fluorite are transparent to $\lambda < 2100$ Å., but show some absorption in the range 1400—1250 Å. K films show weak absorption from 1700 Å., the intensity of absorption increasing with decreasing λ . No evidence of transparency with Li films has been obtained. J. W. S.

Alternating intensities in the spectrum of P₂. F. A. JENKINS (Physical Rev., 1935, [ii], 47, 783). L. S. T.

Spectra of phosphorus, P II, P III, P IV. H. A. ROBINSON (Physical Rev., 1935, [ii], 47, 799; cf. this vol., 397). L. S. T.

Deep terms in ions of the isoelectronic sequence Cl I to Mn IX. S. G. WEISSBERG and P. G. KRUGER (Physical Rev., 1935, [ii], 47, 798).—Vals. of deep terms and ionisation potentials are tabulated. L. S. T.

Molecular spectra of the sulphur group. B. ROSEN and F. BOUFFIQUX (Bull. Acad. roy. Belg., 1936, [v], 22, 885—893).—The broad emission bands of Te₂ vapour reported by Désirant (cf. this vol., 1040) were photographed and analysed to longer λ ; they resolve into narrow bands degraded towards the red. Intensity fluctuations are discussed. The new infra-red band system of S₂ (cf. *ibid.*, 537) photographed at high dispersion showed that certain of the narrow bands are groups of lines of S I. An analysis of 7 bands of S₂ is given. New measurements of the complex bands in the red part of the principal system of S₂ are reported (cf. *ibid.*, 127). N. M. B.

Lifetimes of potassium doublets λ 4047—4 and λ 3447—6. D. SINCLAIR and H. W. WEBB (Physical Rev., 1936, [ii], 50, 440—445).—The life-

times were measured by the a.c. excitation method; a special NaH vac. photo-cell was used to measure the radiation from a K cell containing a hot cathode and two anodes. The K v.p. range was 4×10^{-5} — 10^{-2} mm. The respective lifetimes, accurate to 1%, were 3.79×10^{-7} and 8.50×10^{-7} sec. Radiation emitted after electron excitation followed a simple exponential law. No change of lifetime was found for the whole pressure range; this could be accounted for by assuming that only 10% of each of the $\lambda\lambda$ groups is re-emitted at the same λ .
N. M. B.

Term analysis of the first spectrum of vanadium (V I). W. F. MEGGERS and H. N. RUSSELL (J. Res. Nat. Bur. Stand., 1936, 17, 125—192).—Complete tables of the lines and terms of the V I spectrum are given, and the electronic configurations responsible for the observed terms have been identified in nearly all cases. The ionisation potential of neutral V atoms is calc. to be 6.71 volts.
O. J. W.

Connexion between the deep terms of the elements of the iron series. M. A. CATALÁN and M. T. ANTUNES (Z. Physik, 1936, 102, 432—460).—The expression for the energy of spectral terms based on the Slater method is discussed, and the energy of terms of certain configurations is calc. Empirical relationships between observed term vals. are discussed.
A. J. M.

Connexion between the Rydberg numbers of the deep terms in the iron series. M. A. CATALÁN and F. POGGIO (Z. Physik, 1936, 102, 461—479).—The observed abs. term vals. and Rydberg nos. for the $3d^m4s$ and $3d^m4s^2$ configurations are compared with those calc. from Catalán and Antunes' formula (see above), and a no. of empirical rules are derived.
A. J. M.

Absorption processes in the halogen spectra. R. S. MULLIKEN (J. Chem. Physics, 1936, 4, 620—621).—The interpretation of the absorption continuum of Br₂ preferred by Acton *et al.* (this vol., 1167) may apply to that of Cl₂, but is inapplicable to that of I₂. The transition ${}^1\Pi \leftarrow {}^1\Sigma^+$ is not so weak in the halogens as hitherto supposed.
J. G. A. G.

Third spectrum of krypton. C. J. HUMPHREYS (Physical Rev., 1935, [ii], 47, 799—800).—The spectrum characteristic of the Kr⁺⁺ ion has been selected from the various Kr spectra excited in a Geissler tube discharge. 369 lines extending from 2100 to 7400 Å. have been classified as arising from 88 levels of Kr III.
L. S. T.

Hyperfine structure of Y II lines. P. G. KRUGER and C. N. CHALLACOMBE (Physical Rev., 1935, [ii], 47, 509).—Data are tabulated. A nuclear moment of $\frac{1}{2}$ is indicated for Y.
L. S. T.

Quenching of cadmium resonance radiation (3261) by hydrogen. H. C. LIPSON and A. C. G. MITCHELL (Physical Rev., 1935, [ii], 47, 638).
L. S. T.

Ultra-violet I₂ fluorescence. D. T. WARREN (Physical Rev., 1935, [ii], 47, 642).
L. S. T.

Intensity distribution in the line emission spectrum of caesium. F. L. MOHLER (J. Res. Nat. Bur. Stand., 1936, 17, 45—54).—The intensity dis-

tribution in the *S*, *D*, and *F* series of the Cs emission spectrum has been measured. For the *D* series intensity measurements have also been made for a columnar discharge, and for the 5466 and 5503 Å. lines the intensity variation with current and pressure is described.
D. J. W.

Paschen-Back effect in the hyperfine structure of the caesium resonance line λ 8522 Å. H. KOPFERMANN and H. KRÜGER (Z. Physik, 1936, 102, 527—533).—The Paschen-Back effect was investigated in the case of 16 field-parallel components of the Cs I line, λ 8522 Å. ($6^2S_{1/2} - 6^2P_{3/2}$) using a magnetic field of 9700 Gauss. The nuclear moment of Cs is 7/2.
A. J. M.

Wave-length measurements in the spectra of the neodymium arc and the standard Pfund iron arc. G. R. HARRISON and W. W. BARTLETT (Physical Rev., 1935, [ii], 47, 799).
L. S. T.

Near infra-red spectrum of mercury. I. O. MASAKI, K. KOBAYAKAWA, and T. MORITA (J. Sci. Hiroshima Univ., 1936, 6, 291—297).—The spectrum was photographed with supersensitised plates, and full data and classifications are tabulated.
N. M. B.

Line absorption of mercury vapour for individual hyperfine structure components of the 2537 Å. line. K. ZUBER (Helv. phys. Acta, 1935, 8, 370—380; Chem. Zentr., 1935, ii, 3890).—Assuming that the mean life of the 2^3P_1 level is the same for all isotopes, the results accord with the fine structure scheme of Schüler and Keyston.
J. S. A.

Stepwise fluorescence in mercury vapour: the 3650 line. L. A. TURNER (Physical Rev., 1935, [ii], 47, 807).
L. S. T.

Isotope effect of ionised mercury hydrides (HgH⁺/HgD⁺). S. MROZOWSKI (Z. Physik, 1936, 102, 545—547).—The results of Hori *et al.* (this vol., 1168) are not sufficiently accurate to warrant the conclusion that there are deviations from the usual isotope formula in the case of the ionised Hg hydrides.
A. J. M.

Zeeman effect of the lead line $6p^2 \ ^3P_2 - 6p.7s \ ^3P_1$ (λ 4058 Å.). S. SATÔ (Sci. Rep. Tôhoku, 1936, 25, 207—216).
O. D. S.

Deep terms in the spectra of Pb v and Bi vi. G. K. SCHOEPFLE (Physical Rev., 1936, [ii], 50, 538—542; cf. A., 1935, 424; Mack, *ibid.*, 1292).—Full data for $\lambda\lambda$, classifications, energy levels, and transitions are tabulated for 69 terms involving 205 lines of Pb v, and 40 terms involving 94 lines of Bi vi.
N. M. B.

Paschen-Back effect. ${}^2S^2P$ multiplets in strong fields. P. JACQUINOT (Physical Rev., 1936, [ii], 50, 573).—The resolution of the *s* components reported by Green (cf. this vol., 653) had been previously effected (cf. A., 1935, 423).
N. M. B.

Distribution of the energy in the extreme ultra-violet of the solar spectrum. W. W. COBLENTZ and R. STAIR (J. Res. Nat. Bur. Stand., 1936, 17, 1—6).—The distribution of energy in the extreme ultra-violet of the solar spectrum within and outside the earth's atm. has been calc. It seems

incorrect to assume that the radiation is similar to that of a black body at 6000° abs. Apparatus is described for measuring the spectral quality and total intensity of ultra-violet solar radiation by means of a photo-electric cell and filter radiometer transported aloft in sounding balloons. O. J. W.

Ultra-violet absorption spectrum of Nova Herculis 1934. H. E. GREEN (Month. Notices Roy. Astron. Soc., 1935, 95, 694—704).—Lines of Fe II, Ti II, Cr II, V II, and Mn II were identified.

CH. ABS. (e)

Arcs in inert gases. III. G. E. DOAN and W. C. SCHULTE (Physical Rev., 1935, [ii], 47, 783—784).—The non-arcng phenomenon reported (A., 1934, 935) for low-current arcs also obtains in high-current welding arcs. In A of $\approx 99.0\%$ purity, crater formation and penetration do not occur. L. S. T.

Processes at the cathode of arc discharges. O. BECKEN and K. SOMMERMEYER (Z. Physik, 1936, 102, 551—561).—Two types of discharge at C and W cathodes are described, which are regarded as due to thermal and auto-electronic emission respectively. O. D. S.

Condensed discharge. Z. BAY (Z. Physik, 1936, 102, 507—526).—Short-lived collisions of high intensity were produced in H₂, N₂, Ne, and Ne-Hg mixture by the condensed discharge, and the electrical and spectral properties of the discharge were investigated. Very high c.d. were obtained, and the resulting spectra showed corresponding variations with c.d. A. J. M.

Gas reactions in silent discharge at atmospheric pressure. I. New type of screened point discharge with transition of strong current form of discharge to a weaker. P. A. THIESSEN and H. BARTEL (Z. tech. Physik, 1935, 16, 285—293; Chem. Zentr., 1935, ii, 3891).—The discharge characteristics are described. J. S. A.

Photographic effective wave-length. P. ROSSIER (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 83—85).—Differences between visual and micro-photometric measurements of the distances of diffraction spectra from the central image and resulting differences of $\lambda\lambda$ are examined mathematically. N. M. B.

Precision X-ray wave-length measurements. L. G. PARRATT (Physical Rev., 1935, [ii], 47, 882—883).—A discussion. L. S. T.

Energies of X-ray photoelectrons. L. W. ALVAREZ (Physical Rev., 1935, [ii], 47, 636).—New vals. of these energies favour the crystal rather than the grating scale of X-ray λ (cf. this vol., 1040). L. S. T.

Absorption of X-rays in the wave-length range 50 to 200 X. M. T. JONES and T. R. CUYKENDALL (Physical Rev., 1935, [ii], 47, 643).—Absorption coeffs. in this range have been measured for C, Na, Al, K, Ni, Cu, Nb, Mo, Ag, Sn, Ta, and Pb. L. S. T.

Production of X-radiation by very fast electrons. E. McMILLAN (Physical Rev., 1935, [ii], 47, 801).—As indicated by theory, radiation is emitted by paraffin, Al, and Pb when they stop the β -particles

given by active ³²P or by Cl activated by deuteron bombardment. L. S. T.

K β Spectra of chlorine and sulphur. H. TAZAKI (J. Sci. Hiroshima Univ., 1936, 6, 299—305).—Using LiCl, NaCl, and KCl on a Cu, and S and K₂SO₄ on an Al, anticathode, the spectra were photographed with long exposure, revealing many fine spark lines of Cl and new lines of S. Full $\lambda\lambda$ and ν/R and $\sqrt{\nu/R}$ vals. are tabulated, and semi-Moseley diagrams are given and discussed. N. M. B.

Relationships between atomic number and effect of chemical binding on the K $\alpha_{1,2}$ doublet of some of the lighter elements. N. G. JOHNSON (Z. Physik, 1936, 102, 428—431; cf. A., 1935, 908).—The effect of chemical binding on the K $\alpha_{1,2}$ lines of ¹²Mg and ¹³Al has been investigated. With the compounds used there is a displacement of the lines, compared with the positions of those of the free elements, towards shorter $\lambda\lambda$, the effect being a max. in the case of the fluorides Na₃AlF₆ and MgF₂. The displacements for the oxides of elements of at. no. 12—16 (Mg—S) when plotted against at. no. lie on a smooth, almost rectilinear curve. A similar curve is obtained for fluorides. A. J. M.

New lines in the K series spectrum of tungsten. J. C. HUDSON, H. G. VOGT, and A. H. ARMSTRONG (Physical Rev., 1935, [ii], 47, 809). L. S. T.

Widths of certain L-absorption edges. A. E. SANDSTRÖM (Phil. Mag., 1936, [vii], 22, 497—513).—The effect of thickness of absorbing screen, time of exposure, and the broadening effect of the spectrograph on the width of the L-absorption edges of some elements has been examined. The full widths of the L_{II} and L_{III} and some L_I edges of elements between Zn and Te were measured, together with their asymmetry. The latter was, in most cases, very pronounced. Curves are given showing the variation of the width of the edge with at. no. The L_{II} and L_{III} curves have the same shape, but the few points obtained for L_I edges seem to require a different curvature. A. J. M.

L Spectra of radium (88). H. HULUBEI (Compt. rend., 1936, 203, 542—543; cf. this vol., 399).—Emission and absorption lines of the L spectra of Ra have been determined and the electron levels tabulated. R. S.

K Spectra and conductivity electrons of solid and liquid aluminium. J. FARINEAU (Compt. rend., 1936, 203, 540—541).—The α bands and the short-wave limits of the β bands of solid and liquid Al are the same, but the structure of the β_2 bands is different in liquid Al. It is suggested that the M electrons are only loosely bound and subject to perturbations connected with the lattice structure. R. S.

Calculation of the X-ray energy level widths of Au (79). E. RAMBERG and F. K. RICHTMYER (Physical Rev., 1935, [ii], 47, 644; cf. A., 1935, 138). L. S. T.

Form and breadth of Compton lines. H. KAPPELER (Helv. phys. Acta, 1935, 8, 314; Chem. Zentr., 1935, ii, 3361).—Data are given for N, Ne,

Li, C, and NaF. The form of the Compton line is dependent on the nature of the scattering particle.

J. S. A.

Auger effect for Au (79) and the origin of certain L-satellites in X-ray spectra. E. RAMBERG and F. K. RICHTMYER (Physical Rev., 1935, [ii], 47, 805).

L. S. T.

Radiative Auger effect. F. BLOCH and P. A. ROSS (Physical Rev., 1935, [ii], 47, 884—885).

L. S. T.

Photo-electric properties of zinc. C. F. DE VOE (Physical Rev., 1936, [ii], 50, 481—485).—The work function of a vac.-distilled Zn surface, corresponding with the long-wave limits 2900—2930 Å., was 4.24 volts at 1.5×10^{-8} mm. pressure, and decreased, with rise of air pressure, to a min. at about 10^{-6} mm. and then increased. He and N₂ had no effect to pressures of 3 mm. and 10^{-3} mm., respectively.

N. M. B.

Free path of conductivity electrons. A. PAPAETROU (Z. Physik, 1936, 102, 539—544).—The Bloch method of calculating electrical conductivity from the interaction between electrons and heat waves is simplified by avoiding the use of an integral equation.

A. J. M.

Passage of fast electrons through matter. H. J. BHABHA and W. HEITLER (Nature, 1936, 138, 401).—The probability for production of secondary electrons when a fast primary electron passes through varying thicknesses of matter has been calc. A primary electron of 2×10^9 e.v. passing through a thickness equiv. to 1.6 cm. of Pb produces, on the average, 2 positive and 2 negative electrons with energies $> 2 \times 10^7$ e.v.

L. S. T.

Properties of an electron which rolls without slipping and of radius varying inversely as the velocity. T. V. IONESCU (Compt. rend., 1936, 203, 537—539).—The properties of free and orbital electrons can be accounted for.

R. S.

Positive and neutral rays. IV. Effective cross-sections for neutralisation. A. ROSTAGNI (Nuovo Cim., 1935, [ii], 12, 134—153; Chem. Zentr., 1935, ii, 3362).—For the neutralisation of A⁺, Ne⁺, and He⁺ in A, Ne, and He, respectively, the effective cross-section rises with decreasing velocity of the ions to a max. between 20 and 30 volts, and then decreases for low velocities.

J. S. A.

Absorption and diffusion of positive rays in gases. A. ROSTAGNI (Atti R. Accad. Sci. Torino, 1935, I, 70, 472—486; Chem. Zentr., 1935, ii, 3362).—Data are given for A⁺, Ne⁺, and He⁺ in A, Ne, and He, respectively.

J. S. A.

Potential for light excitation in mercury by collisions with Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺. O. HENLE and W. MAURER (Physikal. Z., 1936, 37, 659—661; cf. this vol., 1167).—The potentials required for the appearance of lines due to alkali metals in the light caused by collision of the ions with Hg have been determined. The potentials at which the various lines appear are: Hg < 500, Li⁺ and Na⁺ \gg 9000, K⁺ > 9000, Rb⁺ < 9000, Cs⁺ about 1400 volts.

A. J. M.

Filament sources of positive ions. J. P. BLEWETT and E. J. JONES (Physical Rev., 1936, [ii], 50, 464—468).—Efficient filament sources of alkali-metal ions were obtained by heating synthetic alkali Al silicates. Studies of emission of the Li sources as a function of composition show that β -eucryptite, Li₂O, Al₂O₃, 2SiO₂, is the most satisfactory. Ions of Mg, Ca, Sr, Ba, Al, Ga, In, Ti, V, Mn, Y, and Ce are emitted when the oxide of the respective metal is raised to white heat on a W filament. Mass-spectrograph analyses of ion beams were made; for Al, negative ions of mass 27, probably Al⁻, were observed.

N. M. B.

Approximate numerical values of the atomic field and radial wave functions of the silver ion. (MISS) M. M. BLACK (Mem. Manchester Phil. Soc., 1934—1935, 79, 29—33).—Calculations of the approx. at. field and wave functions of Ag⁺ have been computed by the method of self-consistent field.

R. S. B.

Products of ionisation in methane. J. A. HIPPLE, jun., and W. BLEAKNEY (Physical Rev., 1935, [ii], 47, 802).—The ions CH₄⁺, CH₃⁺, CH₂⁺, CH⁺, C⁺, H₂⁺, and H⁺ have been observed by the usual mass-spectrograph method. Excepting H₂⁺, which may be an impurity, these ions are primary products. The appearance potentials are 13.7, 14.7, 15.7, 23, 27, —, and 31 volts, respectively. No negative or doubly-charged ions were observed. CD₄ and CHD₃ show characteristics similar to CH₄.

L. S. T.

Separation of isotopes by centrifuging. J. W. BEAMS and F. B. HAYNES (Physical Rev., 1936, [ii], 50, 491—492).—The possibility of adapting a new air-driven centrifuge, giving "velocity separation" as well as centrifugal separation, is investigated by experiments on N₂-CO₂ mixtures, relative to rotor speed and design. A change in *d* of fractions of CCl₄ was observed.

N. M. B.

Production of helium of mass three? H. D. SMYTH, G. P. HARNWELL, W. BLEAKNEY, and W. W. LOZIER (Physical Rev., 1935, [ii], 47, 800—801).—A discussion of doubts concerning the interpretation of previous results (this vol., 301).

L. S. T.

Oxygen isotopes. W. BLEAKNEY and J. A. HIPPLE, jun. (Physical Rev., 1935, [ii], 47, 800).—Mass-spectrographic analyses of > 100 samples of O₂ from various sources give vals. of ¹⁶O : ¹⁸O around 500. Commercial O₂ varies in isotopic concn. from tank to tank, suggesting that refinements of some at. wt. determinations are meaningless without a simultaneous isotopic analysis. Fractionation of the O isotopes produced by electrolysis of H₂O is approx. 1.01.

L. S. T.

Chemical differences between nitrogen isotopes. H. C. UREY and A. H. W. ATEN, jun. (Physical Rev., 1936, [ii], 50, 575; cf. Ogawa, this vol., 1079).—Preliminary results of attempted separations by fractionation and exchange reaction methods are reported.

N. M. B.

Mass-spectrograph analysis of beryllium. W. BLEAKNEY, J. P. BLEWETT, R. SHERR, and R. SMOLUCHOWSKI (Physical Rev., 1936, [ii], 50, 545—546).—A new ion source for positive-ray analysis was developed

in the form of a mol. beam from a hot oven; ions were produced in the beam by electron impact and focussed on the slit of the mass spectrograph by electric fields. Application to Be revealed only ^9Be . The upper limit for ^8Be was 1 part in 10,000.

N. M. B.

Mass-spectrograph study of Ba, Sr, In, Ga, Li, and Na. M. B. SAMPSON and W. BLEAKNEY (Physical Rev., 1935, [ii], 50, 456—460).—Using a 180° -type mass-spectrograph of 22 cm. radius with 1400 gauss magnetic field, an analysis was made of the ions from coated filaments. Peaks for Sr at 84, comprising 0.5% of the total Sr current, and for Ba at 134, comprising 1.8% of the total Ba current, are interpreted as new Sr and Ba isotopes. A third isotope of In was not found. Relative abundances of ^{69}Ga and ^{71}Ga were 38.8% and 61.2%, respectively. ^5Li and ^{22}Na , reported by Brewer (cf. this vol., 918), were not confirmed.

N. M. B.

Variations of the at. wts. of terrestrial elements. V. I. VERNADSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 129—133).—A review and discussion of the isotopic compositions of elements.

A. J. E. W.

Ranges of particles emitted by samarium. L. LEWIN (Nature, 1936, 138, 326).—In addition to α -particles of 1.150 cm. range, ionising particles of 0.13 cm. range contributing approx. 35% of the total ionisation due to α -particles are emitted by Sm.

L. S. T.

Emission of protons by samarium. J. A. BEARDEN and W. R. KANNE (Physical Rev., 1935, [ii], 47, 639).—Two groups of α -particles (cf. this vol., 130) differing in range by 2 mm., but no proton emission (cf. A., 1934, 713), have now been detected.

L. S. T.

Diffusion of radioactive atoms. J. A. GRAY and J. F. HINDS (Physical Rev., 1935, [ii], 47, 813).—The relative rates of deposit of Ra-*D*, -*E*, and -*F* on plates placed above a source of Ra-(*D*+*E*+*F*) from Rn have been compared with the equilibrium vals. These atoms diffuse through thin metal foils, the Ra-*E* more easily than -*D* and -*F*.

L. S. T.

Excitation curves for fluorine and lithium. L. R. HAFSTAD, N. P. HEYDENBURG, and M. A. TUVE (Physical Rev., 1936, [ii], 50, 504—514; cf. A., 1935, 1296, 1297).—Results are given of observations of increased accuracy, using a corona-free, 10,000-megohm voltmeter-resistor for voltage measurements, on the α -particles from Li and the γ -rays from Li and F, when bombarded with protons of energies up to 1000 kv. A weak multiplet structure in F is indicated in the region 500—700 kv., with a broad but fairly prominent "resonance" at 650—700 kv.

N. M. B.

α -Activity excited in cerium and caesium by neutrons. E. FÜNFER (Physikal. Z., 1936, 37, 693—694).—Contrary to Döpel (this vol., 659) no marked activity could be excited in Ce (using CeO_2) or in Cs (using CsCl) by bombardment with neutrons.

A. J. M.

High-frequency parallel rod method for the determination of α -ray speeds. T. R. WILKINS,

W. RAYTON, and H. ST. HELENS (Physical Rev., 1935, [ii], 47, 812).

L. S. T.

α -Ray and proton tracks in photographic emulsions. T. R. WILKINS, W. RAYTON, and H. ST. HELENS (Physical Rev., 1935, [ii], 47, 812).— α -Ray and proton tracks showing Rutherford scattering have been observed; an analysis of the tracks observed when collimated α -rays fall on a H_2CrO_4 -sensitised emulsion has been made.

L. S. T.

α -Particle scattering by deuterons and protons. H. MARGENAU and E. POLLARD (Physical Rev., 1935, [ii], 47, 640).—For α -particle collision with protons anomalous scattering is detected at the range of a 1.7 cm. α -particle; for *D* the α -particle range is 1.3—1.6 cm.

L. S. T.

Precise measurement of three radium-*B* β -particle energies. F. T. ROGERS, jun. (Physical Rev., 1936, [ii], 50, 515—523; cf. Scott, A., 1934, 1284).—Vals. of $H\rho$, where *H* is the magnetic field required to produce a radius ρ of curvature of path, measured for the three most intense Ra-*B* β -particle lines by a precise magnetic spectrograph method, are 1406.0, 1671.1, and 1931.5 gauss cm., accurate to 1 part in 3000, and the corresponding energies are 1.512×10^5 , 2.044×10^5 , and 2.610×10^5 e.v.

N. M. B.

Scattering of γ -rays. R. S. SHANKLAND (Physical Rev., 1936, [ii], 50, 571).—Experiments previously described (cf. this vol., 265) are extended with modified apparatus.

N. M. B.

γ -Radioactivity with continuous spectrum. New unitary field theory. E. C. G. STUECKELBERG (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 64—69).—Energy considerations are discussed. A new field theory, analogous to that of Born, uses spinors instead of vectors, and considers the electron, neutrino, proton, and neutron as different quantum states of a single elementary particle.

N. M. B.

Neutron effects in a photographic emulsion. D. W. MUELLER and H. A. BARTON (Physical Rev., 1935, [ii], 47, 796; cf. A., 1935, 1441).—The proton and α -particle tracks produced by the passage of neutrons through photographic emulsions have been investigated.

L. S. T.

Absorption cross-sections of thermal neutrons. C. T. ZAHN, E. L. HARRINGTON, and S. GOUDSMIT (Physical Rev., 1936, [ii], 50, 570).—The back scattering of slow neutrons from a thick layer is measured by immersing a detector foil in a liquid and comparing the activity caused by the neutrons for the bare foil with that when the neutrons have been screened on one side. Hence the absorption cross-sections can be calc. (cf. Bayley, below). Approx. results are obtained with dil. Cd salt solutions.

N. M. B.

Diffusion of slow neutrons. D. S. BAYLEY, B. R. CURTIS, E. R. GAERTNER, and S. GOUDSMIT (Physical Rev., 1936, [ii], 50, 461—463).—The effect of Ag, Cu, C, and Cd on the diffusion in H_2O of slow neutrons, as indicated by the decrease of activity of Rh and Ag foil detectors, was investigated and plotted. The interpretation of data on the back

scattering of neutrons (cf. Mitchell, this vol., 541) is discussed. N. M. B.

Behaviour of slow neutrons at different temperatures. E. AMALDI and E. SEGRÈ (Physical Rev., 1936, [ii], 50, 571).—Measurements of the reflexion coeff. of paraffin for thermal neutrons show that the result is the same at liquid air and at room temp. Hence the mean free path and mean life of the neutrons in paraffin cannot be independent of their velocity, and scattering is not isotropic. N. M. B.

Bragg reflexion of slow neutrons. D. P. MITCHELL and P. N. POWERS (Physical Rev., 1936, [ii], 50, 486—487).—Using large MgO single crystals, data for relative reflexion and scattering indicate that the observed reflexion of slow neutrons is in accord with the Bragg relation between their de Broglie λ and the grating space of the crystals. N. M. B.

Influence of temperature on the "groups" of slow neutrons. A. ARSENJEWA-HEIL, O. HEIL, and C. H. WESTCOTT (Nature, 1936, 138, 462).—The radioactivity induced in Ag at 20°, 77°, and 290° abs. by slow neutrons of different energies, the A, B, and C groups of Amaldi and Fermi, has been determined. All three groups are affected by changes in temp. The assumption that the absorption coeff. of B varies inversely as the velocity of the neutrons is erroneous. L. S. T.

Absorption of neutrons in silver and cadmium. N. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 235—236).—The absorption of neutrons in Ag remains practically unchanged with increased thickness of paraffin whereas in Cd there is a steady increase. The region of intense absorption in Ag begins when the velocity of the neutrons is substantially $>$ in the corresponding region in Cd. W. R. A.

Absorption of thermal neutrons in silver at low temperatures. V. FOMIN, F. G. HOUTERMANS, I. V. KURTSCHATOV, A. I. LEIPUNSKI, L. SCHUBNIKOV, and G. SCHTSHEPKIN (Nature, 1936, 138, 326—327).—Data obtained at 20.4°, 77°, and 290° abs. are discussed in relation to a Maxwellian distribution for the energies of the neutrons. L. S. T.

Nuclear reactions due to neutrons of 2 m.e.v. energy. E. T. BOOTH and C. HURST (Nature, 1936, 138, 367—368).—No appreciable activity was observed when Mn, Cr, Al, Zn, Si, Fe, Ni, Ca, and Mg were bombarded for periods varying from 20 min. to 6 hr. by neutrons of approx. 2 m.e.v. energy obtained by bombarding D₂ with D ions. L. S. T.

Scattering of neutrons by protons. M. A. TUVÉ and L. R. HAFSTAD (Physical Rev., 1936, [ii], 50, 490—491).—Corr. measurements for 600—1200 kv. neutrons from C, with precautions to eliminate the effect of any neutrons of energy $<$ 300 kv., agree with the predictions of Wigner's formula. N. M. B.

Nuclear chemistry and the scattering of protons in collisions with neutrons. D. M. GANS and W. D. HARKINS (Physical Rev., 1935, [ii], 47, 795—796). L. S. T.

Capture and scattering of neutrons. H. A. BETHE (Physical Rev., 1935, [ii], 47, 640).—Theoretical. L. S. T.

Scattering of fast neutrons by heavy nuclei. C. H. FAY (Physical Rev., 1936, [ii], 50, 560—567; cf. Dunning, A., 1935, 1186).—Mathematical. An investigation neglecting polarisation indicates that effects due to this are small. N. M. B.

Neutron absorption of boron and cadmium at low temperatures. V. FOMIN, F. G. HOUTERMANS, A. I. LEIPUNSKI, L. B. RUSINOV, and L. V. SCHUBNIKOV (Nature, 1936, 138, 505).—The effect of temp. on the absorption of neutrons in Fermi's group C by B and Cd using the 2.3 min. Ag activity as detector has been measured. The absorption curve of Cd has a selective character. L. S. T.

Effect of hydrocarbons at low temperatures on slow neutrons. W. F. LIBBY and E. A. LONG (Physical Rev., 1936, [ii], 50, 575—576).—Ag targets were bombarded with slow neutrons passed through paraffin cylinders or through a thickness of *n*-heptane. Ag activities plotted against temp. for the range 25—300° abs., obtained by the gradual warming of liquid H₂, support the assumptions that the neutrons are at the temp. of the hydrocarbon, and that the proton capture and Ag capture cross-sections are \propto 1/(neutron velocity). N. M. B.

Bond effect in the action of protons on neutrons. W. F. LIBBY and E. A. LONG (Physical Rev., 1936, [ii], 50, 577).—The slowing power of protons on slow neutrons was investigated with liquid and solid H₂, paraffin, and AcOH, using Ag targets (cf. preceding abstract). There is a nearly identical Ag activity whether the Dewar flask is filled with low-temp. H₂ or with a solution of the same proton density at room temp. Results indicate that the neutrons are cooled to a mean temp. \sim 150° abs., and the expected increase in Ag activity is nearly offset by the increase in capture by protons. N. M. B.

Resonance energy of cadmium for neutron capture. E. SEGRÈ and C. T. ZAHN (Physical Rev., 1936, [ii], 50, 577—578).—The results of Powers (cf. *ibid.*, 49, 650) and of Rasetti (cf. this vol., 264) are considered in terms of the Breit-Wigner formula for the cross-section involved. An approx. resonance energy of 0.05₂ volt and a half-width of about the same val. are deduced. N. M. B.

Resonance levels for absorption of neutrons. J. ROTBLAT (Nature, 1936, 138, 545).—The ionisation currents due to slow neutrons from Po+Be produced in a B-coated chamber have been measured in absence and presence of absorbers of Cd, Cd+Ag, Au, and I as KI, and the resonance levels of the neutrons calc. L. S. T.

Names of and symbols for the artificially radioactive elements. G. M. PETTY (Science, 1936, 84, 183).—The prefix *radio-* and symbol *ra-* are suggested. L. S. T.

Symbols for the artificially radioactive elements. S. C. LIND (Science, 1936, 84, 228—229).—Rd is suggested as a prefix for the natural radioactive elements and "rd." for the artificial ones. L. S. T.

Analysis of the data on radioactivity induced by neutron bombardment. C. N. WARFIELD (Physical Rev., 1935, [ii], 47, 796—797).—Eight generalisations are put forward. L. S. T.

Correlation of nuclear disintegration processes. M. S. LIVINGSTON and R. D. EVANS (Physical Rev., 1935, [ii], 47, 795; cf. this vol., 919).—The known artificial nuclear transformations and natural radioactive processes are classified under one of 14 generalised type reactions. The 200 or more reactions can be represented diagrammatically. L. S. T.

Radio-helium. T. BJERGE (Nature, 1936, 138, 400).—Bombardment of finely-pptd $\text{Be}(\text{OH})_2$ by neutrons from $\text{Be}+\text{Rn}$ produces a radioactive gas of half-period approx. 1 sec. in the $\text{Be}(\text{OH})_2$ (cf. this vol., 773). The gas is ${}^3\text{He}$ or possibly ${}^4\text{He}$. L. S. T.

β -Ray spectrum of radio-helium. T. BJERGE and K. J. BROSTRÖM (Nature, 1936, 138, 400).—The energy distribution of radio-He (cf. preceding abstract) has been measured. The upper limit of the spectrum is probably 3.7 ± 0.5 m.e.v. Probable reactions are ${}^2\text{Be} + \frac{1}{2}n \rightarrow {}^2\text{He} + {}^4\text{He}$ and ${}^3\text{He} \rightarrow {}^3\text{Li} + e^-$. L. S. T.

Low-voltage disintegration of lithium with lithium. C. A. WHITMER and M. L. POOL (Physical Rev., 1935, [ii], 47, 795).— α -Particles are produced by bombardment of a Li target with multiply-charged Li ions accelerated by a potential of approx. 120 kv. LiOH and LiOD give a larger yield than pure Li, but a Be target gives no results. L. S. T.

(A) Deuteron-induced radioactivities. J. J. LIVINGOOD. **(B) Deuteron-induced radioactivity in tin.** J. J. LIVINGOOD and G. SEABORG (Physical Rev., 1936, [ii], 50, 425—434, 435—439).—(A) Bombardment of elements with 5-m.e.v. deuterons gave the following results: commercial Cu decays with half-life 130 ± 10 days, emitting γ -rays and very slow electrons; Zn emits electrons with half-lives 97 ± 10 , 25 ± 2 , 12 ± 1 , and 1 ± 0.3 hr., the third being probably due to radio- ${}^{64}\text{Cu}$; Sb gives electron activities with half-lives 50 ± 4 days, 68 ± 2 and 24 ± 2 hr.; corresponding results for Ru are 46 ± 3 , 11 ± 2 days, 39 ± 1 and 4 ± 1 hr. Bi yields electrons of 5 days half-life and α -particles increasing in no. to a const. val. after 3 weeks; this is interpreted as the synthesis of Ra-E thus: ${}^{209}\text{Bi} + {}^2\text{H} \rightarrow {}^{210}\text{Bi}$ (i.e., Ra-E) + ${}^1\text{H}$, followed by its decay to Po and thence to Pb.

(B) Sn was bombarded with 5-m.e.v. deuterons and chemically analysed for transmutation into radioactive In, Sn, and Sb isotopes. The In fraction shows strong electron emission of 26 ± 2 hr. half-life and a very weak activity of half-life probably several months. The Sn ppt. emits an intense electron group of half-life 28 ± 2 hr. and a weak activity as for In. Two Sb isotopes are formed with half-lives 13.3 ± 1 hr. and 112 ± 30 days. Short period activities from bombarded Sn are of 12 ± 2 and 45 ± 5 min. half-life. Absorption curves in Al are given and possible transmutations discussed. N. M. B.

Radioactive isotopes of bromine. C. H. JOHNSON and F. T. HAMBLEN (Nature, 1936, 138, 504).—

After exposure to neutrons for 1 week liquid Br gives an activity of approx. 24 hr. half-period. AgBr pptd. from irradiated aq. NH_4Br gives a similar effect. The reactions ${}^{79,81}\text{Br} + \frac{1}{2}n \rightarrow {}^{79,81}\text{Sc} + {}^1\text{H}$ or ${}^{75,78}\text{As} + {}^4\text{He}$ are excluded. This activity is probably due to another radioactive isotope of Br or to an excited Br nucleus, since it has not been possible to separate it from the 18 min. and 4.2 hr. activities observed by Fermi *et al.* Possible reactions are discussed. L. S. T.

Measurement of single corpuscular rays in presence of intense γ -rays. H. POSE (Z. Physik, 1936, 102, 379—407).—A description is given of apparatus used for the investigation of nuclear transformations brought about with α -particles. Results obtained with Al are similar to those of Duncanson and Miller (A., 1934, 1284). A. E. M.

Specific ionisation of cosmic radiation. M. G. E. COSYNS (Nature, 1936, 138, 284).—Sp. ionisations of cosmic rays in H_2 , He, and A are recorded. L. S. T.

Measurements of cosmic ray intensity in a deep [coal] mine. J. BARNÓTHY and M. FORRÓ (Nature, 1936, 138, 325, 399).—Cosmic rays penetrate a layer equiv. to a thickness of 1500 m. of H_2O , corresponding with particles of an energy $> 10^{12}$ e.v. L. S. T.

Search for protons in the primary cosmic-ray beam. C. G. MONTGOMERY, D. D. MONTGOMERY, W. E. RAMSEY, and W. F. G. SWANN (Physical Rev., 1936, [ii], 50, 403—407).—Measurements of ionisation spurts above an assigned size are an indication of the presence of charged particles towards the end of their range. Results indicate an upper limit of the no. of protons as 5% of the total no. of cosmic rays at sea level. N. M. B.

Variation of cosmic ray intensity with sidereal time. B. F. J. SCHONLAND, B. DELATIZKY, and J. P. GASKELL (Nature, 1936, 138, 325). L. S. T.

Longitude effect of cosmic radiation. M. S. VALLARTA (Physical Rev., 1935, [ii], 47, 800; cf. A., 1935, 560). L. S. T.

Structure of cosmic rays. II. B. TRUMPY (Z. Physik, 1936, 102, 691—696).—No confirmation is obtained of the results of Hilgert and Botha (cf. this vol., 658) that by passage of cosmic rays through coal photons are formed which produce showers in Pb. O. D. S.

Angular distribution and number of pairs (C-rays) produced by cosmic ultra-radiation in lead. B. PÜSCHEL (Physikal. Z., 1936, 37, 661—663).—A curve is given showing the angular distribution of C-rays in terms of coincidences per hr. at different angles. The max. occurs at $7-12^\circ$. A. J. M.

Production of cosmic ray showers. A. BRAMLEY (Science, 1936, 84, 206—207).—Theoretical. L. S. T.

Absorption analysis of the Hoffmann collisions. J. BÖGGILD and A. KARKOV (Naturwiss., 1936, 24, 588—589).—An experiment described indicates that the collisions are accompanied by a soft radiation. A. J. M.

Dependence of burst production on atomic number. C. G. MONTGOMERY and D. D. MONTGOMERY (Physical Rev., 1936, [ii], 50, 490; cf. this vol., 133).—Investigation of bursts originating in small thicknesses of Mg, Fe, Sn, and Pb shows that the rate of production of bursts \propto (at. no.)². Results indicate that the nuclei remain intact under the impact of cosmic rays, and that the building-up process involved in burst formation is not one of pair production. N. M. B.

Production and absorption of cosmic-ray showers [in lead]. R. H. WOODWARD and J. C. STREET (Physical Rev., 1935, [ii], 47, 800). L. S. T.

Absence of cosmic rays from Nova Lacertæ. J. BARNÓTHY and M. FORRÓ (Nature, 1936, 138, 544—545). L. S. T.

Interaction of the neutron and proton. Y. NISHINA, S. TOMONAGA, and H. TAMAKI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 61—69).—Mathematical. Experimental results are explained on the basis of simultaneous Heisenberg exchange forces and Majorana forces. N. M. B.

Energy states of valency electrons in some metals. I. (2) Absolute values of some X-ray levels of zinc. M. SATO (Sci. Rep. Tôhoku, 1936, 25, 197—201).—Theoretical. Energy levels calc. for Zn are: *K* term 711·880 Ryd., valency electrons E_1 0·960, E_2 0·840, E_3 0·600, E_4 0·581, E_5 0·545, and E_6 0·021 crystal Ryd. units. O. D. S.

Coulomb energy of ³He. S. S. SHARE (Physical Rev., 1936, [ii], 50, 488—489).—Mathematical. The difference in binding energies of ³H and ³He is approx. equal to the calc. Coulomb, energy, supporting the view that, except for the Coulomb repulsion between protons, the neutron-neutron and proton-proton attractions are equal. N. M. B.

Electric quadruple moment of the nucleus ¹²³I. (A) T. SCHMIDT. (B) S. TOLANSKY (Nature, 1936, 138, 404—405, 405).—(A) The I nucleus has a negative electric quadruple moment $< -0·5 \times 10^{-24}$, the negative sign indicating that the charge distribution is flattened in the direction of the spin axis.

(B) The moment suggested can only be considered tentative. L. S. T.

Nuclear states and moments. D. R. INGLIS (Physical Rev., 1935, [ii], 47, 813; cf. A., 1935, 278).—A discussion. L. S. T.

Relation between hyperfine structure and atomic nuclei. H. SCHÜLER and H. KORSCHING (Z. Physik, 1936, 102, 373—378).—Certain rules for the building up of at. nuclei are formulated from a consideration of hyperfine structure data. The relative abundance of isotopes of all elements for which the data are available conforms to these rules. H. C. G.

Dependence of nuclear forces on spin. C. F. VON WEINSÄCKER (Z. Physik, 1936, 102, 572—602).—Mathematical. The dependence of nuclear forces on the spin orientation of protons and neutrons is investigated. O. D. S.

Magnetic moment of the proton. H. HÖNL (Naturwiss., 1936, 24, 637—638).—Theoretical. It is shown that the magnetic moment of the proton is about 3 nuclear magnetons (1 nuclear magneton = 1 Bohr magneton/1840). A. J. M.

Gyromagnetic properties of the hydrogens. J. M. B. KELLOGG, I. I. RABI, and J. R. ZACHARIAS (Physical Rev., 1936, [ii], 50, 472—481).—The nuclear moments of the proton and deuteron were measured by the method of at. beams, independently of at. velocity distribution, and the signs of the moments by the method of non-adiabatic transitions in a weak magnetic field. Results are: μ_H 2·85 ± 0·15; μ_D 0·85 ± 0·03 nuclear magnetons; signs of both moments are positive. N. M. B.

Conservation of energy in radiation processes. E. J. WILLIAMS and E. PICKUP (Nature, 1936, 138, 461—462).—Further experiments on the production of photo-electrons in A by X-rays confirm the light-quantum theory and the applicability of conservation principles to X-radiation processes (cf. this vol., 660). L. S. T.

Energy levels of light nuclei. G. BECK (Physical Rev., 1935, [ii], 47, 809—810).—Theoretical. L. S. T.

Nature of energy states in solids. F. H. SPEDDING (Physical Rev., 1936, [ii], 50, 574).—In view of discrepancies arising from the application of the theory for the behaviour of energy levels of an atom subjected to the electric fields of other atoms in a cryst. solid, as developed by Penny (cf. A., 1932, 985) and Frank (cf. this vol., 19), results of a spectroscopic study of the energy levels of Nd, Sm, Er, and Dy are reported. Energy level separations as found from absorption spectra are compared with those predicted by theory. N. M. B.

Interaction of heavy nuclear particles. D. IVANENKO and A. SOKOLOV (Nature, 1936, 138, 246).—Theoretical. L. S. T.

Correlation between electromagnetic theory and wave mechanics. L. T. DEVORE (Physical Rev., 1935, [ii], 47, 638). L. S. T.

Approximate determination of the atomic wave functions of chromium. A. PORTER (Mem. Manchester Phil. Soc., 1934—1935, 79, 75—81).—Calculations for Cr and Cr⁺ have been made using the differential analyser. R. S. B.

Validity of X-ray crystal methods of determining *e*. J. W. M. DUMOND and V. L. BOLLMAN (Physical Rev., 1936, [ii], 50, 524—537).—Measurements with extremely finely powdered calcite give conclusive evidence in favour of the X-ray crystal method. The val. of *e* is 4·799 ± 0·007. Several new unexplained crystal diffraction effects are described. N. M. B.

Application of the Franck-Condon principle to continuous absorption spectra of diatomic molecules. H. TRIVEDI (Proc. Acad. Sci. U.P., 1935, 4, 59—70).—Theoretical. CH. ABS. (e)

Determination of the atmospheric transparency coefficients for different spectral rays and the density of atmospheric ozone. N. P.

LUGIN (J. Geophys. U.S.S.R., 1935, 5, 58—76).—Transparency data and vals. for the $[O_3]$ are given.

CH. ABS. (e)

Isotopes and molecular asymmetry. T. IRDALE (Nature, 1936, 138, 292).—It is suggested that asymmetric mols. containing Me and F should be examined for optical resolution.

L. S. T.

Absorption spectrum of hydrogen peroxide vapour. R. S. SHARMA (Proc. Acad. Sci. U.P., 1934, 4, 51—58).—The ultra-violet absorption spectrum of 3, 10, and 30% aq. H_2O_2 terminates abruptly at 2055 Å., corresponding with $H_2O_2 + 136.1$ kg.-cal. = $2H + O_2$. The recombination spectrum corresponds with $H + HOO = H_2O_2 + 59.6$ kg.-cal. CuO in the absorption tube became reddish, showing the presence of at. H.

CH. ABS. (e)

Spectroscopic investigation of chemical reactions of OH in the electric discharge. A. A. FROST and O. OLDENBERG (Physical Rev., 1935, [ii], 47, 788).—OH produced by the electric discharge through H_2O vapour has a lifetime of the order of $\frac{1}{2}$ sec. The chief process by which OH disappears is indicated to be the three-body process $OH + OH + M \rightarrow H_2O_2 + M$.

L. S. T.

Ultra-violet absorption spectra of the deutero-ammonias. W. S. BENEDICT (Physical Rev., 1935, [ii], 47, 641).—Spectrograms of NH_3 containing varying amounts of D have been obtained over a wide range of temp. and pressure. Vibrational analyses have been made for NH_3 , NH_2D , NHD_2 , and ND_3 .

L. S. T.

$^{15}S-^{15}S$ Band system of copper deuteride. M. A. JEPPESEN (Physical Rev., 1936, [ii], 50, 445—449).—Full data and analysis of the system photographed at high dispersion are tabulated and const. are evaluated. The electronic isotope displacement of CuD relative to CuH is 19 cm.^{-1}

N. M. B.

Pressure effect on the C band of strontium hydride. R. F. HUMPHREYS and W. R. FREDRICKSON (Physical Rev., 1936, [ii], 50, 542—545; cf. A., 1935, 1443).—At low H_2 pressures the emission spectrum of the 3808 Å. band of SrH shows a sharp break-off at $R(18)$, but at high pressures the lines extend to $R(49)$. Perturbations due to resonance and predissociation are present. Frequency assignments are tabulated, and electronic configurations and probable dissociation energies are discussed.

N. M. B.

Band spectrum of silicon fluoride. R. M. BADGER and C. M. BLAIR, jun. (Physical Rev., 1935, [ii], 47, 881).—A re-examination of the violet spectrum obtained in the Si fluoride discharge reveals two systems with considerable overlapping. Previous conclusions (A., 1927, 1005) are invalidated. The emitter is probably SiF.

L. S. T.

Absorption spectra of the vapours of sulphur monochloride and thionyl chloride and their constitutions. H. TRIVEDI (Proc. Acad. Sci. U.P., 1935, 4, 263—268).—The ultra-violet absorption spectra of both S_2Cl_2 and $SOCl_2$ show two bands at 2740, 2135 and 2980, 2040 Å., respectively. The differences in energy between the beginnings of the

bands correspond with that between the $3P$ and $1D$ states of S (for S_2Cl_2) and of O (for $SOCl_2$). The structures are $S:S:Cl_2$ and $O:S:Cl_2$.

CH. ABS. (e)

Band system of TiCl. A. E. PARKER and A. H. PARKER (Physical Rev., 1935, [ii], 47, 812).—The four-headed band system extending from 4340 to 3730 Å. has been analysed.

L. S. T.

Band spectrum of arsenic oxide and lead oxide. E. N. SHAWHAN and F. MORGAN (Physical Rev., 1935, [ii], 47, 199; cf. A., 1935, 562).—The band spectrum of AsO has been investigated in emission and in absorption. Two systems of double double-headed bands have been analysed.

L. S. T.

Far ultra-violet absorption spectra and ionisation potentials of the alkyl halides. I. [Methyl halides.] II. [Ethyl and higher halides.] W. C. PRICE (J. Chem. Physics, 1936, 4, 539—547, 547—551).—I. The absorption spectra of MeI, MeBr, and MeCl have been photographed in the region 2000—1000 Å. The bands are due to excitation of non-binding electrons in the halogen atoms, and the ionisation potentials deduced from the Rydberg series are: MeI 9.49 and 10.11 volts, MeBr 10.49 and 10.80, and MeCl 11.17 and 11.25, in general accord with theory (cf. A., 1935, 562). The vibrational nature of the bands is discussed and the three spectra are correlated.

II. The Rydberg series found in the range 2000—1000 Å. lead to the ionisation potentials EtI 9.30 and 9.88, and EtBr 10.24 and 10.56 volts. Other halides gave very diffuse bands, and continuous absorption from C-C and C-H linkings interfered. The ionisation potentials of consecutive members of the homologous series probably diminish asymptotically to a limiting val.

J. G. A. G.

Mutual optical effect of neighbouring colour carriers in a molecule. H. FROMHERZ, W. AUMÜLLER, and C. O. STROTHER (Z. Elektrochem., 1936, 42, 680).—For dihalogenated paraffins with at least one CH_2 between the halogen (Br or I) atoms, the light absorption is const. and equal to the sum of the absorptions of the individual groups. When the halogen atoms are nearer, and especially when they are the same, the absorption band shifts towards longer λ . This effect is increased when the H near the halogens is replaced by alkyl.

J. W. S.

Light absorption and tautomerism of uric acid. H. FROMHERZ and A. HARTMANN (Z. Elektrochem., 1936, 42, 687).—The absorption spectrum of uric acid has been measured in pure H_2O and in presence of excess of $HClO_4$ and of NaOH, comparison being made with the absorption spectra of substituted uric acids of definite keto- and enol forms. The results indicate that in H_2O or acid, uric acid is in the keto-form, but addition of a little NaOH shifts the absorption bands towards longer λ , corresponding with the enol form. This is a halochromatic effect due to dissociation of a H atom, and is compared with the change in absorption between dissociated and undissociated CO_2H groups.

J. W. S.

Influence of substituents on the ultra-violet absorption spectra of simple and double-linking

conjugated benzene chromophores. M. PESTEMER, T. LANGER, and F. MANCHEN (Monatsh., 1936, 68, 326—348).—The absorption spectra of BzCl, CHPhCl₂, CPhCl₃, styrene, CPhMe, and PhCHO and of their NH₂-, CN-, and NO₂-substitution products have been studied in the region 25,000—50,000 cm.⁻¹, and compared with those of C₆H₆ and PhMe compounds. The effect of the substituents on both the *A* (38,500—43,400 cm.⁻¹) and *B* (49,000—52,000 cm.⁻¹) bands of the conjugated systems Ph·C:C and Ph·C:O is to shift them towards longer λ , the effects being in the order $p > m > o$. This is the same order as the effect of substituents on the *B* band for PhMe, but the reverse of that for the *A* band. The relative effects of the NH₂- and of the NO₂- and CN-groups are in accord with their respective negative and positive characters. J. W. S.

Absorption spectra of anils of aliphatic ketones. Absorption in the ultra-violet and structure of anils and α -ethylenic amines.—See this vol., 1242.

Optical absorption of the porphyrins. VII. A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1936, 177, 165—192; cf. this vol., 1178).—Introduction of vinyl groups into the dihydroporphin system (I) shifts the absorption max. towards the red and at times intensifies them, but does not alter the type of the absorption curve. γ -Substitution with weak chromophoric groups has little effect. Introduction of a CO at 3 causes the curve to change to the "rhodin" type, band I of the spectrum being depressed and shifted towards the blue. Oximation raises band I and shifts it towards the red. CO at 6 does not give rise to the rhodin type of curve. It is inferred that nucleus III differs in structure from nuclei I and II, and has no double linking at 5:6, and that in this nucleus are located the optically active centres of the system (cf. A., 1935, 1383). Chlorin *p*₆ and pseudochlorin *p*₆ have different absorption curves and are in some way stereoisomeric. The purpurins and rhodins seem to have the (I) framework. Mg in (I) only displaces the fluorescence bands towards the red. R. C.

Ultra-violet absorption spectra of thyroxine, thyronine, tyrosine, di-iodotyrosine, and thyroglobulin.—See this vol., 1249.

Gossypol. R. GRÜNBAUMÓWNA and L. MARCHLEWSKI (Biochem. Z., 1936, 286, 295—296).—An absorption curve of gossypol acetate showing max. at 3780 and 2390 Å. and a min. at 3220 Å. is given. P. W. C.

Nuclear vibration bands of solid carbon dioxide. W. DAHLKE (Z. Physik, 1936, 102, 360—372).—Apparatus for determining the absorption of thin layers of solid CO₂ at about 100° abs., throughout the spectrum from the visible to 17 μ , is described. Three absorption bands are obtained similar to the rotation-vibration bands found in the gas. The possibility of mol. rotation in solid CO₂ is discussed. A. E. M.

2.73 μ Absorption band in fused silica. D. G. DRUMMOND (Nature, 1936, 138, 248—249).—The view that this band is due to CO₂ contamination is favoured (cf. this vol., 921). L. S. T.

Diffuse infra-red transmission of solids. J. D. HARDY and C. MUSCHENHEIM (Physical Rev., 1935, [ii], 47, 789). L. S. T.

Fundamental absorption bands of the deutero-ammonias. M. V. MIGOTTE and E. F. BARKER (Physical Rev., 1936, [ii], 50, 418—424; cf. *ibid.*, 1935, [ii], 47, 892).—The four fundamental vibration bands of ND₃ were observed in infra-red absorption, ν_3 being double as in NH₃; the parallel frequencies are: $\nu_1 = 2420$, $\nu_3 = 749.2$ and 745.8 , the perpendicular are: $\nu_2 = 2556$, $\nu_4 = 1191.3$ cm.⁻¹ The rotational structure of ν_3 is completely resolved. The moments of inertia of ND₃ are: $C = 8.985 \times 10^{-40}$ with respect to the symmetry axis, and $A = 5.397 \times 10^{-40}$ g. cm.² for any perpendicular axis. The height of the mol. pyramid is 0.360×10^{-8} , and distance between D atoms 1.645×10^{-8} cm. The potential curve is discussed. N. M. B.

Vibrational levels of cyclopropane. G. W. KING, R. T. ARMSTRONG, and L. HARRIS (J. Amer. Chem. Soc., 1936, 58, 1580—1584).—The infra-red absorption and Raman spectra have been determined, and the results are discussed. E. S. H.

Absorption spectrum of heavy methane (MeD) in the photographic infra-red. W. H. J. CHILDS and H. A. JAHN (Nature, 1936, 138, 285).—The absorption spectrum of MeD from 12,000 to 6000 Å. shows none of the lines of CH₄. A region of intense absorption extends from 8350 to 9000 cm.⁻¹ with a strong, broad max. at 8617 cm.⁻¹ Similarities with the spectrum of CH₄ are pointed out. L. S. T.

Infra-red absorption spectra of acetic acid and acetic anhydride. E. K. PLYLER and E. S. BARR (Physical Rev., 1935, [ii], 47, 793; cf. this vol., 34). L. S. T.

Raman effect. LX. Polarisation measurements. 1. Experimental method. A. W. REITZ (Z. physikal. Chem., 1936, B, 33, 368—386).—The sources of error in polarisation measurements are discussed, and suitable apparatus and the experimental technique described. R. C.

Raman spectra and the latent heat of fusion of non-associated substances. C. J. PHILLIPS (Physical Rev., 1935, [ii], 47, 792).—When applied to 38 org. and inorg. substances in the cryst. and liquid states, the relation $\lambda = mNh_c/JML_f$, when m is 1, 2, . . . and L_f is the latent heat of fusion, gives λ which agree closely with the observed infra-red absorption bands. The relation apparently holds only for non-associated substances. In glass the SiO₂ group may vibrate independently to a certain extent. L. S. T.

Raman spectrum of thiophosphoryl chloride. V. N. THATTE (Nature, 1936, 138, 468—469).—Prominent shifts in the Raman spectra of POCl₃ and PSCl₃ are compared. The slight reduction in the vals. for the latter is attributed to substitution of O by S. L. S. T.

Raman effect in solutions of magnesium sulphate of varying concentrations. E. M. COON and E. R. LAIRD (Physical Rev., 1935, [ii], 47, 889).—Any change in frequency due to concn. (N to $4.5N$) is $\lambda > 1$ or 2 wave nos. L. S. T.

Raman effect and molecular structure. L. SIMONS (Finska Kem. Medd., 1936, 45, 77—97).—A review, with special reference to C_6H_6 .

M. H. M. A.

Raman spectrum of deuterioethanol. S. MIZUSHIMA, Y. MORINO, and G. OKAMOTO (Bull. Chem. Soc. Japan, 1936, 11, 553).—Raman lines closely corresponding with those of EtOH have been observed. The band 3370 ± 80 cm^{-1} , attributed to the OH linking, is displaced to 2510 ± 50 cm^{-1} in EtOD.

R. S.

Raman effect of heterocyclic compounds of the dioxan type. L. MÉDARD (J. Chim. phys., 1936, 33, 626—630; cf. A., 1934, 1289).—The Raman spectra of dioxan (I), dichlorodioxan, thioxan (II), dithian (III), and morpholine have been determined. The vibration frequency of CH_2 is determined by linking to O or S since the CH_2 line 1415 of (III) and the corresponding lines 1445—1460 of (I) appear at 1415—1452 in (II). Lines attributable to the cyclic structure are absent, in agreement with the aliphatic properties of the compounds.

R. S.

Modification of the Raman spectrum of dioxan by dissolved materials. A. SIMON and F. FEHÉR (Z. Elektrochem., 1936, 42, 688—691).—Polar solutes modify the Raman spectrum of dioxan, the CO-frequencies being diminished and the CH-frequencies raised. The changes are due to electrostatic effects and not to formation of mol. compounds. The shape of the solute mol. and the type and location of its dipole have a greater influence than the magnitude of the dipole moment or the deformability of the mol. The results are discussed with reference to Raman frequencies in complicated mols. and in binary mixtures.

J. W. S.

Raman spectra and the structure of benzene. G. DUPONT and R. DULOU, with (in part) V. DESREUX (Bull. Soc. chim., 1936, [v], 3, 1639—1661).—The principal Raman frequencies and their relative intensities are tabulated for *cyclo*-hexane and -hexene, C_6H_6 , PhMe, PhEt, PhPr, *o*-, *m*-, and *p*-xylene, *m*-, *p*-, and *o*-cymene, *ψ*-cumene, mesitylene, thiophen, *allooimene*, PhOH, NH_2Ph , *p*- C_6H_4EtOMe , *p*- C_6H_4PrOMe , eugenol, *isoeugenol*, dihydroeugenol, saffrole, *isosaffrole*, and dihydrosaffrole. It is concluded that in C_6H_6 a form predominates which may be represented by a formula of hexagonal symmetry, e.g., the Stark-Pauli formula, and is responsible for the aromatic properties, but a second form, corresponding with Kekulé's formula, is also present in small quantities.

J. W. S.

Raman spectrum of heavy benzene C_6D_6 . R. W. WOOD (Physical Rev., 1935, [ii], 48, 488; cf. A., 1935, 1189).

L. S. T.

Raman spectra and vibrations of di- and tetra-deuterobenzene. O. REDLICH and W. STRICKS (Monatsh., 1936, 68, 374—382; cf. this vol., 663, 922).—The Raman spectra of *o*- and *m*- $C_6H_4D_2$ and of a mixture of the $C_6H_2D_4$ isomerides have been determined. The frequencies calc. from the valency energy model of C_6H_6 differ considerably from the observed frequencies, but a generalised model is developed which is in satisfactory accord for C_6H_6 ,

p- $C_6H_4D_2$, 1:2:4:5- $C_6H_2D_4$, and C_6D_6 . The Ca salt of polycarboxylic acids of C_6H_6 when heated with $Ca(OH)_2$ yields only a mixture of isomerides.

J. W. S.

Raman spectrum of hydroxyquinol trimethyl ether. S. FRIED and B. SUSZ (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 124—126; cf. Kohlrausch, A., 1935, 146).—Raman data for 1:2:4- $C_6H_3(OMe)_3$ are reported.

N. M. B.

Raman spectra of *cis*- and *trans*-isoeugenol. E. PERROTET and B. SUSZ (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 120—124; cf. this vol., 923).—Raman frequencies for the pure commercial substance (80% *trans*, 20% *cis*) and for the two isomerides are tabulated. *iso*Eugenol contains all the frequencies of these two forms with the exception of 1629 cm^{-1} . The vals. for *trans* show an approx. const. difference from those for *cis*, the former being the higher.

N. M. B.

Raman effect. LVIII. Raman spectra of organic substances. Nitrogen compounds. I. Simple amines. K. W. F. KOHLRAUSCH. LIX. Raman spectra of organic substances. Nitrogen compounds. II. Amino- and hydroxy-acetic acids and esters. L. KAHOVEC and K. W. F. KOHLRAUSCH (Monatsh., 1936, 68, 349—358, 359—373).—LVIII. The Raman spectra of NH_2Me , NH_2Et , NH_2Pr^a , $NHMe_2$, and NMe_3 have been determined and compared with those of Me_2O , Me_2S , and $MeOEt$.

LIX. The Raman spectra of $NH_2 \cdot CH_2 \cdot CO_2H$ and its Me, Et, Pr^b , and Bu^a esters, $(NH_2)_2CH \cdot CO_2H$ and its Me and Et esters, $OH \cdot CH_2 \cdot CO_2H$ and its Me, Et, Pr^b , and Bu^a esters, $NH_2 \cdot CH(OH) \cdot CO_2H$ and its Me and Et esters, $EtCO_2H$ and its Pr^b and Bu^a esters, $CH_2Cl \cdot CO_2H$, and $CH_2Br \cdot CO_2H$ have been determined in the solid state and/or in aq. solution.

J. W. S.

Raman spectrum of piperidine. S. M. MITRA (Z. Physik, 1936, 102, 697—699).—A new line at $\Delta\nu=1451$ is observed in this spectrum.

O. D. S.

Excitation of Raman spectra of substances with the aid of "optical catalysers." K. PROSAD and D. K. BHATTACHARYA (Nature, 1936, 138, 510—511).—The method used for glass (this vol., 270) has been extended to H_2O , MeOH, EtOH, $COMe_2$, C_5H_5N , and aq. HNO_3 , traces of $KMnO_4$ being added to produce absorption bands in these media. The importance of the new technique for the study of Raman spectra is discussed.

L. S. T.

Raman spectra of gallic acid, of its derivatives, and of tannin. B. SUSZ and S. FRIED (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 69—74; cf. A., 1935, 1446).—Raman data are recorded and discussed for pyrogallol, gallic acid, Me gallate, Me trimethylgallate, triacetyl gallic acid, and tannin.

N. M. B.

Induced ultra-violet fluorescence and its release by visible light. O. GLASSER and I. E. BEASLEY (Physical Rev., 1935, [ii], 47, 570).—The ultra-violet fluorescence of certain substances following exposure to X- or γ -radiation is found to persist for unexpectedly long periods of time. It is markedly increased when the irradiated compounds are exposed to visible light. Of the 25 substances examined, NaCl, KCl, rock-salt, and fluorite crystals showed

these effects most clearly. Impurities inhibit the subsequent induction of the fluorescence. L. S. T.

Scintillations of zinc sulphides in α -rays. G. DESTRIAU (J. Chim. phys., 1936, 33, 587—625; cf. A., 1931, 1108).—ZnS screens free from Canada balsam have been prepared from a suspension of ZnS in EtOH. Using a Po source, it has been shown that the no. of scintillations—distance curve varies with the specimen of ZnS. For a given specimen, the curvature is the sharper the smaller is the ZnS crystal and the richer the crystal in phosphorogen. Whilst the concn. of phosphorogen runs parallel to the [Cu], there is no direct proportionality, and only a part of the Cu appears to be active. Theoretical curves in agreement with the experimental results have been derived and the influence of crystal size, concn. of phosphorogen, and the no. of centres excited by an α -particle have been investigated. The view that scintillations involving only one active centre are visible is discussed in relation to data on the min. of visual perception. The mean duration of the scintillations, determined microscopically by a rotating-disc method, increases with the concn. of active phosphorogen and is a max. in crystals of approx. 27 μ , but there is no relation between the sensitivity to α -rays and phosphorescent power of ZnS. The effect of infra-red light, and the relation between the sensitivity to α -rays, X-rays, and triboluminescence, are discussed. Only one specimen of ZnS showed luminescence in the electric field. R. S.

Fluorescence of the salts of trivalent europium in aqueous solutions. J. LARIONOV and A. SEIDEL (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 115—118).—Fluorescence spectrum data are given. Three narrow bands in the red occur only with solutions containing SO_4^{2-} , and are ascribed to Eu^{+++} . One narrow band and two broad bands in the blue-ultra-violet region are of general occurrence: the latter coincide with bands observed in solutions of Ce and Y earth salts. A. J. E. W.

Effect of visible light on the ultra-violet fluorescence of various compounds previously irradiated with Röntgen or γ -rays. O. GLASSER and I. E. BEASLEY (Physical Rev., 1935, [ii], 47, 789).—The ultra-violet fluorescence of NaCl, KCl, NaBr, rock-salt, and fluorite crystals following exposure to X- or γ -radiation is markedly increased by exposure to visible light. With NaCl the emitted radiation has a max. near 2450 Å. L. S. T.

Luminescence of calcite. I. Fluorescence spectrum of Japanese calcite in ultra-violet light. E. IWASE and T. KURONUMA. II. Thermoluminescence. III. Alteration of the fluorescence spectrum by previous heating. E. IWASE (Bull. Chem. Soc. Japan, 1936, 11, 513—522, 523—528, 528—538).—I. All specimens did not fluoresce but band max. were observed at 625—635, 460—470, 515—520, and 560—570 m μ . Calcites from mineral veins gave a reddish-orange fluorescence, whilst stalactitic calcites gave a whitish fluorescence.

II. A no. of thermoluminescence bands have been determined, but no relation between thermoluminescence and fluorescence could be obtained.

III. The fluorescence of white-fluorescing calcites is affected by previous heating, whilst that of the orange-red type is not. Bands in the Arakawa calcite can be attributed to the presence of rare-earth metals. R. S.

Fluorescence of chlorophyll in its relation to photochemical processes in plants and organic solutions. J. FRANCK and R. W. WOOD (J. Chem. Physics, 1936, 4, 551—560; cf. A., 1935, 681).—Chlorophyll, illuminated in org. solutions, behaves as though excited chlorophyll, HChph^* , which is free from adsorbed mols., has a small probability of fluorescing and a greater probability of pre-dissociating into a H and monodehydrochlorophyll. The products of dissociation react with any O_2 present unless O_2 -acceptors, RH, are also present which take up the excitation energy by collision of the second kind or by intramol. energy exchange within a complex HChphRH (I) and protect HChph (II) against oxidation, whilst the RH is oxidised after initial formation of H and R or HChphR (III). The change of intensity of the fluorescence with period of illumination in presence of O_2 and certain acceptors is interpreted in terms of the inferred properties of the complexes (III) and (I). The fluorescence of (III) is $>$ that of (I). Determinations of the similar variations in the intensity of fluorescence with time of illumination of living leaves in presence of O_2 (cf. A., 1935, 1038) are consistent with photosynthesis and photo-oxidation of org. substances adsorbed to (II) taking place in the plant, but (II) is not itself photo-oxidised. The "light saturation" of photosynthesis *in vivo* may arise from photo-oxidation. The time of half life of (III) is approx. 0.02 sec. J. G. A. G.

Emission of aromatic compounds containing the carbonyl group. N. PRIKLESHAeva (Acta Physicochim. U.R.S.S., 1935, 3, 195—201).—In the fluorescence of PhCHO and C₆H₅COCH₃ vapours the excitation is primarily localised in the C₆H₅ ring, whereas the subsequent emission is localised in the CO group. O. J. W.

Biologically active radiation. III. Supposed photographic detection of earth rays according to Dobler. B. ROMEIS, J. WÜST, and J. WIMMER (Strahlenther., 1935, 54, 114; Chem. Zentr., 1935, ii, 3745).—No satisfactory evidence of the photographic action of "earth rays," or of their being electromagnetic radiation of about 1 mm. λ , has been brought forward by Dobler. J. S. A.

Photo-electric threshold of uranium, calcium, and thorium treated with limited amounts of oxygen. H. C. RENTSCHLER and D. E. HENRY (Physical Rev., 1935, [ii], 47, 807).—A shift in the photo-electric threshold towards the longer λ occurs when surfaces of Th, U, or Ca react with a small amount of O_2 . L. S. T.

Photo-electric primary current in an alternating field in potassium bromide crystals containing colour centres. A. NAUMANN (Ann. Physik, [v], 27, 233—242).—The photo-electric conductivity of crystals of KBr containing electrically formed colour centres has been measured for alternating

currents of frequency between 10^2 and 10^5 sec.⁻¹ Ohm's law is obeyed. The conductivity increases with frequency to a saturation val. The ratio conductivity/light absorbed is of the same order of magnitude for the saturation conductivity and for the static conductivity determined at much lower light intensity. It is deduced that the mobility of the photochemically produced electrons is not reduced by the block structure of the crystal. O. D. S.

Analysis of photo-electric data. R. J. CASHMAN and N. C. JAMISON (Physical Rev., 1936, [ii], 50, 568—569; cf. Fowler, A., 1931, 1106).—The comparative results of plotting photo-electric current per quantum of light absorbed or per unit intensity of incident radiation are examined. N. M. B.

Correlation of secondary electron emission with photo-sensitivity and the thermionic effect. A. DOBROJUBSKI (Z. Physik, 1936, 102, 626—628).—Photocell layers Cs—Cs₂O—Ag, Ag₂O—Ag, and Cs—Ag₂O—Ag were considered. O. D. S.

Nature of the barrier plane in the cuprous oxide photovoltaic cell. J. W. BALLARD and E. D. WILSON (Physical Rev., 1935, [ii], 47, 794).

L. S. T.

Colouring and luminescence of crystals under the influence of Becquerel rays. K. PRZIBRAM (Z. Physik, 1936, 102, 331—352).—A general review of modern work on the colour and luminescence of crystals produced naturally or artificially by pressure or by radioactive emission. Attention is given to the fluorites, alkali halides, and bivalent rare earths.

H. C. G.

Electrical observations during the formation and re-formation of colour centres in potassium bromide and chloride crystals. G. GLASER (Ann. Physik, 1936, [v], 27, 217—232).—Measurements have been made of the spectral distribution of the photo-electric current in sensitised crystals of KBr and KCl during the photochemical formation of colour centres. No correlation was found between this and the absorption spectrum associated with the *U*-centres. It was correlated with the absorption spectrum of the "*X*-centres," which underlies that of the *U*-centres, and is similar in form to that of the pure crystal. It is deduced that the photo-electric current is a secondary effect due to the illumination of *X*-centres, which probably result from foreign mols. in the crystal. O. D. S.

Ionisation of liquids by X-rays. L. S. TAYLOR and F. L. MOHLER (Physical Rev., 1935, [ii], 47, 805).—An extension of previous work (A., 1935, 148) to CS₂, ligroin, tetrahydronaphthalene, and their mixtures. L. S. T.

Structure of electrolytic oxide films. H. BETZ (Z. Physik, 1936, 102, 548).—The breakdown potential of Ta₂O₅ films determined by Rummel (this vol., 923) is < the val. obtained by Just (A., 1933, 555). A. J. M.

Structure of electrolytic oxide films. T. RUMMEL (Z. Physik, 1936, 102, 549).—A reply to Betz (preceding abstract). A. J. M.

Measurement of low conductivities and dipole losses with long waves. C. SCHRECK (Ann. Physik, 1935, [v], 27, 261—284).—A method is described by which conductivities of the order of 10^{-13} ohm⁻¹ cm.⁻¹ and dipole losses in liquids can be measured at λ from 170 to 18,000 m. The dielectric const. is determined simultaneously. Data are given of the dipole losses in this region of PrOH, BuOH, and amyl alcohol, glycerol, and aq. solutions of sucrose and fructose. The dielectric const. of mixtures of EtOH and C₆H₆ is determined and the mol. polarisation of EtOH calc. O. D. S.

Electric properties of crystals. I, II. (SIR) W. BRAGG (Proc. Roy. Inst., 1936, 29, 225—230, 290—295).—Lectures.

Reactivity in solid state at ordinary temperature. II. A. SERRA (Period. Min., 1935, 6, 179—183; Chem. Zentr., 1935, ii, 3743; cf. A., 1935, 716).—The electrical conductivity of Cu, Fe, Ag, Ni, and Pb wires was increased by contact with finely powdered realgar, Sb glance, Cu glance, haverite, marcasite, and pyrolusite. Sb glance in contact with Ag foil produces a stain of Ag₂S. J. S. A.

Influence of electric moment on the number of molecules of base fixed by a salt.—See this vol., 1241.

Theory of dielectric polarisation. J. G. KIRKWOOD (J. Chem. Physics, 1936, 4, 592—601).—A mol. treatment of the polarisation of a non-polar dielectric in a homogeneous field shows that small but significant deviations from the Clausius-Mosotti formula are to be expected. The magnitudes of the corrections are discussed. J. G. A. G.

Dielectric constant for pure liquid and solid substances. I. K. HØJENDAHL (Kem. Maanedst. nord. Handelsbl. kem. Ind., 1935, 16, 53—55; Chem. Zentr., 1935, ii, 3748).—Vals. are recorded for C₂H₂Cl₄. J. S. A.

Peculiarities of dielectric constant versus pressure curves for vapours. J. D. STRANATHAN (Physical Rev., 1935, [ii], 47, 794).—For H₂O vapour deviation of the $(\epsilon-1)/(\epsilon+2)$ -pressure curve from linearity is due not to conductivity but to adsorption on the insulator surfaces and the consequent increase in polarisation contributed by these additional mols.

L. S. T.

Polar properties of 1:4- and 1:2-dihydronaphthalene. Polar character of the tetralin molecule. M. PUCHALIK (Acta phys. polon., 1934, 3, 179—185; Chem. Zentr., 1935, ii, 3370).—The dipole moment of 1:4- and of 1:2-dihydronaphthalene is 1.4×10^{-18} e.s.u. The polar asymmetry of the tetralin mol. is thus to be attributed mainly to a change in the C₆H₄ nucleus. H. N. R.

Liquid propane. Electrical conductance and dielectric constant. G. GLOCKLER and R. E. PECK (J. Chem. Physics, 1936, 4, 624).—The conductivity is $< 5 \times 10^{-13}$ ohm⁻¹ at 1 kilocycle between -90° and 15°. The dielectric const. at 0° is 1.61 and the temp. coeff. -0.00124. J. G. A. G.

Molecular rotation in solid aliphatic alcohols. C. P. SMYTH and S. A. MCNEIGHT (J. Amer. Chem.

Soc., 1936, 58, 1597—1600).—The dielectric consts. of solid MeOH, BuⁿOH, and *n*-octyl alcohol (I) have been determined from liquid-air temp. to the m.p. There is evidence of dipole rotation in MeOH between 159.9° abs. and the m.p. Absence of dipole rotation in BuⁿOH and (I) and the absence of transitions in many other alcohols show that OH does not rotate inside the mol., but the whole MeOH mol. rotates above the transition point (159.9° abs.).

E. S. H.

Non-rotation of molecules in a number of solids. S. A. McNEIGHT and C. P. SMYTH (J. Amer. Chem. Soc., 1936, 58, 1718—1722).—The dielectric consts. of solid NH₂Me, Et₂O, COMe₂, COPh₂, and succinic acid have been determined over a wide range of temp. and frequency. Mol. rotation cannot be postulated.

E. S. H.

Molecular rotation of solid arsine and other hydrides. C. P. SMYTH and S. A. McNEIGHT (J. Amer. Chem. Soc., 1936, 58, 1723—1728).—Dielectric consts. and sp. conductances of solid HCN and H₂Se have been determined from liquid-air temp. to the m.p., and those of AsH₃ from liquid-H₂ temp. to the b.p. over the frequency range 0.5—50 kilocycles. Solid HCN shows no mol. rotation; H₂Se mols. rotate freely even at liquid-air temp.; AsH₃ rotates freely down to 32.1° abs., where a transition, accompanied by anomalous dispersion, occurs. The mols. rotate the more readily the smaller are their dipole moments.

E. S. H.

Indication of a decrease in the polarisability of a non-polar molecule by pressure. A. MICHELIS, C. MICHELIS-VERAAT, and A. BIJL (Nature, 1936, 138, 509—510).—Graphs showing the relation between the Clausius-Mosotti function *P*, which ∝ the polarisability of the mol., and *d*, the pressure, and the change in kinetic energy of the internal motion of the mols., Δ*K*, are reproduced from calculations based on recent isotherm data for CO₂. The decrease of *P* with an increase in pressure and in Δ*K* is practically linear.

L. S. T.

[Refractometry.] W. GEEFCKEN (Z. physikal. Chem., 1936, B, 33, 405).—Errors in previous papers (A., 1929, 1233; 1931, 905) are corr.

R. C.

Refractive indices of ordinary and heavy ammonia. O. E. FRIVOLD, O. HASSEL, and S. RUSTAD (Nature, 1936, 138, 330).—*n* for ND₃, determined for various λλ between 4358 and 6562.9 × 10⁻⁸ cm., is slightly < *n* for NH₃.

L. S. T.

Refractometric studies in normal methyl ketones.—See this vol., 1363.

Optical properties of non-polar liquids. H. MUELLER (Physical Rev., 1936, [ii], 50, 547—559).—Mathematical. A theory of refraction, Kerr effect, and light scattering is developed from considerations of the quasi-cryst. grouping of neighbouring mols., the anisotropy of the Lorentz forces, and potential barriers of various heights. Results are applied to C₆H₆. Hindered rotation and cybotactic grouping suffice to explain deviations from classical theory.

N. M. B.

Kerr constants of the hydrogen halide gases. C. H. D. CLARK and E. C. HUMPHRIES (Nature,

1936, 138, 248).—Calc. vals., which appear to support the theory previously advanced (this vol., 1051), are given.

L. S. T.

Kerr effect with nitrotoluene. F. GABLER and P. SOKOB (Naturwiss., 1936, 24, 570).—The effect of temp. on the Kerr const., *B*, of *o*- and *m*-C₆H₄Me·NO₂, at λ 5461 Å. has been determined, and is expressed by empirical equations.

A. J. M.

Polarisation of light and some technical applications. A. F. C. POLLARD (Nature, 1936, 138, 311—314).

L. S. T.

Magnetic rotation of lanthanum and neodymium chlorides in aqueous solution. C. M. MASON, R. D. GRAY, and G. L. ERNST (J. Amer. Chem. Soc., 1936, 58, 1600—1604).—Data are recorded for λλ 5893 and 5460.8 Å. at 10—50° and compared with corresponding data for Al. The Verdet consts. of the solutions have been calc.; those for NdCl₃ vary linearly with 1/*T*. Mol. rotations of aq. NdCl₃ vary with temp. according to (*T*—32.6)*D* = —790.1.

E. S. H.

Calculation of the polarisation ellipsoid of a molecule. T. NEUGEBAUER (Z. Physik, 1936, 102, 305—316).—A method for calculating change in polarisability of an ion due to external influence is described. Anomalies in the calc. polarisabilities parallel and perpendicular to the long axis of a mol. are due to incorrect application of methods for spherically symmetrical ions.

L. G. G.

Structure of benzene. I. Problem and experimental method. W. R. ANGUS, C. R. BAILEY, C. K. INGOLD, and C. L. WILSON. II. Direct introduction of deuterium into benzene and the physical properties of hexadeuterobenzene. C. K. INGOLD, C. G. RAISIN, and C. L. WILSON. (Appendix: Vapour pressure of hexadeuterobenzene. C. R. BAILEY and B. TOPLEY.) III. Raman spectra of liquid benzene and hexadeuterobenzene. W. R. ANGUS, C. K. INGOLD, and A. H. LECKIE. IV. Infra-red absorption spectra of liquid and gaseous benzene and hexadeuterobenzene. C. R. BAILEY, J. B. HALE, C. K. INGOLD, and J. W. THOMPSON. V. Fluorescence spectra of benzene and hexadeuterobenzene vapour. VI. Resonance emission spectrum of benzene and hexadeuterobenzene. C. K. INGOLD and C. L. WILSON. VII. Coincidental frequencies in the infra-red and Raman spectra of benzene and hexadeuterobenzene. VIII. Assignment of vibration frequencies of benzene and hexadeuterobenzene. W. R. ANGUS, C. R. BAILEY, J. B. HALE, C. K. INGOLD, A. H. LECKIE, C. G. RAISIN, J. W. THOMPSON, and C. L. WILSON (J.C.S., 1936, 912—915, 915—925, 925—931, 931—941, 941—954, 955—966, 966—971, 971—987).—I. The difficulty of reconciling the transformations of the aromatic nucleus with its stability is discussed. Although Pauling and Wheland's theory (A., 1934, 15) is successful in bringing the stability of the ring into line with its chemical transformations, it cannot explain certain difficulties, the most important of which is the appearance of identical frequencies in the Raman and infra-red spectra (see VII). Experimental methods for the

investigation are outlined. Since substitution of D for H does not alter nuclear changes, only effects arising from changes in at. masses influence vibration frequencies, and definite numerical relationships between the frequencies of corresponding normal vibrations of two isotopically related mols. are calculable if some mol. model is assumed. Only C_6H_6 and C_6D_6 are discussed; a scheme is given for investigating other D-substituted benzenes.

II. The exchange reaction, $PhH + DO \cdot SO_3D \rightleftharpoons PhD + HO \cdot SO_3D$ is utilised to prepare C_6D_6 containing only 1% of C_6D_5H . Data for m.p., b.p., mol. vol., and mol. refraction for C_6D_6 and for a series of partly deuterated benzenes are given and discussed. V.p. measurements with a differential tensimeter are recorded. A statistical treatment of the v.p. difference of isotopic mols. is developed to explain the higher v.p. of C_6D_6 .

III. Raman spectra of C_6H_6 and C_6D_6 are obtained and compared with previous data. Peak and integrated intensities of the principal lines have been measured photometrically and are correlated by photographing an artificial mixture of 50 mols.-% of C_6H_6 and C_6D_6 . Polarizations of all the principal lines are recorded. The C_6H_6 spectrum has 8 strong lines (fundamentals), 14 weak lines, 16 very weak lines, and 4 satellites of the strong line at 992 cm.^{-1} . For C_6D_6 , 7 strong (fundamental) and 19 weak lines are found.

IV. To make comparison more trustworthy, the same samples of C_6H_6 and C_6D_6 were examined as vapour and as liquid between 1 and 22μ . C_6H_6 vapour has 15 and liquid C_6H_6 24 bands. Previous data are discussed and differences between results are explained, particularly for three bands previously recorded, but not now confirmed, for the vapour; these three bands, however, appear in the liquid C_6H_6 spectrum. C_6D_6 vapour gives 16 bands, liquid C_6D_6 27. Mappings of the complete spectra, contours of strong bands, intensities, and P-R and doublet separations are given and discussed.

V. The ideal case for the production of fluorescence and resonance spectra is outlined and experimental arrangements are detailed. The fluorescence spectra of both vapours are given and microphotometric intensities and series assignments are recorded. The spectra are accounted for by assuming 3 electron levels and 2 vibration frequencies; numerical formulæ are given.

VI. The resonance spectrum of C_6H_6 falls into sections of 989 cm.^{-1} and 9 such sections are discussed; the eight component frequency differences are derived from which the series assignment of band max. is made. The corresponding spectrum of C_6D_6 comprises sections each 944 cm.^{-1} in length and has 7 component frequency differences. Correlation of the C_6H_6 and C_6D_6 bands leads to a satisfactory pairing, 4 pairs being definitely identifiable. The other 3 pairs and a non-paired low frequency are provisionally characterised as fundamentals, inactive both in Raman and infra-red spectra.

VII. If the benzene mol. is a plane, regular hexagon and, therefore, has a centre of symmetry, selection rules forbid the appearance of the same frequencies in both infra-red and Raman spectra. Several coincident frequencies reported previously had led

to the conclusion that the mol. could not be a plane, regular hexagon. A table of 18 suggested coincidences in C_6H_6 and 12 in C_6D_6 is compiled from data in III and IV. By comparing Raman frequencies with infra-red frequencies of liquid C_6H_6 more coincidences are found than with those of the vapour. Cohesive forces in the liquid deform the mol. sufficiently to cause a breakdown in strict selection rules and strong Raman frequencies appear in the liquid infra-red spectra but not in the vapour; strong infra-red frequencies appear faintly in Raman spectra: frequencies, inactive in both, appear fairly strongly in liquid infra-red, feebly in Raman, and are absent from infra-red vapour spectra. All the suggested coincidences are discussed and no evidence for the absence of a centre of symmetry is obtained.

VIII. In the theory of point groups the symbol which represents the symmetry classification of a plane, regular, hexagonal benzene model is D_{6h} ; those for the Kekulé and trigonally puckered models are D_{3h} and D_{3d} , respectively. The symmetry classifications of the vibrations of the three models are developed. Benzene has 20 normal modes of vibration. The D_{6h} model has 4 active in infra-red only, 7 active in Raman spectrum only (two polarised), and 9 forbidden in both spectra. For the D_{3h} model, there should be 8 fundamentals in the infra-red, 14 in Raman spectrum (4 polarised), and 7 common to both; whilst the D_{3d} model requires 8 in infra-red, and 9 in Raman spectra (4 polarised). By Teller's product theorem the products of the frequencies of vibrations of the same symmetry class for two isotopically related mols. are in a ratio which can be expressed as a function of the masses of the atoms and the moments of inertia. The numerical vals. for the ratios are given for the D_{6h} model. Experimental data are analysed and frequencies assigned for this model. Raman spectra give 7 strong lines (2 polarised); infra-red give 4 prominent bands: these are the allowed fundamentals. On applying Teller's product rule to these, very good agreement between calc. and observed ratios is found. The order of magnitude of the nine inactive frequencies is discussed and tentative vals. are given. The selection rules which govern the appearance of overtones and combination tones in these spectra are reviewed and assignments of the majority of the observed frequencies are made. The spectroscopic investigation of benzene, thus far, supports the D_{6h} model; there is no definite indication in favour of the D_{3d} structure. The Kekulé model fails to explain the facts.

W. R. A.

Structure of benzene. IX. Direct observation of the fluorescence spectra of benzene and hexadeuterobenzene vapour in the region of absorption. C. L. WILSON (J.C.S., 1936, 1210—1214; see preceding abstract).—The fluorescence spectra of C_6H_6 and C_6D_6 , excited by the Hg 2537 A. line, have been measured at 0.1—0.3 mm., the resonance spectra being quenched by presence of N_2 (760 mm.). The frequencies and relative intensities of the lines in the region 2577—2667 A. are recorded. The results are in accord with previous data.

J. W. S.

Investigation of the binding properties of benzene by physical methods. R. KREMANN (Naturwiss., 1936, 24, 632—635).—A review of the application of physical methods to the study of the linkings in the C_6H_6 mol. A. J. M.

Structure and properties of mononuclear and polynuclear phenanthroline-ferric complexes. A. GAINES, jun., L. P. HAMMETT, and G. H. WALDEN, jun. (J. Amer. Chem. Soc., 1936, 58, 1668—1674).—The analysis, hydration, conductivity, acid-base properties, magnetic susceptibility, and diffusibility of the brown, cryst. substance prepared by reaction of phenanthroline (I) and $FeCl_3$ are consistent with the view that it is tetraphenanthrolinediol-diferric chloride. Other compounds probably exist in the mother-liquor. The low magnetic susceptibility suggests the partial neutralisation of the magnetic moments of the two Fe, and is evidence of a polynuclear structure. The magnetic susceptibility of the blue triphenanthroline- Fe^{III} complex ion = approx. that of $Fe(CN)_6^{4-}$. Stable (I) complexes, the composition of which has been established in the solid state, may add more (I) in solution, forming secondary complexes of lower stability. E. S. H.

Structure of the chlorine monoxide molecule. R. POHLMAN and H. J. SCHUMACHER (Z. Physik, 1936, 102, 678—683).—An alternative interpretation of the infra-red measurements of absorption of Cl_2O by Bailey and Cassie (cf. A., 1933, 1228). O. D. S.

Valency and molecular structure. R. F. HUNTER and R. SAMUEL (Nature, 1936, 138, 411—413). L. S. T.

Transition of covalency to electrovalency. R. F. HUNTER and R. SAMUEL (Chem. and Ind., 1936, 733—740).—From consideration of potential energy relations in diat. mols. with at. binding, ionic binding, and hydrated ions, it is shown that covalency may pass over into electrovalency when the energy min. of the covalent and electrovalent states are sufficiently close for external forces (lattice energy, energy of solvation, van der Waals forces) to cause an intersection with the at. binding curve. The tendency for transition is dependent on the difference, $J-E$, between the ionisation energy of the cation J , opposing ionisation, and the electron affinity E of the anion, favouring ionisation. For compounds with a const. negative ion (e.g., Cl^-), the transition from covalency to electrovalency, as shown by the m.p., b.p., conductivity and hydrolysis of chlorides, runs strictly parallel to the variation of J . J. S. A.

Energy of formation of "cyclol" molecules. D. M. WRINCH (Nature, 1936, 138, 241—242).—Calculations of the approx. energy of formation of cyclol mols. from polypeptides (cf. this vol., 619) indicate that the linking process is facilitated if the appropriate groups are in the form $\cdot C(OH)N\cdot$, and that certain enzymes operate directly on the substrate by imposing this form on some of its $\cdot CO\cdot NH\cdot$ groups. L. S. T.

Energy of formation of "cyclol" molecules. F. C. FRANK (Nature, 1936, 138, 242; cf. preceding abstract).—Estimation of the energy balance of the

linking process postulated for proteins by Wrinch (this vol., 619) indicates the necessity for assuming the existence of an additional source of energy similar to that provided by the strain in the side-chain cross-linkings found in keratin. Hydration also provides part of the necessary additional energy and helps to explain certain properties of proteins observed in degeneration and denaturation. L. S. T.

Relation of the states of the carbon atom to its valency in methane. H. H. VOGEL (J. Chem. Physics, 1936, 4, 581—591).—Resonance of C^{IV} with other valency configurations raises the stability of CH_4 , to a val. slightly $>$ that calc. from the Pauling-Slater configuration. The relative energies of CH , CH_2 , CH_3 , and CH_4 are 4.0, 8.0, 12.1, and 17.0 volts and thus there is no indication that CH_2 is specially stable. This conclusion is discussed. J. G. A. G.

Orbital valency according to an extended Heitler-London method. G. NORDHEIM (Physical Rev., 1935, [ii], 47, 803—804).—An extension of the Heitler-London theory of chemical linking is developed to take into account not only the ground states but also the lowest excited states of the composing atoms. Directional properties of valency in polyat. mols. are explained. L. S. T.

Intramolecular forces between bound atoms. W. ALTAR (Physical Rev., 1935, [ii], 47, 804; cf. A., 1935, 1192). L. S. T.

Provisional computation of the plane vibration frequencies of symmetrical deuteroethylenes. C. MANNEBACK and A. VERLEYSSEN (Nature, 1936, 138, 367).—Calc. vibration spectra of C_2D_4 and the three isomerides $C_2D_2H_2$ are tabulated. L. S. T.

Relation between the energy saturation and polarity of molecules. V. RASUMOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 21—27; cf. this vol., 925).—The "energy saturation" of mols. \propto the degree and duration of approach of the valency electrons to the individual at. in the mols.; the tendency to ionise is inversely, and to partake in addition reactions directly, \propto the energy saturation. These concepts are applied to some facts in org. chemistry. R. C. M.

Significance of the new quantum theory in chemistry. E. HÜCKEL (Z. Elektrochem., 1936, 42, 657—662).—A general survey. J. W. S.

Elements of the quantum theory. VII. van der Waals forces. VIII. Perturbation theory. IX. Helium atom. X. Hydrogen molecule. XI. Slater-Pauling theory of valency linkings. S. DUSHMAN (J. Chem. Educ., 1935, 12, 581—586; 1936, 13, 32—38, 84—92, 132—140, 179—187, 287—294, 330—333, 333—338, 385—393; cf. this vol., 134). L. S. T.

Vibrational frequencies of molecules. H. G. HOWELL (Nature, 1936, 138, 290; cf. this vol., 1052). L. S. T.

Free energies. T. W. DAVIS (J. Chem. Educ., 1936, 13, 376). L. S. T.

Transfer of rotational energy. F. F. RIEKE (Physical Rev., 1935, [ii], 47, 788). L. S. T.

Phenomena of the exchange of wave energy in collisions of molecules. V. KONDRATEV (Uspechi Fiz. Nauk., 1934, 14, 982—1008).—A review.

CH. ABS. (e)

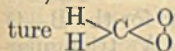
Range of action of surface forces. B. DERJAGUIN (Nature, 1936, 138, 330—331).—Bowden and Bastow's data (A., 1935, 819) do not refute the author's findings that films of $H_2O < 1.5 \times 10^{-5}$ cm. thick have great rigidity.

L. S. T.

Parachor. R. LAUTIE (Bull. Soc. chim., 1936, [v], 3, 1689—1691).—The parachor is shown to follow the formula $[P] = 0.316P_c V_c$, where P_c is expressed in atm. This relation also follows from Aten's formula (A., 1935, 1059). The crit. temp. can be deduced from the parachor.

J. W. S.

Parachor and the structure of formic acid. S. K. RAY (J. Indian Chem. Soc., 1936, 13, 484—485).—Published data are consistent with the structure



E. S. H.

Steady performance of Geiger-Müller counters. B. DASANNACHARYA and G. S. RAO (Nature, 1936, 138, 289).

L. S. T.

Characteristics of Geiger-Müller counters filled with different gases. C. L. HAINES (Physical Rev., 1935, [ii], 47, 791).

L. S. T.

Application of the Geiger point-counter to the measurement of small X-ray intensities. M. PAHL and A. FAESSLER (Z. Physik, 1936, 102, 562—571).—Apparatus for measuring the intensity of X-rays, of high sensitivity below λ 800 X, is described.

O. D. S.

Improved numerical method of two-dimensional Fourier synthesis for crystals. H. LIPSON and C. A. BEEVERS (Proc. Physical Soc., 1936, 48, 772—780).—Mathematical.

N. M. B.

Reduction of space-groups. F. SEITZ (Physical Rev., 1935, [ii], 47, 810).

L. S. T.

Structure-factor graphs for crystal analysis. W. L. BRAGG (Nature, 1936, 138, 362—363).—The use of contoured graphs for determining the configuration of atoms in crystals from X-ray data is explained and illustrated. The analysis of at. positions can thus be expedited.

L. S. T.

Tables for the determination of crystals. A. K. BOLDIREV and V. V. DOLIVO-DOBROVLSKI (Z. Krist., 1936, 93, 321—367).—A summary of a forthcoming set of tables for the identification of crystal specimens from their crystallographic data. For each class of crystals, in the key the crystals are arranged in order of the polar distances of their faces [*i.e.*, angle between (001) and the perpendicular to the face] for all commonly occurring faces; in the sequel they are described fully. The process of identification is thus (1) measurement, (2) determination of the crystal class, (3) determination of the polar distance for each observed form, (4) search for corresponding vals. in the table, (5) confirmation from the details given.

B. W. R.

Classification of crystal structures with defect lattices. L. W. STROCK (Z. Krist., 1936, 93, 285—311).—For "ideal solids" all positions in a theoretical

lattice are occupied by similar particles. If this condition is not fulfilled, there is a "defect lattice," varying in degree from the ideal solid to a state where the lattice of one kind of particle is completely destroyed. A classification is made on this basis of such defect lattices and detailed examples are given; it includes not only those defect lattices which are directly measurable by X-rays, but also the larger micro-lattices.

B. W. R.

Theory of crystal growth. R. KAISCHEV (Z. Physik, 1936, 102, 684—690).—The equation previously developed (cf. A., 1934, 946) can be deduced kinetically.

O. D. S.

Oxide layer on a polished surface. L. H. CALLENDER (Nature, 1936, 138, 291).—Dobinski's results for Cu (this vol., 1055) are confirmed by experiments on polished Al (B., 1927, 724).

L. S. T.

Fourier analyses of X-ray patterns of phosphorus. N. S. GINGRICH and R. HULTGREN (Physical Rev., 1935, [ii], 47, 808; cf. A., 1935, 919).

L. S. T.

Crystal structure of black phosphorus. R. HULTGREN and B. E. WARREN (Physical Rev., 1935, [ii], 47, 808; cf. A., 1935, 919).

L. S. T.

X-Ray determination of residual atomic lattice deformation in pressed duralumin. F. F. KOSOLAPOV and E. F. BACHMETEV (Vestn. Metalloprom., 1934, 14, No. 3, 76—82).—Crystallites with dimensions $> 10^{-1}$ cm. comprise the chief portion of the deformed duralumin. The change in the X-ray diagram is due to lattice distortion, which disappears at 200° (15 min.—1 hr.) or 300° (30 sec.).

CH. ABS. (e)

Change of elastic parameters of single crystals of iron by heating. K. NAKAMURA (Sci. Rep. Tôhoku, 1936, 25, 364—380).—The natural frequency of longitudinal and of torsional vibration of a no. of single crystals of Fe has been measured at intervals from 20° to 560°.

O. D. S.

Intensity of X-rays reflected from zinc. C. ZENER and S. BILINSKY (Physical Rev., 1936, [ii], 50, 489; cf. this vol., 273).—Discrepancies between calc. and experimental vals. of the consts. in the expression for the temp. dependence of the intensity are discussed.

N. M. B.

Anisotropy in the atomic vibrations of zinc crystals. I. Evidence from X-ray scattering. II. Diffuse scattering of X-rays from single crystals. G. E. M. JAUNCEY and W. A. BRUCE. III. (0002) and (1010) reflexions of Mo $K\alpha$ X-rays from powdered zinc. R. D. MILLER and E. S. FOSTER, jun. (Physical Rev., 1936, [ii], 50, 408—412, 413—416, 417—418).—I. A comparison of results of intensity measurements of the various reflexions of Cu $K\alpha$ X-rays from powdered Zn crystals (cf. Brindley, this vol., 3, 15, 538) and measurements on the diffuse scattering of X-rays from single crystals shows that the anisotropy of the thermal vibrations is \gg previously supposed. The root mean square thermal displacements of the atoms are 0.172 and 0.093 Å. along and perpendicular to the *c* axis, respectively. The anisotropy almost explains the anomalous at. structure factor vals. F^2 , as modified

by thermal vibrations, for the (0002) and (10 $\bar{1}$ 0) reflexions, and indicate some asymmetry in the electron structure of the atoms of the Zn crystal.

II. Experiments varying S with ψ , the orientation angle, for a fixed scattering angle ϕ , and varying S with ϕ for two fixed vals. of ψ confirm Zener's formula (cf. this vol., 273) for the Debye-Waller M , in the temp. factor e^{-M} for hexagonal crystals, and the constns. a and b in the expression for M . Results give a higher anisotropy, $a-b=1.66$, than Brindley's val. 0.785.

III. The ratio of the F vals. for the two reflexions is 0.891, using an ionisation method, agreeing with Brindley's val. 0.894 for Cu $K\alpha$ X-rays, using a photographic method. N. M. B.

Asymmetry in metallic zinc and cadmium. H. HERRMANN (Nature, 1936, 138, 290).—Certain discrepancies in the X-ray scattering factors of Zn and Cd (cf. this vol., 412) are ascribed to the asymmetry of the atoms rather than to that in the lattice vibrations. L. S. T.

Asymmetry in metallic zinc and cadmium. G. W. BRINDLEY (Nature, 1936, 138, 290—291).—A reply to Herrmann (cf. preceding abstract). The view that the lattice vibrations are responsible for the asymmetry is maintained. L. S. T.

Eddy arrangement of micro-crystals in metallic wire caused by drawing. T. FUJIWARA and Y. SEIKI (J. Sci. Hiroshima Univ., 1936, 6, 307—312).—Investigations for Al and W wires were made by X-ray radiographs and microscopically. N. M. B.

Soft X-rays and photo-electrons from nickel at different temperatures. S. R. RAO (Current Sci., 1936, 5, 73—74).—The photo-electric efficiencies (E) of Cu and Ni when exposed to soft X-rays (applied potentials 100—150 volts) are independent of temp. in the range 30—500°. E for the 110 face of Ni is 12% < that of polycryst. Ni, this, it is suggested, being associated with the distortion of the crystal surface during bombardment. The soft X-ray emission from well degassed Ni increases with rise of temp., the rate of increase also increasing with rise of temp. No abrupt change was observed at the Curie point. It is concluded that the increase in secondary electron emission observed by Hayakawa (A., 1934, 233) at the Curie point and at potentials above a crit. val. is due to increasing nos. of electrons returning. J. W. S.

Osmiridium. III. O. E. ZVJAGINTZEV and B. K. BRUNOVSKI (Z. Krist., 1936, 93, 229—237).—Rotation and Laue photographs of osmiridium show a type of fibre structure in which the single crystal is divided into blocks set at angles up to $\pm 10^\circ$ from each other. On this basis certain anomalous reflexions in the Laue picture are explained (cf. A., 1935, 440). B. W. R.

Precision measurement of the lattice constant of very pure tantalum. M. C. NEUBURGER (Z. Krist., 1936, 93, 312—313).— $a_0=3.2959\pm 0.0003$ A. at 20°. B. W. R.

Precision measurement of the lattice constant of very pure vanadium. M. C. NEUBURGER (Z.

Krist., 1936, 93, 314—315).— $a_0=3.0338\pm 0.0003$ A. at 25°. B. W. R.

Crystal structure of heat-treated tungsten filaments. R. P. BIEN (Physical Rev., 1935, [ii], 47, 806).—Well-aged filaments showed large crystals, up to 3 cm. in length, extending across the entire diameter of the filament. L. S. T.

α - and β -Ice. N. SELJAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 227).—Orientations of α - and β -ice crystals to the normal to the H₂O surface on which ice formation takes place are given from 0.5° to 10°. W. R. A.

X-Ray analysis of vitreous B₂O₃. B. E. WARREN and O. MORNINGSTAR (Physical Rev., 1935, [ii], 47, 808).—The X-ray scattering curve is that of a typically amorphous pattern showing four peaks. The distribution curve obtained from a Fourier analysis shows peaks at 1.4 and 2.38 A. for the B—O and O—O distances, respectively. A triangular co-ordination with each B linked to 3 O and each O to 2 B is indicated. L. S. T.

Amorphous and crystalline oxide hydrates and oxides. XXVIII. **X-Ray structure and catalytic properties of silver ferrite.** A. KRAUSE, Z. ERNST, S. GAWRYCH, and W. KOCAY (Z. anorg. Chem., 1936, 228, 352—356; cf. this vol., 947, 1080).—The crystal structures of various preps. of AgFeO₂ are similar and show rhombohedral symmetry. The catalytic decomp. of H₂O₂ by AgFeO₂ is relatively slow. J. W. S.

Crystal structure of cuprous ferrite. W. SOLLER and A. J. THOMPSON (Physical Rev., 1935, [ii], 47, 644).—CuFeO₂, rhombic, a 5.96 A., α 29° 26', one mol. per unit cell, space-group D_{3d}^5 , is the only one of several forms of Cu ferrites which is slightly magnetic compared with the cubic form of Cu^{II} ferrite. L. S. T.

Lattice constant of sodium chloride and rock-salt. M. STRAUMANIS and A. IEVIŠ (Z. Physik, 1936, 102, 353—359).—The lattice const. of pure NaCl is $5.6273_7\pm 0.0000_2$ A. at 18°. Three specimens of natural rock-salt from different localities all give the val. $5.6276_8\pm 0.0000_3$ A. at 18°. From measurements between 18° and 67°, the coeff. of expansion is 40.5×10^{-6} . A. E. M.

Crystal structure of germanium disulphide. W. H. ZACHARIASEN (J. Chem. Physics, 1936, 4, 618—619).—GeS₂ crystals are orthorhombic; the unit cell, a 11.66, b 22.34, c 6.86 A., contains 24 mols., and the space-group is Fdd (C_{2h}^{12}). Each Ge is linked tetrahedrally with four S. The angle between two linkings is 103° and the Ge—S distance is 2.19 A. J. G. A. G.

Interatomic distances in orpiment, realgar, sodium sulphoantimonate enneahydrate, and calcium mercuric bromide. W. V. MEDLIN (J. Amer. Chem. Soc., 1936, 58, 1590—1592).—In orpiment and realgar the distance between As and S agrees with the sum of the corresponding covalent radii. In Na₃SbS₄·9H₂O the Sb—S distance is < the sum of the covalent radii. Indefinite results were obtained with CaHgBr₄. E. S. H.

Crystal structure of cupric chloride dihydrate. D. HARKER (*Z. Krist.*, 1936, 93, 136—145).— $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is orthorhombic, a_0 7.38, b_0 8.04, c_0 3.72 Å., space-group $Pbmn$. The structure is found from intensity measurements. The Cu atoms are attached to 2 Cl and 2 O by covalent linkings directed to corners of a square. A similar square formation must occur in $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$. B. W. R.

Crystal structure of ammonium chlorobromiodide. R. C. L. MOONEY (*Physical Rev.*, 1935, [ii], 47, 807—808).—The unit cell, containing 4 mols., has a 6.14, b 8.58, c 10.03 Å.; space-group $Pmcn$ (V_1^{16}). Parameters for NH_4 , Cl, I, and Br are given. The atoms lie in planes perpendicular to the x -axis and separated by a distance $a/2$. The halogen atoms are associated in a strictly linear group with I at the centre. The distance between I and Br atoms in a group agrees with the sum of the at. radii of I and Br as found in I_2 and Br_2 from band spectra. NH_4 is co-ordinated with 4 Cl at a distance of 3.34 Å., 4 Br at one of 3.63 Å., and 2 I at one of 3.79 Å.

L. S. T.

Crystal structure of thallium trithionate, $\text{Tl}_2\text{S}_3\text{O}_6$. J. A. A. KETELAAR and J. K. SANDERS (*J. Chem. Physics*, 1936, 4, 621).— $\text{Tl}_2\text{S}_3\text{O}_6$ crystals are monoclinic and the unit cell, a 13.20, b 7.45, c 7.58 Å., β 91.0°, contains 4 mols. The space-group is C_{2h}^2 ($C2/c$). The crystals are not isomorphous with $\text{K}_2\text{S}_3\text{O}_6$. J. G. A. G.

X-Ray investigation of the structure of ultramarine-blue and its reaction products. E. PODSCHUS, U. HOFMANN, and K. LESCHEWSKI (*Z. anorg. Chem.*, 1936, 228, 305—333).—Ultramarine (I) has a cubic structure with a space-group T_d^2 , similar to that of sodalite, hauynite, and nosean (cf. A., 1929, 749). The S is in a polysulphide state, probably with some in an ionic form. The structures of the Li and Ag substitution products are similar, but in the latter the position of the Ag ions is not quite ideal. The "sulphate-product" obtained by oxidising (I) has a lattice with space-group T^1 . The S atoms are responsible for the colour of (I). J. W. S.

X-Ray diffraction pattern of liquid and solid glycerol films. K. LARK-HOROVITZ and E. P. MILLER (*Physical Rev.*, 1935, [ii], 47, 813; cf. A., 1935, 18).—The apparent sharpening of diffracted lines at lower temp. is due to inhomogeneous radiation. None was observed at room temp. and at -80° . This agrees with the view that the mols. in solid glycerol are distributed at random similarly to mols. in liquids. L. S. T.

Physical investigation of phenyl β -hydroxy- $\beta\beta$ -diphenylvinyl sulphone. H. E. BENT, E. S. LARSEN, and H. BERMAN (*J. Amer. Chem. Soc.*, 1936, 58, 1522—1523).—Crystallographic and solubility (in C_6H_6 and MeOH) data are recorded and compared with corresponding data for Ph α -hydroxy- $\beta\beta$ -diphenylpropenyl sulphone. The compounds may be identical. E. S. H.

Lattice structure of condensed aromatic hydrocarbons and their molecular compounds with trinitrobenzene. E. HERTEL and H. W. BERGK (*Z. physikal. Chem.*, 1936, B, 33, 319—333).—2 : 3-

Benanthracene (I) crystallises in the triclinic system with I_a 7.94, I_b 6.02, I_c 13.5 Å., and 2 mols. in the unit cell. Perylene (II) crystallises in the monoclinic system with I_a 10.3, I_b 10.8, I_c 13.6 Å., space-group C_{2h}^2 , and 4 mols. in the unit cell. The lattice structures of the 1 : 1 mol. compounds of (II) and pyrene with $\text{C}_6\text{H}_3(\text{NO}_2)_3$ (III) have been examined. (I) forms no mol. compound with (III). The lattices of the 1 : 1 mol. compounds of (III) with C_6H_6 and PhMg are able to take up small amounts of (I). An apparatus for vac. sublimation in a const. gas current is described. R. C.

Absorption edges in the X-rays patterns of native and mercerised cellulose. W. A. Sisson, G. L. CLARK, and E. A. PARKER (*J. Amer. Chem. Soc.*, 1936, 58, 1635—1638).—Diffracted general radiation from the 002 and 101 planes in native and the 10 $\bar{1}$ plane in mercerised cellulose produces Br and Ag absorption edges similar in appearance to diffraction lines on the X-ray negative. Absorption edges correspond with some, but not all, of the large interferences reported for cellulose. No spacings $>$ the cellulose unit cell were found. E. S. H.

Shape and properties of thread-like molecules in solution and in the elastic solid state. W. KUHN (*Z. Elektrochem.*, 1936, 42, 692; cf. A., 1934, 959; this vol., 785).—The mean distance between the ends of a long chain mol. is aZ , where Z is the no. of members in the chain and a is a const. The valency angle and nature of the free rotation modify the val. of a . The modulus of elasticity of rubber-like materials $\propto 1/Z$, and so can be used to determine the mol. wt. of the mols. J. W. S.

Elementary lattice of crystallised caoutchouc. K. H. MEYER and W. LOTMAR (*Arch. Sci. phys. nat.*, 1936, [v], 18, Suppl., 61—62; cf. Mark, A., 1928, 1178).—Previous data are corr. The lattice is slightly monoclinic, with a 8.54, b 8.20, c 12.65 Å., β 83°, space-group probably C_{2h}^2 . N. M. B.

Electron diffraction by transmission through thin silica glass films. L. R. MAXWELL and V. M. MOSLEY (*Physical Rev.*, 1935, [ii], 47, 330—331).—The electron diffraction pattern obtained by transmission of 25—38-kv. electrons through thin films of SiO_2 glass is described. L. S. T.

Structure of thin metal layers. R. RIEDMILLER (*Z. Physik*, 1936, 102, 408—416).—The determination of lattice const. of Ni, Au, and Ag by electron diffraction through films vaporised on collodion is described. Various errors are eliminated by photographing a reference pattern simultaneously, and measuring the patterns microphotometrically. The effect of air and H_2 on the films is studied. Lattice const. by this method are about 1% $>$ by X rays. L. G. G.

Structure of some metallic deposits on a copper single crystal as determined by electron diffraction. W. COCHRANE (*Proc. Physical Soc.*, 1936, 48, 723—735).—Ni, Cu, Zn, Cd, Ag, Cr, and Co were deposited electrolytically on etched Cu single-crystals and the structure of the deposits was found by electron diffraction. At small c.d. the layers are oriented except in the case of Zn and Cd. Irregul-

arities (lines and spots) in the Ni and Co patterns are accounted for by assuming repeated twinning on (111) planes. N. M. B.

Gerlach's thermomagnetic electromotive force in some ferromagnetic alloys. N. YAMANAKA (Sci. Rep. Tôhoku, 1936, 25, 174—183).—The e.m.f. produced by the application of a longitudinal magnetic field in a wire down which there is a temp. gradient has been measured for Ni, nichrome, invar, and superinvar. The effect for the alloys is $<$ for Ni. When the temp. is $<$ Curie point the e.m.f. increases with magnetic field and with temp., tending to a saturation val. O. D. S.

Time lag in the magnetisation of soft iron in the upper portion of the hysteresis loop. J. ÔKUBO and N. YAMANAKA (Sci. Rep. Tôhoku, 1936, 25, 163—173).—Measurements have been made of the time variation of magnetic induction in soft iron and Fe-Si-Al alloys after removal of a magnetising current under conditions where μ was nearly const. O. D. S.

Magnetic viscosity at different points of the magnetisation curve. A. MITKEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 175—177).—The best conditions for the observation of the effect of magnetic history on magnetic viscosity are obtained, the magnetisation curve for an iron ring being found by the method of reversals. The viscosity reaches a max. on the steepest part of the curve and decreases exponentially with time. The effect of magnetic history on subsequent viscosity is most marked in weak fields, becoming imperceptible with increase of magnetic field. W. R. A.

Ferromagnetism of iron alloys. M. FALLOT (Ann. Physique, 1936, [xi], 6, 305—387).—The law of the approach to saturation magnetisation as a function of $T^{0.75}$ near 0° abs. is verified. A special apparatus for liquefying small quantities of H_2 for magnetisation experiments, and a recording apparatus for the determination of Curie points, are described. Mean at. moments and Curie points for alloys of Fe with Si, Al, Cr, V, Au, Sn, Pt, and Mn were determined and their variations with the nature and proportion of the added element are discussed. The at. moment of Fe depends on the foreign atoms surrounding the Fe atom in the lattice. N. M. B.

Hall coefficients of alkali metals. C. ZENER (Physical Rev., 1935, [ii], 47, 636).—Theoretical. L. S. T.

Determination of the optical anisotropy constants of absorbing crystal sections from polarisation observations in perpendicularly reflected light. M. BEREK (Z. Krist., 1936, 93, 116—135).—Mathematical. B. W. R.

Optical studies on organic crystals. I. K. S. SUNDARARAJAN (Z. Krist., 1936, 93, 238—248).—A summary of measurements of principal refractive indices and directions of optic axes for 14 aromatic hydrocarbons. The results are discussed in relation to the mol. positions already known from X-ray and magnetic methods. B. W. R.

Effect of crystal boundaries on test specimens consisting of several large crystals. G. SEUMEL (Z. Krist., 1936, 93, 249—283).—The behaviour of test-rods containing several large crystals is studied under strain, the normal polycryst. metal being regarded as the limiting case of such measurements. B. W. R.

Slip, twinning, and cleavage in silicon ferrite (4.17% Si). C. S. BARRETT (Physical Rev., 1935, [ii], 47, 809).—Repeated bending causes cleavage on cube planes [100], and hammering causes twinning (Neuman bands) on icositetrahedral planes [112]. Slip occurs only on rhombic dodecahedral planes [110]. L. S. T.

Crystalline symmetry and shear constants of Rochelle salt. T. TASCHER and H. OSTERBERG (Physical Rev., 1936, [ii], 50, 572).—Interferometer studies of patterns due to shear modes of vibration excited by alternating electric fields of frequency 20—200 kc. per sec. show that, for 12 specimens, the cryst. symmetry is hemihedric with no transitions to the hemimorphic class in the temp. range 0 — 40° . Frequency-temp. curves show negative temp. coeffs. for all three shear modes; all curves show anomalies near 23.5° . N. M. B.

Temperature variation of the elastic moduli of NaCl, KCl, and MgO. M. A. DURAND (Physical Rev., 1936, [ii], 50, 449—455; cf. Balamuth, A., 1934, 836).—The principal adiabatic and isothermal elastic moduli and elastic consts. were measured over 270—480° abs. for NaCl, 80—280° abs. for KCl, and 80—560° abs. for MgO. The Debye characteristic temp. of these at 80° abs., calc. from the adiabatic elastic consts., are 320°, 246°, and 946° abs., respectively. The variation of isothermals with temp. is evaluated and discussed. N. M. B.

High-pressure transitions of bismuth [and antimony]. P. W. BRIDGMAN (Physical Rev., 1935, [ii], 47, 427—428; cf. this vol., 146).—The transition parameters of Bi have been determined at high pressures. Two new modifications of Bi, each denser than the liquid, exist. The transition line between ordinary Bi (I) and the first high-pressure modification (II) is linear and passes through the points 80°, 23,250 kg. per sq. cm. and 180°, 17,850 kg. per sq. cm.; that between (II) and the second high-pressure Bi (III) is also linear and passes through 80°, 26,400 kg. per sq. cm. and 180°, 22,950 kg. per sq. cm. The triple point liquid-(I)-(II) occurs at 184.0° and 17,600 kg. per sq. cm. Estimated vals. for the triple point liquid-(II)-(III) are approx. 187.0° and 22,700 kg. per sq. cm. Sb shows no new modifications in the range examined. L. S. T.

Glassy state of arsenic. W. E. McCORMICK and W. P. DAVEY (Physical Rev., 1935, [ii], 47, 330).—In pure H_2 below 100° , As vapour condenses to an amorphous (X-rays) powder of small particle size; between 100° and 130° , a mixture of powder and coherent sheet, and between 130° and 250° non-cryst. coherent sheet or glass, is obtained. Above 250° , the deposit is distinctly cryst. to X-rays. L. S. T.

Transformation of fluids into the glassy state. H. EBERT (Glastech. Ber., 1935, 13, 73—77; Chem.

Zentr., 1935, ii, 3812).—Glass, when cooled below the transformation interval, behaves as a frozen phase. The transformation curve does not afford decisive evidence of a transformation of higher order.
J. S. A.

Osmotic mol. wt. determination for large molecules. G. V. SCHULZ (Z. Elektrochem., 1936, 42, 692).—The mol. wt. (M) of large mols. can be calc. from their osmotic pressure (p) in solution by the formula $p = RTc/M(1 - cs)$ (c = concn., s = vol. occupied in solution by 1 g. of solute). s is related to p by $p = ks^{-v}$, where k and v are swelling consts. independent of mol. wt. and determinable for smaller mols. of known mol. wt. The vals. of M calc. from these equations are independent of concn. and are in accord with vals. deduced from viscosity and ultrafilter methods. The variation of p with c indicates that no mol. aggregation occurs at higher concn.
J. W. S.

Bismuth crystals. II. Variation of thermoelectric power in transverse magnetic fields. E. GRÜNEISEN and J. GIELESSEN (Ann. Physik, 1936, [v], 27, 243—255; cf. this vol., 930).—The effect of transverse magnetic field on the thermoelectric power of couples of Bi crystals with metals unaffected by the field has been investigated at 0° , -183° , and -195° , with respect to the direction of the field and of the crystal axis. For Bi_{11} at low temp. the thermoelectric power is increased by the magnetic field to an extent varying with the direction of the field. For Bi_1 at low temp. the thermoelectric power is increased or decreased according to the direction of the field. In both Bi_{11} and Bi_1 the thermoelectric power is affected by reversal of the field. The thermoelectric power of a Bi_{11} - Bi_1 couple at -183° and -195° is calc.
O. D. S.

Free path and thermoelectric effects. L. W. NORDHEIM (Physical Rev., 1935, [ii], 47, 794).—A general expression for the mean free path of electrons in metals is derived.
L. S. T.

Destruction of superconductivity by electric current and magnetic field. L. SCHUBNIKOV (Nature, 1936, 138, 545—546).—The data plotted for Sn show that as a necessary condition of superconductivity the magnetic field should be zero in the whole of the vol. and its effective tangential component should be $>$ a crit. val. at any point of the surface of the superconductor.
L. S. T.

New phenomenon in the superconducting transition of tin and tantalum. F. B. SILSBEE, F. G. BRICKWEDDE, and R. B. SCOTT (Physical Rev., 1935, [iii], 45, 794).—With large currents, passage from the superconducting to the normal resisting condition is accompanied by a spontaneous, transitory increase in resistance followed by a slower return.
L. S. T.

Electron theory in metals of any crystal form. M. KOHLER (Ann. Physik, 1936, [v], 27, 201—216).—Mathematical. Theory of electrical conductivity, thermoelectric effect, and the galvanomagnetic phenomena is generalised for metals of any crystal form.
O. D. S.

Effect of electric field on the heat current in gases. H. SENFTLEBEN and W. BRAUN (Z. Physik, 1936, 102, 480—506).—A thin wire heated in an electric field gives out more heat than without the field. The effect was investigated in A and O_2 (non-polar gases) and in EtCl (polar), with variation of pressure, external temp., and temp. of wire. In all cases the effect varied with the square of the field strength, pressure, and temp. of wire. The val. decreased rapidly with increase of external temp. The effect in polar gases is $>$ in non-polar gases. It can be explained as a supplementary convection due to variations in electrostriction, and offers a method of determining the latter in gases.
A. J. M.

(A) Magnetic properties of chromium. L. F. BATES and A. BAQI. **(B) Magnetic properties of amalgams.** L. F. BATES and L. C. TAI (Proc. Physical Soc., 1936, 48, 781—794, 795—809).—(A) The magnetic susceptibility of pure Cr prepared from Cr amalgam was investigated over the temp. range 90 — 620° abs. The mass susceptibility is almost const.; the mean susceptibility is 3.08×10^{-6} e.m.u. per g. at room temp. The effects of impurities are considered in detail, and thermal and magnetic data are discussed on the basis of modern theories of paramagnetism.

(B) The magnetic susceptibilities of a series of amalgams of known concn. of Bi, Cr, Cu, and Mn were studied at room temp. by the Gouy method, the drop-wt. method being untrustworthy for amalgams. The apparent at. susceptibilities in dil. amalgams were: Mn, 0.137 ; Bi, 133×10^{-6} ; Cr, 23×10^{-6} ; Cu, -7.3×10^{-6} e.m.u. Metals diamagnetic in the solid state were paramagnetic in dil. amalgams, with the possible exception of Cu.
N. M. B.

Paramagnetism of the rare-earth sulphates at low temperatures. L. C. JACKSON (Proc. Physical Soc., 1936, 48, 741—746).—Measurements of magnetic susceptibilities of powdered octahydrated sulphates of Yb, Dy, and Er are plotted from room temp. to 14° abs. Results are discussed in terms of the cryst.-field theory of Penny (cf. A., 1932, 985). Measurements on $Nd_2(SO_4)_3 \cdot 8H_2O$ support Gorter (cf. *ibid.*, 448) against Selwood (cf. A., 1933, 1002).
N. M. B.

Acoustical studies. V. Collision efficiencies of deuterium and hydrogen in exciting the lower vibrational states of ethylene. W. T. RICHARDS. **VI. Behaviour of formic and acetic acid vapours.** C. O. STROTHER and W. T. RICHARDS (J. Chem. Physics, 1936, 4, 561—566, 566—569; cf. A., 1934, 588).—V. Sound velocity data in C_2H_4 - D_2 mixtures show that a H_2 - C_2H_4 collision is eight times as effective as a D_2 - C_2H_4 collision in producing transitions in the lower vibrational states of C_2H_4 . The origin of this difference may be found in the uniquely small moment of inertia of H_2 . C_3H_8 behaves as an inert gas in C_2H_4 - C_3H_8 mixtures. The claim to have found rotational dispersion in H_2 is withdrawn.

VI. Thermal decomp. of formic acid at 60° prevents accurate sound velocity measurements. Data for AcOH at 85 — 115° show that the rate of dissociation of the double mols. is $> 10^4$ sec. $^{-1}$ at 85° and 174 mm.
J. G. A. G.

Propagation of sound in partly dissociated gases. H. O. KNESER and O. GAULER (Physikal. Z., 1936, 37, 677—684).—Theoretical. The effect of partial dissociation of a gas on the velocity of waves of short and of long λ , respectively, through it is discussed, and applied to the case of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$.
A. J. M.

Current, breakdown, and supersonic vibrations in dielectric liquids. W. MEYER (Z. Physik, 1936, 102, 279—304).—The influence of supersonic vibrations on the conductivity and dielectric strength of C_6H_{14} , PhCl , Et_2O , CCl_4 , PhMe , and COMe_2 has been investigated. Results are affected by the nature of the electrode surfaces and by the presence of dissolved gas and other impurities in the liquids. The incidence of supersonic vibrations causes a general increase in conductivity and a decrease in dielectric strength.
H. C. G.

Intensity measurements in the diffraction of light by ultrasonic waves. F. H. SANDERS (Canad. J. Res., 1936, 14, A, 158—171).—The relative intensities in the various orders of the diffraction pattern produced when light is passed through a liquid carrying ultrasonic waves have been measured for various ultrasonic intensities and for both progressive and standing wave-fields. The variation with intensity is in accord with the theory of Raman and Nath (this vol., 148, 555).
J. W. S.

Absorption of ultrasonic waves by liquids. P. BIQUARD (Ann. Physique, 1936, [xi], 6, 195—304; cf. this vol., 417).—Using the method of measuring the radiation pressure exerted on an obstacle or an optical method based on diffraction, the absorption in H_2O and several org. liquids of ultrasonic waves of frequency $(4-11) \times 10^6$ was investigated. Absorption coeffs. differed widely from theoretical predictions and the law of proportionality of absorption to v^2 was not always obeyed. Various explanations are discussed.
N. M. B.

Absorption of ultrasonic waves in liquids and related optical phenomena. L. MANDELSTAM and M. LEONTOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 111—114).—Theoretical. The dependence of the absorption coeff. of ultrasonic waves in liquids on frequency and other factors is discussed, and related to the diffraction of light in the transmitting liquid.
A. J. E. W.

Thermal and caloric equation of state of condensed hydrogen isotopes. I. Determination of magnitudes of state. E. BARTHOLOMÉ (Z. physikal. Chem., 1936, B, 33, 387—404).—The results of measurements of the isothermal compressibility of liquid H_2 and D_2 at 16—21° abs. agree with Eucken's equation of state for a condensed substance (A., 1934, 946); the compressibility falls rapidly with increasing pressure. From measurements of the change in vol. on melting under pressure, part of the fusion curve has been traced, and the latent heats of fusion have been calc. The mol. vol. at 0° abs. of H_2 and D_2 are calc. to be 22.9 and 20.3 c.c., respectively. The characteristic temp. of the Debye sp. heat function are 105° and 97° for solid H_2 and D_2 , respectively, the deviation of the ratio of these vals.

from the theoretical val. $\sqrt{2} : 1$ being attributed to the anharmonicity of the potential curve of solid H_2 . From C_p for the liquids, compressibilities have been calc. The results obtained have been used to construct pressure-vol.-temp. and enthalpy-pressure-temp. diagrams for H_2 and D_2 .
R. C.

Determination of heat capacities and heat capacity ratios of gaseous hydrogen cyanide and hydrogen sulphide. W. A. FELSING and G. W. DRAKE (J. Amer. Chem. Soc., 1936, 58, 1714—1717).—Heat capacities have been determined at 30—148° for HCN and 30—110° for H_2S with an accuracy of approx. 1%. C_p/C_v has been determined at 30—75° for HCN and at 10—75° for H_2S with an accuracy of approx. 0.2%.
E. S. H.

Thermodynamic properties of methane. W. C. EDMISTER (Ind. Eng. Chem., 1936, 28, 1112—1116).—Vals. of $(dc_p/dP)_T$, $c_p - c_v$, Joule-Thomson coeff., S , enthalpy, and $\alpha = RT/P - V$ for CH_4 at pressures 1 to 120 atm. and temp. —70° to 200° have been calc. from existing compressibility and sp. heat data.
C. R. H.

Effect on the fundamental units of volume and temperature of the variable isotopic composition of water. E. H. RIESENFELD and T. L. CHANG (Physikal. Z., 1936, 37, 690—692).—The effect of the variability in composition of H_2O from different sources on the accuracy of the definition of the litre and of the Centigrade degree is discussed, and it is concluded that owing to the difficulty of obtaining pure $^1\text{H}_2^{16}\text{O}$ it would be unwise to alter the present definitions. It would, however, be an advantage to specify the source and treatment of the H_2O referred to in the definitions.
A. J. M.

Density and compressibility of solid hydrogen and deuterium at 4.2° absolute. H. D. MEGAW and F. SIMON (Nature, 1936, 138, 244).—Approx. vals. of d , compressibility, and thermal expansion of H and D at 4.2° abs. have been determined in order to show the effect of zero-point energy.
L. S. T.

Density and coefficient of expansion of liquid gallium over a wide range of temperature. W. H. HOATHER (Proc. Physical Soc., 1936, 48, 699—707).—Accurate data for d and coeff. of expansion for the temp. range 30—1000°, obtained by a dilatometric method, are reported. An equation for vol. increase with temp. is found. The calc. mean coeff. of expansion (32.38—310°) is 118.7×10^{-6} .
N. M. B.

Density of hydrocarbon gases and vapours at high temperature and pressure. W. B. KAY (Ind. Eng. Chem., 1936, 28, 1014—1019).— P , V , and T data on eleven petroleum hydrocarbon mixtures are correlated with similar data on pure hydrocarbons by means of the theory of corresponding states. For the mixtures, P_r and T_r are related to a "pseudocrit. point," which is the crit. point of the pure compound of which the P , V , T relations in the superheated region are identical with those for the mixture.
C. R. H.

Reduced volume at the b.p. and additivity. R. LAUTIÉ (Bull. Soc. chim., 1936, [v], 3, 1595—1600).

—The reduced density at the b.p. (T° abs.) is not const. but varies according to $d_c/d_e=2.23+0.1861 \log T_e-8.03 \times 10^{-5}T_e$ to within 2.5%. J. W. S.

Vapour pressure of potassium chloride and caesium iodide crystals. V. DIETZ (J. Chem. Physics, 1936, 4, 575—580).—The v.p. determined by means of a modified abs. manometer are for KCl, $\log_{10} P_{\text{dynes}}=-11,300/T+13.461$ between 847° and 936° abs. and for CsI, $\log_{10} P_{\text{dynes}}=-10,360/T+13.793$, at $767-847^\circ$ abs., from which the heats of sublimation are 51,800 and 47,500 g.-cal. per mol., respectively. Effusion experiments show that the mols. are not associated. J. G. A. G.

Vapour pressure curves and triple points in the temperature range 14—90° abs. F. HENNING and J. OTTO (Physikal. Z., 1936, 37, 633—638).—Data for the v.p. curves of H_2 , Ne, O_2 , and N_2 between the triple point and the b.p. have been obtained using the He gas thermometer. Empirical equations expressing variation of v.p. with temp. are given. For Ne the v.p. of the solid is also given. The triple points are: H_2 13.96° , 54.1 mm., Ne 24.56° , 325 mm., N_2 63.145° , 94.6 mm., O_2 54.33° , 1.2 mm. (all temp. abs.). A. J. M.

Derivation of the equation $PV=RT$. L. McCULLOCH (J. Chem. Educ., 1936, 13, 393—394). L. S. T.

Generalised high-pressure properties of gases. K. M. WATSON and R. L. SMITH (Nat. Petroleum News, 1936, 28, No. 27, 29—36).—Methods which are simpler than the ordinary thermodynamic formulæ are derived for calculating the effect of pressure on heat content, heat capacities, and the Joule-Thomson coeff. from the activity coeffs. Plots of the authors' correlations of compressibility factor (PV/RT) and activity coeffs. are presented. R. B. C.

Joule-Thomson coefficient of oxides of carbon. T. C. HUANG, F. LIN, and C. Y. FU (Z. Physik, 1936, 102, 422).—A correction (this vol., 930). For CO read CO_2 . H. C. G.

Thermal conductivity of deuterium. C. T. ARCHER (Nature, 1936, 138, 286—287).—Vals. obtained for the thermal conductivity at 0° of D_2 prepared by two different methods from 99.95% D_2O are 0.000308₂ and 0.000307₃ g.-cal. per cm. per sec. per degree. L. S. T.

Thermal conductivity of gases with free convection. W. WEIZSÄCKER (Physikal. Z., 1936, 37, 641—650).—The effect of pressure on the free convection of CO_2 , A, H_2 , He, and air for small temp. differences has been investigated. The convection disappears at a temp. characteristic for each gas. A. J. M.

Viscosity of deuterium. H. C. TORREY (Physical Rev., 1935, [ii], 47, 644—645).—Rankine's method gives for the ratio $\eta_{D_2}:\eta_{H_2}$, 1.410 ± 0.03 , yielding 124.4 ± 2.5 micropoises for the η of D_2 at 23.0° . The mol. cross-sections of the H isotopes effective in η thus differ by $<2\%$. L. S. T.

Physical properties of water and other fluids. R. L. DAUGHERTY (Trans. Amer. Soc. Mech. Eng., 1935, 57, 193—196).— η data for H_2O and various

liquids are represented graphically. $P-V-T$ data and vol. modulus of elasticity and sp. heat data for H_2O are given. CH. ABS. (e)

Fluidity and molecular complexity. E. C. BINGHAM and C. E. COOMBS (Physical Rev., 1935, [ii], 47, 645).—Formulæ connecting fluidity and mol. complexity are discussed for normal org. compounds. L. S. T.

Effect of an electric field on the viscosity of eolotropic liquids. Y. BJÖRNSTÅHL (Physics, 1935, 6, 257—264).—An oscillating-disc viscosimeter with connexions for applying a field parallel to the axis of the instrument was used. η increased with increase of either an a.c. or a d.c. field, probably owing to orientation of swarms. A change in electrical conductivity with shear was found. CH. ABS. (e)

Viscosity of aqueous solutions. III. Calculation of the viscosity of mixed solutions. A. BANCHETTI (Gazzetta, 1936, 66, 446—451; cf. A., 1935, 693).—The validity of various formulæ for calculating the viscosity of mixed solutions has been examined for solutions of NaCl+HCl, NaCl+KCl, and HCl+KCl. O. J. W.

Viscosity of supersaturated solution of sucrose. J. COUMOU (Chem. Weekblad, 1936, 33, 542—544).—For supersaturated solutions (75%) of sucrose at 20° η decreases to a const. val. on keeping for 2—3 hr. and increases when the solution is vigorously stirred. S. C.

Binary liquid systems in which compounds are formed. E. ANGELESCU and C. EUSTATIU (Z. physikal. Chem., 1936, 177, 263—276).—Mixtures of aromatic amines with fatty acids at 25° have been studied. The contraction on mixing, ϕ , may be represented by $\phi=Kx^2(1-x)$, where x is the mol. fraction and K and a are consts. The relation between the viscosity, η , and vol. composition of the mixtures may be represented by McLeod's equation (Trans. Faraday Soc., 1924, 19, 6, 17). η is a max. for a mixture containing a greater proportion of acid than corresponds with the composition of the compounds indicated by thermal analysis, a discrepancy which is ascribed to the acids being more highly associated than the amines. Neither the mol. surface energy nor the parachor follows the additive law, but each may be represented by $P=[P_1x+P_2(1-x)](1-K'\phi)$, where P is the parachor or mol. surface energy and K' a const. which is the greater the more capillary active is the acid. The mol. refraction is approx. additive, but n deviates from additivity, the deviation being a max. for a mixture of one mol. of amine with two mols. of acid. R. C.

Properties of metallic solutions. I. V. K. SEMENTSCHENKO (Acta Physicochim. U.R.S.S., 1936, 4, 695—704; cf. this vol., 1192).—The surface tension of amalgams of Mg, Co, Zn, Cd, Ag, Ca, Sr, Pb, Sn, Ba, Li, Na, K, Rb, and Cs has been determined for various concns. There is good agreement with the theory of generalised moments. The effect of minute quantities of impurities on the mechanical properties of metals and alloys, and that of surface-active metals on the mutual solubility of two metals

are discussed. The action of promoters may be explained on the theory. A. J. M.

Diffusion constant and valency of silver in liquid silver amalgam. K. SCHWARZ and R. STOCKERT (*Monatsh.*, 1936, 68, 383—368).—The diffusion const. of Ag in Ag amalgam at 16° is 1.1×10^{-5} sq. cm. per sec., in accord with the bivalency of Ag in these amalgams. J. W. S.

Heat content and heat of formation of molten alloys. H. O. VON SAMSON-HIMMELSTJERNA (*Z. Metallk.*, 1936, 28, 197—202).—The heat contents of Pb-Bi alloys at 400°, 500°, and 600°, Sn-Bi, Pb-Sn, and Pb-Cd alloys at 500°, Pb-Ag alloys at 1000°, and Pb-Sn-Bi alloys at 500° have been determined. The max. heats of alloying calc. from these figures are at 500°: Pb-Bi +1000, Bi-Sn +530, Pb-Sn -250 and Cd-Pb -480 g.-cal. per g.-atom; and at 1000° Pb-Ag -800 g.-cal. per g.-atom. The heats of formation of solid Ag₂Zn₃ and those of solid Cu-Zn alloys on straight lines intersecting at Cu₂Zn₃; calculations of the heat of formation of these alloys at 1000° show that these compounds exist in the liquid state but are strongly dissociated unless a large excess of either component is present. The heats of alloying of Cu and Ni and of Ni and Fe at 1500—1600° vary only slightly from the heats of formation of the corresponding solid solutions. A. R. P.

Relation between the thermal and electrical conductivities of copper alloys. C. S. SMITH (*Physical Rev.*, 1935, [ii], 48, 166—167).—When thermal conductivity is plotted against electrical conductivity at the same temp., the results for all Cu alloys can be represented by a single curve, regardless of composition within wide limits and also of structure or heat-treatment. The curves for 20° and 200° differ in slope, but intersect at approx. the same point on the thermal conductivity axis. All results both at 20° and 200° lie on a single curve when thermal conductivity is plotted against electrical conductivity \times abs. temp. L. S. T.

Hall effect and some other physical constants of alloys. V. Antimony-silver series. W. G. JOHN and E. J. EVANS (*Phil. Mag.*, 1936, [vii], 22, 417—435).—The resistivity, temp. coeff. of resistance, thermo-electric power, d , and Hall coeff. of Sb-Ag alloys have been determined over the complete composition range. The property-composition curves afford no evidence for the existence of a solid solution at the Sb end of the series. Sharp negative max. occur in the thermo-electric power and Hall coeff. curves at 72% Ag, but X-ray analysis shows no sign of a phase change at this composition. A. J. M.

Magnetic susceptibilities of the silver-lead, silver-antimony, and silver-bismuth series of alloys. G. O. STEPHENS and E. J. EVANS (*Phil. Mag.*, 1936, [vii], 22, 435—445).—The d and mass susceptibilities (χ) of Ag-Pb, Ag-Sb, and Ag-Bi alloys have been determined. Annealing has little effect on χ for Ag-Pb alloys, which represent a series of mechanical mixtures throughout the whole composition range. In the Ag-Sb alloys no indication is found of the existence of a solid solution at the Sb

end of the system (cf. preceding abstract). The existence of a solid solution of Bi in Ag up to a concn. of 5.7% Bi is shown. All the alloys examined were diamagnetic. A. J. M.

Longitudinal magneto-resistance effect at various temperatures in nickel-copper alloys. H. MASUMOTO and Y. SHIRAKAWA (*Sci. Rep. Tôhoku*, 1935, 25, 105—127).—The magneto-resistance of Ni-Cu alloys rises with increasing Cu content to a max. at 10% (−195°), 6% (0°), and 4% Cu (100°) and then falls rapidly, reaching zero at 47% (−195°), 33% (0°), and 23% Cu (100°). The max. in the curves is much more pronounced at temp. below 0° than at higher temp. A. R. P.

Quantum theory of electrical conductivity of alloys in superlattice state. T. MUTO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, 30, 99—120).—Theoretical. An expression is derived which connects the influence of temp. and composition on the resistance with the superlattice order of the alloy. Comparison with published results for the Cu-Au system shows fair agreement. J. S. A.

Diffusion experiments as means of simple micrographic detection of compound formation between alloy components in three- and multi-component systems. M. BOSSHARD (*Aluminium*, 1935, 17, 477—481; *Chem. Zentr.*, 1935, ii, 3972—3973).—A cone of the basis metal with one alloy component is pressed into a corresponding seating in a block of an alloy of the basis metal with the second alloying component. After several days just below the solidus temp. the region of the interface is examined micrographically for evidence of diffusion. In the following combinations the changes indicated were so detected: Al-Si: Al-Fe, Al₂Fe \rightarrow Al_xFe_ySi_z (probably Al₆Fe₂Si₃); Al-Si: Al-Mn, MnSi formed; Al-Cr: Al: Si, Al₂Cr \rightarrow CrSi, with vol. contraction; Al-Fe: Al-Cu, Al₂Fe \rightarrow Al₂Cu₂Fe; Al-Ni: Al-Cu, Al₃NiCu₂ or Al₁NiCu₂ formed; Al-Cu: Al-Mg, Al₆Mg₄Cu formed. J. S. A.

Stability of cementite. K. HONDA, K. IWASÉ, and K. SANO (*Sci. Rep. Tôhoku*, 1936, 25, 202—206).—Theoretical. The solubility curve of graphite in austenite is deduced from the equilibrium const. of the reactions: austenite (C-rich) + CO₂ = austenite (C-poor) + 2CO, and C + CO₂ = 2CO. The solubility of graphite above 925° is $>$ that of cementite; it is inferred that cementite is stable above this temp. O. D. S.

System iron-zinc. J. SCHRÄMM (*Z. Metallk.*, 1936, 28, 203—207).—The system has been examined by X-ray, thermal, and magnetic analysis and by micrographical methods. At 20° there are four stable phases: η (hexagonal Zn-rich solid solution), δ (hexagonal "FeZn₃"), Γ (cubic "FeZn₃" with 52 atoms in the unit cell), and α (Fe-rich solid solution). The eutectic point is 419.4°, 0.09% Fe and $<$ 0.03% of Fe dissolves in Zn at the eutectic temp. The δ -field extends from 6.3 to 11.5% Fe at 20° and from 5.8 to 11.5% Fe at 419° and the Γ -field from 20 to 27% Fe at 20—600°. The peritectic horizontal at 780° extends from 54 to 19% Fe, and that at 668° from 20 to 4% Fe, whilst the eutectoid horizontal at 623°

extends from 80 to 27% Fe; α -Fe dissolves 20% Zn at 623°, 10% at 450°, and 8% at 20°, but γ -Fe dissolves a max. of 46% Zn at 780°. The compositions of the δ - and Γ -phases are not in agreement with any of the formulæ previously proposed. A. R. P.

Equilibrium diagram of magnesium-rich magnesium-manganese binary system. H. SAWAMOTO (Suiy.-Shi, 1935, 8, 763—768; cf. this vol., 559).—The new β -phase in the Mg-Mn system is a solid solution of the compound Mg_6Mn , which is formed by the peritectic reaction at 726°.

CH. ABS. (e)

Phase relationships in the nickel-tin system. E. FETZ and E. R. JETTE (J. Chem. Physics, 1936, 4, 537).—With increasing % of Sn, a new phase appears at Ni_3Sn which coexists at 25—35.5 at.-% Sn with a phase (I) having a NiAs-structure. (I) exists alone at 35.5—45 at.-% Sn, but at 40 at.-% Sn and below 500° gives place to a deformed modification. Three new phases, η , θ , and ζ , exist at 51, 54, and 56—62 at.-% Sn, respectively. The ζ -phase coexists with the Sn-phase above 62 at.-% Sn. The solubility of Ni in Sn is very small. J. G. A. G.

Phase equilibria in hydrocarbon systems. XVI. Solubility of methane in four light hydrocarbons. B. H. SAGE, D. C. WEBSTER, and W. N. LACEY (Ind. Eng. Chem., 1936, 28, 1045—1047).—The solubility of CH_4 in $n-C_5H_{12}$, $n-C_6H_{14}$, cyclohexane, and C_6H_6 and the sp. vols. of the mixtures have been determined at 100°, 160°, and 220° F. and at total pressures between 400 and 3000 lb. per sq. in. C. R. H.

Solubility of calcium β -methylbutyrate in water. D. F. HOUSTON (J. Res. Nat. Bur. Stand., 1936, 17, 55—58).—Solubilities at 0—100° are recorded. The results indicate a transition from the penta- to the hemi-hydrate at 36.5°. O. J. W.

Solubility of sodium carbonate in aqueous ammonia. E. I. ACHUMOV and E. A. EZEROVA (J. Appl. Chem. Russ., 1936, 9, 1173—1177).—Solubility data are recorded, for the system $Na_2CO_3-NH_3-H_2O$, at 0°, 10°, and 20°. R. T.

Equilibrium in fluoride systems. I. Solubility of cryolite in aqueous solutions of iron and aluminium salts at 25°. F. J. FRERE (J. Amer. Chem. Soc., 1936, 58, 1695—1697).—Solubility data for Na_3AlF_6 in aq. Fe^{III} and Al chloride, nitrate, and sulphate are recorded. Solubility is greatest in the Al salt solutions. Double salts appear to be formed. E. S. H.

Sodium silicofluoride and aluminium fluoride, and their solubility in water and hydrofluoric acid. N. S. NIKOLAEV, N. A. IVANOV, and S. G. KOLTIPIN (J. Appl. Chem. Russ., 1936, 9, 1183—1190).—The solubility of Na_2SiF_6 and $AlF_3 \cdot 5H_2O$ (I) rises with increasing [HF] and temp. Anhyd. AlF_3 is obtained by drying (I) at 300°. R. T.

Solubility of naringin in water. G. N. PULLEY (Ind. Eng. Chem. [Anal.], 1936, 8, 360).—Data for 6—75° are recorded. Solubility increases little with rise of temp. below 45°, but increases rapidly at >45°. E. S. H.

Relative vapour pressure and aqueous solubility of the solid-solution system β -naphthol-naphthalene. R. WRIGHT and N. E. WALLACE (J.C.S., 1936, 1279—1283).—The solubility of solid solutions of $\beta-C_{10}H_7-OH$ (I) and $C_{10}H_8$ (II) in H_2O at 25°, 65°, and 78° has been determined. At 25° the max. solubility occurs with approx. 50% (I), but at higher temp. the solubility rises with increase in the proportion of (I) until at approx. 80% it rises suddenly to the val. for pure (I). The ratio of the v.p. of (II) in solid solution to that of pure (II) is const. over definite composition ranges at 30° and 55°, indicating the presence of two solid phases in these regions, but this constancy disappears at higher temp. C. R. H.

Laws of separation out of traces of foreign substances during crystallising out of precipitates. N. RIEHL (Z. physikal. Chem., 1936, 177, 224—234).—Theoretical. In slow crystallisation from a supersaturated solution the ratio, r , of the microcomponent (I) to the macrocomponent (II) in the crystal as a whole \propto the ratio of the concns. c_1 and c_2 in the solution at equilibrium. This can be explained only by supposing that in a layer of mols. deposited on the growing crystal $r=c_1/c_2$ at first, but subsequently this is altered by kinetic exchange between crystal and solution. For rapid crystallisation from supersaturated solution in presence of many crystal nuclei the Doerner-Hoskins equation (A., 1925, ii, 381) is valid for the relation between the initial and final vals. of c_1 and c_2 ; this may be explained by supposing that owing to the abnormally high solubility of the nuclei there is metastable equilibrium between the liquid and solid phases. R. C.

Equations for diffusion of gases through metals. W. R. HAM (Physical Rev., 1935, [iii], 47, 645). L. S. T.

Diffusion of hydrogen through highly degassed palladium. J. D. SAUTER and W. R. HAM (Physical Rev., 1935, [ii], 47, 645; cf. this vol., 1194).—Results obtained with highly degassed Pd are recorded. L. S. T.

Diffusion in zeolitic solids. M. H. HEY (Phil. Mag., 1936, [vii], 22, 492—497).—The equations derived in the kinetic theory of zeolitic diffusion previously put forward (A., 1935, 1345) are applied to analcime- NH_3 (I) and Pd- H_2 (II). The calc. diffusion const. of (I) is $(1.2 \pm 0.7) \times 10^{-8}$ sq. cm. per sec., agreeing with the val. given by Tiselius (this vol., 153), whilst that of (II) agrees with the val. given by Jost *et al.* (A., 1935, 1200). A. J. M.

Sorption processes on diamond and graphite. I. Reactions with hydrogen. II. Reactions of diamond with oxygen, carbon dioxide, and carbon monoxide. R. M. BARRER (J.C.S., 1936, 1256—1261, 1261—1268).—I. Isothermals for the chemisorption of H_2 by diamond (I) correspond with a large heat of sorption, the estimated val. being 58 kg.-cal. per g.-mol. compared with 45 kg.-cal. per g.-mol. for sorption by graphite. A comparison of the energy of activation-% saturation curves for (I), graphite, and charcoal indicates that only (I) approaches the ideal adsorbent which consists of perfect crystals

and for which the energy is const. for all degrees of saturation. The admission of O_2 prevents the chemisorption of H_2 by forming a stable oxide film on the (I).

II. At -78° the sorption of O_2 by (I) is nearly all physical. As the temp. is raised chemisorption becomes more pronounced, the O_2 being retained as a film. At $244-370^\circ$, with further admission of O_2 , CO_2 is liberated, and at still higher temp. the O_2 film begins to decompose, CO_2 and CO being formed. CO_2 is reduced by (I) to CO , a small proportion of which is considered to be retained as a film.

C. R. H.

Porosity and sorption properties of activated charcoal. M. DUBININ and E. SAVERINA (*Acta Physicochim. U.R.S.S.*, 1936, 4, 647-674).—A series of activated charcoals, prepared by activation of sugar-C at 850° and 1000° , has been used in the investigation of the adsorption of org. acids, PhOH, methylene-blue, Congo-red, and I from aq. solution and the data have been applied to estimate the porosity of the adsorbent. The adsorption isotherms of C_6H_6 vapour at 20° and 50° , and of MeOH vapour at 20° , on outgassed C were determined at pressures from 10^{-4} mm. to the saturation pressure. The adsorption depends on the activation process, and, for the substances used, agrees well with the Polanyi adsorption potential theory.

A. J. M.

Activated adsorption of hydrogen and carbon monoxide on zinc oxide. Effect of water vapour. R. L. BURWELL, jun., and H. S. TAYLOR (*J. Amer. Chem. Soc.*, 1936, 58, 1753-1755).— H_2O vapour minimises surface reduction of ZnO catalysts and is strongly adsorbed from gas mixtures by those fractions of ZnO surfaces to which the gas mixture first has access. Saturation of ZnO surfaces with H_2O vapour inhibits markedly the activated adsorption of H_2 and CO.

E. S. H.

Adsorption of iodine on quartz glass at temperatures up to 1000° . P. HÖLEMANN (*Z. Elektrochem.*, 1936, 42, 680).—From the v.d. obtained by vaporisation of known amounts of I in vessels with varying areas of internal surface, the adsorption of I on fused SiO_2 has been studied at $150-1000^\circ$ and at v.d. $1.7-3.3 \times 10^{-5}$ g. per c.c. The amount adsorbed (A) \propto the v.d. At $150-400^\circ$ and $850-1000^\circ$ $A \propto 1/T$. It is concluded that for the lower temp. interval the adsorption is mol., and for the upper is at.; the heats of adsorption calc. from the proportionality factors are 1.2 and 15 kg.-cal. per g.-mol., respectively. The no. of "active centres" decreases with rising temp. and is less for at. than for mol. adsorption.

J. W. S.

Adsorption of silver and iodide ions by freshly-precipitated silver iodide. Isoelectric point of the fresh precipitate. I. M. KOLTHOFF and J. J. LINGANE (*J. Amer. Chem. Soc.*, 1936, 58, 1528-1533).—The isoelectric point of freshly-pptd. AgI is p_{Ag} 6.0. At the equivalence potential the excess of adsorbed I' is 0.09% of the total I in the ppt. Adsorption of Ag^+ or I' by the fresh ppt. is in accordance with $\Delta X = K \log C$ in the p_{Ag} range 4-7.2; I' is more strongly adsorbed than Ag^+ . The theoretical ratio

KI:Ag is found in potentiometric titration if the end-point is taken at the isoelectric point instead of at the equivalence potential, and if a correction is applied for excess of Ag^+ in solution.

E. S. H.

Adsorption of barium salts by barium sulphate from solutions in 50% ethyl alcohol. I. M. KOLTHOFF and W. M. MACNEVIN (*J. Amer. Chem. Soc.*, 1936, 58, 1543-1546).—Adsorption of Ba salts from 50% EtOH is $>$ from H_2O ; the Freundlich adsorption isotherm is followed. In a series of Ba salts there is no simple relation between adsorbability and solubility. $KBrO_3$ gives equiv. adsorption of cations and anions. $Ca(BrO_3)_2$ is adsorbed as $Ca(OH)BrO_3$.

E. S. H.

Adsorption at the interface between two fluids. II. Adsorption of five dyes at a paraffin-water and at an air-water interface. C. W. GIBBY and C. C. ADDISON (*J.C.S.*, 1936, 1306-1313).—No adsorption of methylene-blue (I), orange-II (II), Congo-red, Me-orange, or Bordeaux-extra (III) at an air- H_2O interface can be detected. (III) is more adsorbed on a light paraffin- H_2O interface than on a C_6H_6 - or a $PhCl$ - H_2O interface, the other four dyes being less adsorbed on paraffin than on C_6H_6 or $PhCl$. The adsorption curves for (I) and (II) at all three liquid-liquid interfaces rise with the concn. and finally become horizontal. The curves for the other three dyes pass through a max. and then fall towards zero.

C. R. H.

Adsorption of barium chloride from acidic and basic silica sols. Z. BERESTNEVA and V. KARGIN (*Acta Physicochim. U.R.S.S.*, 1936, 4, 675-694).—The Ba-amalgam electrode may be employed for the determination of the activity of Ba^{++} in SiO_2 sols. It has been used to study the adsorption of Ba^{++} from $BaCl_2$ solution by SiO_2 sols at p_H 4.7-11.4. There is no adsorption at $p_H < 8$. The exchange adsorption on coagulation of SiO_2 sols has also been examined. The $[Na^+]$ in alkaline SiO_2 sols remains practically const. during the coagulation by $BaCl_2$.

A. J. M.

Statistical mechanical treatment of adsorption phenomena of gases in organic liquids. I, II. S. HAMAI (*Sci. Rep. Tôhoku*, 1936, 25, 344-356, 357-363; cf. Hildebrand, this vol., 818).—I. Vals. of the const. b in Hildebrand's general solubility equation are calc. statistically and compared with those derived from experimental data. Agreement is not generally satisfactory for solutions of CO_2 and N_2O in org. liquids, but solutions of CO_2 in CS_2 are exceptional.

II. For solutions of HCl in various org. liquids agreement is best for the more symmetrical and less polar solvents.

O. D. S.

(A) Theoretical basis of calculating work of adsorbents, in particular as applied to fractionation of mixtures of gases or vapours. M. DUBININ and S. JAVITSCH. (B) Dynamics of sorption of mixtures of vapours. M. DUBININ and M. CHRENOVA (*J. Appl. Chem. Russ.*, 1936, 9, 1191-1203, 1204-1213).—(A) The adsorption coeff. α of one vapour by another is shown theoretically to be given by $\alpha = (C_1' - C_1)/C_2$, where C_1' is the concn. of one vapour in the issuing air during the period

preceding appearance of the second vapour, and C_1 and C_2 are the initial condens. of the vapours.

(B) The above equation is shown to hold in the case of air containing EtOH and PhMe vapours passed through active C at 20°.

R. T.

Ageing of surfaces of solutions. I. Study of variation of surface tension of solutions with time by the ring method. K. S. G. DOSS and B. S. RAO. **II. Activated accumulation of solute molecules.** K. S. G. DOSS (Proc. Indian Acad. Sci., 1936, 4, A, 11—16, 97—107; cf. this vol., 284).—I. An automatic device for the construction of quartz helical springs is described. The spring is used for measuring the max. pull in the determination of the surface tension of PhMe by the ring method, and the effect of time has been investigated for several liquids. No consistent or reproducible variations were found and the ring method is considered to be unsuitable.

II. An application of the Langmuir-Adam surface pressure technique is described. A fresh surface of benzopurpurin solution shows a fall of surface tension with time; on producing mechanically an overcrowding of solute mols. in the surface, a rise of surface tension with time is found. The measured rate of accumulation of mols. at the surface is very slow and is accounted for on the basis of activated accumulation. This postulate throws light on the time variation of surface tension, the high temp. coeff., and the manifestation of surface pressure. The observations may be applied to the measurement of the efficacy of a substance as a stabiliser of foam.

N. M. B.

Kinetics of selective wetting and surface reactions on metals in presence of electrolytes. I. D. MRLIS and P. REHBINDER (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 123—128).—The spreading of drops of electrolyte solutions on metal plates immersed in C_6H_6 has been studied by observing changes in the contact angle. Spreading is due to hydrophilisation of the surface by corrosion products accumulating at the perimeter of the drop; corrosion of the metal by the drop can thus be studied. Fatty acid in the C_6H_6 phase inhibits spreading owing to adsorption on the metal surface.

A. J. E. W.

Union with complement as a surface reaction. I. Surface tension and adsorption. Model experiments with caffeine solutions. F. SEELICH (Biochem. Z., 1936, 286, 396—407).—Curves show the surface tension at various H_2O -non-miscible org. substance (paraffin, C_6H_6 , $NPhMe_2$, oleic acid, etc.) interfaces when varying amounts of caffeine are added and the relation between surface tension and adsorption is investigated. The bearing of the observations on biological surface reactions is discussed.

P. W. C.

Studies of unimolecular films by the ripple method. I, II. J. SAMESHIMA and T. SASAKI (Bull. Chem. Soc. Japan, 1936, 11, 539—546, 547—552).—I. The relation between mol. area and amplitude of ripple has been determined by the const. surface area method for palmitic (I), stearic, myristic (II), and oleic acids (III), tetradecyl alcohol (IV), and palmitonitrile (V), and the results are in agreement with surface pressure data. The damping action

of the film increases with the vibration frequency of the wave-source (tuning fork), in accordance with hydrodynamical theory. It is suggested that the damping action of oil on ocean waves is due to the subsidence of ripples, entailing a diminution in the resistance to the wind.

II. Oleic and lauric acids, (I)—(V) tripalmitin, triolein, ricinoleic acid, and Et palmitate have been studied using const. oil quantity and varying surface area. The compression and expansion curves show hysteresis with an acid medium, which is attributed to inclination of the mols. in the expanded state. The mol. wt. of mastic, calc. from the area at which the ripples subside, is approx. 3600.

R. S.

Multimolecular films. W. D. HARKINS and R. J. MYERS (J. Amer. Chem. Soc., 1936, 58, 1817—1819).—Multimol. liquid films of stearic, oleic, myristic, and pentadecic acid have been obtained by thickening the films with a liquid paraffin (nujol) of low volatility.

E. S. H.

Contact potentials of reversible soluble films of lauric acid. R. T. FLORENCE, R. J. MYERS, and W. D. HARKINS (Nature, 1936, 138, 405—406).—The changes in surface pressure and in the contact potential when the surface of a solution of lauric acid is swept clean of its adsorbed film and the acid allowed to accumulate at the surface by diffusion from the interior of the solution have been determined. The results indicate the importance of the time factor in the determination of γ for solutions of surface-active materials, and the unsuitability of dynamic methods for materials which require considerable time for equilibrium in the surface.

L. S. T.

Electrical properties of films of ω -bromohexadecic acid. M. GEROVICH and A. FRUMKIN (J. Chem. Physics, 1936, 4, 624).—Films of the acid on the surface of a solution containing 0.01N-KCl and 10^{-4} N-HCl show a large negative interfacial potential owing to the orientation of C-Br linkings. By increasing the acidity of the solution to 10^{-3} N-HCl, the surface pressure is decreased markedly and the potential is changed to a small positive val. probably owing to a change of film structure.

J. G. A. G.

Unimolecular layers of chlorophyll. W. SJOERDSMA (Nature, 1936, 138, 405).—A 3:1 mixture of the *a* and *b* modifications forms unimol. layers on H_2O , 0.01N- and 0.1N- H_2SO_4 . The limiting area per mol. at zero compression is 124 A^2 , and at 26 dynes per cm. the film becomes multimol. On H_2O in equilibrium with CO_2 at atm. pressure the mols. appear to require more space, the limiting area being 132 A^2 . NO has no such effect.

L. S. T.

Permeability of membranes. III. Ionic permeability of non-aqueous liquid layers. K. H. MEYER, H. HAUPTMANN, and J. F. SIEVERS. **IV. Analysis of structure of vegetable and animal membranes.** K. H. MEYER and J. F. SIEVERS (Helv. Chim. Acta, 1936, 19, 948—962, 987—995; cf. this vol., 1065).—III. Diffusion potentials across layers of NH_2Ph , $PhOH$, *m*-cresol, and $CH_2Bu^{\beta}OH$ have been measured at 20° and the mobilities of the participating ions calc. Diffusion is determined by

the mobilities and solubilities of the ions in the non-aq. liquid and there is no selectivity. Partition coeffs. of ions have been determined potentiometrically and published data are discussed.

IV. Diffusion potentials between KCl solutions across vegetable (bracts of *Iris amœna*) and animal (skin of *Bombinator igneus*) membranes have been measured. The former contains acids of high mol. wt. and is permeable to cations, whilst the latter shows only slight permeability. These, and similar data relating to membranes studied by other workers, are used to elucidate their structure. Accumulation of K⁺ in plants is not due to selective solubility in lipins, but to its greater facility of passage through what is essentially a fine-meshed sieve. F. L. U.

Statistical evaluation of sieve constants in ultrafiltration. J. D. FERRY (J. Gen. Physiol., 1936, 20, 95—104).—The sieve const. is evaluated in terms of the calibrated membrane porosity and the particle size. H. G. R.

Viscosity nomograph for salt solutions. D. S. DAVIS (Chem. Met. Eng., 1936, 43, 485).—A nomograph from which η at 25° of 0.1—1.0*N* solutions of 38 salts can be read is supplied. W. L. D.

Viscosity of dilute solutions: technique and measurements with solutions of hydrocarbons. K. H. MEYER and A. VAN DER WYK (Kolloid-Z., 1936, 76, 278—289).—Systematic errors and the corresponding corrections in the determination of η of dil. solutions are discussed. The sp. η of dil. (<1%) solutions of higher hydrocarbons in CCl₄ has been determined with special reference to changes in constitution, concn., and temp. In these series η is not a function of the length of the dissolved mol., but varies in a complicated way with constitution. The variation of η with temp. and concn. shows that the dissolved mols. cannot be regarded as rod-like particles. E. S. H.

High-frequency loss and molecular properties of polar solutions. G. MARTIN (Physikal. Z., 1936, 37, 665—667).—The high-frequency loss for dil. solutions of polar substances in non-polar solvents has been determined in order to verify the dipole theory of high-frequency loss. The dielectric loss for *o*-, *m*-, and *p*-C₆H₄Cl₂ $\propto \mu^2$, as required by theory. The extrapolated loss at infinite dilution for Pr^oOH, *n*-C₈H₁₇·OH, and *n*-C₁₆H₃₃·OH increases with the no. of C in the mol. The effect of η , investigated for solutions of *o*-C₆H₄Cl₂ in C₆H₁₄, C₆H₆, CCl₄, and decalin, the relaxation time being plotted against η , shows that Stokes' law holds in the calculation of relaxation time even for particles of mol. size, if an inner η is assumed, which differs from that determined by macroscopic methods. In non-polar liquids this mol. η is a function of the ordinary η and the mol. vol. A. J. M.

Interdiffusion of acid and base in aqueous solution. C. V. KING and W. H. CATHCART (J. Amer. Chem. Soc., 1936, 58, 1639—1642).—Diffusion coeffs. of HCl and NaOH in presence of NaCl have been determined over a wide concn. range. In the interdiffusion of HCl and NaOH in aq. NaCl the diffusion coeffs. are unchanged if sufficient NaCl is present

initially; in the porous-disc cell the diffusion rates are increased since the concn. gradients become sharper because of neutralisation within the disc. Limitations of the porous-disc cell are demonstrated. E. S. H.

Diffusion of magnesium chloride and nitrate in aqueous solution. L. W. ÖHOLM (Finska Kem. Medd., 1936, 45, 71—76).—Diffusion data are compared with vals. for other properties of the solutions. M. H. M. A.

Viscosities and densities of dilute aqueous solutions of weak electrolytes (*o*-nitrobenzoic acid). A. BANCHETTI (Annali Chim. Appl., 1936, 26, 351—356).— d varies almost linearly with the concn. (c) and the variation of η is given by $\eta - 1 = ac^b$, where a and b are constns. L. A. O'N.

Condition of electrolytes in aqueous solutions. A. H. W. ATEN (Chem. Weekblad, 1936, 33, 555—562).—A lecture. S. C.

Physical characterisation of dissolved ions. II. F.p. and conductivity of very dilute aqueous solutions of alkali halides. J. LANGE (Z. physikal. Chem., 1936, 177, 193—212; cf. A., 1934, 596).—The f.p. and conductivity of solutions of the chlorides and iodides of Li, Cs, and K at 0.001—0.1*N* have been determined. Up to 0.05*N* the results can be expressed by $1 - f_0 = 0.37\sqrt{c} + B_0c$ (f.p.) and $1 - f_\infty = (0.219 + 29.5/\Delta_0)\sqrt{c} + B_\infty c$ (conductivity). For all the salts B_0 and B_∞ are negative and approx. equal, indicating complete dissociation. Each consists essentially of a negative and a positive component. The negative component arises from the finite size of the ions in the sense of the Debye-Hückel theory, varies little from one ion to another, and has the same val. for B_0 as for B_∞ . The positive component originates in the mutual attraction of the ions owing to the short-period perturbations of the movements of the electrons, on the lines of London's theory (A., 1931, 149), and can be approx. calc. by means of this theory; it is greater for B_∞ than for B_0 . R. C.

Hydrochloric and hydrobromic solutions of the salts of cobalt, copper, and bivalent nickel. P. JOB (Ann. Chim., 1936, [xi], 6, 97—144; cf. A., 1935, 582).—Solutions of salts of Co, Cu, and Ni in aq. HCl, HBr, and NaBr have been studied spectrographically. For the Co solutions the absorption is independent of the anion and $\propto [\text{Co}^{2+}]$ for a fixed concn. of acid. The λ - and [HCl]-absorption curves show max., whilst the absorption becomes const. when [HCl] > 13 mols. per litre. The results can be accurately reproduced on the assumption that an intermediate complex CoCl⁺ and a blue complex CoCl₂' are formed. HBr solutions show similar properties, the blue colour appearing, however, at a slightly greater concn. The absorption of Cu²⁺ in aq. HBr increases with the [HBr] to a limiting val. at 10 mols. per litre. Two complexes CuBr' and CuBr₂' are probably formed. The activity coeffs. of NaBr, determined by comparison of the absorption of NaBr and HBr solutions containing Cu²⁺, agree with the results of Harned and Douglas. Solutions of Ni²⁺ in HBr resemble those of Co²⁺ in HBr and contain the coloured complexes NiBr₂ and NiBr₄''. The equilibrium constns. have been calc. in each case and the stabilities of the

complexes compared. CuBr' is more stable than CoBr' , whilst CoBr_3' is less stable than CoCl_3' .

R. S.

Molecular state of red rhenium chloride in solution. F. W. WRIGGE and W. BILTZ (*Z. anorg. Chem.*, 1936, 228, 372—382).—The mol. wt. of anhyd. ReCl_3 (prepared by sublimation in a vac.), calc. from the depression of the f.p. of AcOH , corresponds with Re_2Cl_6 . The dialysis coeff. of its HCl solutions indicates that it exists as HReCl_4 in these solutions. The absorption spectrum of anhyd. ReCl_3 in AcOH , dioxan, H_2SO_4 , or HCl has a max. at about 5100 Å., and a min. at about 4500 Å. Solutions of $\text{ReCl}_3 \cdot 2\text{H}_2\text{O}$ (obtained by exposure of ReCl_3 to moist air) in AcOH or dioxan show two absorption max. at about 5000 and 5400 Å., respectively. The structures of the anhyd. and hydrated salts are discussed. J. W. S.

Light pressure and Brownian movement. M. SATO (*Sci. Rep. Tôhoku*, 1935, 28, 156—162).—The results obtained for the light pressure and mean square of the displacement of a Brownian particle from Planck's radiation law are in good agreement with those derived from Glaser's theory of corpuscular gas (cf. *Z. Physik.*, 1935, 94, 677). A. R. P.

Rheopexy in bentonite. E. A. HAUSER and C. E. REED (*J. Amer. Chem. Soc.*, 1936, 58, 1822).—Fractionation (by high-speed centrifuge) of dispersions of bentonite in H_2O gives completely amieronic fractions which exhibit rheopexy (*A.*, 1935, 933). H. B.

Behaviour of aerosols in the acoustic field. II. Behaviour of suspended matter in oscillating gases at sonic and ultra-sonic frequencies. O. BRANDT (*Kolloid-Z.*, 1936, 76, 272—278; cf. this vol., 794).—The rate of aggregation of the particles (0.2—1.7 μ diameter) in stationary and streaming aerosols of liquid paraffin has been determined for different frequencies by measurement of the rate of fall of the particles and by optical means.

E. S. H.

Effect of an electric field on the intensity of the Tyndall light for different forms of colloidal particles. H. UERLINGS (*Physikal. Z.*, 1936, 37, 655—657).—The effect of an electric field on the Tyndall light from V_2O_5 , blue Au, benzopurpurin, and $\text{Fe}(\text{OH})_3$ sols (all having non-spherical particles) and from Ag, red Au, and mastic sols (with spherical particles) has been examined. The electric field increases the intensity of the light for the former group of sols when the lines of force and the direction of vibration of the electric vector coincide, and the direction of observation is mutually perpendicular to this, and to the direction of the incident light. Sols with spherical particles show no increase in the intensity of the Tyndall light on application of the field. A. J. M.

Structures and forces in colloidal systems. H. FREUNDLICH (*Proc. Roy. Inst.*, 1936, 29, 232—252).—A lecture.

Relations between molecular size, statistical molecular structure, and elastic properties of highly-polymerised substances. W. KUHN (*Kolloid-Z.*, 1936, 76, 258—271; cf. this vol., 785).—Theoretical. E. S. H.

Determination of the specific weights of cellulose solutions. Estimation of the specific weights of the double compounds of cellulose derivatives with organic solvents. W. KUMICHEL and C. TROGUS (*Cellulosechem.*, 1936, 17, 97—102).—From *d* measurements of solutions of cellulose nitrates in COMe_2 and in 4-methylcyclohexanone (I) the sp. vols. of the compounds have been estimated. The vals. found agree with those given by *X*-ray measurements if the unit cell in COMe_2 contains 10 C_6 units, whilst that in (I) contains 6 C_6 units and 6 mols. of solvent (at 20—30°) and 10 C_6 units and 20 mols. of solvent (at 18°). A. G.

Lyophilic colloids. III. Micelle composition. H. KROEPELIN (*Rev. Fac. Sci. Univ. Istanbul*, 1936, 1, 70—76).— Et_2O solutions of rubber show an increased Tyndall effect on addition of small amounts of EtOH or COMe_2 contrary to the theory which is presented. The Tyndall effect increases more slowly than the concn. R. S.

Colloid synthesis by vapour explosions and the colloid-chemical investigation of the disperse systems obtained. N. SATA (*Bull. Chem. Soc. Japan*, 1936, 11, 481—503; cf. this vol., 1198).—Dust, burnt cork, and passage through filter-paper stabilise the Hg sol obtained by the vapour explosion method. Na_2SO_3 coagulates the sol whilst the stability increases to a max. with increasing $[\text{Na}_2\text{S}]$ owing to the formation of stabilising complexes. A similar stability max. obtained with NaI is ascribed to the formation of HgI , which gives a green colour in presence of Hg. The concn. range of stabiliser giving max. stability is diminished by irradiation with ultraviolet light, and more so in the case of Na_2S than NaI . Se sols have been prepared by the vapour explosion method and the influence of stirring and shaking investigated. O_2 increases the stability of the sol by reacting with adsorbed SeH_2 . S sols, similarly prepared, are unstable. R. S.

Coagulation of colloids. XIV. Coagulation of colloidalarsenious sulphide by mercuric chloride. Inadmissibility of viscosity and transparency as general criteria of coagulation. S. S. JOSHI and S. S. KULKARNI (*J. Indian Chem. Soc.*, 1936, 13, 439—447; cf. this vol., 795).—No over-all change of *n* or opacity is observed during coagulation by HgCl_2 , although normal variations in these properties occur during coagulation by CdCl_2 or KCl . These properties do not depend only on the charge, shape, and size of the disperse particles, but on macroscopic properties of the system as a whole. E. S. H.

Variation of cataphoretic velocity of colloidal particles during coagulation. II. J. N. MUKHERJEE, S. G. CHAUDHURY, and J. SEN-GUPTA (*J. Indian Chem. Soc.*, 1936, 13, 428—438; cf. this vol., 1201).—The variation of electrophoretic velocity with time has been determined for sols of As_2S_3 , V_2O_5 , Se, $(\text{UO}_2)_2\text{Fe}(\text{CN})_6$, $\text{Cu}_2\text{Fe}(\text{CN})_6$, and $\text{Fe}(\text{OH})_3$ in presence of various electrolytes. The % increase of velocity is the greater the higher are the concn. of the pptg. electrolyte and the valency of the pptg. ion. The effect also depends on the nature of the sol and of the electrolyte and on the electrolyte content of the

sol and thus runs parallel with the effect on the rate of coagulation. E. S. H.

Ionic interchange in stearic acid sols and the mechanism of coagulation. T. R. BOLAM and A. I. S. DUNCAN (J.C.S., 1936, 1317—1324).—The coagulation of stearic acid (I) by H_2SO_4 and sulphates has been followed; the coagulative effect decreases in the order H_2SO_4 , $MgSO_4$, K_2SO_4 , Na_2SO_4 , Li_2SO_4 . The H^+ liberated from (I) by ionic interchange increases with increasing salt concn., the tendency of the cations to displace H^+ being $Mg^{++} > K^+ > Na^+ > Li^+$. The data support the view that the surface mols. of (I) particles dissociate like a weak acid. C. R. H.

Liesegang rings in non-gelatinous media. II. V. GORE (Kolloid-Z., 1936, 76, 330—333; cf. this vol., 1201).—The formation of periodic structures by diffusion of an electrolyte into sols of metal hydroxides, peptised by another electrolyte, is described. The results support the periodic-coagulation theory. E. S. H.

Sensitising effect of small amounts of alkali on silicic acid sol. V. N. KRESTINSKAJA and N. E. NATANSON (Kolloid-Z., 1936, 76, 313—321).—Experiments on coagulation with NaCl and titration with HCl show that small amounts of NaOH produce complex silicates, which sensitise the sol to electrolyte coagulation, but with increasing amounts of NaOH the product is Na_2SiO_3 , which stabilises the sol. E. S. H.

Oxidation and reduction reactions of colloidal substances. IV. Theory of structure of aggregates of colloid particles. V. N. SKVORZOV (Kolloid-Z., 1936, 76, 322—330; cf. A., 1935, 1208).—The rate of reaction of mono- and poly-disperse sols of MnO_2 and Mn_2O_3 with $H_2C_2O_4$ and H_2SO_4 has been determined. From the results it is inferred that the disperse particles have a zonal structure. Practically monodisperse Mn oxide sols can be prepared by inoculation with a nuclear Au sol. E. S. H.

Colloidal potassium complexes. R. KELLER (Kolloid-Z., 1936, 76, 334—337).—The physiological effects of K^+ and combined K in a negatively-charged colloid are contrasted. E. S. H.

Molecular and colloid solubility of acid and salt dyes, especially benzopurpurin. I. Dissolution of acid dyes in sodium hydroxide. W. OSTWALD and R. WALTER (Kolloid-Z., 1936, 76, 291—313).—Benzopurpurin acid is shown by X-ray analysis to be microcryst.; the crystallites are of about colloid dimensions. The solubility of the dye acid in aq. NaOH is in accordance with the solid-phase rule, reaching a max. for medium amounts of the dye. With increasing [NaOH] the max. is displaced in the direction of increased solubility and increased amount of solid phase. Dissolution by salt formation occurs only when excess of NaOH is present. E. S. H.

Swelling pressure and van der Waals force. G. V. SCHULZ (Naturwiss., 1936, 24, 589; cf. A., 1932, 225, 570).—The dependence of the consts. k and ν in $p = ks^{-\nu}$ (p is swelling pressure, and s is swelling vol.) on the dispersion medium, and their independence of the mol. wt. of the solute make it probable that

swelling and the co-vol. of substances in solution are related to the van der Waals forces between solvent and solute. Assuming this to be true, it is possible to calculate the val. of the force, and a quant. law of force is derived by employing solvation potentials. A. J. M.

Syneresis. III. G. ROSSI and G. SCANDELLARI (Gazzetta, 1936, 66, 459—464; cf. this vol., 935).—The liquid resulting from the syneresis of agar-agar gels containing non-electrolytes is more conc. with respect to these substances than the original gel. The results are discussed. O. J. W.

Molecular state of proteins in mixtures and concentrated solutions. K. O. PEDERSEN (Nature, 1936, 138, 363).—The addition of a protamine (clupein) to serum-albumin lowers the sedimentation const., probably owing to dissociation into mols. of one eighth the original size. Hæmoglobin is also dissociated in presence of other proteins and clupein. L. S. T.

Denaturation and hydration of proteins.—See this vol., 1404.

Limiting high-temperature rotational partition function of non-rigid molecules. VI. The methanol equilibrium. L. S. KASSEL (J. Chem. Physics, 1936, 4, 493—496).—The entropy of MeOH and the equilibrium const. for MeOH synthesis are calc. for two mol. models: (i) with free rotation around the CO linking and (ii) with a torsional oscillation of frequency 700 cm.^{-1} about that linking. The evidence favours (ii) but does not exclude (i). J. G. A. G.

Thermal separation of gas mixtures and its significance in the measurement of chemical equilibria; measurement data for the systems H_2 - H_2S and Ag-S-H. N. G. SCHMAHL and W. KNEPPER (Z. Elektrochem., 1936, 42, 681—686).—A thermal diffusion effect has been observed with H_2 - H_2S mixtures, the effect increasing with increasing temp. difference between different parts of the container and with increasing pressure. The effect at 20° and 400° is a max. with about 40% H_2S and amounts to about 6% difference in $[H_2S]$ between the two regions. Errors which may be introduced in the measurement of thermal equilibria of gases and solids when portions of the vessels are at different temp. are emphasised. Measurements on the equilibrium $2Ag + H_2S \rightleftharpoons Ag_2S + H_2$, corr. for this effect, indicate that discrepancies previously encountered are associated with the use of Ag in thread and powder form, and that these differ in heat content by 153.1 g.-cal. per atom. J. W. S.

Theory of concentrated solutions. XIII. Aqueous solutions of organic compounds. M. EWERT (Bull. Soc. chim. Belg., 1936, 45, 493—515).—Partial v.p.-composition data are recorded for mixtures of 16 org. liquids with H_2O , and are used in calculating activity coeffs. The data are discussed on the basis of thermodynamic theory. H. J. E.

Isotope exchange between water and some organic compounds. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 465—474).—From experiments with org. compounds it is con-

cluded that the isotopic replacement of D atoms occurs only when these are linked to O or N. No replacement was observed with CHCl_3 , Et_2O , and PhCHO . For the remaining compounds the distribution quotients, *i.e.*, the ratios between the at. concn. of D in the total exchangeable H in the compound, and the at. concn. of D in the total H in the H_2O , were NH_2Ph , 1.11; PhOH , 1.07; pyrrole, 0.88; BzOH , 1.0; $\text{CH}_2\text{Ph}\cdot\text{OH}$, 1.10. C. R. H.

Isotopic exchange between aniline hydrochloride and heavy water. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 554—556).—The equilibrium $\text{NH}_2\text{PhCl} + 3\text{D}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_4\text{D}_3\cdot\text{ND}_3\text{Cl} + 3\text{H}_2\text{O}$ is established at 60° after 3 hr. Replacement of the H of NH_2PhCl occurs immediately, but when ND_3PhCl is heated alone to 160° , D wanders into the nucleus. R. S.

Properties of pentadeuterobenzoic acid, $\text{C}_6\text{D}_5\cdot\text{CO}_2\text{H}$. H. ERLIENMEYER and A. EPPRECHT (Nature, 1936, 138, 367).—Vals. recorded are K^{25} 6.6×10^{-5} , mol. heat of combustion 761,380 g.-cal., and solubility 0.34 g. per 100 c.c. of H_2O at 18° . L. S. T.

Primary and secondary dissociation constants of malonic, succinic, and glutaric acids by potentiometric titration. W. L. GERMAN and A. I. VOGEL (J. Amer. Chem. Soc., 1936, 58, 1546—1549).—Data obtained at 25° , using the quinhydrone electrode, are recorded. The calc. primary dissociation consts. agree within 2—4% with those determined by conductivity. E. S. H.

Ionisation constant of hydrazinium hydroxide. G. C. WARE, J. B. SPULNIK, and E. C. GILBERT (J. Amer. Chem. Soc., 1936, 58, 1605—1606).—Ionisation consts. of N_2H_5^+ as an acid and of $\text{N}_2\text{H}_5\text{OH}$ as a base have been determined at 15° , 25° , and 35° with the aid of the glass electrode. E. S. H.

Polyhalides. IV. Formation and dissociation of polyhalides of ammonium and substituted ammonium bases. S. K. RAY and R. R. BHATTACHARYA (J. Indian Chem. Soc., 1936, 13, 456—463; cf. A., 1934, 599).—The conditions of formation and dissociation of NH_4ClBr_2 , NH_4ClI_2 , NH_4BrI_2 , NH_4Br_3 , NH_4I_3 , NMe_4I_3 , and $\text{C}_5\text{H}_5\text{NEtBrI}_2$ in aq. media and the solubility of I in NEt_4I , NEt_4Br , and $\text{C}_5\text{H}_5\text{NEtI}$ and of Br in NEt_4Br and $\text{C}_5\text{H}_5\text{NEtBr}$ at 25° or 30° have been determined. The degree of dissociation of NEt_4Br at 25° and of $\text{C}_5\text{H}_5\text{NEtBr}$ at 30° has been calc. from conductivity measurements. E. S. H.

Equilibrium between isopropyl alcohol and acetone in presence of alcohol-dehydrogenase. Oxido-reduction potential of the system $\cdot\text{CH}(\text{OH}) \rightleftharpoons \cdot\text{CO}\cdot$. R. WURMSER and S. FILITTI-WURMSER (J. Chim. phys., 1936, 33, 577—586; cf. this vol., 936).—The attainment of equilibrium has been followed potentiometrically from both sides. It is shown, by comparison of the normal potential E_0 with that of other $\cdot\text{CH}(\text{OH}) \rightleftharpoons \cdot\text{CO}\cdot$ systems, that introduction of $\cdot\text{CO}$ into Pr^βOH increases E_0 by +0.078 volt, whereas E_0 decreases as the ratio NH_2/CO increases. R. S.

Equilibrium constants in terms of activities (cryoscopic). V. *p*-Toluidine *o*-chlorophenoxide and *p*-chlorophenoxide in benzene and in *p*-dichlorobenzene. W. R. BURNHAM and W. M. MADGIN (J.C.S., 1936, 1303—1306).—The activity coeffs. for C_6H_6 and $\text{p-C}_6\text{H}_4\text{Cl}_2$ solutions of the undissociated complexes *p*-toluidine *o*- (I) and *p*-chlorophenoxide (II) at concns. up to 0.05 mol. have been determined cryoscopically. The average vals. for the dissociation consts. are 20.95 and 8.66 for (I) and 48.39 and 16.54 for (II) in C_6H_6 and $\text{C}_6\text{H}_4\text{Cl}_2$, respectively. Each complex is formed exothermally, the heats of formation being —4200 g.-cal. for (I) and —3500 g.-cal. for (II). In discussing dipolar influences and chelation the vals. have been compared with those previously obtained for similar phenol-base complexes. C. R. H.

Alkali-hydrolysis and dissociation constants of diketopiperazines and aniline peptides. M. ODA (J. Biochem. Japan, 1936, 23, 241—266).—The rates of hydrolysis of diketopiperazines (I) or NH_2Ph peptides by 0.5*N*-NaOH are not related to the corresponding rates of enzymic hydrolysis. Electrometric titration indicates that (I) which are hydrolysed by carboxypolypeptidase exist at p_{H} 8 as negatively-charged anions; this probably facilitates formation of enzyme-substrate complexes. Basic and, for the last three, acidic dissociation consts. are given for glycol derivatives of NH_2Ph , *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, and *o*-, *m*-, and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. F. O. H.

Dissociation pressure of magnesium chloride hexahydrate. K. SANO (Sci. Rep. Tôhoku, 1936, 25, 184—186).—Dissociation pressures of $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ between 50° and 110° are given by $\log P_{\text{H}_2\text{O}} = -3473.25/T + 11.2195$. For $\text{MgCl}_2\cdot 6\text{H}_2\text{O} = \text{MgCl}_2\cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$. $\Delta H_{298} = 32146$ g.-cal., $\Delta F_{298} = 9070$ g.-cal., and $\Delta S_{298} = 77.44$ e.u. O. D. S.

Dissociation pressure of copper sulphate pentahydrate. F. SCHACHERL and O. BĚHOUNEK (Nature, 1936, 138, 406; this vol., 1070).—Dissociation pressures of $\text{CuSO}_4\cdot 5\text{D}_2\text{O}$ at 20° , 30° , 40° , 50° , and 60° are 4.4, 9.9, 21.0, 42.1, and 80.9 mm., respectively. L. S. T.

Thermal transitions of copper sulphate pentahydrate: molecular rotation and the dehydration of hydrates. T. I. TAYLOR and H. P. KLUG (J. Chem. Physics, 1936, 4, 601—607).—The heating curve of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (I) from -75° to 160° has been determined by a differential thermocouple method at 690 mm. Small abrupt changes in heat capacity shown at 29° , 35° , and 53.7° are attributed to a change from oscillatory to rotational movement of the H_2O mols. in the crystal. Dehydrations at 96.5° , 102° , and 113° correspond with the formation of the tetra-, tri-, and mono-hydrates, respectively. A view of the mechanism of dehydration of (I) by heat, based on mols. acquiring sufficient vibrational-rotational energy to break from the crystal lattice, is shown to accord with the cryst. structure (cf. A., 1934, 1296). J. G. A. G.

System calcium oxide-ferric oxide. B. TAVASCI (Annali Chim. Appl., 1936, 26, 291—300).—The system has been studied micrographically and the

results compared with those of Sosman and Merwin (A., 1916, ii, 618). The existence of $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and $\text{CaO}\cdot\text{Fe}_2\text{O}_3$, and the decomp. of the latter at 1216° are confirmed, but $\text{CaO}\cdot 2\text{Fe}_2\text{O}_3$, decomp. at 1227° into Fe_2O_3 + liquid, is also found. The eutectic, m.p. 1203° , has the approx. composition $3\text{CaO}\cdot 4\text{Fe}_2\text{O}_3$ and consists of a mixture of $\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and $\text{CaO}\cdot 2\text{Fe}_2\text{O}_3$.

L. A. O'N.

System potassium dichromate-sodium dichromate. A. LEHRMAN, H. SELDITCH, and P. SKELL (J. Amer. Chem. Soc., 1936, 58, 1612—1615).—The liquidus curve is of the simple eutectic type. $\text{Na}_2\text{Cr}_2\text{O}_7$ has m.p. $356.7 \pm 1.0^\circ$. The transition point of $\text{K}_2\text{Cr}_2\text{O}_7$ has been redetermined as $241.6 \pm 1.0^\circ$.

E. S. H.

System $\text{Zn}[\text{Hg}(\text{CNS})_4]$ - $\text{Cu}[\text{Hg}(\text{CNS})_4]$. M. STRAUMANTIS and E. ENCE (Z. anorg. Chem., 1936, 228, 334—340).— $\text{Zn}[\text{Hg}(\text{CNS})_4]$ forms a continuous series of mixed crystals with $\text{Cu}[\text{Hg}(\text{CNS})_4]$ from solutions with a $\text{Cu}:\text{Cu}+\text{Zn}$ ratio $> 33.5\%$. The $\text{Zn}[\text{Hg}(\text{CNS})_4]$ crystal lattice is expanded proportionately to the $[\text{Cu}]$. On crystallising mixtures with $\text{Cu}:\text{Cu}+\text{Zn}$ ratios $> 40\%$, green crystals of $\text{Cu}[\text{Hg}(\text{CNS})_2]$, free from Zn, are also obtained.

J. W. S.

Solid-liquid equilibria in systems of organic components. V. Systems consisting of *o*-, *m*-, and *p*-aminophenol. K. HRYNAKOWSKI and M. SZMYT (Z. physikal. Chem., 1936, 177, 306—316).—The f.-p. diagrams of the ternary and three binary systems have been obtained. *p*- and *m*-Aminophenol combine in equimol. proportions to form an incongruently melting compound. Activity coeffs. in the melts have been calc. The mol. attractive forces increase in the order $o < p < m$ -aminophenol.

R. C.

Ternary systems. XXI. Lead nitrate, ammonium nitrate, and water at 25° . A. E. HILL and N. KAPLAN (J. Amer. Chem. Soc., 1936, 58, 1644—1645).—The solubility of $\text{Pb}(\text{NO}_3)_2$ is increased by NH_4NO_3 , but $<$ by KNO_3 . No double salts have been found as solid phases.

E. S. H.

Systems MCl_2 - HCl - H_2O . II. System CdCl_2 - HCl - H_2O . D. I. KUZNETZOV and A. A. KOSHUCHOVSKI (J. Appl. Chem. Russ., 1936, 9, 1178—1182).—Solubility data are recorded for 25° . The solid phases are $\text{CdCl}_2\cdot\text{H}_2\text{O}$ and $2\text{CdCl}_2\cdot\text{HCl}\cdot 4\text{H}_2\text{O}$, and $\text{CdCl}_2\cdot\text{HCl}\cdot 3\text{H}_2\text{O}$.

R. T.

Systems lithium chloride-water-ethyl alcohol and lithium bromide-water-ethyl alcohol. J. P. SIMMONS, H. FREIMUTH, and H. RUSSELL (J. Amer. Chem. Soc., 1936, 58, 1692—1695).—Equilibrium data at 25° are recorded. The solid phases recognised are LiCl , $\text{LiCl}\cdot\text{H}_2\text{O}$, LiBr , $\text{LiBr}\cdot\text{H}_2\text{O}$, and $\text{LiBr}\cdot 2\text{H}_2\text{O}$. No alcoholates were detected.

E. S. H.

Reduction equilibrium of silver sulphide by hydrogen. K. SANO (Sci. Rep. Tôhoku, 1936, 25, 186—196).—The equilibrium const. for $\text{Ag}_2\text{S}+\text{H}_2=2\text{Ag}+\text{H}_2\text{S}$ between 490° and 660° is expressed by $\log K_p=117.7/T-0.741$. The heat of reaction, change in free energy, and entropy change are ΔH_{298} 2726 g.-cal., ΔF_{298}° 1896 g.-cal., $\Delta S_{298}^\circ=2.79$ e.u., respectively. For $2\text{Ag}+\text{S}(\text{rhombic})=\text{Ag}_2\text{S}(\text{rhombic})$, ΔH_{298}

$=-7486$ g.-cal., $\Delta F_{298}^\circ=-9736$ g.-cal., and $\Delta S_{298}^\circ=7.55$ e.u.

O. D. S.

Effect of structure on reactions of organic compounds. Temperature and solvent influences. L. P. HAMMETT (J. Chem. Physics, 1936, 4, 613—617).—The heat and free energy of ionisation of an org. acid are not equally affected by a substituent. The entropy of ionisation of derivatives of BzOH varies in a manner which is predictable from the dielectric const., ϵ , of the solvent and is closely correlated with the effect of a change of ϵ on the relative strengths of the substituted and unsubstituted acids. Aliphatic acids do not show similar relations and this is probably connected with their less rigid structure. Other equilibria and reaction rates are similarly considered.

J. G. A. G.

Thermodynamic properties of phosphorus compounds. T. F. ANDERSON and D. M. YOST (J. Chem. Physics, 1936, 4, 529—530).—Raman spectrum, electron diffraction, and equilibrium data lead to the following standard virtual entropies (g.-cal. per 1°): P (solid, white) 10.55, P_4 (gas) 66.88, PCl_3 (gas) 74.7, PCl_3 (liquid) 52.8, PCl_5 (gas) 87.7, and PCl_5 (solid) 40.8; the corresponding standard free energies of formation are 0, 585, $-63,570$, $-64,650$, $-72,540$, and $-77,950$ g.-cal., respectively.

J. G. A. G.

Atomic heats of formation and bond energies. F. G. SOPER (J.C.S., 1936, 1126—1130).—Linking energies calc. from the at. heats of formation of org. compounds are only approx. const., the increment in heat of formation between successive members of a homologous series (due to formation of one C-C and two C-H linkings) varying with the nature of the series. However, if the at. heats of formation are corr. for the intramol. potential energy arising from coulombic attractions and repulsions between the constituent atoms (calc. from the dipole moments of the linkings) the linking energies are more nearly const. for the paraffin, alcohol, and alkyl halide series.

J. W. S.

Heat capacity of aqueous solutions of barium chloride. C. M. WHITE (J. Amer. Chem. Soc., 1936, 58, 1615—1620).—Modified apparatus and technique, increasing the precision to $\pm 0.01\%$, are described. Data are recorded for 0.003 — $0.3M$ - BaCl_2 at 25° . The apparent mol. heat capacity is related linearly to $[\text{BaCl}_2]^{\frac{1}{2}}$.

E. S. H.

Heat capacity and entropy of barium chloride dihydrate from 15° to 300° abs. Heat of dissolution of barium chloride dihydrate. Entropy of barium ion. O. L. I. BROWN, W. V. SMITH, and W. M. LATIMER (J. Amer. Chem. Soc., 1936, 58, 1758—1759).—The entropy of Ba^{++} , calc. from the above determinations, is 2.2 e.u.

E. S. H.

Heat capacity of aqueous solutions of carbamide and mannitol. C. M. WHITE (J. Amer. Chem. Soc., 1936, 58, 1620—1623).—Data for 0.01 — $1.0M$ solutions with a precision of $\pm 0.01\%$ are recorded. The apparent mol. heat capacities are related linearly to \sqrt{M} .

E. S. H.

Heats of dissolution of salts in heavy water. E. LANGE and W. MARTIN (Z. Elektrochem., 1936,

42, 662—668).—The heats of dissolution (L) of alkali halides in D_2O and H_2O have been measured. The difference in L for the same salt in D_2O and H_2O (ΔL) varies with both anion and cation. The results are explained by assuming that L is not only produced by the electrostatic effects but is also modified by van der Waals forces and by an absorption of energy in creating space in the solvent for the solute mols.

J. W. S

Thermochemistry of titanium oxides. II. Thermochemical calculations. N. NASU (J. Chem. Soc. Japan, 1935, 56, 659—666; cf. this vol., 682).—The following data are deduced: $2TiO_2 + H_2 = Ti_2O_3 + H_2O$, $\Delta H_{298} = 4700$ g.-cal., $\Delta F_{298} = 5280$ g.-cal., $\Delta S_{298} = 1.95$ g.-cal. per 1° ; $Ti_2O_3 + \frac{1}{2}O_2 = 2TiO_2$, $\Delta H_{298} = -62,530$ g.-cal., $\Delta F_{298} = -59,770$ g.-cal., $\Delta S_{298} = -9.26$ g.-cal. per 1° ; $2Ti + 1.5O_2 = Ti_2O_3$, $\Delta H_{298} = -388,070$ g.-cal.; $2TiO_2 + CO = Ti_2O_3 + CO_2$, $\Delta F_{298} = -6220$ g.-cal. The lattice energy of Ti_2O_3 is 3569 kg.-cal.

CH. ABS. (e)

Thermal data. VI. Heats of combustion and free energies of seven organic compounds containing nitrogen. H. M. HUFFMAN, E. L. ELLIS, and S. W. FOX (J. Amer. Chem. Soc., 1936, 58, 1728—1733; cf. A., 1935, 304).—The heats of combustion at const. vol. of *d*-alanine, *l*-asparagine, *l*-asparagine monohydrate, *l*-aspartic acid, *d*-glutamic acid, creatinine, and creatine have been determined at 25° . The heats of formation and free energies are calc.

E. S. H.

Heats of combustion and formation of dibutyl and diamyl phthalates. H. R. AMBLER (J.S.C.I., 1936, 55, 291—292T).—The vals. recorded are, respectively, 7396 ± 10 and 7713 ± 10 g.-cal. per g. at const. pressure. These vals. agree with those derived from the structure of the compounds, but not with vals. in the literature (cf. Schmidt, B., 1934, 1085).

Single linking energies. III. C-C linking in diphenyldidiphenylene-ethane. H. E. BENT and J. E. CLINE (J. Amer. Chem. Soc., 1936, 59, 1624—1627; cf. this vol., 291).—The heat of oxidation of diphenyldidiphenylene-ethane is about 20 kg.-cal. < that of C_6Ph_6 . Steric hindrance is < with C_6Ph_6 , and the free radical formed by dissociation, phenylfluoryl, has more resonance energy than CPh_3 .

E. S. H.

Thermodynamic extension of the diffusion equation. U. DEHLINGER (Z. Physik, 1936, 102, 633—640).—The Fick diffusion equation is shown to be the special case for ideal mixtures of the author's general diffusion equation (cf. A., 1933, 896). By means of the general equation the probability of change of position is calc. for Au-Ni mixtures from the results of Jodule (*ibid.*, 1006). The probability is greater in the mixed crystals than in either pure phase.

O. D. S.

Conductance of salts (potassium acetate) and the dissociation constant of acetic acid in deuterium oxide. V. K. LA MER and J. P. CHITTUM (J. Amer. Chem. Soc., 1936, 58, 1642—1644).—The Walden const. increases linearly by 1.93% in passing from H_2O to D_2O for KOAc and KCl. From the data

the dissociation consts. of weak acids in D_2O can be calc. with the aid of conductivity data. The dissociation const. of AcOH (0.55×10^{-5} in pure D_2O) shows a marked negative deviation from linearity on passing from H_2O to D_2O .

E. S. H.

Hydrogen cyanide. VIII. Conductivity of electrolytes in anhydrous hydrogen cyanide. Some univalent salts at 18° . J. E. COATES and E. G. TAYLOR (J.C.S., 1936, 1245—1256).—The Λ of 21 salts has been measured from 0.001N to 0.002N, and the ionic mobilities have been calc. on the basis of Walden's rule. In most cases $\Lambda_c = \Lambda_0 - x\sqrt{C}$, although for LiCl, LiNO₃, and LiCNS the val. of x is > that calc. from the Debye-Hückel-Onsager equation on account of incomplete dissociation. The calc. dissociation consts. for these salts are respectively 0.11, 0.07, and 0.043.

C. R. H.

Electrochemical investigation of the ternary system: aluminium bromide-silver and copper halides in ethyl bromide, ethylene dibromide, and benzene. V. A. PLOTNIKOV and E. J. GORENBEIN (Acta Physicochim. U.R.S.S., 1936, 4, 775—790).—The electrical conductivity of the systems AgX-AlBr₃ and CuX-AlBr₃ (X=Cl, Br, I) in EtBr, C₂H₄Br₂, and C₆H₆ has been determined. The sp. conductivity increases with the concn. of halide at first rapidly, and then more slowly, attaining vals. of 10^{-2} in conc. solutions. The conductivity in C₆H₆ is > that in C₂H₄Br₂ for solutions of the same mol. concn., although the dielectric const. (ϵ) of C₆H₆ is < that of C₂H₄Br₂. Similarly the conductivity in EtBr is only twice as great as that in C₆H₆ although ϵ of EtBr is four times that of C₆H₆, and the dipole moment (μ) of EtBr is considerable. It is concluded that the chemical and electrochemical activity of a solvent is not completely characterised by μ , and that ϵ is not the principal const. on which the electrical conductivity of a solution depends. Electrolysis of the above solutions gave Ag and Cu⁺ at the cathode, and Br at the anode, the best deposit being obtained when X=Cl. The decomp. potentials of the Cu⁺ and Ag halides in the above solutions were determined.

A. J. M.

Streamline scattering in electrolytes. W. KANGRO and K. M. WAGNER (Z. Elektrochem., 1936, 42, 669).—The current distribution within and outside the space between the electrodes has been determined. Within the electrode zone the relations are complicated, but for the region outside this zone a streamline scattering const. can be calc. which varies little with the ionic strength or chemical nature of the ions, but is dependent on the conductivity and total c.d. With an angular cathode the distribution within the electrode zone deviates from ideal distribution in a manner analogous to that in the outer region.

J. W. S.

Normal potential of the silver-silver bromide electrode from 5° to 40° . B. B. OWEN and L. FOERING (J. Amer. Chem. Soc., 1936, 58, 1575—1577).—Data have been obtained by comparison with the Ag-AgCl electrode in Na₂B₄O₇ solutions. The Ag-AgBr (fused) electrode is highly reproducible.

E. S. H.

Potential of mercury electrodes in solutions of salts of other metals. T. ERDEY-GRÚZ and P. SZARVAS (*Z. physikal. Chem.*, 1936, 177, 277—291; cf. A., 1935, 706).—The potential, E , of stationary and dropping Hg electrodes in O_2 -free solutions containing salts of other metals and no Hg ions has been measured. For the stationary electrode E is determined by the concn. of the anions present, and is given approx. by $E = E_0 + k \log a_{\pm}$, where a_{\pm} is the mean ionic activity of the solution. With increase in the capillary activity of the anion E becomes more negative and more definite. It must therefore be supposed that E is due to the adsorption of the anion on the Hg; the above relation indicates that Freundlich's isotherm is valid for the adsorption. The adsorbed anion induces a positive charge on the Hg surface, which is therefore left negatively charged by detachment of drops. This negative charge lessens the adsorption of anions until ultimately at a quite small rate of dropping the surface charge, Q , becomes zero, and E assumes a const. val. which does not change with further increase in the rate of dropping. In the ordinary Paschen dropping electrode the E corresponding with zero Q is reached in the same way, and Hg ions play no part in establishing this val. of E (cf. A., 1933, 128). R. C.

Electrode potentials of dilute amalgams. T. ERDEY-GRÚZ and A. VÁZSONYI-ZILAHY (*Z. physikal. Chem.*, 1936, 177, 292—305).—The potentials, E , of stationary and dropping amalgam electrodes of concn. c in solutions free from Hg ions and O_2 but containing ions of the metal in the amalgam, M , have been measured. At concn. up to a certain crit. concn. c_1 ($\sim 10^{-6}$ g.-ion per litre) E at a stationary electrode is independent of c and approx. the same as E for a pure Hg electrode in that particular electrolyte. As c rises above c_1 E begins to be influenced by the M ions, but varies with c much more rapidly than corresponds with Nernst's electrode potential formula. From a concn. c_2 (10^{-5} — 10^{-4} g.-ions per litre) onwards the relation between E and c follows this formula. A dropping electrode behaves similarly to a stationary electrode, except that c_2 is usually higher. It may be supposed that at concns. up to c_1 , E is determined solely by the adsorption of the foreign ions present in solution (cf. preceding abstract). Between c_1 and c_2 E is determined by the distribution of M ions between the solution and the electrode and also by all the other ions present. R. C.

Potential differences at metal-vapour, vapour-liquid, and liquid-metal interfaces of partially immersed electrodes. C. G. FINK and R. C. DEHMEL (*Trans. Electrochem. Soc.*, 1936, 70, Preprint 23, 245—284).—Apparatus is described for determining the p.d. across the vapour between the exposed portion of a partly immersed electrode and the surface of the solution into which it dips. Experiments with Cu, Au, and Pt electrodes in M solutions of their salts gave the following vals. for the p.d.: in presence of O_2 at 1 atm. pressure, Cu +0.175 (temp. 22°), Au -0.33 (26.9°), Pt -0.19 volt (21.1°); in the absence of O_2 the vals. at the same temp. are: Cu -0.151, Au -0.839, Pt -0.76 volt. When O_2 is introduced the ratio of change in

solution potential to change in p.d. existing across the vapour phase in the case of Cu and Au is approx. 1:100, but is nearer unity for Pt. O_2 causes the solution potential of each metal to become less anodic. In cells having Cu or Au electrodes equilibrium potential is rapidly established, but much less quickly in the case of bright Pt electrodes. Natural atm. ionisation is insufficient to render the p.d. across the vapour phase important as a factor in electrode corrosion. J. W. C.

Polarographic studies with the dropping mercury cathode. LX. Influence of buffers and cations on the electro-reduction of fumaric and maleic acids. E. VOPIČKA (*Coll. Czech. Chem. Comm.*, 1936, 8, 349—365).—In HCl and in AcOH-NaOAc buffers the "half-wave potential" depends on the p_H , and remains const. over a wide range of concn. of maleic and fumaric acids. The former is reduced at more positive potentials than is the latter. In LiOH the "half-wave potential" becomes more positive with increase of p_H and in presence of Ca^{++} the fumarate ion is reduced at more positive potentials than is the maleate ion. C. R. H.

p_H values of some alkaline products. A. T. WILLIAMSON and W. G. OAKES (*J. Text. Inst.*, 1936, 27, 1197—1198).—The following p_H vals. are recorded for 0.2% solutions with H and Sb electrodes: NaOH, 12.69; $Na_2SiO_3 \cdot 5H_2O$, 11.94; $Na_3PO_4 \cdot 12H_2O$, 11.67; Na_2CO_3 , 11.17; $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, 10.11; $Na_2B_4O_7 \cdot 10H_2O$, 9.15; $NaHCO_3$, 8.43. A. G.

Electrochemical reduction potential of pyrrole-aldehyde. G. B. BONINO and G. SCARAMIELLI (*Ric. sci. Prog. tecn.*, 1935, 6, II, 111—112; *Chem. Zentr.*, 1935, ii, 3897).—The reduction potential of pyrrole-aldehyde (I) is 1.254 volts and that of PhCHO 1.054 volts; in accordance with conclusions from Raman spectra, the results suggest that (I) is not enolic in structure. H. N. R.

Influence of pressure on the electrode potential in the electrolysis of water. IV. V. SCHISCHKIN and E. KARNAUCH (*Z. Elektrochem.*, 1936, 42, 693—695; cf. A., 1934, 1178).—Sudden increase of pressure from 1 to 100 kg. per sq. cm. slightly diminishes the cathode potential at a Ni electrode in 5*N*-NaOH, whilst release of the pressure increases it again, especially at low c.d. The effect is > 0.008 volt. A similar but smaller effect is observed for the anode potential at Ni and for the cathode potential at Fe electrodes. It is inferred that the decrease in overpotential forms only a small part in the change of p.d. observed in the electrolysis of H_2O under pressure. J. W. S.

Chemical polarisation of the hydrogen electrode by oxygen and the problem of electrolytic corrosion protection. A. E. LORCH (*Trans. Electrochem. Soc.*, 1936, 70, Preprint 15, 173—178).—The H electrode has been polarised by introducing O_2 into the stream of H_2 ; if i is the current required to polarise the electrode to the same extent as the O_2 it is found that $i = k[O_2]$, when k is an approx. const. The current equiv. of the $[O_2]$ is const. over a wide range of p.d. The bearing on protection from electrolytic corrosion is discussed. R. S. B.

Overvoltage ; effect of fusion of the cathode and the effect of temperature on gas polarisation. A. BUTTS and W. A. JOHNSON (Trans. Electrochem. Soc., 1936, 70, Preprint 19, 205—220).—From the variation of voltage with time and temp. at const. c.d. for cells containing Pt anodes and Wood's metal or Ga cathodes in 25% H_2SO_4 it has been shown that no change in polarisation occurs on melting or freezing the cathode, so that H overvoltage is independent of internal physical structure or total energy content of the cathode. Changes in voltage occur with Wood's alloy which has not reached equilibrium, and sharp changes occur with liquid Ga. The H overvoltage is 0.63 ± 0.05 volt at $70-85^\circ$ on Wood's metal and 0.60 ± 0.05 volt at $25-30^\circ$ on Ga.

R. S. B.

Mechanism of the electrolytic liberation of hydrogen at palladium and platinum. L. KANDLER and C. A. KNORR (Z. Elektrochem., 1936, 42, 669).—The difference in form of the c.d.-cathode potential curve in the electrolysis of $2N-H_2SO_4$ with Pt or Pd electrodes when (a) no gas, (b) N_2 , and (c) H_2 is passed through the cathode vessel during the measurement is attributed to the back reaction $H_2 \rightarrow 2H$, which occurs to a considerable extent in presence of excess of H_2 , but is inappreciable when the H_2 is swept away with N_2 .

J. W. S.

Difficulties encountered in the determination of the decomposition potential of molten salts. P. DROSSBACH (Trans. Electrochem. Soc., 1936, 70, Preprint 18, 201—204).—The neglect of the influence of dispersed metal by many previous investigators leads to errors, owing to the development of a polarisation p.d. If anodic and cathodic regions are not separated current efficiency decreases rapidly with rise in temp. and thermodynamic formulæ cannot be applied to determine the heat of reaction. Polarisation processes are discussed.

R. S. B.

Drop of potential in the metallic electrodes of certain electrolytic cells. C. SNOW (J. Res. Nat. Bur. Stand., 1936, 17, 101—124).—Theoretical. Formulæ are derived for the drop of potential in thin metallic electrodes used for the measurement of the electrolytic resistance of solutions.

O. J. W.

Simultaneous discharge of copper and hydrogen in solutions of complex cyanic salts. O. ESSIN and A. MATANZEV (J. Chim. phys., 1936, 33, 631—639; cf. this vol., 32).—The discharge of Cu in solutions containing $CuCN, 1.5KCN$ is accompanied only by a concn. polarisation due to diminution in $[Cu(CN)_2^-]$ and accumulation of CN^- near the cathode. The current distribution between Cu and H^+ discharged simultaneously is in agreement with a theoretical equation.

R. S.

Co-deposition of metals of the same valency in acid solutions. W. G. PARKS and I. M. LE BARON (Trans. Electrochem. Soc., 1936, 70, Preprint 21, 235—239).—For the metal pairs Zn—Cd, Cu—Cd, Ni—Cu, Zn—Cu, and Ag—Tl in solutions of p_H 5, the limiting % concn. in solution at which the added metal is alone deposited varies linearly with log c.d. The respective effects of difference in electrode potential

and in equiv. wt. of the two metals on the limits of co-deposition are discussed.

J. W. C.

Passivity of iron and steel in nitric acid solutions. X. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 981—1054).—Potentiometric data at 70° indicate that activation of Fe occurs by reduction of Fe_2O_3 to FeO. Passivation is hindered by $CO(NH_2)_2$, due to removal of HNO_2 , and facilitated by $AgNO_3$, which forms HNO_2 in presence of Fe. HCl and H_2SO_4 hinder passivation.

J. S. A.

Energy of activation. C. H. MACGILLAVRY (Chem. Weekblad, 1936, 33, 582—593).—A review.

S. C.

Reaction rates of non-isothermal processes. J. SHERMAN (Ind. Eng. Chem., 1936, 28, 1026—1031).—Mathematical. Reaction rates are derived for various time-temp. relations.

C. R. H.

Explosion diagram. E. M. BRUINS (Chem. Weekblad, 1936, 33, 566—570).—A mathematical analysis of various types.

S. C.

Detonation of gaseous mixtures. J. BRETON (Ann. Off. nat. Combust. liq., 1936, 11, 487—546).—Mixtures of known composition of O_2 or air with H_2 , CO , NH_3 , C_3H_8 , isobutane, C_2H_2 , or Et_2O were passed through a glass tube and detonated with Hg fulminate, photographs of the passage of the wave front being taken on a revolving cylinder. The detonation range in relation to the % of combustible gas in the mixture, and the max. rate of propagation, in m. per sec., with the corresponding mixture composition, are given for each of the above mixtures. The lower limit of detonation of $CO-O_2$ mixtures was considerably lower when a small amount of H_2 was added. An increase of the initial pressure extended the detonation range of H_2-O_2 or H_2 -air mixtures. Mixtures in the vicinity of the upper or lower limit produced helicoidal explosive waves. The photographic method enabled a study to be made of the non-luminous phenomena and of the mechanism of rupture of the glass tube as the explosive wave passed.

R. B. C.

Propagation of explosion condensation through air. L. THOMPSON (Physical Rev., 1935, [ii], 47, 811).—The velocity and intensity functions as affected by the quantity of explosive detonated and by the distance from the centre of the pulse at the instant of disintegration have been investigated.

L. S. T.

Latent energy in explosions. W. T. DAVID and A. S. LEAH (Phil. Mag., 1936, [vii], 22, 513—523).—The heat loss and pressure reached in explosions of CO , H_2 , C_5H_{12} (vapour), C_2H_2 , and C_2H_4 with O_2 or air, in different proportions, and at initial pressures of 0.25, 0.5, and 1 atm. have been determined. The amount of incomplete combustion increases as the initial pressure of the inflammable mixture decreases and is considerable at pressures <1 atm. This incomplete combustion is due to long-lived latent energy left in the exploded gases, which varies with the nature of the combustible gas, the nature of the diluent gas, and the pressure of the mixture before explosion.

A. J. M.

Measurements of flame velocity by a modified burner method. F. A. SMITH and S. F. PICKERING (J. Res. Nat. Bur. Stand., 1936, 17, 7—43).—The velocity of propagation of flame in mixtures of air with various combustible gases has been studied by means of the Bunsen-burner method. Data are given on the effect of varying the size of the air-inlet, of changing the velocity of flow of the mixture from the burner, of changing the composition of the mixture, and of different methods of measuring the flame and of calculating the results. Apparatus is described and the limitations of the method are discussed. O. J. W.

Period of induction of cold flames in pentane-oxygen mixtures. B. AIVAZOV and M. NEUMANN (Z. physikal. Chem., 1936, B, 33, 349—367).—The equation $\tau = Ae^{\gamma/T} [(a+b/d^2)/(1+[N_2]/p)]^2 (p-p_0)^2$ has been obtained empirically for the relation between the period of induction of the cold flame, τ , temp., T , vessel diameter, d , pressure, p , min. pressure at which a cold flame is formed, p_0 ($A, \gamma, a, b = \text{const.}$). MeCHO and NO₂ reduce both τ and p_0 . To explain the formation of cold flames it is suggested that the oxidation of hydrocarbons is a slowly developing chain reaction in which there is intercation of the chains, and that the reaction follows the equation $dn/dt = n_0v - gn + fn + f'n^2$, where n_0 is the no. of active centres formed in 1 sec., v the length of the primary chain, g the chain-breaking factor, and f the chain-branching factor, and $f'n^2$ takes account of the chain interaction; f' is very small. At low pressures $g > f$ and the reaction is stationary, whilst at higher pressures $f > g$ and the reaction is autoaccelerated. This theory accounts for the above experimental relation. R. C.

Reaction between ammonia and carbon dioxide. T. YOSHIDA (Proc. Imp. Acad. Tokyo, 1936, 12, 191—194).—H₂O vapour is necessary for the interaction of NH₃ and CO₂. The data indicate that the reaction is of the second order and has a negative temp. coeff. C. R. H.

Relative rates of combination of hydrogen and deuterium with ethylene. A. WHEELER and R. N. PEASE (J. Amer. Chem. Soc., 1936, 58, 1665—1668).—In the homogeneous reaction near 500° the rate of reaction for H₂ is 2.5 times that for D₂; in the catalytic reaction over Cu at 0° the rate for H₂ is twice that for D₂. Exchange reactions are unimportant. E. S. H.

Reactions of deuterium atoms with methane and ethane. E. W. R. STEACIE and N. W. F. PHILLIPS (J. Chem. Physics, 1936, 4, 461—468).—The D atoms were produced by the discharge tube method and by photosensitisation with Hg. The activation energies of the reactions with CH₄ and C₂H₆ are 11.7 and 6.3 kg.-cal., respectively (cf. A., 1935, 457). Experiments with CH₃-C₂H₅ mixtures show that the reaction C₂H₅+CH₃=C₂H₄+CH₄ does not occur under the conditions. The mechanisms are discussed, and the measured activation energy, 6.3 kg.-cal., is that of the reaction D+C₂H₆=C₂H₅+HD; hence the process H+C₂H₆=Et+H₂ has approx. the same energy of activation. The bearing

of these results on the theory of free radical chains is discussed. J. G. A. G.

Prototropy in relation to the exchange of hydrogen isotopes. I. Rates of isomerisation and of hydrogen isotope exchange in unsaturated nitriles. C. K. INGOLD, E. DE SALAS, and C. L. WILSON (J.C.S., 1936, 1328—1334).—The rate of interconversion of Δ^1 -cyclohexenyl- (I) and cyclohexylidene- (II) -acetonitrile in 0.1N-NaOEt-EtOD has been compared with the rates of isotopic exchange between (I), (II), and the system (I) \rightleftharpoons (II) and the medium at 25°. Rapid isotopic interchange (too great to be measured) of 2 H of (I) with D from the medium is followed by slow conversion of (I) into (II), which is in turn more rapid than H exchange between (II) and the medium, and is accompanied by a diminution in the D content of the total nitrile (I)+(II). Contrary to Kandiah *et al.* (A., 1929, 1294), the equilibrium proportion of (II) is indistinguishable from 100%. Analysis of the system (I) $\xrightleftharpoons[k_2]{k_1}$ mesomeric ions $\xrightleftharpoons[k_4]{k_3}$ (II) shows that $k_1 \gg k_2$, $k_3 \gg k_4$, and $(k_1/k_2) \gg (k_3/k_4)$, the equilibrium val. of the ratio (D : H ratio in one exchanging position in the nitrile)/(D : H ratio in the exchanging position in EtOH) being 0.67. The lower D content of (II) than of (I) is explained by the fact that the two positions concerned in exchange in each nitrile both of these in (I) and only one in (II) attain isotopic equilibrium with the medium, the second position in (II) being filled irreversibly, H⁺ being taken up 4.1 times as fast as D⁺. H⁺ is withdrawn from the nitrile 2.75 times as fast as D⁺ by the OEt' ions of the medium. J. W. B.

Homogeneous unimolecular decomposition of gaseous alkyl nitrites. VI. Decomposition of *n*-butyl nitrite. E. W. R. STEACIE and W. McF. SMITH (J. Chem. Physics, 1936, 4, 504—507; cf. this vol., 33).—The rate of decomp. of 4—43 cm. of Bu^oO·NO at 170—212° has been determined by the pressure changes. The reaction is unimol. and homogeneous, and the primary step is BuNO₂=BuO+NO, but the reaction is not simple, as some tarry matter is also formed. The temp. coeff. leads to the energy of activation 36,000 kg.-cal. approx. Comparison shows that at 189.9°, $k_{Me}:Et:Pr:Pr^o:Bu^o = 0.97 : 1.89 : 3.95 : 3.70 : 8.88 \times 10^{-4}$ (cf. A., 1935, 938). J. G. A. G.

Decomposition of azomethane. III. Effect of inert gases. D. V. SICKMAN and O. K. RICE (J. Chem. Physics, 1936, 4, 608—613; cf. this vol., 684).—Kinetic data at 290° and 310° for Me₂N₂—"inert" gas mixtures afford relative activating efficiencies, α , from which the following activating efficiencies per collision are calc.: Me₂N₂ 1.00, N₂ 0.21, CO 0.13, CH₄ 0.20, H₂O 0.46, CO₂ 0.25, D₂ 0.37, and He 0.07. The uniquely low val. for He suggests that exchange of vibrational energy between mols. is more probable than the transition of translational to vibrational energy. The val. of α varies with pressure in mixtures of Me₂N₂ with H₂, C₂H₆, and C₃H₈, and Me₂N₂ initiates a chain decomp. in *iso*-C₄H₁₀. J. G. A. G.

Thermal decomposition of acetone. J. R. HUFFMAN (J. Amer. Chem. Soc., 1936, 58, 1815—

1816).—The unimol. rate coeff. falls at low pressures in accordance with theory based on a free-radical chain mechanism.

E. S. H.

Kinetics of an inverse diene synthesis in the pure liquid state. (A) B. S. KHAMBATA and A. WASSERMANN. (B) A. WASSERMANN (*Nature*, 1936, 138, 368, 369; cf. this vol., 684).—(A) Between 100° and 150° the decomp. of dicyclopentadiene in the pure liquid state follows the Arrhenius equation, and the rate const. is $3 \times 10^{13} e^{-35400/RT}$ sec.⁻¹ in agreement with the const. in paraffin.

(B) Activation energies and temp.-independent factors are given.

L. S. T.

Velocity of hydrolysis of chlorine. E. A. SHILOV and S. M. SOLODUSHENKOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, 3, 15—19; cf. A., 1935, 939).—Measurements were made at 1.2° and 18° by Hartridge and Roughton's flowing stream method (A., 1923, ii, 744) using Schmidt's mixing arrangement (A., 1929, 919); changes of concn. were followed conductometrically. The direct determination gave vals. of the velocity coeff. m in the equation $-d[Cl_2]/dt = m[Cl_2] - n[HOCl][H^+][Cl^-] = 125$ at 1.2° and $=700$ at 18°, in good agreement with those given by the chlorination of PhOH (cf. A., 1926, 831).

R. C. M.

Decomposition of fluosilicate ion in aqueous and in aqueous salt solutions. A. G. REES and L. J. HUDLESTON (*J.C.S.*, 1936, 1334—1338).—The decomp. of SiF_6^{2-} in alkaline solution is unimol., the mechanism being: $SiF_6^{2-} = SiF_4 + 2F^-$ (slow), $SiF_4 + 3H_2O = 4HF + H_2SiO_3$ (rapid), followed by neutralisation of the acid. k is unaffected by alkali concn. or presence of added electrolyte. The degree of initial dissociation of the SiF_6^{2-} (R_0) is deduced, and $K = a_{SiF_4} a_{F^-}^2 / a_{SiF_6^{2-}}$ calc. Added electrolyte decreases R_0 owing to the increase of ionic strength of the solution, in quant. agreement with theory.

A. J. E. W.

Kinetic and equilibrium measurements of the reaction $2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$. A. V. HERSHEY and W. C. BRAY (*J. Amer. Chem. Soc.*, 1936, 58, 1760—1772).—Rate measurements at 25° and ionic strength 0.09 in aq. solutions containing H^+ , Fe^{+++} , Fe^{++} , I^- , I_2 , K^+ , and NO_3^- have been determined and evaluated. Intermediate compounds involved are discussed. Equilibrium data have been determined.

E. S. H.

Kinetics of the reaction between ferric and stannous perchlorates in acid solution. M. H. GORIN (*J. Amer. Chem. Soc.*, 1936, 58, 1787—1795).—Determinations of rate at 55° and 70° give no evidence of a direct reaction between Fe^{+++} and Sn^{++} . The rate-determining step for the reduction of Fe^{+++} is $Fe(OH)_2^+ + Sn^{++} \rightarrow$. When the hydrolysis equilibria are maintained the rate law is $d(Fe^{++})/dt = 2k_3 k_1 k_2 (Fe^{+++})(Sn^{++}) / (H^+)^2$ when $[Fe^{+++}]$ is high compared with $[Sn^{++}]$. The hydrolysis equilibria have been studied in the light of the above rate law.

E. S. H.

Influence of solvents on reaction velocity. Interaction of pyridine and methyl iodide and benzoylation of *m*-nitroaniline. N. J. T. PICKLES and C. N. HINSHELWOOD (*J.C.S.*, 1936, 1353—1357).—The bimol. reactions between C_5H_5N and MeI ,

and between $BzCl$ and $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$, have been examined using various solvents, and vals. of k and the activation energy E obtained. The influence of the nature of the solvent on the consts. P and E in the equation $k = PZ e^{-E/RT}$ (Z = collision no.) is discussed, Z being assumed const. For active solvents, E remains nearly const., P varying in approx. parallelism with the dipole moment of the solvent. For inert solvents E increases. Variations in P are discussed.

A. J. E. W.

Kinetics of acid and alkaline hydrolysis of esters. W. B. S. NEWLING and C. N. HINSHELWOOD (*J.C.S.*, 1936, 1357—1361).—Vals. of k and the activation energy E for the acid and alkaline hydrolysis of a no. of esters in aq. $COMe_2$ solution have been obtained, and are discussed in relation to the equation $k = PZ e^{-E/RT}$ (cf. preceding abstract). For a given ester, P is approx. const. for acid and alkaline hydrolysis, suggesting analogous mechanisms. Possible mechanisms are discussed. Results for P are not in accord with Soper's entropy change relation.

A. J. E. W.

Reaction kinetics of acid hydrolysis of phenolic ethers. R. P. GHASWALLA and F. G. DONNAN (*J.C.S.*, 1936, 1341—1346).—The acid hydrolysis of eight substituted anisoles and four substituted phenetoles by HCl and HBr has been investigated. The reactions are pseudo-unimol. with acid in excess, and formally of the third order with equiv. acid and ether, $[HCl]^2$ occurring in the equation for k . This may be due to the formation of an intermediate oxonium compound the decomp. of which determines k , or to the acid functioning as undissociated mols. The effect of nuclear substituents on k is discussed.

A. J. E. W.

Reaction of paraformaldehyde with cyanide.—See this vol., 1362.

Inflammation of dust clouds.—See B., 1936, 964.

Initial velocities of reduction of hæmatite and magnetite with hydrogen. G. I. TSCHUFAROV and B. D. AVERBUCH (*Z. physikal. Chem.*, 1936, B, 33, 334—348; cf. this vol., 570).—The initial rate of reduction, v , in H_2 at 0.001—0.1 mm. and at 300—800° has been determined. If a piece of magnetite is repeatedly heated in H_2 so that reduction proceeds a stage further each time, v at a given H_2 pressure increases with the no. of heatings, showing that reduction is autocatalysed. In the earlier stages of the reaction there is a period of induction which increases with fall in the temp. or H_2 pressure. These observations are accounted for if it is supposed that reaction begins at active centres on the oxide surface, and when reaction occurs at a centre several new ones are formed. Above 600° the active surface is reduced by recrystallisation of the active centres, resulting in v being much smaller than at lower temp.

R. C.

Autoxidation of unsaturated hydrocarbons. I. P. PANJUTIN, L. HINDIN, and O. VASILJEEVA (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, 2, 183—186).—An $EtOH$ solution of KI and conc. H_2SO_4 was mixed with C_6H_6 and kept in the dark for 4 hr. The amount of unchanged KI was determined by means of oxid-

ation with Fe^{III} salts. Liberated I was absorbed in KI and titrated with $\text{Na}_2\text{S}_2\text{O}_3$. The peroxide no. in g. of I is calc. from a formula. W. R. A.

Kinetics of rapid reactions. II. Starch iodide. H. VON HALBAN and H. EISNER (Helv. Chim. Acta, 1936, 19, 915—927; cf. A., 1935, 1082).—Measurements by the streaming method of the rate of decolorisation of starch iodide by sulphite (I) or thiosulphate (II) indicate that at 25° the rate-determining process is the reaction between I and the reducing agent, the dissociation of the complex being immeasurably rapid. The observed rates decrease with increasing age of the complex and are, *cæteris paribus*, higher for (II) than for (I). The speed of reaction with (I) increases, and with (II) decreases, with increase of $[\text{H}^+]$. F. L. U.

Kinetics of heterogeneous organic reactions. II. Reaction between benzyl chloride and solid silver nitrate in the presence of inert diluents. M. V. NABAR and T. S. WHEELER (Proc. Indian Acad. Sci., 1936, 4, A, 91—96; cf. A., 1935, 1466).—The presence of dry Et_2O , CHCl_3 , and CCl_4 inhibits the reaction, the effect of Et_2O being most marked. The rate of reaction \propto the surface of AgNO_3 present, but is independent of the initial amount of a given mixture of CH_2PhCl and diluent. Results can be reproduced by a kinetic equation based on the assumption that the rate of reaction for a given initial mixture of CH_2PhCl and diluent depends only on the surface of the AgNO_3 . The effect of the diluent may be due to adsorption on the AgNO_3 surface. N. M. B.

Autocatalysis in chemistry and biology. A. MITTASCH (Chem.-Ztg., 1936, 60, 793—794).—A review.

Influence of nitric oxide on the thermal decomposition of dimethyl ether. Gaseous catalysis. P. F. GAY and M. W. TRAVERS (Nature, 1936, 138, 546—547; cf. this vol., 825, 1072).—Small amounts of NO reduce the rate of the thermal decomp. $\text{Me}_2\text{O} = \text{CH}_3 + \text{CH}_3\text{O}$, but larger amounts rapidly increase it. The reaction of NO with Me_2O gives rise to processes resulting in the formation of a short-lived intermediate which can decompose in two different ways. The oxidations can be represented by the equations $\text{Me}_2\text{O} + \text{O} \rightarrow \text{OMe} \cdot \text{CH}_2 \cdot \text{OH}$ (I) $\rightarrow (\text{CH}_4 + \text{CO}_2 + \text{H}_2)$ or $(\text{CH}_4 + \text{CO} + \text{H}_2\text{O})$ and (I) + O $\rightarrow \text{OMe} \cdot \text{CH}(\text{OH})_2 \rightarrow (\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O})$ or $(\text{MeOH} + \text{CO} + \text{H}_2\text{O})$. L. S. T.

Ozone as an oxidising catalyst. XIII. Rate of transformation of systems obtained by ozonisation of aldehydes. E. BRINER and A. LARDON (Helv. Chim. Acta, 1936, 19, 1062—1074; cf. this vol., 1075).—The system PhCHO (I)— BzO_2H (II) is transformed into BzOH at approx. the same rate as is that obtained by ozonisation of (I), whence it is inferred that the peroxide formed in the latter reaction is (II). In support of this, the speed of the reaction between (I) and (II) is greater in C_6H_{14} than in CCl_4 , corresponding with the higher proportion of (II) formed in the former solvent by ozonisation. The speed of reaction between MeCHO and AcO_2H , and the proportion of the latter formed by ozonisation, are greater in CCl_4 than in C_6H_{14} . The course of the

transformation cannot be represented by any of the usual equations, and the process is considered to depend on chain reactions. F. L. U.

Rates of some acid- and base-catalysed reactions, and dissociation constants of weak acids in "heavy" water. J. C. HORNEL and J. A. V. BUTLER (J.C.S., 1936, 1361—1366).—The rates of hydrolysis in H_2O and D_2O of MeOAc , acetal (I), and $\text{CH}(\text{OEt})_3$ (II) in acid solution, and of diacetone alcohol in alkaline solution have been determined by observing changes in n or η . Acid hydrolysis of (I) or (II) was used to determine the ratio of the dissociation consts. of some weak acids in H_2O and D_2O ($K_{\text{D}}/K_{\text{H}}$). This ratio increases as K increases; this is interpreted by a modification of Halpern's theory (A., 1935, 1203), $K_{\text{D}}/K_{\text{H}}$ being determined mainly by the force const. between the proton and the acid anion. A. J. E. W.

Catalytic decomposition of diazoacetate ion in aqueous solution. C. V. KING and E. C. BOLINGER (J. Amer. Chem. Soc., 1936, 58, 1533—1542).—The reaction of $\text{CHN}_2 \cdot \text{CO}_2^-$ with H_2O is extremely sensitive to general acid catalysis. The mol. catalytic const. for H^+ , 3.57×10^8 at 25°, is the highest recorded for any reaction. The mol. catalysis consts. decrease with increasing base or acid concn. There is a linear relation between the mol. consts. and the reciprocal of the base concn., except at low vals. of base concn. Mol. acid consts. at high base concn. agree with the Brønsted theory. Salt effects are described in relation to the mechanism. E. S. H.

Catalytic action of lactoflavin-5'-phosphoric acid.—See this vol., 1418.

Application of transition state method to the heterogeneous reaction on hydrogen electrode; absolute calculation of isotopic interchange reaction velocity, cathodic and anodic currents, and isotopic separation factor. G. OKAMOTO, J. HORIUTI, and K. HIROTA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 223—251).—The transition state method has been applied to the calculation of abs. reaction velocities for the H-Ni electrode, the rate-determining step being $\text{H}_2 + 2\text{Ni} \rightleftharpoons 2\text{H-Ni}$. The authors' experimental results for anodic and cathodic currents, separation factor for H and D, velocity of interchange of H and D in H_2O , and temp. coeffs. of these processes, together with the relative adsorption velocities of H_2 and D_2 on Ni, and overvoltage, are successfully accounted for. The (110) plane of Ni is the most active, and activation of the catalyst probably consists in increasing the extent of the (110) plane, not the no. of active centres. R. S. B.

Activation of specific linkings in complex molecules at catalytic surfaces. II. Carbon-hydrogen and carbon-carbon linkings in ethane and ethane-d. K. MORIKAWA, W. S. BENEDICT, and H. S. TAYLOR (J. Amer. Chem. Soc., 1936, 58, 1795—1800; cf. this vol., 1213).—The exchange reaction between C_2H_6 and D_2 on a Ni catalyst occurs at lower temp. (100—130°) than that required for the reaction to yield CH_4 (160—300°). The formation of CH_4 has been studied kinetically; the surface reaction is

inhibited by H_2 . At low $[H_2]$ the side reactions $2C_2H_6=C+3CH_4$ and $C+2H_2=CH_4$ may predominate. The reaction of C_2H_6 with H_2 in presence of Ni, forming CH_4 , has an activation energy approx. 43 kg.-cal.; the corresponding val. for the reaction with D_2 is approx. 0.5 kg.-cal. higher. The activation energy of dissociative adsorption at the C-C linking is deduced to be $>$ that of the C-H linking. The prep. of C_2D_6 is described. E. S. H.

Water-gas reaction at a platinum surface at low pressure. G. M. SCHWAB and K. NAICKER (Z. Elektrochem., 1936, 42, 670—673).—The reaction between CO_2 and H_2 on a heated Pt wire has been studied at pressure of 0.01—0.1 mm. The temp. coeff. of the velocity of reaction (v) of an equimol. H_2SO_4 -dried mixture at 1300—1500° indicates a heat of activation of 35 kg.-cal. per mol. Excess of CO_2 has little effect on the reaction, which is unimol., but shows an initial period of autocatalysis which disappears when CO is initially present in the reaction vessel. This effect is attributed to preformation of active centres. When the gases are P_2O_5 -dried there is no autocatalysis and the reaction is of zero order, CO has a retarding effect, whilst excess of H_2 is without effect. When the gases are dried to a H_2O -v.p. of 2×10^{-4} mm. by immersion in a bath at -90° , v has a very high temp. coeff. between 700° and 800°, and above about 900° remains const. at a high val. This indicates that with P_2O_5 -dried gases there is a retardation of the reaction, attributed to poisoning of the active centres. J. W. S.

Kinetics of ammonia synthesis on technical iron catalyst.—See B., 1936, 985.

Catalytic methanisation of carbon monoxide in industrial gases.—See B., 1936, 915.

[Catalytic] preparation of ethyl alcohol from ethylene.—See B., 1936, 918.

[Catalytic] preparation of hydrocarbons of the butadiene series from alcohols.—See B., 1936, 970.

[Catalytic] synthesis of acetic acid.—See B., 1936, 970.

Mechanism of [catalytic] hydrogenation of naphthalene.—See B., 1936, 971.

Preparation of nickel-kieselguhr catalysts.—See B., 1936, 986.

Catalytic hydrolysis of *p*-dichloro- and *p*-dibromo-benzene by steam.—See B., 1936, 970.

Structure of the electric double layer of platinised platinum and velocity of hydrogenation of benzene in a liquid medium. B. FORESTI (Gazzetta, 1936, 66, 464—475; cf. following abstract).—The rate of hydrogenation of C_6H_6 suspended in solutions of KCl of varying p_H and in presence of platinised Pt has been measured. There is a max. velocity at about $p_H 0$, which corresponds with the p_H at which the Pt electrode has zero charge. O. J. W.

Relation between the activity of the hydrogen ions of the medium and velocity of hydrogenation of benzene and of oxygen in a liquid medium and in presence of platinum. B. FORESTI (Gaz-

zetta, 1936, 66, 455—459).—The rate of hydrogenation of O and of C_6H_6 suspended in aq. solutions in presence of platinised Pt is greatly influenced by the p_H of the solution, especially when the Pt catalyst is very active. O. J. W.

Temperature coefficient of the electrolytic separation of the hydrogen isotopes. H. F. WALTON and J. H. WOLFENDEN (Nature, 1936, 138, 468).—The temp. variation of the electrolytic separation of the H isotopes at Hg and Ag cathodes has been measured at c.d. \approx 1 milliamp. per sq. cm. At Ag, the separation coeff. falls with a rise in temp., whilst that at Hg is practically unchanged. Addition of α -naphthaquinoline, which might be expected to inhibit any catalytic mechanism, lowers the coeff. markedly in both cases, and changes the sign of the temp. coeff. L. S. T.

Electrolytic preparation of silver salts.—See B., 1936, 1000.

Electrodeposition of cadmium.—See B., 1936, 997.

Theory of electrodeposition of chromium.—See B., 1936, 997.

Influence of various acid radicals on chromium [plate] hardness.—See B., 1936, 997.

Electrodeposition of molybdenum.—See B., 1936, 997.

Causes of electrochemical corrosion of iron and its alloys in moist aerated media.—See B., 1936, 994.

Electrolytic production of ferro-vanadium.—See B., 1936, 996.

Effect of addition of cadmium salts to nickel-plating baths.—See B., 1936, 997.

Electroplating of antimony.—See B., 1936, 997.

Europium. H. N. MCCOY (J. Amer. Chem. Soc., 1936, 58, 1577—1580).—The electrolytic reduction of Eu^{+++} to Eu^{++} is described. The reduction potential of the Eu^{+++} , Eu^{++} electrode is 0.4313 volt. In solutions of Eu^{++} complete absorption of visible light occurs below 4480 Å.; the bands of the absorption spectrum of Eu^{+++} solutions are not shown. The stability of Eu^{++} solutions to oxidation has been investigated. Cryst. $EuSO_4$ is stable in air. Iodometric methods for the determination of Eu are described. E. S. H.

Electrochemical investigations with α -hydroxy-acids. E. TOMMILA (Ann. Acad. Sci. Fennicæ, 1936, A, 46, 1—95; cf. A., 1935, 960).—The electrolytic oxidation of a no. of aliphatic and aromatic α -OH-acids in 2—5*N*-NaOH solution and with bright and platinised Pt, Ni, and Fe anodes has been investigated. With Ni and Fe anodes the reaction proceeds almost independently of anode potential, yielding almost exclusively the corresponding α -keto-acids, whilst at Pt anodes it yields mainly CO_2 and the next lower aldehyde. Under special conditions H_2 and hydrocarbons can be formed at a bright Pt anode, this phenomenon being least common with the lower members of the series. For each α -OH-acid there are two separate regions of oxidation potential,

corresponding with decomp. with and without O_2 evolution, respectively. In some cases periodic oscillation between the two potentials is observed.

J. W. S.

Polarographic studies with the dropping mercury cathode. LXI. Effect of buffer solutions on the reaction of proteins. R. BRDIČKA (Coll. Czech. Chem. Comm., 1936, 8, 366—376).—The catalytic effect of ovalbumin, peptone, and cysteine in lowering the over-potential of the deposition of H ions has been investigated in buffer solutions. The presence of cystine nuclei in the protein is considered essential for the catalytic action.

C. R. H.

Chemical action of electric discharges. XI. Production of nitric oxide by the electric arc at high frequency in mixtures of nitrogen and oxygen at reduced pressure. E. BRINER, B. SIEGRIST, and H. PAILLARD (Helv. Chim. Acta, 1936, 19, 1074—1079; cf. this vol., 571).—Yields of HNO_3 >500 g. per kw.-hr. have been obtained from equimol. mixtures of N_2 and O_2 by combining the use of a high-frequency arc (10^7 cycles) with reduction of the gas pressure to about 70 mm. Such yields are due to the much smaller min. energy required to maintain a stable discharge. Under the conditions stated excess of O_2 in the mixture and addition of Li to the electrodes have a less favourable influence.

F. L. U.

Kinetics of recombination of iodine atoms. E. RABINOWITCH and W. C. WOOD (J. Chem. Physics, 1936, 4, 497—504; cf. this vol., 398, 437).—The equilibrium $I_2 + h\nu \rightarrow I + I$, $I + I \rightarrow I_2$ in the presence of added gases is heterogeneous at low pressures. The atoms recombine mainly by diffusion to the walls, and the dissociation increases with rising pressure. At higher pressures, sp. for the added gas (e.g., 250 mm. in He, 40 mm. in CO_2) there is a fairly sharp transition and the recombination becomes homogeneous. The walls have practically no effect at pressures > the transition val., and the dissociation \propto (light intensity) $^{\frac{1}{2}}$ and (pressure) $^{-\frac{1}{2}}$, in accordance with the theory for recombination by three-body collisions. The velocity coeffs. of the reaction $I + I + X \rightarrow I_2 + X$ for the different added gases, X, are calc., and the order of efficiency in promoting recombination is $He < A < H_2 < N_2 < O_2 < CH_4 < CO_2 < C_6H_6$. At atm. pressure, one binary collision of I atoms in 530 leads to recombination in He, but one in 50 is fruitful in CO_2 (cf. this vol., 801).

J. G. A. G.

Photochemical reduction of nitrates. R. CULTERRA (Gazzetta, 1936, 66, 440—446).—When aq. solutions of HNO_3 or of metallic nitrates are exposed to sunlight, or to the light of a C arc or of a quartz Hg lamp, some reduction to NO_2' takes place. With the Hg lamp radiation reduction to NH_3 may also occur. In both reactions O_2 is evolved. The effect of various factors on the amount of reduction products formed has been studied.

O. J. W.

Theory of desensitisation. LÜPPO-CRAMER (Z. wiss. Phot., 1936, 35, 197—200).—AgBr-collodion emulsions (not dye-sensitised) are scarcely desensitised by the usual dyes. This fact was used by Weber (this vol., 808) for his theory of desensitisation as a

process of oxidation of chemical or optical sensitising substances. Previous work by the author has, however, shown that the latent image of collodion emulsions is resistant to bleaching and other reactions. The facts are therefore more in accord with the older theory that desensitisation is a process of oxidation of at. Ag to Ag^+ ions.

J. L.

Influence of grain size, separation, and distribution on the capability of enlargement of photomicrographs of biological objects. F. BUCHTHAL and G. G. KNAPPEIS (Z. wiss. Phot., 1936, 35, 177—192).—The characteristics of the grains of nine emulsions have been determined by photomicrographs of single-grain layers within the emulsion and by microphotometric records of density. No definite relation between any characteristic and the capability of enlargement could be found. The methods of measurement and the results obtained are fully discussed.

J. L.

Colloid substrate in photosynthesis. M. COPISAROW (Nature, 1936, 138, 509).

L. S. T.

Photochemical decomposition of methane. P. A. LEIGHTON and A. B. ŠTEINER (J. Amer. Chem. Soc., 1936, 58, 1823).— H_2 and unsaturated hydrocarbons (probably C_2H_4) are produced when CH_4 is irradiated with the light transmitted by a thin fluorite window from a H_2 discharge tube.

E. S. H.

Photochemical oxidation of methane, methyl chloride, and methylene chloride sensitised by chlorine. W. BRENSCHÉDE and H. J. SCHUMACHER (Z. physikal. Chem., 1936, 177, 245—262).—When a mixture of Cl_2 and O_2 with CH_4 , $MeCl$, or CH_2Cl_2 is irradiated with light of λ 436 m μ the principal products are HCl and CO; small amounts of $COCl_2$, H_2O , and less volatile org. compounds are also formed. The reaction has a chain mechanism and a quantum yield referred to CO formation rising from about 80 to 800 in the order $CH_4 < MeCl < CH_2Cl_2$. From CH_4 and $MeCl$ reaction proceeds by way of $MeCl$ and CH_2Cl_2 , and CH_2Cl_2 , respectively. Up to the formation of CH_2Cl_2 there is little oxidation of the hydrocarbon radicals participating in the chains. CH_2Cl_2 , however, forms by collision with a Cl atom the $CHCl_2$ radical, which reacts with O_2 to give CO and HCl, some peroxide of short life being an intermediate product; after a period of induction the velocity of this reaction becomes const.

R. C.

Action of ultra-violet light on halogenated hydrocarbons.—See this vol., 1358.

Behaviour of iodine in sensitised decompositions of gaseous organic compounds. R. F. FAULL and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1936, 58, 1755—1758).—Spectroscopic evidence shows that the [I] during sensitised decomp. of gaseous Et_2O , $MeCHO$, $PrCHO$, $(CH_2)_2O$, $MeOH$, HCO_2Me , or CH_2O is very low. Definite chemical reactions are involved in the decomp.

E. S. H.

Photochemical formation of peroxides. VI. Oxidation of formic acid in ultra-violet light by molecular oxygen. Photochemical formation of performic acid. R. CANTENI (Helv. Chim. Acta, 1936, 19, 1153—1158; cf. this vol., 1091).—Peroxide

is formed in both anhyd. and aq. HCO_2H in presence of O_2 on exposure to ultra-violet light of short λ . The peroxide (I), which is not H_2O_2 , is assumed to be performic acid. In presence of HCO_2H (I) decomposes at a rate which increases with its concn., so that a steady concn. is attained, which in the aq. acid is never $>0.75\%$ in consequence of the strong ultra-violet absorption. F. L. U.

Mechanism of decomposition. I. Vapour-phase photolysis of acetic acid. II. Photolysis of formic acid. M. BURTON (J. Amer. Chem. Soc., 1936, 58, 1645—1654, 1655—1657).—I. During photolysis, H atoms, but no free Me radicals, are formed. The production of at. H is favoured slightly by decrease in λ ; none is produced at $\lambda > 2300 \text{ \AA}$. Energies of activation for two reactions involving AcOH and H atoms have been calc. A free-radical mechanism is put forward. The detection of H atoms in presence of free Me is described.

II. No H is produced during photolysis of HCO_2H ; a mechanism for the production of OH is formulated. A reaction with a fairly low energy of activation occurs between H and HCO_2H . Experiments with MeCHO show CHO to be a stable radical at room temp. E. S. H.

Photo-rearrangement of *o*-nitrobenzaldehyde to *o*-nitrobenzoic acid. L. KÜCHLER and F. PATAT (Monatsh., 1936, 68, 275—289).—The quantum yield in the photo-conversion of $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ into $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ in the vapour phase is $>$ for this reaction in solution (cf. A., 1931, 1251; 1935, 48), but is <1 . The mechanism of the reaction is discussed. J. W. S.

Photochemical deamination of amino-acids in water solution. C. WEIZMANN, E. BERGMANN, and Y. HIRSHBERG (J. Amer. Chem. Soc., 1936, 58, 1675—1678).—Glycine, alanine, betaine, and aspartic acid are hydrolysed in aq. solution under the influence of ultra-violet light, yielding corresponding OH-acids. The kinetics and quantum yields of the reactions have been determined and a mechanism is suggested. E. S. H.

Photochemical studies. XXIV. Photochemical chlorination of dichlorobenzenes. C. F. FISK and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1936, 58, 1707—1714).—The rates of photochemical chlorination of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ are equal. The rate \propto the light intensity at low intensities, but \propto some power of the intensity between 0.5 and 1.0 at higher intensities. The rate is independent of $[\text{Cl}_2]$, but \propto $[\text{C}_6\text{H}_4\text{Cl}_2]$. The mechanism is discussed. E. S. H.

Chemical reactions produced by ionisation processes. I. Ortho-para hydrogen conversion by α -particles. H. EYRING, J. O. HIRSCHFELDER, and H. S. TAYLOR (J. Chem. Physics, 1936, 4, 479—491).—Theoretical. The processes occurring in a gas ionised by α -particles are considered. In H_2 , approx. one ion in 5—9 is associated with a mol. Stable states of H_2^- exist, but the probability of formation is very small. Most neutralisation processes involve H_3^+ , and 2—3 H atoms are produced, corresponding with 3—4 H atoms per ion pair formed. At. H is responsible for the large ratio of para- H_2

converted with respect to ions produced by α -particles (cf. this vol., 171). H atoms are removed only slowly by the process $\text{H} + \text{H} + \text{H}_2 \rightarrow 2\text{H}_2$ compared with the speed of recombination at the wall of the vessel, and Hg atoms are not effective. The results accord with the data (*loc. cit.*). J. G. A. G.

Radiochemical synthesis and decomposition of hydrogen bromide. H. EYRING, J. O. HIRSCHFELDER, and H. S. TAYLOR (J. Chem. Physics, 1936, 4, 570—575).—Theoretical. A mechanism is developed whereby the variations of yield per ion pair with change of $[\text{H}_2]$, $[\text{Br}_2]$, and $[\text{HBr}]$ are accounted for quantitatively (cf. this vol., 688). In pure H_2 six H atoms are formed per ion pair, whilst in pure HBr six mols. are decomposed. In equal mixtures of Br_2 and HBr, an electron forms a negative ion from HBr more frequently than from Br_2 . J. G. A. G.

Separation of isotopes. G. CHAMPETIER (Bull. Soc. chim., 1936, [v], 3, 1701—1727).—A lecture.

Exchange between sodium iodide and ethyl iodide. D. E. HULL, C. H. SCHIFLETT, and S. C. LIND (J. Amer. Chem. Soc., 1936, 58, 1822—1823).—Exchange between radioactive NaI and EtI in EtOH at 100° is demonstrated. E. S. H.

Preparation of magnesium hypochlorite.—See B., 1936, 986.

Graduated [thermal] decomposition of barium dihydrogen oxalate dihydrate measured by the emanation method. B. SAGORTSCHEV (Z. physikal. Chem., 1936, 177, 235—240).—There are formed successively $\text{BaH}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$, $\text{BaH}_2\text{C}_2\text{O}_4$, $4\text{BaC}_2\text{O}_4\cdot\text{H}_2\text{C}_2\text{O}_4$ (decomp. above 210°), BaC_2O_4 , and BaCO_3 . R. C.

Mercuric halides, cyanide, and thiocyanate. K. BRAND and I. TÜRK (Pharm. Zentr., 1936, 77, 591—593).— HgCl_2 , HgBr_2 , HgI_2 , and $\text{Hg}(\text{CN})_2$ crystallise with 2, $\text{Hg}(\text{SCN})_2$ with 1 mol. of dioxan of crystallisation which is readily lost in air. Dioxan is a good solvent for recrystallisation of HgI_2 . R. S. C.

Base-exchanging properties of synthetic aluminosilicate materials.—See B., 1936, 986.

Recent developments in the chemistry of the rare-earth group. B. S. HOPKINS (J. Chem. Educ., 1936, 13, 363—368).—An address. L. S. T.

Separation of yttrium from the yttrium earths. H. C. FOGG and L. HESS (J. Amer. Chem. Soc., 1936, 58, 1751—1753).—Y is separated by fractional pptn. with $\text{CO}(\text{NH}_2)_2$ at 90 — 95° . E. S. H.

Extraction of indium from cylindrite, chalcopyrite, and metallic tin. F. M. BREWER and E. BAKER (J.C.S., 1936, 1290—1294).—Sn in metallic Sn is pptd. as SnS_2 , and In subsequently co-pptd. with $\text{Al}(\text{OH})_3$; alternatively, treatment with Cl_2 volatilises Sn as SnCl_4 , leaving In in the residue. Cu and Fe in chalcopyrite are pptd. with nitroso- β -naphthol (I); some In is carried down, and separation is poor with low In content, making this source inconvenient. Pb, Sn, and Sb in cylindrite (an analysis of which is given) are pptd. as sulphides. In is then pptd. (with Fe and Zn) as hydroxide; Fe is separated with (I), and $\text{Zn}(\text{OH})_2$ dissolved out with aq. NH_3 .

Treatment with NaHSO_3 gives in basic sulphite. Elimination of traces of Fe is troublesome.

A. J. E. W.

Concentration of the carbon isotope. H. C. UREY, A. H. W. ATEN, jun., and A. S. KESTON (J. Chem. Physics, 1936, 4, 622—623).—The % of ^{13}C was increased from 1.06 to 1.36 by using CO_2 and aq. KHCO_3 containing carbonic anhydrase in a counter-current fractionating column apparatus.

J. G. A. G.

Corrosion of silica by chlorine.—See B., 1936, 989.

Properties of the oxides of nitrogen. V. Combustion in the system nitric anhydride-ozone. J. T. LEMON and T. M. LOWRY (J.C.S., 1936, 1409—1412).—Mixtures of N_2O_5 and ozonised O_2 (7—8% O_3) contain a blue gas, probably NO_3 . The mixture ignites at $<100^\circ$, burning with a characteristic blue flame and producing N_2O_4 . The NO_3 appears to burn in O_3 with liberation of O_2 : $\text{NO}_3 + \text{O}_3 = \text{NO}_2 + 2\text{O}_2$ or $2\text{NO}_3 = 2\text{NO}_2 + \text{O}_2$. Once the combustion is initiated, a reaction such as $\text{N}_2\text{O}_5 + \text{O}_3 = 2\text{NO}_2 + 2\text{O}_2$ may occur.

A. J. E. W.

Nitrosyl of A. Angeli. L. CAMBI (Ber., 1936, 69, [B], 2027—2033; cf. Oddo *et al.*, this vol., 460).—Anhyd. MeCHO , EtCHO , Pr^cCHO , and BuCHO do not react with $\text{Na}_2\text{N}_2\text{O}_3$; Angeli's reaction with formation of NaNO_2 and $\text{OH}\cdot\text{CR}\cdot\text{N}\cdot\text{ONa}$ is immediately induced by a little H_2O . In anhyd. media $\text{PhSO}(\text{OH})\cdot\text{N}\cdot\text{ONa}$ (I) reacts immediately with MeCHO and EtCHO : (I) \rightarrow $\text{R}\cdot\text{SO}_2\text{Na} + \text{NaNO}$ and $\text{NaNO} + \text{R}\cdot\text{CHO} \rightarrow \text{OH}\cdot\text{CR}\cdot\text{N}\cdot\text{ONa}$. After removal of the excess of aldehyde, the salt-like residue does not give the reactions characteristic of Piloty's acid (II). With MeCHO and EtCHO (II) yields compounds thus: $\text{R}\cdot\text{CHO} + 2\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{OH}$ (III)— H_2O whereas with Pr^cCHO a mixture of $\text{Pr}^c\text{CHO} + 2(\text{III}) - \text{H}_2\text{O}$ and $\text{Pr}^c\text{CHO} + (\text{III}) - \text{H}_2\text{O}$ results. These are decomposed in complex manner by alkali, giving N_2 , N_2O , and traces of NO and yielding products containing N and S (including PhSO_2H), but no hydroxamic acids. Their formation therefore does not involve Angeli's reaction. (II) and $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ do not interact appreciably during several days. (II) appears unchanged by PhCHO in anhyd. Et_2O . *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and (II) slowly yield a brown resin and a colourless, cryst. material which does not give hydroxamic acids with alkali. Contrary to Oddo, therefore, it is concluded that Angeli's hypothesis of nitrosyl as an unsaturated radical logically connects the reactions of widely differing substances which only share the ability to afford HNO when decomposed. Nitrosyl therefore belongs to the group of free radicals and is comparable with $\text{NH}\cdot\text{NPh}$ and $\cdot\text{NPh}$. In gaseous and liquid systems the formation of HNO as intermediate has frequently been observed.

H. W.

Preparation of chemically pure phosphoric acid.—See B., 1936, 930.

Metaphosphoric acids. R. SALIH (Rev. Fac. Sci. Univ. Istanbul, 1936, 1, 77—84).— $\text{H}_6(\text{PO}_3)_6$ has been prepared by the action of H_2S on $\text{Pb}_3(\text{PO}_3)_6$. It is inferred from titration curves that four of the acidities are strong and two are weak.

R. S.

Pyridinium vanadate. S. KATZOFF and R. ROSEMAN (J. Amer. Chem. Soc., 1936, 58, 1785—1786).—The prep. and properties of $(\text{C}_5\text{H}_6\text{N})_3\text{V}_5\text{O}_{14}\cdot\text{H}_2\text{O}$ are described.

E. S. H.

Concentration of the oxygen isotopes. H. C. UREY, G. B. PEGRAM, and J. R. HUFFMAN (J. Chem. Physics, 1936, 4, 623).—By means of a 35-ft. fractionating column with alternate cones rotating, the ratio of the O isotopes in H_2O was changed by a factor of three.

J. G. A. G.

Preparation of amidosulphonic acid and imidosulphonates.—See this vol., 1237.

Reactions in which metal atoms are exchanged between a gaseous and a solid phase. G. BECKER, E. HERTEL, and C. KASTER (Z. physikal. Chem., 1936, 177, 213—223).—If H_2 charged with HCl is passed over Cr and then over Fe at 950° the CrCl_2 first formed reacts with the Fe: $\text{Fe} + \text{CrCl}_2 = \text{FeCl}_2 + \text{Cr}$. The Cr atoms formed on the surface of the Fe diffuse inwards, and new crystallites with a body-centred cubic lattice and consisting of a solid solution of Cr in Fe, apparently free from C, grow inwards from the surface; the depth of penetration may reach 1 mm. In the spaces between the Cr-Fe crystallites and between these and the Fe crystallites C accumulates, forming a eutectic alloy containing Cr 5, C 5, Fe 90%. Cr may be introduced into Ni and Co by a process similar to the above.

R. C.

Effect of molecular nitrogen on molybdenum at high temperatures. P. TURY and S. KRAUSZ (Nature, 1936, 138, 331).—Heating Mo wires electrically in N_2 at 1300° raises the yield point and increases the extension of the wire under load. Cold-worked wires react more slowly with N_2 than annealed. Deformation of nitrated wires restores the properties possessed prior to nitriding, but deformed nitrated wires revert to the nitrated stage after flashing even in A for 1—2 sec. Electrical resistivity is unaltered by nitriding. Heating in H_2 or in a vac. denitrates the wires. Contamination of the wire surface by C and the presence of traces of O_2 and/or H_2O vapour in the gas retard penetration of N_2 into the wire.

L. S. T.

Preparation and determination of elementary fluorine. W. T. MILLER, jun., and L. A. BIGELOW (J. Amer. Chem. Soc., 1936, 58, 1585—1589).—Apparatus and procedure for the prep. of F_2 and determination by absorption in Hg are described.

E. S. H.

Complex nickel compounds. I. Formation and solvation of nickelous chloride in some non-aqueous liquids. D. R. CHESTERMAN and A. S. NICKELSON (J.C.S., 1936, 1300—1302).—The reaction between Ni and HCl dissolved in various org. solvents has been studied. The reaction is more vigorous when the solvent is MeOH , EtOH , Pr^cOH , Pr^iOH , or AcOH than when it is Et_2O , MeOAc , or EtOAc . No reaction takes place in CHCl_3 , CCl_4 , CS_2 , C_6H_6 , PhNO_2 , or light petroleum. The following compounds were isolated: $\text{NiCl}_2\cdot\text{MeOH}$; $\text{NiCl}_2\cdot 2\text{MeOH}$;

$\text{NiCl}_2\cdot\text{EtOH}$; $2\text{NiCl}_2\cdot\text{Pr}^c\text{OH}$; $2\text{NiCl}_2\cdot\text{Pr}^i\text{OH}$;

$2\text{NiCl}_2\cdot\text{AcOH}$; $\text{NiCl}_2\cdot\text{Et}_2\text{O}$;

$2\text{NiCl}_2\cdot\text{MeOAc}$.

C. R. H.

Affinity. LXX. Combination of palladium and phosphorus. G. WIEHAGE, F. WEIBKE, and W. BILTZ [with K. MEISEL and F. WIECHMANN] (*Z. anorg. Chem.*, 1936, 228, 357—371).—Heating of Pd sponge in P vapour at 600—700° yields PdP₂. Thermal analysis of the system Pd-PdP₂ indicates the existence of a very stable *tripalladium phosphide*, Pd₃P, the *compound* Pd₅P₂, and a β-mixed crystal phase of mean composition Pd₅P. M.p., v.p., and X-ray measurements indicate no compounds between Pd₅P₂ and PdP₂. The physical properties of Pd-P alloys of various compositions are described.

J. W. S.

Co-ordination compounds of platinous halides with unsaturated substances.—See this vol., 1369.

Application of statistics to quantitative analysis. A. A. BENEDETTI-PICHLER (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 373—377).—A discussion.

E. S. H.

Calculation of mean error in conductometric titration. J. MIKA (*Z. anal. Chem.*, 1936, 106, 248—261).—A method for the convenient calculation of the true equivalence point, subjective errors being eliminated, is developed.

J. S. A.

Isohydric indicator method [for p_H determination]. S. STENE (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 398—399).—Modified procedure is described.

E. S. H.

Use of adsorption indicators in acidimetry and alkalimetry. S. N. ROY (*J. Indian Chem. Soc.*, 1936, 13, 486—487).—HNO₃ or AcOH can be determined by titration with NaOH in presence of Pb(NO₃)₂ and fluorescein or eosin. A slight excess of alkali ppt. Pb(OH)₂, which adsorbs fluorescein or eosin, giving characteristic, coloured dye complexes.

E. S. H.

Micro-determination of active hydrogen with deuterium oxide. R. J. WILLIAMS (*J. Amer. Chem. Soc.*, 1936, 58, 1819—1820).—The substance is dissolved in D₂O, evaporated to dryness, and the increase of wt. due to replacement of active H by D determined. Results are given for hydroxyproline and CO(NH₂)₂.

E. S. H.

Determination of hydrogen, carbon monoxide, and methane.—See B., 1936, 931.

Qualitative micro-analysis by electrolysis and spectrography. Analysis of a mine water.—See B., 1936, 1022.

Significance of spectrum analysis for waterworks.—See B., 1936, 1022.

Titration of chloride ion with mercuric nitrate solutions, using diphenylcarbazide indicator. I. ROBERTS (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 365—367).—Within a definite range of [H⁺], the procedure gives an accuracy of about 0.3%. HgO can be used as a primary standard in the prep. of the Hg(NO₃)₂ solutions.

E. S. H.

Accuracy of the potentiometric iodide-silver titration. I. M. KOLTHOFF and J. J. LINGANE (*J. Amer. Chem. Soc.*, 1936, 58, 1524—1528).—The error is 0.1% at room temp., 0.048% at 70°, and 0.017% at 90°. At the equivalence potential the ppt. con-

tains an excess of I⁻, due to adsorption. Titration at 90° is recommended.

E. S. H.

Determination of microgram quantities of iodine. R. H. HAMILTON, jun. (*J. Amer. Chem. Soc.*, 1936, 58, 1592—1594).—IO₃⁻ can be reduced quantitatively in hot alkaline solution by N₂H₄·H₂SO₄. KI can be extracted with EtOH from a saturated solution of K₂CO₃.

E. S. H.

Determination of free and combined iodine in [pharmaceutical] iodine preparations.—See B., 1936, 1016.

Micro-determination of iodine and iodides. G. ENDRES and L. KAUFMANN (*Z. physiol. Chem.*, 1936, 243, 144—148).—The procedure (A., 1935, 1167) used for the determination of NH₂OH has been adapted for the determination of 10⁻⁵—10⁻⁴N-I (error about 2%) and of I⁻ in concns. >10⁻⁵N, the concn. of the dye produced being determined by means of a photometer. In the determination of I⁻ the liberated I⁻ must be separated from excess of I⁻ by distillation. The concn. of the dye should be >2 × 10⁻⁵ mol. per litre.

W. McC.

Micro-determination of fluorine. Elimination of effect of chloride. W. D. ARMSTRONG (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 384—387).—Modified procedure, based on titration with Th(NO₃)₄, but using aq. instead of alcoholic solutions, is described. The F contents of dental enamel, dentine, and inorg. phosphates have been determined.

E. S. H.

Sodium hyposulphite solutions for the absorption of oxygen. D. QUIGGLE (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 363).—Na₂S₂O₄ solutions are unstable; only freshly-prepared solutions are useful for O₂ absorption.

E. S. H.

Determining oxygen in boiler-feed water.—See B., 1936, 911.

[Detection of] nitrous and nitric acids in drinking water.—See B., 1936, 957.

Determination of nitrites in presence of nitrates and of certain organic substances.—See B., 1936, 985.

Benzidine phosphomolybdate and its use for the colorimetric determination of phosphoric acid. H. ETIENNE (*Bull. Soc. chim. Belg.*, 1936, 45, 516—538).—Benzidine phosphomolybdate has the formula 3C₁₂H₁₂N₂·2H₃PO₄·24MoO₃·22H₂O. The P is pptd. in this form in HCl solution and the ppt. is dissolved by heating with 2% aq. N₂H₄·H₂SO₄. The resulting blue solution is matched against standards prepared from pure phosphomolybdic acid by treating with aq. N₂H₄·H₂SO₄. 0.2—1.5 mg. of P per 100 c.c. may be determined. As does not interfere. Details are given for the determination of P in cast Fe, steel, minerals, red Cu, and bronze.

H. J. E.

Modifications of the Gutzeit method for determination of arsenic. H. F. CROSSLEY (*J.S.C.I.*, 1936, 55, 272—276T).—The Gutzeit apparatus is modified by the provision of a water cooling-jacket around the staining chamber and a suitable stand to ensure rigidity. Optimum conditions have been determined.

Rapid colorimetric determination of silicon in steel.—See B., 1936, 994.

Volumetric determination of potassium by the sodium cobaltinitrite method. K. SUZUKI and M. KENJO (Rept. Govt. Sugar Exp. Sta., Formosa, 1935, No. 2, 45—55; Internat. Sugar J., 1936, 38, 270).—A modification of the Jendrassik and Takács method (cf. A., 1935, 134) is described; the cobaltinitrite ppt. separated by centrifuging is dissolved in H_2SO_4 , treated with dil. aq. $KMnO_4$, KI added, and the liberated I titrated with $Na_2S_2O_3$. J. P. O.

Determination of sodium in high aluminous material. H. V. CHURCHILL, R. W. BRIDGES, and A. L. MILLER (Ind. Eng. Chem. [Anal.], 1936, 8, 348—349).—Modified procedure, using NH_4F as fusion reagent, is described. E. S. H.

Rapid evaluation of sodium silicate.—See B., 1936, 931.

Sensitiveness of magnesium uranyl acetate reagent to sodium and potassium. C. H. GREENE (Ind. Eng. Chem. [Anal.], 1936, 8, 399—400).—The influence of the vol. ratio of reagent and test solutions and of the addition of EtOH has been investigated. E. S. H.

Determination of sodium and potassium in insoluble silicates. C. C. MILLER and F. TRAVES (J.C.S., 1936, 1390—1394).—The silicate is decomposed by the Lawrence Smith method. Na is pptd. as Na Zn uranyl acetate (cf. A., 1928, 859). Ca interferes, and double pptn. is necessary. K is determined as $KClO_4$ after removal of Ca, Na, and SO_4^{2-} , preferably by preliminary pptn. of K Na cobaltinitrite, which is treated with $HClO_4$, and interfering perchlorates are extracted with $EtOAc-Bu^oOH$. A. J. E. W.

Quantitative separation of lithium, with reference to its determination in insoluble silicates. C. C. MILLER and F. TRAVES (J.C.S., 1936, 1395—1399).—Li may be determined as Li Zn uranyl acetate, $LiZn(UO_2)_3(OAc)_9 \cdot 6H_2O$. Conditions for complete pptn. are crit. Na interferes, and is removed by extracting $LiCl$ and $CaCl_2$ from the mixed anhyd. chlorides with isoamyl alcohol or $COMe_2$; with the former double pptn. is advisable, owing to interference of Ca when present in large quantity. A procedure is given for the determination of Na, K, and Li in silicates (cf. preceding abstract). A. J. E. W.

Qualitative analysis of the alkaline-earth and alkali groups. C. H. GREENE (Ind. Eng. Chem. [Anal.], 1936, 8, 346—348).—A system suitable for laboratory classes is described. E. S. H.

Test-tube flame test applied to the rarer elements. A. R. CLARK (J. Chem. Educ., 1936, 13, 383—384; cf. A., 1935, 1093).—Characteristic flames or residues given by Li, Rb, Cs, Au, Be, B, Sc, In, Tl, Ti, Zr, Ge, Mo, U, Se, and Te are described and sensitivities recorded. The method is especially applicable to a final identification after the usual group separations. L. S. T.

Determining hardness of water.—See B., 1936, 1022.

Qualitative analysis of the ammonia and ammonium sulphide groups and of phosphoric acid. W. FISCHER, W. DIETZ, K. BRÜNGER, and H. GRIENEISEN (Angew. Chem., 1936, 49, 719—731).—An excess of Fe is added, and then aq. NH_3 . The ppt. is dissolved in HCl , Fe is extracted with Et_2O , and Zr, Ti, La, and any co-pptd. Zn, Mn, Co, Ni, Ca, etc. are then pptd. with $NaOH+H_2O_2$. Cr, V, and U are pptd. by treating the filtrate with HCl , $Na_2S_2O_4$, and $NaOH$ successively. P and W are pptd. from the remaining solution by means of $BaCl_2$. Subsequent separations of the sub-groups so obtained follow usual lines. The scheme is expeditious and minimises the loss by adsorption on earlier ppts. of elements present in small amounts. J. S. A.

Analysis of cations of third and second [fourth] groups in presence of phosphate ion. V. J. PETRASCHENJ (Z. anal. Chem., 1936, 106, 241—243).—After pptn. of the second analytical group, $(NH_4)_2S$ and $(NH_4)_2HPO_4$ are added. The ppt. is redissolved in dil. HCl , and Cr and Mn are oxidised completely either by $Na_2CO_3+Br-H_2O$, or by Na_2O_2 . The ppt. is treated with $AcOH$ to dissolve Mg, Ca, Sr, and Ba. Subsequent separations are orthodox. J. S. A.

Spectrographic micro-determination of zinc. A. P. VANSELOW (Ind. Eng. Chem. [Anal.], 1936, 8, 400).—A correction (cf. this vol., 1308). E. S. H.

Electrolytic micro-determination of zinc and its application to brass. P. WENGER, C. CIMERMANN, and G. TSCHANUN. Volumetric micro-determination of zinc. C. CIMERMANN and P. WENGER (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 113—116, 116—119).—Practical details are described; calc. and experimental results are in agreement. N. M. B.

Preparation and some analytical applications of 2:7-diaminofluorine. E. L. NIÑO and F. CALVERT (Anal. Fis. Quím., 1934, 32, 698—701).—An improvement of the technique of Schmidt *et al.* (A., 1931, 1045) is described. The use of 2:7-diaminofluorene (I) is preferred to H_2S for detection of Cd after removal of Cu by means of $KCNS$. In a solution containing 0.2—0.6% of Zn with added EtOH the Zn is determined by addition of (I) in EtOH; the ppt. is dried at 90° . The error is >1 part in 1000. (I) is suitable for the detection of blood peroxidases (cf. Schmidt *et al.*, A., 1932, 242) but not for determination of Zn in presence of Al or of Cd or Cu. F. R. G.

Cause of contamination of precipitates. II. Precipitation processes involving lead salts. Z. KARAOGLANOV (Z. anal. Chem., 1936, 106, 262—272; cf. this vol., 1220).—Further data for Pb salts are reviewed, and advanced in support of the author's theory of contamination by secondary reaction products. The known compounds $Pb(OH)X$ ($X=Cl, Br, I, CNS$) are considered to be such secondary products. Their formation involves the partly ionised complexes PbX' and the degree of contamination follows the extent to which such complexes are present in solution; e.g., contamination with $PbBr_2 > PbCl_2 > Pb(CNS)_2 > PbI_2 > Pb(OAc)_2 = 0$. J. S. A.

Determination of metallic copper in cuprous oxide-cupric oxide mixtures. L. C. HURD and A. R. CLARK (Ind. Eng. Chem. [Anal.], 1936, 8, 380—382).— Cu_2O is sol. in cold aq. NH_3 , CuO is slightly sol., and Cu insol. Addition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ causes reduction of any Cu^{++} entering the solution and prevents reaction between Cu^{++} and Cu . In a CO_2 atm. the Cu-CuO mixture may be isolated and Cu determined by direct dissolution in $\text{FeCl}_2 + \text{HCl}$, followed by titration with $\text{K}_2\text{Cr}_2\text{O}_7$. E. S. H.

Electrolytic application of hydrobromic acid test for copper. G. W. BAKER (Analyst, 1936, 61, 603—604).—0.0002 mg. of Cu per sq. mm. on a steel surface may be detected by using the steel as anode, with a Pt wire cathode tipped with cotton-wool which is moistened with aq. KBr . Traces of Cu produce a purple-red stain. J. S. A.

Determination of mercury in air and absorption of mercury vapour by means of metallic gold. V. MAJER (Coll. Czech. Chem. Comm., 1936, 8, 339—348).—Air is passed at a known rate through glass tubing containing Au leaf. One end of the tubing is then sealed and the other drawn out into a fine capillary. On distilling, the Hg condenses in the capillary and is dissolved in $\text{Cl}_2\text{-H}_2\text{O}$ and either determined colorimetrically or reprecipitated on Fe wire, redistilled in a fine capillary, and determined micro-metrically. The determination of Hg by condensing in liquid air has also been investigated. C. R. H.

Effect of aluminium on the flame spectra of the alkaline earths. Determination of aluminium. R. L. MITCHELL and I. M. ROBERTSON (J.S.C.I., 1936, 55, 269—272T).—The presence of Al reduces the intensity of the flame emission lines of Ca and Sr. This reduction depends on the relative amounts of Ca and Sr present; with sufficient Sr in the solution, Al does not appreciably affect the Ca emission and *vice versa*. The Ca or Sr depression may be used as an indication of the amount of Al present.

Separation and determination of aluminium and zinc. F. H. FISH and J. M. SMITH, jun. (Ind. Eng. Chem. [Anal.], 1936, 8, 349—350).—Al is pptd. as Li aluminate from solutions containing NH_4OAc ; Zn is determined in the filtrate as $\text{Zn}_2\text{P}_2\text{O}_7$. E. S. H.

Arc spectrographic determination of indium in minerals, and association of indium with tin and silver. F. M. BREWER and E. BAKER (J.C.S., 1936, 1286—1290).—Known sources of In are reviewed. The In content of certain Sn, Sb, Ag, Zn, Mn, and Fe minerals, and of specimens of Sn, Cd, and CdO, has been determined spectrographically by the persistence method. Sn ores, particularly sulphides (cylindrite, 0.1—1% In; franckeite, max. 0.1% In), and commercial Sn contained appreciable quantities of In, suggesting a fairly general association of In with Sn. Association in other cases is more sp. Some chalcopyrite samples contained an estimated max. of 0.1% In. A. J. E. W.

Chemical concentration of gallium, indium, thallium, germanium, and rhenium, in their determination in oxide and sulphide ores.—See B., 1936, 931.

Determination of ferrocyanide ion by means of luteocobaltamine chloride. W. A. HYNES, M. G. MALKO, and L. K. YANOWSKI (Ind. Eng. Chem. [Anal.], 1936, 8, 356—357).— $\text{Fe}(\text{CN})_6^{4-}$ is determined by igniting the pptd. $[\text{Co}(\text{NH}_3)_6]_4[\text{Fe}(\text{CN})_6]_3$ and weighing the residue as $8\text{Co}_3\text{O}_4 + 9\text{FeO}_3$. The procedure is suitable in absence of CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, and VO_3^- . E. S. H.

Macro-detection of cobalt. I. F. P. DWYER (J. Proc. Austral. Chem. Inst., 1936, 3, 239—244).—1 part of Co in presence of 1000 parts of Fe may be detected as $(\text{NH}_4)_2\text{Co}(\text{CNS})_4$, which may be extracted with $\text{C}_5\text{H}_5 \cdot \text{OH} + \text{Et}_2\text{O}$, by adding $\text{NaNH}_4\text{HPO}_4$ until the $\text{Fe}(\text{CNS})_3$ coloration is destroyed. Decolorisation with $\text{KHF}_2 + \text{aq. NH}_3$ is applicable, but less sensitive. J. S. A.

Oxidation-reduction indicators for use with dichromate. II. S. COHEN [with R. E. OESPER] (Ind. Eng. Chem. [Anal.], 1936, 8, 364—365).—The prep. and use as indicators of $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$, $\text{NHPh}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{Na}$, and Na diphenylbenzidine-monosulphonate are described. E. S. H.

Determination of chromium, vanadium, and molybdenum in silicate rocks. E. B. SANDELL (Ind. Eng. Chem. [Anal.], 1936, 8, 336—341).—After decomp. of the rock with Na_2CO_3 in the usual way, V is determined with phosphotungstic acid after separation from Cr with 8-hydroxyquinoline (I). In neutral or slightly acid solutions, V^{V} reacts with (I) to give a compound which can be extracted from the aq. solution with CHCl_3 , whereas Cr^{VI} does not react and remains in the aq. layer. Diphenylcarbazide is used as the reagent for Cr, after separation from V. Mo is determined by the $\text{SnCl}_2\text{-KCNS-Et}_2\text{O}$ procedure without previous separation. The method is suitable for determining 0.001% of Cr or V, and 0.0001% of Mo in a 1-g. sample. E. S. H.

Determination of chromium and iron in tanning solutions and in leather.—See B., 1936, 948.

Reducing action of mercury. II. Stability of quinquevalent molybdenum solutions. Determination of molybdenum by reduction with mercury and titration with ceric sulphate. N. H. FURMAN and W. M. MURRAY, jun. (J. Amer. Chem. Soc., 1936, 58, 1689—1692; cf. this vol., 574).— Mo^{V} solutions are sufficiently stable in air at room temp. to be used in analytical procedures which are completed in a few hr. Mo^{VI} is quantitatively reduced to Mo^{V} by shaking with Hg in presence of 2—3.5N-HCl. Mo^{V} can be titrated with $\text{Ce}(\text{SO}_4)_2$ at room temp., using the *o*-phenanthroline- Fe^{++} complex indicator. E. S. H.

Precipitation of uranium, and its separation from alkaline-earth metals by means of pyridine. E. A. OSTROUMOV (Z. anal. Chem., 1936, 106, 244—248).— $\text{C}_5\text{H}_5\text{N}$ ppts. U quantitatively as $\text{H}_2\text{U}_2\text{O}_7$ from solutions of UO_2^{2+} salts. The presence of NH_4 salts is advantageous; in presence of much SO_4^{2-} a large excess of $\text{C}_5\text{H}_5\text{N}$ is necessary. Separation from Ca, Sr, and Ba is quant. J. S. A.

Use of nitrophenylarsinic acid as a reagent for tin. B. TOUGARINOFF (Bull. Soc. chim. Belg., 1936, 45, 542—544).— $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ (0.8% aq. solu-

tion) gives a white flocculent ppt. with Sn^{IV} in HCl or H_2SO_4 solution on boiling. 0.0001 g. of Sn may be detected in 20 c.c. of solution. Hg^{II} , Cu , Ni , Co , Mn , Fe , Cr , Zn , Ba , Sr , Ca , Mg , Bi , and Sb do not interfere. H. J. E.

Colorimetric determination of titanium. M. SCHENK (Helv. Chim. Acta, 1936, 19, 1127—1135).—Substances containing a phenolic OH give with Ti^{IV} in conc. H_2SO_4 in intense red coloration. The intensity decreases with time after 2 hr. The use of $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ permits the determination of Ti in solutions containing 0.2—40 mg. of TiO_2 per litre. The reaction is not affected by other cations, but HNO_2 and HNO_3 must be absent. Operative details are given. F. L. U.

Special reaction of N. A. Tananaev and A. V. Tananaeva for zirconium. I. P. ALIMARIN (Z. anal. Chem., 1936, 106, 276—279).—The reaction, in a more sensitive form, was described by Lundell and Knowles (A., 1920, ii, 60). J. S. A.

Detection of minute quantities of thorium in common materials. R. D. EVANS, G. D. FINNEY, A. F. KIP, and R. MUGELE (Physical Rev., 1935, [ii], 47, 791—792).—The Th emanation flow-technique is inherently inefficient. Four new methods involving counting of α - or γ -rays have been developed. Applied to a series of Sierra Nevada igneous intrusive rocks they indicate that the Th : U ratio is > previously supposed. L. S. T.

Determination of bismuth as phosphate. W. C. BLASDALE and W. C. PARLE (Ind. Eng. Chem. [Anal.], 1936, 8, 352—353).—The procedure is accurate when pptn. is from solutions which contain no Cl^- or SO_4^{2-} , and are approx. 0.2M with respect to HNO_3 , and approx. 0.065M with respect to $(\text{NH}_4)_2\text{HPO}_4$. Na^+ , K^+ , Mg^{2+} , Zn^{2+} , Cu^{2+} , or Ca^{2+} do not interfere; Cd^{2+} and especially Pb^{2+} interfere. Co-pptn. of basic salts is avoided by adjusting $[\text{H}^+]$ and pptg. from a hot solution and digesting for 1 hr. at 80°. E. S. H.

Separation and determination of bismuth with gallic acid. L. KIEFT and G. C. CHANDLEE (Ind. Eng. Chem. [Anal.], 1936, 8, 392).—Pptn. with gallic acid at 70° serves to separate and determine Bi in 3% aq. HNO_3 in presence of Pb , Cd , Cu , Zn , Al , Cr , Fe , Ni , Ba , Ca , Na , and K , but not Sb , Hg , Sn , or Ag . E. S. H.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXXII. Phosphorus, vanadium, and a tannin precipitation series. W. R. SCHOELLER and H. W. WEBB (Analyst, 1936, 61, 585—590).—(a) Small amounts of P, carried down with Ta_2O_5 and Nb_2O_5 on tartaric hydrolysis, are separated by fusion with NaOH followed by extraction with aq. NaCl . Na_3PO_4 , but no Ta or Nb , dissolves. (b) V may be separated from Ti and Ta by twofold pptn. with tannin (I) from $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution half-saturated with NH_4Cl . Ti and Ta are first pptd. by (I); V only on addition of excess of NH_3 . Pptn. of Nb does not occur, or is incomplete. V is separated from Ta and Nb in tartrate solution, by addition of (I)+ NH_4OAc to the neutralised (NH_3) filtrate from the tartaric hydrolysis of Ta_2O_5 and Nb_2O_5 . The ppt. is fused with KHSO_4 , extracted

with (I)+ H_2SO_4 , and repptd. by addition of cinchonine hydrochloride. V in the filtrate is pptd. on adding NH_4OAc . (c) Pptn. by (I), in decreasing acidity of solution, follows the order Ta , Ti , Nb , V , Fe , Zr , Hf , Th , U , Al . Neighbouring metals cannot be separated by fractional pptn. with (I). J. S. A.

Determination of iridium by titration with potassium ferrocyanide. A. A. GRÜNBERG and J. L. MICHELIS (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 179—181).—By titration in H_2SO_4 solution, Ir^{IV} in the form of $(\text{IrCl}_6)^{-}$ can be determined with as great accuracy as by Mohr's salt. W. R. A.

Portable aradiant convection pyrometer. F. T. BARR and R. F. BERGER (Ind. Eng. Chem. [Anal.], 1936, 8, 393—395).—Apparatus and technique are described. E. S. H.

Sensitive thermo-regulator. L. D. GOODHUE (Ind. Eng. Chem. [Anal.], 1936, 8, 387).—Sensitivity is increased by employing the principle of the differential manometer. A range of 0.05° is sufficient to make and break the electrical contact. E. S. H.

Platinum resistance thermometer as a secondary temperature standard between 14° and 90° abs. F. HENNING and J. OTTO (Physikal. Z., 1936, 37, 639—641).—For the calibration of a Pt resistance thermometer, five fixed points are required, according to the equation previously derived (this vol., 1190). Suitable points are the normal b.p. of O_2 , the triple point of H_2 , the normal b.p. of H_2 , the triple point of N_2 , and the β - γ transition point of O_2 . The comparison of the resistance ratios of different Pt thermometers with each other is considered. A. J. M.

Gas furnace with temperature control. D. VAN DUYN (Chem. Weekblad, 1936, 33, 562).—The inner tube of a van den Berg furnace (A., 1934, 162) is enclosed in a brass tube provided with a hole for carrying a thermocouple. Uniform temp. from 500° to 800° can be obtained. S. C.

Determination of thermal expansion of liquids when observation is hindered by the temperature bath. A. LAMBERTZ (Chem.-Ztg., 1936, 60, 755—756).—An Archimedean method is described, the change in apparent wt. of a submerged glass body being determined. J. S. A.

Limiting sensitivity of a radiometer depending on the principle of the gas thermometer. M. VEINGEROV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 119—122).—A radiometer operating by the thermal expansion of gas heated by incident radiation is theoretically more sensitive than other types of instrument. A. J. E. W.

S.N.P. Photo-densimeter [photometer]. A. FAURE and PALLU (Ann. Falsif., 1936, 29, 393—401). E. C. S.

Christiansen filters as polarisers. H. W. FARWELL (Physical Rev., 1936, [ii], 50, 486).—Fibres of viscose and silk, wound on a frame, were used as doubly refracting crystals, and, immersed in CS_2 - C_6H_6 , transmitted green polarised light horizontally and blue polarised perpendicularly. N. M. B.

Frames for protecting and repairing Lovibond colour glasses. E. FREYER (Oil and Soap, 1936, 13, 234—235).—Whole or broken glasses are mounted in light Al slide-holders, with a central window.

E. L.

Simplified and improved cell for liquids in the interferometer. J. W. McBAIN, T. F. FORD, and G. F. MILLS (Rev. Sci. Instr., 1936, [ii], 7, 341—342).—The cell is of block Ag, bored with two tunnels to contain the liquid and carry the light rays; it is suitable for small quantities of liquid, and evaporation difficulties are obviated.

N. M. B.

[Quantitative] spectrum analysis using emission spectra. J. E. MILLS (J. Proc. Austral. Chem. Inst., 1936, 3, 245—250).—The technique of the Gerlach internal standard method is described.

J. S. A.

Apparatus for rapid study of absorption and rotatory power in the ultra-violet. P. GESTEAU (J. Pharm. Chim., 1936, 24, [viii], 201—209).—An ultra-violet spectrograph with polariser attachments is described. It may be employed either for quant. absorption measurements or for determination of α .

W. O. K.

Anomalous diffraction gratings. U. FANO (Physical Rev., 1936, [ii], 50, 573; cf. Wood, this vol., 128; Strong, *ibid.*, 399).—Theoretical.

N. M. B.

Method for accurate titrations. D. B. PALL (Canad. J. Res., 1936, 14, B, 299—300).—A colour comparator is described in which the two tubes on the one side contain H_2O and the coloured solution undergoing titration, respectively, whilst those on the other side contain a solution buffered to the required endpoint p_H and the indicator, and the original solution, without indicator, respectively. The light used is filtered to the colour of the indicator in the buffered tube. The apparatus is of particular use in titration of weak acids with weak bases in coloured solutions.

J. W. S.

γ -Ray sensitivity of tube counters and the measurement of the thorium content of rocks. R. D. EVANS and R. A. MUGELE (Physical Rev., 1935, [ii], 47, 427).—Factors affecting sensitivity are discussed. The feeble γ -radiation from the radioactive impurities in ordinary granitic rocks can be directly measured with the highly-sensitised counters described.

L. S. T.

Counter-controlled cloud chambers. J. C. STREET and E. C. STEVENSON (Rev. Sci. Instr., 1936, [ii], 7, 347—353).—The design and operation of two cloud chambers of the pneumatic rubber diaphragm type are described. One is cylindrical for use with a large electromagnet, and the other is a rectangular one of wood for cosmic-ray shower studies. The expansion ratio is determined by the separation of rigid diaphragm stops.

N. M. B.

Check valve for wash bottles. F. H. SMITH (Ind. Eng. Chem. [Anal.], 1936, 8, 400).

E. S. H.

Gas-absorption vessels. W. M. MARTIN (Ind. Eng. Chem. [Anal.], 1936, 8, 395—396).—A scrubber and a quant. absorption vessel are described.

E. S. H.

Spindle for insulating wires. J. M. STURTEVANT (Ind. Eng. Chem. [Anal.], 1936, 8, 341).

E. S. H.

Apparatus for production of metallic adsorption powders under nitrogen and other gases. F. DURAU (Physikal. Z., 1936, 37, 684—688).—An apparatus for the prep. of powders of hard or soft metals for adsorption and catalysis is described.

A. J. M.

Sensitive manostat for low pressures and its application to the adsorption of hydrogen and deuterium on copper. T. SOLLER, S. GOLDWASSER, and R. A. BEEBE (J. Amer. Chem. Soc., 1936, 58, 1703—1706).—Apparatus for the control of gas pressures to ± 0.005 mm. at any pressure is described. Provision is made for the continuous reading of the vol. of gas entering the system during adsorption. The rates of adsorption of H_2 and D_2 by Cu at 0° and 2.63 mm. are in the ratio 3.35 : 1; the difference in activation energies of adsorption is 0.48 kg.-cal. The temp. inversion in the ratio of adsorbability of H_2 and D_2 has been confirmed.

E. S. H.

Apparatus for dialysis, electro-dialysis, osmosis, electro-osmosis, filtration, and electro-filtration. MEMBRANFILTER G.M.B.H. (Chem.-Ztg., 1936, 60, 767).

E. C. S.

Pneumatic trough. W. H. POWERS and J. WACLAWIK (J. Chem. Educ., 1936, 13, 375).

L. S. T.

Vacuum centrifuge. E. G. PICKELS (Physical Rev., 1935, [ii], 47, 797).—Developments and improvements are outlined (cf. *ibid.*, 336).

L. S. T.

Centrifuging in rotating hollow cylinders. M. SCHLESINGER (Nature, 1936, 138, 549—550).—A new technique for the fractionation of highly disperse systems using relatively moderate centrifugal forces is described.

L. S. T.

Hardness tester for microscopical objects. E. M. H. LIPS and J. SACK (Nature, 1936, 138, 328—329).—Inclusions and structural elements of metallographic specimens may be identified by measurement of their hardness. A hardness tester attached to a microscope is described, and its use is illustrated by reference to a Cu-Al alloy and pearlitic cast Fe containing P.

L. S. T.

[Small] hydrogen sulphide generator. E. GLASGOW (J. Chem. Educ., 1936, 13, 382).

L. S. T.

Action of fume-chambers. E. BREZINA, W. SCHMIDT, and W. SCHWAB (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 171—178).—Observations of the behaviour of fumes in different models of fume-chambers indicate the design necessary for max. efficiency.

M. A. B.

Approach towards the limit in the process of extraction. C. W. GRIFFIN and M. VON SAAF (Ind. Eng. Chem. [Anal.], 1936, 8, 358—360).—Experimental data for the extraction of solutes from one solvent by another solvent are in agreement with theoretical predictions (cf. B., 1934, 223).

E. S. H.

Special head for Kjeldahl distillation apparatus. C. E. WEAKLEY, jun. (Ind. Eng. Chem. [Anal.], 1936, 8, 367).

E. S. H.

Origin of modern chemical symbols and formulæ. J. R. PARTINGTON (Chem. and Ind., 1936, 759—762).

Saint Vincent de Paul and the alchemist. F. WALKER (J. Chem. Educ., 1936, 13, 353—357).

L. S. T.

Joan Baptista van Helmont. J. R. PARTINGTON. Val Helmont's ice and water experiments. T. S. PATTERSON (Ann. Sci., 1936, 1, 359—384, 462—467).—Historical.

Natural classification of chemical substances. R. HOOYKAAS (Chem. Weekblad, 1936, 33, 599—610).—A lecture.

Geochemistry.

Atmospheres of the fixed stars. H. LAM-BRECHT and B. JUNG (Naturwiss., 1936, 24, 577—582).—A review. A. J. M.

Composition of the planetary nebulae. T. L. PAGE (Nature, 1936, 138, 503—504).—Relative abundances of N, O, A, Ne, and S in N.G.C. 7662 and N.G.C. 7027 have been calc. The high abundances of Ne and A relative to O are discussed. L. S. T.

Oxygen content of the stratosphere. E. REGENER (Nature, 1936, 138, 544).—The vol.-% of O₂ decreases from 20.89±0.05 at 14.5 km. to 20.39±0.05 at 28—29 km. L. S. T.

Ozone as a heating factor in the atmosphere. R. PENNDORF (Nature, 1936, 138, 247).—The heating effect due to O₃ is calc. for various atm. layers. A max. occurs at a height of 50 km. where the heating is approx. 10 times the cooling effect. L. S. T.

Size of atmospheric nuclei: deductions from measurements of the number of charged and uncharged nuclei at Kew observatory. H. L. WRIGHT (Proc. Physical Soc., 1936, 48, 675—689).—Formulae are discussed for determining the size of condensation nuclei from observation of the concn. in the atm. of charged and uncharged nuclei and of the no. of small ions of either sign, assuming combination by collision between small ions and uncharged nuclei to be the result of Brownian movement of the former. Assuming that the mass of a small ion is equal to that of 11 H₂O mols., for R.H. <80% the nuclear radius is approx. 3×10⁻⁶ cm., rising to 4.5×10⁻⁶ cm. for 89% R.H. On Köhler's theory of the growth of nuclei in an atm. of increasing R.H., and if the hygroscopic nuclei are of dil. H₂SO₄, the mass of acid in a nucleus in summer is about 18×10⁻¹⁷ g., and in winter 12×10⁻¹⁷ g. N. M. B.

Mineral and medicinal springs of Switzerland. ANON. (Mitt. Lebensm. Hyg., 1936, 27, 49—104, 158—159, 201—203).—Analyses and physical data are recorded.

Surface waters and deep waters in the canton of Geneva. J. BUFFLE (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 129—132; cf. A., 1935, 600).—Mean vals. of the dissolved matter, alkalinity, CaO, and SO₃ of H₂O from wells in different localities and over intervals of 4—27 years are given and discussed. N. M. B.

Petrographic nomenclature. A. K. WELLS (Geol. Mag., 1936, 73, 319—325).—Recommendations made by the British Association Committee, 1932, are summarised. L. S. T.

Geologic deductions from a thermal equation. J. S. DELURY (J. Geol., 1936, 44, 479—495).—A thermal source is indicated for the energy of earth distortion and deformation of the outer lithosphere. Heat is effective for these purposes in direct proportion to the unevenness of its distribution. Radioactive elements, which are regarded as the most important source of heat in outer shells, migrate extensively in geologic time through erosion and movements of magma. Small differences in thermal conductivity and in distribution of radioactive elements lead to large differences in geothermal history. L. S. T.

Contrasted differentiation. A. HOLMES (Geol. Mag., 1936, 73, 228—238).—Critical (cf. Nockolds, *ibid.*, 1934, 71, 31). L. S. T.

Differentiated dyke of Newmains, Dumfriesshire, and its contact and contamination phenomena. W. Q. KENNEDY and H. H. READ (Quart. J. Geol. Soc., 1936, 92, 116—145).—In the granophyric spessartite or markfieldite dyke at Newmains the crystallisation of quartz arises from the breaking-up of plagioclase into albite, epidote, and white mica at a late stage in the consolidation history of the rock. Normal markfieldite is differentiated into basic markfieldite and markfieldite-pegmatite by fractional crystallisation and filter-pressing effect. The junctions of the normal markfieldite against the country rock, a calcareous greywacke, are sharp. Where the markfieldite-pegmatite is in contact with the greywacke, contamination has occurred. This involves a reciprocal reaction whereby the markfieldite-pegmatite loses Al₂O₃, Na₂O, and K₂O, and gains Fe, MgO, and CaO. The chemistry of the contamination process and its influence on the course of mafic crystallisation are discussed. Analyses of the rocks concerned are recorded. L. S. T.

Progressive kinetic metamorphism in the Missi Series near Flinflon, Manitoba. J. W. AMBROSE (Amer. J. Sci., 1936, [v], 32, 257—286).—Pre-Cambrian greywackes and conglomerates show three zones of progressive metamorphism characterised respectively by chlorite, biotite, and garnet. Intruded igneous rocks in the series are also affected in a like degree. These zones are related to the intensity of shearing of the rocks, and it is suggested that the heat developed by this shearing was sufficient to cause the metamorphism. L. J. S.

Minerals in Bates limestone, Lewiston, Maine. L. W. FISHER (Amer. Min., 1936, 21, 321—326).—Igneous intrusions of different types are described. The mineral associations observed in different zones

suggest that the Bates limestone was originally an impure $MgCO_3$ formation. Mineralogical changes produced by various types of metamorphism are described. L. S. T.

Bore-hole investigations in Yellowstone Park. C. N. FENNER (J. Geol., 1936, 44, 225—315).—The structural features of the cores have been examined and temp. and pressures measured. The mineralogy and petrology of cores from various depths are described in detail, and chemical changes which have occurred are discussed. New analyses are recorded. L. S. T.

Geology of a portion of the Savant Lake area, Ontario. G. RITTENHOUSE (J. Geol., 1936, 44, 451—478).—The genesis of two Fe-bearing formations is discussed. L. S. T.

Optics and structure of three-dimensional spherulites. H. W. MORSE and J. D. H. DONNAY (Amer. Min., 1936, 21, 391—426).—The shape and optical properties of artificial spherulites and related aggregates, mainly carbonates, grown by diffusion and metathesis in gelatin have been further investigated (cf. A., 1933, 691). In spite of wide variations in external shape, most of these aggregates belong to the same type of aggregation, due to radiating crystallisation. A mechanism of formation of spherulitic structures is discussed. L. S. T.

(A) Nature of the invisible gold contained in pyrites. (B) Secondary transformations and enrichment of gold in its primary deposits. G. BÜRG (Z. pr. Geol., 1935, 43, 17—26, 65—75, 89—94; Chem. Zentr., 1935, ii, 3897).—(A) The solubility of Au in the system Fe-S decreases as the S content is decreased. On heating the Au enters the pyrites lattice. At 1 atm. the Au-S compounds formed are stable up to 200°. At higher pressures they are stable to 600°. H. J. E.

Microstructures and metallisation of the gold-quartz veins of Cornucopia, Oregon. G. E. GOODSPEED (Econ. Geol., 1936, 31, 398—416). L. S. T.

Quartz from Bavena. P. GALLITELLI (Period. Min., 1935, 6, 105—128; Chem. Zentr., 1935, ii, 3896).—Data are given of the characteristic habit of quartz from Bavena. It is concluded that the quartz was formed at <575°, and separated before the minerals of the pneumatolytic phase. J. S. A.

Relation of the granite-gneiss and the schists and quartzites in W. Africa. P. LEGOUX (Compt. rend., 1936, 202, 2090—2092).—A discussion. H. J. E.

Minerals of Bavena granite: fayalite. E. GRILL (Period. Min., 1935, 6, 129—133; Chem. Zentr., 1935, ii, 3896).—Inclusions are identified as partly oxidised fayalite. J. S. A.

Epidote from Aceglio (Valle Maira). R. RONDOLINO (Period. Min., 1935, 6, 153—167; Chem. Zentr., 1935, ii, 3896). J. S. A.

Copper deposits of the Southern Appalachian region. C. N. FENNER (Econ. Geol., 1935, 30, 928—936).—A discussion of the views of Ross (U.S. Geol. Survey, Prof. Paper 179, 1935). L. S. T.

Copper deposits of the Southern Appalachian region. C. S. ROSS (Econ. Geol., 1936, 31, 428—432).—A reply to criticism (cf. preceding abstract). L. S. T.

Supergene sphalerite, galena, and willemite at Balmat, N.Y. J. S. BROWN (Econ. Geol., 1936, 31, 331—354).—The occurrence of willemite, chlorite, hæmatite, ilvaite, and magnetite, and of a second generation of sphalerite, galena, and chalcopyrite, believed to be of supergene origin, is described. L. S. T.

Asbestos deposits of Thetford district, Quebec. H. C. COOKÉ (Econ. Geol., 1936, 31, 355—376).—The geological setting of the deposits is outlined and the relation of the asbestos veins to faults is described. Theories of origin of the veins are discussed. L. S. T.

Nodular, orbicular, and banded chromite in northern California. W. D. JOHNSTON, jun. (Econ. Geol., 1936, 31, 417—427).—The minerals are described and analyses are given. The genetic significance of the structures is briefly discussed. L. S. T.

Possible age of monazite from Mars Hill, N. Carolina. J. P. MARBLE (Amer. Min., 1936, 21, 456—457).—The monazite crystal described by Schaller (A., 1934, 628) contains Pb 0.152—0.175, Th 5.526—5.596, and U 0.016—0.019%; approx. age 584×10^6 years. L. S. T.

Structure and chemical composition of greenalite. J. W. GRUNER (Amer. Min., 1936, 21, 449—455).—The X-ray diagrams of greenalite (I) from the Fe formation of the Mesabi Range indicate that it is similar in structure to serpentine. The formula approximates to $9FeO, Fe_2O_3, 8SiO_2, H_2O$ or $(OH)_{12}Fe^{II}_9Fe^{III}_2Si_8O_{22}, 2H_2O$. The ratio $Fe_2O_3 : FeO$ varies considerably and some MgO usually replaces FeO. (I) is actually anisotropic, but appears to be isotropic on account of its fineness of grain and dark colour. L. S. T.

Crystallographic data, unit cell, and space-group for berthierite ($FeSb_2S_4$). M. J. BUERGER (Amer. Min., 1936, 21, 442—448; cf. *ibid.*, 205).—The Weissenberg method gives a 11.44, b 14.12, c 3.76 Å; space-group $Pnam (V_2^h)$; $4 FeSb_2S_4$ per unit cell. L. S. T.

Two monzonitic series of the Newry complex. D. L. REYNOLDS (Geol. Mag., 1936, 73, 337—364; cf. A., 1935, 1100).—Analyses and petrographic descriptions of olivine-monzonite and syenite are given. The two converging monzonitic series in the hybrids of Seeconnell, and their relationships, are established on a chemical basis. L. S. T.

Enderbite, a new member of the charnockite series. C. E. TILLEY (Geol. Mag., 1936, 73, 312—316).—The name *enderbite* is suggested for an acid member of the charnockite series characterised by rhombic pyroxene in which plagioclase (oligoclase or andesine) is the essential feldspar. Enderbite from Proclamation Island, Enderby Land, Antarctica, has SiO_2 75.50, Al_2O_3 13.92, Fe_2O_3 0.48, FeO 1.17, MgO 0.52, CaO 3.54, Na_2O 3.64, K_2O 0.74, P_2O_5 none, TiO_2 0.08, MnO none, H_2O —0.30, H_2O+ 0.15, total 100.04%; d 2.67. L. S. T.

Origin of the Salton volcanic domes, Salton Sea, California. V. C. KELLEY and J. L. SOSKE (J. Geol., 1936, 44, 496—509). L. S. T.

Datolite and herderite. H. STRUNZ (Z. Krist., 1936, 93, 146—150).—Herderite, $\text{Ca}(\text{F},\text{OH})\text{BePO}_4$, is monoclinic prismatic, a_0 4.80, b_0 7.68, c_0 9.80 Å, β 90° 6', space-group C_{2h}^2 , and is thus isomorphous with the silicate datolite, $\text{Ca}(\text{OH})\text{BSiO}_4$. A probable structure is discussed. B. W. R.

Analcite rock from Cloudy Bay, Marlborough, New Zealand J. A. BARTRUM (New Zealand J. Sci. Tech., 1936, 18, 120—123).—The shapes of the abundant large crystals of analcite (I) in the tinguaitite described indicate that earlier phenocrysts of nepheline had been replaced by (I) before the rock solidified. After the magma had been injected into fissures (I) crystallised conjointly with ægirine-augite from the aq. magma to form the felted matrix in which the phenocrystic minerals are embedded. A. G. P.

Eulysites and related rock types from Loch Duich, Ross-shire. C. E. TILLEY (Min. Mag., 1936, 24, 331—342).—Eulysite (a type not previously recognised in the British Isles) is a dense rock composed of fayalite, hedenbergite, iron-hypersthene, garnet, magnetite, and apatite. Chemical analyses are given of this and of related hedenbergite-garnet-magnetite-rock and gruncrite-garnet-magnetite-rock. These rocks have probably been formed by the

metamorphism of sediments rich in Fe and SiO_2 , i.e., siliceous Fe ores. L. J. S.

Effects of heat on the optical orientation of plagioclase feldspars. C. T. BARBER (Min. Mag., 1936, 24, 343—352).—Feldspars of different composition after heating at 1000° show no appreciable change in the optical orientation and the optic axial angle. L. J. S.

Reciprocal rôle of alumina in reaction series. A. BRAMMALL (Min. Mag., 1936, 24, 362—366).—The immiscibility gap in the clinoenstatite-diopside series is related to the (NaSi)-(CaAl) replacement in the plagioclase series, the rôle of Al atoms in the two series being reciprocal. L. J. S.

Chlorophyll and hæmin derivatives in organic minerals. A. TREIBS (Angew. Chem., 1936, 49, 682—686).—A review (cf. A., 1935, 727). F. O. H.

Alterations of nitrogen content of organic substances during and after deposition. K. KREJCI-GRAF (Z. pr. Geol., 1935, 43, 97—101; Chem. Zentr., 1935, ii, 3753).—The disappearance of N in sapropel corresponds with the conditions of decomp. in marine deposits. The ratio C:N affords no evidence of the age of sedimentary deposits. J. S. A.

Selenium in Hawaii [soils] and its probable source in the United States.—See B., 1936, 986.

Selenium compounds in soils.—See B., 1936, 1011.

Organic Chemistry.

Algebraic calculation of the numbers of isomers of certain organic compounds. G. POLYA (Z. Krist., 1936, 93, 415—443).—Mathematical. The "symmetry formula" for the basic substance is fundamental; from it by simple algebraic substitution the no. of possible isomerides of various types is directly derived. Formulæ are summarised for the chief org. series. B. W. R.

Steric hindrance. E. DE ROY VAN ZUYDEWIJN and J. STURMAN (Chem. Weekblad, 1936, 33, 540—542).—From a theoretical discussion it is concluded that steric hindrance, although highly probable in some cases, is not yet proved. It is doubtful whether deceleration of a reaction by surrounding the functional group with substituents is purely a question of spatial configuration. S. C.

Reactions of deuterium atoms with methane and ethane.—See this vol., 1344.

Dehydrogenating cracking of ethane. P. FERRERO and E. DELTOMBE (Bull. Soc. chim. Belg., 1936, 45, 455—492).—The reaction was studied by a flow method at 700—1250°/0.1—1 atm. The main reaction is a decomp. into C_2H_4 and H_2 . The C_2H_4 is a max. at 900—950° and the proportion formed increases with the rate of flow. CH_4 is formed in a secondary reaction which entails Me radicals, and increases with rise in temp. C_2H_2 is formed by decomp. of C_2H_4 at >830°. Small amounts of liquid

products (max., approx. 25% of C_2H_6 decomposed) were formed. These were polymerisation products derived from butadiene and C_2H_2 , formed by the dehydrogenation of C_2H_4 , and varied in composition between $\text{C}_n\text{H}_{1.3n}$ and $\text{C}_n\text{H}_{1.6n}$. H. J. E.

Action of ultra-violet light on halogenated hydrocarbons. II. E. MÜLLER and K. EHRMANN (Ber., 1936, 69, [B], 2207—2210; cf. A., 1932, 830).—Prolonged irradiation of $(\cdot\text{CHCl}_2)_2$ with passage of dry N_2 does not lead to elimination of HCl or other marked change. The production of $\text{CHCl}_2\cdot\text{COCl}$ in presence of air (*loc. cit.*) therefore proceeds $(\cdot\text{CHCl}_2)_2 \rightarrow \text{CHCl}_2\cdot\text{CCL}_2\cdot\text{OH} \rightarrow \text{CHCl}_2\cdot\text{COCl}$. Under these conditions CHCl_3 and C_2HCl_3 remain unchanged. $(\cdot\text{CH}_2\text{Cl})_2$ does not appreciably absorb ultra-violet light, but is relatively greatly changed thereby in presence of air. The production of $(\cdot\text{CCl}_2\cdot\text{CHCl}_2)_2$ is attributed to the action of excited O. No part is played by O in the conversion of $\text{C}_2\text{H}_2\text{Cl}_4$ into C_2HCl_3 by boiling alkali since a precisely similar effect is produced by boiling anhyd. $\text{C}_5\text{H}_5\text{N}$. Irradiation with light of short λ in presence of O_2 converts $(\cdot\text{CH}_2\text{Cl})_2$ into $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, C_2HCl_5 smoothly into $\text{CCl}_2\cdot\text{COCl}$, and C_2HCl_3 into $\text{CHCl}_2\cdot\text{COCl}$ with traces of HCl. $\text{CH}_2\cdot\text{CCl}_2$ and $(\cdot\text{CHCl})_2$ evolve much HCl (even in N_2) and give resinous products. Under the experimental conditions, COCl_2 is not obtained from ethylenic compounds. PhCl is unchanged when irradiated in presence of O_2 . CH_2PhCl passes slowly

into BzOH with probable intermediate formation of PhCHO. CPhCl_2 rapidly and completely gives BzCl. H. W.

Organic laboratory chemistry. VI—VIII. E. F. DEGERING (J. Chem. Educ., 1936, 13, 377—382).—Methods for the prep. of $(\cdot\text{CH}_2\text{Br})_2$ and NH_2Ph are detailed. Various pieces of apparatus are described. L. S. T.

Ozonisation of triple linkings. C. D. HURD and R. E. CHRIST (J. Org. Chem., 1936, 1, 141—145).— $\text{CPh:C}\cdot\text{CO}_2\text{H}$, CPh:CH , Δ^{α} -hexinene (details for large-scale prep. of pure hydrocarbon given), Δ^{α} -heptinene, 1-ethinylcyclohexan-1-ol, and ethinylfenchyl alcohol on ozonolysis with 5 and 10% O_3 in CCl_4 followed by hydrolysis of the resulting ozonides give rise to the acids expected on cleavage of the triple linkings in 42, 59, 51, 59, 52, and 61% yield, respectively. H. G. M.

Proposed mechanism for mercury catalysis in acetylene addition reactions. G. F. HENNION, R. R. VOGT, and J. A. NIEUWLAND (J. Org. Chem., 1936, 1, 159—162).—A scheme involving the formation of a highly reactive intermediate compound, $\text{R}\cdot\text{C}(\text{OB})\cdot\text{CR}'\cdot\text{HgA}$, during the addition in presence of HgA_2 of BOH (B=H, alkyl, acyl, aryl, etc.) to an acetylene $\text{CR}:\text{CR}'$ to form $\text{R}\cdot\text{CH}_2\cdot\text{CR}'(\text{OB})_2$ is advanced, and shown to be in accord with, but not proved by, the known facts. H. G. M.

Reactions of alkylacetylenes. XIV. Reaction of butylacetylene with hydrogen bromide. C. A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1806—1808).—Addition of HBr to $\text{CH}:\text{CBu}$ (I) containing an appreciable amount of peroxides (II) [derived from (I)] occurs rapidly at 0° and gives varying amounts (according to time and amount of HBr) of α -bromo- Δ^{α} -hexene (III) and $\alpha\beta$ -dibromohexane (IV). In absence of (II) reaction occurs much more slowly; thus (I) and HBr (>2 mols.) in presence of quinol and FeBr_2 [which rapidly destroys (II)] at $15^\circ/12$ hr. afford β -bromo- Δ^{α} -hexene (V), $\beta\beta$ -dibromohexane (VI), b.p. $83.5\text{--}84^\circ/24$ mm. [hydrolysed (Ag_2SO_4 in 10% H_2SO_4) to COMeBu], a little (III), and much unchanged (I). (III) and (V) also react rapidly with HBr in presence of (II) to give (IV); in absence of (II), (III) yields a little (IV), whilst (V) affords (IV) and (mainly) (VI). H. B.

Acetylene polymerides and their derivatives. XXVI. Reaction of halogeno-ethers with vinylacetylene. H. B. DYKSTRA (J. Amer. Chem. Soc., 1936, 58, 1747—1749).— $\text{CH}_2\cdot\text{CH}\cdot\text{C}:\text{CH}$ (I), $\text{CH}_2\text{Cl}\cdot\text{OMe}$, and BiCl_3 in Et_2O -pyrogallol (antioxidant) at $5\text{--}15^\circ$ give mainly α -chloro- ε -methoxy- $\Delta^{\beta\gamma}$ -pentadiene (II), b.p. $60\text{--}61^\circ/10$ mm. (presumably formed by a 1:4-addition), and some γ -chloro- ε -methoxy- $\Delta^{\alpha\gamma}$ -pentadiene (III), b.p. $46^\circ/10$ mm. (II) rearranges to (III) when treated with CuCl and 18% HCl in Et_2O at $20\text{--}40^\circ$. (II) and (III) are oxidised (KMnO_4) to $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ and $\text{OMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, respectively. (III) and maleic anhydride in COMe_2 at 50° give (after hydrolysis with H_2O) 4-chloro-3-methoxymethyl- Δ^4 -tetrahydrophthalic acid, m.p. $163\text{--}165^\circ$; (II) does not react. (III) polymerises (rate accelerated by light, heat, and catalysts) to a rubber-like resin. γ -Chloro- ε -ethoxy-

b.p. $44^\circ/4$ mm., and ε -butoxy-, b.p. $67^\circ/2$ mm., $\Delta^{\alpha\gamma}$ -hexadienes and α -chloro- ε -ethoxy-, b.p. $56^\circ/4$ mm., and ε -butoxy-, b.p. $79^\circ/2$ mm., $\Delta^{\beta\gamma}$ -hexadienes are similarly prepared from (I) and the appropriate $\text{OAlk}\cdot\text{CHMeCl}$. H. B.

Substitution of fluorine for other halogens by use of mercurous fluoride and iodine. Preparation of methyl fluoride. F. SWARTS (Bull. Acad. roy. Belg., 1936, [v], 22, 781—783).—On the basis of a mechanism previously indicated (this vol., 712) MeF is prepared in 80% yield by gradual addition of Hg_2F_2 (1 mol.) to I (1 mol.) in MeI (>2 mols.). J. T. A.

Condensations by sodium. VII. General method for stopping the Wurtz reaction at the intermediate organometallic stages. A. A. MORTON and I. HECHENBLEIKNER (J. Amer. Chem. Soc., 1936, 58, 1697—1701; cf. this vol., 966).—Addition of n -amyl chloride to Na powder (excess) in C_5H_{12} or light petroleum at $0\text{--}38^\circ$ and subsequent treatment (after initial reaction ceases) with CO_2 gives $\text{C}_5\text{H}_{11}\cdot\text{CO}_2\text{H}$ (22—44.2%) and $\text{CHBu}(\text{CO}_2\text{H})_2$ (I) (8—24%). Analogous results are obtained with (in order of decreasing yield) n -hexyl chloride, PhCl , Bu^nCl (Bu^nBr), *tert.*-amyl chloride, β -chloro- γ -methylbutane, and Pr^nCl . Evidence indicating that (I) is not formed by way of $\text{C}_5\text{H}_{11}\cdot\text{Na}$ is discussed. $\text{C}_5\text{H}_{10}\cdot\text{Na}_2$ has a greater thermal stability than $\text{C}_5\text{H}_{11}\cdot\text{Na}$. H. B.

Determination of alcohol by Widmark's method. E. FLOTOW and G. NAUENBURG (Pharm. Zentr., 1936, 77, 580—581).—An automatic pipette is described for delivering a fixed vol. of $\text{H}_2\text{SO}_4\text{--CrO}_3$ during this determination. Distillation is replaced by keeping overnight, which obviates some causes of inaccuracy. R. S. C.

New types of racemisation reactions. E. BERGMANN and A. BONDI (J. Amer. Chem. Soc., 1936, 58, 1814).—The formation of $(-)\beta$ -methyl- α -diethyl- n -amyl alcohol, b.p. $92\text{--}93^\circ/32$ mm., $[\alpha]_D^{25}\text{--}13.04^\circ$ in COMe_2 , from $l\text{-CHMePr}^+\cdot\text{CO}_2\text{Me}$ (I) and MgEtBr supports the suggestion (A., 1935, 1223) that $dl\text{-CHMePr}^+\cdot\text{CPh}_2\cdot\text{OH}$ [from (I) and MgPhBr] results owing to the equilibrium $\text{CHMePr}^+\cdot\text{CPh}_2\cdot\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CMePr}^+\cdot\text{CPh}_2$. These results are in accordance with the greater ease of dehydration of $\text{CPh}_2\text{Alk}\cdot\text{OH}$ than $\text{CAlk}_3\cdot\text{OH}$. The racemisation of β -bromohexane during its conversion into the Grignard reagent (Porter, *ibid.*, 1228) is probably due to the racemisation of the MgRBr by Br^+ ; the reaction is analogous to the racemisation of CHPhMeCl by interaction with Mg or Na (cf. A., 1933, 574; this vol., 803). H. B.

β -Amyloxyethyl esters of p -aminobenzoic acid. H. V. ASHBURN, A. R. COLLETT, and C. L. LAZZELL (J. Amer. Chem. Soc., 1936, 58, 1549—1551).—The requisite $\text{C}_5\text{H}_{11}\cdot\text{OH}$ (20—30 mols.), $(\text{CH}_2)_2\text{O}$ (7 mols.), and conc. H_2SO_4 (1 c.c.) [or, for (I), Al H silicofluoride] at $130\text{--}150^\circ$ give β -*n*-amyl-, b.p. $188.3^\circ/751.1$ mm., β -*iso*amyl-, b.p. $179.8^\circ/750.1$ mm., β - β' -methylbutyl-, b.p. $176.8^\circ/748$ mm., β - α' -ethylpropyl-, b.p. $172.6^\circ/746.4$ mm., β - α' -methylbutyl-, b.p. $173.8^\circ/746$ mm., and β - α' - α' -dimethyl-

propyl- (I), b.p. 168.4°/745.4 mm., *-oxyethyl alcohols*; the *p-nitrobenzoates* (prep.: A., 1933, 48) have b.p. 191.5—192.5°/4 mm. (II), 184.1—185.1°/4 mm., 188.1—189°/4 mm., 183—184°/4 mm., 186.6—187.6°/4 mm. (m.p. 74.5°), and 164—166°/0.42 mm., respectively, and are reduced (method: A., 1935, 1494) to the *p-aminobenzoates* [that from (II) has m.p. 56.8°; others are viscous oils] (*picramides*, m.p. 115.5°, 140.9°, 129.1°, 136°, 120.8°, and 134.9°, respectively).

H. B.

Influence of nitric oxide on thermal decomposition of dimethyl ether.—See this vol., 1346.

Decomposition of *n*-butyl nitrite.—See this vol., 1344.

Reactions relating to carbohydrates and polysaccharides. XLIX. Mol. wt., molar refraction, f.p., and other properties of polyethylene glycols and their derivatives. A. F. GALLAUGHER and H. HIBBERT (J. Amer. Chem. Soc., 1936, 58, 813—816; cf. this vol., 963).—The mol. wts. of tri- (I), b.p. 115.5—117°/0.1 mm., f.p. -9.4°, tetra- (II), b.p. 144—145.5°/0.1 mm., f.p. -9.4°, penta-, b.p. 174—176°/0.14 mm., f.p. -8.7°, hexa-, b.p. 203—205°/0.3 mm. f.p. 1.3°, and hepta-, b.p. 241—244°/0.6 mm., f.p. 7.7°, *-ethylene glycols*, *tetraethylene glycol monochlorohydrin* (III), b.p. 134.6—136°/0.94 mm., f.p. -54° [by-product during reaction of Na derivative of diethylene glycol (f.p. -10.1°) and (CH₂Cl-CH₂)₂O (IV)], and *diethylene glycol Me₂ ether* [$\beta\beta'$ -*dimethoxydiethyl ether*] (V), b.p. 160.5—161°/756.6 mm. [formed (cf. Cretcher and Pittenger, A., 1925, i, 228) together with a little CH₂:CH-O-CH₂:CH₂:OME from (IV) and MeOH-NaOMe at about 25°], are determined cryoscopically in C₂H₄Br₂. The vals. for (I), (II), (III), and (V) increase regularly with rise in concn.; in the other cases, association is very large at low concns., then decreases to a min., and finally increases. The glycols show an approx. const. increase in mol. refraction with rise in mol. wt. C₂H₄(OH)₂, f.p. -13.2°, (CH₂)₃(OH)₂, f.p. -32°, and (in a smaller degree) *s*-C₂H₄Cl₂ and OMe-CH₂-CH₂:OH appear to form co-ordination compounds with anhyd. CuSO₄.

H. B.

Esters of perchloric acid. J. MEYER and W. SPORMANN (Z. anorg. Chem., 1936, 228, 341—351).—*Me perchlorate*, b.p. 52°, EtClO₄, and *Prⁿ perchlorate*, b.p. 89° can be prepared by distilling a mixture of R₂Ba(SO₄)₂ (R=Me, Et, or Pr) and Ba(ClO₄)₂ into anhyd. Et₂O containing anhyd. CuSO₄, and removing the Et₂O by evaporation. EtClO₄ has also been obtained by very slow addition of anhyd. HClO₄ to EtOH, and MeClO₄ and EtClO₄ by treatment of anhyd. AgClO₄ with RBr in abs. EtOH. MeClO₄ is also produced by treating anhyd. HClO₄ with CH₂N₂. All three compounds explode readily on heating, percussion, or friction. They are readily sol. in Et₂O and EtOH and insol. in H₂O, but are gradually hydrolysed by the latter, the readiness of hydrolysis following the order MeClO₄>EtClO₄>PrClO₄.

J. W. S.

Attempts to prepare cyclic glycerides. Preparation of "tetrachlorodiglycerides" of dicarboxylic acids. M. GOSWAMI and A. SHAHA (J.

Indian Chem. Soc., 1936, 13, 464—466).—Glycerol, the dibasic acid, and POCl₃ at 100° give *di-ββ'-dichloroisopropyl succinate*, b.p. 141—142°/4 mm., *maleate*, b.p. 128—130°/4 mm., *citraconate*, b.p. 228—232°/4 mm., and *phthalate* (I) [from the anhydride (II)], b.p. 260—262°/4 mm. (I) is also obtained from (CH₂Cl)₂CH-OH, (II), and POCl₃.

R. S. C.

Oxidation of formic acid.—See this vol., 1348.

Photolysis of acetic and formic acids.—See this vol., 1349.

Thermal decomposition of the silver salts of carboxylic acids. III. Thermal decomposition of the silver salts of acetic and benzoic acid. S. J. KANEVSKAJA and M. M. SCHEMJAKIN (Ber., 1936, 69, [B], 2152—2157; cf. this vol., 469).—Thermal decomp. of AgOAc affords Ac₂O and large amounts of AcOH, whilst Bz₂O, PhOBz, BzOH, and a small amount of PhOH but not C₆H₆ are derived from AgOBz. In all cases the initial change appears to be decomp. into Ag₂O and the acid anhydride. Subsequently hydration occurs due to H₂O present in the Ag salt or formed by destructive decomp. of the initial acid. PhOH is attributed to the oxidation by Ag₂O of C₆H₆ or Ph formed by thermal decomp. of the anhydride and PhOBz results from nascent PhOH and unchanged Bz₂O.

H. W.

Fluorination of organic compounds. II. P. C. RAY and A. C. RAY (J. Indian Chem. Soc., 1936, 13, 427—428; cf. A., 1935, 733).—CH₂F-CO₂Me, CH₂F-CO₂Et, and CH₂PhF are prepared from the Br-compounds by TlF₂ in hot abs. EtOH. The method is not general, eight compounds failing to react and others not giving pure F-derivatives.

R. S. C.

Configurative relationship of disubstituted acetic and propionic acids containing an ethyl group. P. A. LEVENE, A. ROTHEN, and G. M. MEYER (J. Biol. Chem., 1936, 115, 401—413).—By conversion into hydrocarbons it is shown that configuratively related acids, CHETr·CO₂H (I), CHETr'·CO₂H, and CHMeR·CO₂H, rotate in the same direction and that related acids, (I) and CHETr·CH₂:CO₂H (II), rotate in opposite directions. The previous correlation (A., 1931, 821) of *l*-CHETr·CH₂:CO₂H with *d*-CHETr·CH₂:CO₂H is erroneous. The rotatory dispersion of (I) and (II) is expressed by a single-term Drude equation. [M] given below are calc. least max. [M]_D²⁵. CHETr·CO₂H, m.p. 117—118°, leads to *l-α-ethyl-n-valeric acid* (III), b.p. 95°/8 mm., [M] -2.21° (*cinchonidine* salt), and *Et d-α-ethyl-n-valerate*, b.p. 108°/115 mm., [M] +7.33° (*quinine* salt of the corresponding acid), reduced to *d-β-ethyl-n-amyl alcohol*, b.p. 107°/100 mm., [M] +3.88°, and thence giving the *bromide* (IV), b.p. 109°/130 mm., [M] +1.04°. (III) leads to *l-β-ethyl-n-amyl iodide*, b.p. 132—133°/160 mm., [M] -0.66°, and *l-γ-methyl-n-hexane*, b.p. 92—93°. (IV) leads to *β-ethylhexoic acid*, b.p. 158—159°/79 mm., [M] -3.41°. CH₂(CO₂Et)₂ leads to *d*-(*cinchonidine* salt) and *l-α-ethylhexoic acid*, b.p. 120°/13 mm., [M] -23.5° (*quinine* salt; *Et* ester, b.p. 90°/28 mm., [M] -22.6°), and thence *l-β-ethyl-n-hexyl alcohol*, b.p. 110°/55 mm., [M] -7.72°, *iodide*, b.p.

60°/2 mm., $[M] -24^\circ$, and bromide, b.p. 110—111°/71 mm., $[M] -19.4^\circ$, d- β -ethylheptonic acid, $[M] +7.41^\circ$, and l - γ -methyl- n -heptane, b.p. 115°. R. S. C.

Oxidation of drying oils and cognate substances. I. Oxidation of maleic anhydride compounds of β -elæostearic acid and its triglyceride. II. (A) Oxidation of maleic anhydride compound of α -elæostearic acid. (B) Properties of maleic anhydride compounds of α - and β -elæostearic acids. III. Effect of heat on oxidised β -elæostearin-maleic anhydride compound. R. S. MORRELL and W. R. DAVIS (J.S.C.I., 1936, 237—246T, 261—265T, 265—267T).—Controlled oxidation (H_2O_2 -AcOH) of the maleic anhydride compounds of α - and β -elæostearic acids yields the corresponding (OH)₂-derivatives, whilst hydrogenation (H_2 -PtO₂, H₂O) affords compounds C₁₈H₃₄O₂·C₁₈H₃₄O₃, m.p. 74° and 63°, respectively. The effect of heat on the gels obtained by the gaseous oxidation of β -elæostearin-maleic anhydride compound in AcOH and CCl₄, respectively, is described and a chemical interpretation is suggested. Previous findings (this vol., 313) are described in detail.

F. N. W.

Electrochemical investigations with α -hydroxy-acids.—See this vol., 1347.

Reactions of pyruvic acid with thiolacetic acid and cysteine. E. FRIEDMANN and J. GIRŠAVIČIUS (Biochem. J., 1936, 30, 1886—1891).—When AcCO₂H (I) is mixed with SH·CH₂·CO₂H (II), an exothermic reaction occurs and a white cryst. equimol. compound of (I) and (II) is formed which, on dissolution in H₂O, behaves like a mixture of free (I) and (II) both in its reactions with I and NaHSO₃ and in the fact that (I) and (II) can be isolated therefrom. Cysteine in aq. or EtOH solution reacts slowly with (I) as shown polarimetrically and by iodometric titration. The compound is reasonably stable as judged from its behaviour to I and some colour reagents. P. W. C.

Preparation of homolævulic [γ -keto- n -hexoic] acid. E. FRIEDMANN (J. pr. Chem., 1936, [ii], 146, 159—162).—COEt·CH₂·CO₂Et (purified by way of the NaHSO₃ compound), Na wire, and CH₂Br·CO₂Et in Et₂O give a 66.5% yield of Et₂ propionylsuccinate, b.p. 146—149°/10 mm., and thence by 5*N*-H₂SO₄ an 81% or by *N*-NaOH a 62% yield of γ -keto- n -hexoic acid, m.p. 40° (corr.), b.p. 140—148°/10 mm. (Et ester, b.p. 102—107°/12 mm.).

R. S. C.

Polynuclear heterocyclic rings. X. Determination of the rate of ring closure. M. STOLL and A. ROUVÉ (Helv. Chim. Acta, 1936, 19, 1079—1095; cf. A., 1935, 1251; this vol., 964).—Further examination of the behaviour of OH·[CH₂]₁₄·CO₂H shows that with 45% primary polymerisation the initial rate of reaction based on transformation of the initial products is greater at the start and slower at the end than the rate based on the functional groups. The corresponding velocity coeffs. differ widely from one another, that based on the initial acid declining first rapidly and then slowly to a limiting val., whilst that based on the functional groups falls very rapidly and finally becomes const. The rate of polymerisation to an acid concn. $c=11.7$ g.=

45×10^{-4} mol. per litre is $>$, and after this concn. $<$, the rate of monomeric lactone formation. This concn. determines the point at which the rates are equal, and must therefore be identical with the cyclisation const. The degree of cyclisation increases with the progress of the change. The ratio uni-: bi-mol. acid shows that the max. amount of ter- and quadri-mol. acid is $>8\%$ of the original material and that $>3\%$ of the latter is available for the production of substances of higher mol. wt. Reply is made to Salomon (this vol., 940). H. W.

Nature of the "activated form" of oxalic acid. E. SCHRÖER (Ber., 1936, 69, [B], 2037—2041).—CHO·CO₂H (I) is identified as the "activated form" of H₂C₂O₄, since a solution of the latter which has reacted with KMnO₄ in absence of air until only a slight yellow colour persists gives a violet colour with fuchsin-H₂SO₃. At the same stage of the reaction (I) can be detected with naphthoresorcinol or, more satisfactorily, with carbazole. Little H₂O₂ is produced when solutions of (I) are shaken with air, but its formation becomes copious in presence of Mn⁺⁺. Little H₂O₂ results in old solutions of (I) and none in those which are syrupy or have been boiled, probably on account of polymerisation of the acid. Identical amounts of (I) are found by the aldehyde and Ti reagents; these appear to decrease with increasing acidity of the solution. (I) reduces Hg^{II} salts in warm solution. The reaction of H₂C₂O₄ and MnO₄' in acid solution is given by the partial equations: $4H_2C_2O_4 + 2MnO_4' + 2H^+ \rightarrow 3CO_2 + Mn_2O_3 + 5H_2O$; $H_2C_2O_4 + Mn_2O_3 \rightarrow (I) + 2MnO_2$; $(I) + O_2 + H_2O \rightarrow H_2C_2O_4 + H_2O_2$; $H_2O_2 + MnO_2 \rightarrow H_2O + MnO + O$; $H_2C_2O_4 + MnO_2 \rightarrow H_2O + 2CO_2 + MnO$.

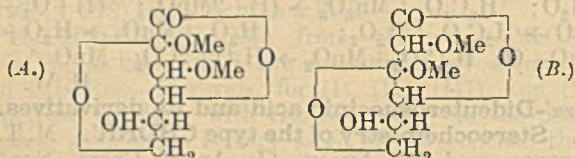
H. W.

$\alpha\alpha'$ -Dideuteriosuccinic acid and its derivatives. II. Stereochemistry of the type CHDRR'. M. T. LEFFLER and R. ADAMS (J. Amer. Chem. Soc., 1936, 58, 1551—1555).—Reduction (D₂, PtO₂, EtOAc) of (a) Et maleate and (b) Et fumarate gives apparently the same Et $\alpha\alpha'$ -dideuteriosuccinate, b.p. (a) 106.5—106.8°/16 mm., (b) 106—106.5°/16 mm., hydrolysed (very dil. HNO₃) to the acid (I), m.p. 184—184.5° (anhydride, m.p. 119.3—119.6°). Fractional crystallisation of (I) failed to indicate more than one form. The brucine, m.p. 216—218° (decomp.), quinine (+H₂O), m.p. (anhyd.) 198—201°, strychnine, m.p. 210° (softens at 190°), and cinchonine (II), m.p. 130—160°, salts of (I) have the same $[\alpha]_D^{20}$ as the corresponding salts (same m.p.) of (·CH₂·CO₂H)₂. Quinine tetradeuteriosuccinate has m.p. 198—201°. Different fractions of (II) showed no mutarotation. The above results indicate that CHDRR' shows symmetry. H. B.

Shellac. IX. Constitution of aleuritic acid. W. NAGEL and W. MERTENS (Ber., 1936, 69, [B], 2050—2052).—Confirmation of the structure OH·[CH₂]₆·CH(OH)·CH(OH)·[CH₂]₇·CO₂H assigned to aleuritic acid (A., 1927, 445) is found in its conversion by successive treatment with COMe₂-H₂SO₄, KMnO₄ (=4 O), and boiling dil. mineral acid into κ -dihydroxyhexadecanedicarboxylic acid, m.p. 125—127° (Mg salt). The corresponding Me₂ ester, m.p. 60—62.5°, yields a diacetate, b.p. 220—230°

(bath)/1 mm., and a CMe_2 derivative, b.p. $185^\circ/3$ mm. H. W.

$\alpha\beta$ -Dimethylascorbic acid and $\alpha\beta$ -dimethyl- ψ -ascorbic acid. F. MICHEEL and G. BISCHOFF (Annalen, 1936, 525, 66—73).— $\alpha\beta$ -Dimethyl- $\delta\epsilon$ -isopropylideneascorbic acid is greatly changed by dil. alkali without yielding derivatives of dimethyl- ψ -ascorbic acid (I) (cf. A., 1935, 1106). Successive treatment of *l*-ascorbic acid with CPh_3Cl and CH_2N_2 affords ϵ -triphenylmethyl- $\alpha\beta$ -dimethylascorbic acid (II), m.p. 159° , $[\alpha]_D^{20} +34.2^\circ$ in $CHCl_3$ (*p*-nitrobenzoyl derivative, m.p. 154° , $[\alpha]_D^{20} +24.3^\circ$ in $CHCl_3$). Removal of the CPh_3 residue from (II) followed by treatment with *p*- $NO_2 \cdot C_6H_4 \cdot COCl$ leads to the known $\delta\epsilon$ -di-*p*-nitrobenzoyl- $\alpha\beta$ -dimethylascorbic acid (III), showing that secondary change does not occur during the action of CPh_3Cl . (II) is isomerised by an excess of dil. alkali to a compound (IV), m.p. 178° , $[\alpha]_D^{20} +34.6^\circ$ in $CHCl_3$, which is not enantiomorphously related to (II). (IV) affords a non-cryst. *p*-nitrobenzoate. Removal of CPh_3 from (IV) followed by treatment with *p*- $NO_2 \cdot C_6H_4 \cdot COCl$ gives (III). Since the ϵ - CPh_3 derivative of dimethylascorbic acid (V) does not become transformed into the similar derivative of (I), it follows that ϵ -OH must be concerned with the isomerisation of (V) to (I), thus excluding the constitution assigned previously (*loc. cit.*) to (I). The mode of participation of ϵ -OH in the formation of (I) is indicated by the observations that (I) does not react with CPh_3Cl and that *p*-nitrobenzoyldimethyl- ψ -ascorbic acid is hydrolysed by $NaOH$ and then loses



Me when treated with 0.1N-HCl at 100° , giving methyl- ψ -ascorbic acid, which reduces Fehling's solution and affords a di-*p*-nitrobenzoylmethyl- ψ -ascorbic acid. The most probable structure of (I) is therefore A or B, of which the former is the more likely since B requires a very ready hydrolysis of glucosidic Me.

H. W.

Kinetics of the reactions of polymeric aldehydes. II. Reaction of paraformaldehyde with cyanide. J. LÖBERING and K. P. JUNG (Ber., 1936, 69, [B], 2147—2151).—Weighed amounts of paraformaldehyde (I) alone and in presence of varied amounts of KCN are shaken at 30° . Determinations of the quantities of dissolved (I) and of (I) utilised in the production of OH-nitrile after definite intervals of time show that the rate of reaction is governed by that of dissolution of (I), and that CN^- has no influence on the velocity of the change, which after an initial period is of the first order. H. W.

Condensation of halogen-substituted aldehydes with nitro-paraffins. F. D. CHATTAWAY, J. G. N. DREWITT, and G. D. PARKES (J.C.S., 1936, 1294—1295; cf. A., 1935, 1224).—Equimol. amounts of chloral and $EtNO_2$ in aq. Na_2SO_3 and Na_2CO_3 at 40 — 70° give $\delta\delta\epsilon$ -trichloro- β -nitro- γ -hydroxybutane, b.p. $95^\circ/0.05$ mm., $115^\circ/2$ mm. (*Ac* derivative, b.p. $98^\circ/$

0.05 mm., $125^\circ/2$ mm.). Butylchloral hydrate yields similarly $\delta\delta\epsilon$ -trichloro- β -nitro- γ -hydroxyhexane, b.p. $138^\circ/0.75$ mm. (*Ac* derivative, b.p. $140^\circ/0.25$ mm.). Chloral and $CH_2Ph \cdot NO_2$ afford $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxy- α -phenylpropane, m.p. 109° (*Ac*-derivative, m.p. 98°). All products are inseparable mixtures of active forms. R. F. P.

Condensation reactions of unsaturated aldehydes. V. Condensation reactions of crotonaldehyde under the influence of different condensing agents. K. BERNHAUER and K. IRRGANG [with K. ADLER, M. MATTAUCH, P. MÜLLER, and F. NEISER] (Annalen, 1936, 525, 43—65).—Immediately before each experiment the crotonaldehyde (I) is distilled in CO_2 and condensation is then effected under N_2 . The proportion of cyclic to open-chain aldehydes depends greatly on the *sec.* amine used. The best yields ($>30\%$) of *o*-dihydrotolualdehyde (II) are obtained by the rapid action of NH_2Et_2 ; prolonged action caused the disappearance of (II) owing to its condensation with (I) to products which resinify readily. With $NHMe_2$ or piperidine (III) the yields of (II) are smaller and relatively best with pure (III) without addition of $AcOH$ (cf. Kuhn *et al.*, this vol., 316). Dicrotonaldehyde, $CHO \cdot CH_2 \cdot CHMe \cdot C(CHMe) \cdot CHO$, is observed only under mild conditions of reaction, and is regarded as the precursor of (II). *p*-Dihydrotolualdehyde is formed mainly by slow action in aq. solution, and probably arises from the condensation of (I) with aldol; it is not produced in presence of dehydrating agents. Octatrienal (IV) appears only in limited amount, best in presence of anhyd. condensing agents or of Na_2SO_4 . Pure (III) or NH_2Et_2 is relatively inefficient, but better results are obtained with their acetates. Max. yields are secured with pure (III) and freshly distilled (I), whereby little (II) results; with the same catalyst and (I) distilled under N_2 less (IV) and more (II) are produced. With this catalyst the addition of $AcOH$ is disadvantageous. Non-cryst. acids are invariable by-products of the condensations. NH_2Ph , $NHPhMe$, $NPhMe_2$, and C_5H_5N have no condensing action and $(-CH_2 \cdot NH_2)_2$ gives only a little (IV). Little condensation and, frequently, much resinification are caused by NH_2Me , NMe_3 , and NMe_4OH . Inorg. bases differ from *sec.* amines in that they never cause formation of cyclic aldehydes. Usually (III) is produced directly from (I), and then suffers partial fission to sorbaldehyde; fission is observed with alkali hydroxides and carbonates, $Ba(OH)_2$, and aq. (III), but not with Na_2HPO_4 , which therefore gives the highest yields of (IV). Dimeric (I) (identified as dimeric crotonic acid, m.p. 64 — 66° or m.p. 71° when very rapidly heated; after re-solidification, m.p. 78 — 81° , independent of the rate of heating) is produced. The position of $Ba(OH)_2$ is exceptional in that it causes formation of (II). Acid catalysts give the highest yields of condensation products, $10\% H_2SO_4$ and $7.5\% HCl$ behaving almost identically; resin formation is very small. Both cause the formation of very little (IV) and give mainly dimeric (I) and its trimeride, m.p. 63° (*semicarbazone*, m.p. 213.5° ; *p*-nitrophenylhydrazone, m.p. 208.5° ; phenylhydrazone, m.p. 139 — 141°), oxidised

to trimeric crotonic acid, m.p. 159.5° (dibromide, m.p. 151°); both are attributed to the intermediate formation of acetaldo.

Gradual addition of H₂O to a mixture of (I), citral, and BaO followed by oxidation of the distilled product with Ag₂O gives a cryst. acid, C₁₄H₂₀O₂, m.p. 99°, probably cyclic in structure. H. W.

Hydrolysis of $\alpha\beta$ -dichloro- β -methylpropane producing isobutaldehyde. J. M. HERSH and R. E. NELSON (J. Amer. Chem. Soc., 1936, 58, 1631—1633).—CMc₂Cl·CH₂Cl, b.p. 38.6—39.2°/70 mm., 106.5°/760 mm., best prepared by low-temp. chlorination of BuⁿCl, is hydrolysed in the vapour phase at 350° by H₂O (ratio 20:1) in presence of catalysts (activated Al₂O₃ being most effective) to PrⁿCHO (90—100% yield on product consumed). H. B.

Refractometric studies in normal methyl ketones. P. CEUTERICK (Bull. Soc. chim. Belg., 1936, 45, 545—564).—The mol. refractivity is determined of a series of α -substituted Et acetoacetates (R=3—10 C), which are hydrolysed (10% NaOH) to the corresponding ketones. The mol. refractivities of the latter indicate that the contribution of CH₂ is 4.612 units at 15° and 4.630 at 30°, which shows that CO does not affect the val. for CH₂ (cf. A., 1933, 815). Assuming the val. for H, the vals. 4.675 and 4.665 are calc. for CO at 15° and 30°, respectively.

J. L. D.

Colorimetric determination of acetone by the salicylaldehyde method. A. RAVIN (J. Biol. Chem., 1936, 115, 511—518).—The method as described is capable of determining 0.0005 mg. of COMe₂ per c.c.

F. A. A.

Addition of acetyl chloride to alkylacetylenes. J. W. KROEGER, F. J. SOWA, and J. A. NIEUWLAND (J. Org. Chem., 1936, 1, 163—169; cf. this vol., 312).—Addition of AcCl to alkylacetylenes CR:CR' in presence of SnCl₄ gives mainly the chloroketones CRCl:CR'Ac (I) with some CRCl:CHR' (II). In this way the following have been prepared: *cis*-, b.p. 97—99°/30 mm., and *trans*-, b.p. 89—91°/30 mm., δ -chloro- γ -ethyl- Δ^{γ} -hexen- β -one, *cis*-, b.p. 117—118°/28 mm., and *trans*-, b.p. 112—113°/28 mm., δ -chloro- γ -n-propyl- Δ^{γ} -hepten- β -one, δ -chloro- γ -n-butyl- Δ^{γ} -octen- β -one, b.p. 140—146°/28 mm., δ -chloro- γ -n-amyl- Δ^{γ} -nonen- β -one, b.p. 115—121°/5 mm., δ -chloro- Δ^{γ} -hexen- β -one, b.p. 46—53°/10 mm., *cis*-, b.p. 62—63°/10 mm., and *trans*-, b.p. 54.5—55.5°/10 mm., δ -chloro- Δ^{γ} -hepten- β -one, *cis*-, b.p. 80°/10 mm., and *trans*-, b.p. 69°/10 mm., δ -chloro- Δ^{γ} -octen- β -one, *cis*-, b.p. 99°/10 mm., and *trans*-, b.p. 89°/10 mm., δ -chloro- Δ^{γ} -nonen- β -one, γ -chloro- Δ^{γ} -hexene, b.p. 113.0—113.5°/748 mm., δ -chloro- Δ^{δ} -octene, b.p. 157.5—159.5°/750 mm., ϵ -chloro- Δ^{ϵ} -decene, b.p. 99—100°/28 mm., ζ -chloro- Δ^{ζ} -dodecene, b.p. 128—129°/28 mm., β -chloro- Δ^{α} -butene, b.p. 57—59°/748 mm. (lit. 61—62°), β -chloro- Δ^{α} -hexene, b.p. 109.5—110.5°/735 mm., β -chloro- Δ^{α} -heptene, b.p. 138—139°/748 mm. (lit. 71°/75 mm.). On keeping, the *cis*- and *trans*-isomerides are converted into an equilibrium mixture. With NaOAc-EtOH the *trans*-compounds give an immediate ppt. of NaCl, obtained only after several days from the *cis*-isomerides. The *trans*-isomeride is obtained on addition of HCl in presence of Cu₂Cl₂ to the appropriate

acetylenic ketone. A mechanism for the formation of (I) and (II) is proposed involving the fission of AcCl into keten and HCl followed by addition of these products to the acetylene. H. G. M.

Dioximes. CXV. G. PONZIO (Gazzetta, 1936, 66, 475—479).—The peroxide of the dioxime of diacetyl glyoxime peroxide (A., 1925, i, 79) is reduced by NH₂OH·HCl in C₅H₅N to dimethyl tetraketone tetraoxime, m.p. 190° (decomp.) [complex Ni salt; (C₅H₅N)₂ salt, m.p. 170° (decomp.); Ac₄ derivative, m.p. 127° (decomp.); Bz₄ derivative, m.p. 209—210°]. Similarly the peroxide of the dioxime of dibenzoyl glyoxime peroxide yields diphenyl tetraketone tetraoxime. E. W. W.

Optical rotatory dispersion in the carbohydrate group. VII. Glucal series. T. L. HARRIS, R. W. HERBERT, E. L. HIRST, C. E. WOOD, and H. WOODWARD (J.C.S., 1936, 1403—1408; cf. this vol., 60).—Absorption spectra and rotatory dispersions are given for xylal diacetate, glucal 3:4:6-triacetate, lactal, lactal hexa-acetate, cellobial, and cellobial hexa-acetate. The data for xylal diacetate are expressed by a one-term Drude-Natanson equation; the other substances require two-term equations. A common low-frequency term, corresponding with an absorption band with λ 2000—2200 Å., indicates dissymmetry of the ethylenic linking. In the xylal series the contributions of the two saturated asymmetric centres cancel out, leaving the full contribution of the ethylenic linking evident; the latter is, however, partly offset by the contribution of the three saturated asymmetric centres in the glucal series. The large difference in $[\alpha]$ in these two series is thus explained. Other observations are in accord with expectation.

R. F. P.

Use of micro-organisms in sugar analysis. II. Quantitative differentiation of fructose and mannose. T. F. NICHOLSON (Biochem. J., 1936, 30, 1804—1806).—Continuing earlier work (A., 1933, 1037), a method is described for determination of mannose (I) which depends on the facts that *Monilia krusei* removes glucose (II), fructose (III), and (I) from solution whilst *Gaffkya tetragena* removes only (II) and (III). Combining the use of these organisms with the use of a strain of *Proteus vulgaris* which removes (II) but leaves (III) and (I), it was possible to analyse mixtures of (I), (II), and (III) and to recover added (III) and (I) from blood and urine filtrates.

P. W. C.

Isomerisation of hydroxyaldehydes. VI. Saccharic transformation of monoses. S. N. DANILOV and A. M. HACHOKIDSE (Ber., 1936, 69, [B], 2130—2141).—The possibilities of the formation of saccharic acids from monoses are discussed in the light of the author's observations with OH-aldehydes (cf. A., 1934, 281). The prep. of glucoconic acid (I), OH·CH₂·[CH·OH]₃·CH₂·CO₂H, m.p. 145°, $[\alpha]_D^{25} +4.99$ in H₂O (Ba salt, $[\alpha]_D^{25} +9.4$ in H₂O; Ca salt (also +1H₂O), $[\alpha]_D^{25} +6.4$ in H₂O; phenylhydrazide, m.p. 176°), by the action of PbO on mono- or di-halogenated glucose triacetates is described. (I) is converted by Ac₂O and NaOAc at 70—80° and then at 96—100° into the Ac₄ derivative, m.p. 110°

(*phenylhydrazide*, m.p. 143°), and by Ag₂O and MeI at 40° into *Me tetramethylglucodeonate* (II), m.p. 81.5°, $[\alpha]_D^{25} + 84.2^\circ$ in H₂O, hydrolysed by aq. Ba(OH)₂ to the corresponding acid, m.p. 92—94° [*phenylhydrazide*, m.p. (indef.), 112—114°]. Glucal, m.p. 60—61°, $[\alpha]_D^{25} - 67.3^\circ$ in H₂O (obtained by hydrolysis of the corresponding triacetate with NH₃-EtOH), is transformed by repeated treatment with Ag₂CO₃ and MeI at 40° into non-cryst. *trimethylglucal*, $[\alpha]_D^{25} + 21.4^\circ$ in H₂O, which with Cl₂ in CHCl₃ at 0° yields 1:2-dichloro-3:4:6-trimethylglucose, $[\alpha]_D^{25} + 121.1^\circ$ in CHCl₃, converted by moist Ag₂CO₃ in CHCl₃ into 2-chloro-3:4:6-trimethylglucose; this with Pb(OH)₂ in H₂O at 18-25° and finally at 80—90° affords *trimethylglucodeonic acid*, OMe·CH₂·CH(OH)·[CH·OMe]₂·CH₂·CO₂H (*Ba* salt; *phenylhydrazide*, m.p. 122—125°), completely methylated to (II). H. W.

Osazones. II. Structure of "anhydro-osazones" and fission of osazones by bases. O. DIELS, R. MEYER, and O. ONNEN (Annalen, 1936, 525, 94—118; cf. A., 1935, 1225).—Dehydration of osazones under the influence of traces of acid appears a general reaction accompanied by the loss of 1 H₂O except in the case of maltose. Frequently the products are stable only as hydrates from which H₂O cannot be removed without decomp.; the Ac derivatives, however, are anhyd. The previous method of formulation, based on the identity of anhydroglucosazone (I) with the osazone of the 3:6-anhydroglucose (II) of Fischer and Zach (A., 1912, i, 678) and Ohle (A., 1928, 871), cannot be maintained, since the pentosazones undergo similar change, and the structure $N \begin{array}{l} \text{CH} \cdot \text{C} \cdot \text{N} \cdot \text{NHPh} \\ \diagdown \quad \diagup \\ \text{NPh} \cdot \text{CH} \cdot [\text{CH}(\text{OH})]_2 \cdot \text{CH}_2 \cdot \text{OH} \end{array}$ is suggested by the conversion of anhydro-osazones by NH₂OH, HCl in EtOH into 4-phenylhydrazono-5-keto-4-phenyl-4:5-dihydropyrazole or its homologues, the inability of N-alkylated osazones to undergo dehydration, and the impossibility of transforming anhydro-osazones into osones by conc. HCl, PhCHO, or *o*-NO₂·C₆H₄·CHO. The alternative constitution $N \begin{array}{l} \text{CH} \cdot \text{C} \cdot \text{NH} \cdot \text{NHPh} \\ \diagdown \quad \diagup \\ \text{NPh} \cdot \text{CH} \cdot [\text{CH}(\text{OH})]_2 \cdot \text{CH}_2 \cdot \text{OH} \end{array}$ is suggested by the general behaviour of 4-pyrazolones, and strongly supported by the observation that the products derived from *l*-arabinose and *d*-xylose are optical antipodes, thus indicating the disappearance of the asymmetry of C₍₃₎. The formation of (II) is not a normal case of osazone production, and slight variations of Ohle's procedure yield a compound, C₁₉H₂₀O₃N₄, m.p. 187—188°, differing from (I) and of unexplained constitution. Osazones are not as sensitive to [OH⁻] as to [H⁺], but are almost universally decomposed by 1% KOH-EtOH into glyoxal-osazone (V) or the products of its dehydration and an OH-acid. The point of scission therefore lies between C₍₂₎ and C₍₃₎. The change is complex and ill-defined.

(I) gives *Ac*, m.p. 170°, and *Bz*, m.p. 161°, compounds and a *COMe*₂ derivative, m.p. 167—168°, converted by boiling MeCN into an *isomeride*, m.p. 220°. The *Ac* derivatives of anhydro-*d*-galactose and anhydrolactose-phenylosazone have m.p. 177°

and 195—196°, respectively. Cellobiosazone is transformed by very dil., boiling H₂SO₄-EtOH into anhydro-cellobiosephenylosazone, C₂₄H₃₀O₈N₄·H₂O, m.p. 245° (decomp.) after softening at 225° (*Ac* derivative, C₃₆H₄₂O₁₄N₄, m.p. 197—198° after softening at about 180°), which is remarkably stable towards alkali. The following *o*-tolylosazones are described: anhydro-*d*-glucose-, m.p. 168—170° (*Ac* derivative, m.p. 149°); lactose-, m.p. 145—155°; anhydrolactose-, m.p. 223—225° (slight decomp.); cellobiose-, m.p. 150—152° after softening at 145°; anhydrocellobiose-, m.p. 223—225° (decomp.); *l*-arabinose-, m.p. 122—123°; anhydro-*l*-arabinose-, m.p. 187—188°; *d*-xylose, m.p. 118—120°; anhydro-*d*-xylose, m.p. 188—189°, $[\alpha]_D^{25} - 57.0^\circ$ in C₅H₅N. The *p*-tolylosazones of anhydroglucose, *d*-galactose (V), and anhydro-*d*-galactose have m.p. 202°, 193°, and 212°, respectively. Anhydro-*l*-arabinosephenylosazone, m.p. 180—181°, $[\alpha]_D^{25} + 35.2^\circ$ in MeOH, and anhydro-*d*-xylosephenylosazone, m.p. 179—180°, $[\alpha]_D^{25} - 32.1^\circ$ in MeOH, are described. The *p*-tolylosazones of glucose and galactose are converted by NH₂OH, HCl in PrOH-H₂O into a substance, C₁₇H₁₆ON₄, m.p. 196°. Treatment of (I) with boiling 1% KOH-EtOH slowly yields the compound, C₁₈H₁₈O₂N₄, m.p. 164°. *d*-Glucosazone (III) when similarly treated affords di- α -phenylazo-ethylene, m.p. 144° (decomp.), the three stereoisomeric forms of (IV), m.p. 220° (decomp.), 155°, and 187°, respectively, and an acid, (?) C₃H₆O₄, isolated as the *brucine* salt, m.p. 188°. (IV) is also derived from the osazones of *d*-galactose, lactose, and maltose. *d*-Glucose-*o*-tolylosazone yields a compound (V), C₁₆H₁₆N₄, m.p. 141°, also obtained from glyoxal-*o*-tolylosazone, m.p. 136°, and KOH-EtOH. *d*-Galactose-*o*-tolylosazone, m.p. 160—161°, is transformed into (V) and a substance, C₂₀H₂₄O₄N₄, m.p. 185°. *d*-Glucose-*p*-tolylosazone yields glyoxal-*p*-tolylosazone, m.p. 238°, not identical with the compound, C₁₆H₁₈N₄, m.p. 238°, derived from (IV), which is transformed by boiling EtOH into a substance, m.p. 205°. Cellobiosazone affords a product, C₁₇H₂₄O₈N₂, m.p. 223° (decomp.), differing in this respect from all other sugars examined. (III) is slowly transformed by 35% NH₂Me in MeOH at room temp. into a compound, C₁₅H₂₅O₃N₅, m.p. 198—199° [normal sulphate, m.p. 237—238° (decomp.)]. H. W.

Crystalline isopropylidene-*d*-threose and simple preparation of *d*- and *l*-threose. M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1936, 69, [B], 1016—1019).— $\text{CMe}_2 \begin{array}{l} \text{O} \cdot \text{CH} \\ \text{O} \cdot \text{CH} \\ \text{H} \cdot \text{C} \cdot \text{OH} \\ \text{CH}_2 \end{array}$ } 1936, 69, [B], 1016—1019).—Successive treatments of benzylidene-arabitol with Pb(OAc)₄ in AcOH and dil. AcOH give *d*-threose, best isolated as the *COMe*₂ derivative (I), m.p. 84°, $[\alpha]_D^{25} - 15.27^\circ$ in COMe₂. The identity of the sugar is established by its almost quant. oxidation to *l*-tartaric acid. H. W.

Characterisation of sugarphosphoric acids and constitution of the pentosephosphoric acid from cozymase. H. VON EULER, P. KARRER, and B. BECKER (Helv. Chim. Acta, 1936, 19, 1060—1062).—Synthetic glucose-6- and ribose-5-phosphoric acid from inosic acid do not give CH₂O when oxidised by

HIO₄, whereas under these conditions ribose-3-phosphoric acid from yeast-nucleic acid gives 0.61 mol. of CH₂O. The pentosephosphoric acid from highly purified cozymase does not yield CH₂O, showing that both pentose mols. are esterified by H₃PO₄ at the primary OH. Cytidylic acid, although containing PO₄ at 3, does not yield CH₂O in consequence of its glucosidification with cytosine. H. W.

Synthesis of glycofuranosides. E. PACSU and J. W. GREEN (J. Amer. Chem. Soc., 1936, 58, 1823—1824).—Galactose Et₂ or dibenzyl mercaptal with HgCl₂ and yellow HgO (to neutralise HCl formed) in EtOH at low temp. gives a good yield of β-ethyl-galactofuranoside. H. B.

Glucose 5-methyl ether. L. VON VARGHA (Ber., 1936, 69, [B], 2098—2102).—Diisopropylidene-glucose 3-*p*-toluenesulphonate is hydrolysed by AcOH at 50° to 1:2-isopropylidene-glucose 3-*p*-toluenesulphonate, [α]_D²⁰ -11.6° in CHCl₃, which with BzCl in CHCl₃ gives 1:2-isopropylidene-glucose 6-benzoate 3-*p*-toluenesulphonate, [α]_D²⁰ -11.4° in CHCl₃, whence the non-cryst. 5-methyl-1:2-isopropylidene-glucose 6-benzoate 3-*p*-toluenesulphonate, [α]_D²⁰ -27.1° in CHCl₃. Alkaline hydrolysis of the latter gives a non-homogeneous product, transformed by Ac₂O in C₅H₅N into 5-methyl-1:2-isopropylidene-glucose 3:6-diacetate (I), m.p. 87°, [α]_D²⁰ -15.2° in CHCl₃. The probability that the removal of the *p*-C₆H₄Me·SO₂ is not accompanied by a Walden inversion and that (I) is a derivative of glucose is strengthened by the almost quant. conversion of 1:2-isopropylidene-glucose 3-*p*-toluenesulphonate into 1:2-isopropylidene-glucose, m.p. 158°, under precisely similar conditions. This view is further confirmed by the mild alkaline hydrolysis of (I) to homogeneous 5-methyl-1:2-isopropylidene-glucose (II), b.p. 145°/0.3 mm., [α]_D²⁰ -13.1° in CHCl₃, transformed by Ag₂O and MeI into 3:5:6-trimethyl-1:2-isopropylidene-glucose, b.p. 138—140°/12 mm., [α]_D²⁰ -27.3° in MeOH. Dil. AcOH at 100° transforms (II) into 5-methylglucose (III), which does not yield a well-defined osazone. Probably (III) is a mixture of several tautomeric forms. The presence of free CHO is established by the immediate reddening of fuchsin-H₂SO₃, instantaneous reduction of KMnO₄, and rapid reduction of cold Fehling's solution. It has [α] ± 0° in H₂O and is not mutarotatory; in EtOH it has [α]_D²⁰ -10.6°, the low val. pointing to the absence of an O bridge. H. W.

Active form of monosaccharides. I. Reactivity of triphenylmethylglucose. A. V. STEPANOV and B. N. STEPANENKO (Ber., 1936, 69, [B], 2046—2049).—Addition of HCN to glucose occurs less readily in 88% than in 10% MeOH due to smaller degree of dissociation of NH₄CN. In 10% MeOH addition is rapid initially but the rate falls and then increases owing to hydrolysis of the nitrile. In 88% or 98% MeOH the increase is not observed. 6-Triphenylmethylglucose reacts more rapidly than glucose. The result is attributed to increased ease of rupture of the O bridge owing to the presence of the negative group. H. W.

Possibility of identifying small amounts of galactose as mucic acid. A. SALVATORI, G.

LAPPONI, and S. BAGLIONI (Atti R. Accad. Lincei, 1934, [vi], 20, 437—444; Chem. Zentr., 1935, ii, 3956).—A method is given for detecting and determining 25 mg. of galactose in 25 c.c. of liquid.

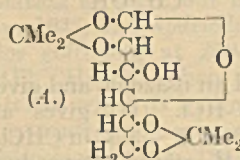
H. N. R.

Open-chain derivatives of *d*-mannose. M. L. WOLFROM and L. W. GEORGES (J. Amer. Chem. Soc., 1936, 58, 1781—1782).—aldehydo-*d*-Mannoseoxime hexa-acetate (I), m.p. 91—92° (lit. 94°), is hydrolysed (H₂C₂O₄·2H₂O in MeOH) to the penta-acetate (II), m.p. 122—123°, [α]_D²⁰ +15° in CHCl₃, which is acetylated to (I) and converted by HNO₂ (method: A., 1934, 1092) into aldehydo-*d*-mannose penta-acetate (III), a syrup [semicarbazone (IV), m.p. 177—178° (decomp.), also obtained by acetylation (Ac₂O-C₅H₅N in the cold) of mannosesemicarbazone]. (III) with EtSH and ZnCl₂ gives the Et₂ mercaptal (Pirie, this vol., 593). (IV) and HNO₂ also give (III), which is oximated to (II). *d*-Mannose thus shows a marked tendency to react in the open-chain form (cf. Deulofeu *et al.*, A., 1934, 394). H. B.

Iodometric determination of fructose. S. STREPKOV (Ann. Chim. Analyt., 1936, [iii], 18, 231—232).—The solution containing fructose (I) is warmed at 48.5—49° with a standard CuCO₃ reagent (II), filtered from reduced Cu₂O, and Cu in an aliquot part is determined iodometrically. (I) is determined from the decrease in titre of (II). J. S. A.

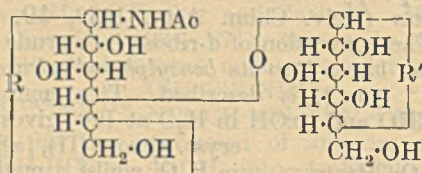
***d*-Diisopropylidenealtrose.** M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1936, 19, 1011—1016).—The conversion of *d*-ribose into crude altrose and of the latter into its benzylphenylhydrazone (I), m.p. 151° (corr.), is described. Treatment of (I) with PhCHO and BzOH in H₂O at 100° gives a non-cryst. altrose (II), [α]_D²⁰ +22° in H₂O, whilst a methylated product (III) results when MeOH at 60—65° is substituted for H₂O. (II) is transformed by COMe₂-CuSO₄-H₂SO₄ into *d*-diisopropylidenealtrose, m.p. 89°, [α]_D²⁰ +28.27° in COMe₂, which does not yield appreciable amounts of acid when oxidised with KMnO₄, and hence is probably A. (III) gives an anhydroisopropylidene-*d*-methylaltroside, C₁₀H₁₆O₅, m.p. 132° after softening at 128°, [α]_D²⁰ -43.04° in COMe₂. H. W.

Mechanism of carbohydrate oxidation. XX. Preparation of oligosaccharide acetates containing dihydroxyacetone constituents. L. C. KREIDER and W. L. EVANS (J. Amer. Chem. Soc., 1936, 58, 1661—1665).—Partly a more detailed account of work previously reviewed (A., 1935, 477). The following is new. β-Cellobiosido-, m.p. 169° (all m.p. are corr.), [α]_D²⁰ -27.1° in CHCl₃ (*p*-nitrophenylhydrazone, m.p. 176°), and β-gentiobiosido-, m.p. 172°, [α]_D²⁰ -25.9° in CHCl₃ (methyl alcoholate, m.p. 110—112°, resolifying with m.p. 171—172°; *p*-nitrophenylhydrazone, m.p. 155°), -dihydroxyacetone octa-acetates are prepared (method: this vol., 827) from OH·CH₂·CO·CH₂·OAc and acetobromo-cellobiose and -gentiobiose, respectively. Attempted



deacetylation (mildest conditions) caused deep-seated changes. H. B.

Action of liquid ammonia on cellobiose octa-acetate. L. ZECHMEISTER and G. TÓTH [with I. PINCZÉSI] (Annalen, 1936, 525, 14—24).—Treatment of cellobiose octa-acetate with liquid NH_3 followed by acid hydrolysis of the product gives cellobiose or its osazone in quant. yield, showing that the reaction remains at the disaccharide stage and that $\text{C}_{(2)}$ and $\text{C}_{(3)}$, the non-reducing half of the biose mols., and the bridge O are not concerned with the position of N. The mixed product is difficult to manipulate after exhaustive acetylation, but it is thereby established that very little of it is formed by union of cellobiose residues. Better results are obtained by gentle acetylation affecting only the NH groups, whereby the more sparingly sol. *acetamidocellobiose* (I) (A ; $R=R'=O$), m.p. 246° (corr.) after softening at 225° , $[\alpha]_D^{20} -20.3^\circ$ in H_2O , is obtained. The position of NHAc follows from the formation of NH_4Cl when (I) is boiled with $N\text{-HCl}$, the very low I val. of (I), its slight reducing power towards Fehling's solution, and the non-formation of an osazone. Treatment of (I) with Ac_2O in $\text{C}_5\text{H}_5\text{N}$ gives the corresponding *peracetate*, m.p. 196° (corr.) after softening at 194° , $[\alpha]_D^{20} -8.4^\circ$ in CHCl_3 , hydrolysed by NaOMe to (I). The mother-liquors from (I) yield *diacetamidocellobiose* (II) (A ; $R=\text{NAc}$, and $R'=O$ or $R'=\text{NAc}$ and $R=O$), $[\alpha]_D^{20} -20^\circ$ in H_2O , which has a very low I val., does not reduce Fehling's solution



(A)

until hydrolysed, does not yield an osazone, and gives NH_4Cl when boiled with $N\text{-HCl}$. (II) gives an Ac_9 derivative, m.p. 196° (corr.), $[\alpha]_D^{20} -3.3^\circ$ in CHCl_3 . Treatment of cellobiose with NH_3 and of the product with Ac_2O in $\text{C}_5\text{H}_5\text{N}$ gives the *substance*, $\text{C}_{40}\text{H}_{55}\text{O}_{26}\text{N}$, m.p. 225° (corr.). H. W.

Semicarbazone and oxime acetates of maltose and cellobiose. *aldehydoCellobiose octa-acetate*. M. L. WOLFROM and S. SOLTZBERG (J. Amer. Chem. Soc., 1936, 58, 1783—1785).—*Maltosesemicarbazone*, m.p. 213° (decomp.), is acetylated ($\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ at $60-65^\circ$ and then at room temp.) to the β -*octa-acetate* (I), m.p. $209-210^\circ$ (decomp.), $[\alpha]_D^{20} +61^\circ$ in CHCl_3 , which contains 7 OAc and 1 NAc (method: this vol., 592). Similar acetylation (at room temp.) of cellobiosesemicarbazone gives the β -*hepta-acetate* (II), m.p. $207-208^\circ$, $[\alpha]_D^{27} -21^\circ$ in CHCl_3 , further acetylated (at 40°) to the β -*octa-acetate* (III), m.p. $240-241^\circ$ (decomp.), $[\alpha]_D^{25} -26.5^\circ$ in CHCl_3 , also containing 7 OAc and 1 NAc. Successive oximation and acetylation of cellobiose hepta-acetate affords β -*cellobioseoxime nona-acetate* (IV), m.p. $195-195.5^\circ$, $[\alpha]_D^{27} -8.5^\circ$ in CHCl_3 , which is not hydrolysed by $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in MeOH . (I)—(IV) all possess ring structures. The cellobiosantioxime octa-acetate of

Zemplén (A., 1926, 822) is probably impure (IV). Cellobioseoxime is acetylated in the cold to an amorphous nona-acetate (which when heated gives cellobionitrile octa-acetate), hydrolysed ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in MeOH) to aldehydocellobioseoxime octa-acetate (V), m.p. $154-155^\circ$, $[\alpha]_D^{28} +30^\circ$ in CHCl_3 , which contains 8 OAc and is converted by HNO_2 into the amorphous aldehydocellobiose octa-acetate, $[\alpha]_D +17.7^\circ$ in CHCl_3 . This reduces Fehling's solution and is oximated to (V). The behaviour of the above cellobiose derivatives on acetylation is the reverse of that of the corresponding glucose compounds (A., 1934, 1092).

H. B.

Verbenalol, aglucone of verbenalin. J. CHEYMOL (Compt. rend., 1936, 203, 543—545).—Emulsion hydrolyses verbenalin (I) to glucose and *verbenalol* (II), $\text{C}_{11}\text{H}_{14}\text{O}_5$, m.p. 133° from Et_2O or 140.5° from AcOH , $[\alpha]_D^{19} -29.07^\circ$ in H_2O (cf. A., 1908, i, 197; 1928, 1137), which contains a lactone ring and a strongly reducing group. The ultra-violet absorption spectra of (I) and (II) are different. (I) with 2.5% H_2SO_4 gives glucose and an *l*-aglucone, which may be (II). J. L. D.

Starch and the Schardinger dextrans. K. FREUDENBERG and W. RAPP (Ber., 1936, 69, [B], 2041—2045).—Detailed instructions are given for the separation of potato starch into amylose, $[\alpha]_{5780}^{20} +203 \pm 1^\circ$ (initial) in 51% H_2SO_4 , $[\alpha]_{5780}^{20} +164 \pm 1^\circ$ in $N\text{-NaOH}$ (acetate, $[\alpha]_{5780}^{20} +172 \pm 2^\circ$ in CHCl_3), and amylopectin, $[\alpha]_{5780}^{20} 206 \pm 1^\circ$ in 51% H_2SO_4 , $[\alpha]_{5780}^{20} +169 \pm 2^\circ$ in $N\text{-NaOH}$. Methylstarch is obtained by treating starch acetate suspended in COMe_2 with NaOH and Me_2SO_4 at 20° and then at 50° ; the processes of acetylation and methylation are repeated, giving a product with 38—39% OMe. Methylation of α -dextrin (I) is effected by adding a solution of K in liquid NH_3 to a solution of (I) in the same solvent at -50° , removing the solvent, and treating the residue with excess of MeI in Et_2O , thus yielding *methyl- α -dextrin* (II), $[\text{C}_6\text{H}_7\text{O}_2(\text{OMe})_3]_5$, m.p. $208-210^\circ$, $[\alpha]_D^{20} +162^\circ$ in CHCl_3 . β -Dextrin is methylated with greater difficulty and ultimately yields a product (III), m.p. (indef.) 190° , $[\alpha]_D^{20} +151^\circ$ in CHCl_3 , with 42.5% OMe (theory 45.5% OMe). Treatment of (II) with boiling 1% $\text{HCl}-\text{MeOH}$ affords trimethylmethylglucoside; no trace of pentamethylglucose can be isolated from it after treatment with BzCl in $\text{C}_5\text{H}_5\text{N}$ at 30° and on hydrolysis it appears to give 2:3:6-trimethylglucose (IV) exclusively. During hydrolysis of (II) and (III) by 51% H_2SO_4 at 20° , $[\alpha]$ rises initially and then sinks to the val. required by (IV). The course of hydrolysis appears the same for each product. The initial rise indicates the presence of a readily ruptured β -union which is not a cellobiose linking. Takadiastase at p_H 4.5 hydrolyses (I) to homogeneous glucose. γ -Dextrin appears to be changed similarly but more complex results are given by β -dextrin. H. W.

Determination of specific weights of cellulose solutions. Specific weights of double compounds of cellulose derivatives with organic solvents.—See this vol., 1337.

Simple enamines with tertiary nitrogen. C. MANNICH and H. DAVIDSEN (Ber., 1936, 69, [B],

2106—2112).—Aldehydes and *sec.* amines in presence of anhyd. K_2CO_3 readily yield diamines which when suitably heated lose 1 mol. of *sec.* amine with formation of enamines, which readily darken when preserved, are moderately stable towards H_2O and alkali, but readily hydrolysed by acids. They add 1 mol. of *sec.* base. They are readily hydrogenated, thus giving a method of converting aldehydes into the corresponding *tert.* amines or into primary or *sec.* amines if the basic component contains CH_2Ph . Condensation of ketones with *sec.* amines does not occur in presence of K_2CO_3 , but can sometimes be effected if CaO is used at a somewhat higher temp. $MeCHO$, piperidine (I), and anhyd. K_2CO_3 at $> 5^\circ$ afford $\alpha\alpha$ -dipiperidinoethane, b.p. $58-60^\circ/0.3$ mm., transformed by distillation at higher pressure into (I) and 1-vinylpiperidine, which is hydrogenated to 1-ethylpiperidine. The following compounds are analogously obtained: 1- Δ^a -propenylpiperidine, b.p. $61-63^\circ/10$ mm., hydrogenated (PtO_2 in cyclohexane) to 1-propylpiperidine; 1- Δ^a -butenylpiperidine, b.p. $70-71^\circ/10$ mm., whence 1-*n*-butylpiperidine, and $\alpha\alpha$ -dipiperidino-*n*-butane; 1- β -methyl- Δ^a -propenylpiperidine, b.p. $65-67^\circ/12$ mm., whence 1-isobutylpiperidine; 1- Δ^a -heptenylpiperidine, b.p. $129-130^\circ/10$ mm., whence 1-*n*-heptylpiperidine, b.p. $121^\circ/13$ mm. (*picrate*, m.p. 98°); diethyl- Δ^a -heptenylamine, b.p. $134-140^\circ/110$ mm., whence diethylheptenylamine, b.p. 198° (*aurichloride*, m.p. 48°); non-homogeneous phenylmethyl- Δ^a -butenylamine (in poor yield), hydrogenated to $NPhMeBu^a$; styryldiethylamine, b.p. $147-150^\circ/16$ mm.; 1-styrylpiperidine, b.p. $174-175^\circ/15$ mm., m.p. $29-30^\circ$, hydrogenated to 1- β -phenylethylpiperidine, b.p. $138-139^\circ/14$ mm.; $\alpha\alpha$ -dibenzylmethylamino- β -phenylethane, an oil, whence benzylstyrylmethylamine, b.p. $171-173^\circ/0.7$ mm., hydrogenated (PtO_2 in EtOH at 45°) to benzyl- β -phenylethylmethylamine, b.p. $135-136^\circ/0.6$ mm. (*methiodide*, m.p. 182°), and ($Pd-C$ in EtOH) to β -phenylethylmethylamine (*hydrochloride*, m.p. $157-158^\circ$); dibenzylstyrylamine, m.p. 120° , hydrogenated (PtO_2 or $Pd-C$) to dibenzyl- β -phenylethylamine (*hydrobromide*, m.p. 213°) or $PhMe$ and $CH_2Ph \cdot CH_2 \cdot NH_2$, respectively; β -piperidino- α -phenyl- Δ^a -propene, b.p. $157-161^\circ/13$ mm., hydrogenated to β -piperidino- α -phenylpropane, b.p. $143-145^\circ/14$ mm. (*hydrobromide*, m.p. 208° ; *methiodide*, m.p. 181°); 1- Δ^a -cyclohexenylpiperidine, b.p. $116-118^\circ/16$ mm., from the base, cyclohexanone, and CaO at 100° during 50 hr., whence 1-cyclohexylpiperidine, b.p. $106-107^\circ/16$ mm. [*methiodide* (II), m.p. 253°]. (II) is transformed by Ag_2O-H_2O followed by heating at 200° into cyclohexylmethyl- Δ^a -pentenylamine, b.p. $108-110^\circ/14$ mm., hydrogenated (PtO_2 in EtOH) to cyclohexylmethylmethylamine, b.p. $113-114^\circ/14$ mm.

H. W.

Formation of enamines and alleneamines from $\alpha\beta$ -unsaturated aldehydes and secondary bases. C. MANNICH, K. HANDKE, and K. ROTH (Ber., 1936, 69, [B], 2112—2123).— $\alpha\beta$ -Unsaturated aldehydes are readily resinified in presence of *sec.* amines, whereby the latter behave entirely as catalyst. If, however, the liberated H_2O is absorbed by much anhyd. K_2CO_3 and the temp. is carefully regulated, additive compounds $NR_2 \cdot CHR \cdot CH : CH \cdot NR_2$ result. The latter readily darken on exposure to air, and are

frequently so unstable that they cannot be distilled in vac. They are very readily hydrolysed. The location of the double linking is established by hydrogenation. When heated they are converted into doubly unsaturated monoamines of the allene type. Gradual addition of freshly distilled acetaldehyde in Et_2O to 45% $NHMe_2-H_2O$ in Et_2O accompanied by introduction of anhyd. K_2CO_3 in successive small amounts at -5° to 0° affords $\alpha\gamma$ -bisdimethylamino- Δ^a -propene, b.p. $52-54^\circ/13$ mm. (60% yield), reduced (PtO_2 in cyclohexane) to $\alpha\gamma$ -bisdimethylaminopropane, b.p. $143-145^\circ$ (*picrate*, m.p. 207° ; *platinichloride*, m.p. 247°). The following are obtained analogously: $\alpha\gamma$ -dipiperidinopropene, b.p. $150-152^\circ/12$ mm. when very rapidly distilled (slow distillation appears to yield polymeric piperidinoallene), hydrogenated (PtO_2) to $\alpha\gamma$ -dipiperidinopropane, b.p. $135-137^\circ/12$ mm. [*platinichloride*, decomp. $230-232^\circ$; *picrate*, m.p. $217-219^\circ$ (decomp.)], and reduced by $Na-Hg$ in 10% $AcOH$ to γ -piperidinopropanol, b.p. $102-104^\circ/12$ mm. (corresponding benzoate hydrochloride, m.p. 186°); $\alpha\gamma$ -bisdimethylamino- Δ^a -butene, b.p. $64^\circ/17$ mm., thermally decomposed into α -dimethylamino- γ -methylallene and hydrogenated to NMe_2Bu^a , $NMe_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot NMe_2$, and $NHMe_3$; $\alpha\gamma$ -dipiperidino- Δ^b -butene (I), hydrogenated (PtO_2 in $MeOH$) mainly to $\alpha\gamma$ -dipiperidinobutane, b.p. $159-160^\circ/18$ mm. (*hydrobromide*, m.p. $272-275^\circ$), and reduced by $Na-Hg$ to γ -piperidinobutanol (*nitrobenzoate hydrochloride*, m.p. 176°); 1-piperidino- γ -methylallene, b.p. $98^\circ/15$ mm. (*aurichloride*, m.p. 91°), from (II) at $130-140^\circ/vac.$, hydrogenated to α -piperidinobutane, b.p. 172° (*picrate*, m.p. 131°); $\alpha\gamma$ -dipiperidino- α -phenyl- Δ^b -propene, m.p. 58° after softening at $55-56^\circ$, whence γ -piperidino- α -phenylpropane and γ -piperidino- α -phenylallene which is too unstable to permit isolation as such, but is characterised as the *picrate*, m.p. 164° , and *hydriodide*, m.p. $211-212^\circ$ (decomp.) after softening at $206-207^\circ$, both of which yield $CHPh \cdot CH \cdot CHO$ when distilled with steam and the latter of which is hydrogenated (PtO_2 in abs. EtOH) to γ -piperidino- α -phenylpropane, b.p. $149^\circ/15$ mm. (*hydrochloride*, m.p. $184-185^\circ$; *hydriodide*, m.p. 138° ; *methiodide*, m.p. $134-135^\circ$), also obtained from $C_5H_{10}N \cdot CH_2 \cdot C : CPh$; α -dimethylamino- $\gamma\gamma$ -dimethyl- Δ^b -octatriene, b.p. $123-124^\circ/12$ mm., hydrolysed to citral and hydrogenated mainly to α -dimethylamino- $\gamma\gamma$ -dimethyl- Δ^b -octadiene [*methiodide* (II), m.p. $178-180^\circ$, which yields NMe_3 when hydrogenated], which passes by addition of H_2O into α -dimethylamino- $\gamma\gamma$ -dimethyl- Δ^b -octen- γ -ol, b.p. $125^\circ/11$ mm. (*hydrochloride*, m.p. $110-111^\circ$; *methiodide*, m.p. $111-112^\circ$); β -methyl- ζ -methylene- Δ^b -octadiene (myrcene), b.p. $56-58^\circ/15$ mm., obtained from (II) and Ag_2O , oxidised by $KMnO_4$ to $COMe_2$, $CH_2(CO_2H)_2$, $AcOH$, and HCO_2H and hydrogenated (PtO_2) to $\beta\zeta$ -dimethyl- Δ^b -octene and thence slowly to $\beta\zeta$ -dimethyloctane; α -dimethylamino- $\gamma\gamma$ -dimethyl- Δ^b -octene, b.p. $99-100^\circ/16$ mm. [*hydrochloride*, m.p. 167° ; *methiodide*, m.p. $220-222^\circ$, degraded (Hofmann) to $\beta\zeta$ -dimethyl- Δ^b -octadiene, b.p. $160-161^\circ$, identical with β -linalolene], transformed by addition of H_2O into a substance, $C_{22}H_{42}ON$, b.p. $128-130^\circ/14$ mm. (hygroscopic hydrochloride, m.p. 96° ; *methiodide*, m.p. $100-101^\circ$), and hydrogenated (PtO_2 in abs. EtOH) to α -dimethyl-

amino- γ -dimethyloctane, b.p. 96°/15 mm. (*hydrochloride*, m.p. 186—187°; *methiodide*, m.p. 242°).

H. W.

Photochemical deamination of amino-acids.—See this vol., 1349.

Preparation of methionine-free natural leucine. S. W. FOX (*Science*, 1936, **84**, 163).—Recrystallisation of the formylated NH_2 -acid yields (50%) a S-free leucine without appreciable racemisation.

L. S. T.

Structure of Wedekind's ketenium compounds. L. L. MILLER and J. R. JOHNSON (*J. Org. Chem.*, 1936, **1**, 135—140).—Wedekind's ketenium compounds (A., 1922, i, 234), formed in small amounts from $\text{CH}_2\text{R}\cdot\text{COCl}$ and $\text{CHR}_2\cdot\text{COCl}$ and $\text{N}(\text{Et})_3$, are shown by hydrolysis and by synthesis to be the diethylamides of the acids, formed from NHEt_2 present as impurity in the $\text{N}(\text{Et})_3$ used. The chief product, CMe_2CO dimeride, of the reaction with Pr^iCOCl is obtained in 60% yield when anhyd. Et_2O or ligroin (60—80°) is used as solvent. The following have been prepared: *isobutyl-*, b.p. 192—194°/740 mm., *phenylchloroacet-*, m.p. 51—51.5°, b.p. 156—158°/4 mm., *dichloroacet-*, b.p. 124—126°/19 mm., and *bromoacet-*, b.p. 114—117°/9 mm., *-diethylamide*.

H. G. M.

Carbamide series. XIII. Nitroalkyl-carbamides and -biurets. T. L. DAVIS and N. D. CONSTAN (*J. Amer. Chem. Soc.*, 1936, **58**, 1800—1803; cf. A., 1933, 383).— $\text{NHR}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{HNO}_3$ ($\text{R} = \text{Et}, \text{Pr}^a, \text{Bu}^a$, m.p. 70—71°, *n-amyl*, m.p. 75°) and conc. H_2SO_4 at <15° give *N-nitro-N'-ethyl-*, m.p. 133—134° (lit. 130—131°), *-N'-n-propyl-*, m.p. 96°, *-N'-n-butyl-* (I), m.p. 80—81°, and *-N'-n-amyl-* (II), m.p. 62°, *-carbamide*, respectively, whilst $\text{NHMe}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{HNO}_3$ affords $\text{NO}_2\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2$ (I) and (II) with NH_2Ph in warm H_2O give *N-phenyl-N'-n-butyl-*, m.p. 129—130°, and *-N'-n-amyl-*, m.p. 92°, *-carbamide*, respectively (also prepared from PhNCO and NH_2Alk); (I) and warm conc. aq. NH_3 afford $\text{NHBu}^a\cdot\text{CO}\cdot\text{NH}_2$. *NN-Dimethyl-*, m.p. 103—104°, *-diethyl-*, m.p. 118°, and *-di-n-propyl-*, m.p. 165°, *-carbamide nitrates* with conc. N_2SO_4 yield the NAlk_2NO_2 ; $\text{CO}(\text{NHMe})_2$ and $\text{CO}(\text{NHEt})_2$ could not be nitrated. α -Methyl- and α -dimethyl-biuret with HNO_3 (*d* 1.42) and conc. H_2SO_4 at <15° give the α' - NO_2 -derivatives, m.p. 99—100° (decomp.) and 114—115° (decomp.) (III), respectively, which with aq. NH_3 afford the original biuret. (III) and NH_2Me , *n-amylamine*, and NH_2Ph in H_2O yield $\alpha\alpha'$ -*trimethyl-*, m.p. 154°, $\alpha\alpha'$ -*dimethyl- α' -n-amyl-*, m.p. 149°, and α' -*phenyl- $\alpha\alpha'$ -dimethyl-*, sublimes about 225°, *-biuret*, respectively; in these reactions (III) probably rearranges to $\text{NMe}_2\cdot\text{CO}\cdot\text{NCO}$ which then reacts with the NH_2R .

H. B.

Optical rotation of configuratively related azides. P. A. LEVENE and A. ROTHEN [with M. KUNA] (*J. Biol. Chem.*, 1936, **115**, 415—428).—In the series, $\text{CHMeR}\cdot[\text{CH}_2]_n\cdot\text{X}$, the results are similar for compounds in which $\text{X} = \text{N}_3$ or halogen only if $n = 0$. *d-sec.-BuOH*, $[\alpha] + 6.82^\circ$, with cold $\text{COMe}_2\text{-HI}$ gives *l-sec.-butyl iodide*, b.p. 111—118°, $[\alpha] - 13.1^\circ$, and thence the *azide*, b.p. 85°/500 mm., $[\alpha] + 16^\circ$, and *d-sec.-butylamine*, $[\alpha] + 0.9^\circ$ (*hydro-*

chloride, $[\alpha] - 0.4^\circ$ in H_2O). *d-Octan- β -ol*, $[\alpha] + 9.6^\circ$, gives *l- β -iodo-*, b.p. 52°/1 mm., $[\alpha] - 33.3^\circ$, *d- β -azido-*, b.p. 68/9 mm., $[\alpha] + 28^\circ$ (homogeneous), $+ 27.4^\circ$ in heptane, and *d- β -amino-n-octane*, b.p. 48°/9 mm., $[\alpha] + 4.19^\circ$ (*hydrochloride*, $[\alpha] - 3.89^\circ$ in H_2O ; *platinichloride*). *d-CHMeEt\cdot\text{CH}_2\cdot\text{OH}*, $[\alpha] - 4.4^\circ$, affords *d- α -iodo-*, b.p. 145—146°, $[\alpha] + 4.18^\circ$, max. $[\text{M}] + 11.1^\circ$, *d- α -azido-*, b.p. 72°/138 mm., $[\alpha] + 7.61^\circ$, max. $[\text{M}] + 11.6^\circ$, and *l- α -amino- β -methyl-n-butane (hydrochloride)*, $[\alpha] - 0.124^\circ$ in H_2O , max. $[\text{M}] - 0.21^\circ$ in H_2O). *d- β -Methylhexyl iodide*, $[\alpha] + 0.37^\circ$, gives *l- α -azido- β -methyl-n-hexane*, b.p. 59—60°/15 mm., $[\alpha] - 0.3^\circ$. *l- β -Methylnonan- α -ol*, $[\alpha] - 2.58^\circ$, yields *d- α -iodo-*, b.p. 86°/4 mm., $[\alpha] + 0.68^\circ$, and *l- α -azido- β -methyl-n-nonane*, b.p. 98—102°/10 mm., $[\alpha] - 0.4$. *l- γ -Methyl-n-pentan- α -ol*, $[\alpha] - 3.2^\circ$, gives *l- α -iodo-*, b.p. 54°/12 mm., $[\alpha] - 7.61^\circ$, and *l- α -azido- γ -methylpentane*, b.p. 145—148°, $[\alpha] - 7.58^\circ$, max. $[\text{M}] - 26.3^\circ$ in heptane. *d- δ -Methylhexan- α -ol*, $[\alpha] + 3.21^\circ$, gives *d- α -iodo-*, b.p. 74—75°/13 mm., $[\alpha] + 3.63^\circ$, max. $[\text{M}] + 26.2^\circ$, and *d- α -azido- δ -methylhexane*, b.p. 157°/418 mm., $[\alpha] + 3.83^\circ$, max. $[\text{M}] + 17.3^\circ$ in heptane. $[\alpha]$ and $[\text{M}]$ are $[\alpha]_D^{25}$ and $[\text{M}]_D^{25}$ (homogeneous) unless otherwise stated.

R. S. C.

Synthesis and refractometric study of saturated α -methylnitriles. C. DE HOFFMANN and E. BARBIER (*Bull. Soc. chim. Belg.*, 1936, **45**, 565—583).—Et α -cyanopropionate (Na derivative) in EtOH with alkyl bromides affords Et α -cyano- α -alkylpropionates. The following are described: *Et α -cyano- α -ethyl-*, b.p. 84—85°/12 mm., *-propyl-*, b.p. 96—97°/11 mm., *-butyl-*, b.p. 105—106°/10.5 mm., *-amyl-*, b.p. 118—119°/10.5 mm., *-hexyl-*, b.p. 132—133°/10.5 mm., *-heptyl-*, b.p. 143—144°/10.5 mm., *-octyl-*, b.p. 155—156°/10.5 mm., *-nonyl-*, b.p. 167—168°/11.5 mm., *-decyl-*, b.p. 180—181°/12 mm., and *-dodecyl-propionate*, b.p. 204—205°/10.5 mm. These are converted by hydrolysis (decarboxylation) into α -methyl-, m.p. 126—128°, *-ethyl-*, m.p. 111.4°, *-propyl-*, m.p. 79.6°, *-butyl-*, m.p. 69.2°, *-amyl-*, m.p. 78.8°, *-hexyl-*, m.p. 80.8°, *-heptyl-*, m.p. 76.4°, *-octyl-*, m.p. 81.4°, *-nonyl-*, m.p. 85.4°, *-decyl-*, m.p. 91.2°, and *-dodecyl-propionamide*, m.p. 96.8°, which with P_2O_5 afford the corresponding nitriles, b.p. 103.4°/753.1 mm., 125.2°/755.2 mm., 146.6°/750.5 mm., 164.8°/761.8 mm., 184.8°/761.8 mm., 85.4°/10 mm., 99.9°/10 mm., 115.4°/10 mm., 133.4°/12 mm., 146.3°/12 mm., and 170.6°/12 mm. Many physical properties of the nitriles are tabulated and the mol. refractivity for CH_2 is calc. as 4.632 at 15° and 4.644 at 30°.

J. L. D.

Behaviour of tautomeric substances towards diazomethane. F. ARNDT (*Rev. Fac. Sci. Univ. Istanbul*, 1936, **1**, 1—8).—A summary of previous work (cf. A., 1933, 146; 1934, 770; 1935, 334; this vol., 59).

H. G. M.

Introduction of silicon into fats. G. KLEIN and H. NIENBURG (*Ber.*, 1936, **69**, [B], 2066—2068).—Esters $[\text{CO}_2\text{R}\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{COR})\cdot\text{CH}_2\cdot\text{O}]_4\text{Si}$ and $[\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}]_4\text{Si}$ are obtained when a mono- or di-glyceride (4 mols.) is heated with $\text{Si}(\text{OEt})_4$ at 150—160°. *Orthosilicates* of the following are described: α -*monostearin*, m.p. 70°; $\alpha\beta$ -*distearin*, m.p.

68°; α -mono-olein, non-cryst.; α -monobutyryn, non-cryst.; $\alpha\beta$ -dibutyryn, non-cryst. H. W.

Organic compounds of mercury. XIV. Reaction of hydroxyethylmercury bromide with diazomethane. R. C. FREIDLINA, A. N. NESMEJANOV, and F. A. TOKAREVA (Ber., 1936, 69, [B], 2019—2021; cf. this vol., 1132).—The action of CH_2N_2 on hydroxyethylmercury bromide (I) in cold Et_2O gives N_2 and an unstable oil which evolves C_2H_4 quantitatively when warmed and gives $\text{CH}_2\text{Br}\cdot\text{HgBr}$ with small amounts of Hg and CH_2O (formed from CH_2N_2). The experiments do not permit a decision between the structures $\text{CH}_2\cdot\text{CH}_2\cdot\text{HgBr}\cdot\text{OH}$ and $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgBr}$ for (I) but the latter is preferred. $\text{CH}_2\text{Br}\cdot\text{HgBr}$ and 2% aq. NaOH yield Hg , CH_2O , and Br^- . HgBr_2 is transformed by a large excess of CH_2N_2 into *Hg dibromomethyl*, m.p. 42—43°.

H. W.

Co-ordination compounds of platinumous halides with unsaturated substances. M. S. KHARASCH and T. A. ASHFORD (J. Amer. Chem. Soc., 1936, 58, 1733—1738).—Compounds $(\text{R}\cdot\text{PtCl}_2)_2$, where $\text{R} = \text{cyclohexene}$ (I), dipentene, pinene, C_2H_4 , isobutene, $\text{CHPh}\cdot\text{CH}_2$, $(\text{CHPh})_2$, or *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$, and $(\text{R}\cdot\text{PtBr}_2)_2$, where $\text{R} = (\text{I})$ or $\text{CHPh}\cdot\text{CH}_2$, have been prepared. The respective m.p. of the above compounds are 145—146°, 151—152°, 138—141°, 170—180°, 144—145°, 169—171°, 191—192°, 155—160°, 150—151°, 153—154°. Optical and solubility data are recorded. E. S. H.

Reduction of aromatic compounds with hydrogen and a platinum oxide-platinum-black catalyst in presence of halogen acid. J. H. BROWN, H. W. DURAND, and C. S. MARVEL (J. Amer. Chem. Soc., 1936, 58, 1594—1596).—Reduction (Adams) of PhBr , PhCl , *p*- $\text{C}_6\text{H}_4\text{Cl}_2$, *p*- $\text{C}_6\text{H}_4\text{Br}_2$, and *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{MeBr}$ gives the cyclohexane and HHal (which activates the catalyst); PhI , *o*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$, 1- $\text{C}_{10}\text{H}_7\text{Cl}$, and 1- $\text{C}_{10}\text{H}_7\text{Br}$ were unaffected. C_6H_6 , PhMe , $\text{C}_6\text{H}_4\text{Me}_2$, *s*- $\text{C}_6\text{H}_3\text{Me}_3$, PhEt , cymene, and Ph_2 are similarly reduced in presence of a little HCl or HBr ; anthracene gives octa- and tetradeca-hydroanthracene but phenanthrene and C_{10}H_8 are unaffected. The following reductions are effected similarly: PhOH to cyclohexanol (occurs more slowly in absence of HHal), EtOBz to $\text{C}_6\text{H}_{11}\cdot\text{CO}_2\text{Et}$, COPhMe to ethylcyclohexane, PhOMe to cyclohexane, and α - and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ to the 5:6:7:8- H_4 -derivatives. H. B.

Decomposition of cyclohexyl bromide in presence of mercuric bromide and the formation of cyclohexene polymerides. F. SWARTS (Bull. Acad. roy. Belg., 1936, [v], 22, 784—790).—Cyclohexyl bromide (0.1 mol.) when heated for 580 hr. with HgBr_2 gave 0.06 mol. of polymerised cyclohexene (I), but the use of HgBr led to no appreciable polymerisation under similar conditions, nor was (I) produced in appreciable yield in the absence of Hg salts. Cu retarded the reaction, which was not appreciably catalysed by Pt . Pure cyclohexene (I) under similar treatment polymerised slightly; hence it is suggested that polymerisation occurs only at the moment of formation of (I). Fractional distillation of the polymerised substance gave cyclohexylcyclo-

hexene and resinous substances. From one fraction, crystallisation from Et_2O gave a substance, C_nH_{2n} , mol. wt. 568, corresponding with about 7 polymerised (I) mols. Some depolymerisation occurred when the resinous material was redistilled. J. T. A.

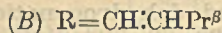
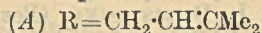
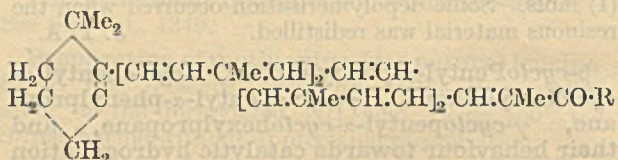
β -cyclopentyl- α -phenylethane, β -cyclopentyl- α -cyclohexylethane, γ -cyclopentyl- α -phenylpropane, γ -cyclopentyl- α -cyclohexylpropane, and their behaviour towards catalytic hydrogenation and dehydrogenation. J. I. DENISENKO (Ber., 1936, 69, [B], 2183—2187).—Addition of cyclopentanone to $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}$ in Et_2O gives 1- β -phenylethylcyclopentan-1-ol, b.p. 140—141°/5 mm., converted by boiling conc. aq. $\text{H}_2\text{C}_2\text{O}_4$ into β -cyclopentyl- α -phenylethane, b.p. 124—125°/10 mm., rapidly hydrogenated (Pt -black in abs. EtOH) to β -cyclopentyl- α -phenylethane (I), b.p. 255—256°/752.5 mm. Passage of (I) with H_2 over Pt-C at 230° yields β -cyclopentyl- α -cyclohexylethane, b.p. 251—252°/752.5 mm., almost completely dehydrogenated by Pt-C at 290° to (I). Similarly, 1- γ -phenylpropylcyclopentan-1-ol, b.p. 136—138°/2.5 mm., is converted successively into γ -cyclopentyl- α -phenylpropane, b.p. 117—118°/3 mm., and γ -cyclopentyl- α -phenylpropane (II), b.p. 271—272.5°/743 mm. (II) is hydrogenated to γ -cyclopentyl- α -cyclohexylpropane, b.p. 268—270°/748.2°, which is dehydrogenated to (II). H. W.

Properties of carotene and lycopene. N. K. DE (Indian J. Med. Res., 1936, 23, 949—956).—Carotene (I) and lycopene (II) behaved similarly towards reagents and adsorbents, but (I) was more sol. and (II) was more readily adsorbed. The spectroscopic absorption in various solvents was determined, and a rough method for the determination of mixtures of (I) and (II), by observing the positions of the absorption max., was devised. NUTR. ABS. (*m*)

Isomerisation of carotenes by chromatographic adsorption. I. ψ - α -Carotene. A. E. GILLAM and M. S. EL RIDI (Biochem. J., 1936, 30, 1735—1742).— ψ - α -Carotene (I), m.p. 166° (uncorr.), formed from β -carotene by repeated adsorption on Al_2O_3 (this vol., 155), is spectroscopically identical with α -carotene (II) but is optically inactive. (I) is isomeric with (II) but whilst (I) is converted into a pigment with absorption max. at longer λ , (II) yields (especially by adsorption on MgO) a pigment (*neocarotene*) with absorption max. at shorter λ . The isomerisation is probably due to rearrangement of double linkings or to geometrical isomerism. F. O. H.

Chemistry of the algæ. II. Carotenoid pigments of *Oscillatoria rubescens*. I. M. HEILBRON and B. LYTHGOE (J.C.S., 1936, 1376—1380; cf. this vol., 259).—The epiphasic pigments consist of β -carotene (I) and myxoxanthin (II), $\text{C}_{40}\text{H}_{56}\text{O}$, m.p. 168—169° (single absorption max. in CS_2 , CHCl_3 , and ligroin) (*oxime*, m.p. 195—196°, absorption max. 463 μ in CHCl_3), which has vitamin-A activity and must therefore contain a β -ionone ring; on microhydrogenation it absorbs 11 H_2 and is thus monocyclic. With $\text{Al}(\text{OPr}^n)_3$ it affords myxoxanthol, m.p. 169—172° (absorption max. 529, 494, 464 μ in CS_2). This is the absorption spectrum of γ -carotene (III)

and analogy with (III) indicates that (II) is (A) or (B). (A) is precluded because (II) has a single absorption max., thus resembling astacene (IV). The enolic



form of (IV) closely resembles (II), wherefore (B) is preferred. The single-banded spectra of pigments such as (II) and (IV) is due to the simultaneous conjugation of the :CO with two ethylenic linkings. The hypochasic pigments include lutein and *myxoxanthophyll*, C₄₀H₅₆₊₂O₇, m.p. 169—170° (absorption max. 518, 484.5, 454 mμ in CHCl₃).

R. F. P.

Reversibility of the Friedel-Crafts reaction. Hydrogenation. L. L. ALEXANDER and R. C. FUSON (J. Amer. Chem. Soc., 1936, 58, 1745—1747; cf. this vol., 205).—Dibenzyl (I) is formed in 27—57% yield when tri- and tetra-arylethanes (or compounds, e.g., CAR:CAR, CHAR:CHAR, CAR₂:CHAR, which, under the conditions used, can give rise to these) are treated with C₆H₆, AlCl₃ (large excess), and dry HCl at room temp. Thus, toluene, CPh₂:CHPh, CHPh₂:CH₂Ph, (CPh₂)₂, (CHPh₂)₂, and β-phenyl-α-di-p-chlorophenylethylene (II), m.p. 116.5—117.5° [obtained by dehydration (AcOH—conc. H₂SO₄) of β-phenyl-α-di-p-chlorophenylethyl alcohol, m.p. 116—117°, which is prepared from CH₂Ph·MgCl and (p-C₆H₄Cl)₂CO], all give (I). (CHPh₂)₂ is formed from toluene, (II), or CPh₂:CHPh with C₆H₆, AlCl₃ (limited amount), and HCl; (CHPh₂)₂ and p-bromostilbene similarly afford CHPh₂:CH₂Ph. The following mechanism for (II) illustrates the general reaction: CHPh:C(C₆H₄Cl)₂ (+C₆H₆) ⇌ CHPh₂:CH(C₆H₄Cl)₂ (+2C₆H₆) ⇌ CHPh₂:CHPh₂ (+C₆H₆) ⇌ CPh₂:CHPh (+H₂) → CHPh₂:CH₂Ph (+C₆H₆) ⇌ CHPh:CHPh (+H₂) → (I). The production of (I) from C₆H₆, AlCl₃, and various halogenoethanes, -ethylenes, and -acetylenes is thus explicable.

H. B.

Principle of vinylogy and the effect of ortho-substituents on the reactivity of benzene derivatives. A. H. BLATT (J. Org. Chem., 1936, 1, 154—158).—Zwecker's comparison (A., 1935, 1112) of the relative reactivities of unsubstituted and o-substituted C₆H₆ derivatives, C₆H₄RX (R=H, Me, etc.; X=CO₂H, CH₂Cl, etc.), with those of HX and RX is shown to be a special case of the principle of vinylogy (cf. Chem. Rev., 1935, 16, 1).

H. G. M.

Hydrolysis of halogenobenzenesulphonic acids with alkali. C. M. SUTER and P. H. SCRUTCHFIELD (J. Org. Chem., 1936, 1, 189—193).—K or Na salts of 1:3:5-C₆H₃X(SO₃H)₂ (I) (X=Cl, Br, I), 1:2:4-C₆H₃Cl(SO₃H)₂, 1:3-C₆H₄I·SO₃H, and 1:3-C₆H₄(SO₃H)₂ have been hydrolysed in a N₂ atm. with 60% aq. KOH (130—160°, 0.25—3 hr.), and (I) (X=Cl and Br) have been fused with KOH (200—310°, 1—3 hr.), and the amounts of Cl' and SO₃'' formed determined. The halogens are more easily hydrolysed than the SO₃H, which, in turn, are hydrolysed more slowly

after hydrolysis of the halogen than before. The ratio of the hydrolysis rates for the halogen and SO₃H is greater in 60% alkali than in fusion reactions.

H. G. M.

Organic substances of high mol. wt. Polybenzyl and its derivatives. II. Synthesis of the polymeride and its viscosity in varying solvents. III. Polynitrobenzyl. S. BEZZI (Gazzetta, 1936, 66, 491—497, 497—504; cf. A., 1935, 1067).—II. Polybenzyl, (C₆H₄:CH₂)_n or CH₂Ph·[CH₂:C₆H₄]_n·C₆H₄:CH₂Cl, obtained by autocondensation of CH₂PhCl (AlCl₃, alone or in PhNO₂, CS₂, or light petroleum), is shown by its viscosity in C₆H₆ and in PhNO₂, at varying concn. and temp., to consist of long-chain mols., and not of micelles.

III. Polybenzyl with HNO₃ (d 1.38) yields an insol. product containing less N than is required by (C₇H₅:NO₂)_n. HNO₃ (d 1.52) gives a mixture of sol. and insol. NO₂-derivatives with N in excess (disubstituted in the terminal rings?). Mol. wt. (cryoscopic) shows that polybenzyls in which the degree of polymerisation is 5 to 24 all give sol. NO₂-derivatives in which it is only 5.5—6.5. The sp. viscosity of the latter is > that of polybenzyls of the same mol. wt. This, and the abnormal viscosity of cellulose, is ascribed to the effect of the functional groups.

E. W. W.

Magnetochemical investigation of organic substances. X. Attempted synthesis of carbon diradicals; existence of diradicals. E. MÜLLER and W. BUNGE (Ber., 1936, 69, [B], 2164—2172).—Attempts to remove Cl completely from 4:4'-dichlorodiphenylmethyldiphenyl ether necessitate the use of Cu powder in boiling C₆H₆, whereby a radical coloration is not observed and the product is a yellow amorphous substance, C₇₆H₅₆O₂, m.p. indef. 140°, apparently a dimeride. It is stable towards boiling SO₂Cl₂, but suffers fission with K-Na, thus resembling Ph₂O. In C₆H₆ at room temp. and at 74° it is completely diamagnetic, and shows no sign of radical content. 4:4'-Di(chlorodiphenylmethyl)-αβ-diphenylethane (Wittig et al., A., 1928, 642) is transformed by Cu powder in C₆H₆ into the almost colourless compound C₄₀H₃₂, which gives a colourless solution in C₆H₆ if heating has been avoided in its prep., but is dark red in the hot solution. At room temp. and at 74° in C₆H₆ the diamagnetic val. of the colourless solid is observed; a paramagnetic deviation corresponding with >2% of radical is excluded. Paramagnetic C diradicals are capable of existence only when there is no possibility of intermol. stabilisation, of passage into a valency-tautomeric quinonoid system, or of equilibration with formation of a polymeric compound.

H. W.

ωω'-Tetraphenylpolyene hydrocarbons; valency tautomerism of unsaturated systems. G. WITTIG and A. KLEIN (Ber., 1936, 69, [B], 2087—2097).—With hydrocarbons

CPh₂:CH·[CH:CH]_n·CH:CPh₂ (n=1, 2, or 3) union with 2 atoms of alkali metal, probably at the ends of the conjugated systems, occurs, but O₂ is without effect even in the presence of PhCHO. Addition of Br appears to take place with avoidance of the CPh₂:CH groups. The tetraphenylpolyenes do not

therefore give stable diyl forms and do not pass into diradicals in presence of O_2 or Br. Tetraphenyl-*p*-xylylene reacts with Na-K in dioxan and the product affords *p*- $C_6H_4(CHPh_2)_2$, m.p. 170—171°, when treated with MeOH. Gradual addition of $Me_2\alpha\alpha'$ -dihydromuconate to LiPh in Et_2O and decomp. of the product with H_2O gives $\alpha\alpha\zeta\zeta$ -tetraphenyl- Δ^{γ} -hexene- $\alpha\zeta$ -diol (I), m.p. 163.5—165°, converted by HCl-MeOH in dioxan into $\alpha\alpha'$ -dimethyl- $\alpha\alpha\zeta\zeta$ -tetraphenyl- Δ^{γ} -hexene, m.p. 209—210°, which with Na-K followed by MeOH in dioxan yields $\alpha\alpha\zeta\zeta$ -tetraphenyl- Δ^{γ} -hexene, m.p. 124—125°. (I) and boiling AcOH containing HCl afford $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\alpha'}$ -hexatriene (II), m.p. 202—204°, which is converted by Na powder in abs. dioxan followed by MeOH into $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\beta\beta}$ -hexadiene (III), m.p. 148—149°, oxidised by $KMnO_4$ in $COMe_3$ to $CHPh_2\cdot CO_2H$ and $OH\cdot CPh_2\cdot CO_2H$, but not $COPh_2$. With Li a similar slow change is observed, whereas with Na-K reaction is much more rapid and gives (III) after short change, but $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\alpha'}$ -hexadiene, m.p. 118—121° (oxidised to $CHPh_2\cdot CH_2\cdot CO_2H$, m.p. 154°), when reaction is prolonged. Partial hydrogenation of (II) gives $\alpha\alpha\zeta\zeta$ -tetraphenylhexane and unchanged (II). In $CHCl_3$ (II) gives a dibromide, decomp. about 133°, but it does not react with I. (II) is unchanged when shaken in C_6H_6 with O_2 alone or in presence of PhCHO or when dry O_2 is passed through its solution in boiling C_6H_6 . $\alpha\alpha\zeta\zeta$ -Tetradiphenyl- Δ^{γ} -hexene- $\alpha\zeta$ -diol, m.p. 238—239°, is converted by HCl in boiling AcOH into $\alpha\alpha\zeta\zeta$ -tetradiphenyl- $\Delta^{\alpha\alpha'}$ -hexatriene, m.p. 320—328° (slight decomp.), which is darker in colour and gives a more marked fluorescence than (II), but is equally indifferent towards O_2 . ($\cdot CH_2\cdot CO_2H$) $_2$, PbO, Ac_2O , and β -phenylcinnamaldehyde (IV) at 140—150° afford $\alpha\alpha\theta\theta$ -tetraphenyl- $\Delta^{\alpha\alpha'}$ -octatetraene, m.p. 198—199°, which in $CHCl_3$ gives a very unstable tetrabromide; it is indifferent to the prolonged action of O_2 . $\alpha\alpha'$ -Dihydromuconic acid, PbO, Ac_2O , and (IV) at 140—150° give $\alpha\alpha\kappa\kappa$ -tetraphenyl- $\Delta^{\alpha\alpha'}$ -decapentaene, m.p. 227—228°, which affords an unstable hexabromide and is indifferent to O_2 . H. W.

$\alpha\delta$ -Diarylbutadienes and related compounds.

I. α -Phenyl- δ -1-naphthylbutadiene. E. FRIEDMANN and W. E. VAN HEYNINGEN (J. pr. Chem., 1936, [ii], 146, 163—165).— $CHPh\cdot CH\cdot CHO$, α - $C_{10}H_7\cdot CO_2H$, Ac_2O , and PbO at 200—230° give 24.9% of α -phenyl- δ -1-naphthylbutadiene, m.p. 109°, which fluoresces in ultra-violet light and has absorption max. at 2360, 2775—2855, and 3260—3370 Å. $\alpha\delta$ -Diphenylbutadiene has absorption max. at 2420 and 3305—3140 Å. R. S. C.

Reaction of metal halides with acetylenic Grignard reagents. J. P. DANEHY and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1609—1610).— $CPh\cdot C\cdot MgBr$ (1 mol.) and $CuBr_2$ (1 mol.) in Et_2O give 72% of $(CPh\cdot C)_2$. $CBu^{\alpha}\cdot C\cdot MgBr$ (I) and $CuBr_2$ at 25° similarly afford $(CBu^{\alpha}\cdot C)_2$ (60%); 55% at -5° and $CBu^{\alpha}\cdot CBr$ (7%); 14% at -5°, which are also formed using $CuCl_2$ at 25° (35 and 5%, respectively) or -5° (30 and 7%, respectively), and from $CBu^{\alpha}\cdot C\cdot MgCl$ and $CuBr_2$ (30 and 1%, respectively). $FeCl_3$ acts similarly. (I) and $AgBr$

give $CBu^{\alpha}\cdot CAg$ (60%), thus affording evidence that the first stage in the reaction between a Grignard reagent and a metal halide (as above) is the formation of an organometallic compound which, if unstable, subsequently decomposes. H. B.

Lattice structure of condensed aromatic hydrocarbons and their molecular compounds with trinitrobenzene.—See this vol., 1327.

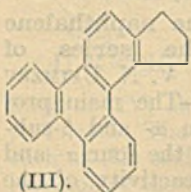
Structure and reactivity of the naphthalene nucleus. I. Orientation in the series of naphthalene and its derivatives. V. N. UFMZEV (Ber., 1936, 69, [B], 2188—2198).—The main properties of $C_{10}H_8$ (difference between α - and β -substituted derivatives; equivalence of the four α - and of the four β -positions; greater reactivity of the α -positions) are adequately expressed by assuming an equilibrium between the forms (I) and (II). The assumption of a displacement (I) \rightarrow (II)



on entry of a substituent into the nucleus explains the preponderating formation of mono-substituted products under mild conditions, since further action occurs with greater difficulty owing to the induced benzenoid character of the second ring; substances with completely similar rings [$Ph_2\cdot C_6H_4(CO)_2\cdot C_6H_4$] usually readily afford derivatives, and only under particular conditions are mono-substituted compounds obtained. Displacement of the equilibrium (I) \rightarrow (II) endows one ring with a more aromatic, the other with an unsaturated, character; further sulphonation causes entry of SO_3H in different positions, but only in the aromatic and difficultly hydrogenated ring, thus explaining the non-production of 1:3- $C_{10}H_6(SO_3H)_2$. Examples from the lit. show that hydrogenation is considerably facilitated in the unsaturated ring, whereas in the other ring it occurs with about the same difficulty as with C_6H_6 . If the structure with non-equiv. rings is considered fundamental to mono-substituted derivatives of $C_{10}H_8$ the entry of a second substituent into the same ring follows the usual rules of C_6H_6 orientation. If it enters the other ring, it is under the influence of a substituent in an unsaturated side-chain, and is subject to the rules of Holleman and Ingold. The processes are illustrated by references to the lit. Contrary to the lit., sulphonation of β - $C_{10}H_7\cdot NHOAc$ in the cold gives mainly 2:8- $NHAc\cdot C_{10}H_6\cdot SO_3H$. Orientation of naphthylamine-sulphonic acids is readily effected by diazotisation, replacement of N_2 by SO_2H by SO_2 in presence of Cu powder, oxidation of SO_2Na to SO_3Na by H_2O_2 , and conversion of $C_{10}H_6(SO_3H)_2$ into $C_{10}H_6(SO_2Cl)_2$. H. W.

cyclopentenotriphenylene. E. BERGMANN and O. BLUM-BERGMANN (J. Amer. Chem. Soc., 1936, 58, 1678—1681).— β -9-Phenanthrylethyl alcohol, m.p. 92° [from Mg 9-phenanthryl bromide and $(CH_2)_2O$ (in $Et_2O-C_6H_6$) or $CH_2Cl\cdot CH_2\cdot OH + MgEtBr$ (reaction occurs when the Et_2O is distilled off)], with $SOCl_2$ in $C_6H_6-NPhMe_2$ gives the chloride, m.p. 82—84°, the Grignard reagent (A) from which with cyclopentanone affords 1-(β -9-phenanthrylethyl)cyclopentanol (I), m.p. 108—109°, and a little $\alpha\delta$ -di-9-phenan-

thylbutane (II), m.p. 214—216°. (I) is dehydrated (KHSO₄ at 160—170°) to 1-(β-9-phenanthryl)-Δ¹-cyclopentene, b.p. 206—207°/1.3 mm., m.p. 50—54.5°, converted by AlCl₃ in CS₂ at room temp. into tetrahydrocyclopentenotriphenylene, m.p. 105.5—107° (picrate, m.p. 161—162°), which is dehydrogenated (Se at 330—340°) to cyclopentenotriphenylene (III), m.p. 171—172.5° (picrate, m.p. 172—173°). (III)



(III) differs from the hydrocarbon, C₂₁H₁₆, to which structure (III) was assigned by Elderfield and Jacobs (A., 1934, 1359). (I) and AcOH-conc. H₂SO₄ do not give (III); the resultant product [from which a hydrocarbon, C₂₁H₂₀, m.p. 117—120° (probably a spiran), is isolable] is dehydrogenated (Se at 320—340°) to (probably) 7-methyl-1:2-benzopyrene, m.p. 157.5—159.5° (picrate, m.p. 153—155°), and 1:2:3:4-dibenzfluorene, m.p. 115—116° (picrate, m.p. 165—167°). 2-Methylcyclopentanone and (A) give (II) and a product which when dehydrated (KHSO₄ at 160—170°) affords a little 1-(β-9-phenanthrylethyl)-2-methyl-Δ¹-cyclopentene, m.p. 73—75°; much 9-ethylphenanthrene, m.p. 62—64°, is formed during the reaction. H. B.

cycloHexylamine and N-dimethylcyclohexylamine. G. BREUER and J. SCHNITZER (Monatsh., 1936, 68, 301—312).—Treatment of cyclohexyldimethylamine in Et₂O with the appropriate amount of conc. H₂SO₄ gives cyclohexylamine sulphate (I), m.p. 338°, and H sulphate, m.p. 117—118°, respectively, also obtained from their components. cycloHexylamine (II) and MeI in Et₂O afford cyclohexylamine hydriodide (III), m.p. 193—194°, and cyclohexyltrimethylammonium iodide, m.p. 263°. (II) and hexyl iodide at room temp. or in Et₂O yield (III), whereas at 100° cyclohexylhexylammonium iodide, m.p. 246°, is produced; cyclohexylhexylamine (IV), b.p. 243—245°/750 mm. (corresponding phenylcarbamide, m.p. 109—110°), is described. In Et₂O (IV) and conc. H₂SO₄ give (I). (III) is also formed from (II) and I in Et₂O; ill-defined dark oils are produced simultaneously. H. W.

Benzoylation of *as*-phenylethylcarbamide. E. A. ABRAHART (J.C.S., 1936, 1273—1274; cf. A., 1884, 1321).—The Bz, m.p. 121°, and p-NO₂·C₆H₄·CO, m.p. 175°, derivatives of NPhEt·CO·NH₂ (I) have been prepared from (I) in C₆H₅N and the respective acyl chloride at room temp. BzCl and (I) at 100° yield NBzPhEt, cyanuric acid, and HCl. F. R.

Action of bases on organic halogen compounds. I. Reaction of aryl halides with potassium amide. F. W. BERGSTROM, R. E. WRIGHT, C. CHANDLER, and W. A. GILKEY. II. Basic catalysis in the dehalogenation of the phenyl halides. R. E. WRIGHT and F. W. BERGSTROM (J. Org. Chem., 1936, 1, 170—178, 179—188).—I. PhX (X=Cl, Br, I, but not F) reacts rapidly with KNH₂ in NH₃ at -33° to give NH₂Ph and some NHPH₂, NPh₃, and p-C₆H₄Ph·NH₂, but only slowly or not at all in boiling Et₂O or C₆H₆. The relative ease of replacement of X was determined by the

“competition” method and follows the sequence Br>I>Cl (F not replaced at 33°), also obtained for replacements involving the *p*-phenylenedihalides. p-C₆H₄MeCl gives p-C₆H₄Me·NH₂ and tarry products. A mixture of mono- and di-phenylamines is also obtained from PhBr and Ca(NH₂)₂ or Ba(NH₂)₂ in NH₃ at room temp.

II. KNH₂ or rather the NH₂⁻ ion catalyses the following reactions in liquid NH₃ at -33°, which proceed slowly or not at all in the absence of catalyst (cf. A., 1924, i, 726; 1931, 1166): NHPH₂K+PhX=NHPH₂+KX; NHPH₂K+PhX=p-C₆H₄Ph·NH₂+KX; NPh₂K+PhX=NPh₃+KX (X=Cl, Br, I); CPh₃K+PhCl=KCl+CPh₄; and the reactions with K quinaldyl and PhCl to give 2-benzyl-, 2-benzhydryl-, and 2-triphenylmethylquinoline. The following reactions, however, in liquid NH₃ at -33° do not take place either alone or in presence of KNH₂: PhCl+KOPh=KCl+Ph₂O and PhBr+KCl=PhCl+KBr. CHPh₂K reacts slowly with PhCl in NH₃ at -33° in the absence of KNH₂ to give CHPh₂ and CPh₄, and catalyses the reaction between NPh₂K and PhCl. In general, the strongest bases (in Brønsted's sense) react most readily with PhX, and only the very strongest (NH₂⁻ and CHPh₂⁻) catalyse reactions between PhX and NHPH₂, etc. H. G. M.

Extensions of the Leuckart synthesis of amines. A. W. INGERSOLL, J. H. BROWN, C. K. KIM, W. D. BEAUCHAMP, and G. JENNINGS (J. Amer. Chem. Soc., 1936, 58, 1808—1811).—Ketones, CORR', are heated with a mixture of HCO₂NH₄ and HCO·NH₂ (used alone with H₂O-sol. and more volatile ketones) at 175—185° (with continuous removal of H₂O by distillation) and the resulting CHRR'·NH·CHO hydrolysed (conc. HCl) to the *dl*-amine (52—85% yield). The following are described: CHPhMe·NH₂; p-C₆H₄Me·CHMe·NH₂; p-C₆H₄Ph·CHMe·NH₂ (178—179°, 220—221°); CHMeBu^o·NH₂ (98—99°, >250°); α-*m*-tolyl-, b.p. 204—205° (113—114°, 164—165°), α-*p*-chlorophenyl-, b.p. 105°/10 mm. (144—145°, 192—193°), α-*p*-bromophenyl-, b.p. 116°/10 mm. (150—151°, 213—214°), α-*p*-anisyl-, b.p. 126°/20 mm. (117—118, 160—161°), α-*p*-phenoxyphenyl- (113—114°, 180—181°), α-*m*-nitrophenyl- (156—157°, 223—224°), and α-2-naphthyl- (151—152°, 198—199°), -ethylamines; fenchylamine, b.p. 190—191° (131—133°, >250°). The m.p. quoted in parentheses are those of the Bz derivative and hydrochloride, respectively. A mixture of neobornyl- (70%) and *d*-bornylamine is obtained from *d*-camphor in presence of PhNO₂. H. B.

Amide condensations. II. Transformations of acetoacetylphenylamide. G. V. TSCHELINCEV and B. M. DUBININ (Ber., 1936, 69, [B], 2023—2026; cf. this vol., 463).—The adaptability of CH₂Ac·CO·NPh₂ (I) to syntheses of the CH₂Ac·CO₂Et type is illustrated. (I) is transformed by cold conc. H₂SO₄ into 2-*keto*-1-phenyl-4-methyl-1:2-dihydroquinoline (II), m.p. 134—135°, in almost quantitative yield. With NHPh₂·NH₂ in Et₂O at 0° (I) gives the corresponding phenylhydrazine, m.p. 171—172°, which passes in boiling xylene into phenylmethylpyrazolone. The successive actions of Na and EtI

in EtOH on (I) lead to α -ethylacetamidiphenylamide, m.p. 70—71°, transformed by conc. H_2SO_4 into 2-keto-1-phenyl-4-methyl-3-ethyl-1:2-dihydroquinoline, m.p. 116—117°. α -Benzylacetamidiphenylamide, m.p. 108—109°, gives a non-cryst. product with conc. H_2SO_4 . Diacetylacetamidiphenylamide, m.p. 123—124°, from $(CH_3NaAc \cdot CO \cdot NPh_2)$ and $AcCl$ in Et_2O , is transformed by conc. H_2SO_4 into (II). H. W.

o- and p-Nitrophenylhydroxylamine. R. KUHN and F. WEYGAND (Ber., 1936, 69, [B], 1969—1974).—Addition of finely powdered o - $C_6H_4(NO_2)_2$ to a solution of ascorbic acid (I) in aq. Na_2CO_3 under N_2 and extraction of the solution with $EtOAc$ after acidification with $AcOH$ gives *o*-nitrophenylhydroxylamine (II), m.p. 74°, which with dil. aq. Na_2CO_3 gives a dark blue solution of the *Na* salt, $OH \cdot N \cdot C_6H_4 \cdot NO_2 \cdot Na$, and with conc. aq. $NaOH$ an intensely reddish-brown solution of the Na_2 salt, $ONa \cdot N \cdot C_6H_4 \cdot NO_2 \cdot Na$, thus explaining the colour reactions of o - $C_6H_4(NO_2)_2$ with aldoses, ketoses, and polyhydric aromatic phenols. For the prep. of (II) it is preferable to start from o - $NO \cdot C_6H_4 \cdot NO_2$ (III), since reaction can then be effected in acid solution and less (I) is necessary. (II) can be determined by running its solution in 50% $EtOH$ into standard $K_2Fe(CN)_6$ under N_2 until the blue colour is permanent, (III) being thus produced. Hydrogenation (PtO_2 in abs. $EtOH$) of (II) gives o - $C_6H_4(NH_2)_2$. Similarly, reduction of p - $C_6H_4(NO_2)_2$ or p - $NO \cdot C_6H_4 \cdot NO_2$ affords *p*-nitrophenylhydroxylamine (IV), m.p. 107°, which in dil. Na_2CO_3 gives a cherry-red solution of the *Na* salt and in dil. $NaOH$ a brownish-yellow solution of the Na_2 salt, which is sensitive to air owing to the catalytic effect of traces of metal, since the colour persists in presence of KCN . (II) is exceedingly unstable and when cryst. passes into a blackish viscous mass within a few hr., but can be preserved for some weeks in an evacuated tube at 0°. (IV) is considerably more stable. H. W.

Fission of tertiary amines by nitrous acid. R. WEGLER and W. FRANK (Ber., 1936, 69, [B], 2071—2077).—*N*-Methylbornylamine, b.p. 88°/15 mm., $\alpha_D^{25} -59.1^\circ$ (improved prep.), is converted by HNO_2 solely into the NO -derivative. Bornyl-dimethyl- or -diethyl-amine is largely converted into camphor and, under certain conditions, scarcely any *tert.* amine can be regenerated. The best method for the separation of *sec.* and *tert.* amine is secured by use of a large excess of $NaNO_2$ in cold 15—20% H_2SO_4 . Fission of *tert.* amines by HNO_2 appears general, and takes place most rapidly in $AcOH$ at 40—80° or, much more slowly, at room temp. N_2O_3 in dil. $AcOH$ can replace $NaNO_2$, or, better, N_2O_3 can be passed into the amine in $AcOH$, whereby the change takes place with marked evolution of heat. The smallest alkyl residue attached to N is removed as aldehyde or ketone. Cyclic residues appear somewhat more firmly attached than aliphatic residues of equal size, but CH_2Ph is removed at least as readily as Me , thus giving a parallel with von Braun's observation on the fission with $BrCN$. Reaction with *tert.* amines containing one or more readily eliminable groups is quant., giving NO -compounds and aldehydes or the corresponding acids in amount showing the

absence of appreciable secondary change. The course of the reaction is uncertain, but the aldehyde appears to be a primary product. The change $NR_2R' + HNO_2 \rightarrow NR_2 \cdot NO + R'OH$ is unlikely, since $R'OH$ ($CH_2Ph \cdot OH$) is not oxidised by HNO_2 alone or in presence of *tert.* amine or NO -compound. The following substances appear new: *nitroso-benzylethylamine*, an oil; *-benzylmethylamine*, b.p. 145°/18 mm.; *-dibenzylamine*, b.p. 140°/0.2 mm.; *-cyclohexylethylamine*, b.p. 140°/17 mm.; *-ethylcoctylamine*, b.p. 147°/15 mm. H. W.

Reactions of 8-nitro- α -naphthylamine and its derivatives. H. H. HODGSON and J. H. CROOK (J.C.S., 1936, 1338—1341).—4:8-Dinitroaceto- α -naphthalide, m.p. 231° (free amine, m.p. 193°), was the sole product of the action of HNO_3 (*d* 1.5) on 8-nitroaceto- α -naphthalide. Monobromination of the latter in $AcOH + NaOAc$ gave 4-bromo-8-nitroaceto- α -naphthalide, m.p. 202°, hydrolysed to the amine, m.p. 116°, converted (Sandmeyer) into 1-chloro-4-bromo-8-nitronaphthalene, m.p. 107.5°, whilst further bromination gave the 2:4-*Br*₂-compound (I), m.p. 198°, sol. in aq. $NaOH$, hydrolysed to the amine (II), m.p. 150°, converted (Sandmeyer) into 1-chloro-2:4-dibromo-8-nitronaphthalene, m.p. 146°, reduced (West's method) to 8-chloro-5:7-dibromo- α -naphthylamine, m.p. 159° (picrate, m.p. 160°; *Ac* derivative, m.p. 227°). Attempts at direct monobromination of 8-nitro- α -naphthylamine resulted in mixtures, whilst dibromination gave (II), which readily gave a Ac_2 compound, m.p. 190°, with excess of Ac_2O , and was reduced (West's method) to 2:4-dibromo-1:8-naphthylenediamine, m.p. 110—112°. Reduction of (I) with acid $SnCl_2 \cdot AcOH$ or by West's method caused condensation to 7:9-dibromo-2-methylperimidine, m.p. 176—177°. F. R.

Manufacture of aminotrifluoromethylarylsulphonic acids.—See B., 1936, 974.

Manufacture of substituted nitro- and aminochrysenes.—See B., 1936, 973.

Manufacture of aminochrysenesulphonic acids.—See B., 1936, 974.

Manufacture of 3-aminopyrenesulphonic acids.—See B., 1936, 974.

Benzidine phosphomolybdate.—See this vol., 1351.

2:7-Diaminofluorene.—See this vol., 1352.

Azo-dyes and their intermediate products. XVIII. *cis*- and *trans*-forms of stilbene dyes. P. RUGGLI and F. LANG (Helv. Chim. Acta, 1936, 19, 996—1007).—Observations with dyes derived from *cis*-stilbene disprove the hypothesis that substantivity of dyes on cotton depends on their existence in long, thread-like mols. which become attached to the similar mols. of cellulose. The by-products of the action of alkali on p - $NO_2 \cdot C_6H_4 \cdot CH_2Cl$ are formed in minor quantity only and are non-homogeneous; a substance, m.p. 199°, containing 5 O is described. *pp'*-Dinitrotolan, obtained from the dibromide or, preferably, the dichloride of *trans*-*pp*-dinitrostilbene, is reduced (Ni in $EtOAc \cdot EtOH \cdot H_2O$) to *cis*-*pp'*-diaminostilbene (I), m.p. 121° [$(C_6H_5)_2$], m.p. 104°;

Ac_2 , m.p. 172°, and Bz_2 , m.p. 253°, derivatives; *trans-pp'*-dibenzamidostilbene, m.p. 352°], which is unchanged by prolonged treatment with cold or short treatment with boiling *N*-HCl, but is isomerised by the boiling 10% acid to *trans-pp'*-diaminostilbene (II). Both substances are cautiously tetrazotised and coupled with 1:4-NH₂·C₁₀H₆·SO₃H to *cis*- (III) and *trans*- (IV) -stilbene-red [$:CH\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(OH)\cdot SO_3Na$]₂, each of which is a substantive dye, although the existence of (III) as a thread mol. is theoretically excluded. Reductive fission of (III) and (IV) yields (I) and (II), respectively. Similar coupling of tetrazotised (I) and (II) with 1:4-OH·C₁₀H₆·SO₃H yields *cis*- and *trans*-stilbene-violet [$:CH\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(OH)\cdot SO_3Na$]₂, each of which is a substantive dye. H. W.

3:5-Fluoronitroanisole. A. C. DE DEGIORGI (Anal. Asoc. Quím. Argentina, 1936, 24, 1—2).—3:5-Nitroaminoanisole in HCl with NaNO₂ and subsequently 40% HBF₄ yields 3-nitroanisole-5-diazonium borofluoride, decomp. 150° (darkens at 140°), which loses BF₃ on warming to give 3:5-fluoronitroanisole, m.p. 85°. F. R. G.

Action of sodium methoxide and ammonia on 1:3:5-fluorodinitrobenzene and 3:5-fluoronitroanisole. A. C. DE DEGIORGI (Anal. Asoc. Quím. Argentina, 1936, 24, 3—10).—The halogen in 1:3:5-C₆H₃F(NO₂)₂ (A., 1935, 1229) but not in the corresponding Cl-, Br-, and I-compounds, is replaced by the action of NaOMe or NH₃ in EtOH. The F in 1:3:5-OMe·C₆H₃F·NO₂ (preceding abstract) is not replaced by NH₃ in EtOH and is replaced less readily than the F in *m*-C₆H₄F·NO₂ by NaOMe. These results are discussed in relation to the views of De Crauw (A., 1931, 1283). F. R. G.

Orientation of *p*-methoxydiphenyl in the Friedel-Crafts reaction. L. F. FIESER and C. K. BRADSHAW (J. Amer. Chem. Soc., 1936, 58, 1738—1741).—In the Friedel-Crafts reaction, 4-methoxydiphenyl is substituted about 66% in position 4', the remainder in position 3. Solvents have little effect on the ratio. *p*-C₆H₄Ph·OMe, (·CH₂·CO)₂O, and AlCl₃ in cold PhNO₂ give 24.5% of γ -keto- γ -*p*-4'-methoxydiphenylbutyric acid (I), m.p. 200—201° (slight darkening) (*Me* ester, m.p. 99—110°), and 60% of γ -keto- γ -4-methoxy-3-diphenylbutyric acid (II), m.p. 155° (*Me* ester, m.p. 48—49°), readily separable owing to the sparing solubility of the Na salt of (I). Reduction (Clemmensen) of the crude *Me* esters of (I) and (II) affords γ -*p*-4'-methoxydiphenyl-, m.p. 148—149° (previous softening), and γ -4-methoxy-3-diphenyl-, m.p. 109°, -butyric acid, respectively; the latter could not be cyclised (H₂SO₄; acid chloride; Bougault). Oxidation of (I) with KMnO₄-aq. KOH and of (II) with NaOBr gives 4-methoxydiphenyl-4'-, m.p. 248—249° (*Me* ester, m.p. 172—173°), and -3-, m.p. 166—167°, -carboxylic acid, respectively, demethylated (48% HBr, AcOH) to 4-hydroxydiphenyl-4'- (III), m.p. 293—294° (*Me* ester, m.p. 224—225°), and -3-, m.p. 212—213° (*Me* ester, m.p. 93—94°), -carboxylic acid, respectively. (III) is oxidised (aq. KMnO₄) to *p*-C₆H₄(CO₂H)₂. (I) and 2.5% NaOCl at 100° (bath) afford 3-chloro-4-methoxydiphenyl-4'-carboxylic acid, m.p. 275—276° (*Me* ester, m.p.

145—146°), also prepared by oxidation (alkaline KMnO₄) of 3-chloro-4-methoxy-4'-acetyldiphenyl, m.p. 109—110° (from 3-chloro-4-methoxydiphenyl, AcCl, and AlCl₃ in CS₂). 3-Bromo-4-methoxydiphenyl-4'-carboxylic acid, m.p. 270—271° (*Me* ester, m.p. 148—149°), and 3-bromo-4-methoxy-4'-acetyldiphenyl, m.p. 97—98°, are prepared by analogous methods. *p*-C₆H₄Ph·OMe, AcCl, and AlCl₃ in CS₂ (at b.p.), C₂H₂Cl₄ (at 0—20°), or PhNO₂ (at 0—20°) give 65—75% of 4-methoxy-4'- (IV), m.p. 153—154° and some -3- (V), m.p. 62—63°, -acetyldiphenyl. Rearrangement (Fries) of *p*-C₆H₄Ph·OAc affords 4-hydroxy-4'-, m.p. 206—207°, and -3-, m.p. 61—62°, -acetyldiphenyl, which are methylated to (IV) and (V), respectively. H. B.

Condensation of phenols with ethanolamine and formaldehyde. H. A. BRUSON (J. Amer. Chem. Soc., 1936, 58, 1741—1744).—NH₂·CH₂·CH₂·OH (1 mol.) and 30% CH₂O (1 mol.) followed (after 1 hr.) by *o*-C₆H₄Ph·OH (1 mol.) in EtOH, give after heating at 100° (bath) 38% of a hydroxyphenyl-*N*- β -hydroxyethylbenzylamine, OH·C₆H₃Ph·CH₂·NH·CH₂·CH₂·OH, m.p. 116°, also obtained by prolonged interaction of equimol. quantities of the reactants in MeOH at 20—25°. *p*-C₆H₄Ph·OH similarly affords a compound, m.p. 102°, which may be (OH·C₆H₃Ph·CH₂)₂N·CH₂·CH₂·OH, whilst *p*-cyclohexylphenol gives a compound, m.p. 170—171°, of (probably) similar constitution. 5-Chloro-2-hydroxydiphenyl, 2:4-C₆H₃Cl₂·OH, 3-nitro-*p*-cresol, *p*-C₆H₄Bu·OH, *p*-tert.-amylphenol, *p*-NO₂·C₆H₄·OH, and *p*-OH·C₆H₄·COPh similarly yield (probably) 5-chloro-2-hydroxy-3-phenyl-, m.p. 182—183°, 3:5-dichloro-2-hydroxy-, m.p. 199—200°, 3-nitro-2-hydroxy-5-methyl-, m.p. 205—206°, 2-hydroxy-5-tert.-butyl-, m.p. 127—128°, 2-hydroxy-5-tert.-amyl-, m.p. 114°, 5-nitro-2-hydroxy-, m.p. 196°, and 2-hydroxy-5-benzoyl-, m.p. 188—189°, -*N*- β -hydroxyethylbenzylamine, respectively. These substances react further with CH₂O to form resins. Resinous products were obtained from PhOH, cresols, *o*- and *p*-C₆H₄Cl·OH, and *o*-cyclohexyl-, *p*-benzyl-, and *p*- $\alpha\gamma\gamma$ -tetramethylbutylphenols; *m*-C₆H₄(OH)₂ gives an amorphous solid. H. B.

Oxidation of pyrocatechol by tyrosinase.—See this vol., 1417.

cycloHexyltrichloromethylcarbinol. J. W. HOWARD and R. J. BROWN (J. Amer. Chem. Soc., 1936, 58, 1657).—Mg cyclohexyl bromide added to chloral in Et₂O gives cyclohexyltrichloromethylcarbinol, b.p. 119—121°/15 mm. (acetate, b.p. 170°/680 mm.; propionate, b.p. 188°/681.6 mm.; butyrate, b.p. 183°/682.6 mm.; benzoate, b.p. 210°/683.3 mm.), in approx. 30% yield. H. B.

Substituted hydroxybenzyl alcohols. B. DUNNING, jun., F. DUNNING, and E. E. REID (J. Amer. Chem. Soc., 1936, 58, 1565—1568).—2-Hydroxy-4-, m.p. 103°, and -6-, m.p. 80°, -methyl-, -5-ethyl-, m.p. 83°, and -5-propyl-, m.p. 73°, -benzyl alcohol are prepared by reduction (Adams) of the appropriate OH·C₆H₃Alk·CHO (prep.; Reimer-Tiemann), whilst 5-bromo-3-iodo-, m.p. 86°, and 3-chloro-5-bromo-, m.p. 93°, -2-hydroxy-, 6-bromo-3-hydroxy-, m.p. 124°, and 3-bromo-4-hydroxy-, m.p. 128°, -benzyl alcohol are obtained by direct halogenation. The relative

bactericidal (towards *S. aureus*), anaesthetic, and anti-spasmodic activities of the above and *o*-(I), *m*-, and *p*-OH·C₆H₄·CH₂·OH, and the 3:5-Cl₂-, -Br₂-, and -I₂-, 5-Cl-, -Br-, and -I-, and 5-Me derivatives of (I) are determined; the bactericidal activity rises as the partition coefficient, solubility in olive oil/solubility in H₂O, increases.

H. B.

Mechanism of asymmetric synthesis with reference to a new type. J. KENYON and S. M. PARTRIDGE (J.C.S., 1936, 1313—1317).—(+)-*Methyl- α -dibromo-n-propylcarbinol*, b.p. 103°/13 mm., $\alpha_{589.3}^{16} + 2.04^\circ$, $\alpha_{579.0}^{16} + 2.15^\circ$, $\alpha_{540.1}^{16} + 2.46^\circ$, $\alpha_{435.8}^{16} + 4.90^\circ$ (*l*, 0.5), obtained from (-)- α - γ -dimethylallyl alcohol and Br-CHCl₃, is oxidised by CrO₃-AcOH to (+)-*Me α -dibromo-n-propyl ketone*, b.p. 90°/13 mm., $\alpha_{589.3}^{16} + 3.06^\circ$, $\alpha_{579.0}^{16} + 3.34^\circ$, $\alpha_{540.1}^{16} + 3.85^\circ$, $\alpha_{435.8}^{16} + 8.25^\circ$ (*l*, 0.25), whilst (+)- α - γ -dimethylallyl alcohol by similar treatment gives the *dl*-*dibromo-alcohol*, b.p. 112°/20 mm., oxidised to *dl*-*Me α -dibromo-n-propyl ketone*, b.p. 90°/13 mm. Further, the similarly constituted (+)- γ -phenyl- α -methylallyl alcohol (I) with Br-CHCl₃ gives a mixture of two carbinols separated by fractional crystallisation into *d*- (II), m.p. 112—113°, $[\alpha]_{589.3}^{16} + 107.1^\circ$, $[\alpha]_{579.0}^{16} + 115.9^\circ$, $[\alpha]_{540.1}^{16} + 128.0^\circ$, $[\alpha]_{435.8}^{16} + 261.0^\circ$ in CHCl₃, and *l*- α -*dibromo- β -phenylethylmethylcarbinol*, m.p. 87—88°, $[\alpha]_{589.3}^{16} - 97.8^\circ$, $[\alpha]_{579.0}^{16} - 115.4^\circ$, $[\alpha]_{540.1}^{16} - 119.7^\circ$, $[\alpha]_{435.8}^{16} - 224.0^\circ$ in CHCl₃. The latter are oxidised without separation to (-)- α -*dibromo- β -phenylethyl Me ketone*, m.p. 127°, $[\alpha]_{540.1}^{16} - 10.15^\circ$ (*l*, 2; *c*, 2.7 in CHCl₃). Oxidation of the (+)- and (-)-carbinols yields respectively (+)- and (-)-ketones, both m.p. 127°, possibly optically pure since the rotatory powers were of equal magnitude and opposite sign. Addition of Br to the (-) form of (I) gives a (-)- α -*dibromo- β -phenylethylmethylcarbinol*, m.p. 112—113°, the optical enantiomorph of (II), oxidised to the optically pure (-)-ketone. It is thought that asymmetric addition takes place when there is a difference in energy associated with the diastereoisomeric intermediate products, a conclusion supported by the fact that there is an unexpectedly wide variation in the rotatory powers of the ketones obtained by oxidation of the mixtures of dibromo-alcohols by bromination at different temp., the (-)- or (+)-ketone predominating according to whether the temp. is low or high.

F. R.

Asymmetric reaction. Preparation of an alcohol or of its diastereoisomeride, exclusively, by reactions asymmetric or not. F. KAYSER (Ann. Chim., 1936, [xi], 6, 145—248; cf. A., 1924, i, 825).—Hydratropaldehyde with the theoretical quantity of MgPhBr in Et₂O affords (α)- α -*diphenylpropyl alcohol* (I), b.p. 180—182°/17—18 mm. [*phenylcarbamate*, m.p. 116°; *chloride*, m.p. 140°; boiling AcCl containing NaOAc affords an Ac derivative of indefinite b.p. and some of the (β)-acetate]. Similarly, β -*phenylbutaldehyde*, b.p. 120°/35 mm. (prep. described), with MgPhBr affords (α)- α -*diphenylbutyl alcohol* (II), b.p. 183—184°/18 mm. [oxidised to ethyldeoxybenzoin (III); *phenylcarbamate*, m.p. 119°; *chloride*, m.p. 49°; Ac, b.p. indefinite, and Bz, b.p. 110°/20 mm., derivatives]; α -*diphenylpropaldehyde* affords (α)- α -*triphenylpropyl alcohol* (IV), m.p. 92° (cf. A., 1933, 710) [oxidised to benzyldeoxybenzoin

(V); by heating with KHSO₄ a product, m.p. 63°, is obtained identical with that from the (β)-diastereoisomeride; *phenylcarbamate*, m.p. 125°; *chloride*, decomp. when heated; Ac derivative, m.p. 70°]. (I), (II), and (III) are obtained free from the (β)-diastereoisomerides. Methyldeoxybenzoin (VI), (III), and (V) are not reduced by H₂-Pt, -Ni, or -Pd, but with MgBu^oCl, a small amount of *sec*. alcohol, (VIII) (below), and γ δ -*triphenyl- β -dimethylpentan- γ -ol*, m.p. 117°, respectively, are formed. Deoxybenzoin with MeI, EtBr, and CH₂PhBr in warm EtOH containing NaOEt affords (VI), (III), and (V), respectively. (VI) with Na-Hg in EtOH or Na in hot EtOH affords (β)- α -*diphenylpropyl alcohol* (VII), m.p. 48° [oxidised to (VI); *phenylcarbamate*, m.p. 122°; the chloride is identical with that from (I); Ac derivative, m.p. 104°], and a *compound*, (C₁₀H₁₀O)_n, m.p. 266°. Similarly (III) and (V) afford (β)- α -*diphenylbutyl alcohol* (VIII), m.p. 82° [oxidised to (III); *phenylcarbamate*, m.p. 124°; *chloride*, m.p. 78°; Ac derivative, m.p. 53°], and (β)- α -*triphenylpropyl alcohol* (IX), m.p. 87° [oxidised to (V); dehydrated (KHSO₄) to a substance, m.p. 63°; *phenylcarbamate*, m.p. 121.5°; *chloride*, m.p. 90°; Ac derivative, m.p. 90°], respectively. The asymmetric synthesis of one diastereoisomeride exclusively is explained by postulating a sp. influence (leading to distortion) of one alkyl (R) on the position in space occupied by CO with respect to R and R', thereby providing a favoured position for attack by the incoming R'' (from MgR''X). *trans*-Stilbene oxide (X) with MgEtBr affords (VIII) whereas the *cis*-isomeride (XI) gives (II) in poor yield. (X) with CH₂Ph·MgCl gives (IX), whereas (XI) affords (IV). (X) with MgMeI gives a mixture of *di- α -diphenylpropyl ether*, m.p. 138°, a *polymeride* (?), m.p. 282°, of diphenylpropyl alcohol, and a *substance*, m.p. 56°; (XI) with MgMeI affords only stilbene. (X) with MgMeBr gives stilbene and (I), as does (XI). Methylstilbene oxide (A., 1932, 394) with H₂-Ni in EtOH at 35—40° affords (VII). Benzylstilbene with BzO₂H affords *benzylstilbene oxide*, m.p. 65—66°, reduced (Ni-H₂) to (IX). In neither case is there any evidence of the presence of the α -diastereoisomeride, nor of the rupture of both C·O linkings of the oxido-compound.

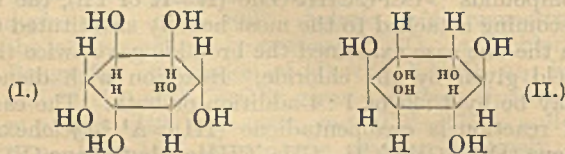
J. L. D.

Addition of alkyl halides to the ethylenic linking. F. STRAUS and W. THIEL [and, in part, G. SZYSZKA] (Annalen, 1936, 525, 151—182).—OMe·CH₂Cl (I) and OMe·CHPhCl (II) add on to unsaturated compounds alone or, better, in presence of HgCl₂ or, best, ZnCl₂, SnCl₄, or SbCl₅, to give compounds >CCl·C·CHR·OMe (R=H or Ph), the Cl becoming attached to the most heavily substituted C. In the one case examined the bromide gave twice the yield given by the chloride. Reaction with dienes may be by 1:2- or 1:4-addition or both. The ease of reaction is cyclopentadiene (III) > $\Delta^{1:3}$ -cyclohexadiene (IV) > CMe₂·CH₂, CMe₂·CHMe > butadiene (V) > mono-unsaturated alicyclic compounds. Yields are usually 70%. The course of reaction is not always certain. Solutions of the alkoxy-halides obtained from the acetal or aldehyde and HCl-MeOH can sometimes be used. *p*-OMe·C₆H₄·CH₂Cl (VI), but not CH₂PhCl, condenses. (CH₂Br)₂O readily condenses by both Br, (CH₂Cl)₂O less readily by both Cl. This

is held to support direct addition of alkyl halides to C in such compounds as $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$. (I) and (V) give α -chloro- ε -methoxy- ε -phenyl- Δ^{β} -pentene, b.p. 126—127°/12 mm. (dibromide, b.p. 150°/0.4 mm.), oxidised by $\text{KMnO}_4\text{-COMe}_2$ to $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 101—102°, and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$. (II) and (V) give (?) γ -chloro- ε -methoxy- Δ^{α} , b.p. 35°/10 mm., 148°/756 mm., and α -chloro- ε -methoxy- Δ^{β} -pentene, b.p. 56°/10 mm., 168°/758 mm. $\text{OMe}\cdot\text{CHPhBr}$ and (V) give α -bromo- ε -methoxy- ε -phenyl- Δ^{β} -pentene, b.p. 92°/0.1 mm., and (VI) gives α -chloro- ε -methoxy- ε -anisyl- Δ^{β} -pentene, b.p. 104°/0.1 mm. (13%). (II) and (IV) yield 1-chloro-2- or -4- α -methoxybenzyl- Δ^1 -cyclohexene, b.p. 112°/0.1 mm., and the 2- or 4- α -methoxy-ethyl, b.p. 81°/10 mm., and -p-anisyl, b.p. 128—129°/0.02 mm., derivatives are also obtained. CPh_3Cl and (IV) afford CHPh_3 and 1-chloro-2-triphenylmethyl- Δ^5 -cyclohexene, b.p. 103°/2 mm. (II) and (III) give a 1-chloro-2- or -3- α -methoxybenzylcyclopentene, b.p. 99—100°/0.1 mm. (I) and $\text{CMe}_2\cdot\text{CH}_2$ give *Me* γ -chloroisoamyl ether, b.p. 81—81.5°/120 mm., 136°/751 mm. (60% with 10% of Bu^nCl), readily hydrolysed by acid or alkali to γ -methoxy-tert.-amyl alcohol, b.p. 51—52°/15 mm., 144°/764 mm. (p-nitrobenzoate, m.p. 72—74°). $\text{CMe}_2\cdot\text{CHMe}$ with (II) gives γ -chloro- α -phenyl- β -methyl-tert.-amyl *Me* ether, b.p. 133—135°/16 mm., and with (I) *Me* γ -chloro- β -methyl-tert.-amyl ether, b.p. 46—46.5°/14 mm., 153°/761 mm., converted by 5% Na_2CO_3 into δ -methoxy- $\beta\gamma$ -dimethylbutan- β -ol, b.p. 159°/750 mm., 58—59°/15 mm., and some α -methoxy- $\beta\gamma$ -dimethyl- Δ^{β} -butene, b.p. 28.5°/15 mm., 115°/750 mm. (II) and $\text{CHPh}\cdot\text{CH}_2$ give α -chloro- γ -methoxy- $\alpha\gamma$ - or - $\alpha\beta$ -diphenylpropane, b.p. 122.5°/0.1 mm. (II) and cyclohexene give 2- α -methoxybenzylcyclohexyl chloride, b.p. 96°/0.2 mm., oxidised to an acid, $\text{C}_{12}\text{H}_{14}\text{O}_2$, m.p. 123.2° (*Me* ester, m.p. 26.5—27°, b.p. 144°/16 mm.), and a little BzOH ; (I) affords similarly 2- α -methoxyethylcyclohexyl chloride (45%), b.p. 89—91°/20 mm., 192°/763 mm. (II) and Δ^2 -dihydronaphthalene give 2-chloro-3- α -methoxybenzyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which, however, decomposes into C_{10}H_8 , HCl , and $\text{CH}_2\text{Ph}\cdot\text{OMe}$, with some formation also of CH_2PhCl ; Δ^1 -dihydronaphthalene reacts more violently, but no pure product was isolated. R. S. C.

Phenyl β -hydroxy- $\beta\beta$ -diphenylvinyl sulphone.—See this vol., 1327.

Cyclitols. III. Configuration of the active inositols. T. POSTERNAK (Helv. Chim. Acta, 1936, 19, 1007—1010; cf. A., 1932, 1127).—Regulated oxidation by KMnO_4 of *l*-inositol (I) (prep. from revertex through quebrachitol described) gives mucic



and *d*-saccharic acid the isolation of which establishes the configurations (I) and (II) for (I) and *d*-inositol, respectively. *d*-Quercitol is therefore 1-deoxy-*l*-inositol. H. W.

Production of steryl glucosides. H. LETTRÉ and A. HAGEDORN (Z. physiol. Chem., 1936, 242,

210—214; cf. MacCorquodale *et al.* A., 1930, 1036).—Cholesterol (I) successively boiled in anhyd. Et_2O with acetobromoglucose (II), Ag_2O , and CaH_2 and acetylated gives cholesteryltetra-acetylglucoside, m.p. 159—160°, $[\alpha]_D^{25} -23.1^\circ$ in CHCl_3 . Similarly dihydro- and dehydro-ergosterol give dihydro-, m.p. 187—188°, $[\alpha]_D^{25} -19.4^\circ$ in CHCl_3 , and dehydro-ergosteryltetra-acetylglucoside (III), m.p. 167—168° $[\alpha]_D^{25} +62.4^\circ$ in CHCl_3 , respectively, and (I) with acetobromolactose yields, after acetylation, the hepta-acetate, m.p. 195°, $[\alpha]_D^{25} -16.3^\circ$, of cholesteryl-lactoside, m.p. 260° (decomp.), $[\alpha]_D^{25} -37.8^\circ$. Together with (III) a substance, m.p. 159—160°, is produced. The glucoside of cholesteryl oxide with hot Ac_2O and NaOAc gives 5-hydroxy-6-acetoxy-3-tetra-acetyl- β -glucosidocholestan (IV), m.p. 212—213°, $[\alpha]_D^{25} -26.4^\circ$, also obtained by the interaction of cholestanetriol and (II) followed by acetylation. (IV) with Na in EtOH gives cholestanetriol-3-glucoside, m.p. 263—265° (decomp.), which yields lather-producing solutions in H_2O . The other glucosides are H_2O -insol. Ergosterylgucoside acquires no antirachitic power on ultra-violet irradiation.

W. McC.

Sterol group. XXVI. 7-Methylenecholesterol. B. BANN, I. M. HELBRON, and F. S. SPRING (J.C.S., 1936, 1274—1276).—7-Ketocholesteryl acetate (I) + 3 mols. of MgMeI gives 7-hydroxy-7-methylcholesterol (II), m.p. 165° (3-mono benzoate, m.p. 175°; 3-monoacetate, m.p. 164°). Dehydration of the mono-benzoate by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ or the Darzens method or sublimation in a high vac. gives 7-methylenecholesteryl benzoate (III; $\text{R}=\text{Bz}$), m.p. 141°, hydrolysed to 7-methylenecholesterol (III; $\text{R}=\text{H}$), m.p. 85° (3 : 5-dinitrobenzoate, m.p. 162°; acetate, m.p. 62—64°), directly isolable from the mother-liquor of (II) and the sole product of (I)+excess of MgMeI , which after irradiation was antirachitically inactive. F. R.

Micro-determination of cholesterol.—See this vol., 1436.

Rates of isomerisation and of hydrogen isotope exchange in unsaturated nitriles.—See this vol., 1344.

Pentadeuterobenzoic acid. H. ERLNMEYER and A. EPPRECHT (Helv. Chim. Acta, 1936, 19, 1056—1059; cf. this vol., 983).—The following consts. of $\text{C}_6\text{D}_5\cdot\text{CO}_2\text{H}$ and BzOH , respectively, are recorded: m.p. 120.9° and 121.7°; solubility in 100 c.c. of H_2O at 18°, 0.34 and 0.28 g.; mol. heat of combustion, 761.38 and 771.4 kg.-cal.; heat of formation from the elements, 106.12 and 91.0 kg.-cal.; normal acidity potential, 205.7±0.3 and 205.6±0.3 mv. H. W.

Asymmetric carbon atom CHDR'' . III. Phenylpentadeuterophenylacetic acid. H. ERLNMEYER and H. SCHENKEL (Helv. Chim. Acta, 1936, 19, 1169—1170; cf. this vol., 467, 604).—*l*- $\text{CHPhBr}\cdot\text{CO}_2\text{H}$, $[\alpha]_D^{20} -145^\circ$ in C_6H_6 , is converted by C_6D_6 in presence of Zn dust into phenylpentadeuterophenylacetic acid, $\text{C}_6\text{D}_5\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, m.p. 144°, $[\alpha]_D \pm 0^\circ$, which could not be resolved into its optical antipodes by morphine or strychnine. H. W.

Halogenation of *o*-sulphobenzoic anhydride. D. TWISS and L. H. FARINHOLT (J. Amer. Chem. Soc., 1936, 58, 1561—1565).—3-Bromo- (I), m.p. 175—176°, 3:6-dichloro- (II), m.p. 121—122°, 3:6-dibromo- (III), m.p. 167—168°, 3:6-di-iodo- (IV), m.p. 243—245°, 3:5:6-tribromo- (V), m.p. 224°, 3:5:6-tri-iodo- (VI), m.p. 287—288°, tetrachloro-, m.p. 158—159°, tetrabromo-, m.p. 216—217°, and tetra-iodo- (VII), decomp. gradually about 300°, *o*-sulphobenzoic anhydrides are prepared by halogenation of $o\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, its anhydride, or, more conveniently, its NH_4^+H^- salt [obtained by hydrolysis (dil. HCl) of saccharin] in (usually) 60% oleum at 150—180°. In some cases I is used as catalyst and the anhydrides are purified by conversion into the corresponding $(\text{NH}_4)_2$ salt and subsequent treatment with SOCl_2 . All except (VII) are readily hydrolysed even by atm. moisture to the acids. The positions of the halogen atoms are determined by removal of the SO_3H from the acids by aq. H_2SO_4 at 200—210°; (I) thus gives $m\text{-C}_6\text{H}_4\cdot\text{Br}\cdot\text{CO}_2\text{H}$; (II), 2:5- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{H}$ and a little $p\text{-C}_6\text{H}_4\text{Cl}_2$; (III), 2:5- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{CO}_2\text{H}$; (V), 2:3:5- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{CO}_2\text{H}$; the I-derivatives are destroyed. Saturation of a conc. solution of tetraiodo-*o*-sulphobenzoic acid in aq. NH_3 with H_2S gives $(\text{NH}_4)_2$ 3:5:6-tri-iodo- [converted by conc. H_2SO_4 at 160° into (VI)] and di-iodo-*o*-sulphobenzoate [which with conc. H_2SO_4 at 150° affords a di-iodo-*o*-sulphobenzoic anhydride, m.p. 221—223°, different from (IV)]. H. B.

Manufacture of basic esters of polyarylacetic acids.—See B., 1936, 975.

Agents of capillary activity [cyclohexylaliphatic acids].—See B., 1936, 975.

Valency problem of the quinquevalent phosphorus atom. II. L. ANSCHÜTZ, F. KOENIG, F. OTTO, and H. WALBRECHT (Annalen, 1936, 525, 297—311; cf. A., 1930, 1429).—The peculiar reactivity of one Cl of PCl_5 is due to electrostatic repulsion of the five electronegative Cl and not to a special type of linking of one Cl. In accordance with this view, the reactivity is depressed if Cl is replaced by OPh or substituted OPh. This is proved for the reaction of $\text{OPh}\cdot\text{PCl}_4$, $(\text{OPh})_2\text{PCl}_3$, $o\text{-COCl}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PCl}_4$, and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PCl}_4$ with H_2O , EtOH, PhOH, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ (I), and indene (II). Chloroindanylophosphorus tetrachloride is purified by pptn. by ligroin from warm PhNO_2 , and then reacts slowly with (I) and not at all with (II), but rapidly with H_2O , EtOH, or PhOH by loss of HCl from the nucleus. The following are described. Ph_3PO_4 , m.p. 45°; salicylic acid phosphate ("phosphosal"); $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}_3\text{H}_2$; *o*-anisoylphosphorus dichloride, b.p. 130—131°/13 mm., and tetrachloride, cryst.

R. S. C.

Derivatives of β -amino- α -hydroxy- α -phenylpropionic acid. B. CROCCA (Gazzetta, 1936, 66, 533—539).— CH_2BzCl , HCN, and NH_3 yield β -chloro- α -hydroxy- α -phenylpropionic acid, m.p. 132°. This with aq. NHMe_2 (reaction completed at 110°) gives the NH_2Me_2 salt, m.p. 251° (decomp.), of β -dimethylamino- α -hydroxy- α -phenylpropionic acid, of which the *Me*, b.p. 155—156°/14—15 mm., and *Pr*^a, b.p. 171—172°/14—15 mm., esters yield respectively

(BzCl) *Me* (I), m.p. 163° (decomp.), and *Pr*^a β -dimethylamino- α -benzoyloxy- α -phenylpropionate hydrochloride (II), m.p. 177—178° (decomp.). *Pr*^a β -dimethyl- (III), m.p. 136°, and β -diethyl-amino- α -acetoxy- α -phenylpropionate hydrochloride (IV), m.p. 134°, are obtained similarly. *Pr*^a β -chloro- α -hydroxy- α -phenylpropionate, b.p. 173°/14—15 mm., with NHMe_2 at 100° gives β -dimethylamino- α -hydroxy- α -phenylpropiondimethylamide, b.p. 173°/14—15 mm. (I) and (II) are surface anaesthetics, and, intramuscularly, antipyretics; (III) also, subcutaneously, has depressor action, as, in a less degree, has (IV), with increased toxicity. E. W. W.

Constitution of isomeric dichlorofluorenone-carboxylic acids formed by the action of sulphuric acid on 3:3'-dichlorodiphenic acid. E. H. HUNTRESS and E. R. ATKINSON (J. Amer. Chem. Soc., 1936, 58, 1514—1518).—The keto-acid, $\text{C}_{14}\text{H}_8\text{O}_2\text{Cl}_2$, previously obtained (A., 1933, 1293) from 3:3'-dichlorodiphenic acid (I) and conc. H_2SO_4 at 170°, is 1:6-dichlorofluorenone-4-carboxylic acid (II), new m.p. 248—249°, which results by isomerisation of the first-formed 1:6-dichlorofluorenone-5-carboxylic acid (III). The inconsistent titration (*loc. cit.*) of (II) is due to solvation. Dehydration of (I) with conc. H_2SO_4 at 80—90°/24 hr., 95—104°/1 hr., or 125°/1 hr. gives (III), but at 125°/5 hr., 135—145°/4 hr., or 150—160°/1 hr., (II) results. Isomerisation does not occur with H_3PO_4 at 215°; (I) thus affords (III) whilst 5:5'-dichlorodiphenic acid (IV) yields (II). 1:6-Dichloro-5-aminofluorenone (*loc. cit.*) is deaminated to 1:6-dichlorofluorenone (V). (II) and conc. H_2SO_4 at 200—215° give 4:6-dichlorofluorenone (VI) (and a little unidentified material), also similarly obtained from (I), (III), and (IV) at about 200°, (V) at 150° (rearrangement not complete at 125°), and 1:8-dichlorofluorenone (VII) at 180—190°. Neither decarboxylation nor rearrangement occurs with (II) and H_3PO_4 . Distillation of the Ca salts of (I) and (IV) gives (VII) and (VI), respectively. H. B.

Condensation of aldehydes with malonic acid in the presence of organic bases. Condensation of (V) anisaldehyde, (VI) *p*-hydroxybenzaldehyde, (VII) *m*-hydroxybenzaldehyde. K. C. PANDYA and T. A. VAHIDY (Proc. Indian Acad. Sci., 1936, 4, A, 134—139, 140—143, 144—146).—V. Condensation of anisaldehyde with $\text{CH}_2(\text{CO}_2\text{H})_2$ using $\text{C}_5\text{H}_5\text{N}$, lutidine, and isoquinoline gives *p*-methoxycinnamic acid but with other bases the first product is anisylidenemalonic acid. Condensation also occurs without using a base.

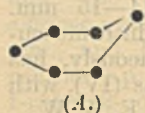
VI. With $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, similar results are obtained, the amount of product, either *p*-hydroxycinnamic or the *p*-coumaric acid, being increased by using a base.

VII. The yields of condensation product with different bases are compared, $\text{C}_5\text{H}_5\text{N}$ giving the best yield at the optimum temp. 105—110°. F. R. S.

Non-existence of multiplanar cyclohexane rings. R. D. DESAI and R. F. HUNTER (Nature, 1936, 138, 548; cf. A., 1935, 1495; this vol., 831, 846).—4:4-Dimethylcyclohexane-1-carboxylic-1-acetic acid and -1:1-diacetic acid, now synthesised from 4:4-dimethylcyclohexanone, each exists in one form only,

thus supporting the uniplanar structure of the *cyclohexane* ring. L. S. T.

Sachse-Mohr theory of the configuration of *cyclohexane* and the application of the Bredt rule to tetrahydro[*iso*]phthalic anhydride. J. BREDT (J. pr. Chem., 1936, [ii], 147, 22—28).—Theoretical. Interconversion of boat into chair forms of a C₆ ring occurs by way of the "sofa" form (A) and the mol. is never planar. By analogy with other systems it is inferred that the anhydride of tetrahydroisophthalic acid is intermol., and that an eight-membered ring containing one O and bridged across the 1:5 positions by one C cannot exist with the bridge containing a double linking. R. S. C.



Chloral derivatives of salicylic acid. N. M. SHAH and R. L. ALIMCHANDANI (J. Indian Chem. Soc., 1936, 13, 475—477).—*o*-OMe·C₆H₄·CO₂H and chloral in conc. H₂SO₄ give 2-methoxy-5-ββ-dichloro-α-hydroxyethylbenzoic acid (I), m.p. 224° (lit. 216°), and a sulphonic acid, converted into (I) by boiling in H₂O. Other salicylic acid derivatives do not undergo this condensation. (I) yields by reduction 2-methoxy-5-ββ-dichloroethylbenzoic acid (II), m.p. 134—135° (lit. 127°), and by H₂SO₄ at 100° 2-methoxy-αββ-tetrachloroethylbenzoic acid, m.p. 138° (lit. 132°), and a small amount of a substance, m.p. 177°. (II) and conc. H₂SO₄ at 100° give 3-carboxy-4-methoxyphenylacetic acid, +H₂O, m.p. 141—142°, and anhyd., m.p. 153°. R. S. C.

Isatdiazide. A. DARAPSKY and B. GAUDIAN (J. pr. Chem., 1936, [ii], 147, 43—52).—Phthalyl chloride (I) and aq. NaN₃ give isatdiazide, *o*-N₃·CO·C₆H₄·NH·CO·N₃ (II), m.p. 101°, and a trace of (?) phthalyl azide. Probably *o*-N₃·CO·C₆H₄·NCO is first formed which then reacts with HN₃, liberated from NaN₃ by products of hydrolysis of (I). With hot dil. aq. NaOH (II) gives anthranilic acid and with NH₂Ph at 100° the dianilide, m.p. 222°, which is stable to acid and alkali, but with conc. HCl at 200—220° gives NH₂Ph and 2:4-diketo-3-phenyltetrahydroquinazoline, m.p. 272°. With hot EtOH (II) gives *o*-phenylenediurethane, hydrolysed by 2*N*-NaOH to *o*-phenylenecarbamide, *o*-C₆H₄(NH)₂CO, m.p. >300°. With conc. NH₃ (II) gives 2:4-diketotetrahydroquinazoline (III) and with N₂H₄ 3-amino-2:4-diketotetrahydroquinazoline, m.p. >280° [benzylidene derivative, m.p. 245—246° (lit. 240°)]; with HNO₂ gives N₂O and (III)]. R. S. C.

Synthesis of substances of possible physiological activity. L. F. FIESER, M. FIESER, E. B. HERSHBERG, H. L. HOLMES, and M. S. NEWMAN (Science, 1936, 83, 558).—Condensation of (CH₂·CO)₂O (I) with α-C₁₀H₇·OMe gives a suitable starting material for the synthesis of 9-methoxyphenanthrene-1:2-dicarboxylic anhydride, m.p. 249—250° (corr.), by reduction, condensation of the ester with Et₂C₂O₄, cyclisation, and dehydrogenation. The 6-methoxy- and 6:7-dimethoxy-derivatives of octahydrophenanthrene-11:12-dicarboxylic anhydride were prepared by addition of butadiene (II) to the unsaturated anhydr-

ides obtained from anisole and from veratrole by condensation with (I), reduction, ester condensation, and cyclisation. The ethers were demethylated after hydrogenation of the active ethylenic linking. 7-Hydroxy-6-methyloctahydrophenanthrene-11:12-dicarboxylic anhydride, m.p. 134·5—135·5° (corr.), was prepared similarly from γ-4-methoxy-3-methylphenylbutyric acid. Phenanthrene-1:2-dicarboxylic anhydride is converted into 1':3'-diketo-1:2-cyclopentenophenanthrene by condensation of the Me₂ ester with EtOAc. 1':3'-Diketo-3:4-cyclopentenophenanthrene, m.p. 201·4—202° (corr.), is obtained similarly. Chrysene, 2:3-dimethyl-6:7-acechrysene, m.p. 222·6—223·1° (corr.), and 6:7-dimethyl-3:4-benzophenanthrene, m.p. 94·5—95° (corr.), have been obtained by extensions of the hydrocarbon synthesis developed by Fieser and Hershberg (this vol., 203). *o*-C₆H₄Me·MgBr and 1:2-C₁₀H₆(CO)₂O give a keto-acid (decarboxylated to β-*o*-toluoylnaphthalene), the ester of which is converted (MgMoX; reduction; cyclisation; reduction) into 5:10-dimethyl-1:2-benzanthracene, m.p. 147—147·5° (corr.) [picrate, m.p. 173·7—174·2° (corr.)]. Addition of (II) and its 2:3-Me₂ derivative to Et 3:4-dihydro-1-naphthoate affords, after hydrolysis, 5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylic acid (morphine numbering), m.p. 137—137·5° (corr.), and its 6:7-Me₂ derivative, m.p. 162—162·5° (corr.). On dehydrogenation, these yielded phenanthrene and 2:3-dimethylphenanthrene respectively. L. S. T.

αδ-Diarylbutadienes and related compounds. II. αδ-Diarylbutadiene-αβ-dicarboxylic anhydrides. E. FRIEDMANN and W. E. VAN HEYNINGEN (J. pr. Chem., 1936, [ii], 146, 166—178; see this vol., 1371).—CH₂Ph·CO₂H and CHPh·CH·CO₂H in boiling Ac₂O give 46·5% of αδ-diphenylbutadiene-αβ-dicarboxylic [β-carboxy-αδ-diphenylpentadienic, phenylstyrylmalic] anhydride (I), m.p. 137·5°. With warm alkali this gives the Na₂, +4H₂O, and K₂ (II), +2H₂O, salts of the corresponding acid. Acidification of (II) in cold H₂O regenerates (I). Hydrogenation (colloidal Pd) of (II) causes absorption of 2 H₂. α-Phenyl-β-p-anisyl- (III), m.p. 176° (Na₂, +3H₂O, and K₂ salt, +2H₂O, of the corresponding acid), and -2-furoylbutadiene-αβ-dicarboxylic anhydride, m.p. 174°, are similarly prepared. The absorption spectra of (I) and (II) and of the K₂ salts show the bathochromic effect of the OMe. R. S. C.

Diphenyl series. IX. Nitration of 2:4'-derivatives of diphenyl. C. FINZI and V. BELLAVITA (Gazzetta, 1936, 66, 421—429).—Diphenyl-2:4'-dicarboxylic acid (I) (dichloride, m.p. 69—70°; diamide, m.p. 233°; dianilide, m.p. 280—281°; di-p-toluidide, m.p. 259—260°; Me₂, m.p. 79—80°, and Et₂ esters) is converted by H₂SO₄ and EtNO₃ into the 4-NO₂-derivative (II), new m.p. 284—285°, and the 4:2'-(NO₂)₂-derivative (dichloride; diamide, decomp. 215°). 4-Nitro-2:4'-diaminodiphenyl (A., 1932, 1025) yields (Sandmeyer) 4-nitro-2:4'-dicyanodiphenyl, m.p. 238—239°, hydrolysed to (II). When 4:2'-dinitrodiphenyl-2:4'-dicarboxylic acid and 2-nitrodiphenyl-2'-carboxylic acid are heated with Cu chromite, they eliminate an NO₂-group, forming 2-nitrofluorenone and fluorenone, respectively; (I), however, yields di-

phenyl-4-carboxylic acid and Ph₂, whilst (II) gives 4-nitrodiphenyl.

E. W. W.

Nitrogenous heterocyclic rings. XXV. *m*-Phenylenedipropionic acid and *m*-diacetylbenzene. P. RUGGLI and A. STAUB (Helv. Chem. Acta, 1936, 19, 962—972; cf. this vol., 866).—Addition of Br to *m*-phenylenediacyrylic acid in AcOH or EtOAc gives the tetrabromide, m.p. 225—227°, purified with difficulty owing to the ready loss of HBr in warm solvents. It is therefore preferable to transform its Me₂ ester, best in EtOAc, into Me₂ *m*-phenylenedi- α - β -dibromopropionate (I), m.p. 146°, transformed from C₅H₅N alone into a brown oil and by C₅H₅N-EtOH (1:3) into Me₂ *m*-phenylenedimonobromoacrylate, m-C₆H₄(CH:COBr·CO₂Me)₂, m.p. 87°. *m*-Phenylenedipropionic acid (II), m.p. 209° [Me₂ (III), m.p. 93°, and Et₂, m.p. 56°, ester], is best obtained by rapidly adding 2 mols. of KOH in EtOH to (I) dissolved in much boiling EtOH and then slowly adding 4 more mols. In the first phase of the change only KBr separates, followed after addition of a further 2 mols. of KOH by the *K* salt of *m*-phenylenedimonobromoacrylic acid, m.p. 215°; this is succeeded by the *K* salt of (II), followed by that of phenylene-1-propionic-3-monobromoacrylic acid, m.p. 161° (dihydrate, m.p. 67°). Treatment of (II) with conc. H₂SO₄ at room temp. yields the unstable isophthaloyldiacetic acid (IV), m-C₆H₄(CO·CH₂·CO₂H)₂, m.p. 116° (decomp.) [Me₂ ester (V), m.p. 68°, best obtained by hydration of (III)]. (IV) and NPh·NH₂ in EtOH at 0° afford the diphenylhydrazone of *m*-acetylbenzoylacetic acid, m.p. 210°, and *m*-diacetylbenzenediphenylhydrazone (VI), m.p. 115°, separates from the mother-liquors when warmed to room temp.; if the change occurs directly at room temp. 1-phenyl-3-*m*-acetylphenylpyrazolonephenylhydrazone, m.p. 230—232° (decomp.), separates and (VI) is obtained from the mother-liquors. (VI) and NPh·NH₂ in boiling EtOH give *m*-phenylene-3:3'-di(phenylpyrazolone), m.p. 263°, also derived from (III); (II) and NPh·NH₂ in EtOH yield the diphenylhydrazine salt, m.p. 166°. (IV) and NH₂·CO·NH·NH₂ at 0° yield the disemicarbazone of (IV), m.p. 232°, and *m*-diacetylbenzenedisemicarbazone, m.p. 240°, or the latter exclusively at room temp. (IV) and NH₂OH·HCl in EtOH at 0° afford *m*-phenylene-3:3'-diisooxazolone, m.p. 190° when rapidly heated, and *m*-diacetylbenzenedioxime, m.p. 204°. Decarboxylation of (IV) is readily effected by 10% H₂SO₄ at 100° whereby *m*-diacetylbenzene, m.p. 32°, is obtained in 70—77% yield. *m*-Acetylcinnamic acid, m.p. 128°, is described incidentally. H. W.

Anthraquinone series. Attempts to synthesise anthraquinonecarboxylic acids of the morindone type. P. C. MITTER and (MISS) T. SENGUPTA (J. Indian Chem. Soc., 1936, 13, 447—449).—Opianic acid, Me 5-bromosalicylate, and H₂SO₄ give 3:4-dimethoxy- α -5'-bromo-2'-hydroxy-3'-carboxymethoxyphenylphthalide, m.p. 215° (Ac derivative, m.p. 210°; corresponding 3'-carboxyphthalide, m.p. 253°), reduced by Zn-10% NaOH to 2:3-dimethoxy-6-2'-hydroxy-3'-carboxybenzylbenzoic acid (I), m.p. 225°. Ring-closure of (I) or its Br-derivative, m.p. 210°, is not effected by H₂SO₄ or P₂O₅. Hot H₂SO₄ sulphonates (I).

R. S. C.

Use of amines for distinguishing geometrically isomeric aldoximes and their acyl derivatives. C. R. HAUSER and E. JORDAN (J. Amer. Chem. Soc., 1936, 58, 1772—1776; cf. this vol., 1253).— α -CHAR:N·OAc (Ar=Ph, *o*- and *m*-NO₂·C₆H₄; *p*-OMe·C₆H₄; 3:4-CH₂O₂·C₆H₃; *o*-C₆H₄Cl; *p*-NMe₂·C₆H₄) are unaffected by C₅H₅N (usually at room temp.) but are converted into α -oximes by NH₂Bu⁺ (at room temp.). β -CHAR:N·OAc (Ar=Ph, *m*-NO₂·C₆H₄; *p*-OMe·C₆H₄; 3:4-CH₂O₂·C₆H₃) with C₅H₅N and NH₂Bu⁺ (heat developed) give nitriles (84—99% yield). It is thus possible to distinguish between the above geometrical isomerides. Similarly, α -CHAR:N·O·CO·NHPh (I) (Ar=*m*-NO₂·C₆H₄; 3:4-CH₂O₂·C₆H₃), α -CHAR:N·O·CO₂Et (Ar=*p*-OMe·C₆H₄; *o*-C₆H₄Cl; *m*-NO₂·C₆H₄; 3:4-CH₂O₂·C₆H₃) and α -CHAR:N·OBz (Ar=*m*-NO₂·C₆H₄; 3:4-CH₂O₂·C₆H₃) are unaffected by C₅H₅N and converted into α -oxime by NH₂Bu⁺, whilst the β -CHAR:N·O·CO·NHPh with C₅H₅N and NH₂Bu⁺ give the nitrile (also formed together with the β -oxime by the action of EtOH-NaOH at 25—30°). NHPh·CO·NHBu⁺ is also obtained from (I) and NH₂Bu⁺. H. B.

Ozonisation of aldehydes.—See this vol., 1346.

Photo-rearrangement of *o*-nitrobenzaldehyde to *o*-nitrobenzoic acid.—See this vol., 1349.

Reactions catalysed by aluminium chloride. XV. Preparation of saturated ketones by addition of acid chlorides to olefines and hydroxylation by aluminium chloride. C. D. NENITZESCU and E. CIORĂNESCU (Ber., 1936, 69, [B], 1820—1823).—AlCl₃ is added gradually to a mixture of cyclopentene (I), AcCl, and cyclohexane (II) at -15° in such a manner that HCl is not evolved; subsequently the temp. of the mixture is gradually raised to 70°, whereby cyclopentyl Me ketone, b.p. 55—56°/16 mm., is obtained in 50% yield. Reaction is C₅H₈ + AcCl = C₅H₈ClAc $\xrightarrow{2H}$ C₅H₉Ac + HCl and 2C₆H₁₂ \rightarrow C₁₂H₂₂ + 2H. The following ketones are prepared analogously: cyclohexyl Me, b.p. 183—184°; dicyclopentyl, b.p. 113—116°/14 mm., from cyclopentanecarboxyl chloride and (I), reduced (Clemmensen) to dicyclopentylmethane, b.p. 208—210°; cyclopentyl cyclohexyl, b.p. 128°/10 mm. (semicarbazone, m.p. 182°), whence cyclopentylcyclohexylmethane, b.p. 223—225°; 2-methylcyclopentyl cyclohexyl, b.p. 138—141°/20 mm. (semicarbazone, m.p. 190°), whence 2-methylcyclopentylcyclohexylmethane, b.p. 239—241°; 1-chloro-2-isovalerylcyclohexane, b.p. 118—120°/14 mm., from cyclohexene (III), isovaleryl chloride (IV), and AlCl₃ in CS₂, and cyclohexyl isobutyl ketone, b.p. 216—219°, from (III), (IV), AlCl₃, and (II), whence isoamylcyclohexane, b.p. 190—191°; 1-chloro-2-hexoylcyclohexane, b.p. 140—143°/15 mm.; cyclohexyl amyl ketone, b.p. 122—125°/11 mm., whence *n*-hexylcyclohexane, b.p. 219—221°. H. W.

Alicyclic compounds. III. Synthesis of β -ketoamines. F. PIRRONE. IV. Schiff's bases of 6- and 2- α -aminobenzyl-2-methylcyclohexanone. F. PIRRONE and (SIGNA.) J. ROSELLI (Gazzetta, 1936, 66, 429—434, 435—440).—III. Interaction of PhCHO, cyclohexanone, and NH₂Ph yields 2- α -anilinobenzylcyclohexanone, m.p. 139—139.5° (oxime,

m.p. 154—155°; *semicarbazone*, m.p. 206—207°; *cyclohexanone* thus reacts in the ketonic form.

IV. PhCHO, 2-methylcyclohexanone, and NH₃ yield 6-, m.p. 180—181° (no oxime or semicarbazone), and 2-*α*-benzylidencaminobenzyl-2-methylcyclohexanone, m.p. 127—128° (oxime, m.p. 238—239°; *semicarbazone*, m.p. 228—229°; *picrate*, m.p. 119—120°).

E. W. W.

Synthesis of 2 : 3-dimethyl-1 : 2 : 3 : 4 : 10 : 11-hexahydrofluorenone. S. FUJISE, Y. HORIUTI, and T. TAKAHASHI (Ber., 1936, 69, [B], 2102—2106).—βγ-Dimethyl-Δ^{αγ}-butadiene (I) and CHPh:CH:CHO at 200° give 2-phenyl-4 : 5-dimethyl-Δ⁴-tetrahydrobenzaldehyde, b.p. 171—173°/3.5 mm. (*phenylhydrazone*, m.p. 131—132°), oxidised by AgNO₃-Ba(OH)₂ in EtOH-H₂O to 2-phenyl-4 : 5-dimethyl-Δ⁴-tetrahydrobenzoic acid, m.p. 159—160°, in very poor yield. Treatment of (I) with CHPh:CH:CO₂Et at 180° gives *Et* 2-phenyl-4 : 5-dimethyl-Δ⁴-tetrahydrobenzoate, b.p. 133—143°/1.5 mm., but the corresponding acid (II), m.p. 159—160°, is best obtained from (I) and CHPh:CH:CO₂H in xylene at 170°. (II) is hydrogenated (PtO₂ in EtOH) to 2-phenyl-4 : 5-dimethyl-hexahydrobenzoic acid, m.p. 128—129° [corresponding chloride (III), b.p. 163—164°/8 mm., and anilide, m.p. 146—149°]. (III) and AlCl₃ in CS₂ afford 2 : 3-dimethyl-1 : 2 : 3 : 4 : 10 : 11-hexahydrofluorenone, b.p. 157—159°/6 mm. (oxime, m.p. 147—151°; *semicarbazone*, m.p. 211—217°). H. W.

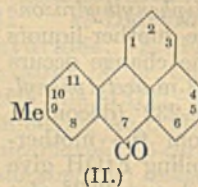
Grignard reagents: their reducing action and rates of addition. M. S. KHARASCH and S. WEINHOUSE (J. Org. Chem., 1936, 1, 209—230).—Previous results and mechanisms proposed for the reducing reactions of Grignard reagents are reviewed. The yield of CHPh₂·OH obtained from COPh₂ and MgBu^αBr is not appreciably affected by temp. or by the order in which the reactants are added to one another, but is affected somewhat by the concn. of the Grignard reagent and by the solvent used. The respective percentages of addition and of reduction (CHPh₂·OH) products formed when the following react with COPh₂ in Et₂O-C₆H₆ are given in parentheses: MgPhBr (90; 0), CH₂Ph·MgCl (95; 0), CH₂Ph·MgBr (52; 0), *p*-C₆H₄Cl·CH₂·MgCl (74; 0), MgBu^αCl (63; 0), CH₂:CH·CH₂·MgBr (72; 5), cyclo-C₆H₁₁·MgBr (—; 7.1), Ph·[CH₂]₃·MgBr (38.5; 20.0), Ph·[CH₂]₂·MgBr (43.2; 32.6), MgBu^αBr (—; 58.6), MgBu^βCl (—; 76.2), MgBu^βBr (—; 91.0), cyclo-C₃H₅·MgBr (—; 94.0). Reduction of COPh₂ by MgRX occurs only when R is of intermediate electronegativity. A mechanism involving dissociation of MgRX into R⁻ and (MgX)⁺ and reduction by R⁻ is proposed and requires the reducing tendency to increase with decreasing electronegativity of R. "Competition" experiments show that the rates of addition of MgRX to COPh₂ also increase with decreasing electronegativity of R. When R is weakly electronegative, the rapidity of the addition reaction is considered to exclude the reduction reaction from observation (cf. A., 1929, 675, 680). Reduction by CPh₂·MgX, an exception to the foregoing generalisations, is considered to occur through a free-radical mechanism. The following appear to be new: *diphenyl-p-chlorobenzylcarbinol*, m.p. 117.5—118.5°,

and *diphenyl-γ-phenylpropylcarbinol*, m.p. 74—75°, dehydrated to ααδ-triphenyl-Δ^α-butene. H. G. M.

Synthesis of phenanthrene derivatives. IV. Propionylphenanthrenes. W. E. BACHMANN and W. S. STRUVE (J. Amer. Chem. Soc., 1936, 58, 1659—1661).—Phenanthrene, EtCOCl, and AlCl₃ in cold PhNO₂ give 2- (I), m.p. 104—105°, and 3- (II), m.p. 55—57°, -*propionylphenanthrene* (*picrates*, m.p. 104.5—107° and 111—113°, respectively), oxidised (3% NaOCl, KOH) to phenanthrene-2- and -3-carboxylic acid, respectively. 9-*Propionylphenanthrene*, m.p. 55—57° (*picrate*, m.p. 105.5—107°), (I), and (II) are prepared from MgEtBr and 9-, 2-, and 3-cyanophenanthrene, respectively. (I) and (II) with Br in Et₂O at 0° afford 2-, m.p. 131.5—133°, and 3-, m.p. 117—118°, -*α-bromopropionylphenanthrene*, respectively, which with CHNa(CO₂Et)₂ in C₆H₆ subsequently hydrolysis (5% NaOH), and decarboxylation give β-2-, m.p. 173—174°, and -3-, m.p. 144—146°, -*phenanthrolybutyric acid*, respectively.

H. B.

Conversion of tolyl naphthyl ketones into methylbenzanthrones. L. F. FISER and E. L. MARTIN (J. Amer. Chem. Soc., 1936, 58, 1443—1445).—*o*-Tolyl α-C₁₀H₇ ketone (I), m.p. 52—53° (from α-C₁₀H₇·MgBr and *o*-C₆H₄Me·CN), and *m*-tolyl α-C₁₀H₇ ketone, m.p. 72—73° (from *m*-C₆H₄Me·MgBr and α-C₁₀H₇·COCl), with AlCl₃+NaCl at 150° both give 9-methylbenzanthrene (II). The conclusion of Mayer *et al.* regarding wandering of the Me group (A., 1930, 1042) is thus valid but is based on unsound



evidence since their (I) [and the (I) of Scholl and Seer (A., 1913, i, 56)] is *o*-tolyl β-C₁₀H₇ ketone (III), m.p. 63—64° (now prepared from *o*-C₆H₄Me·MgBr and β-C₁₀H₇·CN). It is probable that the Friedel-Crafts reaction between *o*-C₆H₄Me·COCl and C₁₀H₈ gives a mixture of (I) and (III). *p*-Tolyl α-C₁₀H₇ ketone, m.p. 83—84° (from α-C₁₀H₇·MgBr and *p*-C₆H₄Me·CN), is converted by AlCl₃+NaCl into 10-methylbenzanthrene (IV), m.p. 158—159°; *m*-, m.p. 76—77°, and *p*-, m.p. 90—91°, *tolyl* β-C₁₀H₇ ketones (from β-C₁₀H₇·CN and C₆H₄Me·MgBr) and (III) do not similarly give benzanthrones. (IV) is oxidised (CrO₃, AcOH) to 7-methylanthraquinone-1-carboxylic acid (V), m.p. 310—312°, and thence [HNO₃ (*d* 1.1) at 200—210°] to anthraquinone-1 : 7-dicarboxylic acid, m.p. 346—348°. (II) similarly affords 6-methylanthraquinone-1-carboxylic acid (VI), m.p. 264—266°, and anthraquinone-1 : 6-dicarboxylic acid, m.p. 336—338°. (V) and (VI) are both decarboxylated (Cu, quinoline) to 2-methylanthraquinone. Anthraquinone-1 : 3-dicarboxylic acid, decomp. 320—325°, is prepared from *m*-xylene, *o*-C₆H₄(CO)₂O, and AlCl₃.

H. B.

Benzanthrene derivatives. IV. New synthesis of benzanthrene derivatives. E. CLAR (Ber., 1936, 69, [B], 1686—1691).—Methyleneanthrone (I) and maleic anhydride (II) in boiling AcOH give the adduct C₂₃H₁₈O₉, m.p. 190—192° (decomp.), whilst when melted together or heated in boiling PhNO₂ they yield *benzanthrene-2 : 3-dicarboxylic anhydride*, m.p. 310° (corresponding *anilide*,

m.p. 288—292°, and *azine*, m.p. >360°). (I) and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ in boiling PhNO_2 afford 3-phenylbenzanthrone, m.p. 183—184°. Under similar conditions benzylideneanthrone and (II) yield 1-phenylbenzanthrone-2 : 3-dicarboxylic anhydride, m.p. 280°. 2'-Anthraquinonylmethylbenzanthrone, m.p. 279—280°, obtained from 2-chloromethylanthraquinone, anthrone, and piperidine in EtOH, condenses with (II) in boiling PhNO_2 to 1-2'-anthraquinonylbenzanthrone-2 : 3-dicarboxylic anhydride, m.p. 316—317°. (I) and *endo*-9 : 10-*o*-phenylene-9 : 10-dihydro-1 : 4-anthraquinone in boiling xylene afford 2' : 3'-benzanthrone-2 : 3-endo-9 : 10-*o*-phenylene-9 : 10-dihydro-1 : 4-anthraquinone, m.p. >360°, which has little affinity for vegetable fibres. 2' : 3'-Benzanthrone-2 : 3-naphtha-1 : 4-quinone, m.p. 286°, from (I) and 2 : 3-dichloro-1 : 4-naphthaquinone in boiling PhNO_2 or from 1 : 4-naphthaquinone, appears identical with the product from $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, benzanthrone, and AlCl_3 . Gradual addition of (I) to a boiling solution of chloranil in xylene gives 5 : 6-2 : 3-benzanthrone-2 : 3-dichloro-1 : 4-benzoquinone, m.p. 300°. If the reagents are used in inverse order and excess of (I) is employed the product is *di*-2' : 3'-2'' : 3''-benzanthrone-2 : 3-5 : 6-benzo-1 : 4-quinone, also obtained from (I) and *p*-benzoquinone in boiling PhNO_2 .

H. W.

Constitution and reactivity. XVI. Constitution of benzanthrone-6-sulphonic acid. Kinetics of the sulphonation of benzanthrone. K. LAUER and K. IRIE (J. pr. Chem., 1936, [ii], 145, 281—286; cf. this vol., 297).—Benzanthrone and H_2SO_4 at 140—150° give *benzanthrone-9-sulphonic acid* (Na salt), the structure of which is proved by chlorination (HCl-KClO_3) to 9-chloro- and 3 : 9-dichloro-benzanthrone and by formation of a violanthrone with KOH-EtOH . Reaction velocities with 80—99% acid at 95—170° show that two sulphonating agents (H_2SO_4 and SO_3) are effecting the reaction. R. S. C.

Magnetochemical investigations of organic substances. XI. Bromobenzanthrone of Brass and Clar. E. MÜLLER and W. WIESEMANN (Ber., 1936, 69, [B], 2173—2174).—Magnetic observations do not indicate the presence of a radical compound in the “uneven bromide” of benzanthrone (this vol., 726).

H. W.

Chrysene. IV. K. FUNKE and J. RISTIC (J. pr. Chem., 1936, [ii], 146, 151—158; cf. this vol., 1113).—Conversion of chrysene-2 : 8-dicarboxylic acid by aq. KOH at 210—220° into chrysene-2-carboxylic acid, m.p. 314°, proves the orientation of 2 : 8-dibromochrysene and all substances derived from it. 2-Acetylchrysene gives the 8-*Br*-derivative, m.p. 142°, which gives oils with CuCN in quinoline and is reduced (Clemmensen) to 2-ethylchrysene (I). (I) gives (Friedel-Crafts) 2-acetyl-8-ethylchrysene, m.p. 131°, reduced to 2 : 8-diethylchrysene, m.p. 145°, and oxidised only to the quinone. 2-Benzoyl-8-ethylchrysene, m.p. 130°, is similarly prepared. 2 : 8-Dibenzoylchrysene (modified prep.) with AlCl_3 gives a dye, not isolated, and a trace of a substance, $\text{C}_{60}\text{H}_{36}\text{O}_6$, m.p. 260°. R. S. C.

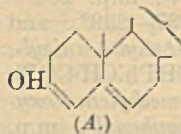
Unsaturated sulphur compounds. III. α - β -Unsaturated ketosulphones. E. P. KOHLER

and R. G. LARSEN (J. Amer. Chem. Soc., 1936, 58, 1518—1522).— $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{SO}_2\text{Ph}$ (I) (from $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$ and PhSO_2H in EtOH) and Br in CHCl_3 give diastereoisomeric *Ph* β -bromo- β -benzoyl- α -phenylethyl sulphones, m.p. 189° (90%) and 209° (<3%; also obtained from $\text{CHPh}\cdot\text{CBr}\cdot\text{COPh}$ and PhSO_2H in EtOH), both of which are converted (at different rates) by KOAc in MeOH or AcOH into the yellow *trans-Ph* β -benzoyl- α -phenylvinyl sulphone (II), m.p. 151°; the colourless *cis*-form (III), m.p. 132°, is prepared from $\text{CPh}\cdot\text{C}\cdot\text{COPh}$ and PhSO_2H in MeOH. (III) is converted by NaOMe into (II), whilst (II) or (III) in CHCl_3 +I in sunlight give an equilibrium mixture [mainly (II)]. *Ph* α -chloro-, m.p. 175°, and α -bromo-, m.p. 124° [decomp. to (II)], β -benzoyl- α -phenylethyl sulphones are obtained from (II) and AcOH-HHal . (II) and MgPhBr in the cold afford *Ph* γ -hydroxy- $\gamma\gamma$ -triphenyl- Δ^a -propenyl sulphone (IV) (+2MeOH), m.p. about 107°, m.p. (MeOH-free) 133° (acetate, m.p. 168°), reduced (H_2 , Pd- CaCO_3 , EtOAc) to the *propyl* sulphone, m.p. 223°, also prepared from (I) and MgPhBr . (IV) and a little AcCl in MeOH give the *Me ether*, m.p. 130°, oxidised (KMnO_4 , COMe_2 , little AcOH) to $\text{OMe}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$; with HCl in C_6H_6 , *Ph* γ -chloro- $\gamma\gamma$ -triphenyl- Δ^a -propenyl sulphone, m.p. about 142° [decomp. to 1-benzenesulphonyl-1 : 3-diphenylindene, m.p. 171°, which is oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$, AcOH) to $o\text{-C}_6\text{H}_4\text{Bz}_2$], results. (II) and MgPhBr in boiling Et_2O afford (IV) and *Ph* γ -hydroxy- $\alpha\beta\gamma\gamma$ -tetraphenylpropyl sulphone, stereoisomeric forms, m.p. 178° and 223° (? 196°), both of which are converted by $\text{AcOH-H}_2\text{SO}_4$ into 1 : 2 : 3-triphenylindene. (II) thus resembles $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{SO}_2\text{Ph}$ (A., 1935, 1241) except in the reaction with MgPhBr . H. B.

Transformation reactions of brominated derivatives of cholesterol. III. Bromination of cholesterol. H. H. INHOFFEN (Ber., 1936, 69, [B], 2141—2147; cf. this vol., 1104).—Treatment of cholesterol (I) in Et_2O at 2° with Br in AcOH gives the dibromide (II), $\text{C}_{27}\text{H}_{42}\text{OBr}_2$, m.p. 162° (decomp.) (*loc. cit.*), and an *isomeride*, m.p. 133°, each of which is transformed into the enol acetate, m.p. 158—159°. Reaction generally occurs immediately but occasionally an induction period is observed. In presence of KOAc (I) does not react with Br; a preliminary enolisation due to HBr is therefore assumed, the enolic form probably being (A).

In confirmation, cholesterol enol acetate (Ruzicka *et al.*, this vol., 991) is transformed by Br in $\text{Et}_2\text{O-AcOH}$ into (II) whereas in presence of KOAc the *Br*₁-ketone (III), $\text{C}_{27}\text{H}_{43}\text{OBr}$, m.p. 132°, is produced. Bromination of (III) in presence of HBr gives (II). The mechanism of the production of (III) and thence of (II) is discussed. H. W.

Constituents of pyrethrum flowers. VI. Structure of pyrethrolone. F. B. LAFORGE and H. L. HALLER (J. Amer. Chem. Soc., 1936, 58, 1777—1780; cf. B., 1936, 812).—Pyrethrolone (I) (3 : 5-dinitrobenzoate, m.p. 145°) is considered to be 5-hydroxy-3-methyl-2- Δ^{γ} -pentadienyl- Δ^2 -cyclopenten-



one (cf. Staudinger and Ruzicka, A., 1924, i, 523). Tetrahydropyretrolone [the Δ^2 -*cyclopentenone*] (II), b.p. 120—125°/0.25 mm., $[\alpha]_D^{20} +11.9^\circ$ in EtOH (cf. *loc. cit.*) (*Me ether*, b.p. 82°/0.35 mm.), prepared by hydrolysis (cold conc. aq. $\text{KHSO}_4 + \text{Et}_2\text{O}$) of its semicarbazone, m.p. 196° [obtained by reduction of the semicarbazone of (I)], contains a quantity of *dl*-tetrahydropyretrolone (III) (semicarbazone, m.p. 170°); (III) is the sole product when hydrolysis is carried out at 100°. 5-Chloro-3-methyl-2-*n*-amyl- Δ^2 -cyclopentenone, b.p. 97—100°/0.6 mm. [from (II) and SOCl_2], is reduced (Zn dust, AcOH) to the optically inactive 3-methyl-2-*n*-amyl- Δ^2 -cyclopentenone [dihydrojasnone] (cf. Treff and Werner, A., 1933, 1296; 1935, 750), which is similarly prepared from (III).

H. B.

β -Methylenebutan- γ -on- α -ol. H. GAULT and L. A. GERMANN (Compt. rend., 1936, 203, 514—516; cf. A., 1933, 1144).—Condensation of CH_2O with $\text{CH}_2\text{Ac}\cdot\text{CH}_2\cdot\text{OH}$ or $\text{CHAc}\cdot\text{CH}_2$ in presence of K_2CO_3 affords $\text{CH}_2\cdot\text{C}\cdot\text{Ac}\cdot\text{CH}_2\cdot\text{OH}$ (cf. *loc. cit.*), which condenses with $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene to 4-hydroxymethyl-4-acetyl-1:2-dimethyl- Δ^1 -cyclohexene, b.p. 155—157°/15 mm., and with δ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene to a mixture of 6-hydroxymethyl-6-acetyl-, b.p. 146—150°/12 mm., and 5-hydroxymethyl-5-acetyl-1:1-dimethyl- Δ^2 -cyclohexene, b.p. 150—153°/12 mm., m.p. 71°.

F. O. H.

Alcoholic ammonia as a reagent for [condensation of] nitro-compounds and unsaturated ketones. D. E. WORRAIL and C. J. BRADWAY (J. Amer. Chem. Soc., 1936, 58, 1607—1608).— γ -Nitro- α -dibenzoyl- $\beta\delta$ -diarylpentanes (A) are obtained by prolonged interaction of MeNO_2 and an excess of $\text{CHAr}\cdot\text{CH}\cdot\text{COPh}$ (except when Ar contains an *o*-substituent) in EtOH- NH_3 ; the presence of H_2O promotes reaction. The intermediate $\text{COPh}\cdot\text{CH}_2\cdot\text{CHAr}\cdot\text{CH}_2\cdot\text{NO}_2$ (Ar = *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4$; m.p. 50—51°, and 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$; m.p. 94—95°) are isolable; these can be similarly condensed with $\text{CHAr}\cdot\text{CH}\cdot\text{COPh}$ to (A). Compounds similar to (A) could not be prepared from EtNO_2 or $\text{CH}_2\text{Ph}\cdot\text{NO}_2$. The following are described: γ -nitro- α -dibenzoyl- $\beta\delta$ -diphenyl-, stereoisomeric forms, m.p. 157—158° (I) and 229—230° (II), - $\beta\delta$ -dianisyl-, m.p. 211—212°, - $\beta\delta$ -di-3:4-methylenedioxyphenyl-, m.p. 192—193°, - $\beta\delta$ -di-*p*-bromophenyl-, m.p. 239—240°, - $\beta\delta$ -di-*p*-tolyl-, m.p. 209—210°, - $\beta\delta$ -di-*m*-bromophenyl-, m.p. 200—201°, - $\beta\delta$ -di-*m*-nitrophenyl-, m.p. 237—239°, and - $\beta\delta$ -dicinnamyl-, m.p. 216—218°; - β -phenyl- δ -anisyl-, m.p. 205—206° (best prepared using $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$ as the second component), - δ -3:4-methylenedioxyphenyl-, m.p. 218—219°, - δ -*m*-bromophenyl-, m.p. 227—228°, - δ -*p*-tolyl-, m.p. 191—192°, and - δ -*m*-nitrophenyl-, m.p. 219—220°; - β -anisyl- δ -*p*-tolyl-, m.p. 196—197°; - β -anisyl-, m.p. 189—190°, - β -*m*-nitrophenyl-, m.p. 218—219°, - β -*p*-tolyl-, m.p. 198—199°, and - β -*m*-bromophenyl-, m.p. 215—216°. - δ -3:4-methylenedioxyphenyl-pentanes. (I) and Br in CHCl_3 and sunlight give a Br-derivative (? mixture), m.p. about 80°. (II) and Br in PhNO_2 afford the β -Br-derivative, m.p. 241—242° (decomp.); in MeOH- NaOMe the γ -Br-derivative, m.p. 205—206° results. The γ -nitro- α -di-*p*-bromobenzoyl- $\beta\delta$ -diphenylpentano

of Kohler and Williams (A., 1920, i, 59) is a mixture of isomerides, m.p. 151—152° and 218—219°.

H. B.

Sexual hormones. XVI. Esters of the testosterone and androsterone series. L. RUZICKA and A. WETTSTEIN [in part, with W. KLARER and J. MEYER]. XVII. Bromination of sterol and androstene derivatives. L. RUZICKA, W. BOSSHARD, W. H. FISCHER, and H. WIRZ (Helv. Chim. Acta, 1936, 19, 1141—1146, 1147—1153; cf. this vol., 991).—XVI. The following esters of testosterone are described: *formate*, m.p. 127—129° (corr.); *propionate*, m.p. 121—123° (corr.); *n-butyrate*, m.p. 111—113° (corr.); *isobutyrate*, m.p. 134—136° (corr.); *n-valerate*, m.p. 109—111° (corr.); *isovalerate*, m.p. 138—140° (corr.); *decoate*, m.p. 55—57° (corr.); *palmitate*, m.p. 72—74° (corr.); *stearate*, m.p. 79—80° (corr.); *H succinate*, dimorphous, m.p. 183—185° (corr.) and 191—193° (corr.), respectively. *Androstane-3-cis-17-trans-diol disuccinate* has m.p. 139—140° (corr.). The *Na* and *Li* salts of androsterone succinate and the *Na*, *K*, and *Li* salts of androstane-3-cis-17-trans-diol 3-succinate are described. The physiological action of the esters is discussed.

XVII. Cholesterol dibromide in C_6H_6 is converted by CrO_3 in $\text{AcOH}\text{-H}_2\text{O}$ at room temp. into Δ^5 -cholestenone dibromide, transformed by boiling aq. KOAc into 6-bromo- Δ^4 -cholestenone (I), m.p. 130—131°, in about 10% yield. The absorption spectrum proves (I) to be an $\alpha\beta$ -unsaturated ketone; it is hydrogenated to cholestenone and coprostanone. If more vigorous conditions are used in the prep. of (I) the product is cholestane-3:6-dione. Similarly, *trans*-dehydroandrosterone is brominated and oxidised to androstenedione dibromide, which in C_6H_6 is transformed by boiling aq. KOAc into 6-bromo- Δ^4 -androstene-3:17-dione, m.p. 170—171° (decomp.). Bromination of the requisite ketone in AcOH yields 2:2-dibromocholestanone, m.p. 194° (*quinoxaline* derivative, $\text{C}_{33}\text{H}_{48}\text{N}_2$, m.p. 184°), 4:4-dibromo-, m.p. 143° (*quinoxaline* derivative, m.p. 200°), and 2:4:4-tribromo-, m.p. 180°, -*coprostanone*. Δ^4 -Cholestenone in CCl_4 does not give a homogeneous product when treated with Br (1—2 mols.) but by use of a large excess of halogen (?) 2:4-dibromo- Δ^4 -cholestenone, m.p. about 180°, is obtained. It does not give a yellow colour with $\text{C}(\text{NO}_2)_4$ or react with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$.

H. W.

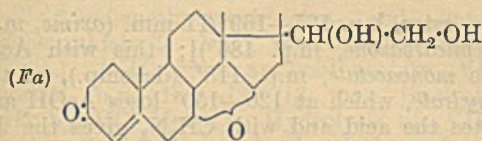
Proposed synthesis of equilenin. M. VANGHELOVICI (Chem. and Ind., 1936, 728).—The proposed path is, ergosterol \rightarrow neocergosterol \rightarrow dehydro- \rightarrow acetyldehydro- \rightarrow neocergosterol \rightarrow acetylenequilenin \rightarrow equilenin.

H. W.

Constituents of the adrenal gland. V. Chemical identification of the androstane skeleton. VI. Methods of separation and isolation of the substances *Fa*, *H*, and *J*. T. REICHSTEIN (Helv. Chim. Acta, 1936, 19, 979—987, 1107—1126; cf. this vol., 475, 605, 704, 854).—V. Reduction (Clemmensen) under mild conditions of the diketone (I) $\text{C}_{19}\text{H}_{26}\text{O}_3$, m.p. 178°, gives small amounts of a crystalline product, m.p. (indef.) 120—143°, oxidised to androstane-17-one and, mainly, a mixture of liquid hydrocarbons, $\text{C}_{19}\text{H}_{32}$, which is somewhat unsaturated and, after

hydrogenation, gives a small proportion of androstane, m.p. 49—51°. Similar results are obtained from androstanedione. The partial formulæ assigned previously to substances *A*, *C*, and *D* thus receive chemical confirmation. No information is afforded of the nature of the third O which is eliminated during the reduction. Zerevitinov determinations establish the presence of 1.14 active H in the OH-ketone (II) $C_{19}H_{28-30}O_2$, m.p. about 236° (corr.) (*loc. cit.*), and 0.15 active H in (I) so that (II) and (I) contain 1 OH and no OH, respectively. Further (II) in boiling C_6H_6 containing C_5H_5N yields a 3 : 5-dinitrobenzoate, m.p. 257—258° (corr.), whereas (I) remains unchanged. Treatment of (I) with a large excess of $NH_2OH \cdot AcOH$ at 130° gives the known dioxime (III) with non-cryst. material analyses of which accord with the presence of about 25% of (III) and 75% of a trioxime. Definite conclusions cannot yet be reached, but the presence of an O bridge, opened under the experimental conditions, is suggested.

VI. The dry residue of the "permutit fraction" of the entire gland is distributed between pentane and 30% MeOH, whereby the cortin activity passes entirely into the aq. layer, from which it is extracted by Et_2O after concn. of the acid liquor. The activity is driven from Et_2O into H_2O , leaving an "ether residue." Concn. and acidification of the aq. layer followed by extraction with Et_2O leads to concentrate C_{13} . The latter is treated with Girard's reagent and from the reactive portions four fractions of $C_{17}A$ ketones are separated by varying the degree of acidity. The *A*-ketone-free residues are heated with the reagent and from the product the $C_{17}B$ ketones are isolated. Substances *A*, *C*, and *D* are thus readily obtained. The product of the oxidation of *E* is identified as adrenosterone (IV) and it is therefore $C_{21}H_{30-32}O_5$. Substance *Fa*, m.p. about 215° (corr.; decomp.) depending largely on the manner of heating, $[\alpha]_D$ about $+200 \pm 8^\circ$ in EtOH, is $C_{21}H_{28-30}O_5$. Its



absorption spectrum shows it to be an $\alpha\beta$ -unsaturated ketone. The cryst. form is very characteristic. It is physiologically inactive. Oxidation of it affords (IV). It appears identical with compound *F* of Wintersteiner and compound *E* of Kendall *et al.*, whose formulation is queried. Substance *H*, m.p. about 163—167°, is obtained from fraction $C_{17}A.III$ by a process which cannot be reproduced with certainty. It appears to be an $\alpha\beta$ -unsaturated ketone, $C_{19}H_{26}O_4$ or $C_{23}H_{32}O_5$. It does not contain OEt. Examination of the "ether residue" (see above) with Girard's reagent is incomplete but (IV), and two further ketones, substances *K* and *L*, m.p. about 175° and about 255° (corr.), have been isolated. Substance *J*, m.p. 216—217° (corr.) after becoming opaque at about 120°, appears to be a polyhydric alcohol, $C_{21}H_{31-36}O_3$, since it is oxidised by CrO_3 to a neutral product of much lower m.p. Its precipitability with digitonin indicates that it is a derivative of chole-

stanol. Reply is made to Mason *et al.* (this vol., 1117). H. W.

6-Keto-3 : 5-diacetoxycholestane. F. SCHENCK (*Z. physiol. Chem.*, 1936, 243, 119—120; cf. Windaus *et al.*, *A.*, 1935, 1363).—The substance having m.p. 169—170°, $[\alpha]_D^{20} -15.4^\circ$ in $CHCl_3$, obtained by oxidising cholesteryl acetate with CrO_3 contains 2 Ac but no active H and hence is 6-keto-3 : 5-diacetoxycholestane. 5-Hydroxy-6-keto-3-acetoxycholestane has m.p. 230—231°, $[\alpha]_D -55.8^\circ$ in $CHCl_3$. W. McC.

Dioximes. CXVI. G. PONZIO (*Gazzetta*, 1936, 66, 479—486; cf. this vol., 1363).—"Benzoylmethylglyoxime peroxide" (*A.*, 1904, i, 427—428), now renamed phenylmethyltriketone-1 : 3-dioxime peroxide (I), new m.p. 161—162°, is converted by $NH_2OH \cdot HCl$ in C_5H_5N into phenylmethyltriketone- α -trioxime (II) (*A.*, 1922, i, 1038) [C_5H_5N , m.p. 130—140° (decomp.), and $NHPh \cdot NH_2$, m.p. 167—168° (decomp.), salts; Bz_3 derivative, m.p. 132—133°]. "Oximinobenzoylmethylglyoxime peroxide" (*loc. cit.*), renamed as the oxime of (I), is similarly reduced to (II), and "anisoyl-" and "oximino-anisoyl-methylglyoxime peroxide," renamed as anisylmethyltriketone-1 : 3-dioxime peroxide and its oxime, are both reduced to anisylmethyltriketone-trioxime, m.p. 195° (decomp.) (Ac_3 , m.p. 133—134°, and Bz_3 , m.p. 150°, derivatives). E. W. W.

System 3 : 4 : 3' : 4'-tetramethoxy- and 3 : 4 : 3' : 4'-bismethylenedioxy-benzophenone. A. OLIVERIO (*Rend. Semin. Fac. Sci. Univ. Cagliari*, 1934, 4, 130—134; *Chem. Zentr.*, 1935, ii, 3910).—A stable equimol. additive compound, m.p. 164°, and two eutectics, m.p. 141—141.5° and 135°, are described. H. N. R.

Stereochemistry of deuterium compounds of the type, CHRR'. 2 : 3-Dideuterocamphane. M. T. LEFFLER and R. ADAMS (*J. Amer. Chem. Soc.*, 1936, 58, 1555—1558).—Reduction (H_2 , PtO_2 , EtOAc) of *l*-bornylene, m.p. 105—106.5°, $[\alpha]_D^{25} -9.57^\circ$ in EtOAc (which thus contains tricyclene), gives camphane, m.p. 145°, $d_1^{152} 0.7458$, $\alpha_D^{25} +0.02 \pm 0.01^\circ$ in EtOAc ($l=1$) (due to some impurity); reduction with D_2 under identical conditions affords 2 : 3-dideuterocamphane, m.p. 143°, $d_1^{152} 0.7552$, of the same rotation. There appears to be no evidence for the activity of CHDRR' compounds (cf. Billmann *et al.*, this vol., 855). H. B.

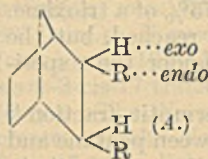
Rotatory power of substituted camphoranilic acids. M. SINGH (*J. Indian Chem. Soc.*, 1936, 13, 467—474).—The following camphoranilic acids are prepared by condensation of the anhydride and amine, $[\alpha]$ given being in MeOH and $COMe_2$, respectively: *o*-, m.p. 171° (decomp. from 165°), $[\alpha]_D +50.6^\circ$, $+45.3^\circ$, and *p*-ethyl-, m.p. 202—203°, $[\alpha]_D +59.2^\circ$, $+47.9^\circ$, *m*-, m.p. 189—190°, $[\alpha]_D +36.9^\circ$, $+30.9^\circ$, and *p*-aceto-, m.p. 224—225°, $[\alpha]_D +67.5^\circ$, $+67.7^\circ$, *m*-, m.p. 210°, $[\alpha]_D +43.2^\circ$, $+34^\circ$, and *p*-nitro-, m.p. 200—203°, $[\alpha]_D +75.6^\circ$, $+71.2^\circ$, *m*-, m.p. 197°, $[\alpha]_D +52.4^\circ$, $+40.5^\circ$, and *p*-fluoro-, m.p. 197°, $[\alpha]_D +42.7^\circ$, $+41^\circ$. The following are obtained by nitration: camphor-2'-nitro-4'-ethyl-, m.p. 140.5°, $[\alpha]_D -62.1^\circ$, -72.9° , 3'-fluoro-2'-nitro-, m.p. 131—132°, $[\alpha]_D -14.4^\circ$, -25° , 4'-fluoro-2'-nitro-, m.p.

171°, $[\alpha]_D -45^\circ$, -49.6° , and *-2'-nitro-4'-acetoanilic acid*, m.p. 202—203°, $[\alpha]_D +51.8^\circ$, $+44.4^\circ$. *Camphor-o-*, m.p. 132—133°, $[\alpha]_D +19.6^\circ$, $+19.7^\circ$, and *-p-ethylphenylimide*, m.p. 123°, $[\alpha]_D +15.9^\circ$, $+14.5^\circ$, are obtained by condensation. *m-*, m.p. 196—197°, $[\alpha]_D +46.3^\circ$, $+41.7^\circ$ (*Ac* derivative, m.p. 220—221°, $[\alpha]_D +25^\circ$, $+23^\circ$), and *p-Aminocamphoranilic acid*, m.p. 220—221°, $[\alpha]_D +57.5^\circ$, $+53.1^\circ$ [*Ac* derivative, m.p. 234—235° (decomp. from 231—232°), $[\alpha]_D +51.1^\circ$, $+48.6^\circ$], are obtained from the NO_2 -acids by $\text{Fe}(\text{OH})_2$. R. S. C.

Ring-isomerisation in the camphene series. P. LIPP, H. DESSAUER, and E. WOLF (Annalen, 1936, 525, 271—291).— ω -Aminoisocamphane (I) with HNO_2 gives a complex mixture by ring changes. Reduction of ω -nitrocamphene (II) by $\text{Zn}-\text{AcOH}$, followed by hydrolysis, gives 59% of camphenolaldehyde. *Camphenilanamide*, m.p. 170—171°, with P_2O_5 gives *camphenilanonitrile*, b.p. 103—105°/12 mm., reduced by $\text{Na}-\text{EtOH}$ to (I) [hydrochloride, decomp. $>250^\circ$, sublimes unchanged in vac.; *platinichloride*; *phenylcarbamide*, m.p. 158° (corr.), and *-thiocarbamide*, m.p. 148° (corr.), and *Bz* derivative (III), m.p. 130—132°]. With $\text{Na}-\text{EtOH}$ (II) affords much (I), *diisocamphylamine*, b.p. 163°/0.13 mm., m.p. 115° [hydrochloride, m.p. 250° (decomp.); *platinichloride*; *oxalate*; *perchlorate*, m.p. 250° (decomp.); *NO-*, m.p. 160° (decomp.), and *phenylcarbamide* derivative, m.p. 150—151° (corr.)], *camphenilone*, and a mixture of *camphenilyl* alcohols (oxidised to the aldehyde). (I) and HNO_2 give *endocamphene* (oxidised by KMnO_4 to *camphenecamphoric acid*, m.p. 134.4—134.8°), a mixture of *R*-homocamphenilols [oxidised to the ketone; *p*-nitrobenzoates (probably impure), m.p. 136—137° (corr.), and 89—91°; with $\text{ZnCl}_2-\text{C}_6\text{H}_6$ gives *endocamphene*], and *N-nitrosoisocamphylethylamine* (IV), b.p. 130—134°/0.8 mm. (IV) with hot fuming HCl gives *isocamphylethylamine* (V), b.p. 109° (corr.)/12 mm. [hydrochloride, m.p. $>300^\circ$; sublimes at about 400° (decomp.); *hydrobromide*; *phenyl-*, m.p. 122—122.5°, and *naphthyl-carbamide*, m.p. 151°, and *Bz* derivative, b.p. 181—183°/0.1 mm.]; this with MeI etc. affords *isocamphylidimethylammonium perchlorate*, *cryst.*, the base from which at 200—250° gives MeOH and *isocamphylmethylamine* (hydrochloride, decomp. 245°; *perchlorate*, decomp. 255°); the *Bz* derivative with PCl_5 gives (III). *Camphenilyl bromide* (prep. by PBr_3), b.p. 99—101°/13 mm., with NH_2Et at 100° affords (IV). R. S. C.

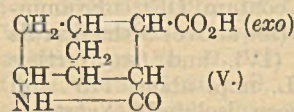
Steric course of addition and substitution reactions. VI. *exo*-Additions of catalytically activated hydrogen to the *dicyclo*-[1:2:2]-heptene ethylenic linking. Configurations of the norborneols and norbornylamines. K. ALDER and G. STEIN [with S. SCHNEIDER, (FRL.) M. LIEB-MANN, (FRL.) E. ROLLAND, and G. SCHULZE]. VII. Catalytic reduction of ketones and ketoximes of the camphor, fenchone, and *isofenchone* series. K. ALDER and G. STEIN [with H. F. RICKERT]. VIII. *endo-exo*-Isomerism. II. K. ALDER and G. STEIN [with (FRL.) E. ROLLAND] (Annalen, 1936 525, 183—221, 221—247, 247—258; cf. A., 1935, 219, 349).—VI. Catalytic hydrogenation under varied

conditions of *dicyclo*-[1:2:2]-heptenes results preponderantly in *cis-exo*-addition of H_2 giving substances of type (A). Addition of H_2 catalytically to *dicyclo*-[1:2:2]-heptanes containing semicyclic CO , $\text{C}'\text{C}$, or $\text{C}'\text{N}\cdot\text{OH}$ also occurs in the *exo*-position to give compounds having one R in the *endo*-position as in (A). Constitutions are rigidly proved. The above rules may also be applied to *dicyclo*heptenes similar to those investigated, but containing in addition two identical substituents on the same C. It follows that the isolated Me of *isocamphane* is *endo*, that α -norborneol has an *endo*-OH, that reaction of α -norbornylamine with HNO_2 occurs with, and that of the β -amine without, Walden inversion. From the point of view of Skita's rule the *dicyclo*-[1:2:2]-heptane system behaves as a substituted *cyclopentane* ring. Hydrogenation (PtO_2) of 3:6-*endomethylene*- $\Delta^{1,4}$ -dihydrophthalic acid in AcOH gives 3:6-*endomethylenehexahydro-cis-endo*-phthalic acid (A; R= CO_2H), m.p. 165°, and a trace of the *trans*-acid, m.p. 94°; hydrogenation of the Me_2 ester in AcOH or MeOH gives only the *cis-endo*-ester, m.p. 55°, also obtained as sole product (PtO_2-AcOH) from Me_2 3:6-*endomethylene*- Δ^1 -tetrahydrophthalate. $\text{CH}_2\text{C}\cdot\text{CO}_2\text{H}$ (modified prep.) and *cyclopentadiene* give 2:5-*endomethylene*- $\Delta^{1,3}$ -dihydrobenzoic acid, m.p. 93—94°, hydrogenated (colloidal $\text{Pt}-\text{AcOH}-\text{HCl}$, PtO_2-AcOH , PtO_2-MeOH , or colloidal $\text{Pd}-\text{H}_2\text{O}$) to 3:5-*endomethylenehexahydroendo*-benzoic acid, m.p. 65—66°. The lactone (I) with hot $\text{KOH}-\text{MeOH}$ gives by hydrolysis, loss of HBr , and ketonisation 3:6-*endomethylene-4-ketohexahydrophthalic acid* (II) (1- CO_2H *exo*, 2- CO_2H *endo*), m.p.



$\text{CHBr}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (*exo*) $\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ (*exo*)
 $\begin{array}{c} | \quad | \\ \text{CH}-\text{CH}-\text{CH} \\ | \quad | \\ \text{O}-\text{CO} \end{array}$ (I) $\begin{array}{c} | \quad | \\ \text{OAc}\cdot\text{C}-\text{CH}-\text{CH} \\ | \quad | \\ \text{O}-\text{CO} \end{array}$ (III.)

186° [Me_2 ester, b.p. 167—169°/11 mm. (*oxime*, m.p. 136°; *semicarbazone*, m.p. 186°)]; this with Ac_2O gives the *monoacetate*, m.p. 118° (decomp.), of the ketone *hydrate*, which at 120—150° loses AcOH and regenerates the acid and with CH_2N_2 gives the *Me ester lactone acetate* (III), m.p. 103°. Hydrogenation (Skita or Adams; AcOH) of (II) gives the lactonic acid (IV), m.p. 134° [as (I) but with H in place of Br]. At 250—260°/vac. (II) gives 3:6-*endomethylene-4-ketohexahydro-cis-exophthalic anhydride*, m.p. 171—175° (loss of H_2O) (*Ac* derivative, m.p. 108°), converted into (IV) by hydrolysis (NaOMe) and methylation. The *oxime*, m.p. 227° (decomp.), of (II) with H_2 -colloidal Pt or H_2 - PtO_2 in AcOH gives the *lactam* (V), m.p. 192° (*Me* ester, m.p. 104—105°), converted by crystallisation from MeOH into an *isomeride*, m.p. 209°, which slowly reverts to (V) when crystallised from EtOAc . *Norcamphoroxime*, b.p. 114—116°/12 mm., with H_2 - PtO_2 (40—50°; 3 atm.) or H_2 -colloidal Pd at 40—50° gives *norbornylendoamine* (hydrochloride, m.p. 295°; *picrate*, m.p. 179—180°) with a little *dinorbornylendoamine* (*picrate*, m.p. 193°) and *dinorbornylendo-*



ethylamine (picrate, m.p. 249°; obtained by reduction of a little Ac derivative formed by the solvent); with Na-EtOH much bornyl-endo- and a little -exo-amine are formed.

[BODE]. *d* and *n* of the *endo*-forms are > those of the *exo*-forms of monocarboxylic acids, but both have about the same $[M]$. *d* and *n* of the *cis*-forms of the dicarboxylic acids are > those of the *trans*-forms, but $[M]$ are about the same.

VIII. Hydrogenation of ketones and ketoximes of the camphor, fenchone, and *isofenchone* series is highly selective, but owing to the *as*-substitution the above rules of configuration cannot be applied. *d*-(—)-Camphoroxime gives (colloidal Pt-AcOH at 50°/3 atm., or PtO₂) almost entirely *d*-(—)-neobornylamine, m.p. 184° (*carbamide* derivative, m.p. 109°). 2:5-Diketocamphane gives (PtO₂; AcOH; 50°/3 atm.) a 2:5-*dihydroxycamphane*, m.p. 263°; its *dioxime*, m.p. 168—170°, $[\alpha]_D^{25} +60.5^\circ$ in MeOH (a small amount of isomeric *dioxime*, m.p. 236°, $[\alpha]_D^{25} +30^\circ$ in MeOH, is also formed), gives 2:5-*diaminocamphane* (*dihydrochloride* and *diplatinichloride*, m.p. 320°; *dicarbamide*, m.p. 192—193°, and *Ac₂* derivative, m.p. 229—230°). *d*-Fenchoneoxime gives *d*-fenchylamine (hydrochloride, m.p. 293°; *picrate*, m.p. 199°; *carbamide* derivative, m.p. 167°). *dl*-*isofenchone* (VI) gives *dl*- β -*isofenhol*, b.p. 89°/15 mm. [*H phthalate*, m.p. 104—105°; *phenylurethane*, m.p. 101°; oxidised to (VI)], and a trace of the known *dl*-fenhol, now termed α -fenhol; with Na-EtOH a mixture of α - and β -forms is obtained; the β - is converted into the α -form by hot Na-PhMe, but the α -form is stable. *dl*-*isofenchoneoxime* affords *dl*-*isofenchylamine* (*hydrochloride*, m.p. 285°; *picrate*, m.p. 303—304°), converted by HNO₂ into a mixture including probably some β -fenchene hydrate. (VI) and SeO₂ give 1:2-*diketo*-3:5:5-*trimethyl*-3:6-*endomethylenecyclohexane* ("*isofenchonequinone*"), m.p. 49—50°.

VIII. Semicarbazones, m.p. 165° and 166—167°, of 2:5-*endomethylene*- Δ^3 -tetra- and -hexa-*hydroendobenzaldehyde* (VII), respectively, are obtained (cf. lit.). (VII) gives an enol acetate (VIII) and *diacetate*, b.p. 136—137°/13 mm. [hydrolysed to (VII) by HCl-MeOH]. Hydrolysis of (VIII) gives mainly 2:5-*endomethylenehexahydroexobenzaldehyde* (IX), b.p. 66—68°/12 mm. (*semicarbazone*, m.p. 178°), oxidised by O₂-MnO₂ to the *exo*-acid. Hydrogenation (PtO₂) of (VII) in EtOH gives 2:5-*endomethylenehexahydrobenzyl endoalcohol*, b.p. 93—95°/14 mm. (*phenylurethane*, m.p. 134°; *H phthalate*, m.p. 111°), and (IX) gives the corresponding *exoalcohol*, b.p. 89—90°/11 mm. (*phenylurethane*, m.p. 118°; *H phthalate*, m.p. 102—103°), also obtained by similar hydrogenation and subsequent hydrolysis of (VIII).

R. S. C.

Resins. I. German pine turpentine from *Pinus silvestris*, L. H. WIENHAUS H. RITTER, and W. SANDERMANN. II. Additive capacity of the pine resin acids. H. WIENHAUS and W. SANDERMANN (Ber., 1936, 69, [B], 2198—2202, 2202—2206).

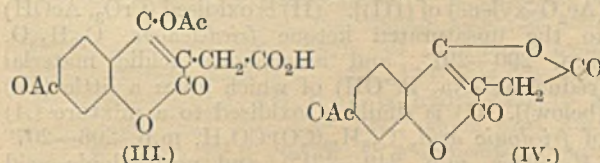
—I. Fresh pine turpentine appears to contain 64.2% of resin acids C₂₀H₃₀O₂ and 35.8% of neutral substances. Its treatment with steam under ordinary conditions and at >50°/30—40 mm. is described.

Repeated crystallisation of the crude acids from MeOH leads to the isolation of a small proportion of sylvic acid (I), m.p. 168—171°, $[\alpha]_D -105.33^\circ$, also obtained by their isomerisation by HCl in AcOH at 100°. Distillation of them under reduced pressure is accompanied by marked fall in $[\alpha]_D$. Treatment of the crude acids with COMe₃ gives a product, m.p. 139—142°, $[\alpha]_D -112.0^\circ$. The ultra-violet absorption spectrum of (I) indicates the presence of a conjugation of ethylenic linkings.

II. The action of maleic anhydride on the primary resin acids (II) of *P. silvestris*, L., occurs at room temp. with marked evolution of heat, and the product is completely identical in cryst. form and m.p. with that obtained from (I) by prolonged heating under pressure. Isomerisation of (II) to (I) does not therefore precede addition. Whereas (I) does not combine with *p*-O:C₆H₄:O at <100°, (II) readily affords the yellow compound (III), C₂₆H₃₄O₄, m.p. 214° (corr.), $[\alpha]_D -148^\circ$ in CHCl₃, which contains one ethylenic linking and is reduced (Zn dust in boiling AcOH or Pt in EtOH) to the colourless substance, C₂₆H₃₆O₄, m.p. 184°. (III) and NH₂Ph in boiling AcOH yield the amorphous product, C₃₂H₄₁O₄N, m.p. 130—140°. With CH₂N₂ in Et₂O esterification of (III) and addition of CH₂N₂ leads to the compound, C₂₈H₃₈O₄N₂, m.p. about 250°, isomerised by Ac₂O at room temp. to the colourless substance, m.p. 270°. Irradiation of (III) in EtOH with ultra-violet light or exposure of its solution in EtOH containing eosin in sunlight leads to a substance, m.p. 196°, transformed by CH₂N₂ into the *Me₂* ester, C₂₆H₃₄O₅(OMe)₂, m.p. 241°. (II) and α -naphthaquinone in MeOH yield the corresponding acid, m.p. 185° [*Me* ester, C₂₆H₂₆O·C₁₀H₆O₂(OMe), m.p. 195°], reduced (Zn in AcOH or H₂-Pt in EtOH) to the H₂-compound, C₂₆H₃₀O₂·C₁₀H₈O₂, m.p. 265°. *p*-Xyloquinone is not added to (II) and at a higher temp. dehydrogenates with production of *p*-xyloquinol. *d*-Pimaric acid present in (II) and distinguished by its stability and the dextrorotatory labile acid of pine resin do not react with quinones. A volumetric determination of the levorotatory labile acid in turpentine is thus indicated.

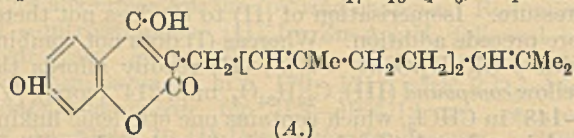
H. W.

Resin components of ammoniacum. II. Constitution of ammosesin. K. KUNZ and L. HOOPS (Ber., 1936, 69, [B], 2174—2182; cf. A., 1935, 219).—Treatment of diacetylammoresin (I) in EtOAc at -20° with 1.5% O₃ leads directly to the aldehyde (II), C₁₅H₁₂O₇, m.p. 137° [*p*-nitrophenylhydrazone, m.p. 194° (decomp.)], in 80—90% yield. Oxidation of (II) with 8% O₃ in EtOAc at -20° yields the corresponding acid (III), m.p. 205° (decomp.)



after darkening at 150° and softening at 165°. When heated for a short time with MeOH or EtOH or at 140—170°/vac. (III) passes into the lactone (IV), m.p. 208° after becoming discoloured at 200°, trans-

formed with loss of Ac by boiling $2N\text{-Na}_2\text{CO}_3$ into the acid, $\text{C}_{11}\text{H}_8\text{O}_6$, m.p. 233° after becoming discoloured at 210° , and converted by boiling MeOH into the compound, $\text{C}_{12}\text{H}_{10}\text{O}_6$, m.p. $158\text{--}5^\circ$ (corresponding *Et* derivative, m.p. $152\text{--}5^\circ$). Oxidation of (IV) with KMnO_4 in COMe_2 affords 4-acetyl- β -resorcylic acid, m.p. 151° . Treatment of (III) with $\text{KOH}\text{-H}_2\text{O}$ at 180° leads to $\beta\text{:}2\text{:}4$ -dihydroxybenzoylpropionic acid, m.p. $199\text{--}200^\circ$ (corresponding *Me*₂-acid, m.p. 147°). Oxidation of (I) with CrO_3 in AcOH at room temp. gives COMe_2 . The material remaining after removal of (II) from the products of the ozonolysis of (I) is distilled with steam, thereby yielding COMe_2 and giving lævulaldehydedi-*p*-nitrophenylhydrazone, m.p. 176° , and a substance, $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_6$, m.p. 187°



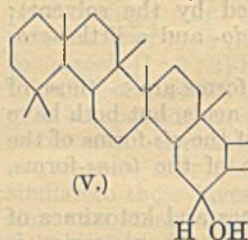
after darkening at 175° , also obtained from synthetic lævulaldehyde. The structure *A* for ammosesinol is therefore confirmed. H. W.

isoChavivic acid. H. LOHAUS (Annalen, 1936, 525, 312—315).—*isoChavivic* acid is obtained in 25% yield with m.p. $134\text{--}136^\circ$ from *Me* γ -bromoisochavicate (dimorphic). It or *isopiperic* acid with I in C_6H_6 or MeOH in light gives piperic acid. The oily *Me* ester is shown by illumination to be at least 75% pure. R. S. C.

Dehydrogenation of ursolic acid by selenium. N. L. DRAKE and H. M. DUVAL (J. Amer. Chem. Soc., 1936, 58, 1687—1688; cf. Ruzicka *et al.*, A., 1932, 517).—Ursolic acid is dehydrogenated (Se at $320\text{--}340^\circ$) to $1\text{:}2\text{:}7\text{-C}_{10}\text{H}_5\text{Me}_3$, $2\text{:}7\text{-C}_{10}\text{H}_6\text{Me}_3$, and the picene hydrocarbon, $\text{C}_{25}\text{H}_{20}$ (? $\text{C}_{24}\text{H}_{18}$) of Ruzicka *et al.* (cf. *loc. cit.*; A., 1934, 530). H. B.

Cerin and friedelin. III. Oxidative degradation of friedelin. N. L. DRAKE and W. P. CAMPBELL. IV. Dehydrogenation of friedelinol. N. L. DRAKE and W. T. HASKINS (J. Amer. Chem. Soc., 1936, 58, 1681—1684, 1684—1687; cf. A., 1935, 1373, 1502).—III. Friedelin (I) is reduced (Na, amyl alcohol) to friedelinol, $\text{C}_{30}\text{H}_{51}\text{OH}$, m.p. $301\text{--}304^\circ$ [iodide, m.p. $224\text{--}226^\circ$ (decomp.); acetate, m.p. $315\text{--}316^\circ$; *Me* ether, m.p. $265\text{--}267^\circ$], the benzoate, m.p. $250\text{--}251^\circ$, of which decomposes at $280\text{--}320^\circ$ in N_2 to BzOH and friedelene (II), $\text{C}_{30}\text{H}_{50}$, m.p. $257\text{--}258^\circ$. (I) and MgPhBr give a little phenylfriedelene, m.p. $269\text{--}271^\circ$; MgMeI affords methylfriedelinol (III), m.p. $316\text{--}319^\circ$, and some methylfriedelene, m.p. $272\text{--}274^\circ$ [also obtained by dehydration (Ac_2O -xylene) of (III)]. (II) is oxidised (CrO_3 , AcOH) to the unsaturated ketone friedelenone, $\text{C}_{30}\text{H}_{48}\text{O}$, m.p. $290\text{--}291^\circ$, and amorphous acidic material [reduction (Na, Pr°OH) of which gives a little (IV) (below)]. (I) is similarly oxidised to a mixture (A) of friedonic acid, $\text{C}_{28}\text{H}_{49}(\text{CO})\text{CO}_2\text{H}$, m.p. $206\text{--}207^\circ$ (*Me* ester, m.p. $249\text{--}251^\circ$), and norfriedonic acid (not isolable); reduction (Na- Pr°OH) of (A) affords friedololactone, $\text{C}_{30}\text{H}_{50}\text{O}_2$, m.p. $309\text{--}312^\circ$, and norfriedololactone (IV), m.p. $289\text{--}291^\circ$. (I) thus contains the $>\text{CH}\cdot\text{CO}\cdot\text{CH}_2$ grouping.

IV. Dehydrogenation (Se at $315\text{--}325^\circ$) of friedelinol (V) gives $1\text{:}2\text{:}7\text{-C}_{10}\text{H}_5\text{Me}_3$,



$1\text{:}2\text{:}8$ -trimethylphenanthrene, an alkylcyclohexene, $\text{C}_{11}\text{H}_{20}$, b.p. $180\text{--}185^\circ$ [further dehydrogenation by Se at 320° (sealed tube) to a product, b.p. $187\text{--}192^\circ$ (brominated to a compound, m.p. $169\text{--}175^\circ$)], and the picene hydrocarbon, $\text{C}_{25}\text{H}_{20}$ (? $\text{C}_{24}\text{H}_{18}$), m.p. $305\text{--}306^\circ$, of Ruzicka *et al.* (A., 1934, 530). The annexed structure is assigned to (V). H. B.

Sapogenins. I. Sapogenins of sarsaparilla root. F. A. ASKEW, S. N. FARMER, and G. A. R. KON (J.C.S., 1936, 1399—1403).—*Smilagenin* (I), m.p. $183\text{--}184^\circ$, $[\alpha]_D^{25} -69^\circ$ in CHCl_3 , has been isolated from Jamaica sarsaparilla root, and forms an acetate, m.p. $150\text{--}151^\circ$, $[\alpha]_D^{25} -59\cdot6^\circ$ in CHCl_3 , and a benzoate, m.p. $181\text{--}181\cdot5^\circ$. (I) is converted by H_2CrO_4 into *smilagenone*, m.p. $156\text{--}157^\circ$, and by PCl_5 into *smilagenyl chloride*, m.p. $194\text{--}195^\circ$, and by reduction ($\text{Na}\text{-C}_5\text{H}_{11}\text{OH}$) into *deoxysmilagenin*, m.p. $132\text{--}133^\circ$. Surface film measurements of the three *Digitalis* sapogenins, sarsasapogenin (II), and (I) show that the formulae for tigogenin and gitogenin are confirmed, but make it necessary to revise the formula for (II), which is closely related to (I). F. R. S.

Constitution of papaveristerol. E. BUREŠ and S. FUCIK (Časopis českoslov. Lék., 1935, 15, 159—167; Chem. Zentr., 1935, ii, 3926).—*Papaveristerol* (I), $\text{C}_{30}\text{H}_{50}\text{O}$, m.p. $134\text{--}134\cdot5^\circ$, $[\alpha]_D^{20} -39\cdot88^\circ$ in CHCl_3 (acetate, m.p. 122° ; dibromide acetate, m.p. $108\text{--}109^\circ$), is isolated from poppy-seed oil soap. (I) is reduced ($\text{Na}\text{-C}_5\text{H}_{11}\text{OH}$) to *dihydropapaveristerol*, m.p. 128° (acetate, m.p. 115°), and oxidised by CuO at $285\text{--}300^\circ$ to *papaveristenone*, $\text{C}_{30}\text{H}_{48}\text{O}$, m.p. $125\cdot5\text{--}126^\circ$ (semicarbazone, m.p. 102° ; oxime, m.p. 85°); the latter is further oxidised (KMnO_4) to a keto-acid, which is then reduced (Clemmensen) to an acid, $\text{C}_{29}\text{H}_{48}\text{O}_2$, m.p. $101\text{--}102^\circ$. The partial formula $\text{C}_{26}\text{H}_{43}(\text{CH}_2\cdot\text{CH}\cdot\text{OH})(\text{CH}\cdot\text{CH}_2)$ is ascribed to (I). H. N. R.

Constitution of Hseh Tsuang seed.—See this vol., 1435.

Dragon's blood.—See this vol., 1435.

Oximation. K. C. GULATI and J. N. RAY (Current Sci., 1936, 5, 75).—Flavone and α -naphthylflavone when boiled with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in aq. $\text{C}_5\text{H}_5\text{N}$ afford oximes, m.p. 237° and 181° , respectively. This method is used successfully in difficult cases. J. L. D.

Styrylpyrylium salts. XVII. Colour phenomena associated with 4-phenylbenzo- β -naphthaspiropyran and 4-phenyl- $\alpha\beta$ -dinaphthaspiropyran. I. M. HELBRON, D. H. HEY, and A. LOWE (J.C.S., 1936, 1380—1383).—2-Ethylchromone and MgPhBr give 4-phenyl-2-ethylbenzopyrylium chloride, which with $2\text{:}1\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHO}$, followed by hydrolysis, affords 4-phenyl-3'-methylbenzo- β -naphthaspiropyran, m.p. $219\text{--}220^\circ$. 7-Methoxy-4-phenyl-3'-methylbenzo- β -, m.p. $256\text{--}258^\circ$, 4-phenyl-3'-methyl- $\alpha\beta$ -di-, m.p. $207\text{--}208^\circ$, and 4-phenyl-3 : 3'-dimethyl-

$\alpha\beta$ -di-naphthaspiropyran are similarly prepared. These substances do not develop colour in boiling inert solvents and the anomalies found by Heilbron *et al.* (A., 1933, 614) no longer exist. F. R. S.

Pigments of cotton flowers. III. Karunganni (*Gossypium indicum*). K. NEELAKANTAM and T. R. SESHADRI (Proc. Indian Acad. Sci., 1936, 4, A, 54—58).—From the petals of Karunganni, *gossypin*, m.p. 230° (decomp.), hydrolysed to gossypetin and glucose, a non-glycosidic substance, $C_{16}H_{12}O_7$, m.p. 255—257° (Ac derivative, m.p. 186—187°), quercetin, herbacitrin, and gossypitrin have been isolated. F. R. S.

Benzoxanthenes. II. W. KNAPP (J. pr. Chem., 1936, [ii], 146, 113—118; cf. A., 1935, 1247).—*Salicylic acid 1-C₁₀H₇ ether* (*o*-1-naphthoxybenzoic acid; from $C_{10}H_7\cdot OH$, *o*- $C_6H_4Cl\cdot CO_2K$, NaOMe, and Cu at 150—200°, m.p. 134—136°, is stable to Ac_2O , but with P_2O_5 in hot C_6H_6 gives 3:4-benzoxanthone, m.p. 162° (corr.) (lit. 155°). Similar prep. of *o*- $CO_2H\cdot C_6H_4\cdot O\cdot C_{10}H_7\cdot 2$ (I) gives also 10% of *naphtha-1':2':2:1-benzofuran*, m.p. 162° (lit. 296°). (I) is stable to Ac_2O , but with P_2O_5 gives 1:2-benzoxanthone, m.p. 145° (corr.) (lit. 140°, 142°). *o*- $OPh\cdot C_6H_4\cdot CO_2H$, m.p. 114°, similarly prepared, gives with P_2O_5 xanthone, m.p. 177° (corr.) (cf. lit.); with Ac_2O it probably gives a mixed anhydride, since xanthone is obtained only after distillation.

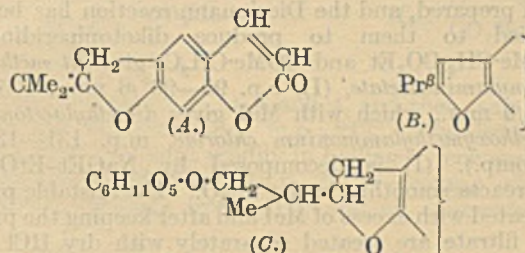
R. S. C.

Alkylacetylenes and their additive products. XIV. Synthesis of dioxolan derivatives from alkylacetylenes. D. B. KILLIAN, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1658—1659; cf. A., 1934, 759).— CH_3CBu (I) with $(\cdot CH_2\cdot OH)_2$ and $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot OH$ in presence of $CCl_3\cdot CO_2H$ and a catalyst (from BF_3 , Et_2O , red HgO, and MeOH) gives 2-methyl-, b.p. 62—63°/20 mm., and 2-methyl-4-chloromethyl-, b.p. 109°/25 mm., -2-butyl-1:3-dioxolan, respectively. Similarly, (I) with $OH\cdot CHPh\cdot CO_2H$ and $OH\cdot CMe_2\cdot CO_2H$ affords 4-keto-5-phenyl-2-methyl-, b.p. 136—138°/19 mm., m.p. 44—45°, and 4-keto-2:5:5-trimethyl-, b.p. 104°/25 mm., -2-butyl-1:3-dioxolan, respectively, whilst Me tartrate yields Me 2-methyl-2-butyl-1:3-dioxolan-4:5-dicarboxylate, b.p. 141—142°/9 mm. Mannitol and (I) give the dioxolan, $\begin{matrix} CHR\cdot O \\ \diagdown \\ CHR\cdot O \end{matrix} > CMeBu$ ($R = \begin{matrix} CH_2\cdot O \\ \diagdown \\ CH\cdot O \end{matrix} > CMeBu$), b.p. 210—212°/9 mm. $CH_2\cdot CH\cdot C\cdot CH$ and $(\cdot CH_2\cdot OH)_2$ similarly afford 2-methyl-2- $\beta\text{-}\beta'$ -hydroxyethoxyethyl-1:3-dioxolan, b.p. 140—142°/20 mm., and the dioxolan, $\begin{matrix} (CH_2\cdot O) \\ \diagdown \\ (CH_2\cdot O) \end{matrix} > CMe\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot$, b.p. 204—206°/20 mm.

H. B.

Natural coumarins. XX. Constitution of nodakenin from *Peucedanium decursivum*, Maxim. E. SPÄTH and P. KATNRATH (Ber., 1936, 69, [B], 2062—2066; cf. Arima, A., 1927, 599; 1929, 430, 914).—Prolonged extraction of the dry roots with pure MeOH at about 300 mm., evaporation of the extract, and treatment of the residue with H_2O yields nodakenin (I), m.p. 218—219° (decomp.), hydrolysed by 3% H_2SO_4 to glucose and nodakenetin (II), $C_{14}H_{14}O_4$, m.p. 192°, $[\alpha]_D^{24} -25.4^\circ$ in $CHCl_3$.

(II) is unaffected by distillation at 280°(bath)/14 mm. or by heating with Al_2O_3 at 260°/vac. but is converted by distillation with P_2O_5 at 120—150°(bath)/1 mm. smoothly into *anhydronodakenetin* (III), $C_{14}H_{12}O_3$, m.p. 138—139°, $[\alpha]_D \pm 0^\circ$ in $CHCl_3$. Catalytic hydrogenation (Pd-sponge in AcOH) of (III) gives deoxydihydro-oreoselone, m.p. 115—117°. This observation combined with the difficulty of dehydration



of (II) leads to the structure C for (I) and, combined with the optical inactivity, to the structure A or B for (III). H. W.

Tannin of Formosan tea leaves. Y. OSHIMA (Bull. Agric. Chem. Soc. Japan, 1936, 12, 103—114, and Proc. Imp. Acad. Tokyo, 1936, 12, 189—190).—Extraction of fresh tea leaves with H_2O gave gallic acid, an amorphous tannin, $C_{30}H_{24}O_{14}$, *l*-epicatechin [identical with that obtained by Freudenberg (A., 1923, i, 697)], and a galocatechin (I), $C_{15}H_{13}O_7$, m.p. 227°, $[\alpha]_D -37.5^\circ$ in H_2O , -67.0° in EtOH (*pentacetate*, m.p. 189°, $[\alpha]_D -21.3^\circ$ in $COMe_3$; Me_5 derivative, m.p. 184°, $[\alpha]_D -15.2^\circ$ in $COMe_3$). The amorphous tannin is *bis*-(5:7:3':4':5'-pentahydroxy)-flavpinacol, proved by its synthesis from phloracetophenone triacetate and gallaldehyde triacetate, hydrolysis of the product to the *chalkone*, $C_{15}H_{12}O_7$, m.p. 278°, and reduction of the latter to the tannin by Zn and AcOH. Reduction of the Me_5 derivative of (I) with Na and EtOH gave α -2:4:6-trimethoxyphenyl- γ -3:4:5-trimethoxyphenylpropane, m.p. 91°, which was synthesised by catalytic reduction of the condensation product of ω -acetoxy-3:4:5-trimethylgallacetophenone with phloroglucinaldehyde Me_3 ether. (I) was synthesised by catalytic reduction of delphinidin Me_5 ether. J. N. A.

Thioindigo syntheses. I. Synthesis of 6:6'-dichloro-4:4'-dimethylthioindigo and 6:6'-dichloro-4:4'-dimethoxythioindigo. R. SHIBATA and T. NISHI. II. Bromination of 6:6'-dichloro-4:4'-dimethylthioindigo, 6:6'-dichloro-4:4'-dimethoxythioindigo, and thioindigo-red. R. SHIBATA and M. OKUYAMA. III. Condensation products of thioindigotin-7:7'-dicarboxylic acid chloride with aromatic amines. R. SHIBATA and A. SASSA (J. Soc. Chem. Ind. Japan, 1936, 39, 280—282B, 282—283B, 283—284B).—I. 3-Chloro-6-cyano-5-methylthioglycolic acid, m.p. 125°, obtained from the corresponding NH_2 -acid, is hydrolysed to the 6-carboxylic acid, m.p. 132—133°, which with NaOH and S gives 6:6'-dichloro-4:4'-dimethylthioindigotin (I). The 4:4'-(OMe)₂-compound (II) is similarly obtained.

II. Bromination of (I) under different conditions yields only the 5:5'- or 7:7'- Br_2 -derivatives, and (II)

similarly affords a Br_2 -derivative. Bromination of thioindigo-red gives coloured dyes.

III. Thioindogotin-7 : 7'-dicarboxyl chloride condenses with amines to form differently coloured dyes.

F. R. S.

Preparation of some β -diketopiperidines. C. GUSTARSSON (Finska Kem. Medd., 1936, 45, 98—103).— δ -Keto-esters containing N in the chain have been prepared, and the Dieckmann reaction has been applied to them to produce diketopiperidines. $NHMe \cdot CH_2 \cdot CO_2Et$ and $COMe \cdot CH_2Cl$ give *Et methylacetonylaminoacetate*, (I), b.p. 95—96°/6 mm., 105—106°/9 mm., which with MeI gives *dimethylacetonyl-carbethoxymethylammonium chloride*, m.p. 131—133° (decomp.). (I) is decomposed by $NaOEt \cdot EtOH$, but reacts smoothly in dry Et_2O . The unstable ppt. is treated with excess of MeI and after keeping the ppt. and filtrate are treated separately with dry HCl to remove Na and yield respectively 3 : 5-diketo-1 : 1-dimethylpiperidinium chloride, pale brown, reddening at 150°, m.p. 208—209° (decomp.), and 3 : 5-diketo-1 : 1 : 4 : 4-tetramethylpiperidinium iodide, m.p. 174.5—175.5°. $COMe \cdot CH_2 \cdot CMe_2 \cdot NH_2$ with $ClCO_2Et(Me)$ gives *N-carbethoxydiacetoneamine* (II), b.p. 105.5—107°/6 mm., and *N-carbomethoxydiacetoneamine*, b.p. 100—102°/7 mm. (II) is decomposed completely by $NaOEt$ in $EtOH$, but smoothly in Et_2O . Among the products is $CHMeBu \cdot OH$.

M. H. M. A.

dicyclo-[1 : 2 : 2]-1-Azaheptane. V. PRELOG and E. CERKOVNIKOV (Annalen, 1936, 525, 292—296).—*Et tetrahydropyran-4-carboxylate* with $Na \cdot EtOH \cdot C_6H_6$ gives 33% of 4-hydroxymethyltetrahydropyran, b.p. 210—214° (*phenylurethane*, m.p. 86—87°), converted by 45% HBr at 100—110° into *ae-dibromo- γ -bromomethylpentane*, b.p. 158—160°/10 mm., which with $NH_3 \cdot MeOH$ at 130—140° gives 31.2% of dicyclo-[1 : 2 : 2]-1-azaheptane (I), m.p. 71° (sinters from 65°), b.p. 120—121°

(hydrochloride, hygroscopic; *platini*- and *auri-chloride*; *picrate*; *picronate*; *methiodide*, hygroscopic; *methoaurichloride*).

R. S. C.

Processes of catalytic dehydrogenation. IX. **Dehydrogenation of hydrogenated derivatives of 2-pyridone.** E. SPATH and F. GALINOVSKY (Ber., 1936, 69, [B], 2059—2061).—2-Ketopiperidine is dehydrogenated by prolonged heating with Pd-sponge at 260—270° to 2-pyridone in 50—60% yield. 1- and 6-Methyl-2-ketopiperidine behave similarly. Better yields are obtained in the similar dehydrogenation of hydro-carbostyryl and -isocarbostyryl and their *N-Me* derivatives.

H. W.

Tautomerism of pyridine homologues. II. **Syntheses in the pyridine series.** A. E. TSCHITSCHIBABIN (Bull. Soc. chim., 1936, [v], 3, 1607—1632; cf. A., 1927, 885).—2- and 4-Alkyl-pyridines and -quinolines are alkylated in the side-chain by $NaNH_2$ and alkyl halides; an excess of base is used to minimise the formation of quaternary salts and olefines. The yield depends partly on the amount of Na derivative present in equilibrium with the base and $NaNH_2$, being greater in the case of γ - than of α -picoline. Isomerides (? 3- or 6-derivatives) are

formed in small amounts and two alkyl groups may enter the same side-chain. The following are thus prepared in 40—80% yield : 2- and 4- β -phenylethyl-, b.p. 164°/20 mm., 2- $\beta\beta'$ -diphenylisopropyl-, b.p. 198°/5 mm. (*picrate*, m.p. 136°), 2- γ -phenylpropyl-, b.p. 199°/2 mm. (*picrate*, m.p. 125°), 2-*n*-amyl-, b.p. 206.5—207° [*picrate*, m.p. 73°; *platini*chloride, m.p. 160° (decomp.)]; a base (*picrate*, m.p. 164°) is also formed], 2-, b.p. 200° (*picrate*, m.p. 105°; *platini*chloride, decomp. >160°), and 4-*iso*amyl- b.p. 225—227° [*picrate*, m.p. 112—113°; *platini*chloride, m.p. 214° (decomp.)], 2-cyclohexylmethyl-, b.p. 118°/12 mm. (*picrate*, m.p. 135°), 2- Δ^2 -butenyl-, b.p. 188—192° (*picrate*, an oil; $HgCl_2$ compound, cryst.), 2- and 4-*n*-propyl- [*picrate*, m.p. 134° (lit. 153°); *platini*-, m.p. 210°, and *auri-chloride*, m.p. 116—118°], 4-*isobutyl*-, b.p. 195° (*picrate*, m.p. 122°; *platini*chloride, m.p. 216°), 4-*n*-butyl-, b.p. 229—230° [*picrate*, m.p. 102—103°; *platini*chloride, m.p. 203° (decomp.)], 2- β -phenylethyl-6-methyl-, b.p. 165°/23 mm. [*picrate*, m.p. 125°; *platini*chloride; a base, $C_{16}H_{13}N$, m.p. 71—72° (*picrate*, m.p. 165°; *platini*chloride), is also obtained], 2- β -phenylethyl-5-ethyl-, b.p. 185—195°/17 mm., 309—312°/760 mm. [*platini*chloride, m.p. 170—172° (decomp.)], 4- α -methylpropyl-, b.p. 187° (*picrate*, m.p. 142°), and 3-phenyl-4- Δ^2 -butenyl-pyridine, b.p. 125—130°/20 mm.; γ -4-pyridyl- $\beta\delta$ -dimethylpentane, b.p. 208—210° (*picrate*, m.p. 115°); δ -4-pyridyl- $\beta\zeta$ -dimethylheptane, b.p. 261° (*picrate*, m.p. 89°; *platini*chloride, m.p. 180°); ε -4-pyridyl-*n*-nonane, b.p. 265—267° (*picrate*, m.p. 114—116°); 4-*n*-propyl- (*picrate*, m.p. 207°), 2- β -phenylethyl- (impure), b.p. 225—230°/12 mm., and 2- $\beta\beta'$ -diphenylisopropyl-quinoline (*picrate*).

R. S. C.

Manufacture of pyridine dyes.—See B., 1936, 924.

Introduction of the triphenylmethyl group. I. E. FUNAKUBO and T. HIROTANI (Ber., 1936, 69, [B], 2123—2130).—Treatment of *isochavibetol* with CPh_3Cl in C_5H_5N at 155° yields *triphenylmethylisochavibetol* (I), m.p. 184—185°, *isochavibetol CPh₃ ether*, (II), m.p. 207—209°, and a sparingly sol., unidentified material. (I) contains OH, OMe, and a double linking in the side-chain. It yields an *acetate*, m.p. 175.5—176°, hydrolysed to (I), a *benzoate*, m.p. 168—169°, a *Me ether*, m.p. 168.5—169°, and a *phenylurethane*, m.p. 215.8—217°. It is unaffected by KOH at 234—236°, but is transformed by HI (d 1.7) at 150° into a substance, m.p. 93—96° after softening at 71°, characterised as the *diacetate*, m.p. 187—188°, and *Me₂* derivative, m.p. 132—137°. (II) contains OMe and a double linking in the side-chain, but not OH. The yield of (I) increases at the expense of (II) when reaction is prolonged. Similarly *isoeugenol*, CPh_3Cl , and C_5H_5N at 150° give *triphenylmethylisoeugenol*, m.p. 208—209° (*acetate*, m.p. 150—150.5°), and *isoeugenol CPh₃ ether*, m.p. 211—212.5°. 1-Triphenylmethylindole, m.p. 211.5—212°, is obtained from indole and CPh_3Cl in boiling C_5H_5N or from Mg indolyl iodide and CPh_3Cl in Et_2O . 1-Triphenylmethyl-2-methylindole, m.p. 215.5—216°, is obtained similarly.

H. W.

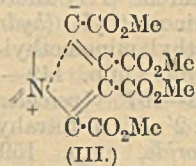
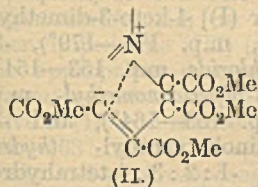
Synthesis of 3-alkyl- and 3-aryl-quinolines. F. L. WARREN (J.C.S., 1936, 1366—1368).— $PhNO_2$, NH_2Ph , and β -ethylglycerol $\alpha\gamma$ - Et_2 ether give 3-

ethylquinoline (picrate, m.p. 196—197°). β -Phenylglycerol $\alpha\gamma$ -Et₂ ether, b.p. 155°/21 mm., obtained from OH-CPh(CH₂Cl)₂, with PhNO₂ and NH₂Ph yields 3-phenylquinoline, and with α -C₁₀H₇·NH₂ forms 3-ethyl- α -naphthaquinoline, m.p. 75·5° (picrate, m.p. 188°).
F. R. S.

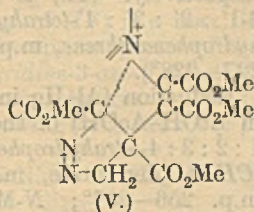
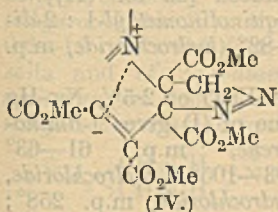
Urethanes as local anæsthetics. III. Alkyl N-8-quinolylocarbamates. R. E. DAMSCHROEDER and R. L. SHRINER (J. Amer. Chem. Soc., 1936, 58, 1610—1612).—8-Aminoquinoline and ClCO₂Alk in Et₂O+aq. Na₂CO₃ give *Me*, m.p. 61·5—62·5°, *Et*, m.p. 66—67°, *Pr*^a, m.p. 58—59°, *Bu*^a, m.p. 40°, *Bu* ^{β} , m.p. 69—70°, *n*- and *iso*-amyl, and *n*-hexyl, N-8-quinolylocarbamates; the hydrochlorides have m.p. 199—201°, 165—166°, 156—157°, 146—149°, 155—165°, 147—149°, 149—152°, and 145—147° (all with decomp.), respectively, and have little or no anæsthetic activity.
H. B.

Derivatives of basically substituted enol and thioenol compounds.—See B., 1936, 920.

Syntheses in the hydroaromatic series. XXVI. Diene synthesis of hetero-rings containing nitrogen. II. Adducts derived from isoquinoline and acetylenedicarboxylic esters. O. DIELS and J. HARMS (Annalen, 1936, 525, 73—94).—The action of (C·CO₂Me)₂ on isoquinoline (I) in Et₂O at 0° and finally at room temp. gives “labile adduct” (II), m.p. 167—169°, and (III), m.p. 142—145°, the latter in relatively very small amount. In solubility and behaviour in ultra-violet light (II) is closely allied

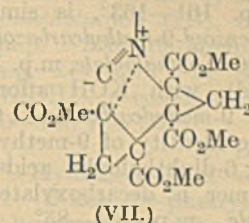
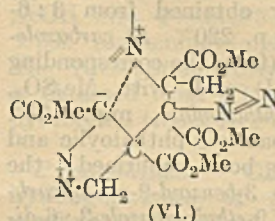


to the “labile” C₅H₅N, quinoline, and stilbazole adducts and its position in the “labile” series is established further by its behaviour towards CH₂N₂. In the first phase two *mono*-adducts, (IV) and (V), result, one of which passes with excess of CH₂N₂ into the *bis*-adduct (VI), m.p. 155—158° (decomp.), whereas the other is stable towards excess of CH₂N₂ and ultimately passes into a substance C₂₂H₂₁N which

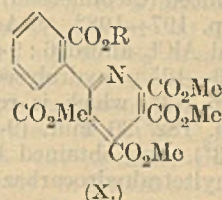
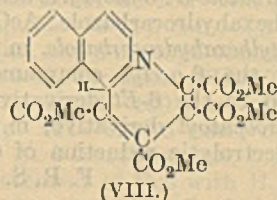


again adds CH₂N₂ and then loses 2 N with formation of the compound (VII), m.p. 207° (accompanied by a substance, C₂₃H₂₃O₈N, m.p. 148—150°). (VI) is converted by HCl into (I) and pyrazoledicarboxylic acid, thus establishing the position of the double linkings in the “unsaturated ester chain.” The CH₂N₂ reaction also proves that these linkings are not equiv. to one another. Hydrogenation of (II) proceeds rapidly (colloidal Pd in MeOH or PtO₂

in AcOH) to a H₂-derivative, m.p. 180°, which adds 2 CH₂N₂, and hence contains the “ester chain”



unaltered and 2 H at 3 and 4, and then very slowly to the H₄-compound, m.p. 217°. Stabilisation of (II) proceeds most readily in boiling xylene and gives the compound (VIII), m.p. 231° (decomp.), also obtained similarly from (III), and an *isomeride*, m.p.



170—172°. (VIII) gives a *perbromide*, C₂₁H₁₈O₈NBr₃, decomp. 140°, a *perchlorate*, C₂₁H₁₈O₈N·ClO₄·0·5H₂O, decomp. 215°, and an *indolizine substance*, C₁₈H₁₅O₆N (IX), m.p. 153°. Treatment of (II) with excess of Br in abs. EtOH yields the *perbromide*, C₁₈H₁₆O₆NBr₃, decomp. 140°, converted by hot aq. K₂CO₃ into the *substance*, C₁₈H₁₄O₆NBr, m.p. 166°, and (IX). Oxidation of (II) by H₂O₂ in AcOH followed by treatment with CH₂N₂, or treatment of (II) with Br in MeOH-H₂O gives the ester (X) (R=Me), m.p. 152° [if Br-EtOH-H₂O is used a similar ester (X; R=Et), m.p. 118—119°, results], hydrolysed and decarboxylated to 2-phenylpyridine.

In contrast with (II), (III) is very unstable and tends to decompose into its components. It adds CH₂N₂, but the intermediate di-adduct loses N₂ during the reaction and gives the *substance*, C₂₃H₂₃O₈N₃, m.p. 168—169°. During very cautious hydrogenation rupture of the mol. occurs, so that the isolable product is a dihydroisoquinoline (*picrate*, m.p. 167°). Stabilisation of (II) is not caused by acids, and the production of small amounts of (VIII) from it in boiling xylene is attributed to a preliminary fission into its components from which (II) is formed, whence (VIII).

The possibility of stabilising the labile adducts of the members of the series depends on the presence of a displaceable H attached to C vicinal to N and of the intact “ester chain.” The presence of the $\Delta^3:4$ -double linking is not essential, since the H₂-derivative of (II) passes when heated above its m.p. into a very characteristic red *isomeride*, m.p. 189°, and is oxidised by Br-MeOH-H₂O to (X) and a *tribromide*, C₂₁H₂₀O₈NBr₃, pale brown needles, decomp. 138°, which slowly pass into a substance, decomp. 145°.

H. W.

Friedel-Crafts reaction in the carbazole series. II. D. R. MITCHELL and S. G. P. PLANT (J.C.S., 1936, 1295—1298).—3:6-Dibenzoylcarbazole and KOH

give carbazole-3:6-dicarboxylic acid (I) (*Et* ester, m.p. 203°); *Et* 9-methylcarbazole-3:6-dicarboxylate, m.p. 161—163°, is similarly obtained from 3:6-dibenzoyl-9-methylcarbazole, m.p. 220°. *Et* carbazole-3:6-diphthaloylate, m.p. 195° (from the corresponding acid), with KOH affords (I) and, with Me_2SO_4 , *Et* 9-methylcarbazole-3:6-diphthaloylate, m.p. 135°. The identity of 9-methylcarbazole-9-phthaloylic and -3:6-diphthaloylic acids has been confirmed; the former is decarboxylated to 3-benzoyl-9-methylcarbazole, m.p. 84—85°. *Et* 9-ethylcarbazole-3:6-diphthaloylate, m.p. 178°, is obtained from the acid. Carbazole, succinic anhydride, and AlCl_3 in PhNO_2 form carbazole-3:6-bis- γ -ketobutyric acid, m.p. 285° (decomp.) [*Et* ester, m.p. 173°; 9-*Me* derivative, m.p. 268° (decomp.), and its *Et* ester, m.p. 142°], reduced (Clemmensen) to carbazole-3:6-dibutyric acid, m.p. 197—198°. 9-Acetylhexahydrocarbazole, AcCl , and AlCl_3 afford 6:9-diacetylhexahydrocarbazole, m.p. 123—125°, hydrolysed to the 6-acetyl compound, m.p. 73°, which is reduced to the 6-*Et* derivative, b.p. 182°/20 mm. (9-*p*-nitrobenzoyl derivative, m.p. 153°), also obtained by electrolytic reduction of 6-ethyltetrahydrocarbazole. F. R. S.

Structure and properties of phenanthroline-ferric complexes.—See this vol., 1324.

Phenanthrene series. XI. Propanolamines of the type $\text{C}_{14}\text{H}_9\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NR}_2$. J. VAN DE KAMP and E. MOSETTIG. XII. Amino-alcohols derived from 1:2:3:4-tetrahydrophenanthrene. A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1936, 58, 1568—1570, 1570—1572).—XI. 2- β -Dimethylamino-, m.p. 104.5—105° (hydrochloride, m.p. 193—193.5°; perchlorate, m.p. 167—167.5°), 2- β -diethylamino- (hydrochloride, m.p. 167—167.5°), 2- β -piperidino-, m.p. 88.5—89° (hydrochloride, m.p. 220—220.5°), 2- β -1':2':3':4'-tetrahydroisoquinolino-, m.p. 133.5—134° (hydrochloride, m.p. 208—209°), 3- β -dimethylamino- (hydrochloride, m.p. 177.5—178°; picrate, m.p. 175.5—176°), 3- β -diethylamino- (hydrochloride, m.p. 155.5—156°; picrate, m.p. 108—109°), 3- β -piperidino- (hydrochloride, m.p. 201—201.5°; picrate, m.p. 162.5—163.5°), 3- β -1':2':3':4'-tetrahydroisoquinolino-, m.p. 118.5—119° (hydrochloride, m.p. 219—220°), 9- β -dimethylamino- (hydrochloride, m.p. 171—171.5°; picrate, m.p. 175—175.5°), 9- β -diethylamino- (hydrochloride, m.p. 135—136°; salicylate, m.p. 113—113.5°), 9- β -piperidino- (hydrochloride, m.p. 184—185°; picrate, m.p. 138—139°), and 9- β -1':2':3':4'-tetrahydroisoquinolino- (hydrochloride, m.p. 228.5—229°), -propionylphenanthrenes are prepared from 2-, 3-, and 9-acetylphenanthrenes (1 mol.), paraformaldehyde (1.5 mols.), and the appropriate $\text{NHR}_2\cdot\text{HCl}$ (1.5 mols.) in isoamyl alcohol. Reduction (H_2 , PtO_2 , 50—70% EtOH) of the above (usually as hydrochlorides) gives 2- γ -dimethylamino- (I), m.p. 97.5—98° (picrate, m.p. 156—157°), 2- γ -diethylamino- (II), m.p. 91—92°, 2- γ -piperidino-, m.p. 128—128.5° (hydrochloride, m.p. 184—185°), 2- γ -1':2':3':4'-tetrahydroisoquinolino-, m.p. 132.5—133° (hydrochloride, m.p. 212.5—213°), 3- γ -dimethylamino-, m.p. 99—100°, 3- γ -diethylamino- (hydrochloride, m.p. 141—143°), 3- γ -piperidino- (III) (hydrochloride, m.p. 185—185.5°), 3- γ -1':2':3':4'-tetrahydroisoquinolino-, m.p.

132.5—133° (hydrochloride, m.p. 212.5—213°), 9- γ -dimethylamino- (perchlorate, m.p. 142.5—143°; picrate, m.p. 167.5—168°), 9- γ -diethylamino-, 9- γ -piperidino-, m.p. 126—126.5° (picrate, m.p. 193.5—194°), and 9- γ -1':2':3':4'-tetrahydroisoquinolino- α -hydroxypropylphenanthrene, respectively. The O-*Bz* derivative hydrochlorides of (I) and (II) have m.p. 219—219.5° and 166—167°, respectively; the O-*Ac* derivative hydrochloride of (III) has m.p. 237.5—238°.

XII. 1-Keto-1:2:3:4-tetrahydrophenanthrene (I) (1 mol.), paraformaldehyde (2.5 mols.), and the appropriate $\text{NHR}_2\cdot\text{HCl}$ (1.2 mols.) in isoamyl alcohol give 1-keto-2-dimethylaminomethyl-, m.p. 66—82° (hydrochloride, m.p. 199—200°), -2-diethylaminomethyl-, m.p. 60—61° (hydrochloride, m.p. 137—138°; picrate, m.p. 163—164°), -2-piperidinomethyl-, m.p. 97—98° (hydrochloride, m.p. 170—220°), and -2-1':2':3':4'-tetrahydroisoquinolinomethyl-, m.p. 121—123° (hydrochloride, m.p. 148—150°), -1:2:3:4-tetrahydrophenanthrenes, which are reduced (H_2 , PtO_2 , 90% EtOH) (as hydrochlorides) to 1-hydroxy-2-dimethylaminomethyl-, m.p. 146—147° (hydrochloride, m.p. 236°), -2-diethylaminomethyl- (II), not obtained cryst., -2-piperidinomethyl-, m.p. 133—134.5° (hydrochloride, m.p. 227—228°), and -2-1':2':3':4'-tetrahydroisoquinolinomethyl-, m.p. 159—160° (hydrochloride, m.p. 217°), -1:2:3:4-tetrahydrophenanthrene, respectively. (II) with $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ or EtOH-HCl at room temp. gives 2-diethylaminomethyl-3:4-dihydrophenanthrene (hydrochloride, m.p. 231—232°). 4-Keto-1:2:3:4-tetrahydrophenanthrene (III) affords [as for (I)] 4-keto-3-dimethylaminomethyl- (hydrochloride, m.p. 178—179°), -3-diethylaminomethyl- (hydrochloride, m.p. 153—154°; picrate, m.p. 149—151°), -3-piperidinomethyl-, m.p. 106—107° (perchlorate, m.p. 163—164°), and -3-1':2':3':4'-tetrahydroisoquinolinomethyl- (hydrochloride, m.p. 159—161°), -1:2:3:4-tetrahydrophenanthrenes, similarly reduced to 4-hydroxy-3-dimethylaminomethyl- (hydrochloride, m.p. 186—187°; O-*Ac*-derivative hydrochloride, m.p. 200°), -3-diethylaminomethyl- (hydrochloride, m.p. 172—173°; picrate, m.p. 177—179°), -3-piperidinomethyl- (hydrochloride, m.p. 178—179°), and -3-1':2':3':4'-tetrahydroisoquinolinomethyl- (IV), m.p. 149.5—151° (hydrochloride, m.p. 181—182°), -1:2:3:4-tetrahydrophenanthrene, respectively. (IV) is dehydrated [as for (II)] to 3-1':2':3':4'-tetrahydroisoquinolinomethyl-1:2-dihydrophenanthrene, m.p. 81—82° (hydrochloride, m.p. 227—228°).

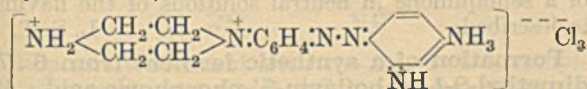
Reduction (Al-Hg in moist Et₂O or 2.5% Na-Hg in EtOH-AcOH) of the oxime of (I) gives 1-amino-1:2:3:4-tetrahydrophenanthrene, m.p. 61—63° [*CHPh*' derivative, m.p. 103—105°; hydrochloride, m.p. 256—257°; *N*-Me (hydrochloride, m.p. 258°; hydriodide, m.p. 243°) and *NN*-Me₂ (hydrochloride, m.p. 216°; picrate, m.p. 177—178°) derivatives]; the oxime of (III) is reduced (Al-Hg) to the 4-NH₂-derivative (hydrochloride, m.p. 267—268°; *NN*-Me₂ derivative hydrochloride, m.p. 202°). H. B.

Acetanilidoalkylbarbituric acids [5-alkyl-5-barbiturylacetanilides]. II. *p*-Carbomethoxy-derivatives. J. A. TIMM and J. B. HOWARD (J. Amer. Chem. Soc., 1936, 58, 1805).—5-Alkylbarbituric acids

and p -CO₂Et·C₆H₄·NH·CO·CH₂Cl give (method: A., 1935, 1507) *Et* 5-ethyl-, 5-isopropyl-, 5-*n*- and -isobutyl-, 5-isoamyl-, and 5-allyl-5-barbiturylacetanilide-4'-carboxylates, all m.p. >225° (decomp.). H. B.

Tetra-alkylbarbituric acids. A. W. DOX (J. Amer. Chem. Soc., 1936, 58, 1633—1635).—Methylation (CH₂N₂) or ethylation (diazoethane) of 5:5-di- and 1:5:5-tri-alkylbarbituric acids gives almost quant. yields of the 1:3:5:5-tetra-alkyl derivatives. The following are described: 1:3-dimethyl-5:5-diethyl- (I), m.p. 37° [also prepared from CEt₂(COCl)₂ and CO(NHMe)₂ at 135—150°], 5-phenyl-1:3-dimethyl-5-ethyl-, m.p. 88—89°, 5-phenyl-1:3-triethyl-, m.p. 129°, 3-phenyl-1-methyl-5-ethyl-5-propyl-, m.p. 78°, 3-benzyl-1-methyl-5:5-diethyl-, m.p. 73°, and -1:5:5-triethyl- and 1:3-dimethyl-5-ethyl-5-hexyl-, b.p. 165—170°/12 mm., -5-isoamyl-, and -5- α -methylbutyl-barbituric acids. The *O*-methyl-5:5-diethylbarbituric acid of Marotta and Rosanova (A., 1932, 1041) is impure (I). H. B.

N-Piperaziny dyes. Azo-dyes. I. V. PRELOG and D. KOHLBACH (Coll. Czech. Chem. Comm., 1936, 8, 377—389).—*N*-Phenylpiperazine (I) and PhN₂Cl give 1-phenylpiperazine-4-azobenzene, m.p. 154—154.5°, decomposed by HCl into N₂, PhOH, and (I). Similarly the substance previously (A., 1934, 196) regarded as *p*-piperazinylazobenzene-*p*'-sulphonic acid is 1-phenylpiperazine-4-azobenzene-*p*-sulphonic acid. However, (I) couples with some diazonium salts in the *p*-position of the Ph; *p*-1-piperazinoazobenzene-*p*'-sulphonamide (II) is thus obtained. 1-Acetyl-4-phenylpiperazine (III) (prep. by Ac₂O or AcCl) with the appropriate diazonium salts gives *p*-1-4-acetyl-piperazinoazobenzene, m.p. 222°, and the *Ac* derivative of (II) and thence *p*-1-piperazinoazobenzene, m.p. 162—163°, and (II). (I) or (III) with HNO₂ gives 1-nitroso-4-*p*-nitrosophenylpiperazine, m.p. 155°, reduced by SnCl₂ to 1-*p*-aminophenylpiperazine (trihydrochloride, m.p. >300°; Bz₂ derivative, m.p. 226.5°), which by diazotisation and coupling yields 2:4-diamino-4'-*N*-piperazinoazobenzene (tetrahydrochloride, an effective bactericide for some, not all, organisms), 2:6-diaminopyridine-3- (IV), 1-phenyl-3-methylpyrazol-5-one-4-, and 2-naphthol-1-azo-*p*-N-piperazinobenzene (dihydrochloride). (IV) gives a red tetrahydrochloride, decomposed by H₂O into a black trihydrochloride (V); the colour of (IV) is a max. in 0.6—1*N*-HCl; this fact, the absorption spectra of the salts and of 2:6-diaminopyridine-3-azo-*p*-dimethylaminobenzene (shows no colour changes in acid; trihydrochloride) lead to the following structure for (V):



R. S. C.

Synthesis of 6-hydroxy-4-methylpyrimidine-5-acetic acid and 4-methyl-5-aminomethyluracil. W. T. CALDWELL and W. M. ZIEGLER (J. Amer. Chem. Soc., 1936, 58, 1749—1751).—4-Methyluracil-5-acetic acid (I), POCl₃, and PCl₅ lead to 2:6-dichloro-4-methylpyrimidine-5-acetic acid, m.p. 156—157°, reduced (method: Gabriel and Colman, A., 1899, i, 638) to 6-hydroxy-4-methylpyrimidine-5-acetic acid,

m.p. 147—149°. The hydrazide, m.p. >375°, of (I) is converted into the azide (II) and thence by 50% AcOH into 4-methyl-5-aminomethyluracil (III), m.p. >335° (darkening) [acetate, m.p. >360° (darkening)]. The *N*-CO₂Et-derivative, m.p. 214—215°, of (III) is obtained from (II) and EtOH; it could not be hydrolysed (conc. HCl at 130—140°) to (III).

H. B.

Pyrimidines. CLII. Hydrogenation and hydrogenolysis of [ethyl 2-keto-[4-phenyl-6-methyl]-1:2:3:4-tetrahydropyrimidine]-5-carboxylate to β -benzyl- and β -hexahydrobenzyl-*n*-butyl alcohol. K. FOLKERS (J. Amer. Chem. Soc., 1936, 58, 1558—1560; cf. A., 1934, 783).—Hydrogenolysis occurs when the ester is treated with H₂ in presence of Cu-Ba-Cr oxides (A) and EtOH at 250° and gives 28.6% of a mixture, b.p. 77—79°/2.5 mm., of β -benzyl- (I), b.p. 81—81.5°/2 mm., and β -hexahydrobenzyl- (II), b.p. 83—84°/2 mm., -*n*-butyl alcohols. CHPh:CAc·CO₂Et is reduced [H₂, (A), EtOH, 160°] to *Et* β -hydroxy- α -benzylbutyrate, b.p. 124—126°/3 mm., dehydrated (P₂O₅ in C₆H₆) to *Et* α -benzylcrotonate, b.p. 125—127°/3 mm.; short treatment of this with H₂ and (A) in EtOH at 250° and subsequent hydrolysis (EtOH-NaOH), gives (I) and α -benzylbutyric acid, b.p. 123—124°/2 mm., whilst more prolonged treatment affords a mixture which is further reduced (Raney Ni, 180°) to (II).

H. B.

Magneto-chemical investigations of organic substances. IX. Magnetic behaviour of nitro-nitrogen-radicals. E. MÜLLER and W. WIESEMANN (Ber., 1936, 69, [B], 2157—2163; cf. A., 1935, 1453).—Wieland's bisdi-*p*-anisylididiphenylhydrazine could not be freed from a solid paramagnetic impurity. The magnetic behaviour of 4:4'-dibenzyl-dipyridinium is not in harmony with the presence of two independent electron spins and supports the quinonoid formulation of the compound. Generally, wherever valency tautomerism with formation of the quinonoid condition is possible the magnetic behaviour is in accord only with such quinonoid structure, whereas the chemical behaviour of the substances points to the existence of free radicals. Attempts to obtain the 4:4'-dibenzyl-dipyridinium subiodide of Weitz gave a compound, m.p. 187—193°, of 1 mol. of radical +1 mol. of subiodide which in the solid condition cannot be regarded as a radical, but further conclusions as to its structure cannot be reached until measurements have been made with its solutions. The magnetic behaviour of tetratolyldiazinium perchlorate supports Weitz' formulation, and since the paramagnetism depends preponderatingly on one spin moment, the alternative NAr₂·NAr₂X is preferred. H. W.

Experiments in the heterocyclic series. E. C. WAGNER and J. K. SIMONS (J. Chem. Educ., 1936, 13, 394).—A correction (cf. this vol., 1000).

L. S. T.

Methyl and phenyl derivatives of nitrophthalhydrazides [nitrophthalaz-1:4-diones]. C. N. ZELLNER and G. DOUGHERTY (J. Amer. Chem. Soc., 1936, 58, 1811—1813).—3-Nitrophthalic anhydride (I) and NHMe·NH₂·AcOH in aq. AcOH (distilled off

during reaction) give two 5-nitro-*N*-methylphthalaz-1:4-diones, m.p. 305° (II) (*Ac* derivative, m.p. 211°) and 273° (III) (*Ac* derivative, m.p. 144°). Similarly, (I) and $(\cdot\text{NHMe})_2$ afford 5-nitro-2:3-dimethylphthalaz-1:4-dione, m.p. 203°, whilst (I) and NMe_2NH_2 yield 3-nitro-*N*-dimethylaminophthalimide, m.p. 200—201°. Methylation (Me_2SO_4 , dil. alkali) of 5-nitrophthalaz-1:4-dione ["3-nitrophthalhydrazide"] (IV) gives two ON- Me_2 derivatives, m.p. 207° and 138—139°, also obtained by similar methylation of (II) and (III), respectively. These results indicate that (IV) is not 3-nitro-*N*-aminophthalimide (cf. Mihailescu and Protopopescu, A., 1930, 1434) but has the constitution assigned. 6-Nitro-*N*-methyl-, m.p. 310—311° and 271—272° (*Ac* derivatives, m.p. 213—214° and 170—171°, respectively), and -2:3-dimethyl-, m.p. 203.5°, -phthalaz-1:4-diones are similarly prepared from 4-nitrophthalic anhydride (V). $\text{NHPh}\cdot\text{NH}_2$ and (V) in *AcOH* give 4-nitro-*N*-anilinophthalimide, m.p. 182°, and a 6-nitro-*N*-phenylphthalaz-1:4-dione, m.p. 253° (*Ac* derivative, m.p. 186°); (I) similarly affords 3-nitro-*N*-anilinophthalimide, m.p. 198—199°. All m.p. are corr. H. B.

3-Aminophthalhydrazide. K. GLEU and K. PFANNSTIEL (J. pr. Chem., 1936, [ii], 146, 137—150).—Me benzisooxazolone-3-carboxylate (I), when heated for a short time with conc. aq. N_2H_4 , gives 3-aminophthaloylhydrazine (II), $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{CO})_2\text{N}\cdot\text{NH}_2$, yellow, m.p. 250—251° or about 257° (slow heating), probably by way of the 3-hydrazide and 3-hydroxylaminophthaloylhydrazine. (II) is also obtained from 3-aminophthalimide (III) and aq. N_2H_4 at 75°. 5-Aminophthalaz-1:4-dione (IV), $\text{NH}_2\cdot\text{C}_6\text{H}_3\begin{matrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{matrix}$, m.p. 328° (hydrochloride, $+0.5\text{H}_2\text{O}$, m.p. 328°, at 100° loses the H_2O rapidly and *HCl* slowly, stable to light), is obtained by heating (I) and N_2H_4 for a longer time, from (III) and N_2H_4 at $>75^\circ$, or by heating (II) above the m.p. or with conc. *HCl*. The *N*-Me derivative of (I) gives 1-methylbenzisooxazolone-4-carbohydrazide, m.p. 173° (decomp.) (hydrochloride, $+\text{H}_2\text{O}$, decomp. 200°), and thence 5-methylaminophthalazdione (V), m.p. about 310—325° (decomp.). (IV) and $\text{Me}_2\text{SO}_4\text{--NaOH}$ give the Me_2 derivative (VI), m.p. 230°. (I) and $\text{NHPh}\cdot\text{NH}_2$ give 3-aminophthal- (or -phthaloyl-)phenylhydrazide (VII), m.p. 222° (*Ac* derivative, m.p. 178°; cf. Bogert *et al.*, A., 1909, i, 305). (II) and (IV), but not (V), (VI), or (VII), are sol. in alkali. (IV) fluoresces in acid, (V) in alkaline solution. (II) and (VI) do not fluoresce. The chemiluminescence of (IV) is best observed with H_2O_2 and a trace of hæmin. The other compounds show no chemiluminescence. R. S. C.

Quinazolines. XLIII. Synthesis of a quinazoline derivative structurally analogous to cusparine. D. PAPA and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 1701—1703).—2-3':4'-Methylenedioxystryryl-4-quinazolone, new m.p. 316—317° (decomp.) (all m.p. are corr.), is reduced (method: A., 1935, 760) to 2- β -3':4'-methylenedioxyphenylethyl-4-quinazolone, m.p. 239—240°, methylated (Me_2SO_4 , aq. *NaOH*) to the 3-*Me* derivative, m.p. 94—94.5°, and converted by $\text{POCl}_3+\text{PCl}_5$ into 4-

chloro- and thence (MeOH--NaOMe) into 4-methoxy-2- β -3':4'-methylenedioxyphenylethylquinazoline, m.p. 67—68°. The following are similarly prepared: 2-*p*-methoxystyryl-, m.p. 284—285°, 2- β -*p*-anisylethyl-, m.p. 213—214°, and 2- β -*p*-anisylethyl-3-methyl-, m.p. 118—118.5°, -4-quinazolone; 4-chloro-, m.p. 125—128°, and 4-methoxy-, m.p. 84.5—85.5°, -2- β -*p*-anisylethylquinazoline. 2-Methyl-4-quinazolone is methylated (Me_2SO_4) to the 2:3- Me_2 derivative, m.p. 111—111.5°. It is now stated that the "galipine" of *loc. cit.* should be galipoline. H. B.

Semiquinones of neutral-red and safranines. L. MICHAELIS (J. Amer. Chem. Soc., 1936, 58, 1816—1817).—Dilution (H_2O) of solutions of neutral-red, phenosafranine, or commercial "safranine" in conc. *HCl* until bluish-violet and subsequent treatment with CrCl_2 or *Zn* dust gives intense green (semiquinone state) and then almost colourless solutions; re-oxidation ($\text{K}_2\text{S}_2\text{O}_8$) reverses the two-fold colour change. H. B.

Synthesis of pyridylisoquinoline derivatives. S. SUGASAWA and M. KURIYAGAWA (Ber., 1936, 69, [B], 2068—2071).—Homoveratrylamine and Et nicotinate at 150—170° give nicotinoyl- β -3:4-dimethoxyphenylethylamide [hydrochloride ($+1\text{H}_2\text{O}$)] transformed by POCl_3 in boiling *PhMe* into 6:7-dimethoxy-1-3'-pyridyl-3:4-dihydroisoquinoline (I), m.p. 123—124° [dimethiodide, m.p. 229° (decomp.)]. The dimethochloride of (I) is hydrogenated (Adams) to the methochloride, decomp. 275°, of 6:7-dimethoxy-1-3'-pyridyl-2-methyl-1:2:3:4-tetrahydroisoquinoline. *N*-Methylhexahydro nicotinoyl- β -3:4-dimethoxyphenylethylamide, m.p. 98°, is converted by POCl_3 in boiling *PhMe* into a non-cryst. base which yields a dihydriodide, decomp. 208—209°, and a dipicrolonate, decomp. 245° after softening at 230°. H. W.

Light absorption and tautomerism of uric acid.—See this vol., 1317.

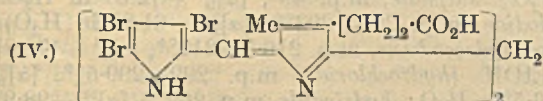
Murexide and leucomurexide. D. DAVIDSON (J. Amer. Chem. Soc., 1936, 58, 1821—1822).—Murexide (I) is obtained in good yield (cf. Kuhn and Lyman, this vol., 1000) from alloxantin and NH_4OAc in boiling glacial *AcOH*. (I) is reduced ($\text{Na}_2\text{S}_2\text{O}_4$, aq. NH_3) to leucomurexide [NH_4 dihydropurpurate], which is readily oxidised [air; $\text{K}_3\text{Fe}(\text{CN})_6$] to (I). H. B.

Semiquinone of the flavin dyes, including vitamin-B₂. L. MICHAELIS, M. P. SCHUBERT, and C. V. SMYTHE (Science, 1936, 84, 138—139).—A colour reaction, affording evidence for the existence of a semiquinone in neutral solutions of the flavins, is described. L. S. T.

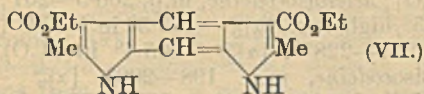
Formation of a synthetic ferment from 6:7-dimethyl-9-*l*-araboflavin-5'-phosphoric acid. R. KUHN, H. RUDY, and F. WEYGAND (Ber., 1936, 69, [B], 2034—2036; cf. this vol., 1418).—6:7-Dimethyl-9-*l*-araboflavin-5'-phosphoric acid (I) gives with the colloidal carrier obtained from the yellow enzyme a non-fluorescent, non-dialysable yellow chromoprotein of high catalytic activity which is resolved into its components by acid. 6:7-Dimethyl-9-*l*-araboflavin is transformed by CPh_3Cl in anhyd. $\text{C}_5\text{H}_5\text{N}$ into 5'-triphenylmethyl-6:7-dimethyl-9-*l*-araboflavin, m.p.

262—263° (decomp.). The corresponding 2' : 3' : 4'-*triacetate*, m.p. 240° (decomp.), is transformed by boiling 80% AcOH into 6 : 7-*dimethyl-9-l-araboflavin* 2' : 3' : 4'-*triacetate*, m.p. 209° (corr.), which when treated with POCl₃ in C₅H₅N gives (I) (*Ag, Na, and Ca salts*). H. W.

Porphyryns. XXXVIII. Synthesis of porphyryns and their derivatives. H. FISCHER, R. J. DOYLE, and W. GLEIM (*Annalen*, 1936, 525, 24—43).—Pyrrole-2-aldehyde (I) and cryptopyrrole-carboxylic acid in AcOH containing 48% HBr give 3' : 5'-*dimethylpyrromethene-4'-propionic acid hydrobromide* (II), darkens above 190° [*Me ester hydrobromide*, m.p. 151° (corr.)]. With Br in AcOH at room temp. (II) gives a mixture of Br₂- and Br₃-derivatives whereas at 100° 3 : 4 : 5-*tribromo-3'-methyl-5'-bromomethylpyrromethene-4'-propionic acid hydrobromide* (III) results; (III) is converted by boiling MeOH or H₂O into 1' : 8' : 1 : 2 : 7 : 8-*hexabromo-3 : 6-dimethyl- α , β -*



γ ,III-*dehydrobilan-4 : 5-dipropionic acid* (IV), m.p. 146°. Analogously (I) and hæmopyrrolecarboxylic acid yield 4' : 5'-*dimethylpyrromethene-3'-propionic acid hydrobromide* (*Me ester hydrobromide*), whence the *hydrobromides* of the Br₂-derivative, decomp. about 210°, and Br₃-compound (V). Treatment of (III) or (V) with (-CH₂CO₂H)₂ and AcCO₂H at 180—190° gives 1 : 5-*dimethylporphin-2 : 6-dipropionic acid* [*Me₂ ester*, m.p. 302° (corr.)], and its *Cu salt*. Et 5-*aldehyde-2-methylpyrrole-3-carboxylate* and Et pyrrole-2-carboxylate in AcOH containing 48% HBr yield Et₂ 5'-*methylpyrromethene-5 : 4'-dicarboxylate hydrobromide*, m.p. 193° (decomp.), which could not be further converted into the corresponding porphyrin or porphin. (I) and 3 Br₂ in Et₂O give 3 : 4 : 5 : 3' : 4' : 5'-*hexabromopyrromethene* (VI), decomp. >160° (*hydrobromide*, decomp. about 160°), which with CH₂O and C₅H₅N gives unchanged material and a *compound*, C₁₉H₆N₄Br₁₀. Addition of CH₂Cl·OEt to Et 2-*methylpyrrole-3-carboxylate* in EtOH, Et₂O, or C₆H₆ gives Et₂ 2 : 6-*dimethyl-4 : 8-dihydrobenzodipyrrole-3 : 5-dicarboxylate* (VII), m.p. 331° (block) after subliming at 280°, also obtained by means of HCl-CH₂O, the constitution of which is established by its reduction (HI-AcOH) to 2 : 3 : 5-*trimethylpyrrole*;



it is possibly identical with the Et₂ 2 : 6-*dimethylbenzodipyrrole-3 : 5-dicarboxylate* of Ruggli *et al.* (this vol., 614). (VI) and 5 : 5'-*dimethylpyrromethene-4 : 4'-dipropionic acid hydrobromide* in AcCO₂H at 190° give *Me₂ porphin-1 : 4-dipropionate*, m.p. 215—216° (*Cu salt*); at 160° *Me₂ 5 : 6 : 7 : 8-tetrabromoporphin-1 : 4-dipropionate*, m.p. 180°, is produced. 3 : 3' : 5 : 5'-*Tetramethyl-4 : 4'-diethylpyrromethene hydrobromide*, (VI), and AcCO₂H at 190° afford 2 : 3-*dimethyl-1 : 4-diethylporphin* (*Cu salt*), whilst at 160° 5 : 6 : 7 : 8-*tetrabromo-2 : 3-dimethyl-*

1 : 4-diethylporphin is produced. *Porphin-1 : 3 : 5 : 7-tetrapropionic acid*, m.p. 265—266°, is derived from 4 : 5 : 3' : 5'-*tribromo-5'-methylpyrromethene-3 : 4'-dipropionic acid hydrobromide* and AcCO₂H at 190°.

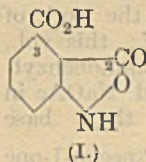
H. W.

Chlorophyll. LXXIV. Quantitative dehydrogenation of phæophorbide-a. H. FISCHER and W. LAUTSCH (*Annalen*, 1936, 525, 259—270; cf. this vol., 1273).—The relationship of the phæophorbide to the porphin series is proved by quant. reaction of phæophorbide-a with Ag₂O (2 mols.) or AgOAc (4 mols.) in hot AcOH (3 min.) to a product, which with CH₂N₂ gives 10-*acetoxyvinylphæoporphyria-a₅ Me₂ ester*, m.p. >360° (additive product with CHN₂·CO₂Me, m.p. 302°; converted into a *hæmin*, m.p. >360°; *oxime*, m.p. >360°). This with H₂-Pd in EtOAc absorbs 3 H₂ to give 10-*acetoxyphæoporphyria-a₅ Me₂ ester*, m.p. 305°, with HBr-AcOH, followed by MeOH, affords 10-*acetoxy-2- α -methoxyphæoporphyria-a₅ Me₂ ester*, m.p. >360°, and a little 2- α -*methoxyrhodoporphyria*, and with MeOH-C₅H₅N, followed by CH₂N₂, gives vinylrhodoporphyria Me₂ ester, m.p. 172°. Structures are confirmed spectrographically. R. S. C.

Chlorophyll and hæmin derivatives in organic minerals.—See this vol., 1358.

Optical absorption of the porphyryns. VII.—See this vol., 1318.

Benzisooxazolone-4-carboxylic acids and indazolone-4-carboxylic acids. K. GLEU and K. PFANNSTIEL (*J. pr. Chem.*, 1936, [ii], 146, 129—136).—Electrolytic reduction of 3-nitrophthalic acid gives quantitatively *benzisooxazolone-3-carboxylic acid* (I), m.p. 191° [*Ag salt*; *Ac*, m.p. 215° (decomp. from 196°), *N-Et*, m.p. 138°, and *N-Me* derivative, m.p. 163° (*Me ester*, m.p. 66°); *Me ester* (prep. by H₂SO₄-MeOH or from the *Ag salt*), +H₂O, m.p. about 110° (decomp.) or (anhyd.) about 119° (*Ac derivative*, m.p. 119°)]. The *N*-substituted but not the *NH* derivatives can be sharply titrated using phenolphthalein. The acid gives by diazo-reactions 3-chloro-, -iodo-, -hydroxy-phthalic acid; if the diazonium solution is treated with KI-SO₂ it gives *indazolone-4-carboxylic acid*, m.p. 312° (decomp.). R. S. C.



Acenaphthene series. II. A. C. SIRCAR and S. C. SEN (*J. Indian Chem. Soc.*, 1936, 13, 482—483; cf. *A.*, 1932, 286).—Acenaphthenequinone, *p*-NHAc·C₆H₄·CHO, and cold NH₃-C₅H₁₁·OH give the oxazole, but more drastic treatment with the same reagents affords the glyoxaline, m.p. 250° (decomp.). Other aldehydes do not react similarly. R. S. C.

Doebner reaction. XII. R. CIUSA and F. BELLINO (*Gazzetta*, 1936, 66, 452—455).—2-2'-*Furylcinchonic acid*, new m.p. 227° (cf. *A.*, 1922, i, 1062), prepared as before, and also by the Doebner reaction, forms *K, Na* (+H₂O), and *Cu* (+0.5H₂O) salts, and a *Me ester*, m.p. 100°. In pharmacological use, it eliminates uric acid from the system in a similar manner to atophan, and is less toxic than the latter. E. W. W.

Vitamin-B₁. XIV. Sulphite cleavage. IV. The thiazole half. E. R. BUCHMAN (J. Amer. Chem. Soc., 1936, 58, 1803—1805; cf. Clarke and Gurin, A., 1935, 1510).— α -Acetyl- γ -butyrolactone and SO₂Cl₂ give the α -Cl-derivative, b.p. 84—86°/3 mm., converted by dil. HCl at 100° into γ -chloro- γ -acetylpropyl alcohol, b.p. 85—110°/3 mm., which with HCS·NH₂ in EtOH at room temp. affords 4-methyl-5- β -hydroxyethylthiazole (I), b.p. 93—95°/2 mm., also prepared (in lower yield) from HCS·NH₂ and the unstable Br-compound from CH₂Ac·CH₂·CH₂·OH and Br in H₂O. (I) and conc. HCl at 145° give 4-methyl-5- β -chloroethylthiazole, b.p. 74—75°/3 mm. H. B.

Synthesis of thiochrome. F. BERGEL and A. R. TODD (Nature, 1936, 138, 406).—Condensation of 4-chloro-2-methyl-5-chloromethylpyrimidine, synthesised from 4-hydroxy-2-methylpyrimidine-5-acetic ester, with 2-amino-4-methyl-5- β -hydroxyethylthiazole gives a product identical with thiochrome prepared from aneurin (A., 1935, 1286). The blue fluorescence shown by thiochrome appears to be a property of the condensed ring system present, since other compounds of this type, which all have a similar fluorescence, have been prepared. This synthesis confirms the structure of aneurin (this vol., 1276).

L. S. T.

l-Peganine from the blossoms and stems of Peganum Harmala. L. A. D. ROSENFELD and D. G. KOLESNIKOV (Ber., 1936, 69, [B], 2022—2023).—l-Peganine, C₁₁H₁₂ON₂, m.p. 212°, [α]_D²⁴—211.0° in CHCl₃ (hydrochloride, m.p. 206—207°; picrate, m.p. 211°; aurichloride, m.p. 132°), isolated from *P. Harmala*, L., appears identical with the alkaloid obtained by Späth (this vol., 489) from *Adhatoda vasica*, Nees. H. W.

Peganine. XII. Peganine derivatives and their picrolonates. E. SPÄTH, F. KUFFNER, and J. LINTNER (Ber., 1936, 69, [B], 2052—2058; cf. this vol., 489).—Mainly a correction of the work of Narang *et al.* (A., 1935, 765, 995, 1387; this vol., 869). Contrary to these authors, *o*-aminobenzylsuccinamic acid is transformed by anhyd. NaOAc in H₂ at 140—150° not into the base CH₂<N=C(CH₂)>CH₂ (I) but into Δ^9 -pegen-1-one (II) identical with that derived from *o*-aminobenzylsuccinimide and further identified by reduction with Na-C₅H₁₁·OH to peganine (III). In an attempt to obtain (I) synthetically *o*-NH₂·C₆H₄·CH₂·OMe is converted by (·CH₂·CO)₂O followed by distillation in a high vac. into the compound, (·CH₂·CO)·N·C₆H₄·CH₂·OMe, m.p. 93—95°, transformed by HBr in C₆H₆ into the corresponding bromide, m.p. 132—134°, which passes into (II) when treated with liquid NH₃ and then distilled in a high vac. The base C₁₁H₁₁N₂ obtained by the reduction of (II) or peganine (IV) is identified as l-*o*-aminobenzylpyrrolidine, not (III); this view is confirmed by the observations that it gives a dipicrolonate whereas (III) affords only a monopicrolonate, m.p. 191—193° (vac.). The electrolytic reduction is complete within 1 hr. The monopicrolonates of (IV), m.p. 177—179° (vac.; decomp.), pegan-3-ol, m.p.

188—190° (vac.; decomp.), and Δ^9 -pegenone, m.p. 236—237° (vac.; decomp.), are incidentally described.

H. W.

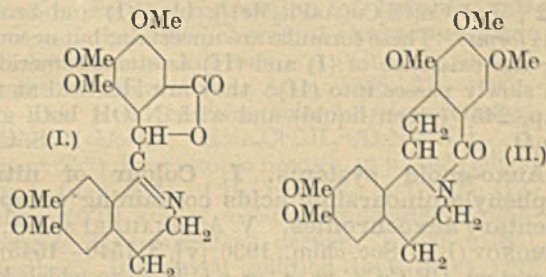
Ethers and hetero-ethers of morphine and its isomerides. B. F. FARIS and L. SMALL (J. Org. Chem., 1936, 1, 194—208).—The prep. of the following derivatives is described; m.p. marked * were determined in an evacuated tube: ethyldihydromorphine, b.p. 170°/high vac., [α]_D²⁴—135.9° in EtOH [H tartrate, m.p. 167°, [α]_D²⁵—59.4° in H₂O; methiodide, m.p. 260°*]; benzylidihydromorphine, m.p. 95—97°, [α]_D²⁴—88.1° in EtOH [hydrochloride (+H₂O), m.p. 233—235°*, [α]_D²⁵—52.1° in H₂O; hydrobromide (+H₂O), m.p. 193—195°*, [α]_D²⁴—44° in H₂O; hydriodide, m.p. 215—217°*, [α]_D²⁴—45.3° in H₂O; perchlorate, m.p. 188—192°, [α]_D²⁵—59.5° in EtOH; methiodide, m.p. 242—244°*, [α]_D²⁴—43.2°; methoxy-methylidihydromorphine, m.p. 99—101°, [α]_D²⁴—154.5° in EtOH (hydrochloride, m.p. 124—126°, [α]_D²⁴—78° in H₂O; sulphate, m.p. 49°, [α]_D²⁴—72.8° in H₂O; methiodide, m.p. 201—203°*, [α]_D²⁴—61.8° in H₂O); heterodihydrocodeine, m.p. 216.5—217°*, [α]_D²⁶—178.0° in EtOH [hydrochloride, m.p. 299—299.5°*, [α]_D²⁶—136.5° in H₂O; hydriodide, m.p. 269°*, [α]_D²⁵—98.9° in H₂O; perchlorate, m.p. 258—260°* (decomp.), [α]_D²⁵—110° in H₂O; hydrogen fumarate, m.p. 215—216°, [α]_D²⁵—110° in H₂O; methiodide, m.p. 260—261°*, [α]_D²⁵—91.4° in MeOH]; heteroethylmorphine (+H₂O), m.p. 110—112°, [α]_D²³—178.8° in EtOH [hydrochloride (+3H₂O), m.p. 241—243°*, [α]_D²⁴—134.9° in H₂O; hydrobromide (+2H₂O), m.p. 285—287°*, [α]_D²⁵—119.2° in H₂O; hydriodide (+2H₂O), m.p. 171—174°, solidifies and remelts at 282°* (decomp.), [α]_D²⁴—115.8° in H₂O; perchlorate, m.p. 249—250°* (decomp.); methiodide, m.p. 255—265°* (decomp.); heteroethylidihydromorphine, m.p. 189—190°, [α]_D²³—164.8° in EtOH [hydrochloride (+3H₂O), m.p. 165—170°*, solidifies and remelts at 274—276°*, [α]_D²⁴—121.7° in H₂O; hydrobromide (+2H₂O), m.p. 282—284°*, [α]_D²⁵—125.1° in H₂O; hydriodide, m.p. 291—293°*, [α]_D²⁵—110.6° in H₂O; perchlorate, m.p. 234—235°*, [α]_D²³—98° in EtOH; methiodide, m.p. 250—251°*, [α]_D²⁵—79.4° in MeOH]; ethyl- α -isomorphine, m.p. 128—130°, [α]_D²³—143.7° in EtOH [methiodide, m.p. 243°*, [α]_D²¹—91.6°]; ethyldihydro- α -isomorphine (+H₂O), m.p. 86—91°, [α]_D²⁴—110° in MeOH [anhyd. base, m.p. 104°, b.p. 130°/high vac.; hydrogen tartrate (+H₂O), m.p. 109—112°, [α]_D²³—66° in H₂O; methiodide, m.p. 277°*, [α]_D²³—76.2° in H₂O]; heteroisocodeine, m.p. 206.5—207°*, sublimes at 155°/high vac., [α]_D²²—185.5° in MeOH (methiodide, m.p. 227—228°*, [α]_D²²—105.4° in H₂O); heterodihydroisocodeine, m.p. 198—200°, [α]_D²⁵—118.1° in EtOH (hydrochloride, m.p. 273—275°*, [α]_D²⁴—111.1° in H₂O; hydriodide, m.p. 287—288°*, [α]_D²⁴—85.2° in H₂O; methiodide, m.p. 245—248°*, [α]_D²⁴—77.9 in H₂O); heteroethyl- α -isomorphine, m.p. 161—162°*, b.p. 170°/high vac., [α]_D²²—205.1° in MeOH [hydrochloride, m.p. 247—248°* (decomp.), [α]_D²⁴—164.2° in H₂O; hydriodide, m.p. 264°* (decomp.), [α]_D²⁴—132.7° in H₂O; hydrobromide, m.p. 255—258°* (decomp.), [α]_D²⁴—150.2° in H₂O; methiodide, m.p. 229—231°*, [α]_D²⁴—131.3° in H₂O]; heteroethyl-dihydro- α -isomorphine, m.p. 210—212°, [α]_D²⁴—128° in EtOH [hydrochloride, m.p. 300°*, [α]_D²⁴—125.7° in

H₂O; *hydriodide*, m.p. 287°*, [α]_D²⁴ -99.5° in H₂O; *methiodide*, m.p. 256—258°*, [α]_D²⁴ -86.1° in H₂O; *ethyl- β -isomorphine*, b.p. 170°/high vac. [*H sulphate*, m.p. 195—198°*, [α]_D²⁴ -136.3° in H₂O; *perchlorate*, m.p. 264—266°* (decomp.), [α]_D²⁵ -113.2° in 40% EtOH; *fumarate*, m.p. 172—175°*, [α]_D²⁴ -100.3° in EtOH]; *ethyl-dihydro- β -isomorphine*, b.p. 210°/high vac. (*perchlorate*, m.p. 231—234°*, [α]_D²⁵ -64.3° in H₂O; *picrate*, m.p. 187—189°*, [α]_D²⁵ -64.8° in EtOH); *heteroethyl- β -isomorphine*, m.p. 209—211°*, [α]_D²⁴ -60.1° in EtOH; *ethyl- γ -isomorphine*, m.p. 183—184°, [α]_D²³ -75° in MeOH [*hydrochloride*, m.p. 298—300°* (decomp.), [α]_D²⁴ -62.7° in H₂O; *methiodide*, m.p. 252—253°*, [α]_D²¹ -40.8° in H₂O]; *ethyl-dihydro- γ -isomorphine*, m.p. 158—159°, [α]_D²³ -36.2° in MeOH (*fumarate*, m.p. 180—192°*, [α]_D²³ -23.7° in H₂O; *methiodide*, m.p. 252—253°*, [α]_D²¹ -40.8° in H₂O); *hetero- ψ -codeine*, m.p. 239—241°*, [α]_D²³ -79.5° in MeOH [*hydrochloride*, m.p. 274—276°* (decomp.), [α]_D²³ -48.6° in H₂O; *hydriodide*, m.p. 185—188° (decomp.), [α]_D²¹ -48.7° in H₂O]; *heterodihydro- ψ -codeine*, m.p. 235—237°*, sublimes at 175°/high vac., [α]_D²³ -83.4° in EtOH (*hydrobromide*, m.p. 256—258°*, [α]_D²⁵ -55.4° in H₂O; *hydriodide*, m.p. 185—187°*, [α]_D²⁵ -52.8° in H₂O); *heteroethyl- γ -isomorphine*, m.p. 215—220°*, [α]_D²³ -43.5° in MeOH [*hydrochloride* (+2H₂O), m.p. 287—290°* (decomp.), [α]_D²³ -30.5° in H₂O; *hydriodide* (+H₂O), m.p. 276—277°* (decomp.), [α]_D²² -23.2° in H₂O]; *heteroethyl-dihydro- γ -isomorphine*, m.p. 220—223°*, sublimes at 175°/high vac., [α]_D²⁵ -20.2° in EtOH (*hydriodide*, m.p. 277—281°*, [α]_D²⁵ -9.1° in H₂O; *methiodide*, m.p. 250—252°*, [α]_D²⁵ -7.2° in H₂O); *benzylmorphine* (*benzylmorphine alcoholic Me ether*), b.p. 180°/high vac. (*hydrochloride*, m.p. 233—236°*, [α]_D²³ -88.9° in H₂O; *H sulphate*, m.p. 247—249°*, [α]_D²³ -90.1° in H₂O; *methiodide*, m.p. 155—157°*, [α]_D²⁴ -75.8° in EtOH); *benzylmethyldihydromorphine*, b.p. 210°/high vac., [α]_D²⁵ -89.1° in EtOH (*methiodide*, m.p. 155—157°*, [α]_D²⁴ -54.60° in H₂O), prepared by benzylation of heterocodeine; *benzyl-dihydrodeoxymorphine-D* (*hydrochloride*, m.p. 249°*, [α]_D²³ -34.4° in EtOH; *hydrobromide*, m.p. 226—227°*, [α]_D²² -29.8° in EtOH; *perchlorate*, m.p. 223—224°*, [α]_D²⁴ -51.5° in EtOH; *methiodide*, decomp. about 70°, [α]_D²⁴ -25.8° in MeOH). *Benzylmorphine N-oxide* has m.p. 236—238°, [α]_D²³ -53.2° in EtOH. H. G. M.

Preparation of apocodeine and its hydrochloride. K. FOLKERS (J. Amer. Chem. Soc., 1936, 58, 1814—1815).—*apocodeine* (+EtOH), m.p. 104.5—106.5° (decomp.), [α]_D²³ -90° in EtOH, m.p. (EtOH-free) 122.5—124.5° [*hydrochloride*, decomp. 260—263° (softens from 140°)], is prepared by a modification of Knorr and Roth's method (A., 1907, i, 790, where it is designated ψ -apocodeine). H. B.

"Methoxyoxypalmitine." N. N. CHOPRA and J. N. RAY (J. Indian Chem. Soc., 1936, 13, 478—481).—2-Keto-4 : 5 : 6-trimethoxy-1 : 2-dihydroisobenzofuran-1-carboxylic acid (prep. from gallic acid Me₃ ether and chloral), +H₂O, m.p. 147°, gives the β -3' : 4'-dimethoxyphenylethylamine, m.p. 154°, and thence (POCl₃) 6 : 7-dimethoxy-1-4 : 5 : 6-trimethoxyphthalido- α -3 : 4-dihydroisoquinoline (I), reduced by Zn dust-AcOH to "methoxyoxypalmitine" (II), m.p. 170°.

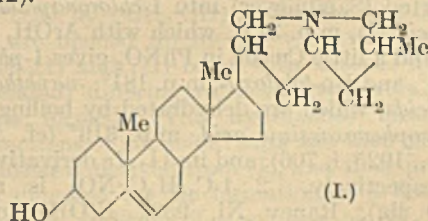
β -2 : 3 : 4-Trimethoxyphenylethylamine (from the propionamide and NaOCl) (*oxalate*, m.p. 185°) was condensed with meconinecarboxylic acid, but did not lead to an isoquinoline derivative.



R. S. C.

Curare alkaloids. II. Tubocurarine and bebeerine. H. KING (J.C.S., 1936, 1276—1279).—Oxidation (KMnO₄) of *O*-methylbebeerine gives a mixture of 5 : 6 : 4'-tricarboxy-2 : 3-dimethoxydiphenyl ether (+2H₂O), m.p. 207° (efferv.) (solidifies and remelts 245°), which is identical with the acid obtained by Faltis from *isobebeerine* (A., 1922, i, 570), 4 : 5 : 5'-tricarboxy-2 : 2'-dimethoxydiphenyl ether (+2H₂O), m.p. 257—258° (efferv.) or (+2.5H₂O) m.p. 145—150° (efferv.), remelts at 262—264° (decarboxylated to 2 : 2'-dimethoxydiphenyl ether), and an acid, C₃₄H₃₀O₁₆·2H₂O, m.p. 283—284°. The latter acid is an intermediate product of oxidation. The results support the structure for bebeerine proposed by Späth and Kuffner (A., 1934, 312). F. R. S.

Occurrence of solanidine in sprouting potatoes. G. R. CLEMO, W. MCG. MORGAN, and R. RAPER (J.C.S., 1936, 1299—1300).—The fresh shoots of different varieties of potato yield 0.04% of solanidine (I). It is suggested that (I) is represented as shown and not as suggested by Soltys and Wallenfels (this vol., 742).



F. R. S.

Action of bromacetates on some alkaloids. L. ESPIL and G. MANDILLON (Compt. rend., 1936, 202, 2177—2179).—Alkaloids containing :NH react with CH₂Br-CO₂Na liberating HBr to form a complex of reduced toxicity; e.g., strychnine is >200 times as toxic as its complex. F. N. W.

Compounds of copper salts with tertiary arsines. G. J. BURROWS and E. P. SANFORD (J. Proc. Roy. Soc. New South Wales, 1936, 69, 182—189).—Cu^I or Cu^{II} salts give the Cu^I co-ordination compounds, CuI,AsPhMe₂, m.p. 127°, CuI,2AsPhMe₂, m.p. 94°, CuCl,2AsPhMe₂, m.p. 127°, CuBr,AsPhMe₂, m.p. 106°, CuNO₃,AsPh₂Me, m.p. 107°, CuBr,AsPh₂Me, m.p. 133°, and CuCl,AsPh₂Me, m.p. 116°. These are insol. in H₂O, sol. in org. solvents, and have approx. normal mol. wts., but are not very stable in solution, giving Cu₂O with NaOH and liberating Cu halides

when boiled for a long time. They are colourless, but slowly become blue in O_2 . With excess of the arsine and Cu^{II} salts the following insol. mixed Cu^I-Cu^{II} compounds are obtained: $Cu[Br_3Cu(AsPh_2Me)_3]$, m.p. 202° , and $Cu[Cl_3Cu(AsPh_2Me)_3]$, blue (I) and brown (II) forms. These formulæ are uncertain, but account for the existence of (I) and (II) as stereoisomerides. (I) slowly passes into (II); they are identical at the m.p. 245° (green liquid) and with $NaOH$ both give Cu_2O . R. S. C.

Auxo-enoid systems. I. Colour of nitro-diphenylaminoarsinic acids containing complementary auxochromes. V. A. ISMAILSKI and A. M. SIMONOV (Bull. Soc. chim., 1936, [v], 3, 1540—1545).—A system, $CR:C'C'C$ or *m*- or *p*- C_6H_4R , in which R is an auxochrome, is termed auxo-enoid. The colour of 3-nitro-4-anilinophenylarsinic acid (I) is due to interaction ("auxo-state") of the NH and NO_2 , the NH assuming onium properties ("functioning as an onium perchrome") and being termed the "principal auxochrome" (or "principal auxo"). If an auxochrome, OH , $NHAc$, OR , or $NH_2-C_6H_4$, is present in the (previously) unsubstituted Ph of (I), it is termed a "complementary auxochrome"; it has a bathochromic effect if in the *p*-position, since it then reinforces the onium properties of the principal auxochrome by inductive forces; if in the *m*-position, its inductive effect opposes the onium properties and causes a lessening of colour. This interpretation is generalised for any "auxo-enoid" system attached to any principal auxochrome. It accounts for the bathochromic effect of introducing *p*- OMe into *Viamine B*. R. S. C.

Reactivity of nuclear chlorine in the isomeric 1:2- and 2:1-chloronaphthalenearsinic acids. G. W. BOWERS and C. S. HAMILTON (J. Amer. Chem. Soc., 1936, 58, 1573—1575).—1:2- $NH_2 \cdot C_{10}H_6 \cdot AsO_3H_2$ is converted (Sandmeyer) into 1-chloronaphthalene-2-arsinic acid (I), m.p. 317° , which with $ArOH$, anhyd. K_2CO_3 , and a little Cu foil in $PhNO_2$ gives 1-phenoxy-, m.p. 322° , and 1-*o*-tolylxy-, m.p. 181° , -naphthalene-2-arsinic acids, which are dehydrated by boiling $AcOH$ to α -benzophenoxarsinic acid, m.p. 319° (cf. Aeschlimann, A., 1925, i, 706), and its 11-*Me* derivative, m.p. 177° , respectively. 2:1- $C_{10}H_6Cl \cdot NO_2$ is reduced [H_2 (40 lb.), Raney Ni , 95% $EtOH$] to 2:1- $C_{10}H_6Cl \cdot NH_2$, converted (Bart) into 2-chloronaphthalene-1-arsinic acid (II), m.p. 296° , and thence (as above) into 2-phenoxy-, m.p. 211° (partly), re-solidifying with m.p. 295° , 2-*o*-, m.p. 295° , and -*p*-, m.p. 225° (partly), re-solidifying with m.p. 273° , -tolylxy-, and 2-*o*-, m.p. $230-231^\circ$, and -*p*-, m.p. $217-219^\circ$, -chlorophenoxy-naphthalene-1-arsinic acids, which are dehydrated ($AcOH$) to γ -benzophenoxarsinic acid, m.p. $278-280^\circ$, and its 8-*Me*-, m.p. 205° (partly), re-solidifying with m.p. 270° , 10-*Me*-, m.p. $215-217^\circ$, 8-*Cl*-, m.p. $216-218^\circ$, and 10-*Cl*-, m.p. 214° , derivatives, respectively. (I) and (II) do not react with NH_2Ph , NH_2Alk , or $AlkOH$; the Cl is thus less reactive than in the corresponding C_6H_6 derivatives (cf. A., 1931, 1173). H. B.

Bismuth derivatives of diphenyl. D. E. WORRALL (J. Amer. Chem. Soc., 1936, 58, 1820—1821).—*p*- $C_6H_4Ph \cdot MgBr$ and $BiCl_3$ give *Bi tri-p-diphenyl*,

m.p. $182-183^\circ$ [*dichloride*, m.p. $198-200^\circ$ (decomp.)], converted ($EtOH-AgNO_3$ in $COMe_2$) into the *dinitrate*, decomp. about 162° ; *dibromide*, m.p. indef. with decomp., which with $BiCl_3$ in Et_2O affords *Bi di-p-diphenyl chloride*, m.p. indef. H. B.

Carbazole. I. Selective metalation. H. GILMAN and R. H. KIRBY (J. Org. Chem., 1936, 1, 146—153).—Carbazole when refluxed with $LiBu^c$ in Et_2O and then treated with CO_2 gives carbazole-1-carboxylic acid. Similarly 9-ethylcarbazole (I) gives its 1-carboxylic acid. Metalation occurs to a slight extent with $CaPhI$, but not with $MgEtBr$. (I) with $Hg(OAc)_2-EtOH-AcOH$ or when fused with $Hg(OAc)_2$ gives 9-ethyl-3-acetoxymercurycarbazole (II), m.p. 156° , and a *dimercurial* (III), m.p. 242° . (II) gives (I) with $EtOH-HCl$, and the 2-iodo- (IV) and 2-chloro-9-ethylcarbazoles when treated, respectively, with $KI-I$ and with $CaCl_2$. (II) with $N_2H_4 \cdot H_2O$ gives *bis*-(9-ethylcarbazyl-3-)-mercury, m.p. 217° , which with $Li-Et_2O$ followed by CO_2 gives 9-ethylcarbazole-3-carboxylic acid, m.p. 226° , also obtained (Grignard) from (IV), from (I) by bromination followed by carbonation of the corresponding Li compound, and by ethylation of Et carbazole-3-carboxylate, followed by hydrolysis. (III) with $KI-I$ gives 3:6-di-iodo-9-ethylcarbazole, also obtained by direct iodination of (I). This with $Cu_2(CN)_2$, KCN , H_2O , and $EtOH$ (sealed tube, 230° , 20 hr.) gives 9-ethylcarbazole-3:6-dicarboxylic acid, m.p. $>320^\circ$ (Me_2 ester, m.p. 187°), also obtained by oxidation with $K_2Fe(CN)_6-KOH-H_2O$ of 3:6-diacetyl-9-ethylcarbazole, m.p. 182° , prepared by ethylating 3:6-diacetylcarbazole (A., 1935, 990). This establishes the positions of Hg in (III). H. G. M.

Magnetochemical investigations of organic substances. VIII. Metal ketyls of 4-pyrones. E. MÜLLER and F. TESCHNER (Annalen, 1936, 525, 1—13).—Magnetic investigations of the K derivatives of 2:6-dimethylpyrone, 2-methylchromone, and 2:3:6:7-dibenzoxanthone exclude the possibility of formulating them as free radicals. Pfeiffer's formulation $R_2C:O \cdots K$ is excluded by chemical evidence. It is therefore necessary to double the formula, thus leading to a choice between $RK \cdot OK + RO$ and $[R(OK)]_2$ ($R=O \begin{matrix} \text{CMe:CH} \\ \text{CMe:CH} \end{matrix} C$). Since the action of MeI leads to a very unstable, reddish-brown perchlorate instead of to Baeyer's colourless trimethylpyrylium perchlorate the latter formulation is advocated with reserve. The magnetic behaviour of the K derivative of xanthone excludes the formulations of Pfeiffer, Schlenk, and Weitz and, combined with analytical behaviour, suggests that it is a quinhydrone-like, complex mol. mixture of eight xanthone mols. or an equilibrium between a pinacoid and a radical form. H. W.

Cross linking formation in keratins. J. B. SPEAKMAN (Nature, 1936, 138, 327).—A discussion of the nature of the linkings responsible for the contraction of wool when treated by various reagents. Permanent setting is explained by the formation of $\cdot S \cdot NH \cdot$ rather than $\cdot N \cdot CH \cdot$ linkings. L. S. T.

New electrochemical method of preparing proteins at the isoelectric point. J. SWYNGEDAUF

(Compt. rend., 1936, 203, 54—57).—The electrolytic method previously described (cf. A., 1934, 961) has been successfully applied to the treatment of ovalbumin and casein. With hæmoglobin, however, the p_H of the high-resistance zone is 3.4 whereas the isoelectric point is about 6.8. C. R. H.

Polysaccharoproteins.—See this vol., 1404.

Handling and weighing absorption tubes in micro-determinations of carbon and hydrogen. D. F. HAYMAN (Ind. Eng. Chem. [Anal.], 1936, 8, 342—343).—The balance room is kept at const. temp., Pregl absorption tubes are used, special precautions are taken when wiping the tubes, and freedom from dust and lint is ensured by examining the tubes visually in a narrow beam of light against a dark ground. The tubes are weighed immediately after wiping and errors due to electrostatic effects are eliminated by maintaining the R.H. of the laboratory at $\leq 45\%$. S. C.

Micro-determination of carbon and hydrogen in compounds containing arsenic, antimony, tin, bismuth, and phosphorus. F. C. SILBERT and W. R. KIRNER (Ind. Eng. Chem. [Anal.], 1936, 8, 353—355).—Satisfactory results are obtained by replacing part of the Pregl universal filling with Pt gauze and a mixture of Pt gauze and Pb_3O_4 . S. C.

Organic micro-analysis. I. Nitrogen by Dumas' method. R. T. MILNER and M. S. SHERMAN (Ind. Eng. Chem. [Anal.], 1936, 8, 331—332).—A simplified all glass micro-combustion apparatus is described. The nitrometer is closed by a ground conical stopper instead of the usual stopcock. A simply constructed, hinged electrical heating element is described and the various corrections to be applied are measured and discussed. S. C.

Formation of nitric acid during the combustion of organic nitrogen compounds in the calorimetric bomb. A. J. PETRICK (J. Chem. Met. Soc. S. Africa, 1936, 37, 1—3).—Org. compounds containing N when burned in O_2 at 30 atm. afford HNO_3 , determined by titration. In S-containing compounds allowance is made for the H_2SO_4 formed, which is determined as $BaSO_4$. The HNO_3 formed accounts for 1.41—11.14% of the N in the compound; high vals. are obtained in the presence of S. J. L. D.

Nesslerisation applied directly to a macro-Kjeldahl nitrogen determination. S. MORGULIS and H. C. SPENCER (Ind. Eng. Chem. [Anal.], 1936, 8, 330).—The wet sample of tissue is weighed on a tared piece of Sn foil folded so as to prevent loss of H_2O and dropped into H_2SO_4 used for the Kjeldahl determination. After digestion the solution is bleached with H_2O_2 , diluted, the Sn ppt. allowed to settle, and NH_3 determined in the clear supernatant liquid by means of Nessler's reagent. S. C.

Modification of micro-Zeisel apparatus for determination of methoxyl and ethoxyl groups. J. J. CHINOY (Analyst, 1936, 61, 602—603). J. S. A.

Microchemical determination of butyric acid. L. KLINO (Mikrochem., 1936, 19, 187—189; cf. A., 1934, 1331).— $PrCO_2H$ is oxidised by H_2O_2 in presence

of Fe to $COMe_3$, which is distilled directly into the Scott-Wilson $Hg(CN)_2$ - $AgNO_3$ reagent. J. S. A.

Determination of lactic acid.—See this vol. 1436.

New reagents for the carbonyl group, their application to the extraction of ketonic substances and the microchemical characterisation of aldehydes and ketones. A. GIRARD and G. SANDULESCO (Helv. Chim. Acta, 1936, 19, 1095—1107).—The prep. of *trimethylcarbohydrazidomethylammonium chloride*, $NMe_3Cl \cdot CH_2 \cdot CO \cdot NH \cdot NH_2$ (I) ("reagent T"), hygroscopic needles, m.p. 192° (slight decomp.), from NMe_3 , $CH_2Cl \cdot CO_2Et$, and $N_2H_4 \cdot H_2O$ in boiling EtOH and of *carbohydrazidomethylpyridinium chloride* (II) (reagent P), decomp. $> 200^\circ$ (corr.), is described. In neutral solution they react very slowly with CO compounds, and generally a large excess of reagent is used in EtOH containing 10% of AcOH; action is then complete in 20—30 min. at the b.p. of the solution. The hydrazones thus produced are cryst. compounds sol. in H_2O and alcohols, insol. in org. media without OH. In approx. neutral solution they are relatively stable, whereas at $p_H < 6$ those of the ketones are rapidly decomposed and those of aldehydes are stable. Separation of aldehyde from ketone is therefore possible by treatment of the mixture with (I) or (II) and of the aq. solution of the product with H_2SO_4 (50 g. per litre); after 1 hr. the liberated ketone is extracted with Et_2O . In practice, (I) and (II) are not suitable for the study of aldehydes. For the isolation of the ketonic fraction of natural materials the latter is dissolved in abs. EtOH and treated with (I) or (II). The resulting solution is poured into iced water containing sufficient Na_2CO_3 to neutralise 90% of the AcOH and then extracted with Et_2O . The aq. solution is made 0.5—1.0N with HCl or H_2SO_4 and kept for 1 hr., after which the ketones are extracted with Et_2O . Emulsification is avoided by suitable use of EtOH or by replacing H_2O by $(\cdot CH_2 \cdot OH)_2$. Possibilities of fractionation are opened up by the very varying rates with which (I) and (II) react with ketones and the (non-correlated) differing rates of hydrolysis of the compounds formed. The hydrazones show the general reactions of alkaloidal salts and their presence in aq. solution if derived from (I), and their presence is readily detected by the formation of a flocculent orange ppt. on addition of a solution of BiI_3 (1 g.), KI (10 g.), and conc. HCl (5 c.c.) in H_2O (to 100 c.c.) or, preferably, by their behaviour towards a solution of HgI_2 (5 g.) and KI (10 g.) in H_2O (100 c.c.). The extraction of oestron from urine of pregnancy and the purification of MeOH from traces of $COMe_2$ are described. H. W.

Micro-determination of fructose in presence of glucose. S. M. STREPKOV (Biochem. Z., 1936, 287, 33—34).—The method depends on the fact that fructose (I) is completely oxidised in 2.5 hr. at 60° by an alkaline Na_2HPO_4 - $K_3Fe(CN)_6$ solution whilst glucose (II) is not attacked. (I) is then determined by iodometric titration of the $K_4Fe(CN)_6$ formed. Tables for reading off the results are given both for (I) in aq. solution and in presence of (II). P. W. C.

Determination of creatinine. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1936, 69,

224—227).—The purple colour given by creatinine (I) and alkaline 3:5-(NO₂)₂C₆H₃·CO₂H is used as a qual. and quant. test. At 0° the colour given by the reagent alone does not interfere for the 15—25 min. required for development of max. intensity by (I). Purified acid gives better results. The test is better than that of Jaffe. R. S. C.

Action of copper salts on benzidine in presence of halides and thiocyanates and a new sensitive test for copper. L. KUHLBERG (Mikrochem., 1936, 20, 153—160).—Benzidine gives a ppt. with Cu⁺⁺ the colour of which varies with the anion present. Br⁻ and CNS⁻ form benzidine-blue. Cl⁻ does not effect the benzidine reaction but produces *o*-tolidine-blue. The mechanism is discussed in terms of the potential Cu⁺⁺/Cu⁺ and the solubility product of the Cu⁺ salt. A reagent containing 0.1 g. of *o*-tolidine +0.5 g. of NH₄CNS in 5 c.c. of COME₂ is recommended for Cu. Strongly oxidising salts must first be reduced with Bi-Hg. R. S.

Sensitive colour reaction of phenol with "fast-red salt B," and its use as drop reaction. Y. KONDO (Mikrochem., 1936, 19, 214—221).—PhOH gives with 0.05—0.1% aq. "fast-red salt B" in presence of Li₂CO₃ a very sensitive red to orange coloration; limit 10⁻⁸ g. of PhOH. Other (polyhydric) phenols give colorations of different shades. J. S. A.

Application of chloroamine in organic analysis. L. VŠETEČKA (Časopis českoslov. Lék., 1935, 15, 51—56; Chem. Zentr., 1935, ii, 3954).—1 mol. of uric acid requires 2 mols of NH₂Cl for oxidation in alkaline solution. A volumetric method based on this reaction is described. H. N. R.

Colorimetric determination of uric acid (Folin).—See this vol. 1436.

Identification of yohimbine. M. L. SHANER and M. L. WILLARD (Mikrochem., 1936, 19, 222—226).—Cryst. ppts. given by yohimbine with metallic chlorides and with the usual alkaloid reagents are described. Identification is best effected through the acid salts, for which microscopic and crystallographic data are given. J. S. A.

The biuret reaction. II. Metal-biuret compounds. III. Protein compounds of copper, nickel, and cobalt. H. JESSERER (Biochem. Z., 1936, 287, 71—83, 84—87; cf. this vol. 1007).—In the complexes of Cu with the following org. bases, 1 atom of Cu is associated with 2 mols. of biuret (I), oxamide (II), or malonamide (III). At the same wt. concn. the strength of colour with (I) is the same as with caseinogen (IV), but the complex with (I) contains three times as much Cu as with (IV). The colour with (I), as with (IV), consists of red and blue components; the latter on long keeping separates, the red component remaining and then containing 1 atom of Cu to 4 mols. of (I). The formulæ of the compounds are discussed. Complexes of (I) in alkaline solution with Ni and Co are prepared in which 1 atom of metal is associated with 3 and 6 mols. of (I), respectively. (II) and (III) give complexes containing 1 atom of Ni to 3 mols. of base.

III [with F. LIEBEN]. Clupein ester hydrochloride gives a complex containing 4 Cu per mol. When the violet Cu-(IV) complex is dialysed, the blue colour separates without decomp. Ni- and Co-(IV) complexes decompose on dialysis. Zn separates the whole of the Cu from the Cu-(IV) complex. No difference in valency was detected in the Cu of the red and blue components. In the Ni- and Co-(IV) complexes 1 atom of Ni replaces 2 Cu and 1 atom of Co replaces 3 of Cu. P. W. C.

Biochemistry.

Gaseous metabolism during controlled restriction of respiration. I. In men with normal hearts. II. In men during dyspnoea. A. LUBLIN (Arch. exp. Path. Pharm., 1936, 182, 427—436, 437—443).—I. Restricted respiration increases the vol. of expired CO₂ and decreases that of utilised O₂ so that the R.Q. increases to vals. >1.

II. Hyperventilation occurs, the utilised O₂ tending to decrease and the R.Q. to increase. F. O. H.

Effect of oxygen lack, variations in the carbon dioxide content of the inspired air, and hyperpnoea on visual intensity discrimination. E. GELLHORN (Amer. J. Physiol., 1936, 115, 679—684). R. N. C.

Respiratory ventilation in the cockroach in air, in carbon dioxide, and in nicotine atmospheres. R. L. KITCHEL and W. M. HOSKINS (J. Econ. Entom., 1935, 28, 924—933). A. G. P.

Rate of elimination of dissolved nitrogen in man in relation to the fat and water content of the body. A. R. BEHNKE, R. M. THOMSON, and L. A. SHAW (Amer. J. Physiol., 1935, 114, 137—

146).—O₂ inhalation results in elimination of dissolved body N₂ in equilibrium with pulmonary N₂, about 98% being removed in 6 hr. in a young well-developed man. Most of the N₂ is stored in the body-H₂O. The N₂ content of a well-nourished dog is approx. the same as that of man. The N₂ elimination curve is exponential. During decompression of divers exposed to high pressures for short periods, the body-fats act as N₂-absorbents and prevent bubble formation. R. N. C.

Position of the oxygen dissociation curve of human blood at high altitudes. A. KEYS, F. G. HALL, and E. S. G. BARRON (Amer. J. Physiol., 1936, 115, 292—307).—At const. *p*_H of the cells, the affinity of hæmoglobin for O₂ tends to decrease at high altitudes. The dissociation curve is displaced to the left of the sea-level curve up to 14,000 ft.; above this level the curve is displaced increasingly to the right. Curves for arterial blood during work are similar to those obtained at rest. The curves for men accustomed to altitudes up to 5340 m. are within the normal limits for men at sea-level. R. N. C.

Effect of altitude on the affinity of hæmoglobin for oxygen. F. G. HALL (J. Biol. Chem., 1936, 115, 485—490; cf. preceding abstract).—The O_2 affinity of human hæmoglobin, determined spectrographically after hæmolysis and dilution, remains unchanged with change in altitude between sea-level and 20,000 ft. F. A. A.

Gaseous equilibria in the lungs at high altitudes. D. B. DILL, E. H. CHRISTENSEN, and H. T. EDWARDS (Amer. J. Physiol., 1936, 115, 530—538).—The partial pressure of O_2 in arterial blood at high altitudes is approx. equal to that of alveolar air. O_2 saturation of arterial blood does not necessarily increase during acclimatisation. R. N. C.

Arterialisation of blood. V. Possibility of influencing gaseous exchange between alveoli and blood. K. KRAMER and H. SARRE (Z. Biol., 1936, 97, 329—342; cf. A., 1935, 371, 878).—Increase in depth of respiration due to lobeline (I) decreases the difference in O_2 tension between alveoli and arterial blood. The initial difference in O_2 tension between alveoli and the pulmonary venous blood is, however, of importance; when high, (I) increases the alveolar tension and diminishes the O_2 -saturation of the venous blood, resulting in an increased difference between alveoli and arterial blood. Adrenaline increases the inflow of blood and considerably displaces the gaseous exchange. The bearing of these and previous data on O_2 -uptake is discussed. F. O. H.

Absorption of water from the small intestine at various degrees of anoxæmia. E. J. VAN LIERE, N. A. DAVID, and D. H. LOUGH (Amer. J. Physiol., 1936, 115, 239—244).—Absorption is increased, an apparent optimum occurring when the blood- O_2 is approx. 10%. R. N. C.

Iodophilic substance of leucocytes. A. GIRARDIN (Jahrb. Kinderheilk., 1935, 145, 140—166; Chem. Zentr., 1935, ii, 3790).—Iodophilic granules of neutrophile leucocytes are shown by treatment of moist blood with I vapour. The normal proportion (20%) is increased in certain infectious diseases, after a meal in sucklings, and in certain metabolic disturbances in children. A. G. P.

Glycolytic activity of blood-corpuscles of normal and diabetic persons. A. CURATOLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 262—263).—The glycolytic activity of washed corpuscles from diabetic blood is < normal. F. O. H.

***In-vitro* and *in-vivo* action of insulin on glycolysis of blood-corpuscles.** A. CURATOLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 264—265).—The glycolysis of corpuscles of non-diabetic persons is unaffected, whilst that of corpuscles of diabetics is diminished, by injection or *in-vitro* addition of insulin. F. O. H.

Products of blood-glycolysis. R. INDOVINA (Boll. Soc. ital. Biol. sperim., 1936, 11, 267—268).—The discrepancy between glucose metabolised and lactic acid (insufficiently) formed by suspension of normal corpuscles in glucose-Ringer's solution at 37° is at least partly due to formation of acid-hydrolysable complexes. F. O. H.

Formation of a phosphorylated compound during *in-vitro* glycolysis. R. INDOVINA (Boll. Soc. ital. Biol. sperim., 1936, 11, 268—269).—Incubation of suspensions of normal blood-corpuscles in glucose-Ringer's solution at 37° produces a complex which on acid hydrolysis yields inorg. P. F. O. H.

Electric impedance of injured and sensitised red blood-corpuscles. H. J. CURTIS (J. Gen. Physiol., 1936, 20, 105—109).—No change in the electrical properties was detected in suspensions injured or sensitised up to the point of hæmolysis. H. G. R.

Properties of red cell surfaces influencing rouleau formation. H. L. WHITE and B. MONAGHAN (Amer. J. Physiol., 1936, 115, 31—37).—The sinking velocity of red cells of different species in 1% gelatin \propto their electrophoretic mobilities at p_H 7.4 and inversely \propto the isoelectric point of the ghosts. Stability in gelatin depends on the free surface energy at the cell-medium interface, which is largely determined by the degree of hydration, and, in turn, by the chemical structure of the cell surface. The surface probably consists of a combination of protein and lipin, the proportion varying with the species. The isoelectric points of washed dog, ox, and rabbit ghosts are 2.7, 3.4, and 4.3, respectively, and are a closer approach to the isoelectric points of intact cells than can be obtained by working with intact cells. R. N. C.

Changes in the permeability to glucose of red corpuscles in shed blood. J. M. D. OLMSTED (Amer. J. Physiol., 1936, 114, 488—490).—Glucose increases rapidly in human corpuscles after the blood has been drawn. The rate of increase in rabbit corpuscles is considerably less, whilst pigs' corpuscles remain impermeable. R. N. C.

Effect of hæmorrhage on hæmoglobin content and distribution in erythrocytes. A. G. ZOCOLLI and A. DE NIEDERHAUSERN (Boll. Soc. ital. Biol. sperim., 1936, 11, 317—318).—Hæmorrhage of 20% of the circulating blood increases the size and hæmoglobin (I) content of the erythrocytes; with severe hæmorrhage the content of (I) per unit vol. and superficial area of the erythrocytes increases. F. O. H.

Hæmoglobin and iron of the blood. I. Determination of the total iron of blood. H. I. COOMBS (Biochem. J., 1936, 30, 1588—1591).—The sample (0.1 ml.) is ashed with H_2SO_4 and HNO_3 , and dipyrityl, glucose, and NaOAc are added. A pink colour develops during 5 min. at 100°; this is stable, and unaffected by Cu^{++} or $PO_4^{'''}$. F. A. A.

Availability of copper from various sources as a supplement to iron in hæmoglobin formation. M. O. SCHULTZE, C. A. ELVEHEJEM, and E. B. HART (J. Biol. Chem., 1936, 115, 453—457).—The Cu of wheat germ, lucerne, brewers' yeast, pig's heart and liver, cysteine Cu^I mercaptide (A., 1933, 382), and Cu aspartate, citrate, nucleinate, and pyrophosphate, in amounts equiv. to 0.01 mg. daily, is readily utilised by anæmic rats to supplement Fe (0.5 mg. daily) for hæmoglobin formation. F. A. A.

Hæmoglobin regulation in chickens. I. W. HARMON (Poultry Sci., 1936, 15, 53—62).—The hæmoglobin (I) level was highest at hatching and at maturity and lowest at 2 weeks of age. Sexual differences in level were not apparent until 8 weeks of age, and in mature birds were in the order, cocks > capons > hens. A splenic reserve of (I) occurs in capons, hens, and 10-week cockerels and pullets, but not in cocks or broody hens. Vals. declined during egg production, but were higher in heavy than in poor layers in corresponding stages. Onset of broodiness and cessation of laying were marked by a rapid increase in (I) vals. A. G. P.

Ultra-violet absorption spectrum of hæmoglobin. G. A. ADAMS (Nature, 1936, 138, 368).—Addition of stromatin (I) causes the 410 m μ absorption band of hæmoglobin (II) to disappear. In red blood (II) may be combined with (I), and the combination may be responsible for the absence of this band in corpuscular (II) (cf. A., 1934, 673). Cholesterol, lecithin, and glutathione have not this effect. L. S. T.

Methylene-blue and hæmoglobin derivatives in asphyxial poisoning. M. M. BROOKS (Amer. J. Physiol., 1935, 114, 160—178).—KCN stabilises the colour of oxyhæmoglobin by forming cyanohæmoglobin, which has the same spectrum; it attaches itself to the Fe ion of hæmoglobin (I) or methæmoglobin (II). Methylene-blue does not form (II) in the blood-stream or defibrinated blood, with or without KCN; it acts as a catalyst rather than as a (I) producer. Reducing agents in the blood-stream, including glucose, prevent (II) formation. NaNO₂ produces (II) when in sufficient concn. to overcome the reducing capacity of the blood. Cryst. derivatives of (I) do not give the above results, owing to the absence of reducing agents. R. N. C.

Plasma-protein regeneration after bleeding in the rat. W. C. CUTTING and R. D. CUTTER (Amer. J. Physiol., 1935, 114, 204—206).—Total proteins recover their original val. 12 hr. after bleeding; the regeneration is decreased by injection of Indian ink. R. N. C.

Crystallisation of serum-albumin from different species. M. GRINSTEIN (Anal. Asoc. Quím. Argentina, 1936, 24, 11—18).—The cryst. form of serum-albumin from man differs from that from the guinea-pig, horse, mule, and ass, those from the last three species being indistinguishable from one another. F. R. G.

Protein content of the serum of ungulates. A. URBAIN and R. CAHEN (Compt. rend., 1936, 203, 277—279).—The total protein of sera of various species (both ruminants and non-ruminants) is similar to that of human serum, except that in sheep it is less, and in equidæ it is slightly higher. P. G. M.

Determination of serum-proteins. K. PLÖTNER (Biochem. Z., 1936, 286, 429—434).—The mean sp. refraction of 22 samples of pathological human serum-protein was 0.00188, a val. agreeing with the accepted val. for horse serum (0.00187). Considerable changes in globulin content do not significantly change the val. P. W. C.

Nephelometry of blood-proteins. III. Nature of the protein-sulphosalicylic acid turbidity reaction. Interrelationship of serum-proteins. K. PLÖTNER (Biochem. Z., 1936, 286, 279—284).—The sulphosalicylic acid turbidity val. of an albumin (I) solution on addition of small amounts of globulin (II) considerably decreases and, after reaching a min., \propto the added (II). The results are explained by assuming that a mol. complex of (II) and (I) (1:2) is formed (cf. this vol. 1008). P. W. C.

Simplification of micro-methods. I. Micro-determination of non-protein-nitrogen of blood. J. PUYAL and A. KUTZ (Anal. Fís. Quím., 1934, 32, 742—747).—The blood is deproteinised by the Hagedorn method and the residual N determined by a micro-Kjeldahl method. The process is quicker and more accurate than that of Bang. L. A. O'N.

Urate distribution in blood. J. H. TALBOTT and J. M. SHERMAN (J. Biol. Chem., 1936, 115, 361—370).—The concn. of urate (I) in serum and cells agrees approx. with the Donnan law applied to blood. The (I) distribution ratio between cells and serum increases with acidity at approx. the same rate as the Cl' ratio. Oxygenation and reduction of blood containing added (I) change the distribution of (I) in the same way as Cl' and HCO₃'. The max. concn. of serum-(I) observed was 1.63 milliequiv. per litre. E. M. W.

Cholesterol. H. W. SOPER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 381—382).—A summary of recent investigations of blood-cholesterol and its influence on dietary habits. CH. ABS. (p)

Fractionation of cholesterol in blood by precipitation as pyridine cholesteryl sulphate and cholesterol digitonide. J. J. DREKTER, A. E. SOBEL, and S. NATELSON (J. Biol. Chem., 1936, 115, 391—399).—Determination of free cholesterol (I) after pptn. as C₅H₅N cholesteryl sulphate gives vals. of 6—10% as opposed to 25—35% after pptn. as (I) digitonide. The former method gives higher vals. for total (I). (I) may exist in serum in a "loosely-bound" form pptd. only by digitonin. In erythrocytes most of the (I) is "unbound," i.e., pptd. by either method. E. M. W.

"Bound" sugar of the blood. I. Influence of protein-fat diets and relation to free blood-sugar. II. Influence of fasting and relation to free blood-sugar. Y. MATSUOKA (J. Biochem. Japan, 1936, 23, 161—170, 171—179).—I. Fat-protein diets have little effect on the combined sugar (I) of dog's blood. With mixed carbohydrate diets, orally administered glucose produces a slight decrease which is enhanced by supplementing the diet with fat+protein but not with fat+protein+carbohydrate. High vals. of (I) are associated with low vals. of free sugar (II).

II. Fasting for 1 week has no effect, whilst fasting for 3 weeks slightly decreases (I). The increase in (I) due to carbohydrate ingestion after a week's fast is > that after 3 weeks' fast; continued ingestion results in a rapid return of (I) to normal vals. High levels of (I) are again associated with low vals. of (II). F. O. H.

Influence of vagi and splanchnics on blood-sugar response to glucose administration. M. AISNER, A. J. GORNEY, and M. S. SEGAL (Proc. Soc. Exp. Biol. Med., 1936, 34, 454—459).—The tolerance of dogs to glucose administered intravenously was not increased by vagotomy. Removal of one adrenal and denervation of the other resulted in a slight but probably insignificant increase in tolerance, whilst cœliac ganglionectomy produced no additional effect.

W. O. K.

Blood-sugar. II. Reduction values of tungstate and mercuric filtrates. Existence of a supposed glucose ester. I. M. LORA TAMAYO (Anal. Fis. Quim., 1934, 32, 858—867).—Filtrates from blood deproteinised by the Folin-Wu method have a glucose (I) content (determined by the author's method; A., 1934, 793) > that of filtrates from Bierry and Moquet's reagent. The probable causes are discussed and it is shown that in presence of inorg. PO_4''' , (I) is carried down in the Hg ppt. F. R. G.

Blood-phosphorus. V. Acid and enzymic hydrolysis of the acid-soluble organic phosphorus. Phosphoglycerate fraction. E. WARWEG and G. STEARNS (J. Biol. Chem., 1936, 115, 567—581).—Acid-hydrolysis of filtrates of human blood deproteinised with $CCl_3 \cdot CO_2H$ is rapid for the first 10 min., the hexose diphosphate being rapidly and the β -glycerophosphate very slowly destroyed. The reaction slows down until after 12 hr. a const. slow rate (unimol. reaction) is attained, the acid-resistant substance being probably phosphoglycerate (I). The org. P is at first more readily hydrolysed by phosphatase at p_H 8.8, but after 24 hr. the optimum shifts to 7.4, which is the same as that of (I) from pig's blood. The ester-P of adult blood consists of approx. 62—75% of (I)-P and 11.4% of P_2O_7'''' -P.

H. G. R.

Blood-sugar, inorganic phosphorus, and phosphatase activity following the intravenous injection of calcium salts. A. CANTAROW, J. T. BRUNDAGE, and E. L. HOUSEL (Amer. J. Physiol., 1936, 115, 1—4).—Ca gluconate or levulate produces in the dog a rise of blood-protein, a rapid fall of sugar, a slower fall of inorg. P, and variable and insignificant changes in serum-phosphatase activity. R. N. C.

Partition of serum-calcium. J. DUCKWORTH and W. GODDEN (Biochem. J., 1936, 30, 1560—1566; cf. A., 1935, 385).—Determinations of Ca^{++} , ultrafilterable, non-ultrafilterable, protein-bound, and total Ca, inorg. P, and protein in the blood-serum of lambs on a basal diet supplemented with maize starch, and of these Ca fractions, inorg. P, and Mg in the serum of a cow after injection of large amounts of aq. Na citrate and in cow's blood *in vitro* after addition of aq. Na citrate indicate that K in the equation of Maclean *et al.* (Amer. J. Med. Sci., 1935, 189, 601) is too variable to aid in the study of Ca partition. The four Ca fractions found by adsorption on $BaSO_4$ and ultrafiltration are real entities. W. McC.

Partition of calcium and inorganic phosphorus in the blood-sera of horses. P. B. PEARSON and H. R. CATCHPOLE (Amer. J. Physiol., 1936, 115, 90—93; cf. this vol., 497).—Inorg. P in the serum of Shetlands is > that in other species. There is no

correlation between total Ca and inorg. P, but significant correlation between total and diffusible Ca and inorg. P. R. N. C.

Cataphoretic investigation of the state of copper in blood-serum. B. EISLER, K. G. ROSDAHL, and H. THEORELL (Biochem. Z., 1936, 286, 435—438).—The total Cu of blood-serum is united with the serum-albumin. P. W. C.

Photometric micro-determination of iron in blood. G. BUCCIARDI (Boll. Soc. ital. Biol. sperim., 1936, 11, 316—317).—Blood is ashed, oxidised by HNO_3 , heated with $H_2SO_4-HNO_3$ followed by H_2O , and, after removal of HNO_3 by urea, Fe^{+++} is determined by addition of NH_4CNS and photometric determination of extinction coeff. F. O. H.

Regulation of the mineral composition of body-fluids in fishes. A. DRILHON and E. A. PORA (Ann. Physiol. Physicochim. biol., 1936, 12, 139—168).—The osmotic pressure of the serum in the carp is normally > that of the surrounding H_2O but, if the salinity of the H_2O is increased by addition of sea- H_2O , the internal osmotic pressure is unaltered until the f.p. depression of the external medium reaches -0.67° . Above this val. the serum is at first hypotonic and equilibrium with more conc. solutions is associated with increase of Na, K, and Ca in the serum. The muscles and not the gills are the chief regulators of the composition of the internal medium. The proteins are stable and unaffected by changes in salinity of the ambient medium. NUTR. ABS. (m)

Physical chemistry of fish blood. A. DRILHON and G. FLORENCE (Bull. Soc. Chim. biol., 1936, 18, 1055—1073).—A study of the buffering power of the serum and the cataphoresis of the serum-proteins shows that during the adaptation of the eel with its protective mucus from fresh to sea- H_2O there is a slow diminution in the alkaline reserve without any change in the protein equilibrium. Without the mucus, however, the change in alkaline reserve is rapid and a slight change in the protein equilibrium takes place. Substitution of aq. KCl for sea- H_2O causes no change in the alkaline reserve, but a displacement of the isoelectric point of the serum-proteins. When the salt- H_2O fish *Muræna* is placed in fresh H_2O , there is a displacement of the isoelectric point of the serum-proteins, although the fish is unaffected by a change to a greater degree of salinity. A. L.

Determination of blood- p_H by the glass electrode. IV. Potential drift of quinhydrone electrode applied to solutions of alkaline buffer, amino-acids, or proteins, or to plasma. H. YOSHIMURA (J. Biochem. Japan, 1936, 23, 187—210; cf. A., 1935, 1143).—The potential drift is due to a chemical change in benzoquinone (I) producing acidic products to an extent dependent on temp., concn. of solution, and p_H . A secondary cause is autoxidation of quinol (II) to (I). Saturation of solutions of $p_H > 5$ with (II) produces a slight acidification due to dissociation of (II). Determinations accurate to 0.02 p_H are afforded by measurements taken within the following times: aq. buffer up to p_H 8, 5 min.; aq. NH_2 -acid or protein, 1 min.; plasma 30 sec. F. O. H.



Validity of determinations of the p_H of whole blood at 38° with the glass electrode. J. SENDROY, jun., T. SHEDLOVSKY, and D. BELCHER (J. Biol. Chem., 1936, 115, 529—542).—With citrate, PO_4''' , and $HCO_3'-CO_3''$ buffers the p_H as determined by the Clark-Cullen (C) H electrode and MacInnes-Belcher glass electrodes A (A., 1933, 689) and B (thin membrane type) were consistent, but with reduced whole blood at various CO_2 tensions, A deviated by a mean of -0.011 from the val. given by C. When standardised with 0.1N-HCl, B gave a val. $0.02 <$ that of C, whilst A gave a similar but less consistent error.

H. G. R.

Relation between viscosity of the blood and the relative volume of erythrocytes (hæmatocrit value). K. K. NYGAARD, M. WILDER, and J. BERKSON (Amer. J. Physiol., 1935, 114, 128—131).—The relation is linear with a hæmatocrit val. $<60\%$, but above this val. η increases more rapidly.

R. N. C.

Control of the circulation of the blood. R. J. S. McDOWALL (Nature, 1936, 138, 488—491).—An extract from an address to the British Association.

L. S. T.

Blood groups, blood transfer, and blood substitutes. A. VON DOMARUS (Naturwiss., 1936, 24, 593—600).—A review.

Accelerating effect of pectin on blood coagulation. O. RIESSER (Klin. Woch., 1935, 14, 958—961; Chem. Zentr., 1935, ii, 3943).—Intramuscular, intravenous, or oral administration of pectin (I) to dogs shortened the coagulation time without producing secondary effects. The action is related to the acid reaction of (I).

A. G. P.

Action of formaldehyde on blood coagulation. A. FISCHER (Enzymologia, 1936, 1, 85—91).— CH_2O inhibits blood clotting by embryo extract. Combination with $-NH_2$ is suggested.

E. D. Y.

Rôle of bivalent metals in the reversible inactivation of jack-bean hæmagglutinin. J. B. SUMNER and S. F. HOWELL (J. Biol. Chem., 1936, 115, 583—588).—Concanavalin-A (I) loses its agglutinating properties (A., 1935, 1143) on contact with dil. mineral acids: this is due to decomp. of Ca, Mn, and Mg compounds and is recovered on neutralisation. Metal-free (I) does not crystallise readily.

H. G. R.

Specific nature of the inhibition of the coagulating effect exerted by tissue extracts on plasma resulting from incubation of tissue extract with blood-serum. C. MOORE, V. SUNTZEFF, and L. LOEB (Amer. J. Physiol., 1935, 114, 1—18).

Blood-clotting: prothrombin fluctuations under experimental conditions. E. D. WARNER, K. M. BRINKHOUS, and H. P. SMITH (Amer. J. Physiol., 1936, 114, 667—675).—Prothrombin (I) in plasma is determined accurately by conversion into thrombin (II) and measurement of the time of coagulation of fibrinogen (III). The normal (I) content of dog plasma is sufficient to form 200 times the amount of (II) necessary to clot (III) in a few sec., but unless thromboplastin is present in large quantities most of the (I) is not utilised. (I) varies slightly in the plasma from different dogs, but is const. in a single animal,

being unchanged by repeated hæmorrhage or drastic diet changes. $CHCl_3$ and P poisoning decrease (I) and (III); with $CHCl_3$ (I) falls before (III) and returns to normal more slowly. (I) remains normal in distemper and turpentine abscess, and in plasma rendered incoagulable by intravenous injection of peptone, or by heparin *in vitro*. Indian ink causes a slight reduction.

R. N. C.

Properties of thromboplastin (aqueous tissue extracts). A. J. QUICK (Amer. J. Physiol., 1936, 114, 282—296).—The time of clotting by tissue extracts decreases as the concn. of the extracts increases until a min. val. is reached, beyond which no further decrease takes place. The thromboplastin (I) concn. in extracts of rabbit brain, lung, and thymus is of the same order. The extracts do not clot purified fibrinogen or prothrombin-free plasma. Extraction of brain extract with fat solvents reduces considerably the thromboplastic potency of the solution, but the extract obtained is only slightly active. The activity of the aq. extracts falls with rising temp., brain extract being less stable than lung extract. The activities of extracts from different animals vary with the species.

R. N. C.

Action of heparin and its relation to thromboplastin. A. J. QUICK (Amer. J. Physiol., 1936, 115, 317—333).—The clotting time of plasma is inversely \propto the thrombin (I) concn.; a corrective factor in the equation decreases with increasing concn. of neutral salts. The relationship is destroyed by minute amounts of heparin (II). (II) is not an antithrombin (III), since it inhibits (I) only slightly with purified fibrinogen, but apparently reacts with a plasma constituent to form a (III). Neutral salts are necessary for the reaction. (II) inhibits clotting of prothrombin-free plasma by (I), the inhibitory effect not being influenced by excess of thromboplastin (IV) and Ca in optimal concn. (II) also inhibits the acceleration in clotting of oxalated plasma by excess of (IV) and Ca in optimal concn.; these results indicate that (IV) does not neutralise (II).

R. N. C.

Inhibiting action of cattle and sheep serum on kidney extracts of cattle and sheep. E. W. THURSTON, J. E. SMADEL, and L. LOEB (Amer. J. Physiol., 1935, 114, 19—24).—The inhibition curve obtained by addition to the mixture of extract and serum of heparin or a Ca inactivator shows the typical form; it results from inactivation of tissue-coagulin and destruction of thrombin during incubation.

R. N. C.

Serologic relation of *Brucella* and *Pasteurella*. L. E. STARR and G. E. SNIDER (J. Infect. Dis., 1934, 55, 384—389).—Cross-agglutination between *Brucella* and *Pasteurella* in cattle sera is demonstrated.

CH. ABS. (p)

Testing of therapeutic serum. I. Antipneumococcus serum *in vivo* and *in vitro*. L. COTONI and J. POCHON (Ann. Inst. Pasteur, 1936, 57, 221—239).—A review of methods for testing sera *in vivo* and *in vitro*. A method which uses the neutralisation of the antibody *in vitro* is described, together with the prep. of the antigen, bacterial emulsion, and solution of the polysaccharide. Advantages are sim-

plicity, rapidity, and economy of material. A serum-standard is not needed.

J. N. A.

Blood-coagulating substance produced by staphylococci, and its relation to disease. M. PIJOAN (Canad. Med. Assoc. J., 1935, 33, 476—481).—Staphylococci generally may produce a toxin, leucocidin, hæmolyisin, necrotoxin, staphylokinase (I), and a fibrinolysin. (I) can be washed from the surface of organisms, is destroyed at 85°, and coagulates oxalated plasma. Clot formation does not depend on the Ca-thrombin mechanism.

CH. ABS. (p)

Antigenic reactions of *Staphylococcus aureus* and its variants. R. E. HOFFSTADT and G. P. YOUMANS (J. Infect. Dis., 1935, 56, 288—296).—Rough and gonidial forms of *S. aureus* afford no protection against smooth and virulent forms. All strains contain heat-stable antigenic fractions in common. Gonidial forms contain a heat-labile fraction in common with rough and smooth forms.

CH. ABS. (p)

Composition of the active principle of tuberculin. XIX. Differences in antigenic properties of various tuberculin fractions; adsorption on aluminium hydroxide and charcoal. F. B. SEIBERT (J. Immunol., 1935, 28, 425—432; cf. A., 1933, 1083).—A purified potent tuberculin-protein derivative was unable to stimulate the production of antibodies but reacted specifically with the antibodies when they were formed by means of the whole tuberculin-protein mol. When injected in a particulate form [adsorbed on $Al(OH)_3$ or C] it stimulated the production of antibodies and inhibited the precipitin reaction between the whole tuberculin-protein antigen and its antibodies.

CH. ABS. (p)

Polysaccharide of the typhus bacillus. III. Agglutinin titre in rabbits. A. SPANEDDA (Boll. Soc. ital. Biol. sperim., 1936, 11, 327—328; cf. this vol., 1010).—Repeated intravenous injection of the polysaccharide produces decreasing febrile reactions, whilst the agglutinin titre increases up to the 4th injection and then slowly falls to a zero val. with subsequent injections; this is probably due to the formation of a sp. antibody.

F. O. H.

Union with complement as a surface reaction.—See this vol., 1335.

Electric impedance and permeability of living cells. J. F. McCLENDON (Science, 1936, 84, 184—185).

L. S. T.

Oxygen and carbon dioxide tensions in the subcutaneous tissues of normal subjects. M. H. SEEVERS (Amer. J. Physiol., 1936, 115, 38—42).—The tensions are of the same order as those previously found for other homothermal animals by the gas depôt method. Final equilibrium between the gas pocket and the surrounding tissues is reached only after 5—7 days, when the foreign body reaction has subsided. After this time the partial pressure of CO_2 remains practically const., whilst that of O_2 varies considerably.

R. N. C.

Micro-determination of fluorine [in dental enamel and dentine].—See this vol., 1351.

Chloride and total base contents of tendon and cartilage. M. WHELAN and H. A. SHOEMAKER (Amer. J. Physiol., 1936, 115, 476—479).—Analytical data are given for muscle, skin, tendon, and cartilage from various sources.

R. N. C.

Distribution of iron in certain tissues of normal and anæmic albino rats. G. WAKEHAM and H. F. HALENZ (J. Biol. Chem., 1936, 115, 429—434).—The prep. and testing of blood-free tissue are described. The Fe content of the washed tissues of normal rats is in the decreasing order: liver, heart, kidney, striated muscle. In anæmic rats, heart contains > liver, but all three lose Fe.

E. M. W.

Determination of sulphur in the extract of the silk-rind of cocoons. G. COLA (Boll. uff. R. Staz. sperim. Seta, 1935, 5, 46; Chem. Zentr., 1935, ii, 4000).—A method of oxidation, followed by pptn. as $BaSO_4$, is described.

H. N. R.

Composition of the eggs of *Tæniarhynchus saginatus* and *Diphyllobothrium latum*. I. A. SMORODINCEV and P. I. PAVLOVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 29—31).—The eggs of the two species contain, respectively, H_2O 72.6, 77.19, org. matter 26.59, 22.30, ash 1.15, 0.66, N 3.57, 3.32, lipins 4.95, 6.88%. In both cases the composition of the eggs differs greatly from that of the worm.

W. McC.

Phosphagen in echinoid muscle and in electrical tissue. E. BALDWIN and D. M. NEEDHAM (Nature, 1936, 138, 506).—The partition of P in the electrical tissue of *Torpedorese* resembles that in the muscles of the rat and the frog. This tissue, like muscle, contains enzymes capable of catalysing the reactions: phosphoglyceric acid \rightarrow phosphopyruvic acid (I); (I) + adenylic acid (II) \rightarrow adenylyl pyrophosphate (III) + $AcCO_2H$; (III) + creatine \rightarrow (II) + phosphagen; and (III) \rightarrow (II) + H_2PO_4 . Certain phosphorylated compounds in presence of enzyme extracts from the jaw muscles of *Sphærechinus granularis* synthesise two phosphagen-like compounds from creatine and arginine, respectively. Echinoid jaw muscle contains enzymes similar to, if not identical with, those reported above.

L. S. T.

Liver-glycogen. IV. Molecular structure of glycogen formed after ingestion of galactose by fasted rabbits. D. J. BELL (Biochem. J., 1936, 30, 1612—1616, and Nature, 1936, 138, 289).—The livers of galactose-fed rabbits and the whole tissue of *Mytilus edulis* yield glycogen, $[\alpha]_D +201^\circ$ in H_2O , containing 18 glucose units per mol., compared with 12 for normal glycogen, but with no other significant difference.

F. A. A.

New Zealand fish oils. I. Composition of eel oil (*Anguilla Aucklandii*). F. B. SHORLAND and I. G. MCINTOSH (Biochem. J., 1936, 30, 1775—1777).—The body- and, more especially, the liver-oil contain vitamin-A. The body-oil (yield 7%; sap. val. 290.4, I val. 122.5) contains 0.8% of unsaponifiable matter. The % of fatty acids resembles those of oils of fresh- H_2O fish examined by Lovern (A., 1933, 183). The production of dihydroxystearic acid by oxidation of the C_{18} unsaturated acids with

alkaline KMnO_4 and the results of bromination indicate the presence of oleic and stearidonic acid. No evidence was found of the presence of linoleic or linolenic acid. W. McC.

Absence of allocholesterol from the organism. E. A. EVANS, jun. (J. Biol. Chem., 1936, 115, 449—451).—No allocholesterol (I) is found in the yolk of hens' eggs, using as a test for (I) the ultra-violet absorption spectrum of $\Delta^{2:4}$ -cholestadiene obtained when (I) is dehydrated in the presence of acid; this test would indicate 0.01% of (I). F. A. A.

Pigments of the retina. II. Sea robin, sea bass, and scup. G. WALD (J. Gen. Physiol., 1936, 20, 45—56; cf. this vol., 1012).—The visual purple (I) in all cases is practically identical, spectroscopically, with that from frogs and the combined pigment epithelium and choroid layer contain vitamin-A, flavin, and an unidentified xanthophyll. The visual yellow of the sea robin retina is irreversibly converted into a p_H indicator at $p_H > 11$. This is not removed to form (I) or -A. H. G. R.

Microchemical detection of pterins in insects. E. BECKER and C. SCHÖPF (Annalen, 1936, 524, 124—144).—The detection of leucopterin is based on the separation of the yellow, cryst. Na salt, the stable Ag salt, and the violet-blue fluorescence of its feebly alkaline solutions. Xanthopterin (I) gives a sharply-defined yellow band which shows an intense yellowish-green fluorescence when adsorbed by Al_2O_3 from 0.01% HCl-MeOH; since the breadth of the band \propto the amount of pigment if the vol. of the solution is restricted an approx. determination may be made. Development by dil. acid decomposes the pigment. The adsorptive power of Al_2O_3 from 0.004*N*-HCl is considerably less. In 20% H_2SO_4 (I) yields a solution with weak but distinct red fluorescence. With somewhat greater amounts the separation of the β -Ba salt is possible. There is no certain method for the microchemical differentiation of (I) and chrysopterin (II). The sole difference is that (II) is more readily adsorbed than (I) from dil. aq. HCl so that homogeneous (II) gives a distinct band and is thus readily detected. In insects, (II) is usually associated with much (I). Detection of small amounts of erythropterin depends on adsorption from dil. acid solution by Al_2O_3 . With natural mixtures, 0.004*N*-HCl is more suitable than MeOH-HCl since it alone affords a clear band of orange colour and dull brown fluorescence. Guanopterin does not give characteristic colour or fluorescence reactions but the characteristic sulphate may be isolated from 0.1—0.2 mg. of material. In the examination of insects for pterins the localisation of pigment at definite positions in the integument, its mode of deposit in the skin tissue, and its microscopic-optical behaviour are as important as the chemical reactions. Preliminary treatment with Et_2O and boiling EtOH only is required but insects should be preserved, if necessary, in abs. EtOH. The pigments are obtained by two extractions with cold 0.5*N*- NH_3 followed by a single extraction with 2*N*- NH_3 . The united extracts are clarified and evaporated over KOH and H_2SO_4 . The subsequent treatment depends on the colour of the residue and is illustrated by several examples. H. W.

New pterins.—See this vol., 1260.

Determination of indoxyl in presence of indole in animal tissue. J. GARCÍA-BLANCO, J. NACLE, and C. HERNÁNDEZ (Anal. Fis. Quím., 1935, 33, 98—104).—Indole (I) is extracted with Et_2O and the indoxyl (II) determined colorimetrically in the acidified solution by means of Obermayer's reagent. (I) increases the amount of (II) lost from the blood and kidney but not the liver of rabbits, during pptn of the proteins. F. R. G.

Denaturation and hydration of proteins. H. NEURATH and H. B. BULL (J. Biol. Chem., 1936, 115, 519—528).— d of natural ovalbumin is $<$ that of heat- or surface-denatured ovalbumin. The vals. for the max. vol. contraction in H_2O are 53, 24.5, and 30 cu. mm. per g., respectively. The vol. contractions have also been measured in various EtOH- H_2O mixtures. H. G. R.

Nature of paranuclein. J. D. HERD (Biochem. J., 1936, 30, 1743—1752).—The rates at which N and P of paranuclein (I) (A., 1926, 970) are rendered sol. in 10% $\text{CCl}_3\text{-CO}_2\text{H}$ by hydrolysis with pepsin, trypsin, papain, and 10% NaOH indicate a P-free, alkali-resistant nucleus containing 20% of the initial N of (I). Data from hydrolyses, physical properties, NH_2 -acid distribution, and combination with I show (I) to consist of two fractions. F. O. H.

Liver-proteins. I. Storage of protein. J. M. LUCK (J. Biol. Chem., 1936, 115, 491—510).—Protein from the blood-free livers of rats may be extracted at 0—3° as four fractions, corresponding with globulin-II, euglobulin, pseudoglobulin, and albumin. In rats kept on a low-protein diet, the amounts in these fractions are 5.07, 4.58, 1.06, and 0.86 g. per 100 g. of liver, respectively. On a high-protein diet these vals. are all 50—60% higher, indicating that no single protein can be regarded as especially involved in protein storage in the liver. On the high-protein diet, the liver increases in wt. as well as in % protein. Under the conditions observed, other organs do not participate in protein storage. F. A. A.

Polysaccharoproteins. X. Rôle of individual amino-acid residues. S. J. VON PRZYŁECKI, K. KASPRZYK, and H. RAFAŁOWSKA (Biochem. Z., 1936, 286, 360—372).—Ovalbumin, lactalbumin, pseudoglobulin, globin, and histone of erythrocytes (goose) have no affinity for P-free polysaccharides (I). Euglobulin, ovoglobulin, fibroin, gelatin, edestin, clupcin, and myosin form symplexes (II) with (I), whilst serum-albumin and caseinogen unite only to a slight extent. The formation of (II) is not dependent on the protein particle size or physical structure nor on the presence of impurities, but (II) are formed only by those proteins which contain considerable amounts of tyrosine or arginine. P. W. C.

Cross-linking formation in keratins.—See this vol., 1396.

Enzymic histochemistry. XVIII. Localisation of peptidase in marine ova. H. HOLTER (J. Cell. Comp. Physiol., 1936, 8, 179—200).—Peptidase activity, in the three species examined, is localised in

the hyaline ground substance (matrix) of the cytoplasm, and is not bound to granular matter.

E. A. H. R.

Colloid osmotic pressure of the body-fluids of fresh-water animals. P. MEYER (Nature, 1936, 138, 287—288).—The vals. are in order of phylogenetic development, but are 20—35% < those of the corresponding marine animals.

L. S. T.

Abnormal fluorescence of human milk. C. GRIEBEL (Z. Unters. Lebensm., 1936, 72, 46—50).—Abnormalities are recorded due to (a) ingestion of 1:8-dihydroxyanthraquinone, (b) a vegetarian diet, and (c) the presence of unidentified cells in the milk.

E. C. S.

Composition of the envelopes of milk-fat globules. G. SCHWARZ and O. FISCHER (Milch. Forsch., 1936, 18, 53—67).—The material surrounding milk-fat globules was isolated by repeatedly washing cream with aq. NaCl, churning, separating butter fat, and pptn. with COMe_3 . The material contained ash 6.95, N 11.25, S 1.12, and P 0.61% in the dry matter. Its protein nature was established and its N distribution determined.

W. L. D.

Rennet test [for milk]. M. F. DUNGERN and G. NELZ (Milch. Forsch., 1936, 18, 46—52).—A semi-micro-method described involves an apparatus similar to that used in the Bürker test for the time of blood clotting. The method is trustworthy under various conditions of temp. and milk acidity.

W. L. D.

Determination of calcium diffusing from milk during compensated dialysis. G. SARZANA (Boll. Soc. ital. Biol. sperim., 1936, 11, 266—267).—Dialysis against isotonic aq. KCl of varying $[\text{Ca}^{++}]$ gives a diffusible Ca fraction of 18—19 and 37—50% for cow's and human milk, respectively, whilst ultrafiltration gives 30—37 and 44—67%, respectively.

F. O. H.

Factors influencing the lactose content of milk. W. E. PETERSEN (Proc. Amer. Soc. Animal Prod., 1936, 58—63).—Increasing the blood-glucose (I) beyond normal levels did not materially increase the lactose (II) content of milk. Lowering (I) or leaving the milk in the udder caused a decline in (II).

NUTR. ABS. (m)

Use of ammonium sulphate serum of milk in serological investigations. M. F. BENGEL and E. BOHM (Z. Unters. Lebensm., 1936, 72, 92). H. KLUGE (*ibid.*, 92).—Polemical (cf. *ibid.*, 71, 405).

E. C. S.

Forces concerned in the absorption of the cerebrospinal fluid. L. H. WEED (Amer. J. Physiol., 1935, 114, 40—45).—The total effective force is compounded of the colloid-osmotic pressure of the blood and a hydrostatic factor.

R. N. C.

Reducing substance in human cerebrospinal fluid. M. MITOLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 332—334).—0.5 c.c. of the fluid from 22 diseased persons reduces 0.75—4.57 (average 2.12) c.c. of 0.01% 2:6-dichlorophenol-indophenol.

F. O. H.

Determination of ethyl alcohol in saliva. J. C. ABELS (Proc. Soc. Exp. Biol. Med., 1936, 34, 504—505).—EtOH is absent from normal saliva, but in intoxication the EtOH content is closely correlated

with that of the blood and also with the degree of intoxication.

W. O. K.

Effects on gastric secretion in dogs of various food substances employed in the treatment of gastric ulcer. A. ALLEY (Amer. J. Digest. Dis. Nutrition, 1934, 1, 555—560).—Milk or cream produced continuous secretion, that with cream being more prolonged and that with milk of higher peptic power. Alkalis increase the vol. and acidity of the secretion. Egg-white, butter, and cream of wheat induced small secretion, that with the last named being of high peptic power and low acidity.

CH. ABS. (p)

Effect on gastric juice secretion of various cooked preparations of haddock and of lobster. A. ALLEY (Amer. J. Digest. Dis. Nutrition, 1934, 1, 182—184).—Lobster caused secretion of shorter duration but of much greater vol., acid and mucin contents than did boiled haddock.

CH. ABS. (p)

Gastric secretagogic value of various digestive secretions. M. S. KIM and A. C. IVY (Amer. J. Physiol., 1936, 115, 386—388).

R. N. C.

Inhibitory effect of the acidity of the gastric contents on the secretion of acid by the stomach. C. M. WILHELMJ, F. T. O'BRIEN, and F. C. HILL (Amer. J. Physiol., 1936, 115, 429—440).—HCl secretion in the dog is progressively inhibited by increasing $[\text{HCl}] > 0.005N$ in a Liebig's extract test meal, inhibition being nearly complete at $0.10N$. The inhibition is of gastric origin, and is probably not due to hormonal action. The composition of acidic and non-acidic fluids entering the stomach is unaffected by the inhibition.

R. N. C.

Improved gastric test meal and a study of the secretory curve in whole stomach pouches and in the normal intact stomach. C. M. WILHELMJ, F. T. O'BRIEN, and F. C. HILL (Amer. J. Physiol., 1936, 115, 5—22).—The meal contains 15 mg. of phenol-red per litre. Regurgitation of duodenal secretions keeps the $[\text{HCl}]$ of the total fluid entering the secreting stomach < the average val. found in isolated pouches. The regurgitated duodenal contents, with a powerful and maintained stimulus e.g., Liebig's extract of meat, are insufficient to lower gastric $[\text{H}^+]$, but prevent or slacken further rise.

R. N. C.

Some properties of Castle's intrinsic factor. C. FLOOD and R. WEST (Proc. Soc. Exp. Biol. Med., 1936, 34, 542—543).—Exposure of normal gastric juice to p_{H} 10.0 for 30 min. destroys peptic activity without materially affecting the intrinsic anti-anæmic factor (cf. A., 1932, 1156). Normal gastric juice produced no reticulocyte response, but, when added to boiled liver, increased the effect of the latter. Purified pepsinogen administered parenterally was inert.

W. O. K.

Volumetric micro-determination of spermine in semen. A. BOLLIGER (Med. J. Australia, 1935, 784—792).—The semen is acidified with $\text{CCl}_3 \cdot \text{CO}_2\text{H}$, the filtrate neutralised with CaCO_3 , and the spermine (I) pptd. as picrate, the picric acid content of which is determined by titration with methylene-blue (A.,

1934, 1322). The (I) content varied from 69 to 117 mg. per 100 c.c. of semen. J. N. A.

Urinary balance and diuresis. S. BELLUC, J. CHAUSSIN, J. COTTET, H. LAUGIER, and T. RANSON (Compt. rend., 1936, 203, 273—275).—Diuresis bears an inverse relationship to salt concn. P. G. M.

Phenolsulphonaphthalein renal function test in dogs. D. A. COLLINS (Amer. J. Physiol., 1936, 115, 27—30). R. N. C.

Nitrogen partition in urine of various primates. M. B. RHEINBERGER (J. Biol. Chem., 1936, 115, 343—360).—Subhuman primates are similar to children in retaining varying amounts of N. Urea, NH_3 , creatinine, and undetermined N are distributed as with children or subjects on a vegetarian diet. Excreted uric acid increases from Old World monkeys to apes in the direction of greater similarity to man. E. M. W.

Neutral sulphur of normal and pathological urines. A. FRIEDRICH and E. BAUER (Z. physiol. Chem., 1936, 242, 261—270).—In healthy human urine the neutral S constitutes 7—13% of the total S. Consumption of protein-rich food increases urinary, neutral, and total S but does not alter the ratio neutral S : total S. The ratio is increased in fevers, in tuberculosis, and sometimes in carcinoma and liver diseases. In a rabbit the ratio was doubled by P poisoning. Increase in urinary neutral S results from diet too rich in protein and from diseases which result in lack of O_2 and decomp. of protoplasm in the organism; except in cystinuria the increase is a measure of the gravity of the disease. W. McC.

Sulphur partition in cat urines following injections of monobromobenzene, cystine, and methionine. R. W. VIRTUE (Proc. Soc. Exp. Biol. Med., 1936, 34, 425—427).—Administration of PhBr to cats results in the excretion in urine of *p*-bromophenylmercapturic acid. The high urinary N found in fasting animals after PhBr administration suggests that the tissues are broken down in order to supply the cysteine required. After injection of cystine and methionine the extra S is excreted in the urine largely as sulphate. W. O. K.

Determination of iron in phosphate-rich material (faeces). RANGIER and LAFRANÇOISE (J. Pharm. Chim., 1936, [viii], 24, 266—268).—The material (e.g., dog's faeces) is boiled with aq. HCl (1 : 1) followed by dil. HNO_3 , filtered, and the filtrate treated with excess of aq. NH_3 , the resulting ppt. [$\text{Ca}_3(\text{PO}_4)_2 + \text{Fe}(\text{OH})_3$] being washed with H_2O and dissolved in boiling dil. H_3PO_4 , and the Fe^{+++} reduced (Zn) and then oxidised with 0.1N-KMnO₄. F. O. H.

Pyruvic acid in urine after hard exercise. R. E. JOHNSON and H. T. EDWARDS (Science, 1936, 84, 140—141).— AcCO_2H , but not AcCHO , appears to be one of the variable constituents of blood and urine during hard exercise. L. S. T.

Excretion of inulin and creatinine at low urine flows by the normal dog. J. A. SHANNON (Amer. J. Physiol., 1936, 114, 362—365).—The mean ratio of simultaneous inulin and creatinine clearance is 0.993 with a standard deviation of 0.048 and max.

variations of +0.097 and -0.083. Neither substance is passively reabsorbed during excretion by the normal kidney. R. N. C.

β -Lactose : effect on the flora of the infant's stool. J. R. GERSTLEY, E. PENRUDDOCKE, and G. LAWRENCE (Arch. Pediatrics, 1935, 52, 552—561).— β -Lactose has the same advantages as α -lactose in the infant's diet, and has a favourable influence on the p_{H} and flora of stools. CH. ABS. (p)

Common salt and other agents. Uses in certain [pathological] conditions. W. W. LANG (Vet. Rec., 1936, 48, 879—886).—A lecture and discussion. Uses of injections of NaCl-Na citrate are considered. A. G. P.

Iron absorption and treatment of anæmia. I, II. G. WALLBACH (Folia hæmatol., 1936, 54, 201—210, 211—216).—I. In mice given 0.01 g. of Fe daily for 8 days, storage of Fe after the same dose in different chemical combinations was very different and did not depend on the solubility in H_2O or the valency of the Fe.

II. After parenteral administration of 0.1 mg. of different forms of Fe certain forms, especially Fe^{II} salts, were deposited in the liver and others, such as reduced Fe, in the epithelial cells of the small intestine, whereas salts such as the citrate remained at the site of injection. NUTR. ABS. (m)

Significance of loss of serum-protein in therapy of severe burns. D. O. WEINER, A. P. ROWLETTE, and R. ELMAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 484—486).—After severe burns H_2O and protein are lost from the blood, which consequently has often an abnormally high erythrocyte count but a low serum-protein content. Administration of solutions containing only glucose and electrolytes is therefore not so effective as is blood-plasma. W. O. K.

Induced chiasma formation in somatic cells by a carcinogenic hydrocarbon [methylcholanthrene]. E. M. HEARNE (Nature, 1936, 138, 291). L. S. T.

Influence of diets containing proteins of various fishes on the growth of tumour in rats. I. S. TOKUYAMA and W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 253—271).—Sarcoma implanted on rats fed on a diet containing 15% of EtOH-extracted protein grew less rapidly when the protein was derived from various fish than from horse meat. The tumour growth rates were correlated with the growth of the animals before tumour implantation. W. O. K.

Transmissible agent in the Rous chicken sarcoma no. 1. J. W. JOBLING and E. E. SPROUL (Science, 1936, 84, 229—230).—The lipin extract of this sarcoma, obtained by the use of a sp. solvent at low temp. under relative anaërobiosis, transmits the tumour when allowed brief contact with chicken tissue extract and promptly inoculated. Tumours do not develop when the lipin extract is inoculated alone or into previously injured breast muscle. L. S. T.

Contents of trypsin, cathepsin, amylase, and lipase in cancerous growths and blood. G. VERCELLANA (Boll. Soc. ital. Biol. sperim., 1936,

11, 328—329).—The enzymes were not found in cancerous growths (excepting amylase, a normal constituent, in a parotid growth) or blood.

F. O. H.

High-sugar diets and dental caries in the white rat. C. D. M. DAY, R. G. DAGGS, and H. J. SEDWICK (J. Amer. Dental Assoc., 1935, 22, 913—925).—Prolonged feeding of diets containing 20—55% of sugar was not conducive to the incidence of caries when sufficient minerals and vitamins were supplied.

CH. ABS. (p)

Diet and dental caries. R. W. BUNTING (J. Amer. Dental Assoc., 1935, 22, 114—122; cf. A., 1934, 99).—High-sugar diets favoured the development of caries in children by influencing the environment of the teeth rather than their resistance. No const. relation was found between caries activity and the Ca, P, or vitamin-C or -D contents of the diet or the chemical composition of blood or saliva.

CH. ABS. (p)

Carbohydrate degradation in relation to dental caries. L. S. FOSDICK and H. L. HANSEN (J. Amer. Dental Assoc., 1936, 23, 401—407).—In the degradation of carbohydrate to lactic acid, with subsequent dissolution of tooth enamel, the enzymes of yeast and tissue play an important part. *In vitro*, human enamel, suspended in a solution of glucose and saliva, was dissolved by the acids produced. NaF prevented dissolution. A correlation of this fact with the low susceptibility of mottled teeth to decay is suggested. A combination of yeast and of (otherwise inactive) *B. acidophilus* was more potent than yeast alone.

NUTR. ABS. (m)

Acid-base balance of diets which produce immunity to dental caries among South Sea Islanders and other primitive races. W. A. PRICE (Dental Cosmos, 1935, 77, 841—846).—The primitive diet was potentially acid-forming. In changing to civilised diets (deficient in certain minerals and vitamins) the potential acidity did not increase with the enhanced susceptibility to caries.

CH. ABS. (p)

Impaired glucose tolerance in certain alimentary disorders of childhood: treatment with liver extract. C. W. ROSS (Lancet, 1936, 231, 556—559).—In celiac disease, chronic intestinal indigestion, and abdominal glandular tuberculosis a flat oral glucose tolerance curve is associated with a high intravenous curve, indicating deficient carbohydrate absorption power from the intestine. Administration of liver extract improves the impaired glucose tolerance.

L. S. T.

Intestinal absorption in celiac disease; effect of liver extracts on carbohydrate metabolism. C. W. ROSS (Trans. Roy. Soc. Trop. Med. Hyg., 1936, 30, 33—60).—Evidence for defective absorption of glucose and a resulting decrease in glucose tolerance, as well as for decreased sensitivity to insulin, is reported. Tests indicated that the factor (probably insulin-kinase), present in total liver extracts, which improves glucose tolerance is not identical with Castle's essential liver factor.

NUTR. ABS.

Chemical aspects of dermatitis. H. E. COX (Chem. and Ind., 1936, 775—781).—An address.

Treatment of severe diabetes in children with protamine insulinate. T. I. BENNETT and A. M. GILL (Lancet, 1936, 231, 416—417).

L. S. T.

Specific dynamic action of protein in pancreatic diabetes. G. C. RING (Amer. J. Physiol., 1936, 115, 419—423).—The calorogenic action of protein (I) in underfed diabetic cats is > normal. Increased metabolism does not affect the action of (I), although those of fat and carbohydrate are reduced. The R.Q. after ingestion of (I) is < that in normal animals. The increased metabolism of diabetes is not due to sp. dynamic action of (I).

R. N. C.

Evidence of altered carbohydrate metabolism in cats with hypothalamic lesions. W. R. INGRAM and R. W. BARRIS (Amer. J. Physiol., 1936, 114, 562—571).—Bilateral lesion in the anterior supra-chiasmatic portion of the hypothalamus, or hypophysectomy, increases the sensitivity of the cat to insulin. The response of blood-sugar to adrenaline is also diminished by severe lesions in the suprachiasmatic region. Lesions in this region abolish the normal response to the hyperglycæmic effect of anterior pituitary suspension (I); hypophysectomy retards the action of (I). Liver-glycogen remains normal.

R. N. C.

Effect of experimental hypothalamic lesions on blood-sugar. R. W. BARRIS and W. R. INGRAM (Amer. J. Physiol., 1936, 114, 555—561).—Lesions at almost any point in the hypothalamus of the cat cause a transient hyperglycæmia. Mild chronic hypoglycæmia generally follows when the lesion is in the anterior portion, particularly if the nucleus filiformis is destroyed or atrophic.

R. N. C.

Blood-lipins in lipæmia retinalis. A. MARBLE and R. M. SMITH (Arch. Ophthalmol., 1936, 15, 86—94).—In lipæmia retinalis occurring in two boys with severe diabetes which had been poorly controlled, the total lipins of the blood amounted to 14.1 and 7.5%, respectively. The greatest increase took place in the fatty acid fraction, with relatively large increases also in the cholesterol and phospholipin fractions.

NUTR. ABS. (m)

Chemistry of muscle in progressive muscular dystrophy. Analysis of biopsy samples from the deltoid. J. A. COLLAZO, J. BARBUDO, and I. TORRES (Deut. med. Woch., 1936, 62, 51—54).—In dystrophic muscle there exists, together with fatty degeneration of the connective tissue, an insufficiency of phosphagen (I) and glycogen (II), (I) being practically absent in severe cases. There is also a marked lack of (II) and lactic acid, and a reduced H₂O content. The inorg. P of muscle is not increased. In a severe case of myasthenia the vals. for muscle-(II) and -(I) were subnormal but not to the extent found in the dystrophies.

NUTR. ABS. (m)

Metabolic studies in osteoporosis. M. ADAMS, W. M. BOOTHBY, and A. M. SNELL (Amer. J. Physiol., 1936, 114, 383—398).—Ca₃(PO₄)₂ fed in large amounts to a patient with senescent osteoporosis produces storage of Ca and P; the extent of the storage is limited by a factor, exhaustion of which results in a decreasing retentive power. Viosterol (I) added to Ca₃(PO₄)₂

renders Ca retention more marked. Ca retention during administration of Ca lactate (II) is > during administration of an equiv. amount of $\text{Ca}_3(\text{PO}_4)_2$; (I) apparently produces little change in Ca balance when (II) alone is given. N is retained throughout; K, Na, and Mg balances are unchanged. R. N. C.

Hydræmia as a factor in the anæmia of pregnancy. H. FELDMAN, E. C. VAN DONK, H. STEENBOCK, and E. F. SCHNEIDER (Amer. J. Physiol., 1936, 115, 69—77).—The H_2O content rises in the blood of pregnant women whilst cell vol., hæmoglobin level, and *n* fall. These changes do not occur in the cow. R. N. C.

Relation of pregnancy and lactation to extirpation diabetes in the dog. F. P. CUTHBERT, A. C. IVY, B. L. ISAACS, and J. GRAY (Amer. J. Physiol., 1936, 115, 480—496).—Glycosuria in depancreatised bitches, maintained with a uniform diet and a dose of insulin (I) permitting slight glycosuria, is increased in early pregnancy, decreased in late pregnancy, and further decreased in lactation. The reduction is due to passage of glucose and glucose-forming substances into the fœtus. Pancreatectomy near term does not cause hyperglycæmia in presence *in utero* of ≤ 3 viable fœtuses. (I) does not suppress the anti-hyperglycæmic effect exerted by the metabolites of near-term pregnancy. The metabolisms of dogs depancreatised before pregnancy and near term show considerable differences, the latter condition being the more analogous to that of the human patient. R. N. C.

Blood-lipins during pregnancy in guinea-pigs. E. M. BOYD and M. D. FELLOWS (Amer. J. Physiol., 1936, 114, 635—641).—Lipæmia becomes marked in the second half of gestation, the increase occurring in the plasma. Total lipins, phospholipins, and free cholesterol (I) are increased to 4 times and neutral fat to 5 times the normal vals., whilst esterified (I) falls 50%, this decrease being continuous and progressive from early pregnancy. R. N. C.

Nutritive value of canavanine (amino-acid). VI. **Influence of canavanine on pregnancy and parturition.** M. OGAWA (J. Agric. Chem. Soc. Japan, 1936, 12, 828—832).—Canavanine is not essential for pregnancy, but it is important for the health of pregnant animals. (Cf. A., 1935, 1417.) J. N. A.

Rôle of acidosis and phosphate retention in the pathogenesis of rickets and rachitic tetany of infants. N. MORRIS, F. J. FORD, and S. GRAHAM (Acta paediat., 1935, 18, 50—91).—The active stage of rickets in two children, one with and one without tetany, was accompanied by increased NH_3 and decreased titratable acid in the urine. Administration of adexolin was followed by an increased retention of Ca and P, a decrease in urinary NH_3 , and an increase in the titratable acid. Before the onset of rickets a child with cœliac disease had an approx. normal output of urinary NH_3 and titratable acid, although mineral retention was poor. The examination of Ca and P balances of children with rickets, with and without tetany, and the administration of P to a patient depleted of Ca through cœliac disease,

failed to show any relation between tetany and high P retention. NUTR. ABS. (*m*)

Blood buffer values in mineral deficiency. I. N. KUGELMASS (Amer. J. Digest. Dis. Nutrition, 1936, 2, 730—732).—The serum of rachitic infants had a much lower buffering power to added acid and alkali than had that of normal infants. NUTR. ABS. (*m*)

Bone-ash in prevention and healing of experimental rat rickets. T. F. ZUCKER (Science, 1936, 84, 162—163).—In curative experiments, supposedly substantial healing effects raise the bone-ash through only approx. one fifth of the interval between the rachitic and the full vitamin-D prevention levels. L. S. T.

Tropical sprue with special reference to intestinal absorption. I. N. H. FAIRLEY (Trans. Roy. Soc. Trop. Med. Hyg., 1936, 30, 9—32).—Decreased absorption of fat (with hypocalcæmia) and of glucose are noted, but starch digestion and protein metabolism are not affected. NUTR. ABS.

Relation of serum-phosphates to parathyroid tetany. J. H. JONES (J. Biol. Chem., 1936, 115, 371—379).—Rats fed on a low-Ca diet with 4% of basic Al acetate show no tetany after parathyroidectomy and the serum-Ca remains high and the -P low. Fasting after parathyroidectomy causes tetany; the serum-P rises and the -Ca falls. With low available P serum-Ca is high enough to prevent tetany on diets deficient in Ca. The P excretion theory of parathyroid function is discussed. E. M. W.

Influence of dietary deficiencies on the transmission of trachoma to monkeys. R. A. HETLER and W. M. JAMES (Amer. J. Ophthalmol., 1934, 17, 1048—1054).—Follicular changes developed in the inoculated eyes of well- and ill-nourished monkeys but not in rats, rabbits, or guinea pigs receiving diets low in vitamins and protein but high in fats. CH. ABS. (*p*)

Effect of diet and vitamins on trachoma. C. E. RICE, R. SORY, J. E. SMITH, P. E. FAED, and A. A. DRAKE (Amer. J. Ophthalmol., 1934, 17, 735—741).—No effects in the course of trachoma were observed. CH. ABS. (*p*)

Metabolism of cartilage. E. G. L. BYWATERS (Nature, 1936, 138, 288).—A reply to criticism (cf. this vol., 1143). L. S. T.

Respiratory metabolism of stimulated frog's muscle. C. L. GEMMILL (Amer. J. Physiol., 1936, 115, 371—375).—The R.Q. averages 0.90, O_2 consumption 357 cu. mm. per g. of muscle per hr., and the tension developed 195 kg. per g. per hr. O_2 consumption and the tension developed under aerobic conditions show a linear relationship. R. N. C.

Age and tissue respiration. J. M. PEARCE (Amer. J. Physiol., 1936, 114, 255—260).—The O_2 consumption of excised mouse tissue decreases as age increases. The greatest fall occurs in the liver, and the least in the kidneys. R. N. C.

Oxidation-reduction in the small intestine and liver of rats during intestinal absorption. G. PERETTI (Boll. Soc. ital. Biol. sperim., 1936, 11, 336—

337).—Following ingestion of olive oil or glucose, the reducing power (to 2:6-dichlorophenol-indophenol) of the liver and, to a smaller extent, of the small intestine and lung tissue increases.

F. O. H.

Oxygen consumption and carbon dioxide production of frog's retina in darkness and light. J. JONGBLOED and A. K. NOYONS (Z. Biol., 1936, 97, 399—408).—The retina, maintained in darkness for 15—60 min. in contact with the pigmented epithelial layer, has an O₂ consumption and a CO₂ production approx. 22—26% > those of the retina exposed to light.

F. O. H.

Effect of bile salts on the oxygen consumption of dog tissues. W. H. STRAIN and M. E. MARSH (Amer. J. Physiol., 1936, 115, 82—89).—With increasing concn. of Na bile salts in Ringer-PO₄-glucose medium, a "crit. inhibitory concn." is reached above which respiration is more or less inhibited. The inhibiting effect of conjugated bile salts is < that of unconjugated salts, whilst that of Na glycololate (which is foreign to the dog) is > that of taurocholate, suggesting specificity in conjugation.

R. N. C.

Regularity of nutritional response to chemical intake. H. C. SHERMAN and H. L. CAMPBELL (Proc. Nat. Acad. Sci., 1936, 22, 478—481; cf. A., 1935, 1154).—Rats from families surviving for 8 generations on a diet poor in "protective foods" responded normally, in respect of growth and development, to supplementary feeding with Ca, vitamin-A and -B₂, and (to a smaller extent) with protein.

A. G. P.

Diet in relation to reproduction and rearing of young. J. F. FEASTER and V. E. NELSON (Amer. J. Physiol., 1936, 115, 147—154).

R. N. C.

Influence of calcium carbonate in the feed of laying hens on digestion. G. D. BUCKNER and A. H. HARMS (Poultry Sci., 1935, 14, 360, 375, 380).—Analysis of the droppings indicates that large amounts of CaCO₃ in the ration lower the digestion of N-free extractives and increase that of protein.

A. G. P.

Availability of calcium salts for bone formation and rickets prevention in chicks. H. J. DEOBALD, C. A. ELVEHJEM, E. B. HART, and J. G. HALPIN (Poultry Sci., 1936, 15, 42—47).—In chicks receiving a basal rachitogenic ration supplemented with various Ca salts and cod-liver oil, the ash content of fat-free bone was higher when the supplement contained P as well as Ca. The Ca in compounds examined (limestone, gypsum, Ca gluconate, bone meal, rock phosphate) was uniformly available for bone formation. If the cod-liver oil given was in crit. amounts, sol. Ca salts (lactate) were more effective than the insol. salts (pptd. silicate). With very insol. silicates the availability \propto solubility in dil. acid and was not influenced by the amount of oil supplied.

A. G. P.

Calcium carbonate versus calcium sulphate in swine rations. C. W. MCCAMPBELL and C. E. AUBEL (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 189—190).—When fed as supplements to a linseed meal-wheat-maize ration, finely

ground limestone and gypsum were similarly effective in respect of influencing the serum-inorg. Ca, inorg. P of whole blood, breaking strength of bones, and daily gain in wt.

CH. ABS. (p)

Refecation in the rat. Preparation of basic materials for deficiency diets. S. BLISS (J. Nutrition, 1936, 11, 1—19).—Refecation is readily produced in rats by feeding diets with potato starch as carbohydrate. Growth of such rats is not attributable to unsuspected vitamin-B contamination of the diet. Raw starch from refected faeces and pure raw potato starch behave similarly towards pancreatic digestion mixtures *in vitro*.

A. G. P.

Purified diet satisfactory for growth, reproduction, and lactation in rats. W. M. COX and M. IMBODEN (Proc. Soc. Exp. Biol. Med., 1936, 34, 443—446).—The diet consisted of casein, 20; dextrin, 55.1; lard, 9.0; protein-free dried extract of brewer's yeast (equiv. in -B₁ to 24% and in -B₂ to 8% of yeast), 4; wheat-germ oil, 1.6; carotene (0.3% in maize oil), 0.3; Ca(OAc)₂ 1; salts, 3.1; and rice cellulose 5.9 parts.

W. O. K.

Vitamin-D content and hæmoglobin-building properties of dehydrated kelp for chicks. M. W. MILLER and G. E. BEARSE (Poultry Sci., 1936, 15, 19—22).—The kelp had little -D activity and did not affect the hæmoglobin content of chick blood.

A. G. P.

Hæmoglobin content of the blood of laying hens on practical poultry rations. M. O. SCHULTZE, C. A. ELVEHJEM, E. B. HART, and J. C. HALPIN (Poultry Sci., 1936, 15, 9—13).—A ration supplying 14 mg. of Fe and 0.5 mg. of Cu per head per day supports heavy egg production without concurrent lowering of the hæmoglobin content of the blood.

A. G. P.

Site of renal elimination of hæmoglobin in the rabbit. I. GERSH (Anat. Rec., 1936, 65, 371—375).

R. N. C.

Effect of previous feeding on the nitrogen excretion of fasting birds. J. C. FRITZ, W. A. HENDRICKS, and H. W. TITUS (Amer. J. Physiol., 1936, 115, 281—286).—N excretion by cocks falls when fasting begins, but on the 2nd and 3rd days rises or falls according as the previous diet was abnormally low or high in protein. After the 3rd day N excretion remains practically const. The source of the protein in the diet does not affect the result. Recovery after fasting is most rapid in birds previously fed with a normal diet.

R. N. C.

Effect of (A) high-fat and (B) high-protein diet on the growth of rats. C. Y. CHEN (Nutrit. Bull. B, April, 1936, No. 3, 23—27, 29—36).—The ill effects of both diets were counteracted by adding a 50% EtOH extract of yeast, but not by a 70% extract.

NUTR. ABS.

Effect of a low-protein ration on the pre-natal and post-natal development of the rat. C. P. THOMPSON (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 177—178).—Low-protein rations did not affect the no. of young per litter but lowered their average wt. and increased the proportion of stillborn. At higher protein levels (17.1%) rats

stored 19% more of the total N ingested than did those receiving 10.2% of protein. CH. ABS. (p)

Rate of growth in relation to plane of protein intake. A. G. HOGAN, S. R. JOHNSON, and U. S. ASHWORTH (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 179—181).—Animals on a high-protein (20%) diet made larger gains in wt., and stored more H₂O and protein but less fat, than did those on a low-protein (10%) diet. CH. ABS. (p)

Digestibility of dietary protein in the ruminant. I. Endogenous nitrogen excretion on a low-nitrogen diet and in starvation. II. Digestibility of protein following a prolonged fast. Nitrogen metabolism. J. C. D. HUTCHINSON and S. MORRIS (Biochem. J., 1936, 30, 1682—1694, 1695—1704).—I. The faecal N excretion of goats and sheep on a N-free diet increases with the quantity of food taken and the presence of fibre in the diet. With the cow, goat, and sheep starvation following a low-N diet causes an increased urinary N excretion, the most notable changes being those of urea (I) and creatine (II); increasing the energy intake on a N-free diet causes a progressive decrease in the urinary excretion of (I) and (II).

II. The greater is the biological val. of the protein and the greater the requirement of the animal for protein, the less is the digestibility; the faecal N excreted under conditions of poor utilisation is volatile at 180°. From studies of the partition of the urinary N of cows after ingestion of food after a period of starvation it is concluded that increased deamination leads to increased (I), NH₃, and NH₂-acid excretion; when the ingested protein is used for tissue anabolism an increase of (II) output occurs. The mean ratio of retained N to S over a long period is similar to that for body tissue. H. D.

Uric acid synthesis in birds. IV. Uric acid synthesis in pigeons; a purine synthesis. (i) Nucleic acid metabolism in the pigeon. (ii) The "precursor" as a carbon source in uric acid synthesis. (iii) Nitrogen source in uric acid synthesis. W. SCHULER and W. REINDEL (Klin. Woch., 1935, 14, 1238—1242; Chem. Zentr., 1935, ii, 3792—3793).—(i) [with A. LEHMER]. Liver is unable to effect fission of nucleic acid or nucleoside, or to oxidise purines to urea.

(ii) [with H. FRIEDRICH]. None of many substances examined can be the precursor of uric acid. Kidneys are unable to regenerate the precursor although they always contain considerable amounts. The production of precursor from liver powder is confirmed.

(iii) [with O. HENZ]. See A., 1935, 1153.

A. G. P.

Choline ester formation in, and choline esterase activities of, tissues *in vitro*. J. H. QUASTEL, M. TENNENBAUM, and A. H. M. WHEATLEY (Biochem. J., 1936, 30, 1668—1681).—A substance considered to be a choline ester (I), which causes eserinated leech muscle to contract, is formed during aerobic incubation of brain cortex slices in the presence of eserine. The rate (*R*) of (I) formation is decreased by CN' and increased 4—5 times by glucose (II) with or without added Ca and K with HPO₄' medium; addition of Ca and K to a (II)-HPO₄' medium increases *R*.

In HCO₃' medium (II) increases *R* in the absence of added Ca'' and K'. Addition of Ca'' and K' lowers *R* so that adding (II) to a Ringer-HCO₃' medium has little or no effect. The possibility that these effects are due to influences on (II) metabolism is suggested. Na lactate, pyruvate, α-glycerophosphate, and glutamate increase *R* < (II) with or without added Ca'' and K'; Na succinate is without influence, also NaF in the presence of (II) although in this case *Q*₁₀ is considerably reduced. Addition of choline or NaOAc is without influence on *R* so that it is assumed that the synthesis of acetylcholine (III) is not from the products of its hydrolysis. Kidney, liver, spleen, and testis do not produce (I) under the conditions in which brain does. The hydrolysis of (III) by tissue slices occurs most rapidly with spleen and it is concluded that there is no relation between the power of an organ to break up (III) and its power to form (I) *in vitro*. H. D.

Oxidation of indole in various organs of the rabbit. J. GARCÍA-BLANCO and J. NACLE (Anal. Fis. Quím., 1935, 33, 105—108).—Indole is oxidised to indoxyl especially in the kidney. F. R. G.

Kinetics of elimination of substances injected intravenously. (Creatinine.) R. DOMINGUEZ, H. GOLDBLATT, and E. POMERENE (Amer. J. Physiol., 1935, 114, 240—254).—Creatinine introduced rapidly into the blood-stream of the dog is dispersed quickly into a large portion of the body-fluids (equiv. plasma vol.) from which it diffuses reversibly into the remainder (tissue vol.), until equilibrium is reached; it is excreted steadily by the kidneys before and after establishment of equilibrium. R. N. C.

Clearance of hexamethylenetetramine in the dog. R. F. PITTS (Amer. J. Physiol., 1936, 115, 706—710).—The clearance ratio of (CH₂)₆N₄ (I) and xylose (II) in the normal dog is independent of the plasma-(I) concn.; hence (I) clearance itself is also independent of plasma-(I). Simultaneous clearances of (I) and (II) are practically identical and about 75% of the simultaneous clearance of creatinine. Phloridzin depresses all three clearances, that of (II) being altered least. R. N. C.

Intestinal absorption of amino-acids. R. HÖBER and J. HÖBER (Proc. Soc. Exp. Biol. Med., 1936, 34, 486—488).—The diffusion of various NH₂-acids and acid amides through the intestinal wall is not a simple function of mol. vol. but shows evidence of sp. selectivity. W. O. K.

Absorption of cystine, methionine, and cysteic acid from intestinal loops of dogs. J. C. ANDREWS, C. G. JOHNSTON, and K. C. ANDREWS (Amer. J. Physiol., 1936, 115, 188—193).—The rate of absorption is max. for methionine and min. for cystine. The amount absorbed in a given period varies with the amount introduced. The amount of NH₂-acid absorbed is the same, whether it is injected as free acid or Na salt; the amount of NaOH absorbed is independent of the NH₂-acid. R. N. C.

Utilisation of glutathione in connexion with a cystine-deficient diet. H. M. DYER and V. DU VIGNEAUD (J. Biol. Chem., 1936, 115, 543—549).—Oral or subcutaneous administration of glutathione

will support growth of rats on a cystine-deficient diet.

H. G. R.

Synthesis of neutral fat by the intestine of diabetic dogs. S. FREEMAN and A. C. IVY (Amer. J. Physiol., 1935, 114, 132—136).—Oleic acid (I) is absorbed from the intestine largely as neutral fat and phospholipin, showing that glycerol is available for fat synthesis in absence of insulin, and that phosphorylation of (I) is not impaired. The increases in cholesterol in the chyle of normal dogs are absent from that of depancreatized animals.

R. N. C.

Ether-soluble lipin-phosphorus, lecithin, and cephalin distribution in the development of the chick. O. E. KUGLER (Amer. J. Physiol., 1936, 115, 287—291).—Phospholipin metabolism reaches its highest stage between the 15th and 17th days of incubation. Lecithin and cephalin run parallel with each other, showing the same fluctuations as Et₂O-sol. lipin-P during development, and maintain a ratio of approx. 3 : 1 in the yolk and the embryo fraction throughout incubation.

R. N. C.

Transformations of adenosinetriphosphoric acid in muscle. IV. Transformation of adenosinetriphosphoric acid in muscle of hibernating animals. O. FEINSCHMIDT (Biochem. Z., 1936, 286, 290—294).—During hibernation, the adenosinetriphosphoric acid (I) and P₂O₇⁴⁻ (II) contents of the muscle of the ground-squirrel *Citellus guttatus* are considerably decreased, (II) to a smaller extent than corresponds with the decrease of (I). Muscle then contains inorg. (II) and free adenylic acid (cf. this vol., 754).

P. W. C.

Creatinuria induced by ingestion of glucose and fructose and by exercise. J. HALDI and G. BACHMANN (Amer. J. Physiol., 1936, 115, 364—370).—Ingestion of glucose (I) and/or fructose (II) by men often causes excretion of creatine (III), whilst carbohydrate metabolism is increased. (II) induces a higher (III) excretion than (I) or (I)+(II). (III) excretion often follows exercise, particularly if this is preceded by ingestion of sugar, (II) again inducing the higher excretion; creatinine excretion is not affected.

R. N. C.

Hexose phosphate metabolism of tumour extracts. C. A. MAWSON (Biochem. J., 1936, 30, 1592—1597).—Lactic acid (I) is not produced from glucose by mouse tumour cell suspensions at 38° or 52°, with or without addition of glutathione (II). Small amounts of (I), not increased by the addition of (II), are produced from hexose diphosphate (III) at 38°; at 52°, larger amounts, considerably increased by the addition of (II), are produced. Dialysis lowers the activity of tumour extracts, which is restored by the addition of (II). The production of (I) from (III) at 52° is greatly reduced by kidney antiglyoxalase.

F. A. A.

Glycogen and the metabolism of carbohydrate. F. G. YOUNG (Lancet, 1936, 231, 237—242, 297—302).—Lectures.

L. S. T.

Avian carbohydrate metabolism. R. SPRAGUE and A. C. IVY (Amer. J. Physiol., 1936, 115, 389—394).—The blood-sugar (I) responses of normal and depancreatized ducks to insulin are similar.

Relatively large doses of adrenaline (II) are required to produce hyperglycemia, normal birds showing a greater response than depancreatized birds, suggesting that (II) and the sympathetic nervous system are of less importance in avian than in mammalian carbohydrate metabolism. Pituiratin does not affect (I). Liver-glycogen (III) is unaffected by depancreatization, and the (III) hydrolysate contains moderate quantities of lactic acid in both cases. The rate of disappearance of glucose from the blood *in vitro* is unaltered by depancreatization. Extracts of duck's pancreas contain an insulin-like substance.

R. N. C.

Mechanism of carbohydrate breakdown in early embryonic development. J. NEEDHAM, W. W. NOWIŃSKI, R. P. COOK, and K. C. DIXON (Nature, 1936, 138, 462—463).—The changes which sugar-like substances undergo in or under the influence of chick embryos of 4—6 days' incubation are summarised and compared with those effected by brain and muscle tissues. Glucose and mannose are the only sugars which give a steady, long-continuing glycolysis; fructose, and disaccharides even when phosphorylated, are unattacked. Lactic acid is quantitatively formed during glycolysis. The embryo does not glycolyse any combination of the P-containing intermediates. The Pasteur effect is very marked. The P distribution in various fractions of the aq. CCl₃·CO₂H extract differs from that obtained with muscle and brain preps.

L. S. T.

"Hunger diabetes" and the utilisation of glucose in the fasting dog. S. SOSKIN and I. A. MIRSKY (Amer. J. Physiol., 1935, 114, 106—109).—Sugar is utilised after evisceration by the normal fasting dog at the same rate as by the normal fed dog. The low R.Q. and other symptoms of "hunger diabetes" are due rather to increased gluconeogenesis than to lack of carbohydrate utilisation.

R. N. C.

Effect of hypophysectomy on gluconeogenesis in the normal and depancreatized dog. S. SOSKIN, I. A. MIRSKY, L. M. ZIMMERMAN, and N. CROHN (Amer. J. Physiol., 1935, 114, 110—118).—The hypophysectomized animal is unable, when its carbohydrate (I) stores are depleted and it is deprived of exogenous (I), to synthesise (I) from fat, but can derive it from protein.

R. N. C.

Carbohydrate metabolism of the heart during pancreas diabetes. H. E. HIMWICH, W. GOLDFARB, and J. F. FAZIKAS (Amer. J. Physiol., 1936, 114, 273—277).—The carbohydrate balance of the heart in both normal and diabetic dogs is positive; this explains the paradoxical storage of cardiac glycogen (I) if a diminished power to oxidise glucose is taken into consideration. The R.Q. of diabetic cardiac tissue is > 0.7, showing that non-fatty substances can be oxidised. O₂ consumption in presence of lactic acid is increased; its oxidation limits storage of (I). Diabetic cardiac tissue can still glycolyse.

R. N. C.

Normal glucose tolerance curves, in the absence of insulin, in hypophysectomized depancreatized dogs. S. SOSKIN, I. A. MIRSKY, L. M. ZIMMERMAN, and R. C. HELLER (Amer. J. Physiol.,

1936, 114, 648—652).—The occurrence of the normal glucose (I) tolerance curve is determined by a homeostatic reaction of the liver, whereby the supply of sugar to the blood is increased in response to the influx of exogenous (I). The rise in (I) stimulates this mechanism, whilst the pancreas and pituitary determine the (I) level at which it comes into play.

R. N. C.

Intermediate metabolism of carbohydrates. H. A. KREBS (Nature, 1936, 138, 288—289).—When added to animal tissues AcCO_2H disappears rapidly even in absence of O_2 ; the products of the anaerobic oxidation are AcOH , CO_2 , and succinic acid. Changes which AcCO_2H undergoes in living cells are described. They are intermediate steps in the biological breakdown of carbohydrates.

L. S. T.

Secretory metabolism of the salivary glands. D. NORTHUP (Amer. J. Physiol., 1935, 114, 46—52).—Simultaneous stimulation of sympathetic and parasympathetic nerves to the submaxillary gland of the dog increases lactic acid (I) and decreases glycogen (II) and creatinephosphoric acid (III) in the gland. The changes produced by sympathetic stimulation alone are $>$ those from parasympathetic stimulation alone, but $<$ those from combined stimulation. Since breakdown of (II) and (III) to (I) occurs during salivary secretion, it is possible that the (II)–(III) mechanism is general for release of energy in tissues where work is done.

R. N. C.

Metabolism of bacteria-free animals. II. Production and excretion of oxalic acid by guinea-pigs. S. BORGSTRÖM (Skand. Arch. Physiol., 1936, 73, 63—66).—Bacteria-free and normal guinea-pigs excreted similar amounts of $\text{H}_2\text{C}_2\text{O}_4$ up to the 15th day after birth, after which the normal animals' excretion remained const., whilst that of the sterile animals rose parallel with the growth curve and after 30 days was 6 times that of the controls.

NUTR. ABS. (m)

Alcohol injected intravenously: effect of habituation on rate of metabolism. H. W. NEWMAN and W. C. CUTTING (J. Pharm. Exp. Ther., 1936, 57, 388—393; cf. A., 1935, 1409).—Oral administration of 6.8 c.c. of EtOH per kg. per day for 13 months did not significantly increase the rate of oxidation of EtOH when injected intravenously into 3 dogs.

J. N. A.

Relation of the urinary chloride rate to the plasma concentration before and after administration of sodium chloride. E. M. MACKAY and L. L. MACKAY (Amer. J. Physiol., 1936, 115, 455—460).—When excretion of urine (rabbit) is high and urea formation directly related to blood-urea, urinary and plasma- Cl' show no uniformity. If NaCl is administered in large doses to increase plasma- Cl' , a curvilinear relationship tends to appear between urinary and plasma- Cl' . There is a Cl' threshold for the rabbit.

R. N. C.

Production of chloride-free solutions by the action of the intestinal epithelium. R. C. INGRAHAM and M. B. VISSCHER (Amer. J. Physiol., 1936, 114, 676—680).— Cl' is almost completely removed from solutions containing SO_4'' placed in the lower ileum. Na_2SO_4 becomes conc. in the intestine,

the increase of osmotic pressure of the cation due to exchange of Cl' for SO_4'' causing an increase in Na' . The normal intestine is impermeable to SO_4'' ; the movement observed is not, however, due to a simple Donnan equilibrium with SO_4'' as the impermeable ion. K' substituted for Na' does not appreciably alter the movement of Cl' .

R. N. C.

Distribution and storage of fluorine in tissues of the laying hen. K. HAMAN, P. H. PHILLIPS, and J. G. HALPIN (Poultry Sci., 1936, 15, 154—157).—All normal tissues, except washed feathers and thyroid, contained F, in amounts decreasing in the order: bones, kidney and liver, muscle, fat. Vals. were increased by feeding raw rock phosphate or phosphatic limestone, bones being affected $>$ soft tissues. In laying hens storage of $\text{F} \propto$ the amount ingested.

A. G. P.

Calcium changes in the plasma resulting from brief severe work and the question as to the permeability of the capillaries to calcium. A. KEYS and L. ADELSON (Amer. J. Physiol., 1936, 115, 539—547).—Ca rises in plasma after brief severe exercise, reaches its max. in 1 min., and then declines logarithmically to reach its resting level in 30—70 min.; the changes are closely parallel to, but slightly $>$, those in plasma-protein. The mechanism of these changes is discussed with reference to "diffusible" Ca.

R. N. C.

Calcium metabolism of laying hens. H. J. DEOBALD, E. J. LEASE, E. B. HART, and J. G. HALPIN (Poultry Sci., 1936, 15, 179—185).—In individual hens blood-Ca remained substantially const. over a 36 hr. period. Deprivation of Ca resulted in a gradual decrease in the CO_2 -free ash of egg shells and laying ceased in approx. 12 days. A portion of the skeletal Ca of hens may be utilised in shell formation. Subcutaneous injection of small amounts of parathormone into Ca-deficient hens had no effect on Ca metabolism, egg production, ash content of bones, or blood-Ca. Large injections increased blood-Ca.

A. G. P.

Rate of bismuth absorption in experimental animals following oral administration. G. E. CLARKE and H. F. MARSH (J. Pharm. Exp. Ther., 1936, 57, 399—409).—Bi in the form of K or Na Bi tartrate or BiOCl when administered orally to guinea-pigs is deposited in the liver, spleen, and kidney. In liver and spleen the highest concn. of Bi occurs after 24 hr. and in kidney between 12 and 48 hr. Bi administered to pregnant animals was found in the foetal liver and placenta, but not in the foetal kidney.

J. N. A.

Magnesium excretion in dogs. Physiology of the colon. III. R. NICOLAYSEN (Skand. Arch. Physiol., 1936, 73, 75—89).—Two dogs of const. wt. (8 kg.) and in N equilibrium on a Mg-free neutral diet excreted in the urine during 10 3-day periods 6—24 mg. of Mg, the faecal excretion being from 18 to 26 mg. These vals. were unchanged after the colon had been short-circuited and the ileum anastomosed with the rectum. In the colon the Mg excretion constituted only a small % of the total amount excreted by the whole gut and remained const. whether the dogs were on a diet deficient or

rich in Mg. Of parenterally injected Mg, 70—90% was excreted by the urine and none appeared in the colon or in the rest of the alimentary canal.

NUTR. ABS. (*m*)

Metabolism of sulphur. II. Metabolism of sulphur and protein in infants and children. A. BLAZSO (J. Physiol. Path. gén., 1936, 34, 120—135).—The urinary concn. and output of S and neutral S fraction per unit of body-wt. in infants were > in older children. Replacement of part of the (boiled or unboiled) mother's milk with cow's milk did not change the relative concns. of the S fractions. The total S in infant's faeces was very small and its concn. was the same as for a child. Of the S fractions, ethereal S was present in greatest concn. in the faeces of the child, whereas in infant's faeces neutral S was greater. In the fasting state the total S and S fractions of the blood-serum were the same for infants and older children. Inorg. S was 8—10 mg. per 100 ml. The ethereal S fraction was < the inorg.

NUTR. ABS. (*m*)

Bone formation. I. Normal bone formation and the constitution of mineral reserves during development. II. Rickets in the growing rat. A. ROCHE and I. GARCIA (Bull. Soc. Chim. biol., 1936, 18, 1014—1026, 1027—1040).—I. During ossification in the normal rat the ratio P/N of the femur and tibia diminishes slightly until the animals reach 25—30 g. wt. The ratio then increases to the original val. when the rats weigh 45 g., and after a short period when the val. is almost const., a steady increase takes place till the wt. reaches 150 g.

II. In young rats fed on a vitamin-D-deficient diet the femur and tibia show development of rachitic lesions until the 16th day. Spontaneous recovery then takes place, being complete after 55 days. These observations are associated with an increase in H₂O and N and a decrease in P and the ratio P/N, this being followed in the period of apparent recovery by normal vals. for H₂O and N, but low P. vals. A. L.

Electrolyte changes in muscle during activity. W. O. FENN and D. M. COBB (Amer. J. Physiol., 1936, 115, 345—356).—Stimulation of rat's muscles through the nerve causes exchange of about 15% of K⁺ for Na⁺, and increases in H₂O and extracellular NaCl, all these changes being reversed during recovery. Frog muscles lose K⁺ only when stimulated directly.

R. N. C.

Effect of fat on the p_{H} of the contents of the duodenum. J. E. THOMAS and J. O. CRIDER (Amer. J. Physiol., 1936, 114, 603—608).— p_{H} becomes neutral or slightly acid, probably through inhibition of gastric secretion and motility.

R. N. C.

Biological action of radiations. Selectivity factors. I. Time factor. J. PALACIOS and H. TÉLLEZ-PLASENCIA (Anal. Fís. Quím., 1934, 32, 677—681).—A theoretical study of the relative rates of destruction of normal and dividing cells.

F. R. G.

Comparative effects of X-rays and neutrons on normal and tumour tissue. J. H. LAWRENCE, P. C. ARBERSOLD, and E. O. LAWRENCE (Proc. Nat. Acad. Sci., 1936, 22, 543—557; cf. this vol., 632).—Per unit of ionisation produced, neutrons are three

times as effective as X-rays in causing the deaths of normal mice, and four times as effective in destroying sarcoma 180 *in vitro*. A marked fall occurs in the no. of white blood cells of mice exposed to either radiation, the min. occurring 4 days after irradiation.

F. A. A.

Radiation sensitivity of "Photodyn." G. KÖGEL (Strahlenther., 1935, 54, 182—184; Chem. Zentr., 1935, ii, 3795).—"Photodyn," a hæmatoporphyrin prep., is active only in the light. Its therapeutic use and a series of radiation experiments are described; it is most sensitive to yellow light.

H. N. R.

Liberation of an acetylcholine-like substance from surviving nerve fibres during electrical stimulation *in vitro*. G. BERGAMI (Boll. Soc. ital. Biol. sperim., 1936, 11, 275—277).—Stimulation of nerve-fibre (dog's vagus or phrenic) in eserine-Ringer's solution produces a substance which resembles acetylcholine in its action on leech-muscle preps.

F. O. H.

Survival of ascarid eggs after centrifuging. H. W. BEAMS and R. L. KING (Science, 1936, 84, 138).—Centrifuging at $1-4 \times 10^5 g$ does not kill eggs of *A. suum*. The killing of cells by centrifuging appears to be due to mechanical distortion or disruption rather than to a disturbance of the spatial relationship of their mol. parts.

L. S. T.

Circulatory and visual effects of oxygen at three atmospheres pressure. A. R. BEHNKE, H. S. FORBES, and E. P. MOTLEY (Amer. J. Physiol., 1936, 114, 436—442).

R. N. C.

Effect of carbon monoxide on recovery of frog skeletal muscle. J. B. HURSH (Amer. J. Physiol., 1936, 114, 625—634).—Excess O₂ consumption and recovery heat production of a stimulated muscle in air are decreased by placing in 79% CO and 21% O₂. The rate of fatigue is the same. Lactic acid (I) concn. is not increased, and the effect of CO is not diminished by CH₂I-CO₂H, indicating that CO does not inhibit oxidation of (I).

R. N. C.

Insensible water loss in relation to water ingestion in man. J. F. HALL, jun., and G. S. McCURE (Amer. J. Physiol., 1936, 115, 670—678).—Rate of insensible perspiration is not increased by ingestion of H₂O or 1% NaCl, or by injections of pituitrin, which, however, produce increases after H₂O ingestion. The rate is increased by ingestion of sucrose, and lowered by dehydration >6% of the body-H₂O.

R. N. C.

The periodic system and biological action. A. LENDLE (Chem.-Ztg., 1936, 60, 833—835).—A discussion.

Physiological effects of mineral salts in natural waters. C. B. POLLARD (J. Amer. Water Works Assoc., 1936, 28, 1038—1043).—A review.

Skeletal changes in rats induced by a diet extremely poor in inorganic salts. M. F. CLARKE, A. L. BASSIN, and A. H. SMITH (Amer. J. Physiol., 1936, 115, 556—563).

R. N. C.

Sodium deficiency [in animals]. H. E. HIMWICH, J. F. FAZIKAS, and M. A. SPIERS (Proc. Soc.

Exp. Biol. Med., 1936, **34**, 450—451).—Dogs, deprived of NaCl by intraperitoneal injection of glucose solutions, showed an increase in blood-urea and total solids, low serum-Cl', and a creatinuria.

W. O. K.

Colloidal potassium complexes.—See this vol., 1338.

Mechanism of the hæmatopoietic action of cobalt. J. M. ORTEN (Amer. J. Physiol., 1936, **114**, 414—422).—Co increases the rate of formation of hæmoglobin and erythrocytes without diminishing the rate of cell destruction.

R. N. C.

Hypoglycæmic and other actions of phosphotungstic acid, phosphomolybdic acid, and allied substances. H. N. MUKHERJEE (Biochem. J., 1936, **30**, 1583—1585).—0.2—0.3 g. of phosphotungstic (I), phosphomolybdic, molybdic, or silicotungstic acids, or Na tungstate, Na vanadate, or NH₄ phospho-18-tungstate, fed by stomach tube to rabbits, has a hypoglycæmic effect comparable with 0.6 unit of insulin. Some of these, especially (I), have a diuretic action. The hypoglycæmic and diuretic actions of (I) were also tested on human diabetic patients, with positive results. The hypoglycæmia lasts longer than that produced by insulin. These substances behave towards benzidine and alkaline phenolphthalein like oxidising enzymes.

F. A. A.

Ætiological studies on formation of skin blisters in viscose workers. W. C. HUEPER (J. Ind. Hyg., 1936, **18**, 432—447).—Blisters occurring on the fingers of doffers are caused by CS₂ in the drip. Protective measures are indicated.

J. N. A.

Changes in skin after cauterisation with dichlorodiethyl sulphide and mineral acids. I. DÖRFFEL and PÖPPING (Virchow's Arch., 1935, **295**, 1—20; Chem. Zentr., 1935, ii, 3945).

A. G. P.

Effect of dichlorodiethylsulphone on brain respiration. R. A. PETERS (Nature, 1936, **138**, 327—328).—The effect of (CH₂Cl-CH₂)₂SO₂ on brain respiration *in vitro* resembles in detail that of CH₂I-CO₂H (A., 1935, 262). The change of lactic acid to AcCO₂H (I) is unaffected, but the further oxidation of (I) is inhibited.

L. S. T.

Effect of 2:4-dinitrophenol (Thermol) on the gas metabolism of pigeons. Z. CATALDO (Boll. Soc. ital. Biol. sperim., 1932, **7**, 767—770; Chem. Zentr., 1935, ii, 3792).—Injection of 2:4-dinitrophenol (I) (<5 mg. per kg.) increases O₂ consumption. Atropine has little influence on this action although the birds become less resistant. During the action of (I) the R.Q. indicates that sugar is first consumed and when this process is well advanced fats are affected.

A. G. P.

Influence of temperature on stimulation of oxidation by dinitro-, dihalo-, and trihalo-phenols. M. E. KRAHL and G. H. A. CLOWES (Proc. Soc. Exp. Biol. Med., 1936, **34**, 567—569).—The stimulating action of 4:6-dinitro-*o*-cresol (I) on the eggs of *Arbacia punctulata* and *Nereis limbata* is max. at concns. of 4—8×10⁻⁶M, independently of the temp. The abs. increase is greatest and the relative increase least at the higher temp. The

optimum % increase in O₂ consumption of rat kidney slices in presence of 2:4:5-trichloro-, 2:4-dichloro-, and 2:4:6-tri-iodo-phenol and (I) at 20° is > at 37°.

W. O. K.

Toxicity and action on guinea-pigs of synthetic *l*-camphor. R. HAZARD and R. LARDÉ (J. Pharm. Chim., 1936, [viii], **24**, 118—120).—The toxicities of the three stereoisomeric camphors are in the order *l*>*dl*>*d*.

W. O. K.

Derivatives of β-amino-α-hydroxy-α-phenylpropionic acid [pharmacological properties].—See this vol., 1377.

Biological analogy of bile acids and sterols. Influence of bile salts on growth and morphogenesis of tadpoles. D. ZIMMET (Arch. Sci. phys. nat., 1936, [v], **18**, Suppl., 136—137).—Na glyco- and tauro-cholate accelerate growth and morphogenesis in the same way as cholesterol.

G. H. B.

Influence of amino-acids on blood-sugar regulation in dogs with Eck fistulæ. L. KESZTYŰS and J. MARTIN (Arch. exp. Path. Pharm., 1936, **182**, 514—520).—Arginine, cystine, and tyrosine increase the blood-sugar of dogs with fistulæ. The inactivity of these NH₂-acids in normal dogs is due to rapid decomp. in the liver. Injection of glycine into normal dogs produces a hyperglycæmia followed after 1 hr. by a hypoglycæmia, probably due to adrenaline- followed by a compensatory insulin-action.

F. O. H.

Rôle of choline in removable shock in the guinea-pig's heart. S. WENT and K. LISSÁK (Arch. exp. Path. Pharm., 1936, **182**, 509—513).—During anaphylactic shock (ox serum) in the isolated, surviving heart, perfusates acquire a slowing action (inhibited by atropine) on the frog's heart but are inactive on leech preps.; acetylation of the perfusates produces a typical acetylcholine activity (frog's heart, leech). The choline content (to which the behaviour of the heart during shock is due) of the heart decreases after shock but the histamine content remains unchanged.

F. O. H.

Comparative effects of pancreas and choline on blood-cholesterol of depancreatized dogs maintained with insulin. I. L. CHAIKOFF and A. KAPLAN (Proc. Soc. Exp. Biol. Med., 1936, **34**, 413—416).—Oral administration of raw pancreas to depancreatized dogs on a suitable basic diet increased their abnormally low blood-cholesterol, but choline in quantities > the amounts present in the lecithin of the raw pancreas was without appreciable effect.

W. O. K.

Effect of acetylcholine on the blood-flow through the stomach and legs of the rat. H. NECHELES, R. FRANK, W. KAY, and E. ROSENMAN (Amer. J. Physiol., 1936, **114**, 695—699).

R. N. C.

Blood-amylase response to acetyl-β-methylcholine chloride in rabbits. A. SCHIFFRIN, L. TUCHMAN, and W. ANTOPOL (Proc. Soc. Exp. Biol. Med., 1936, **34**, 539—540).—In rabbits there is usually but not always a marked increase in blood-amylase after intramuscular injection of acetyl-β-methylcholine chloride.

W. O. K.

Chemical transmission of vagal effects to the small intestine. H. BUNTING, W. J. MEEK, and C. A. MAASKE (Amer. J. Physiol., 1935, 114, 100—105).—Vagal stimulation results in the formation of an acetylcholine-like substance in the splanchnic area. It comes partly from the small intestine, from which it can be removed by perfusion.

R. N. C.

Action of the nitrogenous bases of the gastric juice on blood-pressure, pancreatic secretion, and flow of bile. S. A. KOMAROV (Amer. J. Physiol., 1936, 115, 604—609).—The arginine fraction from canine gastric juice exhibits a histamine-like action on blood-pressure and pancreatic secretion. The lysine fraction increases blood-pressure and stimulates pancreatic and bile flow. The histidine fraction is without effect.

R. N. C.

Physiological importance in nutrition of methods of preparation of foodstuffs. I. Influence of roasting with coffee, coffee substitutes, and similar products. B. BLEYER, W. DIEMAIR, F. FISCHLER, K. TAÜFEL, F. ARNOLD, and H. THALER (Biochem. Z., 1936, 286, 408—428).—The production during roasting of coffee, chicory, wheat, etc. of histamine-like substances is detected chemically and confirmed by biological test on guinea-pig's intestine.

P. W. C.

Action of tyramine in increasing blood pressure in pallid hypertension. H. A. HEINSEN and H. J. WOLF (Z. klin. Med., 1935, 128, 213—222; Chem. Zentr., 1935, ii, 3945).—In chronic nephritis and in malignant nephrosclerosis, tyramine occurs in the blood. It is formed in kidneys by decarboxylation of tyrosine.

A. G. P.

Humoral anti-adrenaline regulation. B. TARAS-WAHLBERG (Klin. Woch., 1935, 14, 793—795; Chem. Zentr., 1935, ii, 3789).—Rabbit and guinea-pig blood contains a substance which causes contraction of the small intestine of guinea-pigs and a decreased blood-pressure in atropinised rabbits. It is dialysable and more resistant to boiling 0.5N-HCl than to 0.5N-NaOH. The activity of the blood is increased by pre-injection of adrenaline.

A. G. P.

Anti-pernicious anæmia principle in stomach. I. Method to improve stomach preparations. E. A. GREENSPON (J. Amer. Med. Assoc., 1936, 106, 266—271).—No response was produced by 40 g. of ventriculin mixed with 200 ml. of H₂O, 0.1 g. of pepsin (I), and dil. HCl and incubated at 38° overnight, when fed to a patient with pernicious anæmia in relapse. Depepsinised gastric mucosa produced a marked reticulocyte response in a case of pernicious anæmia. The activity was destroyed by incubation with (I) and HCl, but not with HCl alone. Since a reticulocyte response was produced in a case of pernicious anæmia by daily oral administration of 250 ml. of normal gastric juice freed from (I) and since a single intramuscular injection of the concentrate of 540 ml. of normal gastric juice freed from (I) produced in 2 cases of pernicious anæmia reticulocyte crises of 24.5 and 21% and increases in the red cell count of 1.8 and 1.6 millions, respectively, it is concluded that (I) destroys the active principle of

the mucosa and that the presence of an "extrinsic factor" is unnecessary in the production of the principle.

NUTR. ABS. (m)

Comparison of the action of insulin and of the hypoglycæmic principle of the jejunum in the pancreatetectomised dog. F. RATHERY, A. CHOAY, and P. DE TRAVERSE (Compt. rend., 1936, 203, 206—208).—Equiv. doses (tested on a rabbit) of an extract (cf. this vol., 1158) of the jejunum of the ox and of insulin injected intramuscularly produce almost identical decreases in the concn. of the blood-sugar of a depancreatized dog; the duration of action of the former is more prolonged.

J. L. D.

Comparative effects of barbituric acid derivatives on isolated heart. R. L. JOHNSTON (J. Pharm. Exp. Ther., 1936, 57, 333—336).—Perfusion of the isolated turtle heart with the Na salts of the following barbituric acid derivatives (concn. 0.0005M) in Ringer's solution at p_H 7.2—7.4 showed that the toxicity decreased in the order: ortal, amytal, nembutal, evipal, phenobarbital, phanodorm, barbital.

J. N. A.

Detoxification of dendrobine by "sodium amytal." K. K. CHEN and C. L. ROSE (Proc. Soc. Exp. Biol. Med., 1936, 34, 553—554).—Na amytal administered to rabbits poisoned by dendrobine hydrochloride can antidote up to 5 min. lethal doses of the alkaloid.

W. O. K.

Anæsthetic properties of "sodium ethylpentylmalonylthiourea." M. G. MULINOS (Proc. Soc. Exp. Biol. Med., 1936, 34, 506—507).—Na ethylmalonylthiobarbiturate (Na pentothal) has a pharmacological action resembling its O-analogue (Na pentobarbital).

W. O. K.

Elimination of cobalt in the bile. F. CAUJOLLE (Bull. Soc. Chim. biol., 1936, 18, 1081—1090).—In dogs under chloralose anæsthesia 3.2% of aq. CoCl₂ injected intravenously is eliminated rapidly in the bile. With a permanent fistula and no anæsthetic the elimination is less rapid.

A. L.

Anæsthetic effects of furan derivatives. V. E. HENDERSON and A. H. R. SMITH (J. Pharm. Exp. Ther., 1936, 57, 394—398).—Furan and its H₄, Me₂, and dimethyltetrahydro-derivatives are of no clinical val. as anæsthetics; the first three produce fatty changes in the liver, a possible mechanism of which is discussed.

J. N. A.

Fishes as test subjects for the biological action of various substances and for the determination of the nature of urease. N. KAWAMOTO (J. Biochem. Japan, 1936, 23, 267—298).—Saponin, adrenaline, and atropine are readily absorbed through the gills of carp in which they exert their characteristic action. The action on the blood-sugar of normal and dialysed aq. insulin thus administered indicates the presence of hyper- and hypo-glycæmic fractions. The gills are impermeable to normal urease preps. but are permeable to tryptically digested preps., whilst on prolonged digestion the activity disappears; the data indicate that urease has a polypeptide structure.

F. O. H.

Destruction of cardio-active glucosides by acids and alkalis. F. T. VON BRÜCKE (Arch. exp.

Path. Pharm., 1936, 182, 444—451).—Data of the action of 0.05—0.1*N*-HCl and -NaOH and of 0.1% Na₂CO₃ at 37° on *Digitalis* glucosides, *g*- and *k*-strophanthin, and cymarin are tabulated. The glucosides are not affected by trypsin or pepsin but are inactivated at gastric acidity and, very slowly, at duodenal alkalinity; decomp. occurs with 0.05—0.1*N*-NaOH at 37°. F. O. H.

Decurarising substances. A. ROSENBLUETH, D. B. LINDSLEY, and R. S. MORISON (Amer. J. Physiol., 1936, 115, 53—68). R. N. C.

Esmodil, a new vagus-stimulant. G. HECHT (Klin. Woch., 1935, 14, 957—958; Chem. Zentr., 1935, ii, 3945).—Esmodil, CH₂:C(OMe)·CH₂·NMe₃Br, is not enzymically decomposed in the organism and is stable in dil. alkali but not in dil. acid. Physiological activities are described. A. G. P.

Pharmacological action of coriamyrtin. (A). A. H. MALONEY. (B). E. E. SWANSON and K. K. CHEN (J. Pharm. Exp. Ther., 1936, 57, 361—375; 410—418).—(A) The min. lethal doses of coriamyrtin (I) for the frog, rabbit, and rat are 10, 0.4, and 1 mg. per kg., respectively. (I) increases the blood-sugar of the rabbit by 13%, has very little effect on blood pressure, but powerfully stimulates respiration. (I) is very toxic, and resembles picrotoxin in its action, which is of very short duration.

(B) (I) abolishes anaesthesia and wakens animals under the influence of a barbiturate. Na amytal is far more effective in combating (I) poisoning than is (I) in counteracting Na amytal poisoning. J. N. A.

Stereoisomeric nature of oxidation and fermentation. G. A. GAUSE (Nature, 1936, 138, 245—246).—The fermentations of glucose by different micro-organisms are more strongly depressed by *l*- than by *d*-nicotine, but the oxidations are more strongly depressed by the *d*-form. In green algae oxidations are direct and sensitive to *d*-nicotine poisoning, but in the frog, fowl, green linnet, etc. oxidations are coupled with fermentations and are more sensitive to the action of *l*-nicotine. The action of the optically-active nictines on the metabolism of mouse tissue is also described. L. S. T.

Effect of atropine and pilocarpine on the emptying time of the human stomach. R. C. HERRIN (Amer. J. Physiol., 1936, 115, 104—112). R. N. C.

Effect of atropine and pilocarpine on gastric emptying in normal and denervated dogs. R. C. HERRIN, A. RABIN, and E. A. BACHHUBER (Amer. J. Physiol., 1936, 115, 113—120). R. N. C.

Blood-sugar level after administration of pilocarpine, atropine, and acetylcholine. M. C. HRUBETZ (Amer. J. Physiol., 1936, 114, 551—554).—Pilocarpine (I) raises blood-sugar (II) in rats, the max. occurring in 15 min. Atropine lowers (II), the max. effect occurring in 90 min., and inhibits the effect of (I). Acetylcholine lowers (II), the min. val. being reached in 20 min. R. N. C.

Action of drugs on choline esterase of brain. F. BERNHEIM and M. L. C. BERNHEIM (J. Pharm. Exp. Ther., 1936, 57, 427—436).—Choline esterase

(I) is greatly inhibited by very small concns. of morphine and apomorphine, and it is suggested that these and possibly other centrally acting drugs may cause accumulation of acetylcholine in brain by inhibiting (I). In most animals the activity of (I) per mg. of dry wt. is greater in the brain than in the serum. J. N. A.

Comparative action of methylephedrine and ephedrine. I. Systemic effects. II. Bronchial effects. C. PAK and B. E. READ (Quart. J. Pharm., 1936, 9, 235—255, 256—267).—I. The circulatory effect of methylephedrine (I) is similar to but < that of ephedrine (II). (I) has an inhibitory effect (probably due to pressor action) on respiration but not the secondary accelerating action of (II). (I) does not stimulate the central nervous system, whilst the toxic effect on rabbits and dogs and dilation of the pupil are < those due to equal doses of (II). Other differences in pharmacological action are described.

II. The bronchial dilator effect of (I) in anaesthetised cats is slower than, but the intensity and duration are approx. equal to, that of (II). (I) and (II) in concns. of 10⁻²—10⁻³% respectively dilate and constrict the isolated bronchioles. F. O. H.

Substituted hydroxybenzyl alcohols.—See this vol., 1374.

Excretion of "skiodan," "diodrast," and "hippuran" by the dog. K. A. ELSOM, P. A. BOTT, and E. H. SHIELDS (Amer. J. Physiol., 1936, 115, 548—555).—Skiodan excretion is independent of its concn. in the plasma, and consistently < that of creatinine (I) by approx. 10%. Diodrast and hippuran excretions depend on their concns. in the plasma. Their clearances are approx. equal to that of (I) at high but greater at low plasma-I. R. N. C.

Effect of various poisons on the movement of chloride against concentration gradients from intestine to plasma. R. C. INGRAHAM and M. B. VISSCHER (Amer. J. Physiol., 1936, 114, 681—687).—Removal of Cl⁻ in presence of SO₄⁻ is abolished by Na₃AsO₃, NaF, H₂S, HgCl₂, and NaCN, in presence of which Cl⁻ moves into the intestine; the increases in [Na⁺] and [SO₄⁻] are also abolished or reversed. Impermeability of the intestinal epithelium to bi- or multi-valent anions is apparently a condition for its performing osmotic work on Cl⁻. R. N. C.

[Pharmacological] action of arsenic and antimony. H. A. OELKERS and E. VINCKE (Arch. exp. Path. Pharm., 1936, 182, 499—503).—The *in-vivo* (rabbits) reduction of oxalacetic to fumaric acid is inhibited by KAsO₃ and K Sb tartrate (cf. Szent-Györgyi *et al.*, A., 1935, 1406), which also diminish the O₂ consumption of liver tissue *in vitro*. Thus the toxic action of As and Sb is mainly due to disturbances of tissue- and organ-metabolism. F. O. H.

Influence of vitamin deficiency on the resistance of rats to neoarsphenamine, mercurochrome, pernocton, and insulin. R. WIEN (Quart. J. Pharm., 1936, 9, 268—297).—The resistance to the toxicity of the three drugs is diminished by deficiency of vitamin-A, -B complex, or -D; that to insulin, as indicated by the blood-sugar curve after injection

of 0.5 unit per kg., is unaltered by deficiency of -A or -D whilst with B-avitaminosis, rats (which have normal fasting blood-sugar vals.) are more sensitive owing to a retardation in the recovery process.

F. O. H.

Antidotal action of magnesium, hydrazine, and phenylhydrazine thioacetates, and hydrazine sulphate in mercurial poisoning. G. DE NITO (Boll. Soc. ital. Biol. sperim., 1936, 11, 323—324).—Enteral, but not parenteral, administration has a significant antidotal action.

F. O. H.

Limitation of fluorine toxicosis in the rat with aluminium chloride. G. R. SHARPLESS (Proc. Soc. Exp. Biol. Med., 1936, 34, 562—564).—The toxic effect of NaF *per os* on the growth and teeth of young rats is antagonised by the addition to the diet of small quantities of $AlCl_3$.

W. O. K.

Poisoning by vapours of beryllium oxyfluoride. I. GELMAN (J. Ind. Hyg., 1936, 18, 371—379).—The toxic effects in man include fever followed after 2—5 days by lung lesions. The symptoms differ from those observed in cases of poisoning by F, HF, SO_2 , or Be oxyfluoride in the form of dust.

J. N. A.

Lead absorption in man. III. Blood-pressure observations. E. L. BELKNAP (J. Ind. Hyg., 1936, 18, 380—390).—The average blood pressures of 81 workers with a heavy Pb absorption varied within normal limits, but tended to decrease slightly over a period of 1—5 years. There was no significant increase in systolic or diastolic pressure.

J. N. A.

Lead in muscle and skin of cattle showing saturnism. KOHN-ABREST (Bull. Acad. vét. France, 1936, 9, 122—123).—Muscles from 3 cattle slaughtered on account of saturnism contained only traces of Pb, but the skins contained 25—40 p.p.m., vals. similar to those reported in fatal cases of saturnism in human beings.

NITR. ABS. (*m*)

Toxicology of selenium. I. Distribution of selenium in acute and chronic selenium poisoning. II. Urinary excretion of selenium. H. C. DUDLEY (Amer. J. Hyg., 1936, 23, 169—180, 181—186).—I. In acute or chronic poisoning induced by feeding inorg. or org. Se compounds Se was found throughout the whole organism. The Se was distributed by the blood, being held chiefly in a protein-like complex. The serum, plasma, and fibrin did not contain Se, but it was present in the centrifuged corpuscles and the clot. It was largely deposited in the liver, kidneys, and spleen in acute cases and in the liver and kidneys in chronic cases. The amounts present in the bile and urine indicated that excretion was mainly by hepatic and renal routes. In the urine the Se was present as an Et_2O -sol., volatile compound. In chronic cases in pigs, 8—20 p.p.m. of Se were found in the hoofs.

II. The urine of men engaged in or near the extraction and processing of Se from electrode slimes in a Cu refinery contained up to 0.069 p.p.m. of Se. The urinary Se in different individuals showed no correlation with the intensity of the symptoms.

NUTR. ABS. (*m*)

Monstrosities produced by the injection of selenium salts into hens' eggs. K. W. FRANKE, A. L. MOXON, W. E. POLEY, and W. C. TULLY (Anat. Rec., 1936, 65, 15—22).—The monstrosities resemble those produced when the hens are fed on wheat containing Se. As, F, and Pb in sublethal doses have no such action.

R. N. C.

Inhibiting effect of sulphur in selenised soil on toxicity of wheat to rats.—See B., 1936, 1011.

Toxicological detection of hydrocyanic acid. Detection of poisoning by very small amounts of hydrocyanic acid. P. R. ORELLA (An. Farm. Bioquim., 1935, 6, 1—11; Chem. Zentr., 1935, ii, 3804).—HCN is best fixed for toxicological analyses by means of $AgNO_3$. The formation of HCN in normal tissues by putrefaction or by the action of $H_2SO_4-H_2CrO_4$ does not occur.

J. S. A.

Toxicity of dioxan. H. H. SCHRENK and W. P. YANT (J. Ind. Hyg., 1936, 18, 448—460).—A *résumé* of work by various investigators. Animal experiments show that the toxicity of dioxan when absorbed through the skin, inhaled, ingested, or given by subcutaneous or intravenous injection is comparatively low, but large doses cause serious harm, the principal damage being to the kidneys and liver.

J. N. A.

Toxicology of Derris.—See B., 1936, 1013.

Lactucarium. II. Enzymes of the sap of *Lactuca virosa*. K. H. BAUER and K. BRUNNER (Pharm. Zentr., 1936, 77, 598—601; cf. A., 1929, 1181).—The fresh sap darkens unless placed immediately in 96% EtOH. The EtOH ppts. amongst other substances two oxidases, a tyrosinase and a laccase, which are almost or entirely absent from the commercial dried sap (lactucarium).

R. S. C.

Enzymes in ontogenesis (Orthoptera). II. The indophenol oxidase. J. H. BODINE and E. J. BOELL (J. Cell. Comp. Physiol., 1936, 8, 213—230).—The indophenol oxidase (I) content of grasshopper eggs has been determined throughout development. The CN' -sensitive respiratory mechanism of the eggs is dependent on, whilst (I) activity is independent of, organisation in the cells. Respiration during diapause is insensitive to CN' , and is unaffected by grinding. As (I) activity shows no diminution during this period, there can be no relation between the normal functioning of (I) and its action in the *in-vitro* oxidation of $p-C_6H_4(NH_2)_2$.

E. A. H. R.

Oxidation product of pyrocatechol when oxidised by means of tyrosinase. H. WAGREICH and J. M. NELSON (J. Biol. Chem., 1936, 115, 459—465).—Two O atoms are concerned in the oxidation of $o-C_6H_4(OH)_2$ (I) in the presence of tyrosinase (II) over the pH range 4.3—8. If the reaction is carried out in the presence of NH_2Ph , a dianilinobenzoquinone (III) is formed, and 3 O are used, over the pH range 4.3—7. If NH_2Ph is added to the oxidised (I), (III) is formed, one O being consumed; this reaction is catalysed by (II). The data indicate that the initial oxidation of (I) involves 2 O per mol.

F. A. A.

Peroxidases. III. Potentiometric determination of activity. B. B. DEY, S. RENGACHARI, and M. V. SITHARAMAN (J. Indian Chem. Soc., 1936,

13, 390—398).—The titration of mixtures of quinol and H_2O_2 against $Ce(SO_4)_2$ cannot be followed potentiometrically (cf. A., 1929, 783; 1930, 727) although H_2O_2 can be determined alone in HCl or AcOH. In determining the peroxidase (I) concn. in plant sap (A., 1931, 1455) this method cannot be used because the reducing substances in sap are oxidised. $Na_2S_2O_3$ and $K_2Cr_2O_7$ can be employed successfully to determine quinol potentiometrically and hence to arrive at the (I) concn. J. L. D.

Poisoning with copper and reactivation in enzymic oxidation-reduction. B. ANDERSSON (Z. physiol. Chem., 1936, 242, 205—209).—Although partly purified cozymase (I), xanthine, and uric acid reactivate the Schardinger enzyme system after poisoning with $CuSO_4$ (cf. Wagner-Jauregg *et al.*, this vol., 895), no reactivation is produced by highly purified (I). W. McC.

Catalytic action of lactoflavin-5'-phosphoric acid. Synthesis of the yellow enzyme. R. KUHN and H. RUDY (Ber., 1936, 69, [B], 1974—1977).—Synthetic lactoflavin-5'-phosphoric acid reacts in neutral solution with the colloidal carrier of Warburg's yellow enzyme forming a non-fluorescent, non-dialysable chromoprotein resolved into its components by dil. acid. The product catalyses the oxidation of the Neuberg or Robison ester, measured by decolorisation of methylene-blue or absorption of O_2 , in exactly the same manner as the natural material. The theory that an enzyme consists of a colloidal carrier and a chemically active group is thus strongly supported and the very sp. type of union is shown by the necessity for $\cdot PO(OH)_2$ at 5' and the flavin nucleus and NH at 3 for partial union with the carrier. H. W.

Components of dehydrogenase systems. XIII. Non-identity of alcohol- and triosephosphoric acid-apodehydrogenases. H. VON EULER, E. ADLER, and S. KYRNING (Z. physiol. Chem., 1936, 242, 215—224; cf. this vol., 1150).—The apodehydrogenase (I) obtained from yeast maceration juice by fractional pptn. with $(NH_4)_2SO_4$, and supplemented with cozymase (II) and flavin enzyme, specifically dehydrogenates EtOH anaerobically [methylene-blue (III) as acceptor] but has no action on dihydroxyacetonephosphoric acid (IV). Hence (I) of EtOH is not identical with (I) of (IV) although both always occur together in non-purified enzyme preps. Both apodehydrogenases combine specifically with (II), which carries H from the donator to the acceptor system. Decolorisation of (III) with hexosediphosphoric acid as substrate occurs only when zymohehexase and (I) of (IV) are present together. (I) specificity probably extends to triosephosphoric acids other than (IV) and hence is significant for the oxidation-reduction mechanism of alcoholic fermentation. W. McC.

Enzymic dehydrogenation of trideuterioacetic acid. R. SONDERHOFF and H. THOMAS (Naturwiss., 1936, 24, 570).—The oxidation of $CD_3\cdot CO_2Na$ by O_2 in presence of yeast cells proceeds at $\frac{1}{2}$ of the rate observed with $NaOAc$. In both cases some of the acetate is incorporated into the cells as carbohydrate and fat, whilst succinic acid is also formed. During

the oxidation of $(CD_3\cdot CO_2)_2Ba$ citric acid is formed. The succinic acid is not pure $(CD_2\cdot CO_2H)_2$, but some replacement of D with H occurs. Similarly the citric acid contains a lower ratio of D/H than corresponds with $HO\cdot C(CD_2\cdot CO_2H)_2\cdot CO_2H$. This confirms the theory of Wieland and Sonderhoff. W. O. K.

Amylase system of rice grain during ripening and germination. K. V. GIRI and A. SREENIVASAN (Nature, 1936, 138, 406—407).—Rice grain contains both α - and β -amylases, which are differentiated by their hydrolysis of amyloamylose and by their p_H optima at 7.0 and 4.6, respectively. Both enzymes are present in dormant seed, largely in a condition not extractable by H_2O , but extractable in an active state by PO_4''' buffer at p_H 7.0. α -Amylase becomes inactive as ripening advances and then active again during germination. The view that amylase arises only during germination of the grains (A., 1933, 1343) is untenable. L. S. T.

Enzymic studies on cereals. V. Saccharifying amylose of well-cleaned rice. VI. Saccharifying amylose of well-cleaned rice. G. YAMAGISHI (J. Agric. Chem. Soc. Japan, 1936, 12, 783—792, 793—799).—V. The optimum p_H of the saccharifying amylose (I) (obtained by extraction with H_2O at approx. 0° for 10 hr.) from unhusked and uncleaned rice and rice bran are 5.0, 4.7, and 6.6, respectively. Purification by dialysis or pptn. with EtOH moves the optimum more to the acid side. The optimum temp. for (I) is 45° . (I) is heat-sensitive.

VI. The optimum p_H vals. of (I) extracted from well-cleaned rice flour with NaCl or papain solutions, and then purified by dialysis or pptn. with EtOH, are 4.5 and 4.3, respectively. In the outer part of the grain nearly all of (I) is readily sol. in H_2O , but in the inner part it is present in an insol. form as (I)-zymogen. J. N. A.

Inulinase. N. K. IYENGAR and M. SREENIVASAYA (Proc. Indian Acad. Sci., 1936, 4, B, 171—177).—Active preps. of inulinase (I) are obtained from species of *Aspergillus* growing on an artichoke medium. PO_4''' stimulates the production of (I) by the mould. The preps. may be dried by $COMe_2$, and (I) is extracted from the dried material by PhMe-saturated H_2O . The content and activity of (I) in dried preps. and extracts are directly related to their P but not to their total or NH_2 -N contents. A. G. P.

Maltase activity of the blood-serum of various species. R. H. BARNES and E. M. MACKAY (Amer. J. Physiol., 1936, 114, 534—537).—Sera from a no. of species show maltase activity, which explains why insulin hypoglycæmia is relieved by maltase or glycogen in these species only. R. N. C.

β -Glycuronosidase. III, IV. G. OSHIMA (J. Biochem. Japan, 1936, 23, 305—311, 311—318; cf. A., 1935, 402).—III. The enzyme is prepared from autolysed extracts of ox spleen by adsorption on kaolin at p_H 2.6—4.4 and elution with $M/15-Na_2HPO_4$.

IV. The optimum p_H is 5.0—5.2 with menthol glycuronate in OAc' buffer as substrate, the reaction being unimol. and having an average temp. coeff. of 2.66 at 30 — 45° and a heat of inactivation of 36.34

kg.-cal. Ultra-violet irradiation inhibits whilst addition of neutral salts accelerates the hydrolysis. The inhibitory action of malic, tartaric, and citric acids and the accelerating action of AcOH, EtCO₂H, Pr^cCO₂H, and lactic acid are correlated with the presence or absence of β-OH. F. O. H.

Glucosulphatase, an enzyme decomposing sulphuric esters of sugars. T. SODA (J. Fac. Sci. Tokyo, 1936, I, 3, 149—222).—Data indicating the content of glucosulphatase (A., 1933, 534), phosphatase, and phenolsulphatase in various classes of molluscs are tabulated. Glucosulphatase (optimum p_H approx. 5; reaction consts. of purified preps. given) has a temp. coeff. of approx. 2 over the range 15—30°, is rapidly inactivated at 80°, and is inhibited to varying extents by sugars and their derivatives (A., 1933, 749; 1934, 560). The physiological rôle of the enzyme is discussed (see also A., 1934, 520; this vol., 378). F. O. H.

Reduction of cozymase. E. ADLER, H. HELLSTRÖM, and H. VON EULER (Z. physiol. Chem., 1936, 242, 225—249; cf. this vol., 1150).—Cozymase (I) is converted by alkaline Na₂S₂O₄ into a yellow substance (II) (absorption max. at 360 mμ) which is quantitatively reconverted into (I) on neutralising or acidifying. Na₂S₂O₄ at p_H 7.5—8.0 and sp. apodehydrogenase (III) in presence of a H donor convert (I) into dihydrocozymase (IV) with intermediate transient production of (II). When (IV) is acidified 20% is reconverted into (I) and 80% into an inactive substance. (IV) is completely reconverted into (II) by flavin enzyme in presence of O₂ and by sp. (III) in presence of H acceptor (MeCHO). (I) is not reduced by Zn in 0.1N-NaOH but is rapidly attacked in N-NaOH with production of a yellow colour. (IV) is not attacked by 0.1N-NaOH at 100° in 30 min. but is slowly reconverted into (I) on keeping, the p_H optimum for the change being 6. (II) rapidly reduces methylene-blue and AgNO₃, whereas (IV) reduces AgNO₃ only very slowly. Possibly the reduction of (I) to (IV) takes place at the N:C linking which joins the C₅H₅N group to the rest of the mol. This linking is probably the only one in the mol. which is unstable to alkali and is also partly responsible for the fermenting power. W. McC.

Re-phosphorylation in presence of cozymase. H. VON EULER, R. VESTIN, and H. HEIWINKEL (Svensk Kem. Tidskr., 1936, 48, 176—183).—In the system, dialysed and aged muscle extract (rabbit)-Mg-phosphocreatine (I), a pyrophosphate (II) fraction is formed by use of (I) in presence of a sufficient amount of a cozymase prep. (III). This action is observed with all samples of (III), independently of method of prep. and degree of purity with the exception of those purified by pptn. with EtOAc from MeOH-HCl. Products isolated as Ag salts from (III) inactivated by heating with alkali are capable of forming (II). Apparently only 20—25% of (III) is utilised in production of (II). Yields are not increased by increase in temp. or concn. of (I) or (III) or by diminishing the acidity of the solution. Re-esterification takes place rapidly. The (II) produced is freed from a large excess of (I) and (III) by pptn. with metals as used in the isolation of adenosine

triphosphate (IV). It is not formed by the addition of the P₂O₇ group to the cozymase mol.; possibly it contains (IV). The substance which acts as substrate in the formation of (II) is probably not identical with cozymase. H. W.

Cozymase pyrophosphate. O. MEYERHOF and W. KIESSLING (Naturwiss., 1936, 24, 557—558; cf. this vol., 1026).—Cozymase pyrophosphate (I) has been prepared in purer form; there are 8 N in the mol. to 4 P and 25 C. (I) is not deaminated by inactivated muscle extract. Fermentation by washed, dried yeast is activated more by (I) than by the same amount of cozymase. E. A. H. R.

Characterisation of sugarphosphoric acids and constitution of the pentosephosphoric acid from cozymase.—See this vol., 1364.

Glyoxalase and its co-enzyme. III. Mechanism of the action of glutathione as co-enzyme. S. YAMAZOYE (J. Biochem. Japan, 1936, 23, 319—334; cf. this vol., 895).—Before conversion into lactic acid (I) and in presence of glyoxalase, AcCHO combines (1:1) with glutathione (II). The compound AcCHO-(II) (isolated as a crude prep., stable to I) is stable in acid solution, decomp. in neutral or, more rapidly, alkaline media to (I)+(II), a reaction catalysed by glyoxalase. In absence of glyoxalase, AcCHO and (II) form a labile complex, readily hydrolysed in neutral or alkaline media to AcCHO and (II) [(I) is not formed] and decomposed by I. F. O. H.

Optical properties of fermentation lactic acids. IV. New enzyme racemise which reveals racemisation of lactic acids. H. KATAGIRI and K. KITAHARA (J. Agric. Chem. Soc. Japan, 1936, 12, 844—852).—With *Lactobacillus plantarum* and *L. pentoceticus* (dl-formers) in a medium containing PhMe and Ca lactate, the velocity of racemisation was high and identical for both forms of the acid. Racemisation of *d*- or *l*-lactic acid or selective decomp. of the *r*-acid was never observed with *L. Sake* (*d*-former) and *Leuconostoc mesenteroides* (*l*-former), even in their resting state. The activity of racemise is only slightly affected by PhMe, but it is sensitive to high temp. (inactivated at 80°). J. N. A.

Substance controlling hydrolysing and synthesising actions of lipase. I. R. ITOH (J. Biochem. Japan, 1936, 23, 299—304).—A detailed account of work already noted (this vol., 895). F. O. H.

Influence of monochromatic light on action of the fat-splitting enzyme in yeast. R. MURAKAMI (J. Agric. Chem. Soc. Japan, 1936, 12, 709—713).—The rate of hydrolysis of castor oil by the enzyme from yeast is increased in monochromatic light, the effect increasing with λ. The rate of hydrolysis is inversely ∝ light intensity. J. N. A.

Absolute activity of choline esterase. L. H. EASSON and E. STEDMAN (Proc. Roy. Soc., 1936, B, 121, 142—164).—The relative rates at which choline esterase (I) hydrolyses choline esters have been compared with the rates for the non-enzymic hydrolysis. This latter rate approx. ∝ [OH⁻] and decreases with increase in the size of the aliphatic acyl group. The rate of enzymic hydrolysis, with *n*-acids, in-

creases with the size of the acyl group, but the introduction of a side-chain diminishes the rate. The influence of p_H on (I) depends on the substrate. For most esters the p_H optimum is >8 . Within the range p_H 6.8—8.0 the hydrolysis of benzoylcholine is uninfluenced by p_H . The inhibitory action of miotine (II) on (I) is const. for the different substrates. (II) is unstable in aq. solution. Prostigmine is stable, and its inhibitory action is used to determine the abs. rate of activity of (I). Under nearly optimal conditions one active centre of (I) hydrolyses 3500 mols. of butyrylcholine and 1490 of acetylcholine per sec. The following β -bromoethyl esters were prepared: *formate*, b.p. 147—148°; *propionate*, b.p. 170—175° (slight decomp.), 73—74°/16 mm.; *n*-, b.p. 82.5°/11 mm., and *iso-butyrate*, b.p. 79°/11 mm. The β -bromoethyl esters with a slight excess of NMe_3 gave *formyl*-, m.p. 142°, *propionyl*-, m.p. 146°, *n-butyryl*-, m.p. 100—101°, and *isobutyryl*-, m.p. 127°, *-choline bromide*.
E. A. H. R.

Optical specificity and activation of arginase. S. EDLBACHER and A. ZELLER (*Z. physiol. Chem.*, 1936, 242, 253—260).—Arginase (I) in concns. usually employed hydrolyses *d*-arginine (II) but not *l*-arginine (III) but when the concn. is greatly multiplied (e.g., 1000-fold) (III) also is quantitatively converted into urea and ornithine. The (I) of pigeon's muscle and kidney and hen's kidney is activated by Mn^{++} , the action on (II) but not that on (III) being affected. NH_2 -acids (ornithine $>$ lysine $>$ glycine $>$ alanine) check the action of (I) on (II) and (III).
W. McC.

Proteolytic enzymes of sprouted wheat. II. J. D. MOUNFIELD (*Biochem. J.*, 1936, 30, 1778—1786; cf. this vol., 637).—In germinating wheat seeds proteinase (I) activity increases tenfold in 7 days at 18° after a lag of 2 days. When the seeds are stored in the dark at 18° power to develop (I) activity on germination steadily decreases, the decrease amounting to about 67% in 2 years. In aq. solution all dipeptidase (II) activity is lost in 5 days at 18° but in 45% aq. glycerol (III) the original level of activity is maintained for 21 days. (I) is stable at p_H 4 and 6 but is destroyed at p_H 8 in <3 days at 18° and (II) is fairly stable at p_H 6 and 8 but is destroyed at once at p_H 4. (III) probably acts by maintaining the original p_H of 6; in aq. extracts the p_H falls to 4—5 in 1—2 days. $NaCN$ activates (I) and (II), the increase in activity being about 60% for (I) with edestin as substrate (max. requirement of $NaCN$ 0.001*M*), the optimal p_H being shifted from 4.1 to 4.8. (II) is less affected but the optimal p_H is shifted also from 7.3 to 7.8 with leucylglycine as substrate and from 7.9 to 8.1 with glycylglycine. W. McC.

Proteolytic enzymes in the tape worm. I. A. SMORODINCEV and K. V. BEBESCHIN (*Bull. Soc. Chim. biol.*, 1936, 18, 1097—1105).—Glycerol extracts of *Taeniarhynchus saginatus* and *Taenia solium* contain pepsin, trypsin, and cathepsin, the tryptic action of extracts of the former being $>$, and the peptic action $<$, that of the latter species. No activation of the cathepsin occurred with H_2S .

A. L.

Selective action of gentian-violet on enzymes. A. Y. WELLS and N. P. SHERWOOD (*J. Infect. Dis.*, 1934, 55, 356—359).—Gelatinases from Gram-positive bacteria were more easily inhibited by gentian-violet (1:400) in acid media than were those from Gram-negative bacteria. Enzymes from the latter liquefied the larger amounts of gelatin. All the enzymes were more active in alkaline media. CH. ABS. (p)

General nature of catheptic enzymes. M. BERGMANN and J. S. FRUTON (*Science*, 1936, 84, 89—90).—A discussion and interpretation of the dual enzyme system of catheptic enzymes. L. S. T.

Conditions for the action of cathepsin in the tissues of the regenerating organs of amphibia. V. N. ORECHOVITSCH (*Biochem. Z.*, 1936, 286, 285—289).— H_2S does not activate the cathepsin (I) of regenerating tissues. Cysteine (II) activates the (I) of normal tissues strongly and, to a smaller extent, that of regenerating tissue. With max. activation, the hydrolysis of gelatin by extracts of regenerating tissues is $>$ that by extracts of normal tissue. The intensity of autolysis of normal tissues with max. (II) activation is $<$ that of the non-activated autolysis of regenerating tissue.

P. W. C.

Determination of peptic activity. III. H. ESCHENBRENNER (*Pharm. Ztg.*, 1936, 81, 967—969; cf. this vol., 520).—The possible influence of the hydrolytic products on the course of proteolysis by pepsin is discussed. Evidence of inhibition could not be obtained from the effect of dialysis or addition of peptones on peptic digestion. Polarographic examination indicates that peptic hydrolysis produces only slight changes in the protein substrate. F. O. H.

Activation of pancreatic trypsin. F. MOCOROA (*Anal. Fis. Quím.*, 1934, 32, 748—756).—From a study of the rates of activation it is concluded that active trypsin (I) is formed from trypsin and kinase, and that its formation is influenced by their concn. and by temp. (I) combines with prokinase to give a kinase. F. R. G.

Specificity of urease. R. BONNET and R. RAZAFIMAHERY (*Enzymologia*, 1936, 1, 55—59).—Heated and unheated urease show no difference in hydrolysing various substituted ureas, amides, and cyanates. Urease is very sp. E. D. Y.

Inhibitory effect of phloridzin and phloretin on kidney phosphatase. H. KALCKAR (*Nature*, 1936, 138, 289).—The inhibitory effect of phloretin on the action of kidney phosphatase is approx. 3 to 4 times that of phloridzin. L. S. T.

Metabolism of the human placenta. O. BUSSE (*Z. physiol. Chem.*, 1936, 242, 271—279).—The placenta contains a phosphatase (I) the activity of which depends on the substrate concn. (max. with 0.15*M*-glycerophosphate at p_H 9). (I) is slightly activated by Mg^{++} , strongly inhibited by cysteine, unaffected by NaF , $EtOH$, and $COMe_2$, and partly purified by fractional pptn. with $EtOH$. The (I) content of the ripe placenta is $>$ that of the unripe and \geq that of the liver, kidney, and small intestine. The zymohexase content of the placenta is only a fraction of

that of muscle. No phosphorylation of inorg. P occurs in the placenta. W. McC.

Alcoholic fermentation in the intact enzyme system of the yeast cell and in the disorganised zymase system. II. R. NILSSON and F. ALM (Biochem. Z., 1936, 286, 373—391).—The fermentation by preps. of intact dry yeast (cf. this vol., 1299) is compared with those by apozymase (I), autolysed dry yeast, and maceration extract and the effect of autolysis and PhMe examined. Yeast which is allowed to autolyse during slow drying loses the power to ferment sugar completely and gives the normal linear curve whilst addition of $\text{PO}_4^{''}$ causes a sharp break in the curve. Maceration juice gives larger deviations and with amounts of $\text{PO}_4^{''}$ below theoretical gives 2 such breaks, the first conditioned by the $\text{PO}_4^{''}$ and the second occurring when one half of the sugar is fermented. (I) + purified co-enzyme gives the normal curve but if the (I) is first dried in air, only half of the sugar is fermented at the normal rate. The changes in the enzyme system are discussed and correlated with similar changes in fermentation with dry yeast at 40° . P. W. C.

Polysaccharides fermented by yeast in wheaten flour. R. GUILLEMET and C. SCHELL (Bull. Soc. Chim. biol., 1936, 18, 1132—1146).—Fermentation of raffinose by baker's yeast in the presence of aq. yeast extract takes place completely, and that of gentianose and stachyose corresponds with 66 and 50% respectively of the carbohydrate added. Fermentation of levosin is, however, much less. Baking flour contains about 0.1% of hexoses, 0.2—0.7% of sucrose, and 1% of a mixture of polysaccharides amongst which is levosin. A. L.

Effect of composition of medium on growth of yeast in presence of bios preparations. I. Effect of magnesium salts. E. I. FULMER, L. A. UNDERKOFER, and J. B. LESH (J. Amer. Chem. Soc., 1936, 58, 1356—1358).—Growth of a strain of *Saccharomyces cerevisiae* on a NH_4Cl - K_2HPO_4 -sucrose medium with added bios II (essential) is markedly increased by small concns. of MgSO_4 [or MgCl_2 or $\text{Mg}(\text{NO}_3)_2$ with K_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$]. K_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ show some activity but MgCl_2 and $\text{Mg}(\text{NO}_3)_2$ do not. H. B.

Action of small quantities of copper on alcoholic fermentation by yeast. Application to wine-making. R. GUILLEMET (Bull. Soc. Chim. biol., 1936, 18, 1125—1131).—The fermentation of aq. glucose by yeast ceases when the yeast has taken up 2.3—2.5 mg. of Cu per g. (dry wt.). The retarding effect of Cu on the fermentation of wine musts, however, takes place only when 500 mg. of Cu per litre are present. This amount is \gg that present after fungicidal treatment of the grapes. A. L.

Comparative action of sodium arsenate, sodium arsenite, and arsenic-protein preparations on respiration and glycolysis of *Saccharomyces cerevisiae*. P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1936, 11, 253—255).—The toxic effect (depression of respiration and glycolysis) gives the order As-gelatin $>$ Na_3AsO_3 $>$ Na_3AsO_4 . F. O. H.

Effect of radium rays on fermentation micro-organisms. Formation of constant variants of yeasts under influence of hokutolit rays. R. NAKAZAWA and M. SIMO (J. Agric. Chem. Soc. Japan, 1936, 12, 699—708).—Morphologically and physiologically distinct variants are produced when yeasts are exposed to hokutolit rays. J. N. A.

Mitogenetic effect on yeast of oligodynamic radiations from metals. M. B. MACDONALD (Iowa State Coll. J. Sci., 1935, 9, 587—595).—Yeast cells multiplied much more rapidly in tubes placed on sheet brass, Fe, Pb, Al, or Ag than on cardboard. In Vitreosil tubes growth was retarded by the metals, probably through excessive transmission of radiations. Protection of the metal surfaces from contact with the atm. diminished their action. Exposure of the medium to metal before inoculation also increased multiplication and the beneficial effect thus obtained was not affected by boiling the treated medium before inoculation. CH. ABS. (p)

Carbohydrates of yeast. K. SILBEREISEN (Woch. Brau., 1936, 53, 317—321, 330—331).—A lecture.

Permeability of yeast cell-membrane.—See B., 1936, 1013.

Micro-organisms of sugar cane juice. R. NAKAZAWA, Y. TAKEDA, and K. SUEMATU (J. Agric. Chem. Soc. Japan, 1936, 12, 749—762).—1 c.c. of juice contained 10^4 to 10^5 micro-organisms consisting of *saccharomyces*, *torula*, *monilia*, and bacteria (mainly *Leuconostoc*). All are able to invert sugar. The juice is well suited to the growth of the organisms, which can be altered by change of p_H , rise of temp., or addition of bleaching powder. J. N. A.

Grouping of *Monilia* by fermentation and precipitin reactions. J. H. LAMB and M. L. LAMB (J. Infect. Dis., 1935, 56, 8—20).—*Monilia* species are divided into 3 groups on the basis of sugar fermentation tests and precipitin reactions. CH. ABS. (p)

Properties of *Aspergillus* species. II. Y. TAKEDA and O. TAKEUCHI (J. Agric. Chem. Soc. Japan, 1936, 12, 853—870).—The optimum temp. for growth and for conidia formation, the permanence and colour of conidia, colour of perithecia, optimum p_H for growth, killing temp., and fermentative or non-fermentative activity for all kinds of carbohydrates are determined for 89 known strains of *Aspergillus* grown on Pfeffer's medium containing 0.5% of oryzanin. J. N. A.

Utilisation of galactose by *Aspergillus niger* and *Penicillium glaucum*. W. H. HERR (Plant Physiol., 1936, 11, 81—99).—Galactose (I) is a poor source of C for these moulds and when used alone retards spore germination and mycelial development. When mixed with glucose, fructose, or mannose, (I) improves growth. Addition of lactose to a sucrose culture medium has little effect on growth. The acidity of media is not an important factor in growth acceleration. A. G. P.

Biochemical method for determining parasitism in *Fusarium*. T. FEDOTOVA (Plant Protection U.S.S.R., 1935, No. 1, 115—118).—Highly parasitic,

weakly parasitic, and saprophytic species contained $\text{NH}_2\text{-N}$ 3—5, 11—19, 19—27, and $\text{NH}_2\text{-N}$ 6—8, 9—28, 35—52 mg. per g., respectively.

CH. ABS. (p)

Nitrogenous metabolism of a micro-organism. W. H. SCHOPFER (Compt. rend., 1930, 203, 201—203).—Cultures of *Phycomyces* on a medium containing 8% of glucose and 0.1% of asparagine show a max. yield of the mould for a definite concn. of vitamin- B_1 . Many other N sources give similar results. The N content of the mould falls to a min. as the yield reaches a max. although all the available N is not utilised. Atm. N_2 plays no part in the process.

J. L. D.

Production of sclerotia by *Rhizoctonia solani*, Kuhn, in pure culture. L. E. TYNER and G. B. SANFORD (Sci. Agric., 1935, 16, 197—207).—No sclerotia were produced in P- or N-free media. Optimum and min. concns. were 31 and 7.5 for P and 560 and 55 p.p.m. for N. Sclerotia appeared with almost equal frequency over a wide range of [K] > 2 p.p.m. Sclerotia formation was restricted with < 20 p.p.m. of Mg in the nutrient. Omission of Ca did not affect development of either sclerotia or mycelium. Sclerotia were produced readily in media of p_{H} 3—9 (optimum 5.5) and were most favoured by temp. of 18—21° and R.H. 60%. Radiations from pitchblende had a stimulatory effect.

A. G. P.

Effects of hypertonic media on the contractile vacuoles of protozoa. J. A. KITCHING (Nature, 1936, 138, 287).—A discussion.

L. S. T.

Chemotherapy of animals infected with trypanosomes by inhibiting carbohydrate metabolism of the parasites with halogenoacetic acids. N. VON JANCSÓ and H. VON JANCSÓ (Biochem. Z., 1936, 286, 392—395).—Trypanosome infection of mice was removed by intraperitoneal administration of $\text{CH}_2\text{Br-CO}_2\text{H}$ and $\text{CH}_2\text{I-CO}_2\text{H}$.

P. W. C.

Physiology of respiration of bacteria. II. Intracellular indophenol reaction. S. YAMAGUCHI (Acta Phytochim. Japan, 1935, 8, 263—283).—The indophenol test was positive with 9 among 24 species examined, and was inhibited by CN^- . With certain species the O_2 absorption was lowered by CO .

CH. ABS. (p)

Bacterial growth and hydrogen-ion concentration. I. In bouillon. II. In peptone water. A. UCHIDA (Japan J. Mikrobiol. Path., 1935, 29, 825—868).—[H^+] decreased at first and increased later (more rapidly in bouillon).

CH. ABS. (p)

Content of hydrolases in some species of bacteria. G. VERCELLANA (Boll. Soc. ital. Biol. sperim., 1936, 11, 329—330).—Trypsin, cathepsin, amylase, and lipase were not found in *B. melitense*, *B. paramelitense*, *B. abortus*, *B. para-abortus*, *B. pyocyaneum*, *Vibrio cholerae*, *Staphylococcus pyogenes aureus*, or *Streptococcus pyogenes*.

F. O. H.

Reactions of organisms on arbutin agar. A. CASTELLANI and M. DOUGLAS (J. Trop. Med. Hyg., 1935, 38, 197—201).—Certain organisms produce brown to black colorations. The reaction does not correspond with the fermentation of arbutin in peptone.

CH. ABS. (p)

Acetic acid bacteria from Formosa. X. Systematic investigations. S. TANAKA (J. Agric. Chem. Soc. Japan, 1936, 12, 726—744).—105 strains are divided into 4 groups, according to the amounts of AcOH and gluconic acid produced on an EtOH-glucose medium.

J. N. A.

Mechanism of biological fixation of nitrogen. III. Economy of carbon during fixation by *Azotobacter chroococcum*, Beij. T. R. BHASKARAN. **IV. Fixation by the mixed microflora of soil in presence of acid products of anaerobic decomposition of carbohydrates.** T. R. BHASKARAN and V. SUBRAHMANYAN (Proc. Indian Acad. Sci., 1936, 4, B, 67—74, 163—170; cf. this vol., 113).—III. The decomp. products of glucose play no part in the fixation of N by *A. chroococcum*, the mechanism of which differs from that by mixed soil flora. During the early stages of sugar decomp. the proportion of C fixed in the slime and bacterial cells is relatively > that of N. Later the ratio is adjusted to the initial level. Growth of the organism and N fixation are closely correlated.

IV. The efficiency of the fixation of N by a mixed flora was improved by addition of the mixture of org. acids etc. obtained by the anaerobic fermentation of sugar. The ratio of C consumed to N fixed is examined under various cultural conditions.

A. G. P.

Utilisation of salicylic acid as an energy-producing food by *Azotobacter* in soil. G. GUITTONNEAU and R. CHEVALIER (Compt. rend., 1936, 203, 211—213; cf. A., 1932, 437).—*Azotobacter* from gardens and fields when grown on SiO_2 gel or the original soil containing Na salicylate (I) utilises (I) better if the soil fertility is high. A pure culture destroys (I), increases the p_{H} of the medium, and fixes N during some days, indicating that no subsidiary bacteria are necessary to enable *Azotobacter* to utilise (I).

J. L. D.

Alcohol- and carbohydrate-oxidising bacteria isolated from fruits: new classification of oxidising bacteria. III. T. ASAI (J. Agric. Chem. Soc. Japan, 1935, 11, 331—340, 377—390, 499—513, 610—620, 674—708; cf. this vol., 113).—Decomp. of sugars and alcohols by numerous species of bacteria is examined. Species growing at higher temp. oxidise glucose (I) to gluconic or glycuronic acid (II) and AcOH to CO_2 , but do not oxidise mannitol (III) or glycerol (IV). Those growing at lower temp. oxidise (I) to (II) or 5-ketogluconic acid, (III) to fructose (V), (V) to kojic acid, and (IV) to $\text{CO}(\text{CH}_2\text{-OH})_2$. They do not oxidise AcOH. The extent of these reactions forms the basis of a classification of species.

CH. ABS. (p)

Thermophilic and anaerobic nature of *Lactobacillus bulgaricus*. J. M. SHERMAN and H. M. HODGE (Science, 1936, 84, 208—209).—Freshly isolated cultures can grow at 60° and vigorously at 55°.

L. S. T.

Quantum relationship of the light-emitting process of luminous bacteria. K. L. VAN SCHOUWENBURG and J. G. EYMERS (Nature, 1936, 138, 245).—One part of the O_2 consumption of *Photobacterium phosphoreum* is completely inhibited by

approx. 0.001M-KCN, and the other decreases slowly with increasing [KCN] and \propto light intensity. 19% of the total O₂ is consumed in the light-emitting process and at 16°, 500 mols. of O₂ are consumed per quantum of light emitted. The efficiency of the light-emitting process depends on various unknown factors.

L. S. T.

Preparation of specific bacterial carbohydrate substances by electrolysis. A. C. H. YEN and T. J. KUBOTCHKIN (J. Infect. Dis., 1935, 56, 238—249).—Passage of a strong electric current through saline suspensions of the organisms causes clarification. Dialysis of the cleared solution removes protein matter, and H₂O-sol. polysaccharides are pptd. from the resulting liquid by EtOH.

CH. ABS. (p)

Comparative behaviour of endotoxins and exotoxins towards trichloroacetic acid. A. BOVIN (Compt. rend., 1936, 203, 284—286).—The anatoxin of *B. diphtheriae* is pptd. by CCl₃·CO₂H at p_H 4, and can be redissolved in PO₄''' buffer of p_H 8. In this way it is possible to concentrate and purify the anotoxins. The purified material contains mineral matter 0.5, N 15.1, and P 0.1%; it yields no sugar, purine, or fatty acid on hydrolysis. The endotoxin, which is a carbohydrate-lipin complex and is responsible for the specificity of the type, is sol. in H₂O at p_H 4.

P. G. M.

Metabolism of *C. diphtheriae*. I. A. TASMAN and A. C. BRANDWIJK (Biochem. J., 1936, 30, 1756—1767).—*Diphtheria* bacteria in a simple culture medium assimilate glucose (I) in concns. \approx 0.2% without detriment to toxin production. When the concn. is 0.5% all (I) is (more slowly) decomposed but toxin production is stopped because of the large amount of acid produced. Much greater concns. of maltose (II) are tolerated, apparently because the velocity of decomp. of (I) by the bacteria is 6 times that of hydrolysis of (II) to (I). During decomp. of sugar the p_H falls until (I) has disappeared and then rises, probably because the acids initially produced from (I) are oxidised to H₂O and CO₂ which converts alkali originally present into CO₃''' and HCO₃'. Production of toxin begins when (I) has practically disappeared, continues for a time at approx. const. velocity, and then ceases abruptly.

W. McC.

Inhibitive effect of vitamin-C on toxin production by *C. diphtheriae*. I. J. KLIGLER (Nature, 1936, 138, 291).—Vitamin-C added in small amounts to a suitable medium inhibits toxin production.

L. S. T.

Diphtheria toxin produced on a semi-synthetic medium. K. ANDO and T. KOMIYAMA (J. Immunol., 1935, 28, 345—352).—On a mineral salt-AcOH-maltose-Difco-proteose-peptone medium at p_H 8.0, *C. diphtheriae* produces a toxin as potent as that obtained in ordinary infusion bouillon.

CH. ABS. (p)

***Cl. welchii*, Type C, Wilsdon (*B. patudis*, McEwen), isolated from sheep in N. Wales.** R. F. MONTGOMERIE and W. T. ROWLANDS (Vet. Rec., 1936, 48, 829—832).—In cases of sheep "strike," a toxin typical of *Cl. welchii* was isolated from blood and other body-fluids.

A. G. P.

Differential character of *Clostridium welchii*, type D. T. J. BOSWORTH and R. E. GLOVER (Proc. Roy. Soc. Med., 1935, 28, 1004—1006).—The toxin prepared in saline becomes much more toxic when mixed with a normal intestinal filtrate. The activating factor is destroyed at 70°. The same amount of antitoxin is required to neutralise the treated and the untreated toxin.

CH. ABS. (p)

Antigenic relation between *Proteus vulgaris* X-19 and typhus *Rickettsia*. III. Antigenic composition of extracts of *P. vulgaris* X-19. M. R. CASTANEDA (J. Exp. Med., 1935, 62, 289—296).—Two polysaccharides, 1 and 4% N, respectively, are pptd. from extracts by EtOH. Both give a negative biuret and a positive Molisch reaction. One, the common antigenic factor in *P. vulgaris* X-19 and typhus *Rickettsia*, is stable to hot alkali, the other is quickly destroyed.

CH. ABS. (p)

Oxidation-reduction potentials in *Salmonella* cultures. I. Development of potential levels characteristic of species. W. BURROWS and E. O. JORDAN (J. Infect. Dis., 1934, 56, 255—263).—The potentials of cultures of individual strains differed only within narrow limits. Those of different species diverged considerably. Species-differences may be due to differences in bacterial substances synthesised.

CH. ABS. (p)

Antigenic structure of the variants of *Staphylococcus aureus*. I. Carbohydrates of the rough and smooth forms. R. E. HOFFSTADT and W. M. CLARK (J. Infect. Dis., 1935, 56, 250—254).—Type-sp. carbohydrates isolated from the two forms differed antigenically and in the manner in which they separated from the proteins of the respective organisms. That from the smooth type was more sol. in hot H₂O, and contained less N, than that from the rough type, from which it also differed in being pptd. by Ba(OH)₂.

CH. ABS. (p)

Ingestion of *Staphylococcus* exotoxin by human volunteers with special reference to staphylococcic food poisoning. C. E. DOLMAN (J. Infect. Dis., 1934, 55, 172—183).—Gastric disturbance followed the ingestion in some cases only. A staphylococcus metabolite rather than the exotoxin was probably the causal agent.

CH. ABS. (p)

Influence of p_H on dissociation of *B. Friedlander* and *M. tuberculosis*. W. STEENKEN (J. Infect. Dis., 1935, 56, 273—276).—The effects of the reaction of various media on attenuation are examined.

CH. ABS. (p)

Effect of formaldehyde on growth of tubercle bacilli. R. D. HERROLD (J. Lab. Clin. Med., 1935, 20, 1165—1167).—Tubercle bacilli are more susceptible to CH₂O than are other common organisms present in sputum.

CH. ABS. (p)

Attenuated (R.I.) tubercle bacilli recovered from silicotic and normal guinea-pigs. G. R. DOWD (Amer. Rev. Tuberc., 1935, 32, 62—72).

CH. ABS. (p)

Ultra-violet absorption of phthiocol, a pigment of the human tubercle bacillus. M. O'L. CROWE (J. Biol. Chem., 1936, 115, 479—484).—The absorption spectrum of synthetic phthiocol (A., 1934, 77)

in 95% EtOH (max. at 385, 334, 278, and 250 m μ) is compared with those of other 1:4-naphthaquinones.
F. A. A.

Concentration and partial purification of bacteriophage. J. H. NORTHROP (Science, 1936, 84, 90—91).—A protein prep. possessing the properties of bacteriophage has been isolated from lysed staphylococcus cultures. Method and properties are described.
L. S. T.

Feulgen reaction of the bacteriophage substance. M. SCHLESINGER (Nature, 1936, 138, 508—509).—The particles of *coli* bacteriophage previously prepared (A., 1934, 1407) are extensively stained by Feulgen's reagent.
L. S. T.

Reactivation of thermally inactivated bacteriophage. A. P. KRUEGER and J. H. MUNDELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 410—413).—Bacteriophage inactivated by heating for 20 min. at 54° in a phthalate buffer mixture at p_H 5.75 is partly reactivated when kept on ice at p_H 8.1. W. O. K.

Selective action of dyes and of other disinfectants on bacteriophage. A. Y. WELLS and N. P. SHERWOOD (J. Infect. Dis., 1934, 55, 195—198).—The phagistatic action of gentian-violet, crystal-violet, PhOH, and NaOH is examined. In general, phages acting on Gram-negative bacteria are more resistant to inhibitory substances than are those which act on Gram-positive organisms.
CH. ABS. (p)

Immunological and chemical investigations of vaccine virus. II. Analysis of elementary bodies of vaccinia. T. P. HUGHES, R. F. PARKER, and T. M. RIVERS (J. Exp. Med., 1935, 62, 349—352).—Washed elementary bodies contain protein 83.1, fat 8.5, ash 0.7, residual H₂O 5.6%. The 2% of undetermined matter includes a trace of carbohydrate.
CH. ABS. (p)

Resistance of the virus of infectious laryngo-tracheitis to certain chemical and physical factors. O. W. SCHALM and J. R. BEACH (J. Infect. Dis., 1935, 56, 210—223).—Effects of temp., exposure to sunlight, p_H , desiccation, and treatment with PhOH, cresol, and NaOH are examined.
CH. ABS. (p)

Attenuation of avian plague virus by X-rays. B. S. LEVIN and I. LOMINSKI (Compt. rend., 1936, 203, 287—288).—A dose of X-rays of 2500—3000 kiloroentgen is required to attenuate plague virus as tested in cockerels. This dose is > that required to kill bacteria (300 kiloroentgen). X-Rays may therefore be used for purification of an ultravirus. P. G. M.

Thermostable activators of bacterial growth from cryptogams. A. SARTORY, R. SARTORY, J. MEYER, and M. J. MERGLEN (Compt. rend., 1936, 203, 280—282).—H₂O-sol. bacterial activators in culture filtrates of *Aspergillus fumigatus*, *Schizosaccharomyces hominis*, *Mucor nigricans*, and *M. plumbeus* manifest themselves only on heating to < 80°. They resist prolonged heating at 120°. The two *Mucor* strains give the best growth with all the cocci used. The growth of *B. diphtheriae* is only slightly affected by any of the filtrates, and that of *B. subtilis* not at all.
P. G. M.

Different effects of some disinfectants on bacterial growth. K. DIERNHOFFER (Milch. Forsch., 1936, 18, 83—86).—On growing a mixture of types of bacteria isolated from cow dung in lactose broth containing various low concns. of KCN, OH-C₆H₃(NO₂)₂, *p*-NO₂-C₆H₄-OH, and theophylline-Na salicylate, a differentiation in the growth of streptococci and Gram-negative bacteria was obtained. 0.05—0.10% of nitrophenols did not affect the growth of streptococci but KCN favoured the growth of Gram-negative organisms.
W. L. D.

Antiseptic and bactericidal action of urea. J. H. FOULGER and L. FOSHAY (J. Lab. Clin. Med., 1935, 20, 1113—1117).—Many bacteria lose viability in 2 hr. in media half-saturated with urea. Staphylococci have a high resistance. Dry urea may be applied directly to suppurating wounds etc. CH. ABS. (p)

Germicidal properties of the soil nema, *Rhabditis pellio*. Schneider. C. MORIYA (Proc. Imp. Acad. Tokyo, 1936, 12, 195—197).—Various pathogenic organisms are destroyed by *R. pellio*.
A. G. P.

Culture media for non-acid products. E. J. CAMERON (J. Assoc. Off. Agric. Chem., 1936, 19, 433—438).—Five media are described and recommended for the detection of all organisms commonly found in such products.
E. C. S.

Culture media for acid products. B. A. LINDEN (J. Assoc. Off. Agric. Chem., 1936, 19, 440—445).—Five media are described and recommended for the detection of bacteria and one for the detection of yeasts and moulds.
E. C. S.

Méker burner with auxiliary flame for bacteriological use. M. E. HIGHLANDS and P. K. BATES (Amer. J. Publ. Health, 1936, 26, 928).
C. J.

Use of micro-organisms in sugar analysis.—See this vol., 1363.

Effect of prolonged administration of hyperglycaemia-producing hormones. F. SERIO (Boll. Soc. ital. Biol. sperim., 1936, 11, 270—271).—Prolonged administration of adrenaline, thyroxine, or pituitary preps. to dogs produces a hypoglycaemia and not a condition simulating diabetes. The mechanism of this phenomenon is discussed.
F. O. H.

Adrenal cortex and cholesterol metabolism. S. THADDEA and W. FASSHAUER (Arch. exp. Path. Pharm., 1936, 182, 477—498).—Intravenous injection of adrenal cortex preps. (I) into dogs decreases the total cholesterol (II) content of the serum, the diminution being mainly of cholesteryl ester (III). The effect does not occur after damage of the reticulo-endothelial system. Bilateral extirpation of the adrenal cortex in cats increases serum-(II) [especially the (III) fraction] and decreases liver- and muscle-(II); subsequent treatment with (I) produces a return to normal vals. and also corrects the absence of hypercholesterolaemia (due to disturbance of fat-absorption) following oral administration of (II). Increased serum-(II) and -(III) occur in Addison's disease. The adrenal cortex probably has a fixative action on (II).
F. O. H.

Adrenal cortex and endogenous carbohydrate formation. G. EVANS (Amer. J. Physiol., 1936, 114, 297—308; cf. A., 1935, 777).—The increase of glycogen (I) in fasting rats exposed to reduced pressure is prevented by hypophysectomy. A parallel increase in N excretion and R.Q. and a fall in O₂ consumption are observed in intact rats. Adrenalectomy abolishes the increase in N excretion; it also reduces excretion of sugar and N in phloridzinised rats. Adreno-medullectomised rats respond to low O₂ tension and phloridzin as do intact rats. The cortical extract of Swingle and Piffner does not alter sugar and N excretion of adrenalectomised phloridzinised rats, nor raise (I) in rats exposed to reduced pressure. Ketosis in phloridzinised rats and rats exposed to reduced pressure is diminished by adrenalectomy. It is concluded that the cortex is concerned with the conversion of protein into carbohydrate.

R. N. C.

Constituents of the adrenal gland. V. Chemical identification of the androstane skeleton.—See this vol., 1382.

Constituents of the adrenal gland. VI. Methods of separation and isolation of the substances Fa, H, and J.—See this vol., 1382.

Carbohydrate and electrolyte changes in the opossum and marmot following adrenalectomy. H. SILVETTE and S. W. BRITTON (Amer. J. Physiol., 1936, 115, 618—626).—Serum- and muscle-Na and -Cl are increased and muscle-H₂O decreased. Na' and Cl' excretion in the urine is < normal. The changes produced in dogs, cats, and rats are strikingly opposite to these. In all species blood-sugar and liver- and muscle-glycogen are decreased. The life-maintaining cortical hormone affects NaCl balance only indirectly, being directly concerned in regulation of carbohydrate metabolism.

R. N. C.

Changes in the rat incisor following bilateral adrenalectomy. I. SCHOUR and J. M. ROGOFF (Amer. J. Physiol., 1936, 115, 334—344).—Calcification of dentine is disturbed.

R. N. C.

Increased salt appetite of adrenalectomised rats. C. P. RICHTER (Amer. J. Physiol., 1936, 115, 155—161).

R. N. C.

Lactation in adrenalectomised rats. R. GAUNT and C. E. TOBIN (Amer. J. Physiol., 1936, 115, 588—598).

R. N. C.

Rôle of potassium in adrenaline action. W. J. R. CAMP and J. A. HIGGINS (J. Pharm. Exp. Ther., 1936, 57, 376—387).—K effects all the typical changes in systems which are produced by adrenaline, and the action of K is obtained after decerebration, bilateral adrenalectomy, and injection of atropine and ergotoxine. K is liberated from the heart by vagus stimulation. The adrenals maintain a const. distribution of K.

J. N. A.

Effect of adrenaline on arterial and venous plasma-sugar and blood flow in dogs and cats. C. F. CORI, R. E. FISHER, and G. T. CORI (Amer. J. Physiol., 1935, 114, 53—68).—The rate of continuous injection of adrenaline (I) solution necessary to produce hyperglycæmia in dogs is > that required for cats. Rates of injection can be found which increase

plasma-sugar (II) without affecting blood-flow. The arterio-venous (II) difference is slightly increased during a period of even (I) hyperglycæmia; insulin injected at the conclusion of the (I) injections causes a considerable increase. The increase of (II) in cats is > in dogs for the same rate of injection of (I).

R. N. C.

Formation of an adrenaline-like substance in autolysing adrenal glands. A. R. LARRAIN, R. G. ROBERTS, and M. M. KUNDE (Amer. J. Physiol., 1936, 115, 662—664).—Autolysis produces a dialysable pressor substance that resembles adrenaline in its chemical reactions, but is not pptd. by conc. aq. NH₃. Its formation continues until the gland is almost completely disintegrated; KCN inhibits its formation.

R. N. C.

So-called virtual adrenaline of the adrenal cortex. J. DEVINE (Biochem. J., 1936, 30, 1768—1774; cf. Abelous and Argaud, A., 1934, 1038, 1143).—Chemical and physiological assays of extracts of adrenal cortex and medulla give no support to the hypothesis of the existence in the gland of "virtual" adrenaline (I) but the distribution of derivatives of *o*-C₆H₄(OH)₂ in the gland suggests that the cortex may be concerned in the production of (I).

W. McC.

Adrenaline and urine formation in the dog. E. F. ADOLPH (Amer. J. Physiol., 1936, 115, 200—209).

R. N. C.

Changes in the circulatory effect of potassium salts due to adrenaline. H. A. MCGUIGAN and J. A. HIGGINS (Amer. J. Physiol., 1935, 114, 207—211).—K' injected intravenously after adrenaline in the dog is as effective in raising the blood-pressure as when injected intra-arterially; an increase in blood-K' is necessary before the action can occur.

R. N. C.

Regulation of oxygen output by erythrocytes. III. Blood glycolysis, insulin, and adrenaline. F. HEMMERICH and F. S. TSCHERNJAK (Biochem. Z., 1936, 286, 344—359).—In men and rabbits, insulin (I) accelerates and adrenaline (II) inhibits glycolysis. After administration of (I) or (II), the opposing hormone is mobilised by the organism and secreted into the blood. In man, activation of glycolysis by (I) is > and of longer duration than inhibition by (II). Since increased glycolysis is bound up with increased output of O₂ by the erythrocytes (this vol., 494), (I) and (II) may be regarded as regulators of the blood respiratory function.

P. W. C.

Enteral absorption of insulin. Protection of insulin against trypsin. F. LASCH and E. SCHÖNBRUNNER (Arch. exp. Path. Pharm., 1936, 182, 452—458; cf. this vol., 525).—Certain basic dyes (I) (e.g., malachite-green), but not acid dyes, protect insulin from inactivation *in vitro* by trypsin (II). Pptn. (indicated by an opalescence when protection is max.) of (I) and (II) occurs.

F. O. H.

Response of the rabbit to insulin. L. B. DOTTI (Amer. J. Physiol., 1936, 114, 538—550).—The % fall in blood-sugar (I) ½ hr. after administration of a fixed dose of insulin (II) is related to the time of onset

of convulsions; the latter, however, is not related to the initial (I). Animals with great sensitivity to (II) require larger injections of glucose to prevent convulsions. The female is more sensitive to (II) and more const. in its responses than the male.

R. N. C.

Protamine insulinate. H. C. HAGEDORN, B. N. JENSEN, N. B. KRARUP, and I. WODSTRUP (J. Amer. Med. Assoc., 1936, 106, 177—180).—Fish sperm protamines combine with insulin (I) to form complexes which have isoelectric points at about p_H 7.3, at which point they are only very slightly sol. in H_2O but somewhat more sol. in serum. The low solubility in body-fluids results in slow absorption of (I) from subcutaneously administered complexes, with hypoglycaemic action about twice as long as that due to the same dose of ordinary (I). The use of protamine insulinate permits a greater stabilisation of the diabetic blood-sugar level than is possible with ordinary (I) and considerably decreases the risk of hyper- and hypo-glycaemia.

NUTR. ABS. (m)

Contrary actions of epiphyseal extracts on blood-ketones. L. CANNAVÒ (Boll. Soc. ital. Biol. sperim., 1936, 11, 273—274).—Aq. and glycerol extracts of fresh pineal gland and Et_2O extracts of $COMe_2$ -dried gland contain a thermolabile principle which lowers blood-ketones (I) whilst $CHCl_3$ extracts of $COMe_2$ -dried gland contain a thermostable substance which increases (I).

F. O. H.

Effect of irradiated ergosterol and parathyroid extract on the rate of disappearance of intravenously-injected calcium chloride. S. FREEMAN (Amer. J. Physiol., 1936, 115, 701—705).—The rate of removal of $CaCl_2$ in normal dogs is uniform. It is decreased by injection of sufficient parathyroid extract or irradiated ergosterol to produce a fasting hypercalcaemia.

R. N. C.

Response of thyroid glands of hypophysectomised newts to injections of phyone and their reaction after cessation of treatment. A. E. ADAMS and F. MARTINDALE (Anat. Rec., 1936, 65, 319—331).

R. N. C.

Thyroid glands of hypophysectomised newts after treatment with anterior pituitary, thyroid, and iodine. A. E. ADAMS and B. GRAY (Anat. Rec., 1936, 65, 69—81).—Only the pituitary hormones stimulate the gland.

R. N. C.

Effects of thyrotropic and adrenotropic principles on hypophysectomised amphibia. W. J. ATWELL (Anat. Rec., 1935, 62, 361—379).—Thyrotropic hormone causes rapid and complete metamorphosis, but adrenotropic hormone produces only slight changes.

R. N. C.

Metabolic aspects of thyroid-adrenal inter-relationship. S. B. BARKER, J. F. FAZIKAS, and H. E. HIMWICH (Amer. J. Physiol., 1936, 115, 415—418).—The rise of O_2 consumption produced by adrenaline in rats is increased by thyroid feeding and decreased by thyroidectomy, this decrease being abolished by thyroid feeding.

R. N. C.

Effect of antithyroidal protective substance on the Reid Hunt test. K. FELLINGER and O. HOCHSTÄDT (Klin. Woch., 1935, 14, 1250—1251;

Chem. Zentr., 1935, ii, 3790).—By means of the MeCN reaction in mice it is shown that the antagonistic action of the protective substance in respect of the thyrotropic hormone is $>$ in respect of the thyroid. The substance acts directly on the gland or on its regulating factors.

A. G. P.

Detection of thyrotropic hormone in tissues other than of the pituitary. A. STURM and W. SCHÖNING (Endokrinol., 1935, 16, 1—8; Chem. Zentr., 1935, ii, 3941).—Many tissues (notably of ovary and kidneys) contain a substance which regulates thyroid secretion. The presumed pituitary-sp. property of the thyrotropic hormone is discussed.

A. G. P.

Effect of thyroxine on the tissue metabolism of excised *Limulus* heart. J. E. DAVIS and A. B. HASTINGS (Amer. J. Physiol., 1936, 114, 618—619).—Metabolism *in vitro* is increased under suitable conditions. This is not due to increased work by the heart.

R. N. C.

Comparison of the calorogenic potencies of *l*- and *dl*-thyroxine and thyroid gland. Thyroxine content of the acid-soluble fraction of the peptic digest of thyroid protein. G. L. FOSTER, W. W. PALMER, and J. P. LELAND (J. Biol. Chem., 1936, 115, 467—477).—*l*-Thyroxine, $[\alpha]_D^{20} -4.4^\circ$, isolated from pig's thyroid, and equiv. doses of thyroid extract, have twice the calorogenic activity of *dl*-thyroxine in guinea-pigs. Thus only the *l*-compound is biologically active. The acid-sol. fractions of a peptic digest of thyroid protein still contain thyroxine, which may be carried down with protein pptts.

F. A. A.

Glycogen content of liver and muscle in the completely hypophysectomised dog. I. L. CHAIKOFF, G. F. HOLTOM, and F. L. REICHERT (Amer. J. Physiol., 1936, 114, 468—472).—Liver- and muscle-glycogen in well-nourished dogs is not altered by hypophysectomy.

R. N. C.

Maintenance of carbohydrate levels in fasted hypophysectomised rats treated with anterior pituitary extracts. J. A. RUSSELL and L. L. BENNETT (Proc. Soc. Exp. Biol. Med., 1936, 34, 406—409).—The abnormal fall in carbohydrate stores which occurs in fasting hypophysectomised rats is prevented by administration of anterior pituitary extracts. The muscle-glycogen may then reach vals. $>$ those of the normal fasting level.

W. O. K.

Relation of the pituitary gland to muscle-creatinine. B. G. SHAPIRO and H. ZWARENSTEIN (Proc. Roy. Soc. Edin., 1936, 56, 164—168).—The hamstring muscles of the right and left legs of *Xenopus laevis* contain on an average 0.399% of creatinine (I). Muscle-(I) decreases by 15% 18 to 22 weeks after hypophysectomy, whilst daily injections of 0.2 c.e. of anterior lobe extracts cause an increase of approx. 30% 3 to 5 weeks after commencing injection. The anterior lobe of the pituitary and muscle-(I) may be indirectly related through some other endocrine organ.

J. N. A.

Source of the blood-acetone resulting from administration of the ketogenic principle of the anterior pituitary gland. I. A. MIRSKY (Amer. J.

Physiol., 1936, 115, 424—428).—The hormone acts only on the liver, without stimulating extra-hepatic fat oxidation. The muscles play no part in the accumulation of blood-ketones, production of which is probably due to decreased carbohydrate utilisation by the liver cells in presence of an increased catabolism of fatty acids arising from accelerated glycogenolysis in the liver.

R. N. C.

Effects of oestrus and spaying on pituitary metabolism. J. VICTOR and D. H. ANDERSEN (Amer. J. Physiol., 1936, 115, 130—137).—The respiratory rate *in vitro* of the anterior pituitary is max. in pro-oestral, and min. in dioestral and spayed, animals. Anaerobic glycolysis and total pituitary metabolism in pro-oestral and oestral are > those in dioestral and spayed animals.

R. N. C.

Action of preparations from the posterior lobe of the pituitary gland on the imbibition of water by frogs. F. K. OLDHAM (Amer. J. Physiol., 1936, 115, 275—280).—The oxytocic and, to a smaller extent, the pressor hormone cause imbibition; the melanophore-dilating hormone is not involved.

R. N. C.

Hormones and pregnancy. W. C. MILLER (Vet. Rec., 1936, 48, 903—911).—A review. A. G. P.

Biological assay of "international standard" oestrin and of certain commercial preparations. F. E. D'AMOUR and R. G. GUSTAVSON (J. Pharm. Exp. Ther., 1936, 57, 472—481).—The rat unit of international standard oestrin is as follows: single injection in oil, 1.3×10^{-6} g.; multiple injection in oil 1.5×10^{-6} g.; single aq. injection 3.8×10^{-6} g., and multiple aq. injection 0.74×10^{-6} g. Aq. commercial preps. decrease considerably in activity on keeping.

J. N. A.

Effect of oestrin on the prostate gland of the albino rat and mouse. D. WELLER, M. D. OVERHOLSER, and W. O. NELSON (Anat. Rec., 1936, 65, 149—163).

R. N. C.

Effect of oestrin on the activity of the anterior lobe of the pituitary. H. L. FEVOLD, F. L. HISAW, and R. GREP (Amer. J. Physiol., 1936, 114, 508—513).—Secretion of luteinising hormone is augmented, but not that of follicle-stimulating hormone.

R. N. C.

Gonad-hypophyseal complex in oestrin-injected rats. S. R. HALPERN and F. E. D'AMOUR (Amer. J. Physiol., 1936, 115, 229—238).

R. N. C.

Persistence of corpora lutea in the pseudo-pregnant rabbit. W. M. ALLEN and G. P. HECKEL (Science, 1936, 84, 161—162).—The persistence of corpora lutea produced by injection of oestrin (I) after a sterile mating indicates that in the rabbit the placenta elaborates (I) which, rather than a placental gonadotropic hormone, causes the corpora to persist.

L. S. T.

Comparative assay of oestrone in the rat and mouse. A. M. HAIN and J. M. ROBSON (J. Pharm. Exp. Ther., 1936, 57, 337—346).—When oestrone (I) is given in 4 doses in oil, the rat unit is approx. 0.0033 mg., when similarly administered in 10% EtOH,

0.0025 mg. For the mouse the units are 0.00009 mg. and 0.00025 mg., respectively. Using oestrone benzoate (II), the rat unit is 0.005—0.01 mg., and for the mouse slightly < 0.0005 mg. With both species a single injection of (II) produces less effect than the same wt. of (I) given in 4 injections. The duration of the oestrus response and the relation between the rat and mouse units are discussed.

J. N. A.

Influence of oestrone on galactin content of male rat pituitaries. R. P. REECE and C. W. TURNER (Proc. Soc. Exp. Biol. Med., 1936, 34, 402—403).—The pituitaries of normal male rats contain a definite quantity of galactin which is increased by subcutaneous injection of hydroxyoestrin benzoate (Oestroform B).

W. O. K.

Sterility in rabbits produced by injection of oestrone and related compounds. G. PINCUS and R. E. KIRSCH (Amer. J. Physiol., 1936, 115, 219—228).

R. N. C.

Spectrophotometric determination of α -oestrone and its derivatives. M. SUREAU and P. GRANDADAM (Compt. rend., 1936, 203, 440—442).—The technique of Chevallier (A., 1935, 906) is adapted. Ultra-violet adsorption coeffs. are determined for α -oestrone and for dihydro-oestrone and its benzoate.

A. G. P.

Isolation of principal oestrogenic substance of liquor folliculi. D. W. MACCORQUODALE, S. A. THAYER, and E. A. DOISY (J. Biol. Chem., 1936, 115, 435—448).—Dihydrotheelin (I), previously isolated from sow ovaries as the *m*-bromobenzoate (Proc. Soc. Exp. Biol. Med., 1935, 32, 1182), is more easily isolated as the di- α -naphthoate. On hydrolysis (I) is obtained in pure cryst. form. (I) isolated from sow ovary is identical with that obtained from theelin.

E. M. W.

Action of a synthetic oestrogenic agent [9 : 10-dihydroxy-9 : 10-di-*n*-propyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthrene] on the anterior pituitary of the castrated female rat. J. M. WOLFE (Amer. J. Physiol., 1936, 115, 665—669).

R. N. C.

Changes in tissue metabolism in oestral, dioestral, and spayed rats. J. VICTOR, D. H. ANDERSEN, and M. R. PREST (Amer. J. Physiol., 1936, 115, 121—129).—O₂ consumption of the liver *in vitro* is max. in oestral and min. in spayed animals; the R.Q. is unaltered. Kidney metabolism does not vary. Infection increases O₂ consumption and the R.Q. of liver but not kidney.

R. N. C.

Effect of ovarian hormone on the basal metabolism of experimental hyperthyroidised rats. T. C. SHERWOOD and L. M. BOWERS (Amer. J. Physiol., 1936, 115, 645—650).—The hormone induces a greater fall in basal metabolism when injected in oil solution than in aq. solution. It accelerates the return of basal metabolism to normal after thyroid feeding.

R. N. C.

Effects of two hypophyseal gonadotropic hormones on the reproductive system of the male rat. R. O. GREP, H. L. FEVOLD, and F. L. HISAW (Anat. Rec., 1936, 65, 261—271).—Follicle-stimulating hormone stimulates the germinal epithelium,

whilst luteinising hormone stimulates the interstitial cells to secrete the male hormone. R. N. C.

Concentration and purification of the gonadotropic substance in urine of ovariectomised and post-menopausal women. L. LEVIN and H. H. TYNDALE (Proc. Soc. Exp. Biol. Med., 1936, **34**, 516—518).—Gonadotropic material may be almost quantitatively pptd. by tannic acid from urine acidified by AcOH to p_H 5.0. The ppt. is extracted with EtOH and then with COMe₂. Purification of the crude tannate is described. W. O. K.

Quantitative relation between follicle-stimulating and luteinising effects in castrate and menopausal urine. U. J. SALMON and R. T. FRANK (Proc. Soc. Exp. Biol. Med., 1936, **34**, 463—466).—Extracts from the urine of female castrates or women past the menopause produced follicle-stimulating and luteinising effects in rats' ovaries according to the dose given. W. O. K.

Effect of divided dosage of gonadotropic extracts in the immature male rat. F. BISCHOFF (Amer. J. Physiol., 1936, **114**, 483—487).

R. N. C.

Industrial extraction of crystalline folliculin. Physical and biological determination. D. VAN STOLK, H. PÉNAU, and R. L. DE LENCÈRE (J. Pharm. Chim., 1936, [viii], **24**, 249—266).—Pregnant mares' urine gives max. yields of the hormone (I) at the 5th—7th month of gestation (cf. Cole and Saunders, A., 1935, 1426). Colorimetric determination of (I) (Kober, A., 1931, 1195) is unsatisfactory with crude preps. A spectrometric method [(I) in EtOH has an absorption max. at 277.5 and min. at 247.5 $m\mu$] and its application to the various stages of purification of (I) during its isolation from urine are described. F. O. H.

Corpus luteum hormone. K. EHRHARDT and A. HAGENA (Endokrinol., 1935, **16**, 51—60; Chem. Zentr., 1935, ii, 3788).—Impure extracts of human placenta give a positive Clauberg-Höhlweg reaction in 20% of cases examined, whereas after removal of follicular hormone 60% of positive tests are obtained. Extracts from pregnancy urine or that from tumour cases seldom contain the corpus luteum hormone; it could not be detected in urine after parental administration. A. G. P.

Effect of progestin on the *in vitro* response of the rabbit's uterus to pituitrin. A. W. MAKEPEACE, G. W. CORNER, and W. M. ALLEN (Amer. J. Physiol., 1936, **115**, 376—385). R. N. C.

Preparation of non-toxic urine fractions for assay of male hormone by the female bitterling test. I. S. KLEINER, A. I. WEISMAN, and D. I. MISHKIND (Science, 1936, **84**, 142).—Dialysis removes the factor toxic to fish in certain urines. L. S. T.

Increasing the effectiveness of testosterone. A. S. PARKES (Lancet, 1936, **231**, 674—676).—Testosterone acetate (I) and propionate (II) are much more effective than the free hormone in restoring the atrophic prostate and seminal vesicles of castrated rats. (II) has a more intense and prolonged action than (I). L. S. T.

Sexual hormones. XVI. Esters of the testosterone and androsterone series. XVII. Bromination of sterol and androstene derivatives.—See this vol., 1382.

Effects of androgenic substances in the rat. W. O. NELSON and T. F. GALLAGHER (Science, 1936, **84**, 230—232).—The effect of male hormone extracts on the testes of hypophysectomised rats, and the effect of androsterone, androstenediol, and androstenedione on the pituitary, mammary gland, and uterus of the spayed rat are described. L. S. T.

Proposed synthesis of equilenin.—See this vol., 1382.

Inter-relationship of vitamins. M. MITOLO (Boll. Soc. ital. Biol. sperim., 1936, **11**, 334—336).—The symptoms occurring in animals fed on diets rich in certain vitamins and lacking in others are described. Those of avitaminosis-D are modified by concomitant hypervitaminosis-A, -B, -C, or -(A+B+C); in the last case, a rachitic condition does not occur. F. O. H.

Experimental polyavitaminosis. G. PERETTI (Boll. Soc. ital. Biol. sperim., 1936, **11**, 338—339).—Symptoms of deprivation of one or more of the vitamins-A, -B, and -C in guinea-pigs are described. F. O. H.

Choice of diet and production of experimental avitaminosis. G. RIGOBELLO (Boll. Soc. ital. Biol. sperim., 1932, **7**, 825—830; Chem. Zentr., 1935, ii, 3791).—Suitable diets for inducing avitaminosis-A, -B, and -D are given. A. G. P.

Relation of vitamin-A to eye development in the pig. F. HALE (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 126—128).—Defective eyes may result from -A deficiency in the mother or in the ration. CH. ABS. (*p*)

Vitamin-A as a prophylactic against the common cold in groups of school children. E. M. TRESS (Amer. J. Digest. Dis. Nutrition, 1935, **1**, 795—796).—Beneficial effects of feeding -A are recorded. CH. ABS. (*p*)

Vitamin-A storage by chickens. A. D. HOLMES, F. TRIPP, and P. A. CAMPBELL (Poultry Sci., 1936, **15**, 71—78).—The -A contents of livers of chickens of varying age and receiving -A supplements are recorded. High-producing flocks receiving a vitamin-rich diet can maintain a sufficient body reserve of -A through the reproductive period. A. G. P.

Cytological study of the action of vitamin-A. P. JOYET-LAVERGNE (Bull. Soc. Chim. biol., 1936, **18**, 1041—1054).—Vitamin-A as determined by the Carr-Price test is present in the nucleolus and chondriome of animal and vegetable cells. A. L.

Photo-chemical decomposition of vitamin-A in alcoholic solution. II. Secondary reaction. A. CHEVALLIER and P. DUBOULOZ (Bull. Soc. Chim. biol., 1936, **18**, 1115—1124; cf. this vol., 1159).—One of the two products produced by irradiation of vitamin-A with light of 365 $m\mu$ is further decomposed with shorter waves giving a series of products. A. L.

Spectrophotographic studies on the antimony trichloride reaction for vitamin-A. I. Relation between tintometer readings and spectral absorption of the blue solution. O. NOTEVARP and H. W. WEEDON (Biochem. J., 1936, 30, 1705—1718).—The absorption spectrum of the $SbCl_3$ -vitamin-A complex changes with time and the variation in the intensity of the 618 and 572 $m\mu$ bands depends on the prep. used. Empirical relations for the extinction coeffs. and the blue vals. are given for the different absorption max., and also a relation for the variation of the blue val. with -A concn. H. D.

Determination of vitamins by chemical methods. I. Vitamin-A in vegetable and animal oils. A. SANTOS RUIZ (Anal. Fis. Quím., 1934, 32, 1217—1224).—A review of the literature. Olive oil contains 3 "cod-liver-oil units" per 100 g. The vitamin-A content of animal and vegetable oils is related to the intensity and time of action of the solar rays to which they have been exposed. F. R. G.

Nutritive effect of tunny, ox liver, and yeast on rats. U. TANGE and K. MICHI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 809—817).—Rats on a diet deficient in B vitamins do not grow so well when the ration is supplemented with tunny or ox liver as when with yeast. The growth-promoting actions of EtOH extracts of yeast were > those from fat-free ox liver, which in turn exceeded those from tunny liver. W. O. K.

Intermediate metabolism of carbohydrates in avitaminosis-B. I. G. PERETTI and F. PORRAZZO (Arch. Sci. biol., 1933, 19, 227—248; Chem. Zentr., 1935, ii, 3791).—Vitamin-B affects carbohydrate metabolism at a stage preceding that of lactic acid production. A. G. P.

Multiple nature of the third factor of the vitamin-B complex. S. LEFKOVSKY, T. H. JUKES, and M. E. KRAUSE (J. Biol. Chem., 1936, 115, 557—566).—Component I (separated from II by adsorption on fuller's earth) of rice-bran extracts prevented dermatitis in rats but was without effect on chickens, whereas II prevented the latter and aggravated the former in absence of I. The deficiency in rats with an EtOH extract of white corn as a source of vitamin-B was multiple in nature, the chief factor lacking being vitamin- B_2 (flavin). H. G. R.

Extraction of vitamin- B_1 from adsorbates. R. D. GREENE and A. BLACK (Science, 1936, 84, 185—186).—The best yields (< 90%) of vitamin from the adsorbate obtained in Seidell's method occur when aq., aq.-EtOH, or EtOH solutions of acid salts of C_6H_5N , quinoline, NH_2Ph , etc. are used as extractants. The salt solutions have an effect > that of acid or base alone. L. S. T.

Pathological changes in the eye in experimental vitamin- B_2 deficiency. K. SEN, N. DAS, and B. C. GUHA (Sci. and Cult., 1935, 1, 59—60). CH. ABS. (p)

Potassium in the brain in vitamin- B_1 deficiency. H. W. KINNERSLEY (Nature, 1936, 138, 368).—No significant difference in the K content of the brains of normal and vitamin- B_1 -deficient pigeons has been detected (cf. A., 1934, 1042). L. S. T.

Vitamin- B_2 concentrates as preventives of black-tongue. L. E. BOOHER and G. H. HANSMANN (Amer. J. Physiol., 1936, 114, 429—435).—Vitamin- B_2 concentrate from low-lactose whey powder, which contains lactoflavin and at least one other thermostable vitamin necessary for growth of rats, prevents or cures black-tongue in dogs. It augments the inferior rate of growth produced in young rats by a diet causing black-tongue in dogs. Liberal quantities of nutritive protein in the diet apparently decrease the - B_2 requirements for growth of rats and prevention of black-tongue in dogs. R. N. C.

Vitamin- B_2 from different sources and coccidial infection. E. R. BECKER and N. F. MOREHOUSE (Proc. Soc. Exp. Biol. Med., 1936, 34, 437—439).—A substance promoting the development of the oocysts of *Eimeria mizairii* in rats is present in various vitamin- B_2 preps., but not in liver. W. O. K.

Significance of vitamin-C in biological oxidation processes of the human lens. P. WEINSTEIN (Orvosi Hetilap, 1935, 79, 874—875).—Vitamin-C, like cystine (I), disappears from the cataractous lens and is found in the covering. Reduced -C acts as a protective agent and retards the oxidation of (I). CH. ABS. (p)

Reversible oxidation of vitamin-C in biological medium or pure solution. N. BEZSSONOFF and M. WOLOSZYN (Compt. rend., 1936, 203, 275—277).—The decolorisation of dichlorophenol-indophenol by ascorbic acid in lemon juice is unaffected by change of pH , but varies in pure solutions. The stability of the vitamin is increased in biological solutions by the presence of other reducing agents. The existence of an oxidised compound of -C, $(C_6H_7O_6)_2$, is postulated. P. G. M.

Meat diet: blood as an antiscorbutic factor. V. STEFANSSON (Science, 1936, 84, 227—228).—A discussion. L. S. T.

Histochemistry. IX. Quantitative distribution of vitamin-C in the adrenal gland at various stages of development. D. GLICK and G. R. BISKIND (J. Biol. Chem., 1936, 115, 551—555).—The concn. is highest in the fascicular zone. It increases in all portions of the gland during growth of the foetus and reaches a max. in the calf. The size and vitamin-C content of the cells increase regularly to the adult stage. H. G. R.

Vitamin-C in an oestrin-producing ovarian tumour. G. R. BISKIND and D. GLICK (Science, 1936, 84, 186).—The relatively low vitamin-C concn. of this tissue supports the view (this vol., 530) that -C is unrelated to oestrin formation in the human ovary. L. S. T.

State of ascorbic acid in plant tissues. G. L. MACK (Nature, 1936, 138, 505—506).—Repetition of the work of Guha and Pal (this vol., 1033) failed to reveal an increase in ascorbic acid (I) content on heating. The cabbages examined did not contain appreciable amounts of combined (I). When the oxidation enzyme is inactivated by heat or EtOH, or inhibited by extraction with sufficiently strong acid,

the total (I) is obtained. The apparent increase on cooking is due to inactivation of the enzyme.

L. S. T.

Variation of vitamin-C content in certain fruits and vegetables.—See B., 1936, 953.

Ascorbic acid oxidase in determining vitamin-C in lens and aqueous humour. L. ROSNER and J. BELLOWS (Proc. Soc. Exp. Biol. Med., 1936, 34, 493—494).—Treatment of extracts of the lens of the eye or of the aq. humour with the enzyme from the Hubbard squash which promotes the oxidation of ascorbic acid (I) (A., 1935, 1023) completely destroys their power of reducing Tillmans' reagent (II). The reducing substance in the lens and humour determined by (II) is therefore (I).

W. O. K.

Use of the phosphotungstic acid method of determining ascorbic acid in urines with low ascorbic acid content. G. MEDES (Biochem. J., 1936, 30, 1753—1755; cf. A., 1935, 1430).—The application of the reagent to urines of ascorbic acid content of $<4 \times 10^{-4}$ g.-mol. per 100 ml. is described.

W. McC.

Determination of ascorbic acid by titration with 2:6-dichlorophenol-indophenol (Tillmans' method). R. STROHECKER and R. VAUBEL (Angew. Chem., 1936, 49, 666—668; cf. A., 1932, 310).—Details of the method given include standardisation of the dye (0.001*N*) with $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, prep. of tissue extracts by dil. AcOH, application of PhNO_2 (in which the dye is sol.) to highly-coloured extracts, and appearance of the end-point under varying conditions.

F. O. H.

Determination of vitamin-C by means of its influence on the body-weight of guinea-pigs. K. H. COWARD and E. W. KASSNER (Biochem. J., 1936, 30, 1719—1727).—A method similar to that used for vitamin-A (A., 1932, 886) is described. The derived relationship is $y = 74.3 + 108.2 \log(\log 10x)$, where y is the mean wt.-increase in g. in 6 weeks and x is the daily dose of ascorbic acid in mg.; that between severity of scurvy and dose is also curvilinear. The method, however, is somewhat inferior to the "tooth" method.

F. O. H.

Value of the acid silver nitrate reaction as a test for ascorbic acid. A. GIROUD and C. P. LEBLOND (Nature, 1936, 138, 247—248).—The absence of a coloration by acid AgNO_3 is not necessarily a proof of the absence of ascorbic acid (I), but a positive reaction in tissue is a sp. test for (I).

L. S. T.

Differential threshold of reaction to vitamin-D deficiency in the house-sparrow and the chick. H. FRIEDMANN (Biol. Bull., 1935, 69, 71—74).—The possible antirachitic properties of the irradiated secretion of the uropygial gland are examined. The threshold of reaction of house-sparrows and starlings to vitamin-D deficiency is markedly different.

CH. ABS. (p)

Mechanism of the action of irradiated ergosterol. I. Development of bone and its mineral content; calcæmia and phosphatæmia. II. Lipin content of bone. L. ROBUSCHI (Boll. Soc. ital. Biol. speriment., 1932, 7, 1025—1028, 1029—1032;

Chem. Zentr., 1935, ii, 3791—3792).—I. Administration of irradiated ergosterol (I) increases the Ca and P contents of blood but not those of bone.

II. (I) affects the lipin content of bone marrow.

A. G. P.

Effect on the antirachitic activity of their milk when ewes were exposed to sunshine and ultraviolet rays. W. G. KIRK, B. H. THOMAS, and C. C. CULBERTSON (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 182—188).—Treatments produced no appreciable effect.

CH. ABS. (p)

Vitamin-D requirements of calves when natural milk is the sole source of the antirachitic factor. J. W. LONG, C. F. HUFFMAN, and C. W. DUNCAN (Milk Plant Month., 1936, 25, No. 7, 30—36).—Growing calves developed rickets when fed a rachitogenic ration containing the same Ca/P ratio as milk. The vitamin-D requirement of a growing calf \propto the rate of gain in body-wt. When winter or early spring milk supplied the only source of -D, 0.3—0.4 U.S.P. unit per lb. of body-wt. daily was sufficient for the requirements of a growing calf provided that the normal level of plasma-Mg was maintained. The higher -D requirement of calves on summer milk is tentatively associated with a difference in Mg metabolism.

W. L. D.

Effect of source of vitamin-D in the diet of chicken on storage of the antirachitic factor. G. M. DEVANEY, H. E. MUNSELL, and H. W. TITUS (Poultry Sci., 1936, 15, 149—153; cf. A., 1935, 1287).—The -D storage of egg yolk was not affected by 8% of fat in the diet. 8% of cod liver-oil (I) in the diet reduced the no., size, and hatchability of eggs. The -D in yolk increases with the (I) or viosterol (II) content of the ration. With a ration containing 2—4% of (I) or 8% of (II), approx. 2% of the ingested -D appeared in the egg yolk. With 2—4% of (II) or 8% of (I), -D storage in yolks was appreciably less although the -D potency of the yolk was increased.

A. G. P.

Determination of vitamin-D. III. Effect of calcification on growth and sex differences in white Leghorn chicks. L. L. LAGHAT and H. A. HALVORSON (Poultry Sci., 1936, 15, 127—135; cf. A., 1935, 417).—Deficiency of vitamin-D affects growth and calcification in females $>$ in males. Females utilise -D more efficiently than do males, and are more suitable for laboratory tests. Seasonal variations, previously reported, in the calcification of rachitic chicks are now explained on the basis of association between body-wt. and bone-ash content. In faster growing birds greater amounts of skeleton are developed and show greater relative amounts of mineral deposition in the skeleton. Results of the A.O.A.C. method of assay are accurately interpreted by means of a simple formula.

A. G. P.

Factors producing rickets present in cereals. O. RYGH (Bull. Soc. Chim. biol., 1936, 18, 1091—1096).—The free fatty acids (I) isolated from oats are antagonistic to the antirachitic action of those from green plants. Concn. of the rachitic factor in the unneutralised fraction of (I) was effected after partial neutralisation.

A. L.

Vitamin-D in Baltic herring. (A) G. BLIX, H. RYDIN, and G. ENGLUND. (B) G. BLIX and G. ENGLUND (Upsala läkarefören. förh., 1936, 40, 175—182; 42, 203—207).—The vitamin-D content of the herring oil was about 200 international units per g., and therefore comparable with that of good cod-liver oil. The fat content of the herrings was a max. at 7—9% in Sept. to Nov. and a min. at 3—6% in Feb. to April. Boiling the herrings in a min. amount of H₂O did not affect the -D val. of the oil.

NUTR. ABS.

Chemistry of calciferol and vitamin-D₃. A. L. BACHARACH (Nature, 1936, 138, 387—389).—A summary of recent work. L. S. T.

Purification of the antihæmorrhagic vitamin by distillation. H. J. ALMQUIST (J. Biol. Chem., 1936, 115, 589—591).—The active fraction of the lucerne-meal concentrate (cf. this vol., 907) distils at 120—145°/1 × 10⁻³ mm. H. G. R.

New factor, not vitamin-B₂, necessary for hatchability. R. B. NESTLER, T. C. BYERLY, N. R. ELLIS, and H. W. TITUS (Poultry Sci., 1936, 15, 67—70).—A mixed grain-lucerne meal ration contains sufficient vitamin-B₂ for hatchability, but lacks a factor necessary for high hatchability. This factor is present in dried pigs' liver and green grass, and, to a smaller extent, in fish meal, desiccated meat meal, and dried buttermilk, but not in whey.

A. G. P.

Electrophoresis of plant cell-contents. A. GUILLIERMOND and N. CHOUCROUN (Compt. rend., 1936, 203, 225—229).—An external field exerts little effect on the contents so long as the cell is living, but prolonged application of a powerful field kills the cell and electrophoresis occurs. On death the nucleus is normally attracted to the positive pole; addition of neutral-red, which is localised during life in the vacuole and is transferred to the nucleus on death, causes migration to the negative pole. P. G. M.

Permeability of membranes.—See this vol., 1335.

Breakdown of fruit and vegetable tissue due to an electric current. W. SEIFRIZ (Plant Physiol., 1936, 11, 195—200).—Tissues of fruits and vegetables when made the cathode of a 110-volt circuit break down to a soft, dark-coloured mass and show a uniform p_n of 12.2. When placed at the anode the tissues remain practically unchanged. The degeneration is attributed to auto-proteolysis catalysed by intracellular enzymes rendered active by reducing conditions at the cathode. Proteolysis is followed by enzymic oxidation and discoloration accelerated by the alkaline medium surrounding the cathode. Phenolic compounds are probably concerned. Potato and onion tissues gelatinise at the cathode and are not discoloured. A. G. P.

Vernalisation. F. G. GREGORY and O. N. PURVIS (Nature, 1936, 138, 249).—Embryos of cereals separated completely from the endosperm can be vernalised in the same way as complete seeds, showing that the cause of vernalisation by low temp. is inherent in the embryo and independent of the metabolism of the endosperm or aleurone layer. L. S. T.

Creeping movements of Spirogyra. D. R. CHESTERMAN and C. L. FOSTER (Nature, 1936, 138, 403—404).—Solutions of electrolytes of concn. $\geq 1\%$ reduce the creeping of *Spirogyra* up the sides of the containing vessel in the dark. Sucrose and glucose up to a crit. concn. reduce climbing and then increase it. The results appear to be related to effects on the respiratory activity of the algal cells. L. S. T.

Changes of apparent ionic mobilities in protoplasm. I. Effects of guaiacol on Valonia. W. J. V. OSTERHOUT (J. Gen. Physiol., 1936, 20, 13—43).—On treatment with 0.01M-guaiacol the order of the apparent mobilities (K > Cl > Na) in the non-aq. protoplasmic surface is reversed. On adding the same concn. to sea-H₂O the p.d. of the cell changes from -10 to +28 mv. and then slowly returns, due to changes in the apparent mobilities of the org. ions in the protoplasm. H. G. R.

Yield and composition of eared and earless maize plants in a selfed line segregating barren stalks. R. J. GARBER, R. B. DUSTMAN, and C. R. BURNHAM (J. Amer. Soc. Agron., 1936, 28, 85—91).—The wt. and sugar content of stems and leaves of earless plants were > those of eared plants. In the entire plants eared individuals showed greater wt., carbohydrate content, and Et₂O extract, but less crude protein. A. G. P.

Dry matter production and metabolism in certain cultivated plants. III. Causes of nitrogen intake and protein formation. S. ODÉN and K. SJÖBERG (Kung. Landtbruks.-Akad. Handl. Tidskr., 73, 780—821; Chem. Zentr., 1935, ii, 3939).—In oats, beans, and cress, increasing N supplies cause increases in yield and total and % N, up to limiting vals. Small additions of N are converted almost completely into protein. The proportional conversion is smaller when large amounts of N are assimilated. A. G. P.

Tissue function and organic solute movement in the sunflower. O. A. LEONARD (Plant Physiol., 1936, 11, 25—61).—Diurnal and seasonal variations in the carbohydrate distribution in the plants are examined. Variation in concns. of simple sugars in leaves correspond with much smaller variations in sucrose (I). The (I) gradient is positive in bark and negative from head to seed. Storage of (I) occurs chiefly in bark, and that of simple sugars in pith. The starch content of all organs is very low except in leaves during the day. Acid-hydrolysable carbohydrate is a temporary storage form and is nearly all translocated from leaves at night. Pith effects storage of NO₃' and some synthesis of NH₂-acids. Gradients of sol. N are positive from leaves to bark but those of total sol., NH₂-, and NH₄'-N are negative up the stem. Amide-N is never abundant and often absent. A. G. P.

Production and physiology of Concord grape vines as affected by variations in the severity of pruning. T. J. MANEY and H. H. PLAGGE (Proc. Amer. Soc. Hort. Sci., 1934, 32, 392—396).—No correlation was found between chemical composition and differences in fruitfulness. CH. ABS. (p)

Influence of the chloride ion on the chlorophyll content of potato leaves. S. BASSLAVSKAJA and M. SIROESCHKINA (Plant Physiol., 1936, 11, 149—157).—The chlorophyll (I) content of field-grown plants was 2—3 times that of pot-cultured plants. Heavy applications of Cl-containing fertilisers lowered the (I) content of field plants to an extent related to their increased H₂O content. The decrease in (I) content (%) of the dry matter of leaves occurred towards the end of the vegetative period. A. G. P.

Chlorolytic action of serum. M. E. SAUER (Plant Physiol., 1936, 11, 159—166).—Serum causes a liberation of chlorophyll (I) from cells of *Euglena gracilis* or *Protosiphon botryoides* if these have been sufficiently altered by contact with strong serum or by heat. The action is related to the lipin content of the serum. Immune serum does not increase the permeability of the cell to (I). A. G. P.

Exudation in cucurbits. A. S. CRAFTS (Plant Physiol., 1936, 11, 63—79).—The mechanism of phloem and xylem exudation is examined. A. G. P.

Absorption of water by the foliage of some common fruit species. W. G. BRIERLEY (Proc. Amer. Soc. Hort. Sci., 1934, 32, 277—283).

CH. ABS. (p)

Effect of ammonium- and of nitrate-nitrogen on the composition of the tomato plant. H. E. CLARK (Plant Physiol., 1936, 11, 5—24).—In sand cultures the use of Ca(NO₃)₂ as N source produced greater fresh wt. of plants but a slightly smaller % dry matter in fresh material. NO₃'-fed plants contained more NO₃', ash, oxalic, malic, citric, and total org. acids, but less glutamine, asparagine, total NH₂-N, sol. org. and insol. protein-N than those receiving NH₄'. The NH₄ content was high in plants supplied with media of higher [NH₄']. Relations between absorption and assimilation of N, accumulation of ash constituents, and the synthesis of org. acids by plants are discussed. A. G. P.

Total nitrogen in developing flowers and young fruits of Valencia oranges. S. H. CAMERON and D. APPLEMAN (Proc. Amer. Soc. Hort. Sci., 1934, 32, 304—207).—Flowers developing early contain more N than those developing later. The petals, stamens, and pistil of mature blossoms contain approx. 45, 30, and 25%, respectively, of the total N and dry matter. CH. ABS. (p)

Translocation of nitrogen in woody plants. W. E. LOOMS (Proc. Amer. Soc. Hort. Sci., 1934, 32, 61—64).—Much protein-N accumulated in the wood and bark of trees and was subsequently utilised in early spring growth. Movement of N from wood and bark was delayed by phloem rings and sol. org. N accumulated below the rings. Inorg. N can pass through normal cell membranes but org. N does not readily penetrate. Its upward and downward movement is confined to the plasmodesmal connexions between living cells, especially in phloem. CH. ABS. (p)

Mechanism of symbiotic nitrogen fixation. A. I. VIRTANEN (Suomen Kem., 1936, 9, A, 69).—The N excreted by root nodules in sterile sand

culture consists of aspartic acid and lysine, with small amounts of NO₂' derived from oximes. The first compound formed in N fixation is probably NH₂OH, which reacts with oxalacetic acid (derived from plant sugars) to produce the oxime and thence, by reduction, aspartic acid. A. G. P.

Diagnosis of plant troubles with diphenylamine. L. H. JONES (Plant Physiol., 1936, 11, 207—209).—Applications of the NHPh₂ test in the examination of physiological disturbances involving N are described. Indications of a photochemical conversion of NH₄' into NO₃' within the plant are recorded. A. G. P.

Effect of boron on growth of certain green plants. A. R. GÉIGEL (J. Agric. Univ. Puerto Rico, 1935, 19, 5—28).—In H₂O cultures of *Spirodela polyrrhiza* B was toxic at concns. >1 p.p.m. and lethal at >5 p.p.m. B caused chlorosis not corr. by Fe but partly cured by K tartrate. *Chlorella* was stimulated by 10 p.p.m. of B, larger proportions of which did not cause chlorosis. B did not lower the availability of Fe. Resistance of plants to B was increased by addition of glucose or sucrose to media. CH. ABS. (p)

Chemical and enzymic studies of the uneven ripening of Concord grapes. J. E. WEBSTER, E. ANDERSON, and F. CROSS (Proc. Amer. Soc. Hort. Sci., 1934, 32, 365—369).—The principal chemical difference between green and coloured grapes is the lower sugar content of the former. CH. ABS. (p)

Seasonal changes in Bartlett pear-leaves. L. D. DAVIS and N. P. MOORE (Proc. Amer. Soc. Hort. Sci., 1934, 32, 131—138).—Ash constituents and N of leaves are examined at various growth stages. There was a consistent loss of N throughout the season especially after yellowing of leaves. CH. ABS. (p)

Absorption, distribution, and seasonal movement of potassium in young apple trees: effect of potassium fertiliser on the potassium and nitrogen contents and growth of trees. R. F. CHANDLER, jun. (J. Agric. Res., 1936, 53, 19—42).—Absorption of K by young trees \propto dry wt. increases. Relative amounts of K in new growth tended to increase and those of 1- and 2-year tissue to decrease throughout the season. In roots K decreased during rapid growth but increased in the later part of the season. The abs. amount of K in all parts of the tree increased with growth; that in leaves decreased after abscission began. New wood added by diameter growth corresponded with current twig growth in respect of [K]. The K content of old leaves was < that of new leaves. The increased intake of K by tissues following use of K fertilisers was in the order leaves > bark > wood. No growth differences could be attributed to the fertiliser. N absorption by trees continued late in the season, whereas K absorption ceased at leaf-fall. The N content of wood and bark decreased during summer through translocation to leaves, but K vals. remained approx. const. A. G. P.

Transformation of sugars in plants. M. NURMIA (Suomen Kem., 1936, 9, A, 70).—Wheat, clover, oats, and horse beans, deprived of starch by storage

in darkness, when cut and placed in sugar solutions absorbed glucose or fructose, partly converted either sugar into the other, and synthesised sucrose (I). (I) was also produced in varying amounts from galactose and maltose, but not from xylose, $\text{CO}(\text{CH}_2\text{OH})_2$, or glycerol. The changes were not affected by PhMe and only slightly retarded by KCN. A. G. P.

Changes in carbohydrate content of wheat plants during the process of hardening for drought-resistance. I. M. VASSILIEV and M. G. VASSILIEV (Plant Physiol., 1936, 11, 115—125).—Hardening of wheat plants by growth with insufficient H_2O until wilting occurs resulted in an initial (24 hr. after wilting) increase in monosaccharides (I) and sucrose (II) and decrease in hemicellulose (III) contents. Subsequently, (II) decreased but (I) and (notably) (III) increased. Immediately after watering (I) decreased and (II) remained at a low level. Fully recovered plants showed lower H_2O and (I) but higher (II) and (III) contents than control plants. The significance of (III) in drought-resistance is discussed. A. G. P.

Distribution of acetaldehyde and alcohol in the apple fruit. E. V. MILLER (J. Agric. Res., 1936, 53, 49—55).—Vals. for various parts of different varieties of apples are given. Storage of prepared samples in refrigerators results in marked increase in MeCHO (I) content. Fruit affected with soft scald or soggy breakdown showed increased amounts of (I) in the peel. Recorded high vals. for (I) in peel are in part due to its production in cells ruptured in paring but accumulation of (I) in peel always follows injury by mechanical means or by physiological abnormality. A. G. P.

Distribution of total soluble solids and catalase in different parts of Jonathan apples. P. L. HARDING (J. Agric. Res., 1936, 53, 43—48).—The sol. solid content of apples was highest in the skin and decreased towards the pith. In fruit affected with soft scald all vals. tended to be < normal. Catalase activity in healthy apples was highest in skin and lowest in the region immediately beneath; in those showing soft scald max. activity occurred in the pith and min. vals. in the diseased portions. A. G. P.

Photosynthesis of formaldehyde from "nascent carbon dioxide" in vitro: importance of respiration in photosynthesis. A. RAM (Proc. Acad. Sci. U.P., 1934, 4, 83—94).—Solutions of AcOH , citric, malic, and lactic acids, glycine, glycogen, COMe_2 , etc., malachite-green, Me-violet, methylene-blue, etc. produce CH_2O (I) on exposure to sunlight. Other simple acids, sugars, and starch produce much smaller amounts. The first group of substances probably produce (I) directly and the second group indirectly through CO_2 and H_2O formed on oxidation. The bactericidal action of dyes may be due to formation of (I). Photosynthesis in plants is aided by energy derived from respiration. (I) is obtained photochemically from CO_3'' or HCO_3' solutions much more readily in the presence of suitable exothermic reactions. CH. ABS. (p)

Photosynthesis in relation to light and carbon dioxide. E. L. SMITH (Proc. Nat. Acad. Sci., 1936, 22, 504—511).—A mathematical relationship is derived and compared with that applicable to other recorded data. The photosynthetic rate is the same function of both $[\text{CO}_2]$ and light intensity.

A. G. P.

Fluorescence of chlorophyll and its relation to photochemical processes in plants and organic solutions.—See this vol., 1320.

Oxidative metabolism of the colourless alga, Prototheca zopfii. H. A. BARKER (J. Cell. Comp. Physiol., 1936, 8, 231—250).—Data are given for the O_2 consumption and CO_2 production corresponding with the assimilation of simple org. compounds by *P. zopfii*. The primary process of assimilation is the oxidation of the substrate to a carbohydrate, which is stored as glycogen, followed by a slower decomp. in the processes of cell synthesis. 50—80% of the substrate C is assimilated. E. A. H. R.

Determination of carbon dioxide production in physiological plant studies. F. L. WYND (Ann. Missouri Bot. Gdns., 1935, 22, 361—363).—Apparatus capable of detecting several g. of CO_2 with an error of >1 mg. over a 12-hr. period is described.

CH. ABS. (p)

Growth and respiration of the *Avena coleoptile*. J. BONNER (J. Gen. Physiol., 1936, 20, 1—11).—During growth the rate of elongation decreases more rapidly than the respiration; HCN or phenylurethane affects both to the same degree. Transport of the hormone into the cell and its action on elongation depend on aerobic metabolism, the cryst. hormone having no effect on respiration. H. G. R.

Respiration of ripening tomatoes. B. N. SINGH and P. B. MATHUR (Current Sci., 1936, 5, 76—78).—The increased liberation of CO_2 by ripening tomatoes is due to an accumulation of CO_2 in the tissues together with a lessened resistance of the peripheral tissues to diffusion. Subsequently CO_2 evolution declines, but the accumulation of CO_2 in the fruit is still marked. Usual methods of measuring respiration rates are thus open to error. J. L. D.

Effect of sulphur on rate of respiration and respiratory quotient in *Chilomonas paramecium*. S. O. MAST, D. M. PACE, and L. R. MAST (J. Cell. Comp. Physiol., 1936, 8, 125—139).—S (present as MgSO_4) is required for the respiration of *C. paramecium*, and probably functions in the oxidation of fat. Starch is transformed into fat, and S prevents the accumulation of the latter by causing its oxidation immediately on formation. E. A. H. R.

Measurement of respiratory exchange in plants. B. N. SINGH and P. B. MATHUR (Current Sci., 1936, 5, 20—22).—A simplification of the Haldane gas-analysis apparatus and the technique, as applied to these measurements, are described. D. C. J.

Vegetable growth-promoting hormones. F. KÖGL (Svensk Kem. Tidskr., 1936, 48, 145—155).—A lecture. H. W.

Action of β -indolylacetic acid on the development of seedlings. T. SOLACOLU and D. CONSTAN-

TINESCO (Compt. rend., 1936, 203, 437—440).—Certain concns. of β -indolylacetic acid (I) retard the development of the radicle of *Phaseolus vulgaris*. Cultures in Knop's solution on cotton to which (I) is added produce a filamentous mycelium-like structure, the normal development of the radicle being entirely suspended. The filaments are derived from proliferations of superficial and meristematic tissue following disturbance of the orientation of tissues effected by (I). A. G. P.

Effect of phenylacetic acid on the growth of tomato plants. H. L. PEARSE (Nature, 1936, 138, 363—364).—Tomato plants sprayed with an aq. 0.1% solution of $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ show increased length of stem and petioles. The % of total dry wt. present as leaf and root are decreased whilst those as stem and petiole are increased. The H_2O content, but not the total dry wt., is increased. L. S. T.

Formation of nodules in legume roots. K. V. THIMANN (Proc. Nat. Acad. Sci., 1936, 22, 511—514).—Experimental data quoted indicate that the formation of nodules may result from the production of auxin in bacterially infected cells. A. G. P.

Relation of root pressure to plant disease. J. JOHNSON (Science, 1936, 84, 135—136).—A discussion. Internal H_2O relations of the host as determined by root pressure may be an important determining factor in predisposition to infection and development of disease. L. S. T.

Adaptation of the micro-Kjeldahl method for determining nitrogen in plant tissues. N. W. STUART (Plant Physiol., 1936, 11, 173—179).—Pregl's method gives results for the total and non-protein-N of plant materials with the same accuracy as does the macro-method. Basic N in plant extracts may be determined without digestion of the phosphotungstic acid and filter-paper. Amides are partly hydrolysed during distillation but total amide- $+\text{NH}_3\text{-N}$ may be satisfactorily determined. A. G. P.

Determination of basic nitrogen. Semi-micro-method applicable to plant tissues. W. W. UMBREIT and P. W. WILSON (Ind. Eng. Chem. [Anal.], 1936, 8, 361—362).—After removing peptides, NH_3 , and amides the sap is treated with phosphotungstic acid in 5% H_2SO_4 and cooled at 0—5° for 48 hr. The ppt. is filtered, dissolved in NaOH, and digested in a semi-micro-Kjeldahl flask with H_2SO_4 containing 0.25% of CuSO_4 and SeO_2 . The method is accurate to 0.1—0.2 mg. of N. S. C.

Determination of small amounts of copper, especially in plants. E. STOLZE (Bodenk. Pflanzenernähr., 1936, 1, 115—132).—The dithiocarbazon (I) method (Fischer, A., 1934, 381) is applied to the examination of plant ash. Small amounts of Fe^{III} salts oxidise (I) and the product forms a Cu compound sol. in CCl_4 and not removed with excess of (I) by washing with aq. NH_3 . Treatment with $\text{Na}_2\text{S}_2\text{O}_3$ reduces the oxidation product. The ratio of Cu in plants to Cu in soil is lower in Cu-rich areas. In the latter, snails have higher Cu and Mn contents. In pot cultures application of CuSO_4 increased the Cu content of plants. The Mn content increased less uniformly. Spraying vines with Bordeaux mixture

increased the Cu and decreased the Mn in washed leaves. A. G. P.

Some ash constituents of alternate-bearing sugar prune trees. L. D. DAVIS (Proc. Amer. Soc. Hort. Sci., 1934, 32, 125—130).—The crop depletes the K and P in wood, bark, and spurs, but only K in leaves. The Ca and Mg contents of leaves are higher in bearing than in non-bearing trees.

CH. ABS. (p)

Correlation of organic and mineral matter contents of mulberry leaves. K. KATO (J. Agric. Chem. Soc. Japan, 1936, 12, 745—748).—The contents of K_2O , P_2O_5 , and SO_4^{2-} are directly and those of CaO and SiO_2 are inversely related to the amount of crude protein, whilst Na_2O is related to the carbohydrate sol. in HCl (*d* 1.15). J. N. A.

Plant roots give off organic acids. J. C. RATSEK (Proc. Amer. Soc. Hort. Sci., 1934, 32, 632—634).—When *Oxalis repens* was grown in H_2O cultures with media containing 100 and 250 p.p.m. of Ca (as CaCl_2), CaC_2O_4 was formed in the medium.

CH. ABS. (p)

Unsaturated fatty acids of hemp oil. Fixed oil from the seeds of *Celastrus paniculatus*, Willd.—See B., 1936, 1003.

Chemical investigation of the leaves of *Epi-medium macranthum* (Yin Yen Ho). Y. F. CHU and Y. S. KAO (J. Chinese Chem. Soc., 1936, 4, 312—321).—The EtOH extract of the leaves contains glucose, ceryl alcohol, hentriacontane, phytosterol, palmitic, stearic, oleic, and linoleic acids, and icaricide (?), $\text{C}_{27}\text{H}_{52}\text{O}_{12}$, m.p. 273—274° (Ac derivative, m.p. 149—151°), hydrolysed to anhydroicaritin (?), m.p. 219—220°. F. N. W.

Carbohydrates of *Allium* bulbs. V. Carbohydrates of *A. odorum* and *A. cepa*. VI. Chemical and physical properties of scorodose. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1935, 11, 548—551, 552—557; cf. A., 1935, 1435).—V. The carbohydrate distribution is recorded for both species. The principal cold- H_2O -sol. carbohydrate of bulbs of *A. odorum* is scorodose (I). None occurred in the leaves. (I) was not detected in bulbs of *A. cepa*.

VI. (I) from *A. scorodoprasum* has $[\alpha]_{\text{D}}^{25} -41.54^\circ$ in H_2O , is pptd. by $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, and is easily hydrolysed by dil. $\text{H}_2\text{C}_2\text{O}_4$. 0.3—0.5% HCl at 37° produced fructose from (I). Intestinal extracts and pancreatin hydrolysed (I) only very slowly.

CH. ABS. (p)

Polysaccharides of *Iridaea laminarioides*. III. T. TADOKORO and K. YOSHIMURA (J. Chem. Soc. Japan, 1935, 56, 655—658; cf. this vol., 534).—Polysaccharides sol. in 2% NaOH gave *d*- and *l*-erythrose on hydrolysis with 5% H_2SO_4 .

CH. ABS. (p)

Constituents of *Actinidia callosa*, Lindl., var. *rufa*, Makino. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1936, 12, 721—725).—An analysis of the bark and of sugars extracted with cold and hot H_2O , hot EtOH, and 5% KOH is given. The mucilage contains galactose and arabinose; the tannin from bark belongs to the pyrocatechol series. J. N. A.

Chile seed. W. A. BUSH (J. Amer. Chem. Soc., 1936, 58, 1821).—The seeds contain H_2O 6.25, oil 26.1, and meal 67.65% (protein 28.92, fibre 29.1, ash 5.61, and carbohydrates 36.37%). The oil, which resembles tomato-seed oil, has d_{25}^{25} 0.918, n_D^{25} 1.4738, acid val. 2.18, I val. (Hanus) 133.5, Ac val. 7, sap. val. 192, and contains 1.7% of unsaponifiable matter. H. B.

Cyanogenetic glucosides in Australian plants.
III. *Eucalyptus cladocalyx*. H. FINNEMORE, S. K. REICHARD, and D. K. LARGE (J. Proc. Roy. Soc. New South Wales, 1936, 68, 209—214; cf. A., 1930, 1627).—Fresh loppings of the young branches gave 0.32% (dried 0.5%) of HCN by maceration with H_2O , and no more by addition of the enzyme (I) of sweet almonds. After 7 years they gave only 0.06% (dried) in H_2O and 0.105% after addition of (I). Another fresh sample of young suckers gave after drying 0.5% of HCN. The isolation of prunasin (II) by percolation with $COMe_2$ is described. One sample of *E. viminalis* leaves gave no HCN, another gave 0.09%. 10% of (II) is obtained from *Eremophila maculata*, best by $COMe_2$. R. S. C.

Reduced glutathione content of certain oil-bearing nuts. D. ZIMMET (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 135—136).—The reduced glutathione content of (peeled) walnuts, brazil nuts, hazel nuts, almonds, and arachis nuts was 20—40 mg. per 100 g. G. H. B.

Chemical examination of the Chinese drug, Tu Hao. Y. F. CHI and Y. M. LEE (J. Chinese Chem. Soc., 1936, 4, 305—311).—The $EtOH$ -sol. portion contains glucose, phytosterol, palmitic, stearic, oleic, and linoleic acids. F. N. W.

Constitution of the Chinese drug, Hseh Tsuang seed. T. H. TANG (J. Chinese Chem. Soc., 1936, 4, 324—334).—From the light petroleum extract a basic unsaturated aromatic compound, $C_{11}H_{10}(OH) \cdot OMe$, m.p. 82.5—83.5° (Ac derivative, m.p. 85°; Bz derivative, m.p. 69°; hydrochloride, m.p. 102°; dibromide, m.p. 147.5—148°), is obtained. The Et_2O -sol. fraction consists of the glycerides of the following acids: saturated 4.56, oleic 46.25, and β -linoleic 45.81, and unsaponifiable matter 0.38%. F. N. W.

Dragon's blood. G. HESSE [with W. KLINGEL] (Annalen, 1936, 524, 14—24).—Extraction of the crude material with Et_2O followed by addition of light petroleum yields the crude resin (I). The acids which remain in the mother-liquors are transformed by boiling $AcOH$ into abietic acid, m.p. 155—163°, $[\alpha]_D^{25}$ —80.0° in 96% $EtOH$, whereas by crystallisation from $COMe_2$ a product, m.p. 155—162°, $[\alpha]_D$ —40.6° to —42.3° in $EtOH$, is obtained. Enrichment of (I) in pigment is effected by pptg. it from amyl alcohol-HCl by Et_2O , and chromatographic analysis (Brockmann's Al_2O_3) of the product in $CHCl_3$ affords the following substances: *dracocarmin*, $C_{31}H_{26}O_5$ (also $+1CHCl_3$), m.p. 293° (decomp.) somewhat dependent on the rate of heating (hydrochloride, m.p. $>350^\circ$); *dracorubin*, $C_{28}H_{24}O_7$, decomp. 270—280° after changing colour at 220° (hydrochloride, decomp. 295°); an unidentified violet pigment. The substances do not appear to contain a sugar component. H. W.

Colouring matter of the corolla of *Rhododendron obtusum* f. *hinode*. I. Isolation of quercetin. K. HAYASHI (J. Pharm. Soc. Japan, 1933, 53, 1093—1098).—Quercetin is obtained from the $MeOH-HCl$ extract after pptn. of anthocyanin with Ph. CH. ABS. (p)

Anthocyanin pigment of the winesap apple. I. J. DUNCAN and R. B. DUSTMAN (J. Amer. Chem. Soc., 1936, 58, 1511—1514).—The pigment, isolated from the skins by a modification of Willstätter and Burdick's method (A., 1917, i, 44), is idæin chloride (Willstätter and Mallinson, A., 1915, i, 282). H. B.

Polyene pigments of the orange. I. L. ZECHMEISTER and P. TUZSON (Ber., 1936, 69, [B], 1878—1884).—The ethereal oil from the skin is removed by steam-distillation in vac. or chromatographically if the isolation of cryptoxanthin (I) is not required. Partial success is achieved by chromatography of the total hydrolysed extract or by chromatography followed by hydrolysis of the separated zones. Whereas the native pigment is stable, certain polyene alcohols become changed immediately after separation from the pigment wax, probably owing to CO_2 or traces of acid in the laboratory air. Many fractions resinify in CS_2 . (I), zeaxanthin+lutein, and violaxanthin have been isolated, with a new carotenoid, *citrawrin* [*oxime*, m.p. 181—182° (corr.)], probably a polyene OH-aldehyde formed by oxidation of a C_{40} compound in the tissue. H. W.

Composition of orange skins. P. R. V. D. R. COREMAN (J. Pomology, 1936, 14, 205—215).—Spraying with Pb arsenate had no direct action on the skin constituents examined. Metabolic activity is greater in the pulp during the growing season. Supplies of Ca and P to the skin are probably accumulated during the early growth stages. Ca is associated with the structure of cell wall material. In the skin pectin is probably almost as important as sugar in metabolic processes. Sugar predominates in the pulp. A. G. P.

Isomerisation of carotenes by chromatographic adsorption. I. ψ - α -Carotene.—See this vol., 1369.

Carotenoid pigments of *Oscillatoria rubrescens*.—See this vol., 1369.

Pipi (Brazilian drug). R. A. D. DA SILVA (Rev. Flora med. Brasil., 1935, 1, 477—487; Chem. Zentr., 1935, ii, 3946).—The plant, *Petiveria tetrandra*, Gomes, contains a non-cryst. substance, *petiverin*, of alkaloid character. A. G. P.

Highly-active constituent of the bark of *Piscidia erythrina*. F. HAUSCHLD (Arch. exp. Path. Pharm., 1936, 182, 317—323).—Fractionation of the light petroleum-sol. substances gives a yellow amorphous prep. which is extremely toxic (approx. 20% < rotenone) to fish, rats, etc. (min. lethal dose in rats 0.1—0.3 mg. per 100 g.). Saponins present are not concerned in the toxicity excepting with fish. F. O. H.

New derivatives of the lignin from Spanish *Pinus sylvestris*. III. Spectroscopic study of the wood. L. LEMMEL (Anal. Fis. Quím., 1935, 33, 39—44).—An account of work previously reviewed (A., 1934, 335; 1935, 84). F. R. G.

Examination by dark-ground illumination of the nuclei of cells grown *in vitro* and treated with hypotonic solutions. O. M. OLIVO and M. BOSKOVICH (Boll. Soc. ital. Biol. sperim., 1936, 11, 243—245).—Hypotonic aq. NaCl renders invisible the nuclei and, more slowly, the nucleoli of fibroblasts of chick embryo; the effect is due to change in osmotic pressure. F. O. H.

Influence of grain size, separation, and distribution on the capability of enlargement of photomicrographs of biological objects.—See this vol., 1348.

Relative acidity of histological fixing fluids. A. PETRUNKEVITCH and G. E. PICKFORD (Anat. Rec., 1936, 65, 461—465).—The p_H of a no. of fluids are listed. R. N. C.

Staining of the nuclei of cells grown *in vitro*, treated with hypertonic solution, and examined under dark-ground illumination. O. M. OLIVO and M. BOSKOVICH (Boll. Soc. ital. Biol. sperim., 1936, 11, 245—247).—Modifications occurring in stained preps. are described. F. O. H.

Isotonic solutions of colloidal silver. R. DESCHAMPEAUX (J. Pharm. Chim., 1936, [viii], 24, 268—269).—A stable prep. is afforded by adding 1.4 c.c. of 5% aq. $Na_2S_2O_4$ ($Na_2S_2O_3$?) and 0.10 g. of colloidal Ag (French Codex) to 90 c.c. of 10% aq. NaCl, the vol. being made up to 100 c.c. with H_2O . F. O. H.

Ashing of plant material. W. D. STEWART and J. M. ARTHUR (Contr. Boyce Thompson Inst., 1936, 8, 199—215).—Ashing at 450° in O_2 gives more trustworthy results than ashing in a muffle at 650°. Volatilisation losses at the higher temp. were due to CO_2 and Cl'. At 450° there was no loss of KCl, K_2CO_3 , $MgCO_3$, $CaCl_2$, or $CaCO_3$. At higher temp. some KCl and $CaCl_2$ were lost. All sulphates were stable at all temp. examined. Addition of H_2SO_4 to facilitate ashing in the determination of total bases was unsatisfactory owing to non-volatilisation of H_3PO_4 . A method of ashing in an electric furnace in a current of O_2 is described. A. G. P.

Macro-Kjeldahl nitrogen determination.—See this vol., 1397.

Nitrogen not titratable by Kjeldahl's method. F. SERIO and S. FIANDACA (Biochim. Terap. sperim., 1933, 20, 201—215; Chem. Zentr., 1935, ii, 3956).—Determination of N by elementary analysis gives higher results with urine (especially diabetic) than a wet method; the difference is ascribed to compounds containing nuclear N. H. N. R.

Prevention of foaming in distillations. W. M. BENDIEN (Chem. Weekblad, 1936, 33, 547).—Troublesome foaming in micro-Kjeldahl determinations of blood-albumin is prevented by the addition of 3—5 drops of a 0.5% solution of cholesterol in EtOH to each 20 c.c. of liquid. S. C.

Determination of lactic acid, and, in particular, lactacidæmia. C. PI-SUÑER BAYO and J. F. PI (Anal. Fis. Quim., 1934, 32, 843—857).—The influence on the method of Friedemann *et al.* (A., 1927, 800; 1929, 677; 1933, 488) of the procedure for removing

proteins (the Folin-Wu method is recommended), duration of the oxidation by $KMnO_4$, and the efficiency of the cooling of the receiver is discussed, and the necessity for a blank determination is emphasised. The technique used is described and typical analyses of Zn lactate and blood are recorded. F. R. G.

Determination of formic, acetic, and propionic acids in bacteriological culture media. A. TASMANN (Chem. Weekblad, 1936, 33, 574—576).—The sample is acidified with H_2SO_4 and phosphotungstic acid to ppt. proteins, centrifuged, and the clear solution steam-distilled. Total acids are determined in the distillate by titration, and HCO_2H by pptn. with $HgCl_2$. A separate sample of distillate is treated with $K_2Cr_2O_7-H_2SO_4$ to remove HCO_2H , and AcOH and $EtCO_2H$ are determined by the "half distillation val." method. S. C.

Colorimetric determination of uric acid (Folin) with delayed colour-formation. G. BERGAMI, E. BOERI, and P. BAER (Boll. Soc. ital. Biol. sperim., 1936, 11, 277—279).—Curves giving the increase in colour with time for standard amounts of uric acid (I) are applied to the determination of (I) by Folin's method (A., 1933, 845). F. O. H.

Nickel nitroprusside as external indicator for iodometric determination of reduced glutathione. D. ZIMMET (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 132—134).—The indicator is added to a series of tubes each containing 2 c.c. of the neutralised tissue extract with amounts of 0.002N-I differing by 1 drop, the approx. amount of I required being determined by preliminary titration. The end point is reached when the ppt. after centrifuging is no longer coloured rose. The sensitivity, 1 in 4×10^6 , is dependent on exact neutralisation to bromothymol-blue. G. H. B.

Determination of glutathione in biological material. F. HARTNER and E. SCHLEISS (Mikrochem., 1936, 20, 163—179; cf. A., 1935, 422).—The quantity of I which reacts with glutathione (I) varies with the conditions, but Br from $NaBr + KBrO_3$ gives const. vals. (I) in biological fluids is adsorbed on $Cd(OH)_2$ or $AgCl$ and determined by the Br method. Details of macro- and micro-methods are given. R. S.

Micro-determination of cholesterol as pyridine cholesteryl sulphate. A. E. SOBEL, I. J. DREKTER, and S. NATLSON (J. Biol. Chem., 1936, 115, 381—390).—Free cholesterol (I) is separated from its esters and other lipins by conversion into C_5H_5N cholesteryl sulphate and pptn. with light petroleum. The (I) in the ppt. is determined by the Liebermann-Burchard reaction. The (I) obtained from hydrolysis of the esters is separately determined. The advantages of this over the digitonin method are discussed. E. M. W.

Electrolytic enrichment of arsenic in biological fluids. J. VAN CALKER and A. PITTONI (Biochem. Z., 1936, 286, 297—300).—A method is described whereby traces of As in biological fluids can be collected at the anode and so conc. prior to determination. P. W. C.