

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1936.



General, Physical, and Inorganic Chemistry.

- Absorption spectrum of hydrogen. II. The D state in the term scheme of hydrogen from photographs of H_2 and D_2 .** H. BEUTLER, A. DEUBNER, and H. O. JÜNGER (*Z. Physik*, 1935, 98, 181—197; cf. A., 1935, 1291). A. B. D. C.
- Ground state of (H_2), the molecular ion (H_2^+), and wave mechanics.** O. W. RICHARDSON (*Proc. Roy. Soc.*, 1935, A, 152, 503—514).—The agreement between the vals. of the fundamental consts. of the ground state of the H_2 mol. (i) as determined by experiment, and (ii) as calc. by wave mechanics, is discussed. The properties of the mol. ion (H_2^+) as predicted by wave mechanics are compared with those predicted empirically from a study of various excited states of (H_2). L. L. B.
- Fine structure of D_2 with increased resolution.** R. C. WILLIAMS and R. C. GIBBS (*Physical Rev.*, 1936, [ii], 49, 40; cf. this vol., 127).—A correction. N. M. B.
- Energy states of doubly excited helium.** T. Y. WU (*Physical Rev.*, 1934, [ii], 46, 239). L. S. T.
- Doubly-excited states in helium.** F. G. FENDER and J. P. VINTI (*Physical Rev.*, 1934, [ii], 46, 77—78). L. S. T.
- Absorption of fluorspar [transmitted] ultra-violet light by carbon black, gold, and rhombic sulphur.** G. RATHENAU (*Physica*, 1936, 3, 42—60). C black has an absorption max. at approx. 2500 Å., and a min. at approx. 1700 Å.; Au has an absorption max. at about the latter λ . S layers, transparent to ultra-violet light, were made by vaporisation in vac. on to a CaF_2 plate at -80° . S absorbs at about 3500 Å., and there is another band at 1800 Å. The results are discussed in relation to the at. and mol. spectra. A. J. M.
- Light yield in the nitrogen spectrum excited by electron collision.** O. HERRMANN (*Ann. Physik*, 1936, [v], 25, 166—184).—The excitation function of the negative bands of the N spectrum and the abs. yield for 3 negative and 5 of the second positive group of N_2^+ and N_2 band spectra have been determined. A. J. M.
- Dependence of intensities of rotation lines of a band on the conditions of excitation.** O. HERRMANN (*Physikal. Z.*, 1936, 37, 100—103).—The intensities of the lines in the R branch of the $0 \rightarrow 0$ band of the negative N_2 group at 3914 Å. have been determined for excitation with electrons of various velocities. A. J. M.
- Excitation of the auroral green line by metastable nitrogen molecules.** J. KAPLAN (*Physical Rev.*, 1936, [ii], 49, 67—69; cf. A., 1934, 827).—The excitation in tubes which show the two new afterglow spectra of N_2 is described. The conditions of excitation are compared with those in the night-sky and in the aurora borealis, in which cases, it is suggested, the 1S_0 state of O which is responsible for the green line is produced by collisions of O atoms and metastable N_2 mols. in the $A^3\Sigma$ state. N. M. B.
- Hopfield's Rydberg series and the ionisation potential and heat of dissociation of nitrogen.** R. S. MULLIKEN (*Physical Rev.*, 1934, [ii], 46, 144—146; cf. A., 1931, 1343). L. S. T.
- Predissociation of the oxygen molecule.** P. J. FLORY (*J. Chem. Physics*, 1936, 4, 23—27).—Optical data for O_2 are interpreted as indicating that the initial process in the photochemical reactions of O_2 due to light in the region of Schumann-Runge band absorption is the formation of normal 3P atoms by predissociation rather than the reaction of an optically excited mol. with a normal mol., as hitherto supposed. M. S. B.
- Arc spectra of fluorine and potassium.** B. EDLÉN (*Z. Physik*, 1936, 98, 445—460).—85 FI lines between 6000 and 9500 Å. are tabulated. A. B. D. C.
- Intensity measurements in the spectra of neon and argon excited by electron collision.** O. HERRMANN (*Ann. Physik*, 1936, [v], 25, 143—165).—Efficiency determinations for the excitation of the Ne and A spectra by electron collision have been made by an abs. method. The scattering of electrons and their angular distribution are taken into account. The abs. yield and excitation probabilities for 54 A lines, and the excitation functions for 52 Å and 16 Ne lines are recorded. Comparison of the abs. yields of 7 Ne and 7 A lines belonging to the same term shows no simple connexion between the two gases. A. J. M.
- Intensity distribution of neon lines.** E. LAU (*Physikal. Z.*, 1936, 37, 110).—Polemical against Schütz *et al.* (A., 1935, 907). A. J. M.
- [Intensity distribution of neon lines.] W. SCHÜTZ (*Physikal. Z.*, 1936, 37, 110—111).—A reply to the above. A. J. M.
- Absolute transition probability of potassium.** E. F. M. VAN DER HELD and J. H. HEIERMAN (*Physica*, 1936, 3, 31—41).—The abs. intensity of light emitted

by K atoms in a C_2H_2 -air flame, the flame temp., and the no. of emitting particles have been determined, and the abs. transition probabilities of the resonance lines of K calc. The abs. transition probabilities were also obtained for the sharp and diffuse series by photographic comparison with the resonance lines, using light of known colour temp. A. J. M.

Arc spectrum of rubidium. K. W. MEISSNER (Z. Physik, 1935, 98, 353—354). A. B. D. C.

Fine structure in the (2D) series limit terms of the I^+ spectrum. S. TOLANSKY (Proc. Physical Soc., 1936, 48, 49—56; cf. A., 1935, 137).—Classifications and fine-structure data are tabulated for I^+ , and fine structure analyses of 14 lines of the 2D system and interval factors for 12 terms are given. Large interval factors associated with the $5d$ electron terms of the 4S and 2D systems are correlated with observations for Sn II, and are due to perturbation by terms with large fine structure. Two types of perturbation in the fine structures are observed.

N. M. B.

Nuclear spin of iodine. II. Fine structure in the arc spectrum and a fine structure perturbation effect. S. TOLANSKY (Proc. Roy. Soc., 1935, A, 152, 663—672; cf. A., 1935, 137).—The fine structures of 13 of the classified lines of the I arc spectrum (6300—4760 Å.) have been measured. The nuclear spin is confirmed as $5/2$. The $6s^4P_{5/2}$ is perturbed.

L. L. B.

Absorption spectra of cerium, neodymium, and samarium. F. W. PAUL (Physical Rev., 1936, [ii], 49, 156—162; cf. King, this vol., 2).—Data for λ and intensities of 600 Ce, 450 Nd, and 1500 Sm lines are tabulated in the region 12,000—2500 Å.

N. M. B.

Absolute intensities in the spectrum of a low-pressure quartz mercury-vapour discharge burner. A. J. MADDOCK (Proc. Physical Soc., 1936, 48, 57—62).—Abs. intensities of the main $\lambda\lambda$ in the range 6000—2400 Å. are tabulated and discussed theoretically in relation to results for high-pressure arcs (cf. A., 1935, 800). Therapeutic effects are examined.

N. M. B.

Collision-induced emission. W. M. PRESTON (Physical Rev., 1936, [ii], 49, 140—144).—A new continuous spectrum associated with the weak forbidden Hg 2269.80 Å. line has been found in a low-pressure Hg discharge with a few cm. pressure of A or He added. It is attributed to radiation from excited Hg atoms in the 3P_2 metastable state perturbed by the close approach of rare gas atoms. N. M. B.

Thallium II spectrum. C. B. ELLIS and R. A. SAWYER (Physical Rev., 1936, [ii], 49, 145—150).—The Tl spectrum from the hollow-cathode discharge in He has been photographed in the range 9250—600 Å. Full data, classifications, and assignments for 115 previously known lines and 160 new lines which locate 35 new levels are tabulated. N. M. B.

Hyperfine structure and the depolarisation of resonance radiation by a magnetic field. A. ELLETT (Proc. Iowa Acad. Sci., 1934, 41, 251).

CH. ABS. (e)

New "bright" method for investigation of the Stark effect with a homogeneous field. W. STEUBING and J. A. SCHAEFER (Ann. Physik, 1936, [v], 25, 97—123).—The method enables very bright spectra to be produced in a measurable homogeneous electric field, and makes it possible to examine the Stark effect of some atoms and mols. which are difficult to excite by other methods. A. J. M.

Analysis and interpretation of the nebular spectrum of Nova Herculis. M. BLOCH and J. DUFAY (Compt. rend., 1935, 201, 1463—1465).—Lines are due to H I, He I, He II, O II, N II, C II, O III, N III, and probably C III. T. G. P.

Absorption of monochromatic X-ray beams, of wave-length in the region 50—20 X units, in lead, tin, copper, and iron. J. READ (Proc. Roy. Soc., 1935, A, 152, 402—417; cf. A., 1934, 577).—A curve relating the absorption coeff. of Pb and the λ has been obtained. The photo-electric absorption coeffs. calc. from this are 7—20% > corresponding vals. obtained from Gray's empirical law (A., 1931, 281).

L. L. B.

Fluorescence X-ray yields from K shells of atoms. R. J. STEPHENSON (Physical Rev., 1934, [ii], 46, 73—74).—A criticism and a revision of vals. (cf. A., 1934, 577).

L. S. T.

Dose measurement of very soft X-rays. E. WILHELMI (Physikal. Z., 1936, 37, 103—107).—The method employs an ionisation chamber of sufficient length to absorb the rays almost completely.

A. J. M.

Effects of chemical binding on the X-ray $K_{\alpha_{1,2}}$ doublet lines of sulphur studied with a two-crystal spectrometer. L. G. PARRATT (Physical Rev., 1936, [ii], 49, 14—16).—Using FeS, Cu_2S , $MgSO_4$, $BaSO_4$, and PbS targets, ionisation curves were recorded, and effects of binding on λ , on the $\alpha_1 \rightarrow \alpha_2$ separation, and on the doublet contour were measured. The λ shift of the $SK_{\alpha_{1,2}}$ lines from sulphates to sulphides was observed in the process of shifting.

N. M. B.

Excitation potential of $K_{\alpha_{3,4}}$ satellite lines. L. G. PARRATT (Physical Rev., 1936, [ii], 49, 132—139).—The K_{α} satellite lines intensity-X-ray tube voltage curve has been determined for the Ti $K_{\alpha_{3,4}}$ lines. For voltages > 11 kv. the ratio satellite intensity/Ti K_{α_1} line intensity is 2.21%; the ratio of peak intensities α_4/α_1 is 0.69%. The Ti $K_{\alpha_{3,4}}$ excitation potential is 5450 ± 100 volts, in good agreement with the calc. voltage, 5455, required to produce a state of KL_{III} ionisation in the Ti atom, and supporting the Wentzel-Druyvesteyn theory of $K_{\alpha_{3,4}}$ satellite line origins.

N. M. B.

Absorption ratio within the L-shell. H. SCHWARZ (Ann. Physik, 1935, [v], 23, 571—588).—Measurements of the fluorescence radiation of Sn excited by the K_{α} lines of Cr (2.285 Å.), Cu (1.54 Å.), and Mo (0.71 Å.) lead to intensity ratios for the three lines, which correspond with the three L-levels.

A. J. M.

Asymmetry of the electric charge distribution in the $^{201}_{80}Hg$ nucleus. H. SCHÜLER and T. SCHMIDT (Z. Physik, 1935, 98, 239—251).

A. B. D. C.

Emission constants of single- and poly-crystalline materials. A. RECKNAGEL (Z. Physik, 1935, 98, 355—362).—Theoretical. Richardson's emission const. A for a single crystal can be double that for polycryst. samples of the same material. A. B. D. C.

Thermionic emission from tungsten and thoriated tungsten filaments. W. B. NOTTINGHAM (Physical Rev., 1936, [ii], 49, 78—97).—Electron emission has been investigated as a function of applied potential from a few volts retarding to 1400 volts accelerating. The electron energy distribution was deficient in slow electrons. The negative temp. coeff. of the work function for pure W is 4.3×10^{-5} volt per degree. Electron emission data in accelerating fields show large deviations from the Schottky mirror image theory. N. M. B.

Photo-electric effect for the L-shell. H. HALL and W. RARITA (Physical Rev., 1934, [ii], 46, 143). L. S. T.

Spark potential for electrolytic valve action. W. BÄR (Z. Physik, 1935, 98, 267—279). A. B. D. C.

Shot effect of secondary emission. I. M. ZIEGLER (Physica, 1936, 3, 1—11).—A method of measuring fluctuations in the current in a vac. tube by comparing them with the definite fluctuations brought about in another tube by the pure shot effect is described. A. J. M.

Electron-microscopic investigations of electron emission from cold metals. A. WEHNELT and W. SCHILLING (Z. Physik, 1935, 98, 286—287).—A cold Mo cathode emits electrons from independent points; these centres last for several min. and then suddenly cease to emit, whilst new centres appear. A. B. D. C.

Electron-optical structural image and emission from barium-nickel cathodes. E. BRÜCHE (Z. Physik, 1935, 98, 77—107).—Changes in heated cathodes during electron emission have been followed by the electron microscope. A. B. D. C.

Electron-optical images of emitting wires. H. MAHL (Z. Physik, 1935, 98, 321—323).—Images of W and Mo wires are reproduced. A. B. D. C.

Pressure of a degenerate electron gas and related problems. (SIR) A. EDDINGTON (Proc. Roy. Soc., 1935, A, 152, 253—272).—A straightforward deduction of the formula $P = K\sigma^{5/3}$ ($P = \text{min. electron pressure corresponding with an electron density } \sigma$) from relativistic principles is given. The pressure is found directly, and not by way of the hamiltonian. The usual (Dirac) theory of the phenomena follows from the present basis. The results are applied to a determination of the val. of the cosmical const. The existence of a vast no. of occupied negative energy levels is one of the essential consequences of the analysis. L. L. B.

Reflexion coefficient of electrons. M. J. COPLEY and T. E. PHIPPS (Physical Rev., 1934, [ii], 46, 144). L. S. T.

Scattering of slow electrons by diatomic molecules. J. B. FISK (Physical Rev., 1936, [ii], 49, 167—173).—Mathematical. The Ramsauer effect is treated by a method analogous to that used for

atoms. Total cross-sections for elastic scattering are calc. in terms of three parameters related with band spectroscopy. Results for incident electron velocities 0—40 volts for N_2 , O_2 , and H_2 are in good agreement with experiment. N. M. B.

Electron attachment and ion formation in gases. W. ROGOWSKI (Z. Physik, 1935, 98, 399—414).—The mass action law is applied with success to formation of ions in gases. A. B. D. C.

Energy losses by positive ions to probes in the plasma of gas discharges. W. MOLTHAN (Z. Physik, 1935, 98, 227—238).—Probe heating \propto probe potential to 200 volts, indicating that the accommodation coeff. for the ions is much < 1 , and that there is a negligible electron emission from the probe. A. B. D. C.

Retardation of hydrogen positive rays by metals. H. BÄTZNER (Ann. Physik, 1936, [v], 25, 233—262).—The velocity decrease of H^+ particles with 4—60 e.k.v. in passing through films of Al, Cu, Ag, Sn, and Au has been measured. The relative at. retarding powers for this energy region depend on the at. vol. rather than on the at. no., in contrast to the relation for high energy. Vals. for the range of the particles in Al are calc. L. J. J.

Negative atomic hydrogen ions. W. H. BENNETT and P. F. DARBY (Physical Rev., 1936, [ii], 49, 97—99).—Negative at. H ions have been directly observed at the heads of striations in discharges in H_2O vapour; they form readily in these regions of high density of slow electrons, but are easily lost by collision. N. M. B.

Determination of the conditions for inelastic collision with the aid of slow K^+ ions. O. SCHMIDT (Z. Elektrochem., 1935, 42, 8—21).—Theoretical. The significance of experimental results (A., 1934, 863, 937) is discussed. E. S. H.

Collision of K^+ ions with inorganic and organic gases. III. Effective cross-section [of particles] and area of mass-spectrographic distribution curves. O. SCHMIDT (Ann. Physik, 1936, [v], 25, 92—96; cf. A., 1935, 5).—For const. max. intensity, the area F of the curve of scattering \propto pressure of the gas and is related to the effective cross-section Q . For pure scattering in similar gases $F/Q = a = \text{const.}$ (Xe, Kr, A, and CO_2 , N_2 , $MeCl$). For other gases, the val. of a and the loss of energy on impact either increase (inert gases) or decrease (paraffins and olefines and He) with decreasing mass. L. J. J.

Relative at. wt. of oxygen in water and in air. M. DOLB (J. Amer. Chem. Soc., 1935, 57, 2731).—The at. wt. of O in air is 16.00008 if that of O in Lake Michigan H_2O is 16.00000. E. S. H.

At. wt. of gallium. G. E. F. LUNDELL and J. I. HOFFMANN (J. Res. Nat. Bur. Stand., 1935, 15, 409—420).—Conversion of pure Ga into Ga_2O_3 through $Ga_2(SO_4)_3$, $Ga(OH)_3$, or $Ga(NO_3)_3$ and ignition at 1200—1300° gave at. wt. of Ga 69.74. Ga_2O_3 has d 5.95. A. R. P.

At. wt. of rubidium. E. H. ARCHIBALD, J. G. HOOLEY, and N. W. F. PHILLIPS (Trans. Roy. Soc.

Canada, 1935, [iii], 29, III, 155—162, and J. Amer. Chem. Soc., 1936, 58, 70—72).—The at. wt., determined from the Ag : RbCl ratio, and using Johnson's method of determining the nephelometric end-point, was 85.48 (cf. A., 1931, 584). H. J. E.

Mass ratio of hydrogen and deuterium from band spectra. W. W. WATSON (Physical Rev., 1936, [ii], 49, 70—72).—Corrections of B_e rotational consts. for uncoupling terms and interactions between nuclear and electronic motions for some diat. hydride and deuteride mols. are calc. If $H=1.0081$, D must be $>$ the generally accepted val. 2.01423, and is approx. 2.0148 (cf. Aston, A., 1935, 677). N. M. B.

Mass ratio of the lithium isotopes from the spectrum of Li_2 . G. M. ALMY and G. R. IRWIN (Physical Rev., 1936, [ii], 49, 72—77; cf. *ibid.*, 1935, [ii], 48, 104).—Rotational and vibrational analyses of the ${}^1\Sigma \rightarrow {}^2\Sigma$ Li_2 band system are tabulated. The mass ratio Li^7/Li^6 calc. from the observed isotope effect is 1.16640 ± 0.00016 , and the mass coeff. 1.04077 ± 0.00004 . A small electronic isotope shift, -0.064 ± 0.010 cm.⁻¹, has been found. N. M. B.

Alpha-particle yield from lithium under proton bombardment. N. P. HEYDENBURG, C. T. ZAHN, and L. D. P. KING (Physical Rev., 1936, [ii], 49, 100—101).—Observed thick film yields for the proton energy range 40—225 kv. are in good agreement with those of Herb (cf. A., 1935, 1186) at higher voltages. N. M. B.

Measurement of β -radiation from radium in r-units. H. SMEREKER and K. JURIS (Strahlenther., 1935, 52, 327—337; Chem. Zentr., 1935, i, 3249).—Measurement by the method described shows the unfiltered β -radiation to be 200 times as strong as the γ -radiation. J. S. A.

Quantum energy of some nuclear γ -rays. R. FLEISCHMANN (Naturwiss., 1936, 24, 77—78).—The quantum energy of γ -rays emitted by neutron bombardment was determined by the coincidence method of Bothe *et al.* (A., 1929, 116), to avoid scattering effects. The absorption of secondary electrons emitted by the action of the γ -rays on Al was determined. The quantum energies are $>$ those obtained by the direct absorption method (this vol., 6). Quantum energy shows dependence on at. no. similar to the packing fraction. A. J. M.

Emission of γ -quanta on disintegration of lithium by fast protons. K. ALEXOPOULOS (Z. Physik, 1935, 98, 336—341).— γ -Quanta are emitted on bombardment with protons of 450 e.kv. A. B. D. C.

Rayleigh scattering of hard radiation by heavy atoms. W. FRANZ (Z. Physik, 1935, 98, 314—320).—Theoretical. Rayleigh scattering of $4.7 \text{ X } \gamma$ -radiation by Pb should amount to 1% of the Klein-Nishina scattering. A. B. D. C.

Scattering of the Th-C'' γ rays. C. C. LAURITSEN and J. R. OPPENHEIMER (Physical Rev., 1934, [ii], 46, 81). L. S. T.

Production of electron-pairs by γ -rays in krypton. M. N. S. IMMELMAN (Naturwiss., 1936, 24, 61—62).—The probability of production of an

electron-pair in Kr by γ -rays from Th-C'' ($h\nu=2.6 \times 10^6$ ev.) is about $\frac{1}{3}$ of the probability of production of Compton electrons with energy $> 1.25 \times 10^6$ ev. Examination of 300 Wilson photographs gave 51 Compton electrons of the above energy, and 4 electron-pairs. A. J. M.

Determination of neutron intensities by means of Fermi electrons from rhodium. R. DÖPEL (Physikal. Z., 1936, 37, 96—100).—The Fermi effect with Rh has been investigated with a view to its use for determining the intensity of a weak beam of neutrons mixed with strong γ -rays. There are two emissions of electrons, half-life 35 sec. and 3.8 m. The initial intensity ratio of the short- to the long-lived is 6.7, and half-val. thickness of Al for absorption of the electrons is 0.45 mm. for both emissions. The optimum conditions for the determination of neutron intensities are examined, and the prep. of neutron standards for comparative work is described. A. J. M.

Neutrons from the disintegration of deuterium by deuterons. T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1936, [ii], 49, 19—21; cf. this vol., 6; Crane, A., 1934, 714; McMillan, A., 1935, 559).—The excitation functions for the emission of neutrons from D and Be by D_2 were investigated in the energy range 0.5—0.9 m.e.v. The yield of neutrons from a D_3PO_4 target varied nearly linearly, and from a Be target nearly exponentially, with the bombarding energy. The no. of neutrons from Be increases from $\frac{1}{3}$ to 3 times as many as from D_3PO_4 in the range. The neutrons from D are nearly homogeneous, with 2.55 m.e.v. max. energy. The energy of the disintegration is 3.21 ± 0.13 m.e.v. N. M. B.

Absorption of residual neutrons. J. TUTIN (Nature, 1936, 137, 34).—Neutrons may be captured in energy levels outside the nucleus. L. S. T.

Absorption law for slow neutrons. F. RASETTI, E. SEGRÈ, G. FINK, J. R. DUNNING, and G. B. PEGRAM (Physical Rev., 1936, [ii], 49, 104).—The validity of the Fermi-Bethe absorption law was tested by measuring the absorption of neutrons by a thin film of Cd and of Ag on the edge of a disc rotating at high velocity with and against, respectively, the neutron beam. For Ag the law is obeyed, but for Cd a change of 6.3% in the absorption coeff. indicates that the capture cross-section varies with the velocity less rapidly than $1/v$, where v is the neutron velocity (cf. following abstract). N. M. B.

Velocities of slow neutrons. G. A. FINK, J. R. DUNNING, G. B. PEGRAM, and D. P. MITCHELL (Physical Rev., 1936, [ii], 49, 103; cf. A., 1935, 1441).—Velocity distribution curves for slow neutrons from sources at room temp. and liquid air temp. are given and discussed. N. M. B.

Slowing down of neutrons. G. C. WICK (Physical Rev., 1936, [ii], 49, 192—193).—Fermi's statement, that an impact of a neutron with a proton reduces, on an average, the neutron energy by $1/e$, is explained (cf. A., 1935, 910). N. M. B.

Influence of the velocity of slow neutrons on their capture by certain nuclei. P. PREISWERK and H. VON HALBAN, jun. (Nature, 1935, 136, 1027).—

The radioactivation of Ag by neutrons from a Be + Rn source at different temp. after traversing paraffin wax with a Cd shield interposed at various distances indicates that the cross-section for neutron capture varies inversely as the velocity of the neutrons relative to the Ag atoms. Contrary to Moon and Tillman (A., 1935, 802), cooling the paraffin wax to 90° abs. increases the radioactivity induced in I by 10%.

L. S. T.

Energy of disintegration of radio-phosphorus [P³⁰]. C. D. ELLIS and W. J. HENDERSON (Proc. Roy. Soc., 1935, A, 152, 714—723).—The energy of the upper limit of the positrons from [P³⁰] is found to be $2.9 \pm 0.1 \times 10^6$ volts, corresponding with the formation of the product nucleus Si³⁰ in its ground state. Assuming that this energy determines the difference of internal energy of Si³⁰ and P³⁰, it is found, on the basis of existing data, that the difference in mass of Al²⁷ and Si³⁰ is the same whether calc. from ${}_{13}\text{Al}^{27} + {}_2\text{He}^4 \rightarrow {}_{14}\text{Si}^{30} + {}_1\text{H}^1$, or from the two stages ${}_{13}\text{Al}^{27} + {}_2\text{He}^4 \rightarrow {}_{15}\text{P}^{30} + {}_0n^1$ and ${}_{15}\text{P}^{30} \rightarrow {}_{14}\text{Si}^{30} + e^+$.

L. L. B.

New artificial radioactive elements. II. O. D'AGOSTINO (Gazzetta, 1935, 65, 1071—1087; cf. A., 1935, 276).—The identification of 17 active elements obtained by neutron bombardment of Li, B, Na, Al, P, Cl, K, Mn, Cu, Zn, Ga, As, Sc, Ag, Cd, In, Sb, I, Ba, W, and Re and some experiments on the separation of radioactive isotopes are described.

O. J. W.

Radioactivity produced in thorium and in uranium by means of neutron bombardment. O. D'AGOSTINO and E. SEGRÈ (Gazzetta, 1935, 65, 1088—1098; cf. A., 1934, 826).—In the Th activity produced by neutron bombardment two periods have been established, viz., 1 min. and 24 min. The latter is due to a new isotope of Th. The 13 and 100 min. activities of U are not due to any element of at. no. 80—92, but to an element 93 or 94 and at. wt. 239.

O. J. W.

Angular distribution of the products of artificial nuclear disintegration. J. GIARRATANA and C. G. BRENNECKE (Physical Rev., 1936, [ii], 49, 35—40).—Using special technique, measurements, accurate to $\pm 8\%$, of the angular distribution of α -particles from the disintegration of Li by fast protons showed that the emission is random in direction.

N. M. B.

Capacity of the elements for disintegration. Results of old and new methods. G. STETTER (Physikal. Z., 1936, 37, 88—95).—A critique of the scintillation method of investigating at. disintegration, and discussion of results obtained by more modern methods.

A. J. M.

Production of cosmic-ray showers at a considerable depth below ground-level. D. H. FOLLETT and J. D. CRAWSHAW (Nature, 1935, 136, 1026).—Much of the radiation which penetrates 60 m. of H₂O must consist of positive or negative electrons.

L. S. T.

Secondary effect of cosmic rays. A. SCHWEGLER (Z. Physik, 1935, 98, 288; cf. A., 1935, 1297).

A. B. D. C.

Fluctuations in cosmic-ray ionisation as given by several recording meters at the same station.

R. L. DOAN (Physical Rev., 1936, [ii], 49, 107—122).—Intensity variations over 10 weeks are recorded and analysed. Statistical agreement is found. The barometer effect is 1—2% per cm. Hg. Marked ionisation increase during rainfall is probably due to γ -radiation from active deposits brought down from the upper atm. Time distribution of ionisation bursts is purely random, with no evidence of barometer effect on burst frequency.

N. M. B.

Super-Novae and cosmic rays. W. BAADE and F. ZWICKY (Physical Rev., 1934, [ii], 46, 76—77).

L. S. T.

Penetrating power of asymmetric component of cosmic radiation. S. A. KORFF (Physical Rev., 1934, [ii], 46, 74—75).

L. S. T.

Analysis of ultra-radiation. B. GROSS (Physikal. Z., 1936, 37, 12—18).—Theoretical. The energy of a primary ray is calc. as a function of depth and range.

A. J. M.

Excitation function of lithium under proton bombardment. M. OSTROFSKY, G. BREIT, and D. P. JOHNSON (Physical Rev., 1936, [ii], 49, 22—34).—The yield of α -particles in the bombardment of Li with protons for different depths and widths of the "potential well," and the asymptotic form of the dependence of the collision cross-section on velocity at low velocities, are calc. Estimates of the theoretical variation of the yield with velocity are made for Li⁷+H². The "well" for the quant. representation of the α -particle reaction is compared with the mass of Be⁸, and both can be fitted by attributing the formation of Be⁸ from Li⁷ to the addition of a proton into a p level.

N. M. B.

Radiative collision between fast charged particles. C. MÖLLER (Proc. Roy. Soc., 1935, A, 152, 481—496).—Mathematical. A correspondence method, which is relativistically invariant and forms an immediate generalisation of the method previously used in the treatment of the non-radiative collision of fast particles, is developed for the treatment of the radiative collision between two particles. (Cf. A., 1931, 1109.)

L. L. B.

Apparent failure of the photon theory of scattering. R. S. SHANKLAND (Physical Rev., 1936, [ii], 49, 8—13).—Using Ra-C γ -radiation and air, Al, Be, filter-paper, and paraffin scatterers, coincident discharges were recorded in special Geiger-Müller electron and photon counters at various angles. There were fewer coincidences in the correct positions than expected, and those observed could be accounted for as chance coincidences due to the finite resolving time of the apparatus. Results do not agree with the photon theory of scattering.

N. M. B.

Exchange forces and the structure of the nucleus. J. H. BARTLETT, jun. (Physical Rev., 1936, [ii], 49, 102; cf. Feenberg, this vol., 134).—The possibility of a Heisenberg exchange followed by a Majorana exchange, i.e., an interchange of spin co-ordinates and not of space co-ordinates, is examined.

N. M. B.

Interaction of light nuclei. II. Binding energies of the nuclei H_1^3 and He_2^3 . H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1935, A, 152, 693—705).—The validity of the variation method as applied to H_1^2 is examined by comparing results obtained by its use with exact solutions. The method must be used with caution in determining binding energies due to short-range interactions. The binding energies of H_1^3 and He_2^3 can be explained by introducing attractive forces between the neutrons on the one hand and the protons on the other. The attraction between two neutrons must be much $<$ that between a neutron and a proton, so the existence of a stable n_0^2 nucleus is precluded. The anomalous attraction between two protons at small distances must also be much $<$ that between a neutron and a proton, and cannot be sufficient to produce a stable nucleus He_2^3 . (Cf. A., 1935, 274.) L. L. B.

Energies of nuclear reactions. H. A. WILSON (Proc. Roy. Soc., 1935, A, 152, 497—502).—The energies of 17 nuclear reactions are discussed, and in order to make the reaction equations consistent, the vals. of some of the energies are revised. The at. wts. of the 13 light elements involved are calc. from the reaction energies, and vals. obtained in good agreement with those of Bethe (Physical Rev., 1935, [ii], 47, 634) and of Oliphant *et al.* (A., 1935, 803).

L. L. B.

Recombination of neutron with proton. S. KIKUCHI, K. HUSIMI, and H. AOKI (Nature, 1936, 137, 30—31).—From the relative intensities of the γ -rays emitted under neutron bombardment by H_2O and aq. H_3BO_3 and an aq. solution of a Cd salt, the mean cross-section found for the recombination of neutron with proton lies between 8.3×10^{-28} and 3.0×10^{-26} cm.²

L. S. T.

Spontaneous disintegration of proton or neutron according to the Fermi theory. H. C. WOLFE and G. E. UHLENBECK (Physical Rev., 1934, [ii], 46, 237).

L. S. T.

Neutron collisions and the β -ray theory of Fermi. A. NORDSIECK (Physical Rev., 1934, [ii], 46, 234—235).

L. S. T.

Energy of removal of neutrons and α -particles from nuclei and α -instability below the radioelements. E. D. EASTMAN (Physical Rev., 1934, [ii], 46, 238—239).—A discussion emphasising the α -instability of elements of relatively low at. no. (cf. A., 1934, 939).

L. S. T.

Hydrogen atom. V. FOCK (Z. Physik, 1935, 98, 145—154).—Group theory describes very simply many of the phenomena associated with the H atom, including the Compton effect for bound electrons.

A. B. D. C.

Singular magnetic poles. B. O. GRÖNBLOM (Z. Physik, 1935, 98, 283—285).—Theoretical.

A. B. D. C.

Creation of electron pairs by fast charged particles. H. J. BHABHA (Proc. Roy. Soc., 1935, A, 152, 559—586).—Mathematical. The creation of electron pairs by the collision of fast charged particles is calc., taking into account the effect of screening. The probability of the creation of a pair

as a function of impact parameter is investigated, and various cases are treated which have not been considered before. Most of the formulæ can be derived by a method similar to that given by Weizsäcker (A., 1934, 712).

L. L. B.

Light aberration and the Doppler effect. K. PAPELLO (Z. Physik, 1936, 98, 490—495).—Aberration of light from stars depends on the distance of the star from the earth, and the relative or abs. velocity of the observer, indicating that the velocity of light is a function of time.

A. B. D. C.

Orbits of electrons in magnetrons with space charge. H. AWENDER, A. THOMA, and D. M. TOMBS (Z. Physik, 1936, 98, 534—535).—A correction (cf. this vol., 4).

A. B. D. C.

Probability of radiative processes for very high energies. L. W. NORDHEIM (Physical Rev., 1936, [ii], 49, 189—191).—Mathematical. The present theory (cf. Bethe, A., 1934, 1150) is modified for high energies and cosmic-ray phenomena.

N. M. B.

Temperature dependence of free electron susceptibility. E. C. STONER (Proc. Roy. Soc., 1936, A, 152, 672—692).—Mathematical. Various formulæ required in the application of the Fermi-Dirac statistics to the calculation of magnetisation are given in a convenient form, and calculations are made of the magnetisation as a function of H and T for the spin and diamagnetic effects considered separately or together, at both low and high temp. Under certain conditions the formulæ derived will hold approx. for electrons in metals.

L. L. B.

Magnetic moment of the neutron. A. LANDÉ and D. R. INGLIS (Physical Rev., 1934, [ii], 46, 76).—Disagreement with Schueler's val. of -1.65 magnetons (A., 1934, 580) is expressed.

L. S. T.

Interpretation of present values of nuclear moments. G. BREIT and I. I. RABI (Physical Rev., 1934, [ii], 46, 230—231).—A discussion of recent speculations on the magnetic moment and nature of the neutron and proton.

L. S. T.

Progression of nuclear resonance levels with atomic number. H. MARGENAU and E. POLLARD (Physical Rev., 1934, [ii], 46, 228; cf. A., 1935, 804).

L. S. T.

Disintegration of H^2 and the stellar abundance of H^2 and H^3 . H. H. GOLDSMITH (Physical Rev., 1934, [ii], 46, 78—79).

L. S. T.

Electric quadrupole moments of some atoms and the magnetic moment of the proton. H. SCHÜLER and T. SCHMIDT (Z. Physik, 1936, 98, 430—436).—Lack of symmetry shown by Cu, As, Eu, Lu, Hg, and Bi nuclei indicates rod- and plate-like electric charge distribution, and gives a magnetic moment of 1.5 for the proton in these nuclei.

A. B. D. C.

Relativistic self-consistent field. (Miss) B. SWIRLES (Proc. Roy. Soc., 1935, A, 152, 625—649).—Mathematical. A relativistic treatment of a many-electron atom on the lines of the self-consistent field method with "exchange" is developed. Tables are given from which the expression for the

total energy of an atom containing *s*, *p*, *d* electrons may be constructed. L. L. B.

Band spectrum of OH⁺. F. W. LOOMS and W. H. BRANDT (Physical Rev., 1936, [ii], 49, 55—67).—Full data are given for two bands at 3332 and 3565 Å. in the electrodeless discharge in pure H₂O vapour (cf. Rodebush, A., 1934, 39) and for new bands at 3695 and 3893 Å., which are, respectively, the (1,0), (0,0), (1,1), and (0,1) bands of OH⁺. Rotational analysis shows that they correspond with a ³Π → ³Σ⁻ transition in which the ³Π state is inverted. Multiplet intervals in both states are determined from the 9 strong branches and the satellite branches. Λ-type doubling and perturbations are examined. The ³Σ⁻ state concerned in the transition and the perturbing state are mol. levels which dissociate into the ground states of O and H⁺ and O⁺ and H, respectively. N. M. B.

Rotation constants B, D, and Y for the ³Π terms of TiO, C₂, CO, PH, AlH, and NH. A. BUDÓ (Z. Physik, 1936, 98, 437—444).

A. B. D. C.

Absorption spectrum of copper hydride. B. GRUNDSTRÖM (Z. Physik, 1935, 98, 128—132)

A. B. D. C.

Strontium deuteride and hydride spectra. W. W. WATSON, W. R. FREDRICKSON, and M. E. HOGAN, jun. (Physical Rev., 1936, [ii], 49, 150—155; cf. A., 1932, 439; 1935, 1443).—Analyses of the *B* and *C* band systems of SrD and of part of the *D* system of SrH are reported. N. M. B.

Isotope effect for gold hydride (AuH/AuD). T. HEIMER (Naturwiss., 1936, 24, 78).—The arc emission band spectrum of AuD has been examined, and compared with results for AuH. A. J. M.

Anomalous rotation of HgH molecules. F. F. RIEKE (Physical Rev., 1934, [ii], 46, 236—237).

L. S. T.

Absorption bands of gaseous HI. D. E. KIRKPATRICK (Physical Rev., 1936, [ii], 49, 104).—Measurements of the centres of the 1 ← 0 and 2 ← 0 absorption bands gave the vals. 2260 ± 30 and 4416 ± 75 cm.⁻¹, in agreement with Salant (cf. A., 1931, 545) and Nielsen (cf. A., 1935, 806). N. M. B.

Band spectra of BiBr, BiCl, BiF, and BiI in absorption. F. MORGAN (Physical Rev., 1936, [ii], 49, 41—46).—Data and vibrational analyses are reported. BiBr has two systems for each of the isotopes Br⁷⁹ and Br⁸¹ with origins at 4045.7 and 4869.1 Å., the latter system degrading to the red. BiCl has a system in the range 3600—4000 Å. for both Cl³⁵ and Cl³⁷, in addition to a system at 4300—5500 Å. (cf. Saper, A., 1933, 207). Vibrational analyses are confirmed by the respective isotope shifts. A system 4150—4900 for BiF, and a system 4150—4300 Å. for BiI have been observed and analysed. N. M. B.

Absorption spectra of PbF, PbCl, and PbBr. F. MORGAN (Physical Rev., 1936, [ii], 49, 47—50).—Data and vibrational analyses are given. PbF has a single system of double-headed bands in the range 4100—5300 Å. PbCl has a system with origin 4571.8 Å. for each of the isotopes Cl³⁵ and Cl³⁷. PbBr has a system in the range 4400—5400 Å. for

both Br⁷⁹ and Br⁸¹. Analyses are confirmed by the respective isotope shifts; all the bands degrade to the red. N. M. B.

End-isotope effect for triatomic molecules. M. WEHRLI (Naturwiss., 1936, 24, 14—15).—The end-isotope effect has been investigated for TeCl₂, the relative abundance of the mols. being TeCl₂³⁵:TeCl₂³⁵Cl³⁷:TeCl₂³⁷=1:0.32:0.10. In contrast to diat. mols. there is no simple connexion between the isotopic splitting, Δ*v*, and the frequency, except in two special band series, one due to excitation of symmetrical vibrations only, and the other to excitation of the antisymmetrical and deformation vibrations. The isotopic factor, *f*₁, is 0.0131 (theory for linear mol. 0.0139). A. J. M.

Absorption spectra of the chlorides and oxychlorides of sulphur. R. K. ASUNDI and R. SAMUEL (Proc. Physical Soc., 1936, 48, 28—34; cf. A., 1935, 680).—Absorption curves, in the visible and ultra-violet, are given for the vapours of SCl₂, S₂Cl₂, SOCl₂, and SO₂Cl₂. Heats of formation and linking energies are derived, and results are correlated with photodissociation processes. N. M. B.

Spectrophotometric studies. II—V.—See this vol., 221.

Extinction of mesomorphic liquids in a magnetic field. Y. BJÖRNSTÄHL (Z. physikal. Chem., 1935, 175, 17—37).—Melts of *p*-azoxyanisole, *p*-azoxyphenetole, and *p*-azoxyanisolephenetole have been examined. The extinction coeff., ε, is unaffected by a transverse field, and there is no dichroism in the field. The depolarisation of linearly polarised light by the liquid is changed in the field. In a longitudinal field ε decreases with increasing field strength, *F*, ultimately approaching a limit. If ε is measured with rising and falling *F*, hysteresis may appear. For moderate *F* ε decreases in jumps with rising *F*. In a given longitudinal field ε is independent of the temp. It is difficult to account for these observations on the swarm theory of mesomorphic liquids. Ornstein's theory (A., 1935, 20) is criticised. R. C.

Absorption spectra of tautomeric selenazoles. R. F. HUNTER (Nature, 1935, 136, 1030).—The ultra-violet absorption curve of 1-hydroxybenzelenazole (I) in MeOH is practically identical with that of 1-keto-2-methyl-1:2-dihydrobenzelenazole and distinct from that of the *O*-Me ether. In aq. NaOH the curve of (I) is moved to the left (deformation) and there is a decrease in the max. due to the production of the ion C₆H₄<Se>N<CO on which tautomeric change depends. 1-Thiolbenzelenazole shows marked similarity to thiazole analogues in the ultra-violet region; the curve for MeOH solution is similar to that of 1-thio-2-methyl-1:2-dihydrobenzelenazole.

L. S. T.

Ultra-violet absorption spectra of some complex aromatic hydrocarbons. I. W. V. MAYNEORD and E. M. F. ROE (Proc. Roy. Soc., 1935, A, 152, 298—324).—An investigation has been made of the ultra-violet absorption spectra of EtOH solutions of C₆H₆, C₁₀H₈, anthracene, 1:2-benzanthracene, 1:2:5:6-dibenzanthracene, phenanthrene, and their

derivatives, and of chrysene, picene, pyrene and its derivatives. The spectra of chemically related compounds are compared, and the effects of the addition of various groups are noted. Changes have been observed in the absorption spectra on cooling the solutions to -183° .
L. L. B.

Ionic dispersion in the extreme infra-red. C. H. CARTWRIGHT (Physical Rev., 1936, [ii], 49, 101—102).—A study of the absorption coeff. and reflecting power curves of H_2O and of KI and KCl solutions indicates that the dispersion of electrolytes in the extreme infra-red can be pictured classically, according to Maxwell's equations, by considering the ions to follow in translation the alternations of electromagnetic waves. The motion of the ions decreases in amplitude, because of inertia and friction, with increasing frequency of radiation. In electrolytes of KCl and KI the ions seem to move with respect to the H_2O mols. except for friction. N. M. B.

Choice of spectral reference rays in the study of every infra-red region (photographic infra-red), especially for the determination of fluorescence spectra. C. DHÉRE and O. BIERMACHER (Compt. rend. Soc. Biol., 1935, 120, 1162—1166).—Standard reference lines for the infra-red are A 912.4 and 1064 $m\mu$, Hg 1014 and the combined He, Cu, and Ag spectra for 500—850 $m\mu$. Acid porphyrin solutions show fluorescence bands between 667.8 and 728.2 $m\mu$, coincident with the two Cu lines. R. N. C.

Infra-red absorption spectrum of water and alcohols in non-polar solvents. E. L. KINSEY and J. W. ELLIS (Physical Rev., 1936, [ii], 49, 105).—Absorption curves in the range 1.0—2.5 μ for H_2O dissolved in CS_2 and for MeOH in CCl_4 , compared with those for liquid and vapour H_2O and MeOH, show vapour-like characteristics and strong OH bands, indicating that the interaction between mols. in the liquid is weakened or destroyed in solution, and that the interaction affects, relatively, only the polar part of the mol. N. M. B.

Rotation-vibration spectrum of acetylene in the photographic infra-red. G. W. FUNKE and G. HERZBERG (Physical Rev., 1936, [ii], 49, 100).—Data and interpretations of 3 new \perp and 6 new \parallel bands are reported and discussed. N. M. B.

Quantitative absorption measurements of the CH overtones for simple hydrocarbons. I. Halogen derivatives of methane, ethane, and ethylene. B. TIMM and R. MECKE (Z. Physik, 1935, 98, 363—381).—Photometer measurements are given for the third CH overtone in spectra of $CHCl_3$, CH_2Cl_2 , $MeCl$, $CHBr_3$, CH_2Br_2 , $MeBr$, C_2HCl_5 , $C_2H_2Cl_4$, $C_2H_3Cl_3$, $C_2H_4Cl_2$, $EtCl$, Pr^iCl , $C_2H_2Br_4$, $C_2H_4Br_2$, $EtBr$, C_2HCl_3 , $C_2H_2Cl_2$, and C_2H_3Cl . Absorption intensity \propto to the no. of CH groups, the halide atom having little influence on the electrical properties of an aliphatic CH linking. Transition moments are calc. and used to determine variation of dipole moment with nuclear separation in a homopolar linking. A. B. D. C.

Rotation-vibration spectra of methyl halides in the photographic infra-red to 1.11 μ . H.

VERLEGER (Z. Physik, 1935, 98, 342—352).—Resolved vibration bands are given for MeCl, MeBr, and MeI, and give moments of inertia for the axis normal to the symmetry axis of 60, 80, and 90×10^{-40} g.-cm.²; that about the symmetry axis is 4.1×10^{-40} for all three. A. B. D. C.

Infra-red evidence for the existence of an isomeric form of HCN. D. WILLIAMS (J. Chem. Physics, 1936, 4, 84).—The infra-red spectrum of a saturated solution of HCN has a strong band at 4.76 μ and a much fainter band at 4.95 μ . Since a shift of approx. 0.2 μ represents the difference between the band for org. cyanides and their isomeric forms at 4.5 μ the absorption at 4.95 μ is attributed to a small quantity (about 2%) of the isomeride HNC. M. S. B.

Relations between electrochemical constants, infra-red spectrum, and reaction properties. F. VLÈS (Compt. rend., 1935, 201, 1475—1477).—The $\lambda\lambda$ of the bands calc. from the previous relationship (A., 1935, 444) for BzOH, NH_2Ph , anthranilic acid, and methylene-blue, and for the decomp. of $CO(NH_2)_2$ by urease, are ascribed to sp. groups of atoms. T. G. P.

Infra-red spectra of amino-acids and polypeptides. E. HEINTZ (Compt. rend., 1935, 201, 1478—1480; cf. A., 1935, 1053).—Data are recorded for glycine, *dl*-alanine, *l*-cystine, cysteine, *l*-leucine, *d*-glutamic acid, *d*-arginine, *dl*-proline, tyrosine, *l*-histidine, phenylalanine, three peptones, and an albuminose of casein. The vals. confirm the previous relationship (A., 1935, 444). T. G. P.

Raman spectrum of deuterium. II. Intensity and polarisation characters. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 477—482; cf. A., 1935, 1445).—Data are recorded and classified. Vibration lines are polarised; rotation lines are nearly completely depolarised. H. J. E.

Raman spectra of carbon and silicon tetrachlorides. R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1935, 2, A, 452—458).—Two new lines of low intensity were found for CCl_4 (434, 145 cm^{-1}). A new line at 440.5 cm^{-1} was found for $SiCl_4$. The origin of these lines is discussed. H. J. E.

Raman spectrum and fundamental vibration frequencies of silane (SiH_4). F. B. STITT and D. M. YOST (J. Chem. Physics, 1936, 4, 82).—Two Raman lines have been found for SiH_4 and, combined with the infra-red data of Steward and Nielsen (A., 1935, 914), have led to the following arrangements of fundamentals: ν_1 2187, ν_2 978, ν_3 2183, and ν_4 910 cm^{-1} . M. S. B.

Raman spectra of some formates and the constitution of formic acid. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 615—620).—The Raman spectra of HCO_2Na , $(HCO_2)_2Ca$, $(HCO_2)_2Cd$, and $(HCO_2)_2Pb$ have been measured for the solids and their aq. solutions; average frequencies for the HCO_2 ion are 2834, 2732, 1717, 1534, 1347, and 857 cm^{-1} . These frequencies are compared with those of HCO_2H , HCO_2Me , $AcOH$, and $NaOAc$. The existence of the lines 2834 and 2732 cm^{-1} proves the presence of the

CH group. The 1534 cm^{-1} line, of doubtful origin, is characteristic of formates. J. W. S.

Raman spectrum of oxalic acid. W. R. ANGUS and A. H. LECKIE (J. Chem. Physics, 1936, 4, 83—84).—Contrary to Hibben's conclusion (this vol., 9), the frequencies 1661 and 1759 are present in the spectrum of solid $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and are as strong as the corresponding frequencies in aq. solution. This agrees with Rao's data (A., 1935, 807) on the assumption that the latter were obtained from the $2\text{H}_2\text{O}$ crystals. M. S. B.

Raman spectrum of dioxan. A. SIMON and F. FEHÉR (Ber., 1936, 59, [B], 214—217).—Repeated freezing and melting of dioxan causes a gradual lowering of the m.p., apparently due to the formation of a polymeric form. Evidence of isomerisation to acetaldehyde ethylene diacetal is not obtained. The Raman spectrum of dioxan gives results correcting and expanding those of Villars (A., 1931, 145). H. W.

Raman effect of acetylenes. II. Di-iodoacetylene, liquid acetylene, and deuterioacetylenes. G. GLOCKLER and C. E. MORRELL (J. Chem. Physics, 1936, 4, 15—22; cf. A., 1935, 146).—A new type of apparatus is described. Data are recorded for C_2I_2 , liquid C_2H_2 , and gaseous C_2H_2 , C_2HD , and C_2D_2 . Marked differences between the spectra of liquid and gaseous C_2H_2 indicate mol. distortion in the liquid state, so that the mol. is no longer linear. Free energies have been calc. and the equilibrium const. for $\text{C}_2\text{H}_2 + \text{C}_2\text{D}_2 \rightleftharpoons 2\text{C}_2\text{HD}$ has been determined at temp. 273—700° abs. M. S. B.

Fundamental frequencies of acetylene. G. GLOCKLER and C. MORRELL (Physical Rev., 1934, [ii], 46, 233).—The frequencies 382 (5), 618 (2), 631 (5), 1762 (1), 1959 (10), 3338 (5) cm^{-1} have been found by Raman scattering in liquid C_2H_2 . L. S. T.

Spectrum and force constants of the ethylene molecule. L. G. BONNER (J. Amer. Chem. Soc., 1936, 57, 34—39).—The Raman and infra-red absorption spectra in the photographic region have been reinvestigated. Three new Raman lines and 11 new infra-red absorption bands have been found. Frequency vals. have been assigned to all the 12 fundamental vibration modes of the C_2H_4 mol., on the basis of the new data, and 8 of the force consts. of the mol. have been obtained. E. S. H.

Constitution of the $\alpha\beta$ -dihalogen derivatives of ethane. H. C. CHENG (J. Chim. phys., 1935, 32, 715—724).—Cabannes and Rousset's apparatus (A., 1933, 446) has been used for measuring depolarisation of the Raman lines of $(\text{CH}_2\text{Cl})_2$, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Br}$, and $(\text{CH}_2\text{Br})_2$. It is concluded that the *cis*- and *trans*-forms of these compounds should coexist in the liquid state, and an attempt is made to classify the fundamental frequencies due to each form. J. W. S.

Raman spectrum of deuterobenzene. R. C. LORD, jun. (J. Chem. Physics, 1936, 4, 82—83).—The Raman spectrum given by Wood (A., 1935, 1189) for C_6D_6 requires force consts. much > usually ascribed to C_6H_6 linkings. It is suggested that some of the lines are attributable to $\text{C}_6\text{D}_5\text{H}$. M. S. B.

Raman spectra of benzene and its derivatives. K. W. F. KOHLRAUSCH (Physikal. Z., 1936, 37, 58—79).—A review. A. J. M.

Partial interpretation of the Raman and infra-red spectra of benzene. E. B. WILSON, jun. (Physical Rev., 1934, [ii], 46, 146—147).—Raman-active and infra-red-active fundamentals of C_6H_6 have been assigned to definite modes of vibration of the regular plane hexagon model. The doublet at 1600 cm^{-1} in the Raman spectrum is explained on the basis of quantum-mechanical resonance between ν_8 and $\nu_1 + \nu_6$. The suggestion that the spectra of C_6H_6 are incompatible with hexagonal symmetry is not justified. L. S. T.

Molecular scattering of light: Cabannes-Daure effect, critical opalescence of binary mixtures. A. ROUSSET (Ann. Physique, 1936, [xi], 5, 5—135; cf. A., 1934, 473, 830, 1302).—The continuous spectrum surrounding the exciting line in the scattering of light by liquids (Cabannes-Daure effect) is attributed to part of the anisotropic scattering due to variations of mol. orientations. The arrangement of cybotactic groups limiting the relative orientations of the axes of the mols. changes the statistical wt. of the rotational levels so that the intensity max. of the *P* and *R* branches are approx. identical with that of the fundamental line. In presence of strong permanent moments the anisotropic scattering of a vibrating mol. is wholly in the *Q* branch, explaining the weak intensity of the Cabannes-Daure effect in strongly polar mols. Measurements of the depolarisation factors ρ for $\text{H}_2\text{O}-\text{Pr}^n\text{CO}_2\text{H}$, $\text{C}_6\text{H}_{14}-\text{PhNO}_2$, $\text{NH}_2\text{Ph-cyclohexane}$, and $\text{H}_2\text{O}-\text{NEt}_3$ show that on approaching the crit. temp. of complete miscibility ρ reaches a min. and increases rapidly near the crit. point, indicating that the scattering due to variations of the mol. field increases more slowly than the opalescence near the crit. point. The sharp rise of ρ is attributed to a partly depolarised secondary scattering increasing more rapidly in intensity than in the case of the primary scattering. The law of variation of opalescence with λ is deduced, intensity of scattering in two directions relative to the incident beam and variations of $\lambda\lambda$ are examined, and results are discussed in relation to available theory. N. M. B.

Raman spectra of amino-acids and related compounds. I. Ionisation of the carboxyl group. J. T. EDSALL (J. Chem. Physics, 1936, 4, 1—8).—Raman spectra have been determined for four NH_2 -acids, their hydrochlorides and Et esters of two, HCO_2H , AcOH , EtCO_2H , $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, and their Na salts, NH_3MeCl , NH_3EtCl , $\text{CO}(\text{NH}_2)_2$, MeOAc , and COMe_2 . For aliphatic acids there is a shift of the C:O frequency from 1670 to 1720 on dissolution in H_2O , but no similar shift for MeOAc and COMe_2 . The presence of NH_3^+ attached to the α -C increases the same frequency by approx. 20. On ionisation of CO_2H the C:O frequency vanishes, lines of the region 1200—1420 undergo characteristic changes, and, in general, the frequency of a powerful line in the region 750—930 is increased by 20—40, whilst each additional Me group on the α -C decreases it by approx. 50, and, finally, the C-H frequency in HCO_2H is

decreased. Certain strong frequencies in NH_3Me and NH_3Et are decreased by ionisation. M. S. B.

Dust effects. L. ŠPLAIT (Z. Physik, 1935, 98, 396—398).—Polemical, against Mitra (A., 1935, 1301). A. B. D. C.

Collision broadening of Rayleigh lines in compressed gases. E. KAPPLER (Ann. Physik, 1936, [v], 25, 272—278).—Theoretical. The undisplaced component is not broadened by collisions, provided that the incident frequency is far removed from any characteristic frequency of the mol. The intensity distribution observed by Weiler (A., 1935, 1190) is not the effect of collisions on the rotational wings of the Rayleigh line. L. J. J.

Collision broadening of the undisplaced component of radiation scattered by carbon dioxide at high pressures. E. KAPPLER and J. WEILER (Ann. Physik, 1936, [v], 25, 279—280).—Up to 59 atm. pressure, radiation scattered through 90° shows no broadening either in the Q branch or in the polarised Tyndall scattering (cf. preceding abstract). L. J. J.

Resonance fluorescence of benzene. II. G. R. CUTHBERTSON and G. B. KISTIAKOWSKY (J. Chem. Physics, 1936, 4, 9—15).—Previous work (A., 1932, 1189) has been amplified and corr. On absorption of the Hg line 2536 Å. the changes of the quantum no. of one vibration only (990 cm^{-1}) of the non-excited C_6H_6 mol. are unrestricted in fluorescence. The changes for other vibrations are ≥ 1 (or 2 if required by selection rules). Five frequencies other than the above have been identified: 432, 791, 1542, 2557, and 3174 cm^{-1} . For C_6D_6 the frequencies 944 ($\Delta\nu$ unrestricted) and 2460 have been observed. The quenching of the resonance fluorescence of C_6H_6 in He, H_2 , N_2 , CO_2 , and cyclohexane consists in a change to high-pressure fluorescence, and some new high-pressure fluorescence bands have been observed. The resonance spectra of PhF and PhMe are nearly continuous even at 0.01 mm. pressure. The fluorescence of PhEt and PhCl is too faint to be examined. M. S. B.

Fluorescence of ruby, sapphire, and emerald. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 459—465).—New bands in the fluorescence spectrum of ruby have been measured. That of sapphire is very similar. Emerald gave two sharp lines at $\lambda\lambda$ 6806, 6835 Å., together with diffuse bands. H. J. E.

Fluorescence of some pure substances. E. CANALS, P. PEYROT, and R. NOËL (Compt. rend., 1935, 201, 1488—1489; cf. A., 1935, 1058).—Vals. for the depolarisation factors (ρ) and the relative intensities of fluorescence for eight alcohols are recorded. The spectra lie between 4400 and 4900 Å. T. G. P.

Extinction of fluorescence of methylene-blue by ferrous iron. H. HELLSTRÖM (Naturwiss., 1935, 24, 76—77; cf. A., 1935, 1087).—The relative intensity of fluorescence of methylene-blue (I) at various $[\text{Fe}^{2+}]$ and p_{H} 3 (citrate buffer), and at various p_{H} and const. $[\text{Fe}^{2+}]$ has been determined. The intensity of fluorescence rapidly diminishes on adding Fe^{2+} , the extinction velocity being dependent on p_{H} . There

may be an unstable compound of (I) and Fe^{2+} which readily dissociates. A. J. M.

Fluorescence of porphyrins. I. A. STERN and H. MOLVIG (Z. physikal. Chem., 1935, 175, 38—62; cf. A., 1926, 885; A., 1935, 808, 1444).—Fluorescence spectra in dioxan have been determined. Porphyrins which in the positions 1—8 of porphin have substituted Me, Et, and various Me ester groups have five fluorescence bands in the visible. As with the absorption spectra, the position of the max. varies little with the nature of the substituents. The positions of the max. of the principal bands are near those of the red bands in the absorption spectra. Porphyrins with vinyl groups have four fluorescence bands in the visible, the max. of which are shifted towards the red compared with those of porphyrins without unsaturated groups. Porphyrins containing both unsaturated and CO groups and γ -substituted porphyrins may have fluorescence spectra different from the above. The effect of varying substitutions in dihydroporphin on the fluorescence spectrum is much greater and more complicated than with porphin, but certain regularities, observable in absorption spectra, emerge, and may assist in the determination of constitution. The fluorescence spectra of two solid porphyrins and an Al salt have been determined. Solid pyromethenes have one fluorescence band in the visible, usually between 590 and 640 μ . R. C.

Porphyrin-gelatin phosphorescence.—See this vol., 346.

Quantum theory of the phosphorescence of crystal phosphors. T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 171—206).—Mathematical. J. W. S.

"Optimum" concentration of active foreign substances in crystal phosphors. G. SCHUMANN (Z. Physik, 1935, 98, 252—261).—This optimum concn. is not uniquely defined, factors such as prep. of the crystal and conditions of observation having been overlooked. A. B. D. C.

Optical and electrical properties of didymium glass. K. PROSAD, D. K. BHATTACHARYA, and L. M. CHATTERJEE (Z. Physik, 1935, 98, 324—335).—Fluorescence bands of Dy glass are identical with the Raman spectrum obtained from incident $\lambda\lambda$ equal to those of absorption bands. Photo-conductivity has been determined using sunlight and that transmitted by yellow and blue filters. A. B. D. C.

Luminescence of solid solutions of rhoduline. S. I. GOLUB (Physikal. Z. Sovietunion, 1935, 7, 49—57).—The spectra of the fluorescence and phosphorescence of solid solutions of rhoduline in sugar are identical. CH. ABS. (e)

Study of thermoluminescence in some crystals. T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 28, 207—220).—Thermoluminescence is studied in terms of the excitation of an electron of an impurity atom, usually a rare-earth metal, by a heat quantum, followed by photo-emission. Variation of bands with temp., disappearance with

time, and the effect of heating the crystal and then treating with X-rays are interpreted theoretically.

R. S. B.

Mitogenetic radiation. J. B. BATEMAN (Biol. Rev. Camb. Phil. Soc., 1935, 10, 42—71; Chem. Zentr., 1935, i, 3294).—A crit. review. The existence of mitogenetic radiation is unproven, and its allocation to the ultra-violet region is improbable.

J. S. A.

Relation between the photo-potential and the chemical properties of photo-sensitive organic substances. H. T. NGA (J. Chim. phys., 1935, 32, 725—740).—As with inorg. electrodes, the photo-electric potential of org. substances appears only in presence of H₂O. The effect appears instantaneously only with mols. containing atoms of variable valency, the NH₂-group being the most active. All compounds containing this group are not photo-sensitive, nor are their leuco-derivatives, but a mixture shows the effect, as does a dye to which is added the leuco-base of a less readily reducible dye. It is concluded that in these compounds the effect is due to displacement of the oxidation-reduction equilibria, produced by the primary photolysis of H₂O.

J. W. S.

Flow method applied to space charge and ionic processes in oil. K. CHRIST (Z. Physik, 1935, 98, 23—65).—The method of a fluid flowing at right angles to an electric field has been applied to dielectric liquids; it shows the transference of a positive charge from metal to oil, and the presence of space charge when an electric current passes through the oil. It can be used to measure ionic mobilities.

A. B. D. C.

Superposition of field distribution and conductivity. W. O. SCHUMANN (Z. Physik, 1935, 98, 72—74).—Theoretical discussion of inhomogeneous dielectrics.

A. B. D. C.

Determination of dielectric constants of organic liquids at radio-frequencies. I. Carbon tetrachloride and chloroform. R. M. DAVIES (Phil. Mag., 1936, [vii], 21, 1—41).—The resonant circuit method was used to obtain the dielectric consts. of CCl₄ and CHCl₃, C₆H₆ being employed as standard. Vals. obtained at 20° and 25°, respectively, were: CCl₄ 2.236₀, 2.226₇; CHCl₃ 4.796₄, 4.708₆.

A. J. M.

Density and molecular polarisation of menthol and borneol. H. HARMS (Z. physikal. Chem., 1935, B, 30, 440—442).—The dipole moments of *l*-menthol and *l*-borneol are (1.62 ± 0.03) × 10⁻¹⁸ and (1.65 ± 0.03) × 10⁻¹⁸ e.s.u., respectively. The association in C₆H₆ solutions has been examined.

R. C.

Molecular volume of alkanes.—See this vol., 309.

Dispersion of air, krypton, and xenon in the short-wave ultra-violet. W. KRONJÄGER (Z. Physik, 1935, 98, 17—22).—Dispersion is given down to 2026 Å.

A. B. D. C.

Refractive indices and dispersions of volatile compounds of fluorine and boron. Carbon tetrafluoride, nitrogen trifluoride, fluoroform, carbon-nitrogen compound of fluorine (CF₃N)₂, boron hexahydride, and nitrogenous boron hydride, B₃N₃H₆. K. L. RAMASWAMY (Proc. Indian

Acad. Sci., 1935, 2, A, 630—636).—Measurements have been made with a Rayleigh type interferometer at room temp. and for λ 4359—6440 Å. Combining with dielectric const. data (this vol., 139) the vals. of the electronic and at. polarisation are deduced. (CF₃N)₂ and B₃N₃H₆ have appreciable vals. of at. polarisation. From the variations of *n* with pressure the compressibilities of the gases have been deduced.

J. W. S.

Refractometric investigations in the series of saturated normal nitriles. B. DARAGAN (Bull. Soc. chim. Belg., 1935, 44, 597—624).—*d*₄²⁰ vals. for various temp., and *n*²⁰, *n*^{54.4}, *n*⁷⁴, and *n*⁹⁵ for the He_{red}, He_{yellow}, He_{green}, He_{violet}, H_a, D, H_g, and H_γ lines are recorded for the series MeCN to C₁₃H₂₇CN. The mol. refractions are calc. and the increments for each CH₂ deduced. The results are in accord with data for paraffins (A., 1934, 132), but diverge from those for glycols.

J. W. S.

Rotatory dispersion of aliphatic aldehydes. P. A. LEVENE and A. ROTHEN (J. Chem. Physics, 1936, 4, 48—52; cf. A., 1934, 12, 1293).—Rotatory dispersion curves of aldehydes of the type CHMeEt·[CH₂]_{*n*}·CHO have been determined in the visible and ultra-violet regions. The ·CHO band at λ 2950 is active and the sign of its contribution changes as *n* changes from 0 to 1 and higher members. The magnitude of the contribution varies periodically with the no. of C between the ·CHO and the asymmetric C.

M. S. B.

Photographic measurement of the magnetic rotatory dispersion of water. I. T. PIERCE and R. W. ROBERTS (Phil. Mag., 1936, [vii], 21, 164—176).—The magnetic rotation of H₂O for 11 lines of the Hg spectrum from 5780 to 2483 Å. has been determined, and a formula has been derived for the dispersion of the Verdet const.

A. J. M.

Magnetic birefringence in solutions of organic substances. I. S. W. CHINCHALKAR (Proc. Indian Acad. Sci., 1935, 2, A, 525—531).—Data are recorded for several aromatic hydrocarbons with two or more C₆ rings in the mol., dissolved in CCl₄, EtOH, Et₂O, or EtOAc. For Ph₂ and most of its simple derivatives the mol. magnetic birefringence is approx. 4 times, for *m*-C₆H₄Ph₂ approx. 9 times, and for C₆H₃Ph₃ approx. 16 times that of C₆H₆, indicating that the C₆ rings in these mols. are either coplanar or parallel. When the C₆ rings are condensed, the magnetic and optical anisotropies are > when they are separate.

H. J. E.

Thiele's theory of partial valency in terms of electrons. F. E. RAY (Proc. Iowa Acad. Sci., 1934, 41, 157—160).—A discussion.

CH. ABS. (e)

Theory of liquids. V. T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 466—476; cf. A., 1935, 1198).—The application of the theory in the calculation of surface tension, internal pressure, cohesion, mol. vibration, internal latent heats, and compressibilities is reviewed.

H. J. E.

Parachors and chemical constitution. VI. Quadrivalent tellurium compounds. B. SINGH and R. KRISHNAN (J. Indian Chem. Soc., 1935, 12, 711—714; cf. A., 1928, 355).—The parachors of

α -dimethyltelluri-dichloride, -dibromide, and -nitrate have been determined and are in good agreement with vals. calc. on the basis of a shell of 10 Te valency electrons. R. S.

Parachor and molecular refraction of hydrazine and [its] aliphatic derivatives. L. D. BARRICK, G. W. DRAKE, and H. L. LOCHTE (J. Amer. Chem. Soc., 1936, 58, 160—162).—Vals. for parachors (figures given after compound) agree with those calc. from Sugden's consts. (A., 1924, ii, 662), but differ considerably from those calc. from the consts. of Mumford and Phillips (A., 1929, 1219): N_2H_4 , 90.7, $(CMe_2 \cdot N)_2$, 302.2, $(CMeEt \cdot N)_2$, 379.8, $(\cdot NHPr^{\beta})_2$, 327.1, $(\cdot NH \cdot CHMeEt)_2$, 400.8, $(\cdot NPr^{\beta})_2$, 318.4, $(\cdot N \cdot CHMeEt)_2$, 395.5, $CMe_2 \cdot N \cdot NHPr^{\beta}$, 313.7, $CMeEt \cdot N \cdot NH \cdot CHMeEt$, 387.6, 3 : 5 : 5-trimethylpyrazoline 288.4. The mol. refractions of these compounds agree with the calc. vals. provided (i) each N in the N-N and N-N linkings is given the primary amine val. and (ii) the C-N linking is given the val. of C-C and the N that of a sec.-amine. H. B.

Predissociation limit of CO at 11.6 volts. R. SCHMID (Physikal. Z., 1936, 37, 55—56).—New spectral evidence is given for the existence of a predissociation limit for CO at 11.6 volts (cf. A., 1935, 1299). A. J. M.

Highly dilute flames of K-I₂. E. E. ROTH (Magyar chem. Fol., 1934, 40, 65—81; Chem. Zentr., 1935, i, 2311).—The heat of the secondary gas reaction is sufficient to excite only the red, but not the violet, K doublet. The heat of dissociation of K₂ is calc. as 187 kg.-cal. from the diminution in light intensity on superheating the reaction zone. J. S. A.

Plano-radiate compounds. H. J. BACKER (Chem. Weekblad, 1936, 33, 67—71).—A survey of published data indicates that, whilst in compounds of the type CX₄ the X are distributed symmetrically in space, in compounds of the type C₆X₆ (C₆=benzene ring) they take up a symmetrical radial arrangement in the plane of the C₆ ring. The resultant compounds are characterised by high m.p., readiness to crystallise, chemical stability, and volatility. D. R. D.

Exchange of energy between diatomic gas molecules and a solid surface. J. M. JACKSON and A. HOWARTH (Proc. Roy. Soc., 1935, A, 152, 515—529).—The theory of the accommodation coeff. developed by Jackson and Mott for monat. gases (A., 1932, 1074) has been extended for diat. mols. The gas mol. is treated (a) as an oscillator, when the exchange of energy between the rotations of the gas mol. and the vibrations of the solid is negligible, and (b) as a plane rotator, when the effect of the rotations is small for H₂ and larger for O₂. L. L. B.

Distance between molecules and the determination of the volume they occupy in the liquid state (by density). A. E. MAKOVETZKI (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 83—102).—Expressions are derived for calculating intermol. distances in liquids, the results differing from those derived from van der Waals' equation. CH. ABS. (e)

Dependence of interatomic distance on single linking-double linking resonance. L. PAULING, L. O. BROCKWAY, and J. Y. BEACH (J. Amer. Chem. Soc., 1935, 57, 2705—2709).—Using experimental vals. for C-C linkings, a function showing the dependence of interat. distance on linking character for single-double linking resonance is plotted. The electronic structure of mols. containing double or triple linkings or aromatic nuclei and of mols. containing C-Cl linkings adjacent to double linkings, and the dependence of linking angles on single-double linking resonance are discussed. E. S. H.

Radial distribution method of interpretation of electron diffraction photographs of gas molecules. L. PAULING and L. O. BROCKWAY (J. Amer. Chem. Soc., 1935, 57, 2684—2692).—Tests on CCl₄ and other tetrahalides, Br, Cl₂, C₆H₆, CS₂, and COS show that the radial distribution function given by a sum of Fourier terms corresponding with the rings of an electron diffraction photograph of gas mols. provides vals. of the important interat. distances accurate to 1 or 2%. Revised vals. of interat. distances and linking angles for several substances are given. E. S. H.

Effect of electric and magnetic fields on the properties of gases. A. A. ZAITZEV (Uspek. Fiz. Nauk. U.S.S.R., 1934, 14, 1009—1019).—A discussion. CH. ABS. (e)

Dissociation of some molecules with free valencies. H. LESSHEIM and R. SAMUEL (Phil. Mag., 1936, [vii], 21, 41—64; cf. A., 1935, 1057).—In the case of the mols. BeF, MgF, CaF, SrF, BeO, MgO, CdF, BeCl, MgCl, and CaCl, there is good agreement between the energy of excitation of the products of dissociation and the terms of the metal atom if the ground level of the mol. is correlated to the *sp³P* term of the metal. Correlation of the ground level to the repulsive term *s²1S* is also possible in some of these mols. A. J. M.

Statistical perturbation theory. II. Perturbation calculations with exchange for the Thomas-Fermi theory. P. GOMBÁS (Z. Physik, 1936, 93, 417—429; cf. this vol., 134). A. B. D. C.

Polymerisation and condensation. E. K. RIDEAL (Trans. Faraday Soc., 1936, 32, 3—10).—A general review of the present state of knowledge regarding types of linking, mechanical properties, swelling and dispersion, and mol. wt. of highly polymerised substances, and the kinetics of their production. F. L. U.

Influence of van der Waals forces and primary linkings on binding energy, strength, and orientation, with special reference to artificial resins. J. H. DE BOER (Trans. Faraday Soc., 1936, 32, 10—37; cf. A., 1934, 727).—The mutual orientation of C₆H₆ rings parallel to their planes is discussed with reference to the van der Waals and repulsive forces. In calculating the tensile strength of either NaCl or synthetic resins of the PhOH- or *m*-cresol-CH₂O type, the inclusion of van der Waals forces still further increases the discrepancy between theory and observation, which is attributed to weakness due respectively to defects in the lattice and to the

smallness of the no. of C-C linkings actually formed compared with the no. possible. In the case of well-oriented cellulose derivatives the calc. vals. agree with experiment. Calculation of the relative positions of C_6H_6 rings in polystyrene indicates that they will tend to lie perpendicular to the direction of the aliphatic C chains, a conclusion in agreement with the observed strongly negative fluxional birefringence.

F. L. U.

Absolute measurement of efficiency of X-ray fluorescent screen. O. GAERTNER (Z. tech. Phys., 1935, 16, 9—12; Chem. Zentr., 1935, i, 3100; cf. A., 1935, 273).—A Cd tungstate screen absorbed 50% of the incident X-radiation, and emitted 0.54% as visible light.

J. S. A.

Intensity of interference lines in Debye X-ray diagrams. N. SELJAKOV, A. STEFANOVSKI, and J. HURGIN (Z. Physik, 1935, 98, 66—71).—Variation of the lattice area covered by the incident beam when its angle is varied accounts for anomalous intensities of different orders of reflexion from chemical catalytic lattices; these anomalies measure the extent of defects in the lattice.

A. B. D. C.

Precision measurements with the Debye-Scherrer method. II. M. STRAUMANIS and A. LEVINŠ (Z. Physik, 1936, 98, 461—475; cf. this vol., 181).—The film is extended to give interference rings around the incident and exit portions of the primary beam; this allows measurement of the film to be made independently of camera and film curvature dimensions. Accurate lattice consts. are tabulated for Al, As_2O_3 , Au, Fe, Fe_2O_3 , MgO, NaCl, Pb, $Pb(NO_3)_2$, Si, $TiCl_4$, W, and WO_3 .

A. B. D. C.

Relation between mechanical strain and intensity of X-rays reflected by a quartz plate. III. E. FUKUSHIMA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 1—14; cf. this vol., 15).—The increase in intensity of the interior reflexion of X-rays transmitted through a quartz plate under the influence of heterogeneous strain has been studied theoretically.

R. S. B.

Effect of temperature on the reflexion of X-rays by crystals. I. Isotropic crystals. C. ZENER and G. E. M. JAUNCEY. II. Anisotropic crystals. C. ZENER (Physical Rev., 1936, [ii], 49, 17—18, 122—127).—I. A short derivation of the Debye-Waller temp. factor in the reflexion of X-rays from isotropic crystals is given.

II. Mathematical. The temp. factor e^{-M} is a function of reflexion plane orientation. The case of metals with hexagonal symmetry is treated. The ratio of the const. M for reflexion \perp to and \parallel to the principal axis is 1.80 and 1.73 for Zn and Cd, respectively.

N. M. B.

X-Ray studies of crystals vibrating piezoelectrically. C. V. BERTSCH (Physical Rev., 1936, [ii], 49, 128—132; cf. Colby, A., 1934, 1296).—Intensity investigations for quartz and Na K tartrate, using Laue patterns and regular reflexion from the crystal surfaces, are reported.

N. M. B.

Systematic packing of spheres, with particular relation to porosity and permeability. L. C.

GRATON and H. J. FRASER (J. Geol., 1935, 43, 785—909).—The geometry of close-packing is discussed.

L. S. T.

Orientation of molecules of liquids from the X-ray scattering pattern. A. PETERLIN (Physikal. Z., 1936, 37, 43—52).—The theoretical scattering curve for CCl_4 is calc., and agrees well with the experimental curve of Pierce (A., 1932, 12).

A. J. M.

Schiller structure. R. T. COLONY (Amer. Min., 1935, 20, 828—837).—A discussion.

L. S. T.

Tabulation of crystal forms and discussion of form-names. A. F. ROGERS (Amer. Min., 1935, 20, 838—851).

L. S. T.

Metallic surfaces and thin films with particular reference to aluminium. BRITISH ALUMINIUM Co. (Intelligence Memo., 49 pp.).—An exhaustive review.

Disperse structures. I. Systematics. V. S. VESELOVSKI. II. X-Ray investigation of the disperse structures of graphitic substances. V. S. VESELOVSKI and K. V. VASILIEV (J. Phys. Chem. U.S.S.R., 1934, 5, 977—981, 982—995).—I. A review of crystal structure and classification.

II. X-Ray data for graphitic substances are discussed.

CH. ABS. (e)

Crystalline boron. S. VON NÁRAY-SZABÓ (Naturwiss., 1936, 24, 77).—Cryst. B (Merck) consists chiefly of the adamantine form, together with irregular hexagonal leaflets of the graphitic form. X-Ray investigation gave for the adamantine form (tetragonal), a 12.55, c 10.18, identity period along [110], 17.61 Å., and for the graphitic form (rhombohedral), a 17.64, b 25.0, c 10.26 Å.

A. J. M.

Crystal structure of solid oxygen. L. VEGARD (Z. Physik, 1935, 98, 1—16).— γ - O_2 has a cubic structure, space-group T_h^h , the unit cell containing 8 rotating mols. ordered in pairs; the pair centres form a face-centred cubic structure of closest spherical packing for the pairs. β - O_2 has a rhombohedral cell of 6 mols.

A. B. D. C.

Crystalline properties and magnetic anisotropy of distilled bismuth. A. GOETZ, O. STIERSTADT, and A. B. FOCKE (Z. Physik, 1935, 98, 118—127).—High-vac. distillation of Bi produces a microcryst. layer 0.5—0.1 mm. thick carrying a macrocryst. conglomerate of similarly oriented crystals.

A. B. D. C.

Isomorphism of Mg_3Al_2 and α -manganese. F. LAVES, K. LÖHBERG, and P. RAHLFS (Nachr. Ges. Wiss. Göttingen, 1934, [ii], 1, 67—71; Chem. Zentr., 1935, i, 3103).—Complete analysis of the crystal structure of " Mg_3Al_2 " shows the space-group to be T_h^h , a 10.54 Å., with 58 atoms per unit cell, giving a true formula $Mg_{17}Al_{12}$.

J. S. A.

Structure of aluminium carbonitride, Al_5C_3N . M. VON STACKELBERG and K. F. SPIESS (Z. physikal. Chem., 1935, 175, 140—153).— Al_5C_3N has a hexagonal structure; a 3.280, c 21.55 Å., $Z=2$, space-group C_{6v}^4 . The lattice consists of hexagonal at. planes, 5 Al planes interleaved with 3 C planes and 1 N plane forming a layer, which consists of two parts similar in structure to Al_4C_3 and AlN, respect-

ively. The lattice of AlN has a 3.104, c 4.965 Å. 2.15 Å. is deduced by Zachariassen's method as the mean "univalent radius" of the N^{III} ion. Apparently AlN is able to hold some Al₄C₃ in solid solution.

R. C.

Crystal structure and colloid-chemical properties of vanadium pentoxide. J. A. A. KETELAAR (Chem. Weekblad, 1936, 33, 51—57).—V₂O₅ forms hemimorphic rhombic crystals of space-group C_{2v}^2 , with 2 mols. in the unit cell; a 11.48, b 4.360, c 3.555 Å., and $d_{\text{calc.}}$ 3.37. The structure is built up of chains of O tetrahedra linked by shared corners, accounting for formation of elongated micelles in colloidal solution.

D. R. D.

Structure of thin films of metallic oxides and hydrates. N. SMITH (J. Amer. Chem. Soc., 1935, 58, 173—179).—Electron diffraction indicates that oxide films removed from heated metals are polycryst., showing no evidence of preferred orientation or pseudomorphism. The film on Ni is NiO, Cu₂O on Cu, and Fe₃O₄ mainly on Fe. Hydroxide pptts. from salt solutions are cryst., but show evidence of distortion.

E. S. H.

Complex nitrites of iron, cobalt, nickel, and copper: structure and magnetic susceptibility. L. CAMBI and A. FERRARI (Gazzetta, 1935, 65, 1162—1190).—The prep. of 15 compounds $M^I M^{II} [Fe(NO_2)_6]$ is described ($M^I = K, NH_4, Tl$; $M^{II} = Ba, Sr, Ca, Pb, Hg, Cd$). Vals. of lattice const. and $d_{\text{calc.}}$, obtained from X-ray measurements, are given. Comparison with previous data shows that the mol. vols. of the complex ions $[Fe(NO_2)_6]^{IV}$, $[Co(NO_2)_6]^{IV}$, and $[Ni(NO_2)_6]^{IV}$ are 120.3, 123.5, and 128.9, respectively. Magnetic susceptibility measurements show that $[Fe^{II}(NO_2)_6]^{IV}$ is predominantly diamagnetic like $[Co^{III}(NO_2)_6]^{IV}$, whereas $[Co^{II}(NO_2)_6]^{IV}$ is paramagnetic (1 Bohr magneton) like $[Cu^{II}(NO_2)_6]^{IV}$.

O. J. W.

Crystallography of hexa- ω -bromomethylbenzene. J. BEINTEMA, P. TERPSTRA, and W. J. VAN WEERDEN (Rec. trav. chim., 1935, 54, 962—969).—The hexagonal unit cell of C₆(CH₂Br)₆ contains 3 mols. and has a 11.373, c 5.377 Å., but the crystal has a rhombohedral lattice with a 9.621 and α 116° 36'. It is concluded that the atoms of each mol. are coplanar, and that each Br lies on a circle of radius 3.75 Å.

J. W. S.

X-Ray study of symmetrical trinitrotoluene and cyclotrimethylenenitroamine. R. HULTGREN (J. Chem. Physics, 1936, 4, 84).—C₆H₂Me(NO₂)₃ is orthorhombic with a 14.85, b 39.5, c 5.96 Å. For 16 mols. per unit cell $d_{\text{calc.}}$ is 1.710 (lit. 1.654). The crystals of cyclotrimethylenenitroamine are also orthorhombic. X-Ray analysis gives a 11.5, b 13.2, c 10.6 Å. For 8 mols. per unit cell $d_{\text{calc.}}$ is 1.82.

M. S. B.

Alkaline-earth cacodylates. II. R. TIOLLAIS (Bull. Soc. chim., 1936, [v], 3, 87—95).—Cacodylates of Ca, Sr, and Ba belong to the monoclinic system, with $a : b : c = 3.363 : 1 : 2.414, 1.813 : 1 : 2.335, 1.5737 : 1 : 1.3332$, respectively. Forms found present are Ca: ph_1m and pa_1h_1m , Sr: $pmb_{1/3}b_1h_{1/2}$ and $pme_1b_{1/3}b_1h_{1/2}$, Ba: pa_1h_1m , $pa_1e_1h_1m$, pa_1m , and

$pa_1h_1mb_{1/2}$. The Sr salt shows twinning (cf. *ibid.*, 70).

E. E. A.

Fine structure of plant chitin. G. VAN ITERSOM, jun., K. H. MEYER, and W. LOTMAR (Rec. trav. chim., 1936, 55, 61—63).—X-Ray examination of plant chitin from *Phycomyces* is described and the results are compared with those previously recorded for animal chitin (cf. A., 1935, 753). An arrangement of the acetylglucosamine residues in the elementary cell of plant chitin fibres is suggested.

E. E. A.

X-Ray spectrography of polymerides, particularly those having rubber-like extensibility. J. R. KATZ (Trans. Faraday Soc., 1936, 32, 77—94).—A general discussion of the interpretation of X-ray spectrograms of cryst. and amorphous polymerides. Synthetic rubbers should be made under control by X-ray analysis. No polymeride of isoprene has yet been found to have the X-ray characteristics of natural rubber. Spectrographic data indicate that the extensible units in rubber and in polymerides with similar properties are single mols.

F. L. U.

Dependence of cybotactic groups on specific volume. R. D. SPANGLER (Proc. Iowa Acad. Sci., 1934, 41, 253—254; cf. A., 1935, 1297).—X-Ray diffraction data are recorded for Et₂O near its crit. point. The cybotactic groupings depend more on sp. vol. than on temp. The indications of groups disappear at about the crit. sp. vol.

CH. ABS. (e)

Effect of crystal size on lattice dimensions. G. I. FINCH and S. FORDHAM (Proc. Physical Soc., 1936, 48, 85—94).—Lattice const. of the Li, Na, and K halides are determined by the electron-diffraction method. Slight divergences from results by X-ray diffraction indicate that crystal size appreciably influences lattice dimensions.

N. M. B.

Electron-diffraction investigation of carbonyl chloride, the six chloroethylenes, thiocarbonyl chloride, α -methylhydroxylamine, and nitromethane. L. O. BROCKWAY, J. Y. BEACH, and L. PAULING (J. Amer. Chem. Soc., 1935, 57, 2693—2704).—The C—Cl distances determined vary between 1.67 and 1.73 Å., which is 5—20% < the normal single linking val. The decrease is due to the partial double linking character caused by resonance resulting from the conjugation of an unshared pair of electrons on the Cl atom with the adjacent double linking. The vals. for the angle Cl—Cl—X are smaller than the tetrahedral val. for the angle between a single and a double linking for the same reason. The vals. for other interat. distances are in good agreement with the accepted covalent radii.

E. S. H.

Diffuse rings produced by electron scattering. L. H. GERMER (Physical Rev., 1936, [ii], 49, 163—166; cf. A., 1933, 657).—Two diffuse diffraction rings have been obtained by electrons scattered from vaporized ZnS, and from unpolished surfaces of SiC and Cu₂O, contrary to the view that such rings from polished metal surfaces are evidence that the surfaces are amorphous. The possibility of an amorphous layer on polished metals is not excluded.

N. M. B.

Structure of ice II. R. L. McFARLAN (J. Chem. Physics, 1936, 4, 60—64).—X-Ray analysis of ice II indicates a side-centred orthorhombic cell, a 7.30, b 4.50, c 5.56 Å. The cell contains 8 mols., has the symmetry of space-group V^5-C222_1 , and gives d 1.21. The transition from ice I to II breaks up the H_2O mol. and gives an ionic crystal for II.

M. S. B.

Structure of ice. W. H. BARNES (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 53—60).—A crit. discussion of the structure proposed by Bernal and Fowler (A., 1933, 1106).

H. J. E.

Structure and entropy of ice and of other crystals with some randomness of atomic arrangement. L. PAULING (J. Amer. Chem. Soc., 1935, 57, 2680—2684).—The H_2O mols. in ice are so arranged that each is surrounded by 4 others, each mol. being oriented so as to direct its 2 H towards two of the four neighbours, forming H linkings. Only one H lies near each 0-0 axis. There are $(3/2)^N$ such configurations for N mols., giving a residual entropy of $R \log_2 3/2 = 0.805$ e.u., in good agreement with the experimental val.

E. S. H.

Crystal structure from data on magnetic susceptibilities. O. M. JORDAHL (Physical Rev., 1934, [ii], 46, 79).—Experimental results on the crystal structure of $CuSO_4 \cdot 5H_2O$ (A., 1934, 243) agree with the conclusions of the author (*ibid.*, 241) deduced from an analysis of the magnetic data.

L. S. T.

X-Ray investigation of the solid solution nature of nitrate-contaminated barium sulphate precipitates. G. H. WALDEN, jun., and M. U. COHEN (J. Amer. Chem. Soc., 1935, 57, 2591—2597).—Apparatus and technique for determining the lattice parameters of powdered crystals with a precision of 0.01% are described. A study of the lattice parameters of $BaSO_4$ ppts., containing NO_3^- in absence of all foreign cations other than H^+ , shows that the contaminant enters the $BaSO_4$ lattice with formation of a solid solution. The general problem of ppt. contamination is discussed in the light of the results.

E. S. H.

Crystal structure and constitution of $BF_3 \cdot 2H_2O$. L. J. KLINKENBERG and J. A. A. KETELAAR (Rec. trav. chim., 1935, 54, 959—961).— $BF_3 \cdot 2H_2O$ is isomorphous with NH_4ClO_4 , its orthorhombic unit cell containing 4 mols. and having a 8.74 ± 0.06, b 5.64 ± 0.03, c 7.30 ± 0.10 Å. These cell dimensions are almost identical with those of NH_4BF_4 , viz., 8.89 ± 0.05, 5.68 ± 0.05, and 7.21 ± 0.03 Å., respectively. This is interpreted as indicating that the formula should be written $(OH_3)(BF_3OH)$.

J. W. S.

Physical investigations on alkali halide crystals. R. HILSCH (Angew. Chem., 1936, 49, 69—73).—A lecture on published work concerning optical properties and electrical conductivity, especially of crystals containing excess of alkali or halide ions.

E. S. H.

Effect of thermal and mechanical tempering on the back electromotive force and current-voltage curves of rock-salt crystals. A. VENDEROVITSCH and R. DRISINA (Z. Physik, 1935, 98, 108—117).—The effects of tempering NaCl crystals

on deviations from Ohm's law show that these deviations are due to the presence of a high-voltage polarisation.

A. B. D. C.

Variation of alternating-current resistance of nickel in longitudinal magnetic fields. M. M. SEN GUPTA, H. B. MOHANTY, and S. SHARAN (Z. Physik, 1935, 98, 262—266).—A.-c. measurements are free from many irregularities found with d.c. Hysteresis is less for a.c. (cf. A., 1935, 267).

A. B. D. C.

Phenomenon in transformations [in metals and alloys] extending over a temperature range. A. SCHULZE (Z. Metallk., 1935, 27, 251—255).—Magnetic transformations and the change from regular to random orientation of the atoms in the lattice are preceded by inflexions in the curves of electrical resistance, temp. coeff. of resistance, and thermal expansion. This anomaly is shown by Fe, Ni, and Ni-Fe alloys (magnetic transformations) and by Au-Cu and β -Zn-Cu alloys (lattice reorientation).

A. R. P.

Magnetic behaviour of nickel wire under high torsion. R. GANS (Ann. Physik, 1936, [v], 25, 77—91).—Theoretical.

L. L. J.

Processes of technical magnetisation. I. Weiss' theory of the technical magnetisation curve. K. H. R. WEBER (Z. Physik, 1935, 98, 155—180).

A. B. D. C.

Relation of spontaneous and true magnetisation to [optical] emissivity. W. GERLACH (Ann. Physik, 1936, [v], 25, 209—212).—The anomalous resistance-temp. curve of Ni in the neighbourhood of the Curie point is associated with a similar anomaly in the emissivity-temp. curve for long λ , in accordance with the Hagen-Rubens relation. Both effects are quantitatively related to the spontaneous magnetisation; data for λ 24 μ and 8.7 μ are recorded from 100° to 310°. True magnetisation depresses the emissivity, in further agreement with theory.

L. J. J.

[Optical] emissivity of nickel. E. LÖWE (Ann. Physik, 1936, [v], 25, 213—222; cf. preceding abstract).—Measurements of total radiation and radiation at a series of λ from < 4.5 to 24 μ for polished Ni between 100° and 450° are recorded. Magnetisation has no effect on the total emission, but for $\lambda > 8$ —10 μ the emission at the Curie point is depressed 0.6% in a field of 4000 gauss.

L. J. J.

Effect of tension on magnetisation [of nickel] above the Curie point. G. SCHARFF (Ann. Physik, 1936, [v], 25, 223—232).—The Curie temp. is independent of tension. Ferromagnetic and true magnetisation can be distinguished by the effect of tension, since the former is depressed, the latter unaffected. Ferromagnetisation can be detected up to 12° above the Curie point.

L. J. J.

Transverse magnetic effect. J. E. VERSCHAFFELT (Wis. nat. Tijds., 1934, 7, 53—66; Chem. Zentr., 1935, i, 3638).—Theoretical.

J. S. A.

Surface magnetisation in ferromagnetic crystals. L. W. MCKEEHAN and W. C. ELMORE (Physical Rev., 1934, [ii], 46, 226—228; cf. this vol., 145).

L. S. T.

Variation of volume magnetostriction and Weiss' factor with temperature and lattice constant. M. KORNETZKI (*Z. Physik*, 1935, 98, 289—313).—Ferromagnetic substances showing vol. magnetostriction should have Curie points that vary with vol. Measurements on Fe, Fe-Ni, and Ni-Cu alloys between 20° and 90° confirm this. A. B. D. C.

Behaviour of single crystals of aluminium of different degrees of purity prepared from the molten metal and by recrystallisation. F. GISEN (*Z. Metallk.*, 1935, 27, 256—261).—Single crystals of 99.5—99.998% Al can be prepared (i) by maintaining the metal at 800—820° until all nuclei disappear, then cooling very slowly without disturbance to < the m.p., or (ii) by drawing rod to 40—45% reduction, annealing at 250° for 15 hr. to obtain a fine-grained structure, stretching 0.5—1%, and slowly heating from 430° to 480° during 45 hr. The crit. shear strength of crystals prepared by method (ii) decreases almost linearly with decreasing purity from about 300 g. per sq. mm. for the 99.998% metal to 70 g. per sq. mm. for the 99.5% metal, whereas that of crystals prepared by method (i) is < 20 g. per sq. mm. irrespective of the purity. This difference is ascribed to the more pronounced mosaic structure of crystals prepared by method (ii); X-ray examination confirms this theory. A. R. P.

Strength and modulus of elasticity of amorphous materials, related to their internal structure. R. HOUWINK (*Trans. Faraday Soc.*, 1936, 32, 122—131).—The internal structure of asphalts, resins, and glass is discussed, and their tensile strengths and vals. of Young's modulus are compared. Smekal's theory of "Lockerstellen" is adopted to account for the discrepancy between calc. and observed strengths, weaknesses in macromols. of an insol. PhOH-CH₂O resin being due to non-reaction between such reactive groups as happen to be out of alignment. F. L. U.

High elasticity of three-dimensionally polymerised amorphous materials in relation to their internal structure. R. HOUWINK (*Trans. Faraday Soc.*, 1936, 32, 131—143; cf. preceding abstract).—"High elasticity," *i.e.*, elastic deformation which > 1%, is observed in asphalts and glass, in which it may reach 20% and is connected with a viscosity range of 10¹¹—10¹³ poises. In hardening resins at about 120° it reaches 240%. A relation between the conditions for high elasticity and the formation of insol. elastic three-dimensional networks is shown, and calculations are given to explain changes of Young's modulus, yield val., and strain at the yield val. when such structures are formed. F. L. U.

Inorganic substances with rubber-like properties. K. H. MEYER (*Trans. Faraday Soc.*, 1936, 32, 148—152; cf. A., 1935, 1450).—The elastic behaviour and X-ray patterns of elastic S and of polyphosphonitrilic chloride are described. They present many analogies with org. polymerides, and their extensibility is attributed to long flexible chains of mols. which become straight when stretched, and undergo flexion by Brownian movement when ten-

sion is relaxed, with consequent shortening of the specimen. F. L. U.

Constitution of the crystallised part of cellulose. IV. Elasticity of cellulose. K. H. MEYER and W. LOTMAR (*Helv. Chim. Acta*, 1936, 19, 68—86).—The influence of moisture, temp., orientation, and tension on the modulus of elasticity *E* of several natural cellulose (I) fibres and some derivatives of (I) has been determined using Polanyi's dynamometer and also an acoustic method of measurement. The temp. coeffs. of the tension are zero or negative except for (I) acetate, which gives a positive val. like rubber, because of its amorphous structure. In the other fibres, with a cryst. network, the attractive forces between the atoms, or the deformation of the valency angles, are responsible for the elasticity. *E* for natural fibres of high orientation, such as ramie, hemp, and linen, approaches a val. of approx. 11,000 kg. per sq. mm. ±10%, which is close to the val. calc. for the (I) model if the angular forces are 20% of the principal valency force. Artificial (I) fibres or (I) derivatives have vals. of *E* between 100 and 5000 kg. per sq. mm. M. S. B.

Crystal plasticity. V. Completion of the rate of slip formula. E. OROWAN (*Z. Physik*, 1935, 98, 382—387; cf. A., 1934, 949).—A term is added to the earlier rate of slip formula to take account of forces arising in the crystal opposed to the applied force: these are likely to be significant for org. crystals. A. B. D. C.

Variation of the adiabatic elastic moduli of rock-salt between 80° and 270° abs. F. C. ROSE (*Physical Rev.*, 1936, [ii], 49, 50—54).—Balamuth's method for measuring Young's modulus of a cubic crystal (cf. A., 1935, 154) is extended to the measurement of all the elastic moduli of any solid crystal below 0°. Data for the variation with temp. of the adiabatic and isothermal elastic moduli and elastic consts. of rock-salt in the range 80—270° abs. are given. N. M. B.

Relation between heat of transition and transition point of enantiotropic modifications. J. A. M. VAN LIEMPT (*Rec. trav. chim.*, 1935, 54, 934—936).—An equation is derived connecting heat of transmission with the temp., and the at. frequencies and densities of the modifications at the transition temp. Direct confirmation is lacking owing to absence of data, but by substituting the ratio of the at. frequencies by the ratio of the abs. temp. at which the forms have equal sp. heats, the calc. transition temp. for Sn and S are of the same order as the experimental vals. J. W. S.

Rates of vaporisation of metals in a gaseous atmosphere. J. A. M. VAN LIEMPT (*Rec. trav. chim.*, 1936, 55, 1—6).—A formula is derived which is in agreement with experimental data and with Weber's formula. The deviations which are observed at high pressures are explained. E. E. A.

Mol. wt. of polystyrenes and shape of the molecules in solutions. R. SIGNER (*Trans. Faraday Soc.*, 1936, 32, 296—307).—Experiments on mol. wts. of polystyrenes as determined by ultracentrifuging and on their fluxional birefringence lead

to the conclusion that in certain solvents the mols. are linear, straight for the fractions of lower, and curved for those of higher, mol. wt. (cf. A., 1933, 23, 902; 1935, 162, 700).

F. L. U.

Rendering visible standing ultrasonic waves in transparent solid substances. III. Optical strain analysis of elastic vibrations. E. HIEDEMANN and K. H. HOESCH (Z. Physik, 1935, 98, 141—144; cf. A., 1935, 1312).—Longitudinal and transverse waves give different patterns. A. B. D. C.

Determination of ultrasonic velocity in 52 organic liquids. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1935, 2, A, 497—511).—Data for 52 liquids (hydrocarbons, alcohols, ketones, halogen derivatives, etc.) at 23—24.5° are given. Aromatic compounds in general gave higher velocities than did aliphatic compounds. Mols. with electric moment, or long mols., also gave high velocities. Adiabatic compressibility data are tabulated. H. J. E.

Longitudinal thermoelectric effect. VI. Mercury. J. L. CH'EN and W. BAND (Proc. Physical Soc., 1936, 48, 164—167; cf. A., 1935, 1312).—The Benedicks e.m.f. in Hg in an unrestricted glass tube undergoes a reversible decrease with rising temp. It is suggested that there is an anisotropic quasi-cryst. arrangement of the surface mols. depending on temp. N. M. B.

Thermomagnetic properties of nickel. II. W. BAND and Y. K. HSÜ (Proc. Physical Soc., 1936, 48, 168—177; cf. *ibid.*, 1935, 47, 910).—Curves are given for the homogeneous thermoelectric e.m.f. in pure Ni wire 1 mm. diameter for tensions \geq 8 kg. Benedick coeffs. are found as functions of magnetic field and tension. An antisymmetric part of the e.m.f. with respect to the magnetisation has been discovered. Evidence suggests that the homogeneous effect is controlled by the regularity of the micro-crystals in the wire. N. M. B.

Ionic complexes of polymeric compounds. G. WALTER (Trans. Faraday Soc., 1936, 32, 396—402).—Determination of the electrical conductivity of mono- and poly-meric methylenecarbamides in HCO₂H in conjunction with that of the mol. wt. in the same solvent and of the NH₂ end-groups reveals the presence of ionic complexes. The rôle of the latter in the formation of resins from CO(NH₂)₂ and CH₂O is discussed. F. L. U.

Electrical conductivity of alkali metal flames. W. KISSELMANN and A. BECKER (Ann. Physik, 1936, [7], 25, 49—73).—The conductivity of Li, Na, K, Rb, and Cs chloride vapours in the Méker burner flame at 1250—1950° abs. has been investigated. In the metal-free flame the conductivity-temp. relation corresponds with electron emission by a component of ionisation potential 2.50 volts. For the metal vapour, the conductivity \propto the square root of the total metal concn.; the conductivity-temp. relation is independent of the concn., and corresponds approx. with electron emission by free metal atoms formed by chemical dissociation. L. J. J.

Phase-equilibrium of superconductors in a magnetic field. H. LONDON (Proc. Roy. Soc., 1935, A, 152, 650—663).—Mathematical. The disturbance

of superconductivity by a magnetic field is treated thermodynamically (A., 1935, 689). A threshold val. of the c.d. and not of the magnetic field is the decisive quantity. L. L. B.

Superconductivity of thin metallic films. A. D. MISENER and J. O. WILHELM (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 5—11).—The transition temp. for Pb films falls rapidly as the film thickness is decreased below 9×10^{-5} cm. The films were deposited electrolytically on constantan wire cores. H. J. E.

Effect of magnetic fields on the superconductivity of thin films of tin. A. D. MISENER, H. G. SMITH, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 13—21).—The crit. magnetic field necessary to interrupt the superconducting state of Sn is greater for thin films than for massive Sn. Hysteresis effects occurred in thin films. H. J. E.

Magnetic anisotropy of naturally occurring substances. I. Mother of pearl. P. NILAKANTAN (Proc. Indian Acad. Sci., 1935, 2, A, 621—629).—From measurements of the abs. susceptibility and magnetic anisotropy of the naure of *Turbo*, *Haliotis*, *M. margaritifera*, *Mytilus viridis*, and *Nautilus pompilius* it is concluded that the *c* axes are in each case normal to the elementary lamina. The *a* and *b* axes are probably in some cases distributed at random and in others the *a* axis is approx. along the line of growth. J. W. S.

Magnetism and polymerisation. J. FARQUHARSON (Trans. Faraday Soc., 1936, 32, 219—226).—Polymerisation is accompanied by a change in diamagnetic susceptibility, measurement of which can be used to find the mol. wt. of the product with an accuracy which decreases with increase in the degree of polymerisation. Results of experiments with (CH₂:CMe)₂, cyclopentadiene, CNCl, and PhNO are given. F. L. U.

Electrical resistance and magnetic susceptibility of sugar carbon submitted to various thermal treatments. P. CORLIEZ (Compt. rend., 1935, 201, 1486—1488; cf. this vol., 143).—Vals. are recorded for specimens heated from 1000° to 2000°. T. G. P.

Character of linking in the carbon monoxide molecule. R. I. JANUS and J. S. SCHUR (Physikal. Z. Sovietunion, 1935, 7, 19—25).—A simple method of measuring the magnetic susceptibility of gases is described. The val. for CO is $-118 \pm 6 \times 10^{-7}$. CO contains a triple linking. CH. ABS. (e)

Diamagnetism and change of state. P. S. VARADACHARI (J. Annamalai Univ., 1935, 5, 18—26).—Evidence is given that the decreased magnetic susceptibility of many aromatic compounds on solidification is due to the decomp. on fusion of polymerides present in the solid state. The sharp lines in solid C₆H₆ and Ph₂O (cf. Gross, A., 1935, 564) may be due to such polymerides. H₂O is considered in the light of Raman data. Differences between the susceptibilities of the liquid and vapour states of org. compounds are eliminated if the v.d. is taken into account in calculating mol. susceptibility. N. M. B.

Magnetochemistry of rhenium: metallic rhenium and septavalent rhenium. N. PERRAKIS and L. KAPATOS (Praktika, 1934, 9, 121—125; Chem. Zentr., 1935, i, 3110).—Measurement of the magnetic susceptibility of Re_2O_7 gives for Re^{VII} the same val. as found by Albrecht and Wedekind for metallic Re. For Re prepared by reduction of NH_4ReO_4 , the author's previous val. was confirmed. χ for KReO_4 and NH_4ReO_4 are recorded. J. S. A.

Diamagnetic susceptibilities of salts forming ions with inert gas configurations. II. Alkaline halides. G. W. BRINDLEY and F. E. HOARE (Proc. Roy. Soc., 1935, A, 152, 342—353).—The method previously described (A., 1935, 149) has been used to determine the diamagnetic susceptibilities of the halides of Li, Rb, and Cs. The results indicate that the susceptibilities are additive within the limits of experimental error except for LiCl, LiBr, and LiI, and CsCl, CsBr, and CsI. It is suggested that the low vals. in the latter cases are due to deformation of the ions produced by (a) the close approach of the negative ions in the Li salts, and (b) the change of crystal structure in the Cs salts. A series of ionic susceptibilities for ions in crystals of the rock-salt type is derived. L. L. B.

Temperature coefficient of susceptibility of tetrahydronaphthalene. B. N. RAO (Current Sci., 1935, 4, 404—405).—The susceptibility, studied in the range 23—70°, showed no temp. effect. The abs. val. was -0.688×10^{-6} , showing no variation with field strength. N. M. B.

Temperature of the Langmuir hydrogen flame. H. VON WARTENBERG and H. J. REUSCH (Nachr. Ges. Wiss. Göttingen, 1934, [ii], 1, 141—145; Chem. Zentr., 1935, i, 2654).—The temp. of an at. H flame was determined by the reversal of lines of the Li flame, using the solar image as comparison. Near the electrode 4600—4800° was recorded. J. S. A.

Temperature rise in a material of which the thermal properties vary with temperature. J. H. AWBERY (Proc. Physical Soc., 1936, 48, 118—124).—Mathematical. N. M. B.

Polymorphism. H. E. PHIPPS and J. H. REEDY (J. Physical Chem., 1936, 40, 89—100).—An accurate method for determining the transition temp. of sol. substances by means of a dipping refractometer is described. Examination of NH_4NO_3 III petrographically indicates that it is orthorhombic. Redetermination of the transition point of CCl_4 by heating and cooling curves gives $-47.66 \pm 0.2^\circ$. The effect of impurities on this is much > on the m.p. M. S. B.

Temperature dependence of free electron specific heat. E. C. STONER (Phil. Mag., 1936, [vii], 21, 145—160).—Mathematical. The Fermi-Dirac statistics are applied to obtain the variation of energy and sp. heat over the whole temp. range, the range of validity of the formulæ being specially considered. A. J. M.

Equation for approximating heat capacities of gases calculated from spectral data. I. N. GODNEV (J. Amer. Chem. Soc., 1936, 58, 180—181).—The proposed equation has been applied satisfactorily

to data for CO, N_2 , and S in the range 100—5000° abs. E. S. H.

Rotation and entropy of hydrogen sulphide. K. CLUSTUS and A. FRANK (Naturwiss., 1936, 24, 62).—There is no difference between the entropy of H_2S calc. thermodynamically and statistically, in contrast with H_2O . There is therefore no zero-point rotation of its *o*-modification. This difference between H_2O and H_2S is connected with the existence of a no. of solid phases of H_2S under ordinary pressures, whereas only one stable form of H_2O exists. A. J. M.

Thermal data on organic compounds. XV. Heat capacity, entropy, and free energy data for the isomeric butenes. S. S. TODD and G. S. PARKS (J. Amer. Chem. Soc., 1936, 58, 134—137; cf. A., 1935, 825).—The heat capacities of the four isomeric butenes have been determined between liquid-air temp. and their respective b.p. The mol. entropies and free energies of formation have been calc. The thermodynamic stability varies considerably with the configuration of the mol. E. S. H.

Glass. XII. New heat capacity data for organic glasses. Entropy and free energy of *dl*-lactic acid. G. S. PARKS, S. B. THOMAS, and D. W. LIGHT. **XIII. Glass formation by a hydrocarbon polymeride.** J. D. FERRY and G. S. PARKS (J. Chem. Physics, 1936, 4, 64—69, 70—75).—XII. Sp. heat measurements have been made on $\text{Bu}^{\beta}\text{OH}$, *dl*-lactic acid (I), and γ -methylhexane in glassy, liquid, or incompletely cryst. states by Nernst's method. As with other glass-forming substances (cf. A., 1930, 1359), there is a transition region over a temp. interval of 8—20°, depending on the nature of the glass and its thermal history. Through this temp. interval the material passes from a hard glass to a more or less viscous liquid, whilst the sp. heat rises rapidly. The sp. heat of cryst. (I) has also been determined at different temp. The heat of fusion of the crystals at 289.9° abs. is 30.1 g.-cal. per g. The entropy and free energy of formation of (I) have been calc.

XIII. Polyisobutene, average mol. wt. 4000, forms a glass of nature similar to those of low mol. wt. The transition region, through which the sp. heat increases by 32%, is 192—202° abs. The expansion coeff. has been measured at 160—300° abs. and increases by 200% between 185° and 205° abs. In agreement with the behaviour of other glass-forming substances, η , at the mean transition temp., is approx. 10^{13} poises. The influence of mol. structure on glass formation is discussed. M. S. B.

Purification and physical properties of organic compounds. XII. Lower aliphatic bromides. E. L. SKAU and R. McCULLOCH (J. Amer. Chem. Soc., 1935, 57, 2439—2440; cf. this vol., 290).—Revised data for the b.p., f.p., and *d* of Et, Pr ^{α} , Pr ^{β} , Bu ^{α} , Bu ^{β} , and *n*-amyl bromides are recorded. E. S. H.

Regularities in the m.p. of polyenes. R. KUHN and C. GRUNDMANN (Ber., 1936, 69, [B], 224—227).—The same regularities are observed in the absorption and fluorescence spectra of the purely aliphatic polyenes and of the $\omega\omega'$ -diphenylpolyenes. In expect-

ation of further physical regularities it is found that the m.p. of polyenes are to a first approximation a linear function of the no. of conjugated double linkings. The inclination of the graphs is nearly identical for aldehydes, carboxylic acids, and their Me esters, but is steeper for the alcohols. Among *cis-trans*-isomerides the *cis*-forms ($H_2C_2O_4$, maleic, *cis-cis*-muconic acid) show a different sequence of m.p., and the 2-furylidene-polyene-aldehydes and -carboxylic acids do not conform to the scheme. The following new or amended m.p. are recorded: sorbaldehyde, m.p. -17° ; Me sorbate, m.p. 15° ; decatetraenoic acid, m.p. 226.5° .

H. W.

Time of melting of thin fuses. II. J. A. M. VAN LIEMPT and J. A. DE VRIEND (*Z. Physik*, 1935, 98, 133-140; cf. A., 1935, 289).—Currents, *I*, up to 20 times the limiting current require a time, *t*, for fusion, where $I^2t = \text{const.}$

A. B. D. C.

Thermochemical properties of nitrous oxide. T. C. SUTTON, H. R. AMBLER and G. W. WILLIAMS, (*Proc. Physical Soc.*, 1936, 48, 189-202).—The conditions of initiation and of pressure under which direct decomp. will propagate progressively and explosively through N_2O are examined. The heat of formation, determined by explosive thermal decomp. at 42 atm., is -19.52 ± 0.1 g.-cal. per mol. at const. pressure. A simple method for comparing *p* for two gases is applied to N_2O and CO_2 over 10-45 atm.

N. M. B.

Continuation of vapour-pressure curve above the critical point. F. KRÜGER (*Physikal. Z.*, 1936, 37, 56-58).—Theoretical. The methods of Eucken (A., 1934, 1062) and of Trautz and Ader (*ibid.*, 723) gave identical results in the neighbourhood of the crit. point.

A. J. M.

Vapour pressure of glycols. O. J. SCHIERHOLTZ and M. L. STAPLES (*J. Amer. Chem. Soc.*, 1935, 57, 2709-2711).—V.p. (10-760 mm.), *n*, and *d* are recorded for ethylene, $\alpha\beta$ - and $\alpha\gamma$ -propylene, $\alpha\gamma$ - and $\beta\gamma$ -butylene glycols.

E. S. H.

Isopiestic method of determining the vapour pressures of salt solutions. A. JANIS (*Proc. Roy. Soc. Canada*, 1935, [iii], 29, III, 87-89).—A modification of Sinclair's method for use with larger samples is described (cf. A., 1933, 587).

H. J. E.

Coefficient of expansion of silver iodide and of the halides of thallium. G. JONES and F. C. JELEN (*J. Amer. Chem. Soc.*, 1935, 57, 2532-2536).—A differential wt. dilatometer, which acts simultaneously as a thermo-regulator, is described. The following mean cubical coeffs. of expansion have been determined: Pyrex glass 9.85×10^{-6} , PhMe 1.111×10^{-3} , AgI -1.6×10^{-6} , TlCl 1.59×10^{-4} , TlBr 1.53×10^{-4} , TlI 1.35×10^{-4} .

E. S. H.

Melting curves and compressibilities of nitrogen and argon. P. W. BRIDGMAN (*Proc. Amer. Acad. Arts Sci.*, 1935, 70, 1-32; cf. A., 1935, 156).—The m.p. and vol. changes on melting were determined at pressures up to 6000 atm. The heats of fusion were calc. *P-V-T* data are given.

CH. ABS. (e)

Viscosity of deuterium oxide and its mixtures with water at 25° . G. JONES and B. J. FURNWALT

(*J. Chem. Physics*, 1936, 4, 30-33).— η is nearly a linear function of *d*. An expression relating fluidity to the increase in *d* over that of ordinary H_2O is shown to be valid to 0.006% over the whole concn. range, whilst Bingham's equation is valid to 0.01%.

M. S. B.

Absolute measurement of the viscosity of liquid tin. A. J. LEWIS (*Proc. Physical Soc.*, 1936, 48, 102-110; cf. Stott, A., 1933, 895).—Using the capillary flow method, η , with independent correction for kinetic energy, was measured for the temp. range $235-330^\circ$. The temp. variation of η and the val. at the f.p. agree with Andrade's theory (cf. A., 1934, 356).

N. M. B.

Association of substances which are solid at ordinary temperatures [determined] by the fluidity method. E. C. BINGHAM and J. E. HATFIELD (*Physics*, 1935, 6, 64-68).—The fluidities of $BzOH$, $C_{10}H_8$, $CH_3Ph \cdot OBz$, $Me_2C_2O_4$, $Et_2C_2O_4$, $Pr_2C_2O_4$, and succinic, glutaric, and adipic acids, and of mixtures of $BzOH$ and $C_{10}H_8$ with $CH_3Ph \cdot OBz$ were measured. A viscosimeter bath suitable for use up to 230° is described.

CH. ABS. (e)

Molecular dimensions from viscosity studies. R. M. THEIS and H. B. BULL (*J. Physical Chem.*, 1936, 40, 125-131).—The viscosity of stearic acid and lecithin in CCl_4 has been determined and a linear relation observed between $c\eta_0/(\eta-\eta_0)$ and *c*, where η_0 and η are the viscosities of the solvent and solution, respectively. The possibility of applying Eisen-schitz' equation (A., 1932, 121) to determine the ratio of the length of the solute mols. to their diameter is discussed.

M. S. B.

Partial molal volumes of ammonia and hydrogen in liquid ammonia-hydrogen mixtures under pressure at 100° . R. WIEBE and T. H. TREMEARNE (*J. Amer. Chem. Soc.*, 1935, 57, 2601-2603).—Data are recorded and their thermodynamic significance is discussed.

E. S. H.

Density of solutions of alkali metal halides in liquid ammonia. W. C. JOHNSON and R. I. MARTENS (*J. Amer. Chem. Soc.*, 1936, 58, 15-18).—Data are recorded for solutions of the chlorides, bromides, and iodides of Li, Na, and K in liquid NH_3 between -32° and -60° over as wide a concn. range as solubility permits.

E. S. H.

[Refractive index of] mixtures of piperine and iodides. S. GRUM-GRSHIMAILO (*Trans. Inst. Econ. Min. U.S.S.R.*, 1934, No. 61, 21-23, 27-28).—The vals. of *n* recorded for piperine, SbI_3 , and AsI_3 differ from those given by Larsen (*U.S. Geol. Surv. Bull.* 679, 1921).

CH. ABS. (e)

Raman effect in mixtures of oleum and nitric acid. J. CHÉDIN (*Compt. rend.*, 1936, 202, 220-222; cf. A., 1935, 807).—The mixtures afford evidence of association between N_2O_5 and SO_3 ; the characteristic spectral effects are very different from those accompanying the association of SO_2 and H_2SO_4 in $H_2S_2O_7$.

T. G. P.

Magnetic susceptibilities of nitric acid solutions. S. P. RANGANADHAN and M. QURESHI (*Current Sci.*, 1935, 4, 404).—The susceptibility-concn.

curve over the range 4—65% HNO_3 shows marked departure from linearity. The g -ionic susceptibility of the NO_2 ion is -20.83×10^{-6} . Min. in the curve correspond with $\text{HNO}_3 + 50\text{H}_2\text{O}$, $+6\text{H}_2\text{O}$, $+4\text{H}_2\text{O}$, and $2\text{HNO}_3 + 5\text{H}_2\text{O}$. N. M. B.

Constitution of liquid zinc amalgams. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1935, 57, 2657—2662).—Analysis of published e.m.f. data shows that the deviations can be explained on a polymerisation hypothesis which assumes the existence of Zn_2 and Zn_3 in equilibrium with monat. Zn. E. S. H.

Binary mixtures. IV. L. PIATTI (Angew. Chem., 1936, 49, 77—78; cf. A., 1934, 1301).—The b.p. of binary mixtures (0—100%) of o -, m -, and p -cresol with COMe_2 and C_6H_6 , respectively, have been determined. The vals. are $<$ those calc. from the mixture rule. E. S. H.

Azeotropic and constant evaporating mixtures. S. I. SKLJARENKO and M. K. BARANAJEV (Z. physikal. Chem., 1935, 175, 203—213; cf. this vol., 281).—It is deduced that $v_1/v_2 = (p_1/p_2)\sqrt{(D_1/D_2)}$, where v_1 and v_2 are the rates of evaporation of the components of a binary liquid mixture having the diffusion coeffs. D_1 and D_2 and partial v.p. p_1 and p_2 . A mixture in which x_1 and x_2 are the mol. fractions of the components will evaporate without change in composition if $x_1/x_2 = (p_1/p_2)\sqrt{(D_1/D_2)}$, an equation which has been confirmed by experiment. Mixtures for which the vapour given off at a particular temp. has the same composition as the liquid do not, in general, evaporate without change of composition at that temp. R. C.

Orthobaric azeotropes. Esters—hydrocarbons. M. LECAT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 253—265; cf. A., 1930, 680).—315 binary systems involving 44 hydrocarbons and 72 esters have been studied. The b.p., composition, and heats of formation of the azeotropes are given. R. S.

B.p. and composition of the vapour phase of the ternary system ethyl acetate—ethyl alcohol—water. V. A. KIREEV, I. J. KLINOV, and A. N. GRIGOROVITSCH (J. Chem. Ind. Russ., 1935, 12, 936—940).—B.p. data and the composition of the vapour phases are recorded. R. T.

Viscosity measurements of the ternary system diopside—albite—anorthite at high temperatures. S. KÔZU and K. KANI (Proc. Imp. Acad. Tokyo, 1935, 11, 383—385).—Data are recorded for the temp. range 1150—1575°. In a homogeneous melt, η varies linearly with the temp. but the slope increases suddenly when the primary phase begins to crystallise. E. S. H.

X-Ray and electrical investigation of the copper—gold system. C. H. JOHANSSON and J. O. LINDE (Ann. Physik, 1936, [v], 25, 1—48; cf. A., 1926, 112; 1927, 400).—A new regular structure (CuAu II) in the region 50 at.-% has been identified, and its lattice dimensions are measured. CuAu II has rhombic symmetry, and is a modification of the tetragonal form (CuAu I). The unit cell is the 4-atom face-centred cell repeated 10 or 11 times. CuAu II is stable at low temp. for the regions 36—47 and 53—

65 at.-% Au; for 47—53% it can be obtained only by quenching from 420°. The relations between the lattice structures, and the influence of heat-treatment, are discussed. In the region 65—80 at.-% Au a cubic structure is found. The sp. resistance for the entire range has been measured. L. J. J.

Ferromagnetic increment of resistance of copper—nickel alloys. B. SVENSSON (Ann. Physik, 1936, [v], 25, 263—271).—Data are recorded for the sp. electrical resistance of nine Cu—Ni alloys with 11—90 at.-% Ni between 0° and 500°. The ferromagnetic component of the resistance has a max. val. at approx. 80 at.-% Ni. L. J. J.

Solid solubility of magnesium in aluminium. S. KISHINO (J. Chem. Soc. Japan, 1935, 56, 322—324).—The determination of the solubility of Mg in Al by microscopic examination, or by electrical resistance measurements, is difficult for $< 5\%$ of Mg. CH. ABS. (e)

M.p. of eutectics. Lipowitz alloy and Wood's metal. S. J. FRENCH (Ind. Eng. Chem., 1936, 28, 111—113).—The cooling and melting curves of the Lipowitz alloy (Bi 50, Pb 27, Sn 13, Cd 10%) and Wood's metal (Bi 50, Pb 25, Sn 12.5, Cd 12.5%) coincide approx. over the greater part of the const.-temp. region, giving the same m.p. and f.p., viz., 71.7° and 69.7°. The former approaches the quaternary eutectic more closely than does Wood's metal. Discrepancies in published vals. may be due to undercooling or to Hg as an impurity. It is suggested that names for the alloys should be discarded, and that composition and m.p.—f.p. range should be substituted. R. S. B.

Ternary diagram of aluminium—copper—silicon system. K. MATSUYAMA (Kinz.-no-Kenk., 1934, 11, 461—490).—The Al—Cu, Cu—Si, and Al—Si diagrams have been reinvestigated. In the system Al—Cu—Si there are 18 monovariant curves and 8 nonvariant points. The α , β , γ , and δ solid solutions of the systems Cu—Al and Cu—Si are contiguous. In the solid state there are 9 monovariant curves and 2 nonvariant points. CH. ABS. (e)

System iron—cementite—manganese carbide—manganese. R. VOGEL and W. DÖRING (Arch. Eisenhüttenw., 1935—1936, 9, 247—252).—Contrary to previous statements, Mn and Mn_3C do not form a continuous series of solid solutions, but a complicated series of reactions occurs during cooling. The liquidus curve passes through a min. at 3.5% C, 1160°, and Mn_3C undergoes a transformation at 1050°, the temp. of which is gradually decreased by addition of Mn to 920° at 3.5% C (eutectoidal point). At 740° in alloys with $> 1.2\%$ C the γ -Mn solid solution undergoes a eutectoidal transformation into α -Mn + α - Mn_3C . The γ - β -transformation point of Mn is lowered by addition of C from 1140° to 840°, whereas the β - α point is raised from 740° to 840° (0.9% C). The complete diagram and micrographs showing characteristic structures of alloys within the various fields are included. In the ternary system Fe—Mn—C the equilibria resemble those in the Fe—C system up to 60% Mn; in alloys with a higher Mn content complicated reactions occur due to the allotropic changes

in Mn and Mn_3C ; thus the section through 70% Mn contains 17 phase fields. In the Mn corner of the ternary diagram there are 4 planes of four-phase equilibrium, one of which corresponds with a ternary eutectoidal change: $\gamma\text{-Mn} = \alpha\text{-Mn} + \gamma\text{-Fe} + \alpha\text{-Mn}_3\text{C}$; the eutectoid contains Fe 25, Mn 77.95, C 2.05% (640°).

A. R. P.

Properties of the oxides of nitrogen. II.

Binary system $N_2O_3\text{-H}_2O$. III. Pseudo-binary system $N_2O_4\text{-H}_2O$. T. M. LOWRY and J. T. LEMON.

IV. Formation of two liquid layers in mixtures of nitrogen peroxide and water. T. M. LOWRY, E. LLOYD, and W. V. LLOYD (J.C.S., 1936, 1—6, 6—10, 10—17).—II. Two liquid phases are formed over a wide range of mixtures. The limiting mixtures correspond with 42—97 wt.-% N_2O_3 at 0° and 48—95% at 20°. A max. temp. of separation was observed at 55° and 65% N_2O_3 . Escape of NO into the gaseous phase lowers all the temp. and the crit. solution temp. is possibly 20° > that recorded. A quaternary point, at which the gaseous and two liquid phases are in equilibrium with ice, occurs at -33.3° and 36% N_2O_3 , and another, with N_2O_3 as the solid phase, may occur below -103° at > 98% N_2O_3 .

III. Two liquid phases are formed over a wide range. A max. temp. of separation was observed at 67° and 89% N_2O_4 . Escape of NO into the gaseous phase probably lowers the temp. Homogeneous aq. solutions deposit ice down to -50° and up to 33% N_2O_4 and a compound of unknown composition over a narrow range down to -56° and up to 44% N_2O_4 . Non-homogeneous mixtures containing > 44% N_2O_4 deposit $HNO_3, 3H_2O$ from the upper aq.-acid layer, at temp. up to a max. of -22.5°. The lower layer of liquefied gas deposits N_2O_4 , either in the ordinary stable form or in a metastable form which melts 11° lower.

IV. The composition of the two liquid layers has been determined by analysis. The limits within which two liquid layers are formed in the system $H_2O\text{-}N_2O_3\text{-}N_2O_5$ at 0° and 20° are shown on triangular diagrams.

E. E. A.

Solubility of gas mixtures in liquids under pressure.

I. Solubility in water of carbon dioxide from admixture with hydrogen at 20° and 30° and under total pressures up to 30 kg. per sq. cm. I. R. KRITSCHEVSKI, N. M. SHAVORONKOV, and V. A. AEPPELBAUM (Z. physikal. Chem., 1935, 175, 232—238).—A thermodynamic method is described for calculating the solubility of components of gas mixtures in liquids in the case where the thermodynamic potential of the dissolved gas is not affected by the presence of other dissolved gases. The experimental results show that if the pressure is not too high the solubility of CO_2 in H_2O at a given fugacity is the same whether the gas is pure or mixed with H_2 .

R. C.

Ratio of rates of evaporation of different liquids in moving air. S. I. SKLJARENKO and M. K. BARANAJEV (Z. physikal. Chem., 1935, 175, 195—202).—It is deduced theoretically and confirmed experimentally that for two liquids of v.p. p_1 and p_2 evaporating under the same conditions in a current

of air $v_1/v_2 = (p_1/p_2)\sqrt{\{[D_1/(B-\frac{1}{2}p_1)]/[D_2(B-\frac{1}{2}p_2)]\}}$, where v_1 and v_2 are the rates of evaporation, and D_1 and D_2 the diffusion coeffs. of the vapours, and B is the barometric pressure.

R. C.

Dependence of rate of evaporation on nature of gas flowing over the surface of the evaporating liquid. S. I. SKLJARENKO and M. K. BARANAJEV (Z. physikal. Chem., 1935, 175, 214—218; cf. preceding abstract and this vol., 280).—If the vapour of the liquid is heavier than the gas passing over the surface, $v_1/v_0 = \sqrt{(D_1/D_2)}$, where v_1 and v_0 are the rates of evaporation into, and D_1 and D_0 the diffusion coeffs. of the vapour into, the gas and air, respectively. If the vapour is the lighter, as in the evaporation of H_2O into air, allowance must be made for convection currents.

R. C.

Principles of gas exsorption. III. A. GUYER, B. TOBLER, and H. FARMER (Chem. Fabr., 1936, 9, 5—7; cf. A., 1934, 592, 1065).—The apparent "evasion coeff." and rate of loss of gas from falling drops of H_2O is independent of the height of fall, and therefore of the velocity of fall. The relative loss of gas increases with increasing height of fall. The relative loss of gas from a H_2O stream falling against an air resistance increases with the height of fall and with decreasing cross-section of the stream. Reduced pressure has only a slight influence on the loss of gas. This is related to the degree of disturbance of the H_2O , which is a function of the air pressure. J. W. S.

Diffusion of gases through metals. II. Diffusion of hydrogen through aluminium. C. J. SMITHELLS and C. E. RANSLEY (Proc. Roy. Soc., 1935, A, 152, 706—713; cf. A., 1935, 692).—The rate of diffusion of H_2 through Al above 400° depends on the state of the surface. The highest rate is given with a surface freshly scraped in H_2 , but it rapidly falls, and after several hr. reaches a steady val. which is only 0.1 of the initial rate. This low rate is obtained with an anodically oxidised surface. The effects of temp. and pressure are represented by Richardson's equation.

L. L. B.

Diffusion of water vapour through copper. J. H. DE BOER and J. D. FAST (Rec. trav. chim., 1935, 54, 970—974).—At about 800° H_2O vapour diffuses at the rate of about 1.9×10^{-12} g.-mol. per sq. cm. per sec. through Cu 1 cm. thick, when the pressure difference is 1 atm. The rate of diffusion of H_2 under similar conditions is 230×10^{-12} g.-mol. per sq. cm. per sec. The diffusion of N_2 through Cu, if existent, is very slow. H_2O vapour does not diffuse through chrome-Fe, whilst at 900° the rate of diffusion of N_2 is $> 6.9 \times 10^{-12}$ g.-mol. per sq. cm. per sec.

J. W. S.

Diffusion of helium through fused silica. E. O. BRAATEN and G. F. CLARK (J. Amer. Chem. Soc., 1935, 57, 2714—2717).—Measurements at -78° to 562° show that the rate of diffusion \propto pressure and inversely \propto the thickness of SiO_2 . Two vals. for the activation energy have been obtained, depending on the temp. region.

E. S. H.

Diffusion of silver in glass. O. KUBASCHEWSKI (Z. Elektrochem., 1936, 42, 5—7).—The rate of diffusion and variation with temp. have been

determined. The amount of Ag taken up depends primarily on the availability of O_2 , showing that it is not a case of simple diffusion of Ag^+ . E. S. H.

Equilibrium between strontium sulphate and water at various temperatures. G. GALLO (Annali Chim. Appl., 1935, 25, 628—631).—The solubility of $SrSO_4$ in H_2O increases from 0.0121 (g. per 100 c.c. of solution) at 5° to 0.0141 at 40° , then decreases to 0.0113 at 95° ; both pptd. $SrSO_4$ and calcined celestine give similar vals. The influence of NH_4Cl , NH_4NO_3 , and $(NH_4)_2SO_4$ on the solubility is studied. E. W. W.

Re-determination of the solubility of chloropentammine cobaltic chloride. F. J. GARRICK (Nature, 1935, 136, 1027—1028).—The compound purified by an improved method (A., 1935, 1335) gave 0.00925 and 0.0211 g.-mol. per litre at 0.20° and 25.00° , respectively. L. S. T.

Solubilities and free energies of some metallic sulphides. S. E. RAVITZ (J. Physical Chem., 1936, 40, 61—70).—The solubility data for the sulphides of Zn, Pb, Cu, Tl, Ag, and Cd have been examined and the solubilities recalcd. with the help of recent activity data. Free energies of formation have also been calc. M. S. B.

Solubility of oxalic acid and oxalates of the alkaline earths in mineral acids. I. H. TRAPP (J. pr. Chem., 1936, [ii], 144, 193—210).—The solubility of $H_2C_2O_4$ in 0—16.46% HCl , 0—46.96% H_2SO_4 , and 0—29.35% H_3PO_4 at $20 \pm 2^\circ$ is recorded. With K_2SO_4 and $CaSO_4$ it forms $KHC_2O_4 \cdot H_2C_2O_4$, and $CaC_2O_4 \cdot 2H_2O$, respectively, until the concn. of H_2SO_4 is 12 and 13%, respectively, at $20 \pm 2^\circ$. Lower concns. of H_2SO_4 suffice to dissolve the salts at higher temp. $NaCl$ and $MgSO_4$ form $Na_2C_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ and $MgC_2O_4 \cdot 2H_2O$, respectively. $BaCl_2$ gives $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ until the concn. of HCl is 4.5% and above this concn. $BaC_2O_4 \cdot H_2C_2O_4 \cdot 3H_2O$. R. S. C.

Equilibrium in the system lithium phthalate-phthalic acid-water. S. B. SMITH, W. A. STURM, and E. C. ELY (J. Amer. Chem. Soc., 1935, 57, 2406—2408).—Solubility data at 0° , 25° , and 50° have been obtained. The compound $LiHC_8H_4O_4 \cdot 2H_2O$ is formed at these temp. and can be crystallised at temp. $\leq 60^\circ$. E. S. H.

Solubility of metals in crystals of halides. G. TAMMANN (Z. anorg. Chem., 1935, 226, 92—96).—Solutions of metals in their solid halides (e.g., Na in $NaCl$, Ca in CaF_2) are discussed from the point of view of their similarity to solutions of one metal in crystals of another. F. L. U.

Precipitation processes. I. Connexion between ratio of concentrations of reactants and precipitation of silver thiocyanate and cyanide. B. TEŽAK (Z. physikal. Chem., 1935, 175, 219—231; cf. A., 1934, 593).—The pptn. curve (graph of turbidity 4 min. after mixing the reacting solutions against reactant concn.) exhibits two max. if the stabilising effects of the two reacting ions are large but approx. equal. The max. at the lower concn. is due to the isoelectric point, and the other to the reduction in solubility and stability and to the rapid formation

of pptn. centres. If the stabilising effect of the ion of variable concn. is very great, or there is considerable tendency to complex formation, the first max. only is observed, whilst if both ions have but a slight stabilising effect the second max. only is present. R. C.

Distribution of thorium-C'' in thallium salt solutions. J. ZIRKLER (Z. Physik, 1935, 98, 75—76).—The separation of the Tl isotope $Th-C''$ from a solution containing Tl' and Tl''' does not depend on the total mass of the ions present, but on the amounts of Tl^{205} and Tl^{203} . A. B. D. C.

Adsorption of hydrogen and deuterium on copper at low pressures. R. A. BEEBE, G. R. LOW, jun., E. L. WILDNER, and S. GOLDWASSER (J. Amer. Chem. Soc., 1935, 57, 2527—2532).—At -78° and $0-2$ mm. the rate of adsorption is less for D_2 than for H_2 , but equal amounts are adsorbed at equilibrium. At 0° H_2 is more strongly adsorbed, but at 125° it is adsorbed $< D_2$. The differential heats of adsorption are identical for H_2 and D_2 . E. S. H.

Adsorption of hydrogen on tungsten. J. K. ROBERTS (Proc. Roy. Soc., 1935, A, 152, 445—463).—The method used depends on the fact that the accommodation coeff. of Ne is different for a bare surface and for a surface with an adsorbed film on it. Saturation occurs at a partial pressure of H_2 of the order of $< 10^{-1}$ mm. and the process is one of chemisorption, which takes place rapidly at these low pressures at 79° abs. The heat of adsorption and amount of gas adsorbed have been measured on a single fine wire. The film is stable at negligibly low pressures at room temp. There is strong evidence for the view that the H_2 is adsorbed as atoms, with one atom for each W atom in the surface. The binding is of the same type as that of O_2 on W. The bearing of the data on the general problem of H_2 adsorption and on that of activated adsorption is considered. L. L. B.

Composite films of oxygen and hydrogen on tungsten. J. K. ROBERTS (Proc. Roy. Soc., 1935, A, 152, 477—480).—When an O_2 mol. is adsorbed on a W surface already covered with H_2 , a mol. of H_2 is ejected into the gas phase. The behaviour of H_2 in the presence of a surface partly covered with O_2 is also considered. The data support the theory that activated adsorption of H_2 is connected with the interaction between H_2 and surface O_2 , either adsorbed or forming an integral part of the solid lattice. L. L. B.

Adsorbed films of oxygen on tungsten. J. K. ROBERTS (Proc. Roy. Soc., 1935, A, 152, 464—477; cf. preceding abstract).—Experiments show that a second mol. film of O_2 , which is quite stable at room temp., is formed on top of the well-known stable film (A., 1931, 782). The heats of adsorption and no. of mols. adsorbed in each film have been measured. Consideration of the process of building up an immobile film by the adsorption of the two atoms of a diat. mol. on neighbouring solid atoms shows that such a film necessarily has gaps in it. The no. of these gaps has been measured, and the amount of O_2 in the second film found to correspond with adsorption on the gaps in the first. The possible

rôle of these gaps in the diffusion of O_2 into W is discussed. The accommodation coeffs. for Ne striking the at. and the mol. film are deduced.

L. L. B.

Sorption of ammonia and other gases by arsenic trisulphide. N. MORITA (J. Chem. Soc. Japan, 1935, 56, 325—332).—The sorption velocity of NH_3 by As_2S_3 varies with the mode of prep. of the As_2S_3 . The product at room temp. corresponds with $As_2S_3 \cdot NH_3$. The behaviour of NH_2Et is similar.

CH. ABS. (e)

Adsorption of gases by virgin salt surfaces. F. DURAU and A. HORN (Z. Physik, 1935, 98, 198—226).—Observations have been made with $NaCl$, $CdCl_2$, and $NaNO_3$ which were melted, freed from impurities, and powdered in high vac. A. B. D. C.

Adsorption on chromite catalysts. J. C. W. FRAZER and C. G. ALBERT (J. Physical Chem., 1936, 40, 101—112).—The "activated adsorption" of O_2 and CO on Cu chromite (I) at 100—200°, as distinct from the van der Waals adsorption, has been determined in order to see what relation it bears to the catalytic activity of (I) in the oxidation of CO . Activation energies of the adsorption have been calc. The activated adsorption of O_2 increases with rise of temp., but that of CO attains a max. and then falls. This behaviour may be due to entirely separate processes taking place at the surface of (I). The results suggest that it is the activated adsorption of O_2 which determines the catalytic activity of the surface. Possible mechanisms are discussed. M. S. B.

Adsorption at crystal-solution interfaces. VIII. **Influence of dyes and other organic compounds on the crystal habits of barium and lead nitrates.** (Miss) P. P. DAVIS and W. G. FRANCE (J. Physical Chem., 1936, 40, 81—87).—The habit assumed by crystals of $Pb(NO_3)_2$ and $Ba(NO_3)_2$, separating from pure solutions and solutions containing dyes or other org. substances, indicates that they approximate most closely to the distorted CaF_2 structure. The results are in general agreement with the theory previously put forward to account for adsorption and habit modification (cf. A., 1933, 20). The effect of a mixture of two dyes is approx. additive. M. S. B.

Adsorption of dyes on previously ignited gels. J. SPILCHAL (Coll. Czech. Chem. Comm., 1935, 7, 521—536).—Basic dyes, e.g., methylene-blue, Me-violet, are not adsorbed from aq. solution by ignited $Al(OH)_3$ gel (I). The adsorption of acid dyes, e.g., Congo-red (II), eosin, and Bordeaux-red, is high, but decreases to very low vals. as the drying temp. of (I) is raised to 1200°. Ignited $Fe(OH)_3$ gels behave similarly. An unstable space lattice of the γ - Al_2O_3 is indicated. The adsorption on bauxites (III), which have a smaller internal surface than (I), and of (II) on (I), decreases as the grain size increases. The adsorptive power of (III), heated at 1000°, increases towards basic dyes, probably owing to an increase of the internal surface of the grains. J. G. A. G.

Maximal adsorption. I. Maximal adsorption of sparingly soluble acids and bases by

different active charcoals. H. BRINTZINGER, A. SCHALL, and H. G. BEIER (Kolloid-Z., 1936, 74, 29—32).—Max. adsorption is defined as the amount of substance adsorbed at a given temp. by 1 g. of the adsorbent from a saturated solution. Determinations with salicylic acid and quinine are reported. E. S. H.

Adsorption of lead nitrate by metastannic acid. A. G. BOSIN and M. M. SHULKINA (J. Appl. Chem. Russ., 1935, 8, 1287—1290).—When $Sn-Pb$ alloys are dissolved in HNO_3 part of the $Pb(NO_3)_2$ formed is adsorbed on the SnO_2 ; the amount (C_2) of Pb adsorbed by a const. amount of SnO_2 is given by $C_2 = 4\sqrt{C_1}$, where C_1 is the amount of Pb found in the solution. R. T.

Adsorption at the interface between two fluids.

I. Adsorption of methylene-blue, methyl-orange, Congo-red, and orange II at benzene-water and chlorobenzene-water interfaces. C. W. GIBBY and C. C. ADDISON (J.C.S., 1936, 119—127).—The adsorption, at various concns. in H_2O , at $H_2O-C_6H_6$ and $H_2O-PhCl$ interfaces and the interfacial tensions have been measured. The results show marked quant. deviations from the predictions of Gibbs' equation in all cases, although this equation gives vals. of approx. the right order and in closer agreement with the observed results than with Lewis' data. Two types of concn.-adsorption curve are found. The type differs according to the adsorbate, but is independent of whether the interface is $H_2O-C_6H_6$ or $H_2O-PhCl$. Curves for Congo-red and Me-orange have the qual. features of a Gibbs curve; those for methylene-blue and orange II have not. The area of the interface occupied by the adsorbed mol., reckoned as monomeric, in the region of max. adsorption is calc. For methylene-blue and orange II, the adsorbed layer, on either interface, is unimol., but for the other two dyes, the surface concn. on C_6H_6 is $<$, and on $PhCl$ about twice as great as, that which is represented by a unimol. layer. E. E. A.

Kinetics of adsorption of vapours by highly active adsorbents. M. V. POLJAKOV, I. E. NEIMARK, and I. M. MALKIN (J. Phys. Chem. U.S.S.R., 1934, 5, 1079—1081).—Data for the adsorption of C_6H_6 and $PhMe$ by a mixture of C and SiO_2 gel at 0—36° are recorded. The change in the character of the isotherm with fall in temp. is attributed to the onset of capillary condensation. CH. ABS. (e)

Application of Polanyi's potential theory to the van der Waals adsorption of gases on iron synthetic ammonia catalysts. P. H. EMMETT and S. BRUNAUER (J. Amer. Chem. Soc., 1935, 57, 2732—2733).—Isotherms for the adsorption of A and N_2 by $Fe_2O_3-Al_2O_3$ catalysts are in accordance with the theory. E. S. H.

Specific heat and binding conditions of adsorbed argon on charcoal. H. M. CASSELL (J. Amer. Chem. Soc., 1935, 57, 2724).—Published sp. heat evidence suggests that the adsorbed atoms are capable of one-dimensional vibration only. E. S. H.

Temperature dependence of the surface tension of solutions. R. V. MERTZLIN and N. A.

TRIFONOV (J. Phys. Chem. U.S.S.R., 1934, 5, 1146—1163; cf. A., 1935, 928).—Data are recorded for the systems PhMe-Pr^oCO₂H (12—100°), C₅H₅N-NPhEt₂ (18—100°), allylthiocarbimide-NPhEt₂ (16—130°), quinoline-Bu^oOH (0—140°), thymol-EtOAc (15—70°)

CH. ABS. (e)

Effect of light on surface tension of soap solutions. II. L. D. MAHAJAN (Z. Physik, 1935, 98, 388—395; cf. A., 1931, 1228).—Max. lowering by irradiation is observed with 6.25×10^{-4} g. of Na oleate per c.c., and with ultra-violet light.

A. B. D. C.

Electrokinetics. XVI. Streaming potentials in small capillaries. H. B. BULL and L. S. MOYER (J. Physical Chem., 1936, 40, 9—20).—A mathematical treatment is given for the streaming potential in capillaries < those to which Smoluehowski's theory in its simple form applies. The change in the viscosity of H₂O with capillary size is discussed and an equation is derived to show the relationship between the back pressure produced by electro-osmotic effects and the mechanical pressure. A method for determining the average pore radius is described. For quartz and glass diaphragms, the theoretical crit. pore radius is not the same as that found experimentally. The potential-concn. and flow-concn. curves are anomalous for quartz and glass diaphragms with pores < the crit. size, but normal for cellulose.

M. S. B.

Wetting and spreading properties of aqueous solutions. Oleic acid-sodium carbonate mixtures. H. L. CUPPLES (Ind. Eng. Chem., 1936, 28, 60—62; cf. B., 1935, 1129).—The surface tensions and interfacial tensions against mineral oil have been determined for oleic acid-aq. Na₂CO₃ mixtures containing approx. 0.1—1% of oleic acid, and approx. 1—4 mols. of Na₂CO₃ per mol. of oleic acid. The spreading coeff. $s = \sigma_{oil} - \sigma_{soap\ solution} - \sigma_{interface}$ varies much less with the ratio of alkali to acid than with oleic acid-NaOH mixtures, especially at high concn. of acid. Unlike the NaOH mixtures, the Na₂CO₃ mixtures at high acid concn. have excellent wetting properties over the whole range of mol. ratios, and a high val. of s is easy to maintain.

R. S. B.

Wetting hysteresis caused by dispersity. I. R. KLJATSCUKO (Kolloid-Z., 1936, 74, 90—97).—Wetting isotherms for several minerals have been determined and the importance of the adsorption of surface-active substances is confirmed. The relation to flotation is discussed.

E. S. H.

Spreading of ovalbumin. (Miss) M. G. TER HORST (Rec. trav. chim., 1936, 55, 33—42).—The area of spreading increases with rise of temp., but the velocity of spreading shows an optimum at 25°. The area of the coherent film is little influenced by temp., but that of the compressed film rapidly increases with rise in temp. until at 50° both films probably become identical and the p.d. between the two films vanishes.

E. E. A.

Ageing of surface of solutions. K. S. G. DOSS (Current Sci., 1935, 4, 405).—A freshly formed surface of 0.002M solution of benzopurpurin, investigated by the surface-pressure method, showed a regular fall of surface tension with time, accompanied by the

formation of a surface film. If overcrowding of the surface mols. is produced by shifting the barrier, the surface tension increases with time. The observed rate of accumulation of solute mols. is far < the calc. collision frequency and is > doubled for 20° temp. rise, in agreement with the view that the adsorption is of the activated type.

N. M. B.

Collapse of unimolecular films of palmitic acid on acid solutions. R. J. MYERS (J. Amer. Chem. Soc., 1935, 57, 2734—2735).—The curve obtained when the collapse pressure vals. are plotted against p_H is S-shaped. The mid-point of the curve differs from that of the neutralisation curves for fatty acids. This appears to indicate increased activity of palmitic acid when oriented at a H₂O surface.

E. S. H.

Periodic phenomena in diffusion and adsorption. I. Use of membranes. H. WAELSCH, S. KITTEL, and A. BUSZTIN (Kolloid-Z., 1936, 74, 22—29).—Periodic variations in concn. have been observed in the diffusion of salts in blood corpuscles and plasma. Similar periodicity has been obtained in a colloid model by allowing KCl to diffuse from aq. solution into a gelatin sol, from which it is separated by a membrane.

E. S. H.

Effects of some factors on rhythmic crystallisation. M. J. MACMASTERS, J. E. ABBOTT, and C. A. PETERS (J. Amer. Chem. Soc., 1935, 57, 2504—2508).—The periodic crystallisation of aq. K₂Cr₂O₇, Na₂Cr₂O₇, and (NH₄)₂Cr₂O₇ has been investigated. Differences in temp. and concn. have little effect, but the phenomenon may be inhibited by foreign anions, the effect increasing in the order Cl' < SO₄' < NO₃'. The spacing of the periods agrees with that observed in the Liesegang phenomenon and in the crystallisation of periodic structures from melts.

E. S. H.

Structural changes taking place on ageing of freshly-prepared crystalline precipitates. V. Thermal ageing of freshly-prepared lead sulphate. VI. Perfection and ageing of lead sulphate precipitated under various conditions. VII. Kinetics of the distribution of thorium-B through fresh lead sulphate. VIII. Influence of agitation on the ageing and speed of distribution of thorium-B. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1935, 57, 2573—2577, 2577—2579; 1936, 58, 116—120, 121—122; cf. A., 1935, 715).—V. Sintering of the particles occurs markedly at 400° and very slowly at 300°. At lower temp. internal thermal ageing occurs, due to the high speed of evaporation of lattice ions on the active surface. At still lower temp. thermal ageing is promoted by adsorbed and occluded H₂O.

VI. The effects of concn. of Pb(NO₃)₂ and K₂SO₄ and of temp. on the nature of PbSO₄ ppts. and their rate of ageing have been studied.

VII. During the initial stages of the ageing of fresh PbSO₄ the recrystallisation is mainly unidirectional and an enrichment of Th-B in the recryst. sulphate occurs; with prolonged shaking, successive recrystallisations occur, ultimately leading to homogeneous distribution.

VIII. The speed of distribution of Th-B when

shaken with freshly-pptd. PbSO_4 is independent of the speed of agitation so long as the ppt. is prevented from settling. The speed of ageing of PbSO_4 in aq. $\text{Pb}(\text{NO}_3)_2$ is independent of the amount of ppt. and the speed of agitation. The recrystallisation is not an Ostwald-ripening process. E. S. H.

Influence of nature of the membrane and temperature on the osmotic system of water and oxalic acid. F. A. H. SCHREINEMAKERS, (Miss) J. C. LANZING, and C. L. DE VRIES (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1067—1074; cf. A., 1931, 1007; 1932, 334, 691).—The system H_2O -membrane-aq. $\text{H}_2\text{C}_2\text{O}_4$ has been investigated when one of the liquids is maintained invariant. With Cellophane at 20° , H_2O and $\text{H}_2\text{C}_2\text{O}_4$ diffuse in opposite directions, with pig's bladder both H_2O and $\text{H}_2\text{C}_2\text{O}_4$ diffuse to the left at 0° , but at 20° with invariant aq. $\text{H}_2\text{C}_2\text{O}_4$, H_2O and $\text{H}_2\text{C}_2\text{O}_4$ diffuse to the left until the H_2O contains approx. 5% of $\text{H}_2\text{C}_2\text{O}_4$ and then H_2O diffuses to the right. The relations at 0° and 20° are discussed. J. G. A. G.

Osmotic complex with two stationary liquids. F. A. H. SCHREINEMAKERS and J. P. WERRE (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 982—988).—Changes in composition with time have been investigated for the system $A|B|C|D$, where A is H_2O , D is a NaCl solution of definite concn., and B and C represent solutions of NaCl and Na_2CO_3 . The concn. of NaCl in B passes through a min. J. W. S.

Osmotic complexes in which one or more liquids proceed along a closed curve during osmosis. I. F. A. H. SCHREINEMAKERS and C. L. DE VRIES (Rec. trav. chim., 1935, 54, 945—955).—The changes of composition with time in systems consisting of solutions in series contact through semipermeable membranes are discussed, with special reference to aq. $\text{NaCl} + \text{Na}_2\text{CO}_3$ solutions, H_2O forming one invariant phase. J. W. S.

Electrodialysis. G. S. VOZDVISHENSKI (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 99—101).—If the H_2O in the electrode spaces in electro-dialysis is left unchanged, the c.d. and rate of dialysis increase, even if the voltage is kept const. Gluten containing NaCl (ash content 1.70%) was electro-dialysed by this method, using a parchment membrane. It took 5 hr. at 30 volts, or 1 hr. at 100 volts, to obtain a product with 0.14% of ash. CH. ABS. (e)

Simple lyotropic effects (viscosity). E. M. BRUNS (Rec. trav. chim., 1936, 55, 13—16).—Different lyotropic formulæ are discussed and the idea of crit. ions is explained. The viscosities of 0.25*N* solutions of electrolytes containing (1, 1)-, (1, 2)-, (2, 1)-, and (2, 2)-valent salts can be calc. from a single formula. E. E. A.

Optical behaviour of dissolved ions and its significance for the structure of solutions of electrolytes. I. Influence of temperature and effect of salts on optical absorption of 2 : 4-dinitrophenoxide ion. G. KORTUM (Z. physikal. Chem., 1935, B, 30, 317—355).—The extinction coeff., ϵ , of the 2 : 4-dinitrophenoxide ion (I) at 436

$m\mu$ in aq. solution at 20° and 25° remains const., in presence of foreign salts independent of the salt concn., c , up to concns. beyond those at which the ionic properties influenced by electrostatic interactions, e.g., conductivity, vary appreciably with c . At higher salt concns. ($c > 0.01$) the absorption bands of (I) shift, but the magnitude and direction of the shift are an individual property of the foreign salt present. At these concns. there is no parallelism between the change of ϵ with c and the change of the activity coeff. of (I) with c . The effects cannot be explained by deformation by the cations accumulating in the ionic atmosphere or by ionic association. In general, the salt anion has a sp. effect on ϵ commensurate with that of the cation. The effects of salts on the optical properties of an ion seem to depend on the interaction between the ion and the solvent, rather than on direct deformation in the Coulomb field of force of the added ions. Calculation shows that small changes in the field of force due to ion-dipole interaction will have optical effects as large as deformation in the Coulomb field of the ions. The optical effects of non-electrolytes on (I) are similar to those of electrolytes. The effect of temp. on the long-wave absorption band of (I) suggests an electron affinity spectrum. A review of the entire optical data for aq. solutions of electrolytes indicates that at small and moderate concns. the solute is present as isolated solvated ions, the mutual deformation of which is largely negligible compared with their interaction with the H_2O mols. R. C.

Optical rotation and circular dichroism, and absorption and refraction in solutions. W. KUHN (Z. physikal. Chem., 1935, B, 30, 356—378).—The non-sp. part of the effect of the solvent results in the circular dichroism, D , and the optical rotation, α , each being multiplied by the factor $(n^2+2)/3$ on passage from the gaseous to the dissolved state, whilst the contribution of an absorption band to the normal absorption and sp. refractive power, r_L , is multiplied by the factor $K = [(n^2+2)/3]^2/n$. Consequently, relations between D and α and between r_L and absorption are not changed by going over from the gaseous to the dissolved state, provided that the magnitudes for the appropriate state are consistently used. This is confirmed by existing experimental data. The anisotropy-activity factor observed with a solution must be multiplied by $(n^2+2)/3n$ to reduce it to the gaseous state. In calculating f vals. from the intensity of absorption bands in solutions, allowance must be made for the factor K . R. C.

Dielectric constants of strong electrolytes and the Debye-Falkenhagen theory. M. JEZEWSKI (Physikal. Z., 1936, 37, 52—55).—New measurements of the dielectric consts. of strong electrolytes by a resonance method show that the Debye-Falkenhagen theory is in agreement with experiment for dil. solutions. At higher concns. and higher temp. the change of dielectric const. is $<$ that given by the theory. A. J. M.

Form and dielectric behaviour of thread-like molecules in solutions. W. KUHN (Z. physikal. Chem., 1935, 175, 1—16).—The dipole moment of a zwitterion $\propto \sqrt{Z}$, where Z is the chain length, and

$r^2 \propto Z$, where r^2 is the mean square distance between the positive and negative charges on the ion. r_b^2 , the mean square of the distance between the ends of the mol. taking account of the attraction between the two charges, increases slightly more rapidly than $\propto Z$, which agrees with the observation that $dD/dc \propto Z$ (D =dielectric const., c =concn.). Only when $Z > 25$ does the difference between r_b^2 and r^2 fall below about 40%. The calc. orientation polarisation on applying a field to a solution containing zwitterions is the same whether the zwitterions are supposed to behave as rigid dipoles capable of rotating, but not of changing in length in the field, or whether the variation in the distance between the charges with the field strength is taken into account. The internal field in aq. solutions of NH_2 -acids is much weaker than $(4\pi/3)P$ (cf. A., 1934, 959, 1291). R. C.

Diffusion of compounds of high mol. wt. IV. Rod-like molecules. M. TANIGUCHI and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 728—730B; cf. A., 1935, 1072).—The diffusion consts. (D) of squalene and fractions crystallised from solid paraffin have been determined in C_6H_{14} and Et_2O . $D = \eta kT (\log l/d + 0.69) / 2\pi l$, where l and d are the mol. length and thickness, η =viscosity of the medium, and k =gas const. For squalene $l=31.2$, $d=5.3$ Å., and for the paraffin fractions $l=29.2$ — 39.7 , $d=4.0$ Å. These vals. are in good agreement with those deduced from X-ray measurements.

R. S. B.

Spierer lens and colloidal structure. W. SEIFRIZ (Ind. Eng. Chem., 1936, 28, 136—140).—A reply to criticism of the use of the lens (A., 1926, 931) in the study of colloidal structure. R. S. B.

Preparation of colloid solutions by the silent electric discharge. IV. S. MIYAMOTO (Kolloid-Z., 1936, 74, 32—35; cf. A., 1935, 932).—The prep. of hydrosols and alcossols of Cu_2O and Cu_2S , and also of hydrosols of Hg and HgS from corresponding salt solutions is described. The relative stability of the sols is indicated. E. S. H.

Water-soluble colloidal lead. A. F. GERASIMOV and B. M. KOZUREV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 119—125; cf. A., 1930, 1114).—The prep. of a substance containing 16.5% of Pb is described. The properties of a 1% colloidal Pb solution after dialysis are described.

CH. ABS. (e)

Emulsification of mercury. L. J. KREMNEV (J. Phys. Chem. U.S.S.R., 1934, 5, 1051—1061; cf. A., 1934, 729).—Suspensions of oxides and certain slightly sol. salts stabilise the Hg globules by forming protecting layers. Results obtained with oxides or hydroxides of Ca, Mg, Ba, Zn, Hg, Pb, Cu, Fe, and Si, and Hg_2Cl_2 , HgI_2 , HgBr_2 , ZnCO_3 , PbSO_4 , BiONO_3 , and HgS in association with various electrolytes are described. Stabilisation is also produced by Prussian-blue, Congo-red, night-blue, benzopurpurin-4B, benzopurpurin-10B, and chrysofenin. In presence of oxidising or chlorinating agents, HgO or Hg_2Cl_2 can act as an emulsifier for Hg.

CH. ABS. (e)

Application of a simple air-driven spinning-top centrifuge to colloid-chemical problems.

J. W. MCBAIN and R. F. STUEWER (Kolloid-Z., 1936, 74, 10—16).—Apparatus, technique, and applications are described, with some preliminary results on the sedimentation velocity of agar sols and swelling pressure of the gels. E. S. H.

Effect of heat-treatment on hydrous chromic oxide sols. G. H. AYRES (J. Amer. Chem. Soc., 1936, 58, 18—22).—The effect of heating the sols at temp. up to 260° is to decrease η in the lower temp. ranges, but to increase η at the higher temp. At 250 — 260° conc. sols set to rigid gels and dil. sols are finally pptd. Heat-treatment reduces the stability of the sols towards flocculation by K_2SO_4 . E. S. H.

Electrolytic double layer. E. J. W. VERWEY (Wis. nat. Tijds., 1934, 7, 89—100; Chem. Zentr., 1935, i, 3640).—The formation of a double layer with AgI sols is discussed. H. J. E.

Viscosity relationships in emulsions containing milk fat. A. LEVITON and A. LEIGHTON (J. Physical Chem., 1936, 40, 71—80).—The viscosity η of emulsions containing milk fat does not vary, within the limits of experimental error, with variations in the degree of dispersion of the fat phase, provided that fat clusters enclosing a portion of the continuous medium are not formed. Such formation causes a rise in η . An empirical expression for the relation between η and the fat content of these emulsions has been found. For low concns. of fat it reduces to Taylor's equation (A., 1932, 1195). The apparent vol. of the continuous medium associated with the fat clusters per unit vol. of dispersed fat represents the clumping index of cream and ice-cream mixes. It is determined from η vals. of the mix and the continuous medium. M. S. B.

Relation between absorption and scattering of light in white sols. B. TEŽAK (Kolloid-Z., 1936, 74, 16—22).—Determinations of absorption and scattering of light in different spectral regions by sols of colophony and cellulose acetate of different concn. are in accordance with the Lambert-Beer law. The influence of λ , particle radius, and polydispersity is discussed. E. S. H.

Dispersion of the Kerr effect of certain colloidal solutions. Time of relaxation of the electrokinetic potential. J. ERRERA, J. T. G. OVERBEEK, and H. SACK (J. Chim. phys., 1935, 32, 681—704; cf. A., 1929, 135).—The electrical birefringence of colloidal solutions of V_2O_5 , benzopurpurin (I), polystyrene (II), and *p*-azoxyanisole (III) has been measured at frequencies 10^3 — 6×10^7 cycles per sec. The birefringence of V_2O_5 sols increases with increasing field towards a saturation val., and it also increases with increasing concn. and age. The dispersion suggests that there are two components, one positive and decreasing rapidly at frequencies $> 10^6$ and the other negative and decreasing at frequencies $> 10^4$. The dispersion of the dielectric const. (ϵ) of these sols is confirmed and the negative part of the birefringence is attributed to high vals. of ϵ . The birefringence of (I) is negative and diminishes rapidly at frequencies $> 10^6$, whilst that of (III) is positive and accompanied by marked dichroism. No bire-

fringence could be detected with (II). The dispersions at $>10^6$ cycles per sec. can be explained in terms of the time of relaxation of the electro-kinetic potential.

J. W. S.

Maxwell effect in colloids. A. M. TAYLOR (Trans. Faraday Soc., 1936, 32, 307—310).—Methods are suggested for discriminating between theories of streaming double refraction which assume on the one hand optical anisotropy of the particles and on the other hand the production of elastic strain in particles normally isotropic.

F. L. U.

Constitution of hydrous oxide sols from X-ray diffraction studies. H. B. WEISER and W. G. MILLIGAN (J. Physical Chem., 1936, 40, 1—7).—X-Ray diffraction photographs of moist Al_2O_3 , SnO_2 , and In_2O_3 gels prepared from the hydrous oxide sols give the patterns for $\gamma-Al_2O_3 \cdot H_2O$, SnO_2 , and $In_2O_3 \cdot 3H_2O$, respectively. In sols containing chloride this is not present as basic salt, but is adsorbed.

M. S. B.

Constitution of hydrous oxide gels and sols. H. B. WEISER and W. O. MILLIGAN (Trans. Faraday Soc., 1936, 32, 358—374).—A review of evidence leads to the conclusion that gelatinous ppts. of oxides consist of agglomerates of minute crystals of oxide or hydroxide which hold large amounts of H_2O by adsorption and capillary forces. In hydrous oxide sols containing chloride the latter is adsorbed, not bound in the form of basic salts or Werner complexes.

F. L. U.

Colloid-chemical processes at high temperatures. S. I. DJATSCHKOVSKI (Kolloid-Z., 1936, 74, 51—57).—The effect of heating several hydrosols at high temp. in an autoclave has been investigated. Typical hydrophobic sols undergo coagulation; hydrophilic sols undergo complex changes, involving loss of electrolyte and desolvation. $Fe(OH)_3$ is re-solvated at the highest temp. used. V_2O_5 passes into a mol. form, leading to crystallisation of HVO_3 .

E. S. H.

Acclimatisation phenomenon in colloid-chemical processes. V. N. KRESTINSKAJA (Kolloid-Z., 1936, 74, 45—51).—Published work is discussed.

E. S. H.

Reaction of organic anions with basic thorium chloride hydrosols. Reversal of charge with salts of the hydroxy-acids and with nitric acid. A. W. THOMAS and C. B. KREMER (J. Amer. Chem. Soc., 1935, 57, 2538—2541).—Hydroxy-org. anions reverse the charge of the sol, producing anionothorate micelles. Negative sols are also produced by peptising $ThO_2 \cdot xH_2O$ with K salts of the above anions. Conc. HNO_3 also reverses the charge of the positive sols. The order of deoliation of basic $TiCl_4$ sols and subsequent formation of crystalloid solutions with conc. inorg. acids is $H_2SO_4 > HCl > HNO_3$.

E. S. H.

Ageing and reactivation *in vitro*. I. Ageing of gum arabic. D. KOTSOVSKY (Kolloid-Z., 1936, 74, 88—90).—Gum arabic sols age at a rate which is inversely \propto to the vol. of solution. The surface tension-time curves show irregular, periodic variations, the amplitude of which is greater in dil. than in conc.

solutions. The shape of the curve, but not the general rate, is influenced by addition of electrolytes.

E. S. H.

Heat of imbibition of cellulose in water and in certain technical organic solvents at 25°. K. P. MISCHTSCHENKO and M. Z. PRONINA (J. Appl. Chem. Russ., 1935, 8, 1164—1169).—The heat of imbibition of cellulose has been measured in an ice calorimeter for H_2O , HCO_2H , $MeOH$, and triacetin. Vaseline oil gives no heat effect, whilst the rate of evolution of heat in $(\cdot CH_2-OH)_2$ and glycerol is too slow to permit measurement.

R. T.

Interaction of cellulose esters with solvents. A. P. OKATOV and Z. I. EMMANUILOVA (J. Appl. Chem. Russ., 1935, 8, 1248—1264).—When SiO_2 gel is immersed in H_2O or C_6H_6 , heat is evolved in two stages which correspond with wetting of the surfaces and with swelling of the gel. When cellulose nitrate is placed in $EtOH-Et_2O$, the greatest heat effect is obtained for equimol. mixtures, which have also the greatest negative heat of mixing; the evolution of heat in this case involves a third factor, viz., disruption of aggregates to yield sols. Imbibition proceeds most rapidly at low temp. and high pressures, whence it follows that the most homogeneous films would be obtained by cold-pressing the partly solvated product.

R. T.

Dependence of the swelling power of potato starch in warm water on the kind and amount of cations contained therein. E. WIEGEL (Kolloid-Z., 1936, 74, 58—66).—The effect of acid treatment on the viscosity (η) of starch sols has been investigated. After neutralisation with alkalis the sol has a relatively greater initial η and a lower end η . Alkaline-earth cations cause a relatively lower initial η , but scarcely change the end val.; the sols are more turbid and less sensitive to electrolytes than those containing alkali ions. The practical significance of the results is discussed.

E. S. H.

Relation between the chemical and colloidal structure of proteins. A. FODOR and S. KUK (Kolloid-Z., 1936, 74, 66—87).—Results obtained by non-hydrolytic degradation of gelatin and casein by glycerol at 930—150° are further discussed (cf. A., 1933, 730).

E. S. H.

Laws of motion of thixotropic plastic liquids. M. BUNIN (J. Phys. Chem. U.S.S.R., 1934, 5, 996—1003).—A discussion.

CH. ABS. (e)

Lyophilic colloids. XXVI. Coacervation. III. Complex coacervation of the system gum arabic-gelatin. II. H. G. B. DE JONG (Kolloid-Beih., 1936, 43, 213—271; cf. A., 1935, 821).—The composition of the two layers formed by mixing aq. gum arabic and gelatin sols has been investigated. Under optimal conditions of coacervation the coacervate contains the components in the same ratio as in the whole system for a series of isohydric mixtures. The H_2O content of such a coacervate is at a min. between p_H 3.3 and 3.5. Addition of a desolvating non-electrolyte (e.g., $EtOH$) increases the colloid content of the coacervate, but addition of neutral salts decreases it. The coacervate can take up excess of one of the components. The aq. layer also con-

tains gum arabic and gelatin; the conditions determining the amount of these components are discussed.

E. S. H.

Silicic acid gels. VI. Influence of temperature and acid on the time of set. C. B. HURD (J. Physical Chem., 1936, 40, 21—26).—The times of set of silicic acid gels made by mixing aq. Na silicate with aq. AcOH, tartaric, citric, or succinic acids of varying concn. have been determined at 25.1°, 38.4°, and 53.0°. The relation between log (time of set) and $1/T^\circ$ abs. is shown to be linear and heats of activation have been deduced. The average vals. for the four acids are 17,140, 17,530, 16,940, and 17,190 g.-cal., respectively (cf. A., 1932, 1202).

M. S. B.

Diffusion coefficient and apparent radius of the cupric ion in silica gels. W. G. EVERSOLE and E. W. DOUGHTY (J. Physical Chem., 1936, 40, 55—60; cf. A., 1935, 702).—The rate of diffusion of CuCl_2 into SiO_2 gels has been determined by a photometric method. The most probable val. of the diffusion coeff. of Cu^{++} in H_2O is 4.6×10^{-6} sq. cm. per sec. The effective radius of hydrated Cu^{++} appears to be approx. 5.2×10^{-8} cm.

M. S. B.

Influence of neutral salts on the optical rotation of gelatin. III. Effect of the halides of lithium, sodium, rubidium, and caesium. IV. Rotatory dispersion of gelatin in sodium iodide solutions. D. C. CARPENTER and F. E. LOVELACE (J. Amer. Chem. Soc., 1935, 57, 2337—2342, 2342—2346).—III. The $[\alpha]_D$ at 0.5° and 40° of a 0.7% solution of gelatin (calfskin) (I) at p_H 6—7 is lowered (more marked at 0.5°) by the halides in the order $\text{I} > \text{Br} > \text{Cl}$; when the concn. of added salt is fairly high the cation exerts a minor lowering effect, viz., $\text{Li} > \text{Cs} > \text{Rb} > \text{Na}$. For the alkali gelatinates in absence of added salt the magnitude of $[\alpha]_D$ is in the order $\text{K} > \text{Rb} > \text{Cs} > \text{Na} > \text{Li}$.

IV. The $[\alpha]_D$ of solutions of (I) (0.7704 g. per 100 solution) containing NaI have been measured at 0.5° and 40° for 5 wave-lengths. The rotatory dispersion, which obeys a single-term Drude equation, is governed by an absorption band at 2200 Å., in which region (I) has a high absorption. The "gel" \rightarrow "sol" transformation is considered to be a process of dissociation or association of the mol. of (I). Application of Lucas' method (A., 1930, 1095) of analysis to the data shows that only two optically active species exist in solutions or gels of (I).

H. B.

Myoglobin. I. Solubility in ammonium sulphate solutions.—See this vol., 359.

Colloid chemistry of edestin. III. Capillary-electric effects produced during the peptisation of edestin by solutions of electrolytes. K. HOLWERDA (Biochem. Z., 1936, 283, 253—262; cf. this vol., 158).—The shifting of the zone of peptisation towards higher salt concns. on the acid side of the isoelectric point is a consequence of the auto-complex capacity of edestin (I), but diminution or removal of this does not suffice to cause peptisation and the solubility of (I) in neutral salt solutions does not depend on this capacity alone.

W. McC.

Salting-out and peptisation of edestin by mixtures of two salt solutions. K. HOLWERDA (Bio-

chem. Z., 1936, 283, 280—291; cf. Büchner *et al.*, A., 1931, 1125).—The effects of small amounts of NaCl, NaI, and NaCNS on the salting-out of edestin by Na_2SO_4 are similar to those produced in the case of gelatin, there being no antagonistic effects, but KF has an antagonistic effect on peptisation by NaCl, adsorption of F' being then negative. The antagonism observed between NaCl and multivalent cations probably has another cause (effect of oppositely charged centres, auto-complex action).

W. McC.

Plant colloids. XLII. Influence of crystalloids on the state of amyloses, with special reference to thread-forming power. M. SAMEC [with P. BENKOVIČ] (Kolloid-Beih., 1936, 43, 272—286; cf. A., 1935, 165).—The viscosity of dil. amylose solutions is lowered by small amounts of electrolytes, but raised by larger amounts; the spontaneous coagulation by ageing is retarded by electrolytes or org. crystalloids. Conc. amylose solutions (6%) increase in consistency as the concn. of the added crystalloid is increased; at a certain stage the mixtures have good thread-forming properties.

E. S. H.

Phase rule in colloid chemistry. W. D. BANCROFT (J. Physical Chem., 1936, 40, 43—45).—Theoretical.

M. S. B.

Exchange reactions with deuterium. I. Deuterium and hydrogen chloride. P. C. CROSS and P. R. LEIGHTON (J. Chem. Physics, 1936, 4, 28—30).—An apparatus for measuring exchange equilibria and rates of exchange between D_2 and H-containing compounds is described. Data for the equilibria $\text{H}_2 + 2\text{DCl} \rightleftharpoons \text{D}_2 + 2\text{HCl}$ and $\text{H}_2 + \text{DCl} \rightleftharpoons \text{HD} + \text{HCl}$ have been obtained and are in satisfactory agreement with theoretical vals.

M. S. B.

Thermal equilibrium of the cis-trans-isomerides of dichloroethylene at high temperatures. W. MARONEY (J. Amer. Chem. Soc., 1935, 57, 2397—2398).—The investigations previously reported (A., 1934, 831) have been extended to 975°.

E. S. H.

Present state of the problem of electrolytic solutions. C. A. KRAUS (J. Chem. Educ., 1935, 12, 567—573).—At lower concns. the properties of electrolytes in solvents are satisfactorily accounted for by interaction between ions in accord with the Coulomb law of force. In solvents of high ϵ , electrolytes are completely dissociated into ions and only long-range interactions need be considered, but when ϵ is low, short-range interactions must be taken into account. As ϵ falls, these interactions become of increasing importance and the formation of triple ions as well as ion pairs must be considered. In solvents of very small ϵ more complex interactions, which occur at higher concns., lead to the formation of complex, neutral, and probably charged aggregates. No present theory adequately accounts for the properties of electrolytic solutions at higher concns. New conductance data for various electrolytes in liquid NH_3 , and $\text{C}_2\text{H}_4\text{Cl}_2$, the f.p. and the ϵ of solutions in C_6H_6 , are recorded and discussed.

L. S. T.

Statistical treatment of strong electrolytes. S. LEVINE (Proc. Roy. Soc., 1935, A, 152, 529—559).—It is shown that Kramer's theory of strong

electrolytes (A., 1927, 626) is valid if the ordinary Coulomb forces between the ions are assumed. The deviations from the inverse square law, due to saturation and hydration effects on the H_2O dipoles, and to the polarisation, van der Waals, and exchange forces between two typical ions, are accounted for by means of a correction term in the expression for the energy of interaction. L. L. B.

Transition cases in the distribution of ions. R. M. FUOSS (J. Amer. Chem. Soc., 1935, 57, 2604—2607).—A crit. concn. exists, above which free and pair-associated ions become indistinguishable (cf. A., 1935, 488). At higher concns. the simple laws of dil. electrolyte solutions are no longer obeyed.

Hydration of ions. O. SCHMITZ-DUMONT (Z. anorg. Chem., 1935, 226, 33—45).—Theoretical. Brintzinger's method (A., 1935, 579, 582, 824) based on the coeff. of dialysis does not enable electrostatically bound H_2O to be distinguished from that present as an aquo-complex. E. S. H.

Sourness of acids. R. M. BEATTY and L. H. CRAIG (J. Amer. Chem. Soc., 1935, 57, 2347—2351).—Sourness is defined in terms of the normality of aq. HCl of equal sourness. The sourness of unbuffered solutions of some org. acids is given by x/K , where x is the vol. of a PO_4''' buffer required to bring a unit vol. of the acid to p_H 4.4, and K is a const. characteristic of the buffer used. E. S. H.

Monoalkyl phosphites and their hydrolysis.—See this vol., 312.

Effect of temperature on the ionisation constants of some dibasic acids. I. JONES and F. G. SOPER (J.C.S., 1936, 133—137).—When the distance (r) between the ionising centres is $> 4.0 \text{ \AA}$., corrections for anisotropy and compressibility may be ignored without appreciable error, and it has been possible to determine r for many symmetrical dibasic acids at various temp. The p_H changes during the neutralisation of *cis*-caronic acid (I) show no marked displacement with temp. change, and with phenolphthalein, contrary to the observation of Baeyer, there is no indication of monobasicity at room temp., although temp. markedly affects the inflexion point at the second neutralisation. The second ionisation const. of (I) is 0.49×10^{-8} , and the disappearance of the inflexion at higher temp. is attributed to increased hydrolysis of the salt. To obtain a sharp end-point in the titration of such weak acids, titrations should be made at low temp. For a const. val. of r , the ratio of the first and second ionisation consts. K_1/K_2 increases with temp. for all acids studied, except those having *cis*-structures, and possible causes of this are discussed. Values of $K_1 \times 10^5$ for (I) and *trans*-caronic acid are 459 and 15.2 respect. Caronic acid is compared with other dicarboxylic acids.

E. E. A.

Effect of certain sugar alcohols and their anhydrides on the dissociation of boric acid. J. C. KRANTZ, jun., (MISS) M. OAKLEY, and C. J. CARR (J. Physical Chem., 1936, 40, 151—154).—The two polyhydric alcohols, mannitol and dulcitol, have an effect on the titration curve of H_3BO_3 much $>$ that

of the anhydrides mannitan, mannide, and dulcitan. *iso*Mannide has no effect. M. S. B.

Hydrogen-ion dissociation curve of the crystalline albumin of the hen's egg.—See this vol., 360.

Physico-chemical properties of mercurous perchlorate solutions. E. NEWBERY (Electrochem. Soc. Preprint, 1936, 69, 57—73).—The prep. and purification of $Hg_2(ClO_4)_2$ is described. The existence of the tetrahydrate is confirmed and this is shown to be stable below 36° . From 36° to $> 100^\circ$ the stable hydrate is $2H_2O$. The transition point is lowered in strongly acid solution. Hydrolysis occurs in three stages the products being $Hg_2O, Hg_2(ClO_4)_2$ (I), $Hg_2(OH) \cdot ClO_4$ (II), and HgO , respectively. The degree of hydrolysis is 2.5% in 0.1M solution. In more conc. solution the hydrolysis is $>$ anticipated because (I) is a weaker base than (II). The degree of ionisation (α) of the salt appears to increase with the concn. Conductivity data suggest that $\alpha = 128\%$ in the saturated solution (3.93M) at 25° . The view is expressed that in dil. solution the basic salt formed by hydrolysis is non-ionised and that, in very conc. solutions, Hg_2^{++} is dissociated into $2Hg^+$ by the action of the negatively charged ions present in large concn. Hg^+ perchlorate may be used for a Hg coulometer, for sp. gr. determinations in mineralogy, for cleaning Hg, for the prep. of pure Hg_2Cl_2 or Hg_2SO_4 , and as a reagent for halogens, SO_4''' , PO_4''' , AsO_2''' , and CrO_4''' . M. S. B.

Equilibria in solutions of tri-ionic electrolytes. K. JABŁCZYŃSKI and R. LEGAT (Rocz. Chem., 1935, 15, 351—359).—Cryoscopic and conductivity data are applied in the estimation of the equilibria const. for the ionisation of Ba, Sr, Ca, and Mg chlorides in accordance with the general formula $MCl_2 \rightleftharpoons M^{++} + 2Cl'$. R. T.

Carbamate equilibrium. I. Equilibrium of amino-acids, carbon dioxide, and carbamates in aqueous solution; with a note on the Ferguson-Roughton carbamate method. W. C. STADIE and H. O'BRIEN (J. Biol. Chem., 1936, 112, 723—758).—It is the amphanion $COO^- \cdot R \cdot NH_2$ and not the zwitterion $COO^- \cdot R \cdot NH_3^+$ of NH_2 -acids which forms carbamates with CO_2 . The ionisation of these, which behave as dibasic salts at $p_H > 7$, is discussed. Mass-action equations for the carbamate equilibrium of NH_2 -acids and CO_2 in aq. solution are given, together with const. calc. under various conditions. By the use of carbonic anhydrase, the Ferguson-Roughton carbamate method can be used when much free CO_2 is present. J. N. A.

Activity coefficient of ions. (MILLER) M. QUINTIN (Compt. rend., 1936, 202, 123—125; cf. A., 1935, 826).—The e.m.f. of the cells Cd (amalgam, two phases) | $CdCl_2(m)$ | KCl sat. | $KCl 0.1N$ | Hg_2Cl_2 | Hg and $Ag | AgCl | CdCl_2(m) | KCl sat. | KCl 0.1N | Hg_2Cl_2 | Hg$ have been measured at 25° for $m = 0.001$ — 0.1 . From the data the calc. radii (Debye a) of Cd^{++} and Cl^- are 5.4 and 2 \AA ., respectively. The former val. agrees with the $6 \pm 1 \text{ \AA}$. calc. from data using $CdSO_4$ (A., 1927, 729). T. G. P.

Activity coefficients of lead chloride in aqueous solutions of barium nitrate. H. D. CROCKFORD

and H. O. FARR, jun. (J. Amer. Chem. Soc., 1936, 58, 87—89).—Activity coeffs. and the \bar{a} parameter have been calc. from e.m.f. determinations of the cell $\text{Pb-Hg (2-phase)}|\text{PbCl}_2 (m_1), \text{Ba(NO}_3)_2 (m_2)|\text{AgCl-Ag}$.
E. S. H.

Activity coefficients of sulphuric acid in anhydrous ethyl alcohol from electromotive force data. A. W. SCHOLL, A. W. HUTCHISON, and G. C. CHANDLEE (J. Amer. Chem. Soc., 1935, 57, 2542—2544).—The data have been obtained from e.m.f. measurements of the cell $\text{H}_2|\text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4(s)|\text{Hg}$.
E. S. H.

Fundamentals of chemical thermodynamics. P. VAN RYSSELBERGHE (Chem. Rev., 1935, 16, 37—51).—A review.
CH. ABS. (e)

Exact significance of the thermodynamic quantities $\Delta F'$ and $\Delta F''$. P. VAN RYSSELBERGHE (Chem. Rev., 1935, 16, 29—35).—Theoretical.
CH. ABS. (e)

Independent components in the phase rule. A. F. GERASIMOV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 114—119).—A discussion.
CH. ABS. (e)

Integrated form of the equation for calculating change of equilibrium with temperature. J. B. AUSTIN (J. Amer. Chem. Soc., 1935, 57, 2428—2434).—The equations relating change of solubility with temp. are converted into a more convenient form. Experimental vals. fall on a straight line when plotted against temp., or the reduced temp., on double logarithmic co-ordinates. The approx. equation for v.p. leads directly to the rules of Ramsay and Young and of Dühring.
E. S. H.

System stannic chloride-hydrogen chloride. A. CHRÉTIEN and G. VARGA (Compt. rend., 1935, 201, 1491—1493).—Thermal data show the formation of $\text{SnCl}_4 \cdot 5\text{HCl}$, m.p. -94.7° , and $\text{SnCl}_4 \cdot 2\text{HCl}$, m.p. -85° , and three eutectic points.
T. G. P.

System antimony iodide-sodium iodide-water. F. FRANÇOIS (Compt. rend., 1935, 201, 1489—1491).—Isotherms at 15° , 35° , and 60° indicate the formation of $\text{SbI}_3 \cdot 2\text{NaI} \cdot 8\text{H}_2\text{O}$ and $\text{SbI}_3 \cdot \text{NaI} \cdot 6\text{H}_2\text{O}$.
T. G. P.

Thermal analysis of the systems iodine-LiI, -KI, -RbI, or -TlI. J. A. FIALKOV and G. A. KUZMENKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 127—139).—Polyiodides are not formed when the iodides are fused with I, indicating that the presence of a solvent is essential for their formation.
R. T.

Purification and physical properties of organic compounds. X. F.p. diagram for the system acetanilide-propionanilide. E. L. SKAU and L. F. ROWE (J. Amer. Chem. Soc., 1935, 57, 2437—2438; cf. A., 1935, 1077).—The Beckmann method is unsatisfactory. A static method shows that the system forms a compound with incongruent m.p.
E. S. H.

Binary systems of *p*-dichlorobenzene with diphenyl, naphthalene, and triphenylmethane. R. E. MORRIS and W. A. COOK (J. Amer. Chem. Soc., 1935, 57, 2403—2406).—A simple eutectic is shown

in each system. Solubilities, eutectic temp., and compositions are approx. those calc. for ideal solutions.
E. S. H.

Physical-chemical properties of the chlorohydrin and of the dichloride of Δ^{β} -butene. I. N. BUSCHMAKIN, M. M. GOLIDMAN, and K. I. KUBTSCHEVSKAJA (Sintet. Kautschuk, 1935, 4, No. 1, 33—35).—Equilibrium data are recorded for the binary and ternary systems formed with H_2O .
CH. ABS. (e)

Solid-liquid equilibria in ternary systems in which incongruently melting compounds are formed. III. K. HRYNAKOWSKI and M. SZMYT (Z. physikal. Chem., 1935, 175, 83—98).—The systems salicylic acid- $\text{CO(NH}_2)_2$ -urethane and $\text{PhOH-CO(NH}_2)_2$ -urethane each exhibit one eutectic point and two peritectic points.
R. C.

(A) Lower transition point of the mutual system $\text{Na}_2\text{SO}_4\text{-NH}_4\text{HCO}_3\text{-H}_2\text{O}$. (B) Mutual aqueous system $\text{Na}_2\text{SO}_4\text{-NH}_4\text{HCO}_3\text{-H}_2\text{O}$ at -17° . A. P. BELOPOLSKI and S. J. SCHPUNT (J. Appl. Chem. Russ., 1935, 8, 1126—1135, 1136—1142).—(A) The transition point, corresponding with the equilibrium $2\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + 2\text{NH}_4\text{HCO}_3 \rightleftharpoons \text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O} (I) + 2\text{NaHCO}_3 + 16\text{H}_2\text{O}$, is shown by solubility measurements to be at 7° .

(B) Equilibrium relations have been determined at -17° . (I), which is unstable at $< -16^\circ$, can exist at lower temp. in presence of NH_4HCO_3 .
R. T.

Equilibria in the systems (A) $\text{MgCO}_3\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$, (B) $\text{Na}_3\text{PO}_4\text{-NaCl-H}_2\text{O}$. A. P. OBUCHOV (J. Appl. Chem. Russ., 1935, 8, 1143—1148, 1149—1151).—(A) [with E. I. GORDON]. The double salt $\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3$ crystallises from an aq. solution of Na_2CO_3 which has been saturated with MgCO_3 at 35° .

(B) [with M. N. MICHALOVA]. Equilibrium data are recorded for the systems at 25° and 105° . The solubility of Na_3PO_4 falls rapidly with increasing $[\text{NaCl}]$.
R. T.

System cobalt chloride, ammonium chloride, ammonia, water. M. CHATELET (Compt. rend., 1936, 202, 216—217).—The formation of the ions $[\text{CoNH}_3]$ and $[\text{Co(NH}_3)_3]$ is said to have been detected by calorimetric measurements.
T. G. P.

Determination of change of free energy in reactions of type $A(s) + B(s) = AB(s)$ and application to dolomite problem. F. HALLA [with F. RITTER] (Z. physikal. Chem., 1935, 175, 63—82).—A method for determining the change in free energy, ΔF , in the formation of double compounds by solubility measurements is described. Application to the formation of dolomite (I) from its solid components shows that under 1 atm. this occurs spontaneously above -34° and ΔF° is 590 ± 50 g.-cal. at 25° and 740 ± 30 g.-cal. at 38.8° , and that ΔH is -2840 ± 350 g.-cal. at $25\text{--}32^\circ$. For dolomitisation, $2\text{CaCO}_3 + \text{Mg}^{++} = (\text{I}) + \text{Ca}^{++}$, $\Delta F = -190 \pm 50 + 1430 \log \frac{[\text{Ca}^{++}]}{[\text{Mg}^{++}]}$ g.-cal. at 25° and $120 \pm 30 + 1365 \log \frac{[\text{Ca}^{++}]}{[\text{Mg}^{++}]}$ g.-cal. at 38.8° . The direction of this process is therefore determined almost entirely by the ratio $[\text{Ca}^{++}] : [\text{Mg}^{++}]$ in the solution, and under the conditions of temp. and concn. prevailing in the sea dolomitisation should occur spontaneously. The

following solubility products have been obtained: MgCO_3 , 1.8×10^{-8} at 25° , 1.6×10^{-8} at 38.8° ; CaCO_3 , 3.83×10^{-9} at 38.8° ; (I), 3×10^{-17} at 25° , 1.8×10^{-17} at 38.8° . Lewis and Randall's sp. ionic activity coeffs. have been successfully used to calculate solubility product from a single solubility. The variation in solubility of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ with temp. is given by $m = 0.4344 - 0.0111t + 0.04953t^2$. Heats of dissolution in $2N\text{-HCl}$ have been measured.

R. C.

Heats of dissolution of ferric chloride in water and in aqueous hydrochloric acid. W. KANGRO and R. FLÜGGE (Z. physikal. Chem., 1935, 175, 187—194).—Differential and integral heats of dissolution and dilution at 20° have been determined. The heat of dissolution in aq. HCl falls rapidly with increasing [HCl]. When [HCl] is $\approx 10\%$ the decrease is quantitatively accounted for by fall in the activity of the H_2O , but at higher concns. there are discrepancies, which are probably connected with association. Sp. heats of aq. FeCl_3 solutions have been determined at 20° .

R. C.

Hydrazine. Heats of dissolution of hydrazonium salts at 25° . II. E. C. GILBERT and V. C. BUSHNELL (J. Amer. Chem. Soc., 1935, 57, 2611—2612; cf. A., 1935, 303).—Data for hydrazonium dibromide (anhyd. and hydrated) and sulphate are recorded. Partial mol. heats of dissolution of solute and solvent (H_2O) have been calc. for the bromide. The heat capacity of aq. hydrazonium sulphate at 25° has been determined.

E. S. H.

Thermochemistry of azoimide. P. GÜNTHER, R. MEYER, and F. MÜLLER-SKJOLD (Z. physikal. Chem., 1935, 175, 154—169).— HN_3 is conveniently prepared by heating NaN_3 with stearic acid in vac. and condensing at not below -75° . When the gas explodes under reduced pressure very little NH_3 is formed. The heat of formation of the gas at const. vol. is -70.9 ± 0.5 kg.-cal. per mol. The v.p. of the liquid has been determined from near the triple point to near the b.p. (35.7°). At 12.4° the mol. heat of evaporation is -7.3 ± 0.1 kg.-cal. The total heat of dissolution of the gas to give a $0.16N$ solution is 9.7 ± 0.1 kg.-cal. per mol. These data confirm the recorded heat of formation (Roth and Müller, A., 1929, 755). For the liquid at $0-21^\circ d = 1.126/(1 + 0.0013t)$.

R. C.

Heat of combustion of isobutane. F. D. ROSSINI (J. Res. Nat. Bur. Stand., 1935, 15, 357—361).—The heat of combustion of $\text{iso-C}_4\text{H}_{10}$ in O_2 to form CO_2 (gas) and H_2O (liquid) at $25^\circ/1$ atm. is 686.31 ± 0.13 kg.-cal. per mol., hence the heat of formation of $\text{iso-C}_4\text{H}_{10}$ at 25° is 32.2 ± 0.43 and the heat of conversion of the *n*- into the *iso*-form is 1.63 ± 0.15 kg.-cal. per mol.

A. R. P.

Direct carboxylation of carbon compounds.

III. **Free energy of benzoic acid at 522 abs.** W. D. BONNER and C. R. KINNEY (J. Amer. Chem. Soc., 1935, 57, 2402—2403; cf. A., 1933, 1159).—Calculation from published data gives $\Delta F_{522}^\circ = -36,491$ g.-cal.

E. S. H.

Heats of organic reactions. III. Hydrogenation of some higher olefines. IV. Hydrogen-

ation of dienes and of benzene. G. B. KISTIAKOWSKY, J. R. RUTHOFF, H. A. SMITH, and W. E. VAUGHAN (J. Amer. Chem. Soc., 1936, 58, 137—145, 146—153; cf. A., 1935, 825).—III. Heats of hydrogenation (in g.-cal. per mol.) are recorded for Δ^a -heptene ($-30,137 \pm 37$), *as*-methylethylethylene ($-28,491 \pm 36$), Δ^b -pentenes (*cis* and *trans*) ($-27,954 \pm 28$), $\text{CMePr}^a\text{:CH}_2$ ($-27,997 \pm 24$), cyclohexene ($-28,592 \pm 10$), $\text{CMe}_2\text{:CHMe}$ ($-26,920 \pm 10$), and $\text{CMe}_2\text{:CMe}_2$ ($-26,633 \pm 19$). With increasing no. of substituent alkyl groups the heat of hydrogenation is progressively lowered, and the differential effect decreases with increasing no. of substituents. This effect is independent of the chain length of substituent *n*-alkyls, but branched groups have a greater influence.

IV. Heats of hydrogenation are given for allene + 2H_2 ($-71,280 \pm 103$), *zy*-butadiene + 2H_2 ($-57,067 \pm 28$), $\alpha\delta$ -pentadiene + 2H_2 ($-60,790 \pm 64$), $\alpha\epsilon$ -hexadiene + 2H_2 ($-60,525 \pm 43$), $\Delta^{1,3}$ -cyclohexadiene + 2H_2 ($-55,367 \pm 56$), $\text{C}_6\text{H}_6 + 3\text{H}_2$ ($-49,802 \pm 44$), cyclopentadiene + 2H_2 ($-50,865 \pm 47$ g.-cal. per mol.). The data are discussed.

E. S. H.

Single linking energies. I. C-C linking in hexaphenylethane. H. E. BENT, G. R. CUTHBERTSON, M. DORFMAN, and R. E. LEARY. II. **C-C linking in hexaphenylethane.** H. E. BENT and G. R. CUTHBERTSON (J. Amer. Chem. Soc., 1936, 58, 165—170, 170—173).—I. Apparatus and technique for determining heats of reaction, especially for easily oxidised substances, are described. The v.p. of Δ^a -heptene (I) has been determined from 0° to 90° and the heat of vaporisation calc. The heat of hydrogenation of (I), the heat of oxidation of $(\text{CPh}_3)_2$, and the heats of dissolution of the compounds involved in these reactions have been determined. The dissociation of $(\text{CPh}_3)_2$ is due to weakening of the C-C linking and the stabilising effect of the resonance energy of CPh_3 .

II. The heat of hydrogenation of $(\text{CPh}_3)_2$ to form CPh_2 is -40.5 kg.-cal. for solids and -34.8 kg.-cal. in EtOAc solution. The C-C linking is weaker than a normal linking by about 30 kg.-cal.

E. S. H.

Electrical conductivity of potassium chloride in certain mixed solvents. R. N. AGARWALA and D. C. MANDERVILLE (J. Indian Chem. Soc., 1935, 12, 699—705).—Viscosities and sp. conductivities of $\text{H}_2\text{O}-\text{MeOH}$, $\text{H}_2\text{O}-\text{EtOH}$, and $\text{H}_2\text{O}-\text{COMe}_2$ mixtures have been determined together with equiv. conductivities Λ of the corresponding HCl solutions. The plot of Λ against $[\text{KCl}]^{1/2}$ is linear for H_2O and $\text{H}_2\text{O}-\text{EtOH}$, but regularly spaced max. and min. appear in the case of $\text{H}_2\text{O}-\text{MeOH}$ and $\text{H}_2\text{O}-\text{COMe}_2$ which bear no relation to the viscosity. An explanation involving "dipole association" chains of hydrated COMe_2 etc. between the ions has been advanced.

R. S.

Electrical conductivity of solutions of electrolytes in methyl alcohol and acetone at high temperatures. P. C. BLOKKER (Rec. trav. chim., 1935, 54, 975—987).—The conductivities and sp. vols. of solutions of LiCl, LiBr, LiI, NaI, KI, CaI_2 , and $(\text{Pr}^a[\text{CH}_2]_2)_4\text{NI}$ in MeOH and COMe_2 have been measured at temp. up to 218° in special soft steel

bombs lined with Pt. The equiv. conductivities of these solutions show max. at temp. which are the lower the higher is the salt concn. It is shown that the max. are caused by decrease in the dielectric const.
J. W. S.

Conductivity of calcium, strontium, and barium chlorides in anhydrous glycerol. J. SZFER and Z. GAJEWSKI (J. Chim. phys., 1935, 32, 705—714).—For 1—1/16 molar solutions and at 25—200°, the mol. conductivities of CaCl₂, SrCl₂, and BaCl₂ in anhyd. glycerol follow the Kohlrausch law $\Lambda_{\infty} - \Lambda_p = k'\sqrt{c}$. The limiting mol. conductivity is 3.67×10^{-4} at 25° and 35° for all three salts. The mobilities of the cations increase with the mol. wt. The mol. conductivity increases exponentially with temp. at low temp., but above 130° increases linearly.
J. W. S.

Electrochemical investigation of the ternary system AlBr₃-AsBr₃-benzene. V. A. PLOTNIKOV and S. I. JAKUBSON (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 99—109).—Thermal analysis does not suggest compound formation, but freshly prepared solutions of the salts in C₆H₆ conduct electricity; the conductivity falls rapidly to a const. val. after 23 days. The unstable compound AlBr₃.AsBr₃ is postulated.
R. T.

Determination of transference numbers in dilute solutions from limiting ionic conductances. B. B. OWEN (J. Amer. Chem. Soc., 1935, 57, 2441).—Theoretical.
E. S. H.

Ionic mobility. J. J. HERMANS (Z. Physik, 1935, 97, 681—689).—An equation is obtained for the effect of solvent dipoles on ionic mobility, and is solved for infinite dilution. Extension to finite dilution shows that the mobility \propto (concn.)^{1/2}.
A. B. D. C.

Electrical transport of an active deposit of radium in some organic liquids. Z. KLEMENSIEWICZ and K. PROJEKT (Acta Phys. Polon., 1933, 2, 409—415).—Solutions in C₆H₁₄, C₆H₆, PhMe, Et₂O, COMe₂, and EtOH have been examined in an electric field. The amount of Ra deposited on the electrodes decreases with rise in the dielectric const. and the viscosity of the liquid.
Ch. Abs. (e)

Absolute single potential of [calomel] electrode. K. HIROTA and T. MURATA (Bull. Chem. Soc. Japan, 1935, 10, 594—596).—The variation of p.d. with interfacial tension (σ) of Hg has been studied by forcing the Hg upwards through a fine orifice immersed in KNO₃. The height of the jet varies approx. parabolically with the p.d. between jet and the N-calomel electrode, the min. corresponding with the position of max. σ . The mean val. for the N-calomel electrode is 0.563 ± 0.004 volt at 20.6°, in agreement with vals. determined by the dropping Hg electrode.
R. S. B.

Unknown property of the calomel half-cell and the determination of bromide-chloride mixtures. F. L. HAHN (J. Amer. Chem. Soc., 1935, 57, 2537).—The potential is strongly influenced by even very small amounts of Br' in the KCl. The effect may be adapted to the determination of Br'.
E. S. H.

Mercury-mercuric oxide-saturated barium hydroxide and calcium hydroxide electrodes. G. J. SAMUELSON and D. J. BROWN (J. Amer. Chem. Soc., 1935, 57, 2711—2714).—The potential Hg|HgO(s), Ba(OH)₂(s) with reference to the N-H₂ electrode is $+0.1462 - 0.00060(t-25) \pm 0.0002$ volt; that of Hg|HgO(s), Ca(OH)₂(s) is $+0.1923 + 0.00010 \times (t-25) \pm 0.0010$ volt. The ease of prep., constancy, reproducibility, and temp. coeff. of the electrodes have been studied.
E. S. H.

Potential of the Ag(s)|Ag₂CrO₄(s)|CrO₄" electrode. J. Y. CANN and G. B. MUELLER (J. Amer. Chem. Soc., 1935, 57, 2525—2527).—E.m.f. measurements of the cell Ag(s)|Ag₂CrO₄(s)|K₂CrO₄(aq.)|KCl(aq.)|AgCl(s)|Ag(s) at 25° give -0.4463 volt for the normal electrode potential of Ag(s), Ag₂CrO₄(s), CrO₄" ; $\Delta F^\circ = 20,596$ g.-cal.
E. S. H.

Volta effect of electrolytic solutions against water, and characteristics of acidity and basicity. (MILLER) S. VEIL (Compt. rend., 1936, 202, 121—123).—The electrometric potentials of the system Pt-H₂O (gelatin)-salt solution-Pt have been measured (A., 1935, 822). They depend on the concn. and nature of the salt, and are positive at $p_H < 7$.
T. G. P.

Anomalous redox potentials of thiol-disulphide systems. J. W. H. LUGG (J. Indian Chem. Soc., 1935, 12, 706—711).—A theory involving the formation of an ionisable compound between RS and the electrode surface is suggested.
R. S.

Oxidation-reduction potential of reductone. R. WURMSER and N. MAYER (Compt. rend., 1935, 201, 1366—1368; cf. A., 1934, 1072).—The oxidation-reduction potential of the system OH·CH·C(OH)·CHO \rightleftharpoons CO(CHO)₂ at 38° has been studied between p_H 2 and 9. E_0 at p_H 0 is $+0.282$ volt.
T. G. P.

Oxidation-reduction potentials. II. Investigation of a coupled oxidation-reduction equilibrium by photo-electric measurement of light extinction. G. HOLST (Z. physikal. Chem., 1935, 175, 99—126; cf. A., 1934, 968).—The mol. extinction coeff., α , of methylene-blue (I) at 20° in 0.01N-HCl for $\lambda = 546$ m μ increases with the dye concn. PhN·N·SO₃K (II), as a result of chemical interaction, depresses α , whilst NHPh·NH·SO₃K (III) does not affect α . The equilibrium (I)+(III) \rightleftharpoons leucomethylene-blue (IV)+(II) is reversibly displaced by light. In 0.01N-HCl at 20° the equilibrium const. of the dark reaction is 8.2. Irradiation with blue light shifts the equilibrium towards larger concns. of (I); yellow light has the reverse effect. The α of the mixture equilibrated in the dark increases during irradiation when the (I) concn. is small and falls when it is large; in either case it attains a limiting val. as irradiation continues. The p.d., ΔE , between the two reacting reduction-oxidation systems at 20—40° is const. at 0.027 volt, corresponding with an equilibrium const. of 8.5 at 20°. This val. of ΔE is \ll that recorded by Clark *et al.* (U.S. Hyg. Lab. Bull., 1928, No. 151), a discrepancy which may be connected with the variation of potential with dye concn. The heat changes for (II)+H₂ \rightleftharpoons (III) and (I)+

$H_2 \rightleftharpoons$ (IV) (at p_H 2.0) are 30.3 and 31.5 kg.-cal., respectively. R. C.

Decomposition potential of solutions of bromides of metals in fused cadmium bromide. V. A. IZBEKOV and G. J. ZACHARTSCHENKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 121—126).—The decomp. potentials of a no. of bromides in fused $CdBr_2$ fall in the order $Zn < Cd < Pb < Cu < Ag < Sn < Co < Ni < Bi$; the same order holds in fused $AlBr_3$ or $ZnBr_2$. Any member of the above series is displaceable from $CdBr_2$ solution by any of the preceding metals. R. T.

Nature of the residual current [observed with the moving cathode]. I. ZLOTOWSKI (J. Chim. phys., 1935, 32, 750—753).—Polemical against Thon (A., 1935, 705). J. W. S.

Nature of the residual current [observed with the moving cathode]. N. THON (J. Chim. phys., 1935, 32, 754).—Polemical against Zlotowski (cf. preceding abstract). J. W. S.

Simultaneous cathodic and anodic direct-current polarisation of electrodes. II. Anodes of platinum, palladium, and gold. P. S. TUTUNDŽIĆ (Z. Elektrochem., 1936, 42, 21—27; cf. A., 1935, 1205).—The influence of superimposed d.c. of varying direction, p.d., and c.d. on the potential and decomp. potential of Pt, Pd, and Au anodes in $2N-H_2SO_4$ at room temp. has been investigated. E. S. H.

Oxide film on passive iron. W. D. BANCROFT and J. D. PORTER (J. Physical Chem., 1936, 40, 37—42).—The data of earlier investigators suggest that the oxide film on passive Fe (I) is FeO_3 . This is confirmed by e.m.f. measurements in HNO_3 (d 1.20) on Fe made passive by adsorption from aq. K ferrate, by anodic polarisation in KOH, and by treatment with H_2O_2 , CrO_3 , acid $KMnO_4$, or HNO_3 (d 1.35—1.42). The activation of (I) by conc. H_2O_2 is due to decomp. of FeO_3 by the heat evolved when the H_2O_2 is catalytically decomposed at the surface of (I) and not by a reducing action of the H_2O_2 . M. S. B.

Electrometric studies of the precipitation of hydroxides. XIII. Reactions between silver nitrate and methylamine, mono-, di-, and triethylamine, ethylenediamine, aniline, and pyridine in solution. H. T. S. BRITTON and W. G. WILLIAMS (J.C.S., 1936, 96—100; cf. A., 1935, 936).—The formation of complex Ag cations when various org. bases are added to $AgNO_3$ has been studied. The extent to which bases ppt. Ag_2O and the amounts required for redissolution depend on the instability const. of the complex cation, the solubility product of the Ag_2O , and the dissociation const. of the base. Glass electrode titration curves at 18° of $AgNO_3$ with solutions of the bases and electro-titration curves are given. $(CH_2 \cdot NH_2)_2$ forms the ion $Ag[(CH_2 \cdot NH_2)_2]^+$. The modes of pptn. of Ag_2O by the org. bases and by NH_3 are compared. Unlike NH_3 , none of the bases causes the Ag_2O to redissolve when 2 mols. per mol. of $AgNO_3$ have been added. From p_H vals. and e.m.f. data, the instability consts. K_1 of $Ag(NH_2Me)_2^+$ and $Ag(NH_2Et)_2^+$ have been calc. The relatively large vals. of K_1 for complex cations

from NH_2Ph and C_5H_5N show that these are relatively much less stable. E. E. A.

Energy levels in electrochemistry W. D. BANCROFT and J. E. MAGOFFIN (J. Amer. Chem. Soc., 1935, 57, 2561—2565).—The oxidation of dil. aq. H_2SO_3 or Na_2SO_3 is irreversible because, for reduction to occur, the system must pass through an energy level which is $>$ the energy level for nascent H as obtained by electrolysis. The energy level decreases with decreasing concn., rising temp., and activating adsorption. The stabilities of $NaClO_3$ and $NaClO_4$ relatively to $NaOCl$ are related to the intermediate energy levels which must be surmounted for reduction to occur. An irreversible reaction may give a definite c.m.f. E. S. H.

Homogeneous unimolecular decomposition reactions of gases. F. PATAT (Z. Elektrochem., 1936, 42, 85—98).—A review.

Thermal interaction of deuterium and ammonia. A. FARKAS (J.C.S., 1936, 26—35).—The kinetics of the homogeneous exchange reaction between NH_3 and D_2 have been investigated at 680—790° and at 25—400 mm. total pressure. The apparent energy of activation is 62 kg.-cal. and the reaction mechanism (i) $D_2 \rightarrow 2D$, (ii) $NH_3 + D \rightarrow NH_2D + H$, and (iii) $H + D_2 \rightarrow HD + D$ accords with the data assuming that the rate-determining step (ii) is 30—40-fold slower than reaction (iii). The atoms responsible for the exchange reaction are produced by the thermal process (i), the dissociation $NH_3 \rightarrow NH_2 + H$ being negligible. The lower speed of (ii) is due to the higher activation energy, 11 ± 1 kg.-cal., required, and may be partly due to a lower steric factor. This result is in agreement with preliminary experiments on the Hg-sensitised photochemical exchange reaction between D and NH_3 . J. G. A. G.

Occurrence of radicals in the thermal decomposition of molecules and the reaction $Me + H_2$. F. PATAT (Naturwiss., 1936, 24, 62—63).—The radical chain theory of Rice and Herzfeld (A., 1934, 369) can be tested by the p - H_2 method of Geib and Harteck (A., 1931, 1252). In the case of the reactions (i) $Me + H_2 \rightarrow CH_4 + H$ and (ii) $H + \text{org. substance} \rightarrow H_2 + \text{org. radical}$, $[H]/[Me] = k_1[H_2]/k_2[\text{org. substance}]$, where k_1 and k_2 are the velocity coeffs. of (i) and (ii), respectively. $[Me]$ can be determined from $[H]$ if k_1/k_2 is known. In the photochemical decomp. of $MeCHO$ and azomethane in p - H_2 , the difference in energy of activation for reactions (i) and (ii) is negligible. The similar reactions involved in the thermal decomp. of Me_2O etc. give the same result, showing that the radical concn. is $< 1/1000$ of that expected if the decomp. followed the chain mechanism of Rice and Herzfeld. A. J. M.

Rate of combination of bromine atoms. K. HILFERDING and W. STEINER (Z. physikal. Chem., 1935, B, 30, 399—439).—The rate of homogeneous formation of HBr in light, all wall effects being absent, has been measured, and simultaneously the abs. amount of energy absorbed. For a total pressure of 258—1308 mm. the relation between velocity, v , and total pressure agrees with Herzfeld's reaction scheme (A., 1919, ii, 503), so that over this pressure

range [Br], which is measured by v , is determined solely by the rate of energy absorption and the rate of recombination of Br atoms. From the reaction have therefore been deduced the rate of recombination of Br atoms in triple collision with various foreign mols. at 490° abs. A "yield factor," f , can be separated from the velocity coeffs. of these reactions, which has the dimension time and measures the sp. energy transfer. From the vals. of f it appears that the no. of effective triple collisions is practically equal to the total no. of triple collisions calc. by the gas-kinetic theory. For the val. of f it is immaterial whether the mol. takes up energy solely as translational energy or also as rotational and vibrational energy. The variations in effectiveness between different mol. species are due to perturbation of the potential curve of the pair of atoms by the mol. At pressures < 258 mm. the wall exerts an effect. For the transport to the wall of Br atoms formed by the radiation, convection rather than diffusion is responsible, except in a thin film immediately on the wall.

R. C.

Zero-point energy of an activated complex and the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$. O. K. RICE (J. Chem. Physics, 1936, 4, 53—59).—Theoretical. A reaction of which the rate is determined by a transitory activated complex in the formation of which classical degrees of freedom must be frozen out into vibrations must have, at all temp., a positive activation energy increasing with rise of temp. A negative activation energy means the formation of a more or less stable mol. complex. The theory has been applied to the oxidation of NO to NO_2 . M. S. B.

Mechanism of reactions of nitric oxide with oxygen, chlorine, and bromine. I. M. BODENSTEIN. II. Rate of formation and equilibrium of nitrosyl bromide. W. KRAUSS (Z. physikal. Chem., 1936, 175, 294, 295—303).—I. Introductory.

II. At 264—290° abs. K_p (p in atm.) for $2\text{NOBr} \rightleftharpoons 2\text{NO} + \text{Br}_2$ is given by $\log K_p = -13,100/4.571T + 8.025$. The formation of NOBr at all temp. and concns. is a termol. reaction with temp. coeff. 1.10; reported deviations from the termol. law (A., 1918, ii, 162) disappear if the reverse reaction is allowed for.

R. C.

Kinetics of the oxidation of gaseous hydrocarbons. III. Oxidation of acetylene. E. W. R. STEACIE and R. D. McDONALD (J. Chem. Physics, 1936, 4, 75—81).—Measurements have been made by a static method in an apparatus previously employed (A., 1935, 172). The rate of reaction is variable and depends on the condition of the surface of the reaction vessel. It is approx. expressed by $-(d/dt)[\text{C}_2\text{H}_2] = k[\text{C}_2\text{H}_2]^{2.7}/[\text{O}_2]^{0.1}$ if O_2 is in excess. The order diminishes with increase of surface and may fall to 1.4 in a packed vessel. In an empty vessel the ratio CO/CO_2 is independent of pressure, but it falls in a packed bulb and still further decreases with diminishing pressure. The apparent heat of activation is approx. 35,000 g.-cal. Addition of glyoxal causes no change in velocity, but CH_2O decreases it. The oxidation is apparently a chain reaction, the chains being initiated at the walls but not appreciably destroyed there. It is possible that the chain carrier is some

product that precedes glyoxal in the oxidation process. A reaction scheme is suggested. M. S. B.

Explosion waves and shock waves. III. Initiation of detonation in mixtures of ethylene and oxygen and of carbon monoxide and oxygen. W. PAYMAN and H. TITMAN (Proc. Roy. Soc., 1935, A, 152, 418—445; cf. A., 1928, 1099).—The inflammation of mixtures of C_2H_4 and O_2 , which detonate with ease, and of CO and O_2 , which detonate with comparative difficulty, has been studied with a wave-speed camera. The speed of the flame in a tube before shock waves of appreciable intensity are produced depends on the fundamental speed of propagation of flame by the transfer of heat, and on the motion of the gas in which the flame is moving. Detonation may be set up ahead of or within the flame front, due to waves travelling in front of or from behind the flame, to the collision or overtaking of wave and flame or wave and wave, or to the collision of a wave with an obstruction or the closed end of the tube.

L. L. B.

Combustion of hydrocarbons. I. Influence of molecular structure on hydrocarbon combustion. II. Absorption spectra and chemical properties of intermediates. A. R. UBBELOHDE (Proc. Roy. Soc., 1935, A, 152, 354—378, 378—402).—I. Theoretical. A review is made of methods which have been adopted to investigate the combustion of hydrocarbons. The chemical identification of intermediates of oxidation, reaction kinetics, chemiluminescence and emission spectra, the induction period and wall effects, the action of positive and negative catalysts, and the behaviour of isomerides and of substituted hydrocarbons are discussed. The probable importance of vibrational energy, particularly at low temp., is verified, using simple mol. models, and a mechanism for the combustion of the longer-chain hydrocarbons is suggested. This involves a mechanism of chain-branching which accounts for special phenomena observed in the low-temp. region of combustion. Evidence in support of this is obtained from the oxidation of hydrocarbon mols. sufficiently long to permit ring-closure.

II. A study has been made of all the compounds with characteristic absorption spectra which might arise in slow combustion, and of the influence of certain catalysts, such as NO_2 , on the slow combustion of hydrocarbons. The absorption spectra and slow combustion of ring compounds including one O atom have been investigated in an attempt to discover the origin of the band X arising in the slow combustion of the higher hydrocarbons. Since this first appears for C_4H_{10} , it would seem to depend on ring formation of some kind. The conclusion is reached that the formation of O ring compounds is of importance in elucidating the oxidation mechanism of the higher paraffins at low temp. It is suggested that the formation of saturated O rings, such as methyltetrahydrofuran, corresponds with an internal oxidation by the energy-rich peroxide, $\text{Me}[\text{CH}_2]_4\text{OOH} \rightarrow \text{CHMe} \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{matrix} + \text{H}_2\text{O}$, and that the formation of unsaturated O rings occurs when a similar process

takes place with an energy-rich peroxide radical, $\text{Me}[\text{CH}_2]_4\text{O}_2 \rightarrow \text{OH}\cdot\text{CH}\left\langle \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{O}-\text{CH}_2 \end{array} \right\rangle \text{CH}_2 + \text{H}\cdot$. These two compounds are the only ones the presence of which has been definitely indicated, but other modes of ring-closure are not excluded. The formation of peroxides which combine the properties of an olefine and an alkoxy-peroxide is probably due to the peroxidation of unsaturated O ring compounds, since the vinyl ether peroxides which would be formed have the required behaviour. The formation of a substance X with intense absorption band is probably due to the decomp. of a peroxide first formed. Its structure may resemble that of ascorbic acid. L. L. B.

Thermal decomposition of silane. T. R. HOGNES, T. L. WILSON, and W. C. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 108—112).—Determinations at 380—490° over a considerable pressure range show the reaction to be of the first order. The H_2 produced inhibits the decomp.; this does not appear to be due to adsorption of H_2 by Si, and there is no evidence of reaction between Si and H_2 to form SiH_4 . The mechanism of decomp. is discussed. E. S. H.

Thermal decomposition of tert.-butyl and tert.-amyl chlorides, gaseous homogeneous unimolecular reactions. D. BREARLEY, G. B. KISTIAKOWSKY, and C. H. STAUFFER (J. Amer. Chem. Soc., 1936, 58, 43—47).—The reactions have been investigated at 543—645° abs. The activation energies are 45,000±1900 and 46,200±700 g.-cal., respectively; the rate expressions are $k=1.9 \times 10^{14} e^{-46,000/RT}$ sec.⁻¹ and $k=4.5 \times 10^{14} e^{-46,000/RT}$ sec.⁻¹ if the activation energies are regarded as identical. The data are compared with those for the corresponding alcohols. E. S. H.

Thermal decomposition of silver oxalate. J. Y. MACDONALD (Nature, 1936, 137, 152—153).—The rate at which $\text{Ag}_2\text{C}_2\text{O}_4$ decomposes with a rise in temp. \propto the concn. of the original solutions and the relative amounts of the reacting substances, AgNO_3 and $\text{Na}_2\text{C}_2\text{O}_4$. A complex mechanism, which disagrees with the conclusions of Benton *et al.* (this vol., 37), is discussed. L. S. T.

Relative rates of ozonisation of unsaturated compounds.—See this vol., 313.

Carbon dioxide cleavage from dibromomalonic acid. II. (Miss) J. MUUS (J. Physical Chem., 1936, 43, 121—124).—The rate at which $\text{CBr}_2(\text{CO}_2\text{H})_2$ gives up CO_2 at 25° (A., 1935, 709) is also the approx. rate at which it can simultaneously take up Br. A fraction only of the acid reacts with Br and this fraction is independent of [Br] within a large range. It is suggested that an intermediate unsaturated compound is formed on CO_2 cleavage (cf. Pedersen, A., 1934, 737). This may either lead directly to $\text{CHBr}_2\cdot\text{CO}_2\text{H}$ or form a compound reacting with Br to give $\text{CBr}_3\cdot\text{CO}_2\text{H}$. M. S. B.

Highly polymerised compounds. CXXII. Relation between reaction velocity and composition of product of reaction in macropolymerisation processes. G. V. SCHULZ (Z. physikal. Chem., 1935, B, 30, 379—398).—The distribution of mol. wts. in a mixture of polymeride-homologues

has been calc. statistically, assuming that the homologues are built up by chain reactions. The no. of mols. of the degree of polymerisation $P \propto \alpha^P$, where $\alpha=1-k$ (k =ratio of the velocity of the chain-breaking reaction to that of the polymerisation reaction) and is < 1 , but the proportion of such mols. by wt. $\propto P\alpha^P$ and thus passes through a max., the val. of P at which is equal to the mean degree of polymerisation, \bar{P} (1 base-mol. of the mixture contains $1/\bar{P}$ g.-mols.). For an unfractionated polymerisate the val. of \bar{P} determined from the viscosity by Staudinger's law is twice the true val. The above deductions have been confirmed by fractionation of a mixture of polymerised isobutylenes. R. C.

Polymerides and polyfunctionality. W. H. CAROTHERS (Trans. Faraday Soc., 1936, 32, 39—49).—Polymerisations do not conform to a single reaction type (*e.g.*, opening of double linkings), but are to be regarded as intermol. combinations functionally capable of indefinite continuation in one or more dimensions. If f =no. of reactive functions per monomeric mol., then if $f=2$, only linear polymerides can be formed, whereas for any higher val. of f growth may be in two or three dimensions. In general, the extent of reaction (*i.e.*, fraction of original reactive functions lost) $= 2/f - 2/xf$, where x =average degree of polymerisation. Attention is directed to the importance of the distribution of mol. wt., and not merely its average val., in determining the properties of a polymerisation product. F. L. U.

Mechanism of polymerisation. H. DOSTAL and H. MARK (Trans. Faraday Soc., 1936, 32, 54—69).—Polymerisation of unsaturated compounds, not involving condensation, proceeds in two stages, of which the first is the formation of "nuclei" *e.g.*, by collision of two monomeric mols., requires an activation, and may be unimol. or bimol. The second stage, rapid compared with the first, is the growth of chains which may occur and be modified in a variety of ways. Formulae consistent with the mechanism suggested are derived for the reaction velocity. Quant. agreement with experiment is obtained in the case of $\text{CHPh}\cdot\text{CH}_2$. F. L. U.

Kinetics of long-chain disintegration applied to cellulose and starch. K. FREUDENBERG (Trans. Faraday Soc., 1936, 32, 74—75).—Velocity coeffs. (K) of hydrolysis of cello-biose (I), -triose (II), -tetraose (III), and cellulose (IV), and of maltose and starch are given. The vals. of K for (II) and (III) lie between those for (I) and (IV), indicating a continuous sequence from biose to polysaccharide. Heats of activation and steric factors are calc. F. L. U.

Highly polymerised compounds. CXX. Formation of high polymerides of unsaturated substances. H. STAUDINGER (Trans. Faraday Soc., 1936, 32, 97—115; cf. A., 1935, 1319).—A general review of the conditions of formation and the properties of synthetic polymerides is given. In polymerisations not involving condensation a chain mechanism originating in an activated monomeric mol. is best in accord with experimental observations. The physical and colloidal properties of homopolar

polymerides are determined by chain length and are independent of chemical composition. Measurement of the sp. viscosity of dil. solutions of polymerides as a method of determining chain length is valid even for the most highly polymerised substances, but as a measure of mol. wt. only when the chains are unbranched and cross-linkings are absent.

F. L. U.

Kinetics of ring formation and polymerisation in solution. G. SALOMON (Trans. Faraday Soc., 1936, 32, 153—175).—In condensation of substances of the type of $\text{Br} \cdot [\text{CH}_2]_x \cdot \text{NH}_2$ intramol. ring-closure is greatly influenced by the chain length but is nearly independent of the concn., whereas intermol. polymerisation, largely independent of chain length, is affected by the solvent which is a sp. factor in the reaction velocity. A theory of ring-closure by the interaction of terminal groups is advanced, and supported by analysis of kinetic measurements in different solvents, for $x=3-17$.

F. L. U.

Kinetics of polymerisation reactions. C. E. H. BAWN (Trans. Faraday Soc., 1936, 32, 178—183; cf. preceding abstract).—The transition state method, applied to the calculation of reaction velocities, leads to a simple interpretation of the steric factor of bimol. association reactions in terms of the probability of the transition state. Assuming a chain mechanism, the degree of polymerisation is shown to be determined by the magnitude of the steric factor, which is calc. for some simple reactions. F. L. U.

Kinetics of polymerisation of Δ^2 -butadiene in presence of metallic sodium. A. ABKIN and S. MEDVEDEV (Trans. Faraday Soc., 1936, 32, 286—295).—Polymerisation of $(\text{CH}_2 \cdot \text{CH} \cdot)_2$ in presence of Na takes place in both the gaseous and the liquid phase. The reaction is heterogeneous and its rate, at a given pressure, is the same in both phases. An initial period of acceleration is followed by reaction at a const. rate, the former being connected with the formation of primary compounds with Na. Polymerisation proceeds by the successive addition of monomeric mols. to the Na compounds. The inhibiting effect of O_2 has been studied. Experiments were done at 30—35°.

F. L. U.

Kinetic consequences of complex formation in solution. E. A. MOELWYN-HUGHES and A. SHERMAN (J.C.S., 1936, 101—110).—Theoretical. The solvent is responsible for differences between kinetics of reaction in the gas phase and in solution, and the effect is, in general, electrostatic in origin. For convenience, reactions in solution involving other than the rupture or formation of homopolar linkings in non-ionised mols. are divided into the following types: (i) ion-ion, (ii) dipole-dipole, (iii) dipole-induced dipole, (iv) ion-induced dipole, and (v) ion-permanent dipole. The Debye-Hückel expression refers only to interionic attractions, whereas the so-called ionic reactions, in the kinetic study of which the expression has been extensively applied, usually involve interaction between an ion and a dipole as well. Interaction between two mols. with permanent dipoles probably accounts for the existence of several intermol. complexes, and the low velocity of certain

bimol. reactions is attributed to interaction of either dipolar reactant with the solvent. Certain catalytic effects, e.g., AlCl_3 in the Friedel-Crafts reaction, and the existence of hydrates of CH_4 and the rare gases are traced to the interaction of a permanent dipole with an induced dipole. The solvation of ions and the formation of cryst. hydrates imply an ion-permanent dipole interaction, the relation of which to the co-ordinate linking is discussed. J. G. A. G.

Hydrolysis of aryl sulphuric acids. I. G. N. BURKHARDT, W. G. K. FORD, and E. SINGLETON. II. **Kinetic considerations.** G. N. BURKHARDT, A. G. EVANS, and E. WARHURST (J.C.S., 1936, 17—25, 25—26).—I. The hydrolysis by aq. HCl of $\text{X} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{SO}_3\text{K}$, where $\text{X} = o-, m-, p-\text{NO}_2, -\text{Cl}, -\text{Br}, -\text{Me},$ and $-\text{OMe}$, at 48.6° and 78.7° is of first order with respect to aryl sulphate and partly autocatalytic owing to the increase of $[\text{H}^+]$ due to partial dissociation of HSO_4^- formed in the hydrolysis. The SO_4 group is most readily hydrolysed when attached to a position of low electron availability. The logarithms of the velocity coeff. for the $m-$ and $p-$ compounds give a straight-line relation of the type previously described (A., 1935, 1465). Existing data show that the linear relationship is of wide application in the case of $m-$ and $p-$ substituted compounds and is valid for some series of $o-$ derivatives. In terms of the transition-state conception, the influence of substituents on the free-energy changes associated with the equilibria between the initial and transition states, in the reactions considered in respect of velocity, \propto their influence on the free-energy changes between the initial and final states in corresponding dissociations.

II. The acid hydrolysis of $\text{C}_6\text{H}_4\text{Me} \cdot \text{O} \cdot \text{SO}_3\text{K}$ is not catalysed by HSO_4^- . J. G. A. G.

Elimination of chlorine in the hydrolysis of aqueous solutions of chloroacetic acid and chloroacetates. H. M. DAWSON and E. R. PYCOCK (J.C.S., 1936, 153—158; cf. A., 1933, 1125; 1934, 848).—Measurements at 25° and 45° of the initial velocity of hydrolysis of the $\text{CH}_2\text{Cl} \cdot \text{CO}_2$ group, A , in solutions containing (i) undissociated mols. only, (ii) ions only, and (iii) mols. and ions, show that the reaction is, in general, the sum of four independent processes represented by $v = k_1[A'] + k_2[A']^2 + k_3[\text{HA}] + k_4[\text{HA}][A']$. Collisions involving H^+ and those between HA mols. are not measurably effective. At high $[\text{HA}]$, and in presence of much HNO_3 and HClO_4 , v falls below the calc. val. probably owing to a decrease in k_3 . k_1 and k_3 probably relate to bimol. processes involving the H_2O mol., and the relative bimol. velocity coeffs. of the processes at 45° are: mol- H_2O 1, ion- H_2O 1.22, ion-ion 228, mol.-ion 880.

J. G. A. G.

Kinetics of the reaction between α -bromopropionate and silver ions. A. N. KAPPANNA (Proc. Indian Acad. Sci., 1935, 2, A, 512—524).—The hydrolysis of aq. $\text{C}_2\text{H}_4\text{Br} \cdot \text{CO}_2\text{Na}$ is a very slow reaction. The reaction with aq. AgNO_3 at 27° occurs at the surface of AgBr particles. The rate in dil. solution \propto the concn. of each of the reactants, showing the latter to be weakly adsorbed on the catalyst surface. In dil. solutions the rate \propto the amount of suspended AgBr . H. J. E.

Kinetics of the synthesis of ketones by Friedel and Crafts' method. S. C. J. OLIVIER (Rec. trav. chim., 1935, 54, 943—944).—The conclusions of Ulich and Heyne (A., 1935, 1207) were anticipated by the author (A., 1918, i, 228), but no irregularities in the reaction const. were observed. J. W. S.

Kinetics of gaseous Diels-Alder reactions. G. B. KISTIAKOWSKY and J. R. LACHER (J. Amer. Chem. Soc., 1936, 58, 123—133).—Rate coeffs. have been determined as follows: acraldehyde and cyclopentadiene, $k=1.50 \times 10^9 e^{-15.200/RT}$; acraldehyde and isoprene, $k=1.02 \times 10^9 e^{-18.700/RT}$; acraldehyde and butadiene, $k=1.46 \times 10^9 e^{-19.700/RT}$; crotonaldehyde and butadiene, $k=0.90 \times 10^9 e^{-22.000/RT}$. The reactions are of the second order, homogeneous, and only slightly complicated by side reactions. The product of the first of the above reactions, endomethylenetetrahydrobenzaldehyde (A., 1928, 1019), is unstable at elevated temp.: the rate of decomp. is given by $k=2.2 \times 10^{12} e^{-33.600/RT}$. E. S. H.

Constitution and reactivity. XV. Kinetics of the nitration of aromatic compounds in sulphuric acid. K. LAUER and R. ODA (J. pr. Chem., 1936, [ii], 144, 176—192; cf. A., 1935, 1465).—The rate of nitration of anthraquinone (I) by HNO_3 or KNO_3 , measured in 87—100% H_2SO_4 at 15°, 20°, and 25°, is a max. in 89% H_2SO_4 . Q is about 21,750 g.-cal. for HNO_3 and 5 nitrates in 87—95.6% H_2SO_4 , but only 13,300 for KNO_3 in 100% H_2SO_4 . The "action const." varies with the concn. of the acid, being a min. for 87% acid, and is thus responsible for the variation in k . The rate of nitration is affected by the nature of the cation in the order, $\text{H} < \text{NH}_4 < \text{K} < \text{Na} < \text{Ag} < \text{Li}$, which is also the order of relative ease of formation of pyrosulphates. Cations thus act by removal of free SO_3 to form pyrosulphate with consequent diminution in $[\text{H}_2\text{SO}_4]$. Martensen's data for PhNO_2 (A., 1905, ii, 149) lead to similar results. Nitration in aq. H_2SO_4 is considered to be due to $\text{OH}\cdot\text{NO}_2$, but in 100% H_2SO_4 mainly to $[\text{N}(\text{OH})_3]^{+}$. H_2SO_4 containing 3—5% of SO_3 causes sulphonation of (I) in presence, but not in absence, of KNO_3 ; reaction is due to addition of $[\text{N}(\text{OH})_3]^{+}$ to the α -C and of $[\text{HSO}_4]^{-}$ to the β -C, with subsequent elimination of HNO_3 and H_2O . m -Nitration of PhNO_2 is due to $\text{OH}\cdot\text{NO}_2$, and o - p -nitration to $[\text{N}(\text{OH})_3]^{+}$, as is shown by increase in the latter for PhNO_2 from 11.7% in 90% H_2SO_4 to 13.8% in 100% H_2SO_4 . R. S. C.

Benzoin reaction. IV. Kinetics of the benzoin reaction in presence of organic solvents. P. S. REGE and T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 483—489; cf. A., 1935, 938, 1084, 1329).—Inert org. solvents (*e.g.*, C_6H_6 , C_5H_{12} , CCl_4) when added to a mixture of solid KCN and PhCHO cause pptn. of part of the dissolved KCN, and so retard the homogeneous autocatalytic reaction. They do not affect the heterogeneous reaction. OH-compounds [*e.g.*, MeOH , $(\text{CH}_2\cdot\text{OH})_2$] accelerate the reaction, the effect increasing with the no. of OH groups in the mol. H. J. E.

Determination of linear crystallisation velocity. T. FÖRSTER (Z. physikal. Chem., 1935, 175,

177—186).—In the usual method of determining the crystallisation velocity, v , of a non-metallic substance in a tube the temp. of the solid-liquid interface rises with the distance from the wall. This is responsible for the presence on the graph of v against amount of supercooling of a portion of const. v , followed by an abrupt fall, whilst the true curve must exhibit a sharp max. A method of determining the true form of the curve is described. R. C.

Atmospheric corrosion of metals. Iron. I, II.—Sec B., 1936, 150.

Kinetics of reactions in heterogeneous systems. I. Reaction between carbon disulphide and alkali. II. Reaction between benzoyl chloride and water. D. KARVÉ and K. K. DOLÉ (J. Indian Chem. Soc., 1935, 12, 719—732, 733—739).—I. The influence of speed of shaking, temp., amount and concn. of alkali solution, and amount and concn. of CS_2 alone and in petroleum, light petroleum, PhMe , xylene, PhCl , and PhBr has been studied. Reaction occurs chiefly in the homogeneous aq. phase and to a smaller extent heterogeneously. The rate is increased by addition of H_2O_2 , but decreases with additions of NaCl , and does not follow a simple kinetic law.

II. The reaction is purely heterogeneous and the velocity is increased by shaking. Solutions of BzCl in CCl_4 , xylene, CS_2 , PhCl , PhBr , and CHCl_3 react according to a unimol. law and with velocities which decrease in the order named. R. S.

Hydrolysis rates of some monoacid triglycerides under the influence of pancreas extract. I. Influence of the fineness of division of the triglyceride on the hydrolysis rate. K. HOLWERDA, P. E. VERKADE, and A. H. A. DE WILLIGEN (Rec. trav. chim., 1936, 55, 43—57).—Detailed examination of the heterogeneous system triglyceride-pancreas extract has yielded reaction rates which are greatly influenced by the fineness of division of the triglyceride and the relative amounts of the phases. A method for obtaining uniform results has been worked out. E. E. A.

Theory of proton transfer. J. HORIUTI and M. POLANYI (Acta Physicochim. U.R.S.S., 1935, 2, 505—532).—The authors' theory of ionogenic reactions (cf. A., 1934, 1185) is extended to reactions involving proton transfer, viz., electrolytic dissociation of acids (proton donors), prototropy, spontaneous ionisation and separation of H at electrodes, and H-ion catalysis. The order of magnitude of the activation energy of the first three processes, the relation between electrolytic dissociation const. of acids and bases and their catalytic activity, and the Tafel relationship for H overvoltage, are all derived from the theory. The order of magnitude of the catalytic activity of H ions is explained. O. J. W.

Factors governing the formation of nitric acid in the course of combustion of organic substances under a high pressure of oxygen. L. KEFFLER (J. Chim. phys., 1935, 32, 741—749).—The quantity of HNO_3 produced during org. combustions in the bomb calorimeter \propto the rise in temp. in the bomb and the pressure. It increases with

increasing $[N_2] : [O_2]$ ratio in the bomb, but there is evidence that the HNO_3 first formed tends to oppose the further oxidation of N_2 . The results also indicate that there is a negative catalyst for the reaction present in cylinder O_2 , and that its concn. increases as the pressure in the cylinder decreases.

J. W. S.

Polymerisation of gaseous formaldehyde and acetaldehyde. J. E. CARRUTHERS and R. G. W. NORRISH (Trans. Faraday Soc., 1936, 32, 195—208).—Polymerisation of gaseous CH_2O is promoted by HCO_2H vapour. The reaction occurs only on the walls of the vessel, and is complete at 18° . At higher temp. depolymerisation takes place simultaneously and leads to an equilibrium, whilst if the whole vessel is at 100° only the monomeric form can be detected. Polymerisation is bimol. with reference to the CH_2O ; that of $MeCHO$ vapour is also promoted by HCO_2H but not by $AcOH$, and that of CH_2O is promoted by $AcOH$. With $(-CHO)_2$ and HCO_2H reaction does not go beyond the formation of an additive compound. The results are explained by a branching chain mechanism in which the HCO_2H is responsible for both initiation and branching. The ease with which depolymerisation occurs indicates that the simple mols. are linked through O. The results support Staudinger's theory of the catalysis.

F. L. U.

Acid-catalysed enolisation of sec.-butyl ketones.—See this vol., 317.

Kinetics of Friedel-Crafts reaction and activity of mixed catalysts.—See this vol., 322.

Enzymic hydrolysis of glucosides in heavy water.—See this vol., 377.

Adsorption and heterogeneous catalysis. E. C. C. BALY (J.S.C.I., 1936, 55, 9—12T).—The equations already developed (A., 1935, 1084) are extended to cases involving supported catalysts. On certain assumptions, the reaction velocity is a function of one half of the total energy of activation of the reaction. A supported catalyst has a max. efficiency when of a sp. composition, e.g., a unimol. layer of $Al(OH)_3$ on kieselguhr (I), or a termol. layer of NiO or CoO on (I) (cf. A., 1935, 1070). The structure of these surfaces is discussed.

J. G. A. G.

Polymerisation in monolayers. G. GEE (Trans. Faraday Soc., 1936, 32, 187—195).—Changes occurring during the "drying" of the compound of β -elæostearin with maleic anhydride have been followed by measuring the surface pressures at different areas per mol. of a unimol. film on $0.01N-H_2SO_4$. The initial reaction gives rise to an unstable peroxide which may polymerise either directly or after transformation into a more stable form, according to the experimental conditions. The velocity curves indicate that polymerisation proceeds by a chain mechanism in which the chains are terminated by a steric factor. Addition of inert substances like $Me \cdot [CH_2]_{13} \cdot CO_2Et$ to the film inhibits polymerisation by breaking the chains, but does not affect the oxidation. The polymerisation stage is also accelerated by $CoSO_4$, and retarded by quinol. Activation energies are calc.

F. L. U.

Polymerisation of phosphorus. H. W. MELVILLE and S. C. GRAY (Trans. Faraday Soc., 1936, 32, 271—285).— P_4 mols. dissociate to P_2 when passed through a SiO_2 -glass jet at $500-800^\circ$, or by contact with a hot W filament. If P_2 thus formed is condensed under such conditions that it cannot combine to P_4 , the product is red P. The kinetics of dissociation on hot W have been studied in detail. It is shown that only P_2 mols. are in equilibrium with red P, and that discrepancies in the thermal data regarding the interconversion of red and white P are removed by taking into account the thermal change accompanying the dissociation $P_4 \rightleftharpoons 2P_2$.

F. L. U.

Change of magnetic and catalytic properties during the transformation of a mixture of calcium oxide and ferric oxide into calcium ferrite. G. F. HÜTTIG, J. FUNKE, and H. KITTEL (J. Amer. Chem. Soc., 1935, 57, 2470—2477).—Products obtained by heating $CaO + Fe_2O_3$ and $CaCO_3 + Fe_2O_3$ in mol. ratio at different high temp. under varying conditions have been investigated with regard to catalytic activity in the decomp. of N_2O , magnetic susceptibility, powder d , colour, and CO_2 content. The heat of activation and no. of active centres are given for each product. An "active intermediate," which no longer possesses the properties of the original mixture nor those of the cryst. $CaFe_2O_4$, is formed. The most active samples contain up to 60% of the intermediate, which has a magnetic susceptibility of 51.5×10^{-6} and heat of activation (for decomp. of N_2O) of 20,000—25,000 g.-cal. The intermediate is formed as a film at the surface of the particles.

E. S. H.

Platinum catalysts on metallic carriers.—See B., 1936, 101.

System vanadic acid-cupric oxide-silicic acid as catalyst in the formation of sulphuric acid.—See B., 1936, 144.

Is sintering the cause of inactivation of barium-vanadium catalysts?—See B., 1936, 101.

Catalytic air-oxidation of petroleum in the vapour phase.—See B., 1936, 83.

Catalytic hydrogenation of phenolic oil in low-temperature tar. II.—See B., 1936, 132.

Condensation of benzyl chloride and benzene.—See B., 1936, 138.

Ternary catalyst $Cu-ZnO-Cr_2O_3$ as a hydrogenation catalyst. S. S. BALIASNI (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 175—182).—Reduction of $COPhMe$ to $PhEt$ is catalysed more efficiently by Ni than by $91.8 : 6.5 : 1.7$ $Cu-Zn-Cr_2O_3$ at 250° , whilst at $284-289^\circ$ the latter catalyst has no hydrogenating activity.

R. T.

Decompositions of esters and acids by anhydrous zinc chloride.—See this vol., 313.

Electrolytic preparation of deuterium and the separation coefficient α . M. P. APPLEBEY and G. OGDEN (J.C.S., 1936, 163—168).—The large discrepancy between the observed and the theoretical vals. of α ($= [D_2]$ in gas/ $[D_2]$ in liquid phase) is discussed, and the following principles are adopted in the design

of cells for producing D_2O : (a) the electrode metal must be a poor catalyst for the exchange reactions, (b) the H_2 evolved must be removed rapidly from the electrode surface, and (c) local concn. of D_2O at the electrode must be avoided. With very low $[D_2O]$, vals. of $\alpha \ll$ the calc. vals. (0.05—0.10) were obtained, but this is not necessarily a proof that quantum-mechanical leakage is an important factor in the difference of reactivity of H and D atoms, since the observed val. of α is controlled by the uncertain val. of $[D]$ in standard H_2O . J. G. A. G.

Direct introduction of deuterium into benzene by high-frequency current. J. HORIUTI and T. KOYANO (Bull. Chem. Soc. Japan, 1935, 10, 601).—Pure C_6H_6 in presence of 8% D_2O and Pt-black after standing on a pole of a Tesla coil for 10 hr. at room temp. acquired a D content of 0.69%; no change in temp. occurred. In a second experiment the pure C_6H_6 was kept between the poles of a high-frequency oscillator of λ 4 m., and was cooled, the % of D rising from 0 to 0.41. C_6H_6 similarly treated with ordinary H_2O gave no change in d and f.p. No exchange occurred at room temp., even with an oscillator, unless a catalyst was present. R. S. B.

Preparation of oxygen by electrolysis of baryta. E. M. STODDART (Proc. Roy. Soc., 1935, A, 152, 273—277).—Electrolysis of $Ba(OH)_2$, using Ni electrodes, does not always give pure O_2 at the anode. After some time H_2 is liberated as well, probably owing to the reaction $OH + OH = H_2 + O_2$. This can be prevented by coating the anode with a layer of $Ni(OH)_2$. L. L. B.

Influence of small amounts of agar-agar and gelatin on the KG_1 of the anode deposit of silver peroxide. A. GLAZUNOV and K. VALEČKA (Chem. Listy, 1935, 29, 359—361).—The velocity of crystallisation of Ag_2O_2 at the anode in electrolysis of $AgNO_3$ falls with increasing concn. of agar-agar or gelatin from 0 to 0.15%. R. T.

Spectroscopic studies of luminescence at cathode during electrolysis. I. UHARA (Bull. Chem. Soc. Japan, 1935, 10, 559—563).—The spectrum of the luminescence at a Pt wire cathode on electrolysis of 1—3*N*-salt or -acid solutions shows lines identical with those of the arc, and in some cases the spark, spectra of the metals forming cations. The lines of H and H_2 are observed, but anions have no influence on spectra. It is suggested that no luminescence occurs until the c.d. is sufficient to form a film of H on the cathode. The metals which give insol. hydroxide and consequent disappearance of the luminescence with d.c. give prolonged luminescence with 100 volts a.c. R. S. B.

Electrolytic manufacture of aluminium-magnesium alloys.—See B., 1936, 151.

Electrodeposition of bronze.—See B., 1936, 151.

Electrodeposition of zinc and cadmium on aluminium and aluminium alloys.—See B., 1936, 151.

Electrodeposition of cadmium.—See B., 1936, 152.

Hardness of electrolytic chromium. II.—See B., 1936, 152.

Effect of imprisonment of resonance radiation in the decomposition of ammonia and of deuterio-ammonia. H. W. MELVILLE (Proc. Roy. Soc., 1935, A, 152, 325—341; cf. A., 1934, 1078, 1183).—Velocity coeffs. in Hg-photosensitised reactions are usually determined by comparison with the mean life of the $3P_1$ Hg atom, which is assumed to be const. At high Hg-vapour pressures, however, at which experiments are usually made, there is appreciable imprisonment of resonance radiation with the result that the effective mean life is much $>$ its actual val. of 10^{-7} sec. A re-examination of the Hg-photosensitised decomp. of NH_3 , ND_3 , PH_3 , and PD_3 , under conditions where reabsorption is negligible, leads to lower velocity coeffs., in agreement with expectation. It is suggested that the decomp. of NH_3 and ND_3 are brought about in collisions between NH_3 (ND_3) and metastable atoms, derived from quenching collisions between $3P_1$ atoms and NH_3 (ND_3). The former collisions are equally efficient for NH_3 and ND_3 . To account for the greater reactivity of NH_3 , secondary reactions, unconnected with Hg atom processes, are assumed to occur. The suggested mechanism is supported by the fact that in the direct photo-decomp. NH_3 also reacts more quickly, and that the decomp. of ND_3 is more susceptible to inhibition by D than is that of NH_3 by H. L. L. B.

Mathematical representation of photographic blackening curves deduced from the coagulation theory of latent images and using the fundamental hypothesis of Bose-Einstein statistics. G. UNGAR (Z. Physik, 1936, 98, 517—533).—The equation deduced permits closer correlation of blackening with properties of the emulsion. A. B. D. C.

Mercury-photosensitised polymerisation of acetylene. H. W. MELVILLE (Trans. Faraday Soc., 1936, 32, 258—271).—Kinetic analysis of results obtained in polymerising C_2H_2 by light from a quartz-Hg lamp in presence of Hg vapour (pressure \approx 0.0003 mm.) indicates that excited Hg atoms form with a C_2H_2 mol. a complex which then adds on more C_2H_2 mols. by a chain mechanism. The chain length is independent of the C_2H_2 pressure, of surface, and of the rate at which chains are started, and exhibits a max. (100) at 250°. Cessation of growth is due to collision between a C_2H_2 mol. and the growing polymeride, but of a different kind from that causing propagation. The pressure and temp. ranges were 0.05—10 mm. and 20—500°. Polymerisation of C_2H_4 also occurs under the same conditions, but is preceded by formation of C_2H_2 and H_2 , the final product being partly hydrogenated. F. L. U.

Explanation of the course of photolysis of fructose in quartz light using long-wave ultra-violet light. R. CANTIENI (Helv. Chim. Acta, 1936, 19, 86—93).—In long-wave ultra-violet light (glass-filtered quartz light) fructose with the ketone structure decomposes with the evolution of CO, whilst, simultaneously, the ring structure in equilibrium gives CO_2 . In long- and short-wave ultra-violet

light (unfiltered quartz light) H_2 is obtained in addition, but polarimetric measurements also indicate that some of the fructose undergoes change without any evolution of gas. M. S. B.

Connexion between decomposition velocity and concentration of fructose in long-wave ultra-violet light. R. CANTIENI (Helv. Chim. Acta, 1936, 19, 94—96; cf. preceding abstract).—The rate of decomp. of fructose by long-wave ultra-violet light, as measured by gas evolution, reaches a max. for a fructose concn. of 150 g. per 100 c.c. of H_2O . Above this concn. the rate of decomp. remains const., at least up to 200 g. per 100 c.c. of H_2O . The gas evolution from such a solution is approx. half that from an equal vol. of solution of concn. 1 : 10 irradiated by unfiltered quartz light. M. S. B.

Acidity and yellow coloration of fructose at higher temperatures in quartz light. R. CANTIENI (Helv. Chim. Acta, 1936, 19, 96—98).—The acid formation which takes place in fructose solution under the influence of ultra-violet light, and more rapidly at shorter λ , is probably due to HCO_2H formed by the oxidation of the CH_2O proved to be produced by ultra-violet light. The yellow coloration is due to a dark reaction accelerated by the presence of acid and requiring the addition of light energy into heat. M. S. B.

Influence of solvent on the course of chemical reactions. I. Absorption spectrum of anthracene in various solvents. K. LAUER and M. HORIO. II. Photochemical reaction, anthracene \rightleftharpoons dianthracene, in various solvents. III. Kinetics of bromination of anthracene in various solvents. IV. Changes in energy of activation and action constants in substitution reactions of organic compounds as effect of solvent. K. LAUER and R. ODA (Ber., 1936, 69, [B], 130—137, 137—140, 141—145, 146—148).—I. Examination of the absorption spectrum of anthracene in hexane (I), cyclohexane (II), cyclohexene (III), C_6H_6 , EtOH, and AcOH shows that solvents containing double linkings cause displacement of the absorption max. of dissolved aromatic compounds without dipole character or polar groups towards the region of longer λ . Dipolar solvents have so little effect on these solutes that the displacements are within the limits of experimental error. Solvents with double linkings but without dipole act on polar mols. in such a manner that the spectrum proper to the polar group and that due to the aromatic portion of the solute is displaced towards the longer λ . Dipolar solvents have a greater influence than dipole-free solvents on that part of the spectrum due to the dipole of the solute and a less, though distinct, influence on the aromatic portion of the spectrum. The displacements are always in the same sense as those caused by the linear anellation of C_6H_6 nuclei to C_6H_6 .

II. The rate of the photochemical reaction, anthracene \rightleftharpoons dianthracene, has been determined in (I), (II), (III), C_6H_6 , EtOH, and AcOH. Within the limits of experimental error it has the same val. in (I), (II), (III), and EtOH, but is considerably

higher in AcOH and particularly in C_6H_6 . The photo-reaction is parallel to the displacement of the absorption spectra, and double linkings in the solvent have a distinct, accelerating action on the change.

III. Bromination of anthracene in (I) or (II) takes place relatively slowly and at about the same rate in each solvent. In C_6H_6 and EtOH it is equally rapid at 10° , but about twice as fast in EtOH as in C_6H_6 at 15° . In (I), (II), and C_6H_6 (dipole-free solvents) the change occurs with a uniform energy of activation (about 6800 g.-cal.) and the greater rate in C_6H_6 is due to the higher action const. In EtOH and AcOH the energies of activation are 18,600 g.-cal. and 10,850 g.-cal., respectively, and the action consts. are considerably higher, hence the greater rate of change.

IV. The heat of dissolution of Br in (I), AcOH, and EtOH, respectively, is determined at dilutions and temp. similar to those used in the bromination of anthracene. These vals. subtracted from the heats of activation gave a very nearly const. val. which is regarded as the energy val. of the action, anthracene-Br, in the absence of solvent. It is considered that the solvent without dipole exerts an "impact action" which affects the no. of successful collisions of the reacting mols.; whether this is a numerical or spatial action remains undecided. Dipolar solvents, in addition to this action, cause also a change in the heat of activation of the subsequent reaction due to alteration in the energy conditions on dissolution of the reaction partner ("energy action"). H. W.

Photochemical stability of crotonaldehyde. F. E. BLACET and J. G. ROOF (J. Amer. Chem. Soc., 1936, 58, 73—75).—Although ultra-violet light is absorbed by the vapour phase, no decomp. or appreciable polymerisation was observed. The concept of a predominating reverse reaction is put forward as an explanation. E. S. H.

Photochemical decomposition of nitrated phenols. J. MOLNAR (Compt. rend., 1935, 201, 1482—1484).—At $p_H > 13.0$ picric acid is decomposed in ultra-violet light to give picramic and isopurpuric acids, HNO_2 , NH_3 , and HCN, whilst the usual yellow form existing at $p_H < 13.0$ is unaffected. An analogous reaction occurs with 2 : 5-OH- $C_6H_3(NO_2)_2$, *o*- and *p*- NO_2 - C_6H_4 -OH, 2 : 4- and 2 : 6-OH- $C_6H_3(NO_2)_2$, and 2 : 4-dinitro-*o*-cresol decompose at p_H where the red forms exist, the rate of decomp. increasing with p_H . T. G. P.

Catalysed photo-reduction of vat dyes. K. WEBER (Naturwiss., 1935, 23, 849—850).—If a 0.001% aq. solution of thionine (Lauth's violet) (I) containing a small amount of $FeSO_4$ and H_2SO_4 is cooled to 10° and exposed to the light of a powerful arc lamp, the dye is rapidly bleached. The process is reversible. The bleaching takes the longer the higher is the temp. and the weaker the light. Methylene-blue (II), Nile-blue, phenosafranine, and neutral-red, all of which have negative normal reduction potentials, do not behave similarly. (I) has a positive reduction potential. In the case of (II) photo-reduction takes place if the $FeSO_4$ is replaced by $K_4Fe(CN)_6$, which has a more negative reduction potential. The phenomenon can be explained by

supposing that the photo-excited dye mol. F^* has a more positive reduction potential than the unexcited mol. F . The systems F -leuco-base, and F^* -leuco-base are both present. In the dark, Fe^{2+} does not react, but in the light the potential of F^* becomes more positive than that of the Fe^{3+} - Fe^{2+} system, and equilibrium is reached by the formation of leuco-base and Fe^{3+} . The max. of the absorption band of (I) is at 600 $m\mu$, corresponding with an absorption of energy $>$ sufficient for the above change. (II) has a more negative reduction potential than (I) and its absorption max. is at higher λ ; consequently the energy absorbed is in this case insufficient for the reaction to occur. The fact that the photo-reduction does not occur in alkaline solution is explained on similar grounds. A. J. M.

Radiochemical decomposition of deutero-ammonia. J. C. JUNGERS (J. Physical Chem., 1936, 40, 155—158).—The rate of decomp. of ND_3 by α -radiation is $<$ that of NH_3 and also increases more slowly, relatively, with rise of temp. M. S. B.

Action of radioactive substances on proteins. J. LOISELEUR (Compt. rend., 1935, 201, 1511—1513).—Proteins are first hydrolysed, and flocculation follows in the presence of electrolytes. T. G. P.

Heavy hydrogen and heavy water. H. MARK and M. WALD (Protoplasma, 1935, 23, 109—127).—A review.

Production and identification of helium of mass three. W. BLEAKNEY, G. P. HARNWELL, W. W. LOZIER, P. T. SMITH, and H. D. SMYTH (Physical Rev., 1934, [ii], 46, 81—82; cf. this vol., 130).—Evidence for the production of He^3 from D_2 in a mass spectrograph is advanced. The life of the H^3 and He^3 produced is at least 10^8 years. No evidence of the production of He^4 was obtained. Attempts to find He^3 and He^5 in ordinary He were unsuccessful. L. S. T.

Purification and spectroscopic evidence for He^3 . G. P. HARNWELL, H. D. SMYTH, and W. D. URRY (Physical Rev., 1934, [ii], 46, 437).—The purification and isolation of small amounts of He^3 from D_2 circulating in a canal-ray discharge tube are described (cf. preceding abstract). L. S. T.

Preparation of calcium chromate in the wet way. J. MILBAUER and J. DOŠKAŘ (Sborn. Masaryk. Akad. Práce, 1934, 8, 42—59; Chem. Zentr., 1935, i, 3259; cf. B., 1933, 963).—Full details are given. J. S. A.

Common occurrence of trimercury group (HgX_2Hg_2) in complex compounds of mercury (family of turpeths). G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1933, 71, 97—109; Chem. Zentr., 1935, i, 3260).—Basic Hg compounds with 3 atoms of Hg per mol. are referred to a common structural unit $Hg\left\langle \begin{array}{c} X \cdot Hg \\ X \cdot Hg \end{array} \right\rangle A$, where $X=O, S, Se, NH, NR$ or NH_2OH, N_2H_4 , and $CO(NH_2)_2$ residues; $A=Cl_2, Br_2$, or a dibasic acid. The compounds are termed "turpeths" (turpeth mineral, $A=O, X=SO_3$), and the compounds with $X=O, A=(NO_3)_2, SeO_4, TeO_4, (BrO_3)_2, (IO_3)_2, Cl_2$, and Br_2 ; $X=S, A=SO_3, Cl_2$,

$Br_2, F_2, (NO_3)_2, (OAc)_2, (O \cdot COEt)_2, (O \cdot COPr)_2$ are described. J. S. A.

Aluminium carbide, Al_4C_3 , and aluminium carbonitride, Al_5C_3N . M. VON STACKELBERG, E. SCHNORRENBERG, R. PAULUS, and K. F. SPIESS (Z. physikal. Chem., 1935, 175, 127—139).—The compound Al_5C_3N , almost indistinguishable in appearance and properties from Al_4C_3 , is formed by regulated admission of N_2 to a mixture of Al and C at 1800° , being an intermediate product in the nitridation of carbide to nitride, $5Al_4C_3 + 10N_2 = 4Al_5C_3N + 3C + 8N_2 = 20AlN + 15C$. Al_4C_3 takes up at high temp. excess of Al, which separates again on cooling, and the supposed carbides Al_9C_3 and Al_3C_2 (A., 1934, 600) are merely finely disperse mixtures of Al_4C_3 and Al, whilst Al_8C_9 is a mixture of Al and Al_2C_3 . "Amorphous" Al_4C_3 (A., 1933, 917) is identical with the cryst. variety. R. C.

Carbonyl chloride. A. PERRET and R. PERROT (Bull. Soc. d'Encour., 1935, 134, 552—560).—The reactions of $COCl_2$ are summarised and its action on the blood is discussed, especially with reference to the analogy between the effects of $COCl_2$ and of CO. J. W. S.

Colour reaction between nitroprusside and sulphite (Bödeker's reaction). G. SCAGLIARINI (Atti R. Accad. Lincei, 1935, [vi], 22, 155—159).—Treatment of equimol. aq. mixtures of Na nitroprusside and Na_2SO_3 with conc. aq. Zn, Cd, or Ni acetate and $(CH_2)_6N_4$ affords the compounds $(Zn \text{ or } Cd)_2[Fe^{2+}(CN)_5(NO \cdot SO_3)] \cdot 2C_6H_{12}N_4 \cdot 12H_2O$ and $Ni_2[Fe^{2+}(CN)_5(NO \cdot SO_3)] \cdot 2C_6H_{12}N_4 \cdot 8H_2O$ (see A., 1896, i, 197). F. O. H.

Germanium chlorofluorides. H. S. BOOTH and W. C. MORRIS (J. Amer. Chem. Soc., 1936, 58, 90—93).—By reaction of $GeCl_4$ with $SbCl_3$ in presence of $SbCl_5$, there are formed $GeCl_3F$, b.p. $37 \cdot 5^\circ$, m.p. $-49 \cdot 8^\circ$, $GeCl_2F_2$, b.p. $-2 \cdot 8^\circ$, m.p. $-51 \cdot 8^\circ$, $GeClF_3$, b.p. $-20 \cdot 3^\circ$, m.p. $-66 \cdot 2^\circ$, and GeF_4 . The chlorofluorides hydrolyse in moist air more readily than does $GeCl_4$; they are unstable, tending to rearrange to $GeCl_4$ and GeF_4 even at -78° . Under certain conditions they are reduced explosively by Cu to Ge^{II} salts. E. S. H.

Lead ferrites. L. I. PARAMONOV (Tsvet. Metal., 1934, No. 3, 79—88).—Formation of $PbO \cdot Fe_2O_3$ (I) by heating PbO with Fe_2O_3 begins at 665° , and is a max. at 725° . Addition of SiO_2 favours the decomp. of (I). CaO decomposes (I) at 600 — 800° and combines partly with the PbO. CO begins to reduce PbO from (I) at 400° . The reduction is complete at 550° . CH. ABS. (e)

Ammonium salts of arsenic, phosphoric, and antimonie acids, and direct determination of heats of oxidation of arsenic. A. DE PASSILLE (Ann. Chim., 1936, [xi], 5, 83—146).—Full details of the author's prep. of pure As (cf. A., 1934, 742) and work on NH_4 phosphates and arsenates (cf. *ibid.*, 377, 966; 1935, 344, 936) are given. The prep. of $NH_4SbO_3 \cdot 3H_2O$ (I) is described. (I) readily loses H_2O and NH_3 , affording probably $HSbO_3 \cdot 0 \cdot 5NH_3$ at 110° , and Sb_2O_5 at 270° . When As is burned in O_2 at 15—40 atm., the ratio $As_2O_5 : As_2O_3$ increases with $[O_2]$. The heats



of formation from As metal are : As_2O_3 (cubic) 154.7 and As_2O_5 (cubic) 218.3 kg.-cal. J. G. A. G.

Dehydrogenating action of sulphur monoxide. B. S. RAO and M. R. A. RAO (Current Sci., 1935, 4, 406).—On absorption in paraffin or decalin at low temp. SO yielded H_2S . C_2Cl_4 gave no result, the SO being comparatively stable in solution, but yielding H_2S on adding paraffin or decalin. SO gave H_2S readily on treatment with MeOH, and more slowly with EtOH. Micro-analysis confirmed the reaction $2\text{SO} + \text{MeOH} = \text{H}_2\text{S} + \text{CH}_2\text{O} + \text{SO}_2$. The general dehydrogenation is $\text{RH}_2 + 2\text{SO} = \text{R} + \text{H}_2\text{S} + \text{SO}_2$, or possibly in some cases $\text{RH}_2 + \text{SO} = \text{RO} + \text{H}_2\text{S}$.

N. M. B.

Fluorination of sulphuryl chloride : sulphuryl chlorofluoride. H. S. BOOTH and C. V. HERRMANN (J. Amer. Chem. Soc., 1936, 58, 63–66).— SO_2ClF , b.p. $7.1 \pm 0.1^\circ$, m.p. $-124.7 \pm 0.1^\circ$, has been prepared by the action of SbF_3 on SO_2Cl_2 in presence of SbCl_5 under pressure. The latent heat of vaporisation at the b.p. is 6338 g.-cal. At 0° the liquid has d 1.623 and surface tension 17.2 dynes per cm. The gas is hydrolysed by H_2O and readily absorbed by aq. NaOH.

E. S. H.

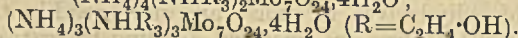
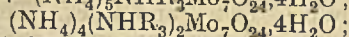
Preparation of selenic acid. L. I. GILBERTSON and G. B. KING (J. Amer. Chem. Soc., 1936, 58, 180).— SeO_2 is oxidised by refluxing with aq. H_2O_2 .

E. S. H.

Molybdenum-blue. F. HEIN, I. BURAWOY, and H. SCHWEDLER (Kolloid-Z., 1936, 75, 35–45).—The reduction of heteromolybdic acids by SnCl_2 has been studied colorimetrically. This reaction and titration of the Mo-blue with KMnO_4 indicate that the product is Mo_4O_{11} .

E. S. H.

Mixed molybdates. F. GARELLI and A. TETTMANZI (Gazzetta, 1935, 65, 1009–1015; cf. A., 1934, 1208).—The prep. of the following compounds is described : $(\text{NH}_4)_5\text{NHR}_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$;

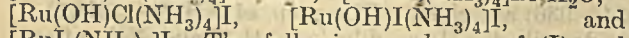
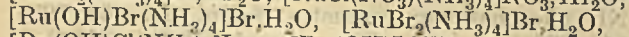
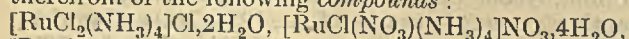


O. J. W.

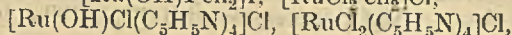
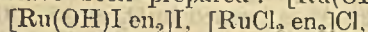
Action of chlorine and bromine on chlorites. G. R. LEVI and M. TABET (Gazzetta, 1935, 65, 1138–1144).—The action of Cl_2 on aq. solutions of $\text{Ca}(\text{ClO}_2)_2$ is quant : $2\text{ClO}_2' + \text{Cl}_2 = 2\text{Cl}' + 2\text{ClO}_2$. With Br a similar reaction takes place in the initial stages, but is followed by an oxidation-reduction process : $3\text{ClO}_2' = 2\text{ClO}_3' + \text{Cl}'$, nearly all the Br remaining in the free state.

O. J. W.

Residual affinity and co-ordination. XXXVI. Constitution of "ruthenium-red." G. T. MORGAN and F. H. BURSTALL (J.C.S., 1936, 41–45).—Ru-red (I) is best prepared by treating RuCl_3 with conc. aq. NH_3 . The constitution of (I), $[\text{Ru}(\text{OH})\text{Cl}(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$, is supported by the prep. therefrom of the following compounds :



and $[\text{RuI}_2(\text{NH}_3)_4]\text{I}$. The following analogues of (I) and derivatives have been prepared : $[\text{Ru}(\text{OH})\text{Cl} \text{en}_2]\text{Cl}$,



$[\text{RuCl}_2(\text{NH}_2\text{Et})_4]\text{Cl}$, and $[\text{Ru}(\text{OH})\text{Cl}(\text{NH}_2\text{Et})_4]\text{Cl}$. The analogues of (I) are less strongly coloured than (I).

J. G. A. G.

Detection and separation of sparingly soluble compounds by concentrated hydriodic acid. E. R. CALEY and M. G. BURFORD (Ind. Eng. Chem. [Anal.], 1936, 58, 63–67).—Examples of the use of conc. HI in the detection and separation of compounds that are insol. in HCl, HNO_3 , or aqua regia are given.

E. S. H.

Calculating the blank [in volumetric determinations]. B. PARK (Ind. Eng. Chem. [Anal.], 1936, 8, 32).—Arithmetical procedure is described.

E. S. H.

Theory of titration in stages of mixtures of acids and bases. S. KILPI (Z. physikal. Chem., 1935, 175, 239–254; cf. A., 1935, 1214).—The conditions for the titratability of such mixtures and of ampholytes have been derived.

R. C.

Colorimetric chemical analyses by means of photo-electric cells. F. CARRANZA (Bol. Soc. Quím. Perú, 1935, 1, No. 5, 7–27).—The % of the incident light transmitted by the unknown solution is determined by means of a photo-electric cell and the concn. deduced by comparison with solutions of known concn. The sensitivity may be increased or decreased by the use of filters of complementary or similar colour, respectively, to the solution. Examples are given of the determination of KMnO_4 in aq. solution, of NH_2 -acids (glycine) by means of the ninhydrin reaction, and of vitamin-A in cod-liver oil.

D. R. D.

Volumetric determination of water in liquids and solids.—See B., 1936, 127.

Argentometric titration of halide, thiocyanate, selenocyanate, and cyanate with adsorption indicators. R. RIPAN-TILICI (Z. anal. Chem., 1936, 104, 16–22).— CN' is titrated with AgNO_3 by Liebig's method, and the titration of Cl' , SCN' , SeCN' , CNO' , etc. continued using fluorescein as indicator.

J. S. A.

Determination of sulphuric acid in solutions containing aluminium, chromium, and ferric sulphate. III. S. A. TOLKATSHEV and J. G. TIROVA (J. Appl. Chem. Russ., 1935, 8, 1271–1283).—25 ml. of aq. $\text{Al}_2(\text{SO}_4)_3$ are titrated with 0.5N-NaOH, an excess of 12 ml. of which is then added; the solution is diluted to 100 ml., and saturated with CO_2 at the b.p., cooled, and diluted to 250 ml., filtered, and excess of alkali in an aliquot part of the filtrate is titrated with 0.5N- H_2SO_4 (Me-orange). $\text{Cr}_2(\text{SO}_4)_3$ is determined analogously, an excess of 10 ml. of 0.5N-NaOH being added per 0.1 g. of Cr_2O_3 in the solution. In the case of $\text{Fe}_2(\text{SO}_4)_3$ treatment with CO_2 is not necessary; the excess of alkali should be 8 ml. per 0.1 g. of Fe_2O_3 . The mean error is ± 0.2 – 0.3% .

R. T.

Stabilisation of 0.1N-sodium thiosulphate solution.—See B., 1936, 144.

Determination of selenium in sulphur.—See B., 1936, 101.

Source of loss of ammonia in Kjeldahl distillations. Method of eliminating this loss. H. S.

MILLER (Ind. Eng. Chem. [Anal.], 1936, 8, 50—51).—Dilution of NH_3 with air in the initial stages causes low absorption, giving an average loss of 1.26% N. By using a modified delivery tube, provided with holes which cause the air bubbles to be broken up, this loss can be reduced to 0.06% N. E. S. H.

Titrimetric determination of phosphoric acid in perchloric acid solution as bismuth phosphate. J. HARMS and G. JANDER (Angew. Chem., 1936, 49, 106—109).—The conductometric titration of H_3PO_4 in HClO_4 solution with aq. BiOClO_4 has been investigated in presence of Mg, Ca, Cu, Zn, Ni, Fe^{II} , Mn, Al, small amounts of Fe^{III} , NO_3 , Cl, H_2SiO_3 , and in artificial fertilisers. With suitable precautions, the method is rapid (10—15 min.) and satisfactory.

T. G. P.

Influence of fluorine on precipitation of phosphoric acid with molybdic acid. H. T. BUCHERER and F. W. MEIER (Z. anal. Chem., 1936, 104, 23—28).—Quant. results for P_2O_5 by the molybdate method of Lorenz, or in presence of 8-hydroxyquinoline, cannot be obtained in presence of F, which must first be removed. J. S. A.

Micro-determination of arsenic in must and wine.—See B., 1936, 119.

Determination of silicon in aluminium alloys.—See B., 1936, 151.

Determination of free carbonic acid in waters containing humus. Y. KAUKO (Ann. Acad. Sci. Fenn., 1934, 39, A, No. 2; Chem. Zentr., 1935, i, 3177).—The method previously described (A., 1935, 34; this vol., 159) is applied to soft surface waters. Decomp. of dissolved H carbonates introduces an error if applied to hard waters. J. S. A.

System of qualitative analysis for the [commoner] anions. J. T. DOBBINS and H. A. LJUNG (J. Chem. Educ., 1935, 12, 586—588).—The anions are separated into six groups, the detailed analysis of which is described. Group I, containing $\text{CO}_3^{\prime\prime}$, F^{\prime} , $\text{C}_2\text{O}_4^{\prime\prime}$, $\text{SO}_3^{\prime\prime}$, $\text{AsO}_3^{\prime\prime\prime}$, $\text{AsO}_4^{\prime\prime\prime}$, $\text{PO}_4^{\prime\prime\prime}$, and tartrate, is pptd. as the Ca salts in alkaline solution; II, $\text{SO}_4^{\prime\prime}$ and $\text{CrO}_4^{\prime\prime}$, as the Ba salts from alkaline solution; III, CN^{\prime} , $\text{BO}_3^{\prime\prime\prime}$, $\text{Fe}(\text{CN})_6^{\prime\prime\prime}$, $\text{S}^{\prime\prime}$, and $\text{Fe}(\text{CN})_6^{\prime\prime\prime\prime}$, as the Zn salts in alkaline solution; IV, $\text{S}_2\text{O}_3^{\prime}$, CNS^{\prime} , Cl^{\prime} , Br^{\prime} , and I^{\prime} , as the Ag salts from slightly acid (HNO_3) solution; V, ClO_3^{\prime} , NO_2^{\prime} , OAc^{\prime} and VI, NO_3^{\prime} are identified without pptn. Sensitivities are recorded. L. S. T.

Use of formaldehyde for the elimination of ammonia and of ammonium salts in qualitative and quantitative analysis. II. Application to detection of metals of the sixth group. A. HEMMELER (Annali Chim. Appl., 1935, 25, 610—617).— NH_4 salts, and their disturbing effect on group VI analysis, may readily be removed by adding CH_2O , thus converting them into $(\text{CH}_2)_6\text{N}_4$ (cf. A., 1934, 1189). The group V filtrate so treated is divided into portions A and B. To A, conc. aq. or solid NaOH is added and $\text{Mg}(\text{OH})_2$ completely pptd.; in half the filtrate Li^{\prime} is detected in the usual way. In the remainder, K^{\prime} is detected by adding AcOH to neutrality (phenolphthalein) followed by freshly prepared $\text{Na}_3\text{Co}(\text{NO})_6$; if there is no ppt., or one of $(\text{CH}_2)_6\text{N}_4$

cobaltinitrite which dissolves completely when treated with conc. NaOH followed by AcOH, K^{\prime} is absent, whilst if a yellow ppt. remains, K^{\prime} is present. In portion B, Na^{\prime} is detected as $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$. $(\text{CH}_2)_6\text{N}_4$ interferes with other qual. tests for K^{\prime} . E. W. W.

Methyl-red as an adsorption indicator. D. M. MUKHERJEE (J. Indian Chem. Soc., 1935, 12, 748—749).—The p_{H} and the sp. conductivity of the solution have been determined after pptn. of AgCl in presence and in absence of Me-red. R. S.

Determination of the radium content of rocks. W. D. URRY (J. Chem. Physics, 1936, 4, 40—48).—The differential method for determining Ra has been applied to rock analysis. The apparatus has an observational limit of $5.5 \times 10^{-14} \times n^{-0.5}$ g. Ra for n hourly readings. He, Ra, U, and Th, and age data are given for Keweenaw trap rocks from different levels, and also data for a geological time scale.

M. S. B.

Detection of cadmium. F. I. TRISCHIN (J. Appl. Chem. Russ., 1935, 8, 1269—1270).—Ag, Pb, Hg, Bi, Fe, Al, Cr, Mn, and Sn are pptd. by adding dil. aq. KI, conc. aq. NH_3 , and 5—6 drops of H_2O_2 to 1 c.c. of solution, the solution is filtered, and excess of KCN and a few drops of aq. Na_2S are added to the filtrate (containing Zn, Co, Ni, Cu, and Cd), when a yellow ppt. is obtained in presence of ≤ 0.00056 mg. of Cd. R. T.

Salts of thiolbenzthiazole.—See this vol., 215.

Direct detection of lead with diphenylthiocarbazon. M. KASAHARA and T. KASAHARA (Klin. Woch., 1934, 13, 1857—1858; Chem. Zentr., 1935, i, 3320).—A colorimetric variation of the method of Bohnenkamp and Linneweh (A., 1934, 1030) is described. H. N. R.

Use of the iodine monochloride end-point in volumetric analysis. III. Titration of thallos salts with permanganate, iodate, and ceric sulphate. E. H. SWIFT and C. S. GARNER (J. Amer. Chem. Soc., 1936, 58, 113—115; cf. A., 1930, 561).— KMnO_4 and $\text{Ce}(\text{SO}_4)_2$ are unsatisfactory. The use of KIO_3 is recommended. E. S. H.

Iodometric determination of copper. Adjustment of hydrogen-ion concentration. W. R. CROWELL, T. E. HILLIS, S. C. RITTENBERG, and R. F. EVENSON (Ind. Eng. Chem. [Anal.], 1936, 8, 9—11).—Park's procedure (A., 1931, 454) is modified. K H phthalate has no material effect on p_{H} of the solution and may be omitted. E. S. H.

Spectrophotometric determination of copper in ores and mattes.—See B., 1936, 105.

Separation of precipitated mercuric sulphide and sulphur in the gravimetric determination of mercury. E. R. CALEY and M. G. BURFORD (Ind. Eng. Chem. [Anal.], 1936, 8, 43).—The HgS-S mixed ppt. is dried and weighed; HgS is dissolved by treatment with cold, conc. HI, and the residual S weighed. E. S. H.

Gravimetric determination of cerous salts. P. SPACU (Z. anal. Chem., 1936, 104, 28—30).— Ce^{III} salts give with $\text{K}_4\text{Fe}(\text{CN})_6$ at room temp. a

ppt. of $\text{CeK}[\text{Fe}(\text{CN})_6]_4 \cdot 4\text{H}_2\text{O}$ which may be weighed as such or dried to the trihydrate at 100° . J. S. A.

Volumetric determination of indium. H. B. HOPE, M. ROSS, and J. F. SKELLY (Ind. Eng. Chem. [Anal.], 1936, 8, 51—52).—In acetate is titrated with $\text{K}_4\text{Fe}(\text{CN})_6$, using diphenylbenzidine as internal indicator. Cl^- must be absent. E. S. H.

Determination of rhenium. I. Qualitative. L. C. HURD (Ind. Eng. Chem. [Anal.], 1936, 8, 11—15).—In the Prescott and Johnson system of analysis Re concentrates with As. Confirmatory tests for Re are described. E. S. H.

Standardisation of permanganate solutions with sodium oxalate. R. M. FOWLER and H. A. BRIGHT (J. Res. Nat. Bur. Stand., 1935, 15, 493—501).—Titration of $\text{Na}_2\text{C}_2\text{O}_4$ with KMnO_4 at $60-90^\circ$ gives vals. for the normality of the latter which may be 0.4% high. 90—95% of the KMnO_4 solution should be added to the aq. $\text{Na}_2\text{C}_2\text{O}_4$ (+5% of H_2SO_4) at $25-30^\circ$, the solution warmed to $55-60^\circ$, and the titration completed as usual. H. J. E.

Colorimetric determination of manganese [in soils] in presence of titanium.—See B., 1936, 114.

Determination of manganese and magnesium in soils and silicate rocks.—See B., 1936, 114.

Use of potassium stannochloride dihydrate $\text{K}_2\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ in determination of iron. E. VOYATZAKIS (Praktika, 1934, 9, 108—111; Chem. Zentr., 1935, i, 3317).—To the strongly acid (HCl) Fe^{3+} solution, NaHCO_3 is added, and then an excess of $\text{K}_2\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ (I) (prep. described). The excess of (I) is titrated back with 0.01*N*-I. J. S. A.

Determination of iron in phosphorites and apatites.—See B., 1936, 144.

Oxidimetric determination of molybdenum. I. Vanadate method. R. LANG and S. GOTTLIEB (Z. anal. Chem., 1936, 104, 1—16).—A neutral MoO_4^{2-} solution is acidified with 15—20 vol.-% of conc. HCl , and 0.2*N*- SnCl_2 is added until no further brown coloration occurs on each addition, reducing Mo^{VI} to Mo^{V} . The excess of SnCl_2 , but not Mo^{V} , is oxidised by adding aq. $\text{Br} + \text{KBr}$, Br being removed by an equal vol. of 0.3*N*- As_2O_3 . NaF is added, and then NHPh_2 in H_3PO_4 as indicator. Mo^{V} is oxidised by addition of 0.1*N*- NH_4VO_3 (I), the excess of which is titrated back with FeSO_4 . Alternatively, after addition of As_2O_3 , the Mo^{V} may be titrated directly with (I), previously oxidised diphenylamine-sulphonic acid being added as indicator shortly before the end-point. The acidity during reduction must be as stated to avoid reduction to Mo^{III} or Mo^{IV} , which oxidises directly to Mo^{VI} with Br . Neutral salts or non-reducible metals do not interfere. In presence of Fe and V the method is impracticable, due to oxidation of Mo^{V} by Fe^{III} and V^{IV} . Large amounts of Cu interfere similarly. Mo may be determined in presence of W by adding NaF before reduction to keep WO_3 in solution; a trace of Cu is added to catalyse the reoxidation of W compounds by Br . J. S. A.

Reduction of uranyl ion in the uranyl oxalate actinometer. E. C. PITZER, N. E. GORDON, and

D. A. WILSON (J. Amer. Chem. Soc., 1936, 58, 67—70).—A method for determining U^{IV} in presence of $\text{H}_2\text{C}_2\text{O}_4$ and UO_2^{2+} is described. In the photolysis of actinometer solutions the complex undergoing unimol. decomp. is $\text{UO}_2(\text{C}_2\text{O}_4)_2^{2-}$, and the source of U^{IV} is $\text{UO}_2\text{C}_2\text{O}_4$. The ionisation of the complex is discussed. E. S. H.

Oxidation of stannous chloride by permanganate. V. V. ZACHAROV and N. V. ZACHAROVA (J. Appl. Chem. Russ., 1935, 8, 1284—1286).— SnCl_2 may be titrated with KMnO_4 in presence of FeSO_4 and H_3PO_4 . R. T.

Determination of the thorium content of rocks. W. D. URRY (J. Chem. Physics, 1936, 4, 34—40).—A method of measuring Th in quantities of the order of 10^{-5} — 10^{-6} g. by determining the α -particle activity of thoron (Tn) in a streaming gas by a counter is described. It is possible to make a simultaneous determination of the Pa/Ra ratio in common rocks. M. S. B.

Organic compounds as analytical reagents. II. Cinchonine iodide as reagent for determination of bismuth. J. B. FICKLEN, I. L. NEWELL, and N. R. PIKE (Z. anal. Chem., 1936, 104, 30—34).—Cinchonine iodide is not strictly sp. for Bi . Data are given as to the interfering effect of other cations. J. S. A.

Stable standardised gold solution. W. C. WILLIAMS (J. Lab. Clin. Med., 1935, 80, 545—549).—Patterson's method (A., 1932, 225) is modified by use of 0.02*N*- KOH , the acid Au salt, and a solution of edestin for standardisation. CH. ABS. (p)

Calorimetric apparatus. W. A. ROTH (Chem. Fabr., 1936, 9, 10—12).—A summary of recent developments in calorimetry. J. W. S.

Maquenne block. R. P. JACQUEMAIN (Bull. Soc. chim., 1936, [v], 3, 142—143).—The disadvantages of the usual Maquenne block are reviewed. A Cr block is recommended. E. E. A.

Combined hydrogen and helium liquefier. B. V. ROLLIN (Proc. Physical Soc., 1936, 48, 18—27).—An apparatus needing only liquid air for the initial cooling, and designed for low-temp. laboratory experiments, is described. N. M. B.

Semi-micro-Cottrell b.-p. apparatus. M. L. WILLARD and D. E. CRABTREE (Ind. Eng. Chem. [Anal.], 1936, 8, 79—80).—The apparatus can be used with 5 c.c. of liquid and gives results accurate to 0.1°. E. S. H.

Electrically-heated m.-p. apparatus. E. DOWZARD and M. J. RUSSO (Ind. Eng. Chem. [Anal.], 1936, 8, 74—75).—The apparatus avoids the use of heating liquids and is suitable for substances with m.p. $\geq 310^\circ$, with a reproducibility of 0.5°. E. S. H.

Stem correction for mercury thermometers. M. EDENHOLM and G. OLSSON (IVA, 1935, 5—10; Chem. Zentr., 1935, i, 3692).—The formula $\Delta t = n_1(t_a - t_e) / (k - n_1 + t_e)$, where t_e = temp. of exposed stem, t_a = observed temp., n_1 = length of exposed stem in degrees, and $1/k$ = apparent coeff. of cubical expansion, is proposed. H. N. R.

General source of radiation for the visible and infra-red spectrum. A. H. PFUND (*Science*, 1935, **82**, 597—598). L. S. T.

Curved quartz crystal X-ray spectrograph. J. W. M. DUMOND and B. B. WATSON (*Physical Rev.*, 1934, [ii], **46**, 316—317). L. S. T.

Large-aperture spectrograph suitable for the ultra-violet. A. ARNULF and B. LYOT (*Compt. rend.*, 1935, **201**, 1480—1482).—A quartz spectrograph, aperture $f/1$, has been constructed using a spherical Al mirror in place of the usual objective. T. G. P.

Self-rectifying gas X-ray tube. R. W. G. WYCKOFF and J. B. LAGSDIN (*Rev. Sci. Instr.*, 1936, [ii], **7**, 35—37).—An instrument previously described (*Radiology*, 1930, **15**, 42) is improved. C. W. G.

Simplified apparatus for fluorescence analysis. A. KARSTEN (*Zement*, 1935, **24**, 158—159; *Chem. Zentr.*, 1935, **i**, 3315).—An apparatus, using activated metal electrodes, is described. H. N. R.

Application of photo-electric methods to the Duboscq colorimeter. G. BERNHEIM and G. REVILLON (*Ann. Falsif.*, 1936, **29**, 5—10).—The photo-electric cell described has a range of sensitiveness similar to that of the human eye, and consists of a small Fe plate supporting semi-conductors which are covered (by cathodic treatment) with a thin layer of an alloy of a precious metal. One of these is inserted under each of the eyepiece prisms of the Duboscq colorimeter, the two being connected through a millimeter in opposition. Solutions tested and the corresponding max. relative matching errors are 0.6% 1.2, 0.05% KMnO_4 10, 2% CuSO_4 (in aq. NH_3) 6, and 10 mg. per litre of methylene-blue 2.2%. J. G.

Determinations with registering spherical cadmium cells. M. BENDER (*Physikal. Z.*, 1936, **37**, 107—110).—Cd photo-cells can be used for determining the ultra-violet in sunlight. A. J. M.

Differential refractometer. D. RAU and W. E. ROSEVEARE (*Ind. Eng. Chem. [Anal.]*, 1936, **8**, 72—73).—The apparatus uses white light and has a sensitivity of 5×10^{-7} . It has been used to determine the concn. of aq. solutions with $n=0.0004-0.002 > n$ for H_2O . The scale readings are nearly a linear function of the difference in n . E. S. H.

Visual conductometry. L. WOLF (*Chem. Fabr.*, 1936, **9**, 46—49).—Two galvanometer-Se-rectifier instruments are used, one in series with the titration cell and the other in parallel. The current in the main circuit is kept const. and the deflexion of the second galvanometer is observed after each addition of alkali. The accuracy can be increased by taking readings with different currents in the main circuit. R. S.

Directionally selective ion counter. L. M. LANGER and R. T. COX (*Rev. Sci. Instr.*, 1936, [ii], **7**, 31—33).—A particle passing between a pair of parallel wire electrodes in a direction parallel to them produces a greater total discharge than one passing in another direction. C. W. G.

Universal camera for electron diffraction at 10—100 kv. H. J. YEARIAN and J. D. HOWE

(*Rev. Sci. Instr.*, 1936, [ii], **7**, 26—30).—Reflected or transmitted electron beams from a hot-filament cathode or from a discharge tube can be used. A wide range of temp. and exposures is available. C. W. G.

Ion sources for mass spectroscopy. A. J. DEMPSTER (*Rev. Sci. Instr.*, 1936, [ii], **7**, 46—49; cf. *A.*, 1935, 677).—A high-frequency alternating spark coupled inductively to a primary oscillating spark circuit is a more convenient source than a vac. vibrator or a large condenser discharge. C. W. G.

Measurement of the breakdown and current-voltage characteristics of liquid dielectrics with direct potentials. E. B. BAKER and H. A. BOLTZ (*Rev. Sci. Instr.*, 1936, [ii], **7**, 50—58).—Currents from 10^{-16} to 10^{-3} amp. can be measured. C. W. G.

High-speed, high-sensitivity photo-electric potentiometer. R. W. GILBERT (*Rev. Sci. Instr.*, 1936, [ii], **7**, 41—46).—The response to changes of input is instantaneous. C. W. G.

Electro-ultra-filtration apparatus. E. J. CZARNETZKY (*Science*, 1935, **82**, 625—626).—An apparatus for the prep. of solutions of protein-Hg compounds is described. L. S. T.

Mounting cell for the bulb type of glass electrode. J. H. HIGHBERGER (*J. Amer. Leather Chem. Assoc.*, 1936, **31**, 32—34).—The apparatus described previously (*A.*, 1935, 1097) is modified to permit the flushing of the saturated aq. KCl and the electrode chamber. D. W.

Modified Gouy's balance for the accurate and quick measurement of diamagnetic susceptibilities. M. B. NEVGI (*Current Sci.*, 1935, **4**, 403).—The modified instrument consists of two tubes, one of which is sealed and contains the paramagnetic substance and acts as a stopper to the other tube containing the diamagnetic specimen. An equation is deduced, and calc. results for nine org. substances are in good agreement with available data. N. M. B.

Utility of broken automatic pipettes. B. N. SINGH and P. B. MATHUR (*Science*, 1935, **82**, 626). L. S. T.

Apparatus for sugar and other titrations. E. S. WEST (*Ind. Eng. Chem. [Anal.]*, 1936, **8**, 62). E. S. H.

Precision pyknometer for liquids. S. T. YUSTER and L. H. REYERSON (*Ind. Eng. Chem. [Anal.]*, 1936, **8**, 61—62).—A modified apparatus is described. E. S. H.

Method of obtaining perfectly polished metallic surfaces. P. JACQUET (*Compt. rend.*, 1935, **201**, 1473—1475; cf. *B.*, 1935, 730).—The Cu specimen, polished in the ordinary way on fine emery, is made the anode in the electrolysis, at a suitable c.d., of aq. H_3PO_4 or $\text{H}_4\text{P}_2\text{O}_7$ containing at least 400 g. per litre, and maintained between 15° and 25° . T. G. P.

Quick method of depositing polonium on silver. M. D. WHITAKER, W. BJORKSTED, and A. C. G. MITCHELL (*Physical Rev.*, 1934, [ii], **46**, 629—630). L. S. T.

Safety device for use with gas-heated Soxhlets. J. C. MACRAE (Chem. and Ind., 1936, 53).—The device cuts off the gas supply if the H₂O supply to the condenser or bath begins to fail. E. S. H.

Efficient fume hood [for laboratories]. G. W. MUHLEMAN (J. Chem. Educ., 1935, 12, 591).

L. S. T.

Apparatus for producing vapours of constant concentration by evaporation of mixtures of liquids of different b.p. E. V. ALEXEEVSKI and G. M. CHRAMOV (J. Appl. Chem. Russ., 1935, 8, 1319—1320).

R. T.

Stirring apparatus for small amounts of liquid. K. PACKENDORFF (J. pr. Chem., 1936, [ii], 144, 211—213).—An electrically operated plunger-stirrer, suitable for mixing small amounts of liquid in a gas-tight or evacuated tube, is described.

R. S. C.

Low-pressure measurements. W. GAEDE (Z. tech. Physik, 1934, 15, 664—668; Chem. Zentr., 1935, i, 3164).—A piece of Al foil is suspended by a quartz fibre in a glass vessel, the pressure and mol. wt. of the gas in the apparatus being deduced from observations of the vibration and damping of the Al. The range of operation is 10—10⁻⁷ mm. Hg. H. J. E.

Laboratory hints. A. VOSMAER (Chem. Weekblad, 1936, 33, 61—62).—The best methods for cutting different kinds of glass tubing and for cutting and boring glass plate are described.

D. R. D.

Laboratory hints. W. VAN TONGEREN (Chem. Weekblad, 1936, 33, 62).—A hole bored in the rubber ejector bulb of a wash-bottle is closed during use by means of a finger.

D. R. D.

Ultramicrometer. C. L. UTTERBACK and H. WIRTH (Physical Rev., 1934, [ii], 46, 328).—Changes in pressure of the order 10⁻³ dyne per sq. cm. can be measured by the arrangement described. L. S. T.

Organic liquids suitable for cloud expansion work. D. D. LOUGHRIDGE and H. C. TRUEBLOOD (Physical Rev., 1934, [ii], 46, 323).—28 liquids have been studied with reference to their min. expansion ratio for condensation on α -particle tracks.

L. S. T.

Amplifier and recording apparatus for α -particles, high-speed protons and neutrons. M. C. HENDERSON (Physical Rev., 1934, [ii], 46, 324).

L. S. T.

Measurement of very low relative humidities. A. SIMONS (Proc. Physical Soc., 1936, 48, 135—144).—An apparatus for measuring dew points down to -40°, corresponding with 0.5—10% R.H., and a hygrometer using wet and dry thermocouples are described. Calibration curves for the hygrometer for 0.5—10% R.H. and 10—90° air temp. are given.

N. M. B.

Automatic recording balance. D. S. BINNINGTON and W. F. GEDDES (Ind. Eng. Chem. [Anal.], 1936, 8, 76—79).—The balance is electrically operated, fitted with oil damping, and counterbalanced for an initial load of 100 g. Wt. losses up to 17 g., with an accuracy of 0.01 g., are recorded without manual attention by an automatic device which places wts. on the pan. A continuous record is obtained on a paper chart by the use of a timed spark.

E. S. H.

Micro-Dumas generation of carbon dioxide. W. S. IDE (Ind. Eng. Chem. [Anal.], 1936, 8, 56).—MgCO₃ is introduced into the closed end of the micro-combustion tube. Before combustion, air is removed from the tube by heating the MgCO₃.

E. S. H.

Check valve. E. L. GREEN (Ind. Eng. Chem. [Anal.], 1936, 8, 40).—The device is designed to prevent the sucking back of liquids when passing a gas through them.

E. S. H.

Ball mill. L. L. QUILL (Ind. Eng. Chem. [Anal.], 1936, 8, 27).

E. S. H.

Determination of the wall correction for the falling-sphere viscosimeter. E. I. FULMER and J. C. WILLIAMS (J. Physical Chem., 1936, 40, 143—149).—Viscosity data have been obtained in the falling-sphere viscosimeter for castor oil, glycerol, solutions of colophony in turpentine, and two samples of honey. An equation has been derived giving the wall correction for vals. of r/R up to approx. 0.500. r and R are the radii of the sphere and the inside of the cylinder, respectively.

M. S. B.

Surface tension by the ring method. Applicability of the Du Nouy apparatus. R. MACY (J. Chem. Educ., 1935, 12, 573—576).—Methods by which data obtained by this method can be brought into line with those given in the International Critical Tables are described.

L. S. T.

Practical application of lifting plate method to determination of surface tension. W. DEKEYSER (Wis. nat. Tijds., 1934, 7, 107—118; Chem. Zentr., 1935, i, 3640—3641).—An expression is developed for the accurate determination of surface tension from the force required to lift a disc from the surface of a liquid.

J. S. A.

Determination of surface tension of saturated aqueous solutions. F. DE BLOCK (Wis. nat. Tijds., 1934, 7, 80—88; Chem. Zentr., 1935, i, 3641).—A lifting-disc method is applied to the determination of the surface tension of saturated solutions, and its dependence on temp.

J. S. A.

Further applications of chemistry to archaeology. W. FOSTER (J. Chem. Educ., 1935, 12, 577—579).—Ancient mortars and cements (Mayan), bees-wax, and Pb are described.

L. S. T.

Geochemistry.

Temperature of atmospheric ozone. J. DEVAUX (Compt. rend., 1935, 201, 1500—1501; cf. A., 1932, 108).—Infra-red spectra indicate a temp. < 0°, which does not suffer appreciable diurnal or seasonal variation.

T. G. P.

Penetration of solar and cosmic rays into fresh-water lakes. G. A. LINHART (J. Physical Chem., 1936, 40, 113—119).—An equation previously deduced (Amer. Math. Month., 1935, 42, 224) is applied.

M. S. B.

Origin of bore-hole water. N. V. TAGEEVA (Ncft. Choz., 1934, 26, No. 7, 63—65).—Analyses are given. The H₂O originated from the ocean, and was later changed by contact with minerals.

CH. ABS. (e)

Radium minerals. V. CHARRIN (Rev. ind., 1935, 65, 19—20; Chem. Zentr., 1935, i, 3701).—A review of the occurrence and extraction of Ra. J. S. A.

Occurrence of minerals in Hungary. R. REICHERT (Földtani Közlöny., 1934, 64, 348—356; Chem. Zentr., 1935, i, 3651).—Microscopic, chemical, and crystallographic data are given concerning Hungarian occurrences of marcasite, quartz in pyroxene andesite, hornblende and biotite, and phillipsite.

J. S. A.

Crystallographic data for Hungarian copper pyrites. SZÁVA-KOVÁTS and K. RESCH (Földtani Közlöny, 1934, 64, 334—341; Chem. Zentr., 1935, i, 3651).—Measurements on Cu pyrites from four sources are given.

J. S. A.

Granodiorite deposit of Štěnovic (near Pilsen) and its relation to neighbouring massifs. A. ORLOV (Věst. stát. Geol. Ust. Čes. Repub., 1934, 10, 97—103; Chem. Zentr., 1935, i, 3651).—The oligoclase granodiorite of Štěnovic contains plagioclase (of oligoclase type, with zoned structure) 50%, quartz 20%, and orthoclase 10%, with amphibole and biotite.

J. S. A.

Chemical-mineralogical investigation of eruptive rocks of the central Sahara and the Sudan. M. E. DENAEYER (Bull. Soc. franç. Min., 1934, 57, 284—337; Chem. Zentr., 1935, i, 3651).—A comprehensive résumé of chemical and mineralogical data.

J. S. A.

Böhmite and bayerite. H. LEHL (J. Physical Chem., 1936, 40, 47—54).—Four definite crystal forms of Al hydroxide are known. Diaspore, Al₂O₃·H₂O, gives α -corundum on removal of H₂O. The other three forms, on losing H₂O, give cubic γ -Al₂O₃. They are, in order of increasing stability, böhmite, Al₂O₃·H₂O, bayerite, Al₂O₃·H₂O, and gibbsite, Al₂O₃·3H₂O.

M. S. B.

Helium content of minerals not emitting α -rays and its explanation. H. J. BORN (Naturwiss., 1936, 24, 73—76).—The origin of He in beryl and in alkali halides, particularly sylvine, is discussed. The He content of beryl is probably due to the action of γ -rays on ${}^4\text{Be}^9$ giving ${}^4\text{Be}^8$ and ${}^0n^1$, the ${}^4\text{Be}^8$ breaking down to ${}^2\text{He}^4$. Sylvine and rock-salt often contain Pb, and the difference in He content of these minerals may depend on the concn. of U, Ra, and Ra-D in the H₂O from which they were originally deposited. Primary rock-salts contain only minute amounts of He. Those containing greater amounts have all been in contact with H₂O at some later period, and the high He content is connected with the high [Ra] in deep waters.

A. J. M.

Thermal decomposition of talc. R. H. EWELL, E. N. BUNTING, and R. F. GELLER (J. Res. Nat. Bur. Stand., 1935, 15, 551—556).—Wt. losses and X-ray data are given. No change in crystal structure occurs up to 800°. At 800—840°, enstatite (I), amorphous

SiO₂, and H₂O are formed. (I) forms clinoenstatite at 1200°, and amorphous SiO₂ forms cristobalite at 1300°.

H. J. E.

Ejected blocks of the Laacher See district. G. KALB (Tsch. Min. Petr. Mitt., 1936, 47, 185—210).—The sanidinites derived from crust. schists are of two types: aegirine-augite-sanidinite (fenite) formed by pneumatolytic injection metamorphism with a phonolitic magma; and biotite-sanidinite formed by pneumatolytic contact metamorphism with an alkali-trachyte magma.

L. J. S.

Aphrosiderite from the granite of the Tatra Mts. B. MAURITZ (Mat. Term. Ért., 1935, 53, 238—247, and Tsch. Min. Petr. Mitt., 1936, 47, 262—269).—Analysis of a chloritic mineral coating a block of granite identifies it with aphrosiderite.

L. J. S.

Yellow rock-salt from Hall in Tirol. K. PRZIBRAM (Nature, 1936, 137, 107—108).—The discovery by Schaubberger of light-sensitive yellow rock-salt from this locality supplies the link, hitherto missing, in the formation of natural blue rock-salt. The absorption spectrum is the same as for rock-salt coloured artificially by Ra rays. The salt shows thermoluminescence, and on exposure to Ra rays it colours quickly; the artificial colour is likewise sensitive to light.

L. S. T.

Petrology of common volcanic rocks of Japan. S. TSUBOI (Proc. V Pacific Sci. Congr., 1934, 3, 2271—2273).—The alkali-lime index for the Japanese volcanic rock series is 65.5. The compositions of pyroxenes are plotted.

CH. ABS. (e)

Chemical composition of the Deccan trap flows of Linga, Chhindwara District, Central Provinces. L. L. FERMOR (Rec. Geol. Surv. India, 1934, 68, 344—360).—The minerals are described. Analyses are given.

CH. ABS. (e)

Occurrence of sphalerite at Ellsworth, Ohio. G. U. GREENE (Amer. Min., 1935, 20, 882—883).—Sphalerite associated with barite or calcite is described.

L. S. T.

Morphology of phenacite from two new occurrences [at Klein-Spitzkopje, South West Africa, and the Morefield mine, Winterham, Amelia Co., Virginia]. F. H. POUGH (Amer. Min., 1935, 20, 863—874).

L. S. T.

Vectorial chemical alteration of crystals. C. FRONDEL (Amer. Min., 1935, 20, 852—862).—Vectorial chemical alteration of crystals occurring in nature is described for pyrite (to haematite), enargite, stibnite (probably to wurtzite), and tourmaline. With barite and celestite, a partial overgrowth of a white opaque substance of later generation may simulate a vectorial alteration. Chemical changes in crystals may be affected by twinning, zoning in composition, and the physical nature of the bounding surface. Nucleation on crystal edges or surface imperfections is described for the topochemical alteration of azurite to malachite.

L. S. T.

Monticellite from San Bernardino County, California, and the monticellite series. W. T. SCHALLER (Amer. Min., 1935, 20, 815—827).—Small

grains of monticellite (I) disseminated throughout a dolomite from the Dewey mine are the purest samples of (I) so far described. The FeO and MnO replacing MgO is < 1.50%. α 1.641, β 1.649, and γ 1.655 are < any other recorded vals. The components of the series MgO, CaO, SiO_2 (I)—FeO, CaO, SiO_2 —MnO, CaO, SiO_2 (glaucochroite) are discussed and their refractive indices given. L. S. T.

Experimental study of the porosity and permeability of clastic sediments. H. J. FRASER (J. Geol., 1935, 43, 910—1010). L. S. T.

Biotite system. A. N. WINCHELL (Amer. Min., 1935, 20, 773—779).—A revision of data and diagrams (cf. A., 1925, ii, 592; 1926, 494). L. S. T.

Occurrence and origin of celestite and fluorite at Clay Centre, Ohio. R. B. MORRISON (Amer. Min., 1935, 20, 780—790).—Descriptive. L. S. T.

Enargite and plumbojarosite at Picher, Oklahoma. A. L. RANSOME (Amer. Min., 1935, 20, 799—805).—Crystals of enargite and plumbojarosite in a specimen from the Barr mine are described. L. S. T.

Thulite in New Mexico. S. A. NORTROP (Amer. Min., 1935, 20, 805—807).—Thulite, d 3.15, occurs in quartz, associated with some actinolite, at Pilar Post Office, Taos Co., New Mexico. An analysis is given. L. S. T.

Quartz paramorphs after tridymite and cristobalite. R. S. MOEHLMAN (Amer. Min., 1935, 20, 808—810).—Abnormal forms of quartz, probably the result of inversion from tridymite and cristobalite, have been observed in Miocene volcanic rocks southwest of Ouray, Colorado. L. S. T.

Composition of asbestos and other fibres of Thetford district, Quebec. H. C. COOKE (Trans. Roy. Soc. Canada, 1935, [iii], 29, IV, 7—19).—Several analyses are given of carefully selected chrysotile of different degrees of softness and harshness, and these are interpreted as mixtures of serpentine ($H_4Mg_3Si_2O_9$), chlorite, talc, brucite, periclase, etc. Harshness seems to be connected with excess of SiO_2 and the presence of more talc and periclase and less H_2O . Analyses of fibrous materials occurring on slickensided surfaces and in faults show that these may range from serpentine to brucite. L. J. S.

Manganese concretions in Nova Scotia lakes. E. M. KINDLE (Trans. Roy. Soc. Canada, 1935, [iii], 29, IV, 163—180).—The nodular or more often disc- or saucer-shaped concretions (3—6 in. across) are formed around pebbles on the bottom of the lakes, and contain MnO_2 35.29, Fe_2O_3 16.56%. They have probably been formed by the action of algae extracting Mn and Fe from the lake water. L. J. S.

Rôle of manganese in minerals. H. OTTO (Tsch. Min. Petr. Mitt., 1935, 47, 89—140).—Several new chemical analyses together with optical data are given of various manganese-bearing minerals (phosphates and silicates), and the results are plotted, together with data from the lit., showing a decrease in n with isomorphous replacement of Fe^{II} by Mn^{II} and an increase with replacement of Zn, Mg, Li,

Ca by Mn^{II} and of Al by Mn^{III} . The varied coloration of Mn minerals and the occurrence of Mn in different kinds of rocks are discussed. L. J. S.

Pyrometasomatic vein deposits at Tepezala, Aguascalientes, Mexico. A. WANDKE and T. G. MOORE (Econ. Geol., 1935, 30, 765—782).—The rock types and ore deposits are described. CaO-silicate minerals occur both as products of wall rock alteration and as gangue minerals in the veins proper. The sulphide ore, chiefly chalcopyrite with minor amounts of pyrite, sphalerite, and galena, is associated with abundant diopside (I), hedenbergite (II), garnet, epidote (III), fluorite, quartz (IV), etc. as vein gangue minerals. The marginal alteration associated with the veins consists of an intergrowth of (I), (II), (III), and (IV). This alteration affects both intruded and intrusive rock and is probably the first work of the solutions as they rose in the fractures. The sequence of mineral deposition is discussed, and a comparison with other pyrometasomatic districts is made. The deposits are considered to be of Tertiary age. L. S. T.

Iron ore deposits of the Ilmpeia River, Eastern Siberia. V. SOBOLEV (Econ. Geol., 1935, 30, 783—791).—The geology and petrology of the district are briefly discussed. The Fe ore deposits, which present a new instance of a special type of magnetite deposits, are described and analyses are given. Their origin also is discussed. L. S. T.

Kaldurga conglomerates and the iron ore series of the Bababudans, Kadur district, Mysore. (A) M. B. R. RAO. (B) C. S. PICHAMUTHU (Current Sci., 1935, 4, 415—417, 417—418).—(A) A criticism of Pichamuthu (cf. A., 1935, 1479). (B) A reply. N. M. B.

Some deposits of lead ores in the state of Minas Geraes. B. A. WENDEBORN (Bol. Min. Agric. [Brazil], 1935, 24, 35—77).—The geology of the region studied (a zone of 1100 km. from Sete Lagoas through Pirapora to Montes Claros, and about 10—20 km. wide) is described with especial reference to, and analyses of, the Pb ores found. E. L.

Lead-bismuth ores in Bleka, Svartdal, Norway. C. BUGGE (Econ. Geol., 1935, 30, 792—799).—The ore (analyses given) occurring at Bleka in quartz (I) veins in a gabbro dyke is mainly galenobismutite with small amounts of bismutite (Bi_2S_3) and traces of galena. Emplectite has also been found. Au-bearing veins also occur and the gangue consists of dominant (I), barite, brown spar, tourmaline, and traces of fluorspar. Chalcopyrite is also important. L. S. T.

Spectrographic evidence on origin of ores of Mississippi Valley type. L. C. GRATON and G. A. HARCOURT (Econ. Geol., 1935, 30, 800—824).—Spectrographic examination shows that sphalerites from many deposits of the so-called Mississippi Valley type appear to contain amounts of Fe, Cu, and Pb, and of the less common elements, especially Cd, Ga, Ge, and In, commensurate with those found in deposits formed by solutions of magmatic origin. The geochemistry of the latter group of elements

in this connexion is discussed. A definite and systematic serial relationship between these sphalerites and those of hydrothermal sphalerites of a magmatic group is indicated. L. S. T.

Steigerite, a new vanadium mineral. E. P. HENDERSON (Amer. Min., 1935, 20, 769—772).—Steigerite (I), $\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot 6 \cdot 5\text{H}_2\text{O}$, similar to fervanite (II), has been found in the U-V deposits of the Gypsum Valley, San Miguel Co., Colorado. (I), n 1.71 \pm 0.005, has V_2O_5 44.44, Al_2O_3 25.14, Fe_2O_3 1.50, H_2O —8.08, $\text{H}_2\text{O} +$ 21.04, total 100.20%. It is bright canary-yellow in colour, insol. in H_2O , and is easily decomposed by mineral acids. X-Ray examination shows that (I) is cryst. giving a pattern different from that of (II). L. S. T.

Pegmatite minerals from near Amelia, Virginia. J. J. GLASS (Amer. Min., 1935, 20, 741—768).—31 mineral species have been identified from the pegmatites of Amelia and eight of these, viz., bertrandite, biotite, chalcopyrite, phenacite, pyrolusite, topaz, triplite, and zinnwaldite, are described in detail for the first time. The physical and optical properties of the two varieties of microlite which occur are compared, and several varieties of sericite (with analyses) are described. The zinnwaldite has SiO_2 43.70, Al_2O_3 22.96, Fe_2O_3 0.59, FeO 11.67, TiO_2 0.32, MgO 0.03, CaO 0.02, Na_2O 0.74, K_2O 9.58, H_2O —0.08, $\text{H}_2\text{O} +$ 1.35, MnO 1.95, F 5.52, Li_2O 1.92, Rb_2O 1.04, Cs_2O 0.10, total 101.58, (less O 2.32) 99.26%. New optical determinations and other properties of nearly all the minerals which occur at Amelia are tabulated. The less common elements, identified by spectrographic analyses in many of these minerals, are recorded. L. S. T.

Lithology of the precipitation of "domanic" shales from the upper Devonian of the western

slope of the Ural mountains. A. A. VAROV (Nef. Choz., 1934, 26, No. 7, 32—37).—The shales contain TiO_2 0.2—0.3, Mn \geq 2.23, Fe_2O_3 \geq 2, total S 2—3, SO_4^{2-} 0.2—0.3%. The P_2O_5 (0.1—0.5%) is higher in the carbonate shales than in the siliceous shales. CH. ABS. (e)

Lithology of the clay facies of the carboniferous in the Samara U-bend of the Volga river. L. A. GULJAEVA (Nef. Choz., 1934, 26, No. 7, 26—31).—The clay from various depths (\geq 1000 m.) contained alkalis 6—10, CO_2 $<$ 6, Mg 1—3%. It was low in Mn, Cl, and H_2SO_4 . CH. ABS. (e)

Enrichment of titania in clays. A. SALMINEN (Suomen Kem., 1936, 9, A, 1—4).—The average TiO_2 content of 27 Finnish clays was 0.68%; that of 12 sands was 0.40%. S. M. N.

Geological aspects of recent research on coal.—See B., 1936, 82.

Geology and presence of petroleum in northern Ferghana. G. I. SCHATOV (Nef. Choz., 1934, 26, No. 10, 21—22). CH. ABS. (e)

Geological characterisation of the Tschikischlyar oil-bearing district in Turkmenia. A. I. KOSUITGIN (Nef. Choz., 1934, 26, No. 7, 49—55).—Analytical data are given for various volcanic, and other, gas and oil producers, on the east shore of the Caspian Sea. CH. ABS. (e)

Athabasca oil sands: apparent example of local origin of oil. M. W. BALL (Bull. Amer. Assoc. Pet. Geol., 1935, 19, 153—171).—The oil occurs as a film around each grain of sand. It is of asphaltic base, very heavy, high in S, and is readily cracked at $<$ the normal temp., yielding 20—35% of gasoline. It is probably a young oil, which has not been geologically cracked. CH. ABS. (e)

Organic Chemistry.

Comparison and critical analysis of physical properties of homologues and isomerides. Molecular volume of alkanes. G. CALINGAERT and J. W. HLADKY (J. Amer. Chem. Soc., 1936, 58, 153—157).—A series of parallel curves is obtained by plotting mol. vol. against no. of C atoms in the longest chain; an arbitrary scale is used. Certain irregularities and the need of new data are discussed. H. B.

Combustion of hydrocarbons. I, II.—See this vol., 294.

Occurrence of radicals in the thermal decomposition of molecules and the reaction $\text{CH}_3 + \text{H}_2$.—See this vol., 293.

Formation of condensation products from simple hydrocarbons. M. W. TRAVERS (Trans. Faraday Soc., 1936, 32, 236—246).—Work previously published (A., 1935, 40) on the pyrolysis of C_2H_6 and condensation of C_2H_4 is reviewed. In presence of H_2 at 550° $\text{CHMe} \cdot \text{CH}_2$ yields C_2H_4 and CH_4 , whilst at the same time condensation proceeds from the initial reactions $2\text{C}_3\text{H}_6 = (\text{C}_3\text{H}_6)_2$ and $\text{C}_3\text{H}_6 + \text{C}_2\text{H}_4 = \text{C}_5\text{H}_{10}$. Preliminary experiments with C_2H_2 indicate

that the state of the SiO_2 -glass surface influences the nature of the reaction. F. L. U.

Development of the intermolecular and intramolecular chains in oxidation of *n*-hexane. W. M. ZAIKOVSKY (Physical Rev., 1934, [ii], 46, 329).—Analytical data of the oxidised air-*n*-hexane mixture are discussed. L. S. T.

Isomerisation of *n*-heptane. G. CALINGAERT and H. A. BEATTY (J. Amer. Chem. Soc., 1936, 58, 51—54; cf. A., 1935, 843).—*n*- C_7H_{16} heated with AlCl_3 gives pentanes (+lower hydrocarbons) 64.6% (of C_7H_{16} reacting), β - and γ -methylpentane 3.4 and 2%, respectively, *n*- C_6H_{14} 0.4%, $\beta\delta$ -dimethylpentane 1.5%, $\beta\beta\gamma$ -trimethylbutane 0.5%, $\gamma\gamma$ -dimethylpentane 0.4%, β - and γ -methylhexane 1.2 and 1.6%, respectively, and polymerisation products 24.4%. The above % are deduced from vals. of *n*, b.p., and crit. solution temp. in NH_2Ph . H. B.

Highly polymerised compounds. [Viscosity of solutions of aliphatic hydrocarbons.] H. STAUDINGER (Ber., 1936, 69, [B], 203—208).—A reply to Meyer *et al.* (A., 1935, 1318). H. W.

Paraffin hydrocarbon from urine of pregnancy.—See this vol., 362.

Mechanism of addition of halogens to ethylenic linkings. R. A. OGG, jun. (J. Amer. Chem. Soc., 1935, 57, 2727—2728).—The following mechanism, which applies to reactions in solution and in the dark, is suggested: $\text{CHR}:\text{CHR} + \text{Br}^- \rightarrow \text{CHRBr}^-\text{CHR} \xrightarrow{\text{Br}-\text{Br}} \text{CHRBr}\cdot\text{CHRBr} + \text{Br}^-$. Addition is thus catalysed by Br^- ; evidence (lit.) supporting this view is given. Since the intermediate carbanion has a stable configuration, stereoisomerides should be formed from *cis*- and *trans*-isomerides; the theories of Carothers (A., 1924, ii, 814) and Ingold (Chem. Reviews, 1934, 15, 225) lead to identical additive products. The above theory also explains the generally observed *trans* addition of Hal. H. B.

Mechanism of polymerisation.—See this vol., 295.

Polymerides and polyfunctionality.—See this vol., 295.

Formation of high polymerides of unsaturated substances.—See this vol., 295.

Polymerisation of unsaturated hydrocarbons. H. I. WATERMAN and J. J. LEENDERTSE (Trans. Faraday Soc., 1936, 32, 251—257; cf. A., 1935, 480).—A review of work previously published. F. L. U.

Peroxide effect in addition of reagents to unsaturated compounds. XI. Solvent effect in addition of hydrogen bromide to isobutene. M. S. KHARASCH and W. M. POTTS (J. Amer. Chem. Soc., 1936, 58, 57—59; cf. A., 1934, 792).—Addition of HBr to isobutene in a vac. in presence of antioxidants and solvents (pentane, CS_2 , EtCO_2H , EtBr , PhCN , PhNO_2 , H_2O) gives 80—92% yields of $\text{Bu}^\gamma\text{Br}$. In presence of ascaridole (0.03—0.04 mol.) and the same solvents a mixture of Bu^βBr (75—87% except in CS_2 when 100%) and $\text{Bu}^\gamma\text{Br}$ (13—25%) results. The data now obtained confirm the conclusion (*loc. cit.*) that solvents affect the velocity, but not the direction, of addition. H. B.

Photoiodination of ethylenic linking at low temperatures. G. S. FORBES and A. F. NELSON (J. Amer. Chem. Soc., 1936, 58, 182—183).—Illumination (through 10 cm. H_2O) of an equimol. mixture of Δ^a -butene (0.01M in CHCl_3) and I at -70° to -60° with light from incandescence lamps causes 98% disappearance of I after 3 hr. (90% in CH_2Cl_2 at -90° to -60°); I does not react with the solvent. Subsequent exposure of the solution in quartz to light from a W-steel spark causes quant. elimination of the I within 1 hr.; when the solution is kept at $20^\circ/100$ hr., 84% elimination of I occurs. H. B.

Dibromide method of determination of butene mixtures. W. G. YOUNG and S. WINSTEIN (J. Amer. Chem. Soc., 1936, 58, 102—104).—Contrary to Pines (A., 1933, 1138) and Komarewsky *et al.* (A., 1935, 192), the reaction rate-dibromide method (A., 1930, 888) is trustworthy. Conversion of mixtures into dibromides (composition not altered by distillation at atm. pressure) does not cause an appreciable change in composition. Differences in composition

of the C_4H_8 prepared by catalytic decomp. of $\text{Bu}^\alpha\text{OH}$ are ascribed to the effects of catalyst and temp. rather than to analytical procedure. H. B.

Application of the structure theory of reactions to Lebedev's synthesis of butadiene from alcohol and to Rice's theory of pyrolysis.—See this vol., 167.

Polymerisation of $\Delta^{\alpha\gamma}$ -butadiene in presence of metallic sodium.—See this vol., 296.

Induced substitution of pentene by chlorine. T. D. STEWART and B. WEIDENBAUM (J. Amer. Chem. Soc., 1936, 58, 98—100).—The following reactions occur between Δ^β -pentene and Cl_2 in CCl_4 at -10° or 25.1° : $\text{CHEt}:\text{CHMe} + \text{Cl}_2 \rightarrow \text{CHEtCl}\cdot\text{CHMeCl}$; $\text{CHEt}:\text{CHMe} + \text{Cl}_2 \rightarrow \text{CHEt}:\text{CH}\cdot\text{CH}_2\text{Cl}$ (I) + HCl. Substitution is favoured by decreasing the $[\text{Cl}_2]$; addition of H_2O , HCl, or powdered glass has no effect. Substitution also occurs, but to a smaller extent, with $\text{CH}_2:\text{CH}\cdot\text{CH}_2\text{Ph}$ but not with $\text{CH}_2:\text{CMeCl}$ (II). A reaction mechanism is discussed. The pseudo-unimol. velocity coeffs. (mols. per litre at 25°) of quaternary salt formation between NMe_3 (ten-fold excess) and (I), $\text{CH}_2:\text{CH}\cdot\text{CH}_2\text{Cl}$, (II), and CCl_4 are 0.109, 0.045, 0, and 0, respectively. H. B.

Dicrotyl [Δ^β -octadiene]. R. LESPIEAU and P. HEITZMANN (Bull. Soc. chim., 1936, [v], 3, 273—277).— $\text{CHMe}:\text{CH}\cdot\text{CH}_2\cdot\text{MgBr}$ and H_2O give a mixture of dicrotyls [Δ^β -octadienes], b.p. 122 — 125° [does not add I; hydrogenated to $n\text{-C}_8\text{H}_{18}$; oxidised to AcOH and $(\text{-CH}_2\cdot\text{CO}_2\text{H})_2$], *trans-trans-dicrotyl*, b.p. $124^\circ/747$ mm., m.p. about -76° (*tetra-bromide*, m.p. 84 — 84.5° , and *-iodide*, decomp. about 100°), and *trans- γ -methyl- $\Delta^{\alpha\epsilon}$ -heptadiene*, b.p. 115° , m.p. about -57° (*di-iodide*, m.p. 155 — 156° ; oxidised to $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$; hydrogenated to γ -methylheptane, b.p. 118.5°). R. S. C.

Mercury-photosensitised polymerisation of acetylene.—See this vol., 299.

Peroxide effect in addition of reagents to unsaturated compounds. X. Addition of hydrogen bromide to methylacetylene (allylene). M. S. KHARASCH, J. G. McNAB, and M. C. McNAB (J. Amer. Chem. Soc., 1935, 57, 2463—2465).—“Normal” addition (in a vac. in absence or presence of antioxidant) of HBr to $\text{CH}:\text{CMe}$ (I) gives CMc_2Br_2 . In presence of ascaridole (II), $\text{CHMeBr}\cdot\text{CH}_2\text{Br}$ is formed; the HBr must be passed into the (I)+(II) at -40° to -33° . (I) is not very sensitive to O_2 . H. B.

Divinylacetylene and its derivatives. P. V. SHAVORONKOV, A. P. ALECHINA, and R. S. SCHTER (Sintet. Kautschuk, 1934, No. 2, 12—14; cf. A., 1933, 694).—Divinylacetylene (I), b.p. 46 — $47^\circ/200$ mm., obtained as a by-product in the prep. of chloroprene from C_2H_2 , polymerises in 7—8 days in air to a gel which explodes on drying and cannot be used in the production of protective films. Antioxidants retard the formation of explosive films, whilst chlorination gives “safety” films. (I) yields *vinyl allyl ketone*, b.p. 85 — $86^\circ/20$ mm., by the addition of H_2O . CH. ABS. (r)

Reaction of butylacetylene with oxygen. C. A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 55—56; cf. A., 1935, 325).—

CH:CBu, freed from olefine by regeneration from CBU:CAg, AgNO₃ with aq. NaCN, forms a peroxide (attempted isolation by distillation caused decomp.); when kept in O₂ at 35—45°/3 months, valeric acid (8 g. from 123 g.) and polymeric material are produced.

H. B.

Catalytic dechlorination of tetrachloroethane. I. Decomposition by active carbon. II. Order of the decomposition reaction of tetrachloroethane. S. YAMAGUCHI (J. Chem. Soc. Japan, 1934, 55, 1227—1231, 1232—1235).—I. The effect of temp. and of various added materials is described.

II. The reaction $2C_2H_2Cl_4 \rightleftharpoons 2C_2HCl_3 + HCl$ is of the second order in the presence of active C.

CH. ABS. (r)

Constitution of the $\alpha\beta$ -halogen derivatives of ethane.—See this vol., 269.

Allylic rearrangements. I. Crotyl and methylvinylcarbinyl bromides. S. WINSTEIN and W. G. YOUNG (J. Amer. Chem. Soc., 1936, 58, 104—107).—Largely a more detailed account of work previously reviewed (A., 1935, 1480). Mixtures of CHMe:CH·CH₂Br, b.p. 2°/5 mm., and CH₂:CH·CHMeBr (I), b.p. -2°/14 mm., 31°/93 mm., are separated by fractional distillation at low temp. in a vac.; higher temp. cause rearrangement. Slow distillation/atm. pressure of a mixture [13% (I)] gives a product containing 87.5% of (I) (cf. *loc. cit.*).

H. B.

Mechanism of the catalytic conversion of alcohols into diethylene hydrocarbons. S. V. LEBEDEV, J. A. GORIN, and S. N. CHUFORETZKAJA (Sintet. Kautschuk, 1935, 4, No. 1, 8—27).—Catalytic decomp. of a mixture of EtOH and MeCHO affords butadiene (I). The influence of varying conditions on the yield of (I) is described. Catalytic decomp. of a mixture of EtOH and Et₂O yields (I), together with C₂H₄ and (CHMe)₂, the proportions depending on the conditions. Mixtures of EtOH with C₂H₄, H₂O, H₂, and BuOH behave similarly; the influence of varying conditions on the yield of (I) is described.

CH. ABS. (r)

Action of sulphuric acid on *sec.*-butyl alcohol. N. L. DRAKE and F. P. VEITCH, jun. (J. Amer. Chem. Soc., 1935, 57, 2623—2625).—*sec.*-BuOH and 75% H₂SO₄ at 80°/48 hr. under pressure give a mixture of (*sec.*-Bu)₂O and $\gamma\delta$ -dimethyl- Δ^{β} -hexene (I) [ozonolysis products, MeCHO, AcOH, and Me *sec.*-Bu ketone (II) (2:4-dinitrophenylhydrazone, m.p. 71.2°)]. Distillation of (I) with a trace of acid gives substances of higher mol. wt. (II) is oxidised (NaOBr) to α -methylbutyric acid (*p*-phenylphenacyl ester, m.p. 70.6°). Whitmore's mechanism of polymerisation by acids explains the production of (I) better than that of Kline and Drake (A., 1935, 192). H. B.

Dehydration of methyl*ditert.*-butylcarbinol. Fission and isomerisation of *ditert.*-butylethylene. I. N. NASAROV (Ber., 1936, 69, [B], 18—21; cf. Whitmore *et al.*, A., 1933, 1140).—Distillation of methyl*ditert.*-butylcarbinol with I affords essentially γ -methylene- $\beta\beta\delta\delta$ -tetramethylpentane, which readily suffers fission when heated with 1:4-C₁₀H₆Br·SO₃H into β -methyl- Δ^{α} -propene and a liquid mixture

containing $\beta\gamma$ -dimethyl- Δ^{β} -butene (about 70%), $\gamma\gamma$ -dimethyl- Δ^{α} -butene (about 3%), and $\beta\gamma$ -dimethyl- Δ^{α} -butene (about 27%). The formation of a radical and its immediate isomerisation, $CH_2:C^*CMe_2 \rightleftharpoons CH_2:CMc^*CMe_2 \rightleftharpoons C^*H_2:CMc^*CMe_2$, is assumed, hydrogenation at the expense of Bu⁷ occurring at C* atoms. The dehydration of methyl*tert.*-butylcarbinol is explained similarly.

H. W.

Fission and isomerisation of olefines which contain a tertiary radical. I. N. NASAROV (Ber., 1936, 69, [B], 21—24).—Methylisopropyl*tert.*-butylcarbinol (I) is transformed by distillation with a trace of I into γ -methylene- $\beta\beta\delta$ -trimethylpentane, smoothly transformed by 1:4-C₁₀H₆Br·SO₃H into β -methyl- Δ^{α} -propene and β -methyl- Δ^{β} -butene, also obtained directly from (I). Ethylisopropyl*tert.*-butylcarbinol, b.p. 188—191°, is dehydrated by I to $\delta\delta$ -dimethyl- γ -isopropyl- Δ^{β} -butene, b.p. 153—158°, which is transformed by 1:4-C₁₀H₆Br·SO₃H into β -methyl- Δ^{α} -propene and, apparently, β -methyl- Δ^{β} -pentene and β -methyl- Δ^{α} -pentene.

H. W.

Polyolysis of geraniol and citral. J. DŒUVRE and R. DESMULE (Bull. Soc. chim., 1936, [v], 3, 196—206).—In presence of Pt or glass wool at 505—510° geraniol (*p*-xenylyurethane, m.p. 69°) gives much isoprene and CMe₂:CH·CHO [*semicarbazone*, m.p. 240° (block); *p*-nitro-, m.p. 161°, and 2:4-dinitro-phenylhydrazone, m.p. 187—188°, with CH₂O, MeCHO, CHMe:CH·CO₂H, (?) CMe₂:CH·CH₂:OH, and a mixture of (? $\beta\eta$ - and $\beta\zeta$ -)dimethyl- $\Delta^{\beta\delta}$ -octadienes, b.p. 67—68°/20 mm., all of which arise by fission of the $\delta\epsilon$ -linking or formation and fission of an internal γ -oxide. Citral gives much CH₂:CHMe and other gases with a complex mixture containing $\beta\zeta$ -dimethyl- $\Delta^{\alpha\epsilon}$ -nonadiene, b.p. 141—143° (corr.)/750 mm., a hydrocarbon, C₁₀H₁₈, b.p. 66°/19 mm., a little isoprene, and a trace of CMe₂:CH·CHO.

R. S. C.

(A) Hexadecenol and tetradecenol in sperm head oil. Y. TOYAMA and T. TSUCHIYA. (B) Hexadecenol in sperm blubber oil. Y. TOYAMA and G. AKIYAMA (Bull. Chem. Soc. Japan, 1935, 10, 572—579, 579—584).—(A) Fractionation of the Ac derivatives of the unsaponifiable matter, b.p. < 180°/15 mm., of sperm head oil, conversion of the unsaturated acetates into their bromides, debromination, and refractionation of the unsaturated acetates affords the Ac derivative, b.p. 195—198°/15 mm. (oxidised by KMnO₄-AcOH to *n*-C₆H₁₃·CO₂H and OAc[CH₂]₈·CO₂H), of Δ^{ϵ} -hexadecen- α -ol (I) (*zoomaryl alcohol*), I val. 93.6, and the Ac derivative, b.p. 165—170°/15 mm. (oxidised to *n*-C₈H₁₇·CO₂H and γ -hydroxyvaleric acid), of Δ^{ϵ} -tetradecen- α -ol (*physeteryl alcohol*), I val. 111.2.

(B) The isolation (by similar methods) of (I) (16 g.) from the unsaponifiable portion (10 kg.; 36.1% of the oil) of sperm blubber oil, is described. J. W. B.

Lipins of tubercle bacilli. XLI. 1. Composition of timothy bacillus wax. 2. Isolation of *d*-eicosan- β -ol and *d*-octadecan- β -ol from the unsaponifiable matter of timothy bacillus wax. M. C. PANGBORN and R. J. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 10—14).—The wax (A., 1931, 526), purified by repeated pptn. from Et₂O with

COMe₂, has m.p. 45°, I val. 20.5, sap. val. 66.9, $[\alpha]_D^{20} +15.1^\circ$ in CHCl₃. Hydrolysis (5% EtOH-KOH in N₂) gives glycerol, trehalose, optically active higher fatty acids, and a dibasic *OH-acid*, C₇₀H₁₃₈O₆, m.p. 56–57°, $[\alpha]_D^{20} +6.1^\circ$ in CHCl₃ [*Ac* derivative, m.p. 40–41°; *Me* ester, m.p. 49° (*Ac* derivative, m.p. 41°)]. The unsaponifiable matter consists almost entirely of higher alcohols since treatment with *o*-C₆H₄(CO)₂O gives nearly quant. conversion into *H* phthalates. Fractional crystallisation of the alcohols (from MeOH) and their phenylcarbamates affords *d*-eicosan- β -ol (I), m.p. 62.5–63°, $[\alpha]_D^{20} +4.2^\circ$ in CHCl₃ (acetate, m.p. 35–37°; benzoate, m.p. 39–40°; phenylcarbamate, m.p. 78–78.5°, solidifies at 76° and remelts at 81°; *H* phthalate, m.p. 60–61°), and *d*-octadecan- β -ol (II), m.p. 56°, $[\alpha]_D^{20} +5.7^\circ$ in CHCl₃ (phenylcarbamate, m.p. 72–73°, solidifies at 66° and remelts at 76–77°). (I) is oxidised (CrO₂-AcOH, 30–40°) to eicosan- β -one, m.p. 58–59° (oxime, m.p. 73–74°; semicarbazone, m.p. 128°), which is also prepared by alkaline hydrolysis of the product from *n*-heptadecyl bromide and CHNaAc·CO₂Et. (II) is similarly oxidised to octadecan- β -one, m.p. 52° (semicarbazone, m.p. 127.5°), also synthesised from *n*-heptadecoyl chloride and ZnMeI.
H. B.

Stability of pinacolates in liquid ammonia solution. C. B. WOOSTER and D. S. LATHAM (J. Amer. Chem. Soc., 1936, 58, 76–78).—(·CMe₂·OH)₂ (I) and (·CPhMe·OH)₂ (II) with NaNH₂ (or CNaPh₃) in liquid NH₃ give the colourless (·CRMe·ONa)₂, which are hydrolysed (NH₄Cl) to the pinacols but no CORMe; ketyl formation [as with (·CPh₂·OH)₂ (cf. Kraus and Bien, A., 1933, 1120)] does not occur. (I) and (II) can be titrated with NaNH₂ using CHPh₃ as indicator. (I) and Na in liquid NH₃ give OH·CMe₂·CMe₂·ONa; (II) undergoes fission to CHPhMe·ONa. Hydrobenzoin is too insol. in liquid NH₃ to react with NaNH₂.
H. B.

Compounds of bivalent carbon. XIV. Bromodimethoxymethane (formyl bromide dimethyl acetal) and its reaction with sodium triphenylmethyl. H. SCHEIBLER and H. J. SCHMIDT (Ber., 1936, 69, [B], 12–15; cf. this vol., 66).—(OMe)₂CH·CO₂H is readily converted by Br in warm CHCl₃ in direct sunlight into bromodimethoxymethane (I), b.p. 55°/12 mm., and *Me H* oxalate, b.p. 75°/12 mm. (*K* salt). (I) and CNaPh₃ in Et₂O under N₂ yield the unstable triphenylacetaldehyde *Me₂ acetal*, which immediately decomposes into CHPh₃ and (not-isolated) *dimethoxymethylene (CO Me₂ acetal)*.
H. W.

Small-scale experiments on the autoxidation of ether. A. RIECHE and R. MEISTER (Angew. Chem., 1936, 49, 101–103).—PhCHO treated with H₂O₂, followed by CH₂Ph·OH and P₂O₅, yields *dibenzyl ether peroxide*, (CH₂Ph·O)₂, m.p. 119°. OH·CHMe·O₂H (I) dehydrated with P₂O₅ in Me₂O at low temp. yields the compound (CHMe·O₂H)₂O. (I) treated with MeCHO and H₂O₂ in Et₂O at 20°, the mixture cooled in Et₂O–solid CO₂, and MeCl added followed by P₂O₅ yields α -ethoxyethyl *H* peroxide, which under appropriate conditions of decomp. gives EtOH, MeCHO, AcOH, H₂O₂, and polymerised

ethylidene peroxide. A complete mechanism for the autoxidation of Et₂O is suggested. T. G. P.

Preparation of ketals of alkylacetylenes with higher alcohols. D. B. KILLIAN, G. F. HENNING, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 80–81; cf. A., 1934, 867).—Addition of CH:CBu to ROH (R=Et–hexyl) containing small amounts of CCl₄·CO₂H and a catalyst (prepared from red HgO and BF₃·Et₂O in MeOH) at $\geq 70^\circ$ gives CMeBu(OR)₂, which are hydrolysed (dil. H₂SO₄) to COMeBu. $\beta\beta$ -Diethoxy-, b.p. 68–69°/18 mm., $\beta\beta$ -dipropoxy-, b.p. 95–97°/18 mm., $\beta\beta$ -dibutoxy-, b.p. 115–117°/18 mm., $\beta\beta$ -diamyloxy-, b.p. 141–143°/18 mm., and $\beta\beta$ -dihexyloxy-, b.p. 143–144°/8 mm., -hexanes are described. $\beta\beta$ -Diethoxy-, b.p. 81–83°/18 mm., $\beta\beta$ -dipropoxy-, b.p. 107–109°/18 mm., $\beta\beta$ -dibutoxy-, b.p. 134–136°/18 mm., and $\beta\beta$ -diamyloxy-, b.p. 148–150°/17 mm., -heptanes are similarly prepared from Δ^2 -heptinene. Ketals could not be prepared from branched-chain AlkOH.
H. B.

Thermal decomposition of methyl hydrogen peroxide.—See this vol., 164.

Monoalkyl phosphites and their hydrolysis. P. NYLÉN (Svensk Kem. Tidskr. 1936, 48, 2–22).—The following monoalkyl phosphites, prepared by the action of NaOH on the appropriate dialkyl phosphite, are isolated as their *Na* salts: *Me*, m.p. 125° (decomp.); *Et*, m.p. 183–185°; *Pr^{\alpha}*, m.p. 195–196°; *Pr^{\beta}*, m.p. 132–133°; *Bu^{\alpha}*, m.p. 177.5–178.5°. *K* for these *H* esters is determined in 3.98*M*-NaCl at 25°. Only the undissociated *H* ester is oxidised by acid 1; the anion is stable towards I. A method for following the hydrolysis of the esters by acids and alkalis is described, and the equilibrium of the system H₃PO₃-EtOH-EtH₂PO₃-Et₂HPO₃-H₂O is determined. The structure of the mono- and di-alkyl phosphites is discussed.
J. N. A.

Hydrolysis of the phosphoric ester of starch and glycogen.—See this vol., 243.

Formation of high polymerides by condensation between metal polysulphides and dihalogenated hydrocarbons and ethers. J. C. PATRICK (Trans. Faraday Soc., 1936, 32, 347–357).—Aliphatic hydrocarbons and ethers having a halogen on each of the terminal C condense with metal polysulphides, e.g., Na₂S₄, to form linear polymerides of high mol. wt. with the respective empirical formulae C₂H₄S₄ and C₄H₈OS₄. Both types frequently exhibit rubber-like properties. By treatment with NaOH half the S is removed, the residual substance losing its rubbery nature if formed from a hydrocarbon, but retaining it if formed from an ether. S can be re-introduced, and (in the former case) rubbery properties restored, by a process analogous to the vulcanisation of rubber. Theories of chemical structure and of the mechanism of the heat-vulcanisation are advanced.
F. L. U.

Preparation of lower alkanesulphonic acids. D. L. VIVIAN and E. E. REID (J. Amer. Chem. Soc., 1935, 57, 2559–2560).—Anhyd. Alk·SO₃H are obtained from conc. aq. solutions after 4–5 distillations at 1 mm.; the pure acids soon darken even in a vac. The following are described: *n*-propane-

b.p. 136°/1 mm., m.p. 7.5°, *n*-butane-, b.p. 147°/0.5 mm., m.p. -15.2°, *n*-pentane-, b.p. 163°/1 mm., m.p. 15.9°, and *n*-hexane, b.p. 174°/1 mm., m.p. 16.1°, -sulphonic acids. The alternation in m.p. resembles that for Alk·CO₂H. H. B.

Interaction of diazonium salts and acetone-sulphonic acid. G. D. PARKES and S. J. M. FISHER (J.C.S., 1936, 83—85).—Diazotised *p*-C₆H₄Br·NH₂ and Na acetonesulphonate give *Na methylglyoxal-p-bromophenylhydrazone-ω-sulphonate*, m.p. 224° (decomp.). The following are similarly obtained: *Na methylglyoxal-phenyl-*, m.p. 195° (decomp.), *-p-chlorophenyl-*, m.p. 228° (decomp.), *-2:4-dichlorophenyl-*, m.p. 270° (decomp.), *-2:4-dibromophenyl-*, m.p. 275° (decomp.), *-o-nitrophenyl-*, m.p. 256° (decomp.), *-m-nitrophenyl-*, m.p. 251° (decomp.), and *-p-nitrophenyl-hydrazone-ω-sulphonate*, m.p. 265° (decomp.). *Na methylglyoxalphenylhydrazone-ω-sulphonate* with Br (1 or 2 mols.) yields *ω-bromomethylglyoxal-p-bromophenylhydrazone*, with 3 mols. of Br gives *βω-dibromo-α-ketopropaldehyde-p-bromophenylhydrazone*, and with excess of Br forms *ββω-tribromo-α-ketopropaldehyde-2:4-dibromophenylhydrazone*. F. R. S.

Esterification as a gas reaction.—See this vol., 164.

Hydrolysis rates of some monoacid triglycerides under the influence of pancreas extract. I.—See this vol., 297.

Catalytic hydrogenation of acid chlorides in the vapour phase at atmospheric pressure. N. FRÖSCHL and C. G. DANOV (J. pr. Chem., 1936, [iii], 144, 217—224).—Hydrogenation (Pd-asbestos) of the appropriate acid chloride at the b.p. gives P_r·CHO (with some CHPr⁺·CHEt·CHO), *isovaleraldehyde* (95%), *γ-butyrolactone* (54%), from *succinyl dichloride*, PhCHO (89%), CH₂Ph·OH + PhEt, and *o*-C₆H₄Me·OMe. S and P compounds must be entirely absent. Raney Ni cannot be used.

R. S. C.

Catalysis in organic chemistry. V. Decompositions of esters and acids by anhydrous zinc chloride. H. W. UNDERWOOD, jun., and O. L. BARR (J. Amer. Chem. Soc., 1935, 57, 2729—2730).—Alk·CO₂H (I) and their Me, Et, Pr, and Bu esters are unaffected by anhyd. ZnCl₂ (II) (cf. A., 1930, 321; 1931, 1034); the amyl esters undergo slow decomp. to (I) and unsaturated hydrocarbon (III). The rate of decomp. of Alk·CO₂Alk' increases with the no. of C atoms in Alk'. The esters of aliphatic dibasic acids (IV) give the Zn salt of (IV) and HCl [which reacts with (III) to form AlkCl]. ArCO₂R decompose to (III) and ArCO₂H (which then gives CO₂ and ArH). All the (III) produced undergo polymerisation; the amount increases with the no. of C atoms. When (II) is insol. in the hot acid or ester no decomp. occurs. Numerous examples are given. CH₂Cl·CO₂H gives CO, CH₂O, and HCl; CCl₃·CO₂H affords CO, COCl₂, and HCl. H. B.

Preparation of acetylenecarboxylic acids with sodamide. Synthesis of ethylpropionic acid. A. E. FAVORSKI and V. O. MOCHNATSCH (Bull. Far-Eastern Branch Acad. Sci. U.S.S.R., 1934, No. 9,

3—6; cf. A., 1888, 1168).—Treatment of *αβ*-C₄H₈Br₂ with NaNH₂ in kerosene, followed by passage of CO₂, gives a 46% yield of *Δ*^α-pentenoic acid, b.p. 81—82°/2 mm., m.p. 50.6°. The prep. from COMeEt and PCl₅, followed by NaNH₂ and CO₂, gave only poor yields. CH. ABS. (r)

Tetradecenoic and dodecenoic acids in sperm oil. I. Tetradecenoic and dodecenoic acids in sperm blubber oil. II. Dodecenoic acid in sperm head oil. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 563—569; 570—573).—I. After fractionation of their Me esters and hydrolysis, the fatty acids (2.4%) of sperm blubber oil (from *Physeter macrocephalus*, L.) are separated into fractions (i) b.p. 172—177°/15 mm., and (ii) b.p. 192—197°/15 mm. By the Pb-soap method (i) affords *Δ*⁸-dodecenoic acid (I), termed *denticetic acid*, converted into a Me dihydroxylaurate which gives *n*-C₆H₁₃·CO₂H and glutaric acid (II) when oxidised with KMnO₄ in COMe₂. Similarly (ii) gives *Δ*⁸-tetradecenoic acid (identical with physeteric acid from sperm head oil), converted into a Me dihydroxy-myristate, oxidised (KMnO₄) to *n*-C₈H₁₇·CO₂H and (II). Neither *Δ*⁸-tetradecenoic nor *Δ*⁸-dodecenoic acid (Hilditch *et al.*, B., 1928, 307) could be detected.

II. (I) is isolated from the unsaturated fatty acids, b.p. 172—177°/15 mm., obtained by usual methods from sperm head oil, and its structure is established as above. J. W. B.

Drying of oils and related unsaturated compounds. R. S. MORRELL and W. R. DAVIS (Trans. Faraday Soc., 1936, 32, 209—215; cf. this vol., 298).—Of the possible combinations between maleic anhydride and *α*- and *β*-clæostearic acids, only one is formed with each, viz., at the pair of conjugated double linkings remote from the CO₂H in the *α*- and nearer the CO₂H in the *β*-acid. The former (I) does not, and the latter (II) does, exhibit "drying" properties at room temp. Changes occurring in both compounds have been studied by measurements of the O₂ absorbed, peroxide val., I val., and viscosity, and by examination of the chemical structure of the products. In (I) only the ethenoid linking in the aliphatic chain is oxidised, yielding a product with ·CO·CH(OH)·, which undergoes no further change. In (II) a similar oxidation occurs at the ring ethenoid linking, whilst the remote aliphatic linking gives rise to a peroxide which is solely responsible for the ensuing polymerisation. Polymerisation in this, and in similar materials such as tung oil, is shown by a steady increase of viscosity which is accompanied by a concomitant disappearance of the peroxide radical. A chemical interpretation, supported by structural evidence, is put forward. The influence of polar and non-polar solvents is discussed.

F. L. U.

Polymerisation in monolayers.—See this vol., 298.

Relative rates of ozonisation of unsaturated compounds. C. R. NOLLER, J. F. CARSON, H. MARTIN, and K. S. HAWKINS (J. Amer. Chem. Soc., 1936, 58, 24—27).—The O₃-absorption curves (cf. Brus and Peyresblanques, A., 1930, 449, 588) for

oleic and elaidic acids, Me oleate, 1-phenyl- Δ^1 -cyclohexene, and stilbene show that rapid addition of 1 mol. to the C:C occurs. The rate of addition decreases considerably with CHPh:CPh₂ and compounds containing $\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot$ (e.g., vinylacetic, crotonic, cinnamic, and itaconic acids; CHMe:CH \cdot CHO); a further decrease is observed with CPh₂:CPh₂ and CHCl:CHCl. With compounds containing 2 or 3 double linkings (e.g., diphenylbutadiene; sorbic and elæostearic acids), rapid addition of 1 mol. occurs; the rate then decreases. With geometrical isomerides which undergo relatively slow addition (e.g., Me fumarate and maleate; mesaconic and citraconic acids), the *trans*-form reacts more rapidly. H. B.

Lipins of tubercle bacilli. XLII. Phthioic acid. M. A. SPIELMAN and R. J. ANDERSON (J. Biol. Chem., 1936, 112, 759—767; cf. this vol., 24).—Phthioic acid, C₂₆H₅₂O₂, m.p. 20—21° (best purified by way of the Me ester, b.p. 158°/0.003 mm., [α]_D²⁰ +12.2° in Et₂O, and characterised as *amide*, m.p. 45°), with CrO₃-AcOH gives only a branched-chain acid, C₁₁H₂₂O₂ (p-C₆H₄Br \cdot CO \cdot CH₂ \cdot ester, m.p. 49—50°; *tribromoanilide*, m.p. 111°). The *methylamide*, m.p. 27°, with PCl₅-C₆H₆ gives indefinite Cl nos. of no constitutive val. Grignard-CrO₃ degradation of the ester gives a mixture (impure *semicarbazone*, m.p. 55—65°). The acid is a polymethylated long-chain acid and probably has at least one Me close to the CO₂H since [α]_D²⁰ +12.56° in Et₂O, is high. The very pure acid retains the physiological properties previously reported. R. S. C.

ϵ -Hexolactone. F. J. VAN NATTA, J. W. HILL, and W. H. CAROTHERS (J. Amer. Chem. Soc., 1936, 58, 183).—Partly a reply to Stoll and Rouvé (A., 1935, 1351). Further details (cf. A., 1934, 392) for the prep. of ϵ -hexolactone are given. H. B.

Highly polymerised compounds. CXXXIII. Viscosity of solutions of glycol esters and dicarboxylic esters. H. STAUDINGER and H. MOSER (Ber., 1936, 69, [B], 208—213).—The observed sp. viscosities of C₆H₆ and CHCl₃ solutions of esters of higher fatty acids and decane- $\alpha\kappa$ -diol and of esters of sebacic and thapsiaic acid agree with those calc. from the formula $\eta_{sp.} (1.4\%) = \eta n$ and the temp. coeff. is the same as that observed with other aliphatic compounds of similar structure, thus showing that $\eta_{sp.}$ of a solution depends essentially on the length of the mol. and is independent of its special structure. With derivatives of propane- $\alpha\gamma$ -diol the observed $\eta_{sp.}$ is lower than the calc. but the temp. effect is normal. A shortening of the chain due to inter-attraction of the O atoms appears to be indicated. The following are incidentally described: *dilaurate*, m.p. 47—48°, *dimyristate*, m.p. 56—57°, and *dipalmitate*, m.p. 62—63°, of decane- $\alpha\kappa$ -diol; *dicetyl sebacate*, m.p. 53.5—54.5°, *dicetyl*, m.p. 62.5—63°, and *dioleyl*, m.p. 35—35.5°, *thapsiate*; *dilaurate*, m.p. 38—39°; *dimyristate*, m.p. 49.0—49.5°, and *dipalmitate*, m.p. 54.5—55.5°, of propane- $\alpha\gamma$ -diol. H. W.

Influence of heat and of the presence of various cations on oxalic acid solutions. A. M. VASILIEV and N. I. PANOVA (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 79—82).—H₂C₂O₄ is volatile

from conc. aq. solution on boiling. Most salts are stable but Mn causes loss of acid even in dil. solution.

CH. ABS. (7)

Oxidation of ethyl hydrogen methylmalonate and of ethyl hydrogen succinate with potassium persulphate. F. FICHTER and J. HEER (Helv. Chim. Acta, 1936, 19, 149—154).—CO₂K \cdot CHMe \cdot CO₂Et and CO₂K \cdot CH₂ \cdot CH₂ \cdot CO₂Et behave when oxidised with KSO₄ in the same manner as when electrolysed according to Crum Brown and Walker, EtCO₂Et and CH₂:CH \cdot CO₂Et being obtained in addition to (\cdot CHMe \cdot CO₂Et)₂ from the former and Et₂ adipate from the latter. Electrosynthesis is therefore an oxidation in the sense 2CO₂H \cdot CHMe \cdot CO₂Et + O = 2CO₂ + H₂O + (\cdot CHMe \cdot CO₂Et)₂ and 2CO₂H \cdot CH₂ \cdot CH₂ \cdot CO₂Et + O = (\cdot CH₂ \cdot CH₂ \cdot CO₂Et)₂ + 2CO₂ + H₂O. The yields of Et₂ esters are less by the oxidative than by the electrolytic method and decrease with increasing mol. wt. of the initial material. Et H methylmalonate has b.p. 111°/1 mm. H. W.

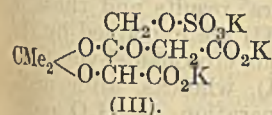
Carbon dioxide cleavage from dibromomalonic acid. II.—See this vol., 295.

Formation of succinic acid by B. coli.—See this vol., 247.

Lichen substances. LXII. Components of Cetraria islandica, Ach. Y. ASAHINA and M. YANAGITA (Ber., 1936, 69, [B], 120—125).—*C. islandica*, Ach., from Hokkaido contains about 4% of a mixture of fatty acids which affords *d-protolichesteric acid* (I), m.p. 106°, [α]_D²⁰ +12.07° in CHCl₃ when crystallised from AcOH, and *l-allo-protolichesteric acid* (II), m.p. 88°, [α]_D²⁰ -56.34° in EtOH, [α]_D²⁰ -49.53° in CHCl₃. Since (II) is transformed by warm Ac₂O into *l*-lichesteric acid and converted by CH₂N₂ into a *pyrazoline* derivative, C₂₂H₃₆O₄N₂, m.p. 68—69°, [α]_D¹⁸ -73.69° in CHCl₃, it is structurally identical with *protolichesteric acid*. It is oxidised by alkaline KMnO₄ to myristic acid. Treatment of the mixture of fatty acids with Ac₂O at 100° gives *dl*-lichesteric acid, m.p. 115°, also obtained from its components. Catalytic hydrogenation (Pd in AcOH) of (II) affords *dihydro*-*l*-allo-*protolichesteric acid*, m.p. 92—93°, [α]_D²⁰ -7.41° in CHCl₃. Similarly, (I) gives *dihydro*-*d*-*protolichesteric acid*, m.p. 106°, [α]_D¹⁸ +34.60° in CHCl₃, transformed by CH₂N₂ into a *pyrazoline* derivative, m.p. 54—55°, [α]_D¹⁸ +190.60° in CHCl₃. Extraction of the thalli of Japanese *C. tenuifolia*, Retz, with H₂O yields *l*-*protolichesteric acid*, m.p. 106°, [α]_D¹⁸ -12.12° in CHCl₃, hydrogenated to *dihydro*-*l*-*protolichesteric acid*, m.p. 106°, [α]_D¹⁸ -30.96°, whence the *pyrazoline* derivative, m.p. 54—55°, [α]_D¹⁸ -183.1° in CHCl₃. H. W.

Action of periodic acid on tartaric acid. P. FLEURY and (MLLE.) G. BON-BERNATETS (J. Pharm. Chim., 1936, [viii], 23, 85—99; cf. A., 1933, 591; Malaprade, A., 1934, 1090).—In the first stage of the reaction, which is complete in 5—10 min., HIO₄ gives up O, 2CHO \cdot CO₂H (I) being produced; in the second, which is complete in 36—48 hr. at room temp. (2 hr. at 37°), (I) is oxidised to HCO₂H and CO₂, taking O from HIO₄. Hence each mol. of tartaric acid requires 3HIO₄ for completion of the reaction. W. McC.

Constitution of isopropylidene-furtondicarboxylic acids. H. OHLE and N. SENGER (Ber., 1936, 69, [B], 160—170; cf. A., 1929, 913; 1931, 72; 1932, 144, 148).—Oxidation of β -diisopropylidene-fructose (I) with KMnO_4 ($\equiv 4\text{O}$) gives K_2 β -isopropylidene-1-furtondicarboxylic acid, ($+\text{H}_2\text{O}$) (II), $[\alpha]_D^{25} +53.2^\circ$ in H_2O [corresponding Ag_2 ($+\text{2H}_2\text{O}$), Ba ($+\text{1.5H}_2\text{O}$), and Ca ($+\text{6H}_2\text{O}$) salts]. (II) is transformed by pyridine-1-sulphonic acid in $\text{C}_5\text{H}_5\text{N}$ into K_2 β -isopropylidene-1-furtondicarboxylate 1-sulphate (III) (*loc. cit.*), so that (II) is the parent of (III). Methylation of the Ag salt of (II) affords α -isopropylidenedioxy- β -carbomethoxymethoxy- γ -butyrolactone (IV), m.p. 89.5° , $[\alpha]_D^{25} +56.6^\circ$ in MeOH , $+64.2^\circ$ in C_6H_6 , which regenerates (II) when hydrolysed by alkali, and Me γ -methoxy- α - β -isopropylidenedioxy- γ -carbomethoxymethoxy- n -butyrate, b.p. 140° (bath)/ 0.05 mm., $[\alpha]_D^{25} +33.8^\circ$ in MeOH , hydrolysed by KOH-MeOH to K_2 γ -methoxy- α - β -isopropylidenedioxy- γ -carbomethoxy- n -butyrate (V), $[\alpha]_D^{25} +45.85^\circ$ in H_2O (corresponding Ag_2 salt). (IV) contains an active H of unknown location. When hydrolysed by acid it evolves CO_2 with much greater difficulty than does (II). When treated with boiling HCl-MeOH it gives (in about 90% yield) hydroxyketonic acid, identified by dehydrogenation with $p\text{-O:C}_6\text{H}_4\text{:O}$ and coupling with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ to the quinoxaline derivative, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_4$. Analogously with (IV), (V) decomposes into COMe_2 , CO_2 , and $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, but the expected dihydroxymethylacetone could not be detected with certainty. (III) has therefore the structure shown and the analogy between fermentative and



oxidative fission is purely formal. Examination of the graphs of the oxidation of (III) by KMnO_4 in alkaline and neutral solution together with previous observations (*loc. cit.*) show that oxidation of (I) proceeds in two fundamentally different manners determined by $[\text{H}^+]$ and $[\text{OH}^-]$, respectively. In alkaline solution the oxidant at first attacks almost exclusively the OH of CH_2OH . In neutral solution oxidation takes place preferentially at the CH linkings of the etherified OH groups.

H. W.

Synthesis of vitamin-C from starch. P. P. T. SAH (Ber., 1936, 69, [B], 158—159).—The synthesis of *l*-ascorbic acid (I) through the following steps is announced; the details will follow. Starch $\rightarrow d$ -saccharic acid $\rightarrow l$ -gulonic acid $\rightarrow l$ -gulonolactone $\rightarrow l$ -gulose $\rightarrow l$ -gulosazone $\rightarrow l$ -gulosone $\rightarrow \alpha$ -keto-*l*-gulonic acid $\rightarrow \text{Me}$ α -keto-*l*-gulonate \rightarrow (I). H. W.

Starch as a starting material for the synthesis of vitamin-C. P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1935, C, 3, 265—277).—A detailed account of the work already reviewed (cf. preceding abstract). The possible, similar use of lactose is suggested.

H. W.

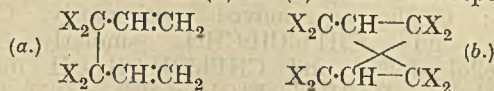
Reactions of vitamin-C.—See this vol., 255.

Constitution of gluconic acids. IV. H. SUTTER, F. ROTTMAYR, and H. PORSCH (Annalen, 1936, 521, 180—197; cf. A., 1935, 1224).—Proof that the thermal decomp. product of gluconic acid (A., 1933, 1143) is $\text{CHEt:CET}\cdot\text{CHO}$ is obtained by its oxidation with Ag_2O to the acid, b.p. $116^\circ/13$ mm. (chloride,

b.p. $62^\circ/13$ mm.; *amide*, m.p. 117°), identical with a specimen synthesised by condensation of $\text{CHEtBr}\cdot\text{CO}_2\text{Et}\cdot\text{Zn}\cdot\text{EtCHO}$ to give the *OH*-ester, b.p. $107\text{—}122^\circ/18$ mm., converted by PCl_5 and subsequent hydrolysis with KOH-EtOH into $\text{CHEt:CET}\cdot\text{CO}_2\text{H}$. The *amides* of tiglic, m.p. 77° , and of $\beta\beta$ -dimethylacrylic acid, m.p. 108° , were prepared for comparison. Glauconic acid (I), m.p. 188° , $[\alpha]_D^{20} +189.6^\circ$ in CHCl_3 , has equiv. 83, and gives a Ag_4 salt which, with MeI-MeOH affords only a Me_2 ester, m.p. 145° . (I) gives a *compound*, $\text{C}_{18}\text{H}_{21}\text{O}_6\text{N}$, m.p. $207\text{—}208^\circ$, with NH_2OH , and a *compound*, $\text{C}_{20}\text{H}_{32}\text{O}_4\text{H}_4$, m.p. 122° , with $\text{NHPh}\cdot\text{NH}_2$. Reduction of (I) with Zn-AcOH affords (mainly) a dicarboxylic acid, $\text{C}_{18}\text{H}_{27}\text{O}_7$, m.p. 209° (Me_2 ester, m.p. 161°), and traces of an acid, $\text{C}_{20}\text{H}_{24(28)}\text{O}_7$, m.p. 201° (Me ester, m.p. $193\text{—}194^\circ$), and a neutral substance, $\text{C}_{18}\text{H}_{22}\text{O}_6$, m.p. 192° . (I) is stable to most oxidising agents, but with NaOCl-NaOH it gives a substance, $\text{C}_{16}\text{H}_{20(22)}\text{O}_4\text{Cl}_2$, m.p. 200° . The structure of (I), which probably contains the system $\text{OH}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{C} \begin{array}{l} \diagdown \quad \diagup \\ \text{C} \cdot \text{O} \cdot \text{CO} \\ \diagup \quad \diagdown \end{array}$ reduced to $>\text{C} \begin{array}{l} \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \\ \diagup \quad \diagdown \end{array} \text{CH}(\text{CO}_2\text{H})\cdot\text{CH}$ is briefly discussed.

J. W. B.

Possibility of ring-chain mesomerism. II. **Properties of $\Delta^{\alpha\epsilon}$ -hexadiene- $\alpha\alpha\gamma\gamma\delta\delta\zeta\zeta$ -octacarboxylic esters.** C. K. INGOLD, M. M. PAREKH, and C. W. SHOPPEE (J.C.S., 1936, 142—153).—The work of Guthzeit and Hartmann (A., 1910, i, 386) on the ester obtained from Et sodiodicarboxyglutaconate and I has been repeated, without complete confirmation. The Me series has also been prepared and the constitution of the compounds is discussed. The observations do not support the *dicyclobutane* formula for the ester nor a structure with fused *cyclobutane* rings, but are in favour of (a) or (b). The corresponding



Me compounds are given in brackets. Oxidation of Et $\Delta^{\alpha\epsilon}$ -hexadiene- $\alpha\alpha\gamma\gamma\delta\delta\zeta\zeta$ -octacarboxylate (I) [Me_8 ester (II), m.p. 139°] with KMnO_4 gives Et_6 $\Delta^{\alpha\epsilon}$ -hexadiene- $\alpha\alpha\gamma\gamma\delta\delta\zeta\zeta$ -octacarboxylate [Me_6 ester, m.p. 218° (decomp.)], which with SOCl_2 yields the Et_6 ester dichloride, $\text{C}_6\text{H}_2(\text{CO}_2\text{Et})_6(\text{COCl})_2$, m.p. $65\text{—}66^\circ$. (I) and HCl afford Et_3 H_2 3-hydroxy-2:4:4:5:5-pentacarboxycyclopentane-1-acetate, m.p. 152° , and its *anilide*, m.p. 152° [Me_4 ester, m.p. 245° (decomp.)], converted into the neutral Et_6 ester, m.p. 71° [Me_6 ester, m.p. 168°]. 3-Hydroxy-2:4:5-tricarboxycyclopentane-1-acetate, prepared by hydrolysis of the foregoing esters, has m.p. 193° , is stable to KMnO_4 , and gives Me and Et esters; the constitution of this substance was given incorrectly by previous authors. Ozonolysis of (I) and (II) gives Et and Me ethane-tetracarboxylate, respectively. (II) and NaOMe afford Me 3-methoxy-2:2:4:4:5:5-hexacarboxycyclopentane-1-malonate, m.p. 193° , whilst thermal decomp. of (II) leads to Me 6-methoxy- α -pyrone-3:5-dicarboxylate. Electrolysis of (II) in H_2SO_4 gives Me_8 dihydro-2:2:4:4:5:5-hexacarboxycyclopentane-1-malonate, m.p. 149° , which with HCl forms the Me_6 H_2 ester, m.p. 252° (decomp.), hydrolysed to 2:4:5-tricarboxycyclopentane-1-acetic acid, m.p. 225° [Ag

salt; *amide*, m.p. 280° (decomp.]. The red Na_4 salt of Guthzeit does not exist. Me 3-hydroxy-2:4:5-tricarboxycyclopentane-1-acetate is dehydrated (KHSO_4) to a mixture of isomeric pentene-1-acetates, reduced to a mixture of acids. F. R. S.

Photochemical reactions of SH-compounds in solution.—See this vol., 171.

Derivatives of β -sulphopropionic acid. L. A. BIGELOW, H. W. SIGMON, and D. H. WILCOX, jun. (J. Amer. Chem. Soc., 1935, 57, 2521—2524).— Me_2 , b.p. 132—133° (slight decomp.)/1 mm., m.p. 17°, Et_2 , m.p. 4°, Pr^a_2 , m.p. -7°, Bu^a_2 , m.p. -25°, and *di*-(phenylethyl), m.p. 59°, β -sulphopropionates are prepared from the anhyd. Ag_2 salt (cf. Rosenthal, A., 1886, 866) and RI . The dry K_2 salt and PCl_5 in C_6H_6 afford the unstable acid chloride (I), $\text{COCl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\text{Cl}$, m.p. $-9\pm 1^\circ$ (cf. *loc. cit.*); the normal *diamide*, m.p. 161°, is prepared. (I) and dry NH_3 in C_6H_6 give (probably) NH_4 β -sulphopropionimide, $\begin{matrix} \text{CH}_2\cdot\text{SO}_2 \\ \text{CH}_2\cdot\text{CO} \end{matrix} > \text{N}\cdot\text{NH}_4$, m.p. 164—168° (decomp.); the corresponding *Ba* salt and H_2SO_4 (1 equiv.) do not give the imide, but afford some (NH_4) $_2$ β -sulphopropionate, m.p. 175—176° (shrinks at 170°), which passes at 111°/3—4 mm. into the NH_4 *H* salt. H. B.

Kinetics of reaction between peracetic acid and aldehydes.—See this vol., 165.

Reduction of aldehydes with aluminium isopropoxide. W. G. YOUNG, W. H. HARTUNG, and F. S. CROSSLEY (J. Amer. Chem. Soc., 1936, 58, 100—102).— $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ is best prepared (58—60% yield) by reduction of $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ with $\text{Al}(\text{OPr}^i)_3$ (I) (from Al and HgCl_2 in Pr^iOH) in Pr^iOH at 110° (bath); COMe_2 is removed continuously. Citronellal and $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ similarly give citronellol (32%) and $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ (68%), respectively. PrCHO in EtOH at 25° or C_6H_6 (b.p.) with (I) gives 30 or 28%, respectively, of Bu^nOH ; $\text{Al}(\text{OEt})_3$ and $\text{OEt}\cdot\text{MgCl}$ (Meerwein and Schmidt, A., 1925, i, 1239) are much less efficient. The reaction mechanism is considered not to be a simple adaptation of the Cannizzaro reaction (cf. *loc. cit.*). H. B.

Constitution of bisulphite additive compounds of aldehydes and ketones. W. M. LAUER and C. M. LANGKAMMERER (J. Amer. Chem. Soc., 1935, 57, 2360—2362).— $\text{CH}_2\text{I}\cdot\text{SO}_3\text{K}$ (I) (from CHI_3 and aq. K_2SO_3) and KOAc at 200—205° give *K* acetoxy-methanesulphonate (II) (crystallographic data given), also formed by acetylation ($\text{Ac}_2\text{O}\text{--AcOH}$) of the KHSO_3 additive compound (III) of CH_2O . (III) is, therefore, *K* hydroxymethanesulphonate. (I) is reduced (Zn dust, $\text{EtOH}\text{--AcOH}$) to MeSO_3K and with aq. K_2SO_3 gives $\text{CH}_2(\text{SO}_3\text{K})_2$. (II) and NH_2Ph afford *K* anilinomethanesulphonate ($+\text{H}_2\text{O}$), converted by aq. KCN into $\text{NHPh}\cdot\text{CH}_2\cdot\text{CN}$ (hydrolysed to $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$). (II) and aq. KCN give $\text{OAc}\cdot\text{CH}_2\cdot\text{CN}$. Hydrolysis (dil. H_2SO_4) of (II) affords CH_2O . $\text{CH}_2\text{I}\cdot\text{SO}_3\text{Na}$ ($+\text{H}_2\text{O}$) is prepared as (I).

H. B.

[Asymmetric] catalysis with organic fibres.—See this vol., 170.

Polymerisation of gaseous formaldehyde and acetaldehyde.—See this vol., 298.

Polymerides of acetaldehyde. M. W. TRAVERS [in part with R. G. SOLLERS] (Trans. Faraday Soc., 1936, 32, 246—249).—By distilling dry air-free MeCHO into a bulb cooled in liquid air, a viscous or gelatinous product is obtained, the v.p. of which is, however, not measurably < that of the ordinary mobile liquid. On exposure to a vac., the product froths and ultimately becomes glassy. It slowly regenerates MeCHO in a sealed tube at 100°. Treatment of MeCHO with $\text{H}_2\text{SO}_4\text{--EtOH}$ at temp. not below -105° produces rapid polymerisation, a liquid compound, b.p. 73—75°, being formed. Its mol. wt., determined cryoscopically, corresponds with $(\text{MeCHO})_2$. It dissociates rapidly at 100°. F. L. U.

Synthesis of deuteroacetaldehyde. J. E. ZANNETTI and D. V. SICKMAN (J. Amer. Chem. Soc., 1935, 57, 2735).—Deuteroacetaldehyde (v.p. 327 mm. at 0°), prepared from C_2D_2 and D_2O —acid— Hg salt, shows the usual aldehyde reactions. H. B.

Decomposition of acraldehyde catalysed by iodine.—See this vol., 167.

Aldehyde condensations with secondary amines (Knoevenagel reaction). R. KUHN, W. BADSTÜBNER, and C. GRUNDMANN (Ber., 1936, 69, [B], 98—107; cf. A., 1931, 1273).—The apparent discrepancy between the authors' results and those of Bernhauer *et al.* (A., 1932, 834) are explained by the observations that homogeneous crotonaldehyde (I) is unchanged by piperidine (II), whereas, after insolation, discoloration and separation of H_2O occur readily. The change is due to crotonic acid (III) formed by autoxidation of (I). AcOH , BzOH , citric or cholic acid can replace (III), but phenols are less efficient. It is therefore probable that the Knoevenagel reaction is generally catalysed by salts of *sec.* bases rather than by the bases themselves and an equimol. mixture of (II) and glacial AcOH diluted with a little abs. EtOH is found very serviceable. Decatetraenal, $\text{Me}\cdot[\text{CH}\cdot\text{CH}]_4\cdot\text{CHO}$, m.p. 107—107.5° (*hydrazone*, complete decomp. 280° after softening and darkening at 190°), is thus derived from (I) and sorbaldehyde or from MeCHO and octatrienal. It condenses with $\text{CH}_2(\text{CO}_2\text{Et})_2$ to *decatetraenalmalonic acid*, which gradually decomposes when heated and is decarboxylated, best by boiling $\text{AcOH}\text{--Ac}_2\text{O}$, to *dodecapentaenoic acid*, m.p. 247° (decomp.); the *Me* ester, m.p. 190.5°, becomes polymerised and autoxidised when exposed to air. *Citrylideneacetaldehyde*, $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$, b.p. 93—94°/0.02 mm., obtained from citral and excess of MeCHO in presence of (I)— AcOH but not of (I), can be preserved unchanged in vac. in the dark, but rapidly resinifies when exposed to air; it has a strong odour of over-ripe pears, and differs in this respect and in its physical consts. from the product of von Braun *et al.* (A., 1934, 1335). The possibility of *cis-trans*-isomerism is not supported by attempted isomerisation by irradiation, I, etc. It gives a *semicarbazone*, m.p. 166—167°, and a 2:4-dinitrophenylhydrazone, m.p. 132—133°. It is transformed by boiling 10% K_2CO_3 into MeCHO and methylheptenone. When

heated with Ag_2O it is oxidised (with partial hydrolysis) to *citrylideneacetic acid*, b.p. $115-120^\circ/0.002$ mm., hydrogenated (PtO_2) to *dl-80-dimethyldecoic acid*, b.p. $160-162^\circ/12$ mm. (*p-bromophenacyl ester*, m.p. 56°). Treatment of it with $\text{Al}(\text{OPr}^\beta)_3$ affords *citrylidene-ethyl alcohol* (*εε-dimethyl-Δ⁸⁸⁰-decatrienyl alcohol*), b.p. $102-105^\circ/0.03$ mm. H. W.

Detection of methylglyoxal and fission of caoutchouc by ozone. R. PUMMERER, G. MATTHÄUS, and W. SOCIAS-VIÑALS [with, in part, F. BRAUN] (Ber., 1936, 69, [B], 170-183).—The possibility of recognising AcCHO in presence of laevulaldehyde (I), MeCHO , and CH_2O (as products of ozonisation of caoutchouc) is impeded by the impossibility of separating (I) and AcCHO by means of $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$. The pptn. of Ni methylglyoxime is not sufficiently complete in dil. solution. The most suitable reagent is $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, which in very dil. solution gives 91% yields of methylglyoxaldisemicarbazone (II) without co-pptn. of laevulaldehydesemicarbazone. (II) is subsequently transformed by 17% H_2SO_4 into methylglyoxal-2 : 4-dinitrophenylosazone (yield 95%). A more complex separation of AcCHO and (I) is effected by *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$. Comparative experiments with O_3 and mesityl oxide in CCl_4 and H_2O give only 7.4% and 18% yields of AcCHO , which are increased to 29% in CHCl_3 at 0° followed by very cautious fission of the ozonide by SO_2 . The mean yield of MeCHO from caoutchouc is 1%, but this is observed only after over-ozonisation. If the action of O_3 is interrupted as soon as the CHCl_3 solution has become stable to Br, the production of AcCHO is $> 0.1\%$ in any case. The view that AcCHO is a secondary product is discounted by the observation that, after a certain period, further over-ozonisation does not affect the yield of AcCHO . If aq. SO_2 is used for fission of the ozonide, AcCHO is not detected even after prolonged ozonisation. A terminal isoprene group with a conjugated system is therefore not present in 1000 isopentene groups of caoutchouc. Guttapercha behaves similarly, giving no AcCHO with or without over-ozonisation if SO_2 is used for fission of the ozonide and about 1% of AcCHO if H_2O at 80° is employed. The occurrence of MeCHO among the products of ozonisation is unexplained. Methylheptenone when ozonised or over-ozonised and then treated with SO_2 does not give AcCHO . Over-ozonisation and subsequent treatment with H_2O at 80° gives 0.6-0.8% of the C skeleton as AcCHO and an almost equiv. amount of $\text{H}_2\text{C}_2\text{O}_4$. H. W.

Enolisation as directed by acid and basic catalysts. III. Acid-catalysed enolisation of sec.-butyl ketones. P. D. BARTLETT and C. H. STAUFFER (J. Amer. Chem. Soc., 1935, 57, 2580-2583).—The rates of racemisation (k_R) and iodination (k_I) of *d*- $\text{COPh}\cdot\text{CHMeEt}$ in AcOH containing HNO_3 (1.19N) (catalyst) at 36.75° are identical. Similarly, k_R and k_I are determined for *d*- $\text{COR}\cdot\text{CHMeEt}$ (R = Me, Et, CH_2Ph , and cyclohexyl) at 25° (and other temp.); the competitive rates of the enolisations involving the H of CHMeEt and R are calc. The mechanism previously advanced (A., 1934, 607) does not permit an explanation of the relationship

between enolisation and alkyl substitution. The vals. of k_R and k_I for menthone (*ibid.*, 153) are revised.

H. B.

Reactions of tagetone. I. T. G. H. JONES (Proc. Roy. Soc. Queensland, 1934, 45, 45-49; cf. A., 1926, 72).—Tagetone (I) is represented as a tautomeric mixture: $\text{COBu}^\beta\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2)_2\cdot\text{CH}\cdot\text{CH}_2 \rightleftharpoons \text{OH}\cdot\text{CBu}^\beta\cdot\text{CH}\cdot\text{C}(\text{CH}_2)_2\cdot\text{CH}\cdot\text{CH}_2 \rightleftharpoons \text{COBu}^\beta\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2$. Reduction of (I) with $\text{Na}\cdot\text{EtOH}$ yields *dihydrotagetol*, $\text{C}_{10}\text{H}_{20}\text{O}$, b.p. $197^\circ/760$ mm., which is not γ^0 -dimethyl- Δ^a -octen- ϵ -ol. Reduction of (I) with Zn dust and $\text{EtOH}\cdot\text{NH}_4\text{Cl}$ yields a non-homogeneous *dihydrotagetone* (II), $\text{C}_{10}\text{H}_{18}\text{O}$, b.p. $186-190^\circ$, with two dimeric products, $\text{C}_{20}\text{H}_{32}\text{O}$, b.p. $115-120^\circ/4$ mm., and $\text{C}_{20}\text{H}_{34}\text{O}_{27}$, b.p. $140-150^\circ/4$ mm. (II) on oxidation yields $\text{Bu}^\beta\text{CO}_2\text{H}$ and a *CO-acid*, $\text{C}_9\text{H}_{16}\text{O}_3$; it is, therefore, $\text{COBu}^\beta\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CHMe}$ containing a little $\text{COBu}^\beta\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2$. Reduction of (I) with Zn and $\text{EtOH}\cdot\text{NaOH}$ yields a *monoketone*, $\text{C}_{20}\text{H}_{34}\text{O}_2$, b.p. $140-150^\circ/4$ mm. (*monoxime*), and an isomeric *diketone*, b.p. $160-170^\circ/4$ mm. (*dioxime*), together with a little low-boiling liquid (*semicarbazone*, m.p. 92.5°). Reduction of (I) with $\text{Na}\cdot\text{Hg}$ and EtOH or with $\text{Al}\cdot\text{Hg}$ and Et_2O affords intractable mixtures of pinacols. Treatment of (I) with H_2S in $\text{NH}_3\cdot\text{EtOH}$ yields a S-containing substance, b.p. $90^\circ/4$ mm. With $\text{Ba}(\text{OH})_2$ in MeOH (I) affords a *CO-alcohol*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, b.p. $75-80^\circ/4$ mm., with COMeBu^β . (I) with MgMeI yields a substance, b.p. $66^\circ/3$ mm., and two *polymerides*, $\text{C}_{20}\text{H}_{32}\text{O}_2$, b.p. $130-140^\circ/4$ mm. and $150-160^\circ/4$ mm. With NH_2OH in alkaline solution an oxime is formed, whilst in dil. H_2SO_4 an *oximinoketone*, b.p. $100-102^\circ/4$ mm., is produced.

CH. ABS. (r)

Steric transformation of sugars. F. JUST (Z. Spiritusind., 1936, 59, 25, 33-34).—A review of the methods used in effecting steric transformation of sugars leads to the conclusion that Walden inversion during fission of the O bridge in anhydro-sugars is more promising preparatively than treatment of the sugars with alkali or $\text{C}_7\text{H}_5\text{N}$ or of unsaturated sugar derivatives with BzO_2H .

H. W.

Structure of *d*-xylomethylose. P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1936, 112, 775-783).—*iso*Propylidene-*d*-xylomethylose and $\text{MeI}\cdot\text{Ag}_2\text{O}$ at 50° give the 3-*Me ether*, b.p. $58-60^\circ/0.3$ mm., $[\alpha]_D^{25} -49.4^\circ$, hydrolysed by hot 1% H_2SO_4 to 3-*methyl-d-xylomethylose*, b.p. $101-102^\circ/0.8$ mm., $[\alpha]_D^{25} +8.1^\circ$ (*phenylosazone*, m.p. $128-130^\circ$), which with $\text{HCl}\cdot\text{MeOH}$ affords α -, b.p. $58-62^\circ/0.3$ mm., $[\alpha]_D^{25} +124.5^\circ$, and β -*methyl-3-methyl-d-xylomethyloside*, b.p. $72-75^\circ/0.3$ mm., m.p. $48-50^\circ$, $[\alpha]_D^{25} -127.9^\circ$. These with $\text{MeI}\cdot\text{Ag}_2\text{O}$ at 50° yield α -, m.p. $34-35^\circ$, b.p. $39-41^\circ/0.5$ mm., $[\alpha]_D^{25} +154^\circ$, and β -*methyl-2 : 3-dimethyl-d-xylomethyloside*, b.p. $38-40^\circ/0.5$ mm., $[\alpha]_D^{25} -102.4^\circ$, respectively, both oxidised by conc. HNO_3 to *d*- $[\text{CH}(\text{OMe})\cdot\text{CO}_2\text{H}]_2$. *d*-Xylomethylose (I) and $\text{Ag}_2\text{O}\cdot\text{H}_2\text{O}$ at 80° give only AgOAc . The rate of lactonisation of *d*-gulomethylose acid indicates formation of γ - and δ -lactones. The structure of (I) is thus confirmed. $[\alpha]$ are in H_2O . R. S. C.

Ring closure in sugar benzoates. M. L. WOLFROM and C. C. CHRISTMAN (J. Amer. Chem. Soc.,

1936, 58, 39—43).—Successive treatment of *l*-arabinose Et_2 mercaptal with CPh_3Cl and $BzCl$ in C_5H_5N at room temp. gives 5-triphenylmethyl-*l*-arabinose Et_2 mercaptal tribenzoate, m.p. 111—112°, $[\alpha]_D^{25} - 25^\circ$ in $CHCl_3$, converted by $AcOH-HBr$ followed by $CdCO_3 + HgCl_2$ in aq. $COMe_2$ into *l*-arabinose 2:3:4-tribenzoate (I), m.p. 162—163°, $[\alpha]_D^{25}$ (in C_5H_5N) $+143^\circ \rightarrow +196^\circ$. Equilibration of *l*-arabinose in C_5H_5N and subsequent treatment with $BzCl$ affords α -*l*-arabinose tetrabenzoate (II), m.p. 160—161°, $[\alpha]_D^{25} + 112.5^\circ$ in $CHCl_3$ [also prepared by benzylation of (I)], converted by cold $AcOH-HBr$ into benzobromo-*l*-arabinose, m.p. 144—145°, $[\alpha]_D^{25} + 203^\circ$ in $CHCl_3$, which is hydrolysed (method: Fischer and Noth, A., 1918, i, 225) to (I). β -*l*-Arabinose tetrabenzoate has m.p. 173—174°, $[\alpha]_D^{25} + 325^\circ$ in $CHCl_3$ (cf. Gehrke and Aichner, A., 1927, 544). The above reactions are considered to support the pyranose structure of (II). *d*-Galactose Et_2 mercaptal tetrabenzoate, m.p. 127—128°, $[\alpha]_D^{25} - 16.5^\circ$ in $CHCl_3$ [from the 6- CPh_2 ether (III) (A., 1935, 734) and $AcOH-HBr$], with $CdCO_3 + HgCl_2$ in aq. $COMe_2$ gives *d*-galactose tetrabenzoate (+ $MeOH$), m.p. 112—113°, $[\alpha]_D^{25}$ (in $CHCl_3$) $-10^\circ \rightarrow +6.5^\circ$. HBr converts (III) (in $CHCl_3$) into 6-bromo-*d*-galactose Et_2 mercaptal tetrabenzoate, m.p. 103—104°, $[\alpha]_D^{25} - 1.4^\circ$ in $CHCl_3$. α -*d*-Galactose pentabenzoate, m.p. 128—129°, $[\alpha]_D^{25} + 187^\circ$ in $CHCl_3$, is prepared by Levene and Meyer's method (A., 1928, 398). Triphenylmethyl-*d*-mannose Et_2 mercaptal tetrabenzoate, m.p. 105—106°, $[\alpha]_D^{25} 0^\circ$, $[\alpha]_D^{25}$ -10.5° in $CHCl_3$ (corresponding tetraacetate, m.p. 133.5—134.5°, $[\alpha]_D^{25} + 36^\circ$ in $CHCl_3$), is converted [as for (III)] into *d*-mannose Et_2 mercaptal tetrabenzoate, m.p. 116—117°, $[\alpha]_D^{25} - 5^\circ$ in $CHCl_3$, and thence into *d*-mannose tetrabenzoate, $[\alpha]_D^{25} - 115^\circ$ in $CHCl_3$. Glucose Et_2 mercaptal pentabenzoate (Brigl and Muehlschlegel, A., 1930, 1022) with $CdCO_3 + HgCl_2$ in aq. $COMe_2$ gives aldehydoglucose pentabenzoate, m.p. 81—82°, $[\alpha]_D^{24} + 40^\circ$ in $EtOH$ (cf. *loc. cit.*). Kunz and Hudson's method of hydrolysis (A., 1926, 941) is applicable to sugar benzoates provided they are appreciably sol. in H_2O . H. B.

Esters of aldehydrol form of sugars. M. L. WOLFROM (J. Amer. Chem. Soc., 1935, 57, 2498—2500).—aldehydoGalactose penta-acetate Et hemiacetal (A., 1930, 1023) with $AcHal$ gives aldehydo-*l*-chloro-, m.p. 174—175°, $[\alpha]_D^{27} - 44^\circ$ in $CHCl_3$, -*l*-bromo-, m.p. 179—181°, $[\alpha]_D^{25} - 79^\circ$ in $CHCl_3$, and -*l*-iodo-, m.p. 152—153°, $[\alpha]_D^{25} - 111^\circ$ in $CHCl_3$, -*d*-galactose hexa-acetates; these compounds are the open chain analogues of the cyclic halogenosugar acetates. Acetylation (Ac_2O and C_5H_5N or $ZnCl_2$ at room temp.) of aldehydo-*d*-glucose penta-acetate affords the hepta-acetate, m.p. 118.5—119.5°, $[\alpha]_D^{25} + 8^\circ$ in $CHCl_3$; aldehydo-*l*-arabinose tetra-acetate gives the hexa-acetate, m.p. 89.5°, $[\alpha]_D^{27} - 27^\circ$ in $CHCl_3$. These $C_1H(OAc)_2$ derivatives are much more stable than the aldehydo-forms. H. B.

Action of hot alkali solutions on carbohydrates. R. S. HILPERT and A. WOLTER (Angew. Chem., 1936, 49, 54—55).—Carbohydrates are heated with aq. Na_2CO_3 , and the amount of acid produced is determined from the CO_2 evolved. This varies from zero for gum arabic to 0.18 g. of CO_2 per g. of mono-

saccharide at 100°. The amount increases rapidly with rise of temp. up to 0.3 at 170°. Sucrose is stable up to 130°. $OH \cdot CHMe \cdot CO_2H$ was not found in the liquors. S. M. N.

Constitution of osazones. L. L. ENGEL (J. Amer. Chem. Soc., 1935, 57, 2419—2423).—The absorption spectra of the osazones (I) of various sugars (e.g., glycerose, glucose, lactose, 3:4:6-trimethyl-, tetra-acetyl- and -benzoyl-glucose) are all markedly similar; the group responsible for the sp. absorption is considered to be

$NHPh \cdot N \cdot CH \cdot C(N \cdot NHPh) \cdot CH \cdot OR$ ($R=H$, alkyl, or acyl). The difference between the curves for (I) and the osazones of $AcCHO$ and Ac_2 (both of which are almost identical) is ascribed to the $C_3 \cdot O$ in (I). The mutarotation of (I) may be due to the establishment of an equilibrium between (I) and their hydrolysis products. A related equilibrium appears to be established between 3:4:6-trimethylglucosephenylosazone, $[\alpha] - 48.8^\circ \rightarrow +61.5^\circ$ (after 188 hr.) (in $EtOH-C_5H_5N$), and $NHPh \cdot NH_2$ (16.3 mols.); the change $[\alpha] - 50.6^\circ \rightarrow +30^\circ$ (after 155 hr.) being observed.

Acetylation (Ac_2O , C_5H_5N) of glucosephenylosazone (II) and fructosephenylmethylsazone (III) gives the Ac_4 derivatives, m.p. 102—104° (corr.). $[\alpha]_D^{25} - 58.5^\circ$ in 95% $EtOH$, and m.p. 126—127° (corr.), $[\alpha]_D^{27} - 184.8^\circ$ in 95% $EtOH$. (III) and $NHPh \cdot NH_2$ in $MeOH$ at room temp. afford glucosephenylmethylsazone; the *p*-nitrophenylphenylmethylsazone, m.p. 223.5—224.5° (corr.), is similarly prepared using *p*- $NO_2 \cdot C_6H_4 \cdot NH \cdot NH_2$. isoPropylidene-galactosephenylosazone, m.p. 183.5—184.5° (corr.), is formed from the galactosazone, $COMe_2$, and P_2O_5 at 0°. Acetylglucose-2:4-dinitrophenylosazone, m.p. 196—197° (corr.), is obtained from $CO(CH_2 \cdot OAc)_2$ [prep. by oxidation ($Na_2Cr_2O_7$, $AcOH-H_2SO_4$) of diacetin described]. Methylation (various conditions) of (II) gives non-homogeneous products. Votoček and Valentin's results (A., 1931, 1274) on the mutarotation of (III) could not be confirmed. H. B.

Photolysis of fructose in ultra-violet light.—See this vol., 299, 300.

Hydrolysis of glucosides and of certain organic compounds by ultra-violet rays.—See this vol., 171.

Synthesis and properties of β -alkylglucosides. S. VEIBEL and F. ERIKSEN (Bull. Soc. chim., 1936, [v], 3, 277—283).— β -Methyl-, ethyl-, m.p. 81—83°, $[\alpha]_D^{20} - 38.6^\circ$ in H_2O (tetra-acetate, m.p. 105—106°, $[\alpha]_D^{20} - 29^\circ$ in C_6H_6 or $EtOH$), -propyl-, forms, m.p. 77—78° (I) and 102—103° (II), respectively, $[\alpha]_D^{25} - 39.3^\circ$ in H_2O [(I) \rightarrow (II) at 90—95°; (II) \rightarrow (I) in $PhMe$ slowly at 30° and rapidly if boiled and then cooled to 70°; tetra-acetate, m.p. 102—103°, $[\alpha]_D^{25} - 27^\circ$ in $EtOH$], and -isopropyl-glucoside, m.p. 128—129°, $[\alpha]_D^{20} - 40.9^\circ$ in H_2O (tetra-acetate, m.p. 136—137°, $[\alpha]_D^{20} - 30.6^\circ$ in $EtOH$), are prepared (a) from penta-acetylglucosidyl bromide and subsequent hydrolysis by a trace of $NaOMe$ and (b) by emulsion from glucose with removal of the excess of glucose by yeast. M.p. are corr. R. S. C.

Synthesis of 1-*d*-glucosidocytosine. G. E. HILBERT and E. F. JANSEN (J. Amer. Chem. Soc., 1936, 58, 60—62).—2:4-Diethoxypyrimidine and acetobromoglucose at 65° give 2-*keto*-4-*ethoxy*-1-*tetraacetyl-d-glucosido*-1:2-*dihydropyrimidine*, m.p. 206° (corr.), $[\alpha]_D^{25} +36.1^\circ$ in CHCl_3 , converted by EtOH-HCl into 1-*d-glucosidouracil* (I) (A., 1931, 100) and by EtOH-NH_3 at 80°/96 hr. in sealed tube into 1-*d-glucosidocytosine* (II) ($+\frac{1}{3}\text{EtOH}$), m.p. 197—199° (sinters at 192°) [*picrate*, m.p. 216—218° (decomp.); *nitrate* ($+\text{H}_2\text{O}$), m.p. 143° (decomp.)], which when kept in a moist atm. passes into a *hydrate*, m.p. about 128° (decomp.). Crystallisation from 90—95% EtOH gives a *hydrate-alcoholate*, m.p. 194—195° (decomp.). Anhyd. (II) is hygroscopic and has $[\alpha]_D^{25} +25.6^\circ$ in H_2O . (II) with 25% H_2SO_4 at 150° gives (probably) a mixture of (I) and (II). 7-*Acetyl*-1-*tetraacetylglucosidocytosine* has m.p. 225°, $[\alpha]_D^{25} +38.1^\circ$ in CHCl_3 . H. B.

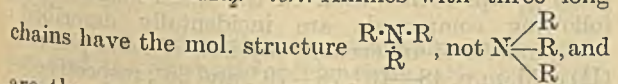
Influence of crystalloids on the state of amyloses.—See this vol., 288.

Plant colloids. XLIII. Influence of chlorine dioxide on the chemical reactions of potato- and wheat-starch. M. SAMEC [with F. ULM] (Kolloid-Beih., 1936, 43, 287—294).—When treated with ClO_2 solutions, starch loses P and N. A considerable amount of P in potato- (but not wheat-) starch resists this action. The treatment also renders the starch more sol., and in some cases causes feeble oxidation. E. S. H.

Kinetics of long chain disintegration applied to cellulose and starch.—See this vol., 295.

Origin of nitrous oxide and hydrogen cyanide formed by certain methods of decomposition of cellulose nitrate. H. MURAUOR (Bull. Soc. chim., 1936, [v], 3, 265—267).—Decomp. of cellulose nitrate leads to HNO , which at low temp. gives N_2O and at high temp. reacts with CH_4 to produce HCN . R. S. C.

Highly polymerised compounds. CXXIII. Measurements of the viscosity of aliphatic amines with long chains. H. STAUDINGER and K. RÖSSLER (Ber., 1936, 69, [B], 49—60).—Determinations of the viscosity of long-chained aliphatic nitriles and primary and *sec.*-amines show the compounds to be unimol. in C_6H_6 and CCl_4 , since the observed η_{sp} . (1.4%) vals. agree with those calc. from the expression η_{sp} . (1.4%) = ny . The temp. coeff. is the same as that of hydrocarbons. With short-chain compounds the observed vals. are < the calc., since the abs. viscosity of the dissolved substance is not sufficiently high in comparison with that of the solvent. The amine mol. has therefore the form $\text{R}\cdot\text{NH}\cdot\text{R}$, not NHR_2 . *tert.*-Amines with three long chains have the mol. structure



are thus comparable with the glyceryl esters. The viscosity of long-chained amines in heteropolar solvents is quite irregular and is little affected by the addition of electrolytes. Since micelle formation is not involved, an adequate explanation of the high sp. viscosity in AcOH is not forthcoming. Amines

and nitriles, like hydrocarbons and esters, exist in solution as thread mols. with the most extended form; from these the crystals are formed and m.p. and solubility of the solids depend greatly on the length of the chains. Nitriles have a somewhat higher m.p. (about 9°) than hydrocarbons with the same no. of chain links. Primary amines and primary alcohols have the same m.p. (20—30° > that of the corresponding hydrocarbons); their mols. are therefore coordinatively united but so weakly that the union is broken in solution. The very low m.p. of *tert.*-amines is explained by their branched structure. *sec.*-Amines with two long chains have m.p. slightly < the corresponding hydrocarbons due to the slightly less regular structure, whilst *Me*-substituted *tert.*-amines have m.p. similar to that of hydrocarbons containing *Et* attached to the central C. The following compounds are incidentally described: *dimyristylamine*, m.p. 56—58.5°; *dicetylamine*, m.p. 65—66°; *dimethylmyristylamine*, liquid at 0°; *dimethylcetylamine*, m.p. about 12°; *dimethylstearylamine*, m.p. about 25°; *methylmyristylamine*, m.p. 24—25°; *methylcetylamine*, m.p. 34—35°; *methylstearylamine*, m.p. 40°; *trimyristylamine*, m.p. 33—34°; *tricyetylamine*, m.p. 42—43.5°; *tristearylamine*, m.p. 54—55°. H. W.

Possible rearrangement reactions of monochloroamine and Grignard reagents. G. H. COLEMAN and R. A. FORRESTER (J. Amer. Chem. Soc., 1936, 58, 27—28).— $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ and NH_2Cl give 92% of $\text{CH}_2\text{Ph}\cdot\text{NH}_2$; $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{MgCl}$ affords 47% of $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{NH}_2$; $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{MgCl}$ (at -20°) yields 14% of $\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}_2$. No indication of the formation of rearrangement products (*viz.*, $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $1:2\text{-C}_{10}\text{H}_6\text{Me}\cdot\text{NH}_2$, and $\text{NH}_2\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2$, respectively) was obtained. H. B.

Kinetics of ring formation and polymerisation in solution.—See this vol., 296.

Reduction of organic compounds by ethanolamines. M. MELTSNER, C. WOHLBERG, and M. J. KLEINER (J. Amer. Chem. Soc., 1935, 57, 2554).—Reduction of anthraquinone, $(\text{NPh})_2$, and COMe_2 occurs when these are heated with $\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_3$ (I); anthranol, NH_2Ph , and Pr^βOH , respectively, are formed. Mixtures of the azo-, azoxy- (II), and NH_2 -derivatives are similarly produced from PhNO_2 and $o\text{-C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$ with (I), $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, or, preferably, $\text{NH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$ in presence of aq. NaOH ; (II) is not formed in absence of NaOH . Chrysoidine is reduced (? by (I)) to $1:2:4\text{-C}_6\text{H}_3(\text{NH}_2)_3$. Aq. solutions of Ag , Pb , Hg , and other metal salts are also reduced. H. B.

Mixed molybdates.—See this vol., 302.

[Derivatives of] ruthenium-red.—See this vol., 302.

Preparation and properties of β -*n*-alkylcholine chlorides and their acetyl esters. R. T. MAJOR and H. T. BONNETT (J. Amer. Chem. Soc., 1936, 58, 22—24).— $\text{OH}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NMe}_2$ (from $\text{OH}\cdot\text{CHR}\cdot\text{CH}_2\text{Cl}$ and NHMe_2 in C_6H_6 at 115—120°) are converted (MeI followed by AgCl) into $\text{OH}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$ ($\text{R}=\text{Et}-n\text{-C}_7\text{H}_{15}$), which are acetylated (method:

A., 1932, 257) to $\text{OAc}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$. The following are described: α -chlorononan- β -ol, b.p. 114.5—116.5°/13 mm. (prep.: Levene and Haller, A., 1928, 737); α -dimethylamino- β -hydroxybutane, b.p. 142—144°/760 mm., -hexane, b.p. 89—90°/25 mm., -octane, b.p. 99—101°/10 mm., and -nonane, b.p. 104—106°/5 mm.; β -ethylcholine chloride, m.p. 174—176° (acetate, m.p. 144—146°), and iodide, m.p. 162—163°; β -n-propylcholine chloride, m.p. 115—117° (acetate, m.p. 168—169°), and iodide, m.p. 198—200°; β -n-butylcholine chloride, m.p. 100.5—102° (acetate, m.p. 186—187°), and iodide, m.p. 90—92°; β -n-amylcholine chloride, m.p. 72—74° (acetate, m.p. 182—184°), and iodide, m.p. 98—100° (lit. 106—108°); β -n-hexylcholine chloride, m.p. 69—71° (acetate, m.p. 169—171°), and iodide, m.p. 109—110°; β -n-heptylcholine chloride, m.p. 97—99° (acetate, m.p. 176—177°), and iodide, m.p. 122.5—123.5°. Pharmacological data are given; none of the acetates is as active as $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$ (cf. Simonart, A., 1932, 1284).

H. B.

Equilibrium of amino-acids, carbon dioxide, and carbamates in aqueous solution.—See this vol., 289.

Feeding experiments with purified amino-acids. VIII.—See this vol., 233.

Synthesis of α -amino- β -hydroxy- n -butyric acids. H. E. CARTER (J. Biol. Chem., 1936, 112, 769—773).—The mixture of isomerides, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ (I), of Abderhalden *et al.* (A., 1934, 638) has no physiological activity. Formylation gives α -formamido- β -methoxy- n -butyric acid, m.p. 173—174°, which after epimerisation by hot Ac_2O - NaOH and hydrolysis with HBr yields a mixture of stereoisomerides of (I), which has about 25% of the activity of the natural acid.

R. S. C.

Canavanine. VI. M. KITAGAWA and A. TAKANI (J. Agric. Chem. Soc. Japan, 1935, 11, 1077—1082).—The similarity in properties of $\text{ONH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and canaline confirms the structure of $\text{ONH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$. Guanidation of α -benzoylcanaline with methylisocarbamide followed by hydrolysis yields (as flavianate) canavanine, which therefore is $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{N}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ (cf. A., 1934, 993).

F. O. H.

Specific rotation of *l*-cystine in relation to degree of neutralisation and p_H . G. TOENNIES, T. F. LAVINE, and (MISS) M. A. BENNETT (J. Biol. Chem., 1936, 112, 493—496).— $[\alpha]_{\text{H}_2\text{O}}^{20-31.5}$ at p_H 0—10.6 are recorded for 0.005*M*-*l*-cystine, prepared from 98—99% pure Li cystinate by adding varying amounts of LiOH and/or HCl . $[\alpha]_{\text{H}_2\text{O}}$ is -225° at p_H about 0.1, -97° at p_H 11.6, and -325° at p_H 3—7 (the isoelectric range). $d[\alpha]/dt$ is $+1.5^\circ$ between 19.3° and 32.05°.

R. S. C.

New synthesis of methionine and a scheme relating certain α -amino-acids. E. M. HILL and W. ROBSON (Biochem. J., 1936, 30, 248—251).—*Et* γ -chloro- α -benzamidobutyrate, m.p. 45°, prepared by treatment of α -benzamido- γ -butyrolactone with HCl in EtOH , gave benzoylmethionine on treatment with NaSMe and subsequent alkaline hydrolysis.

Acid hydrolysis gave methionine (carbamide, m.p. 171—172°; hydantoin, m.p. 117—118°). H. D.

Determination of the stereochemical purity of *l*-cysteine. G. TOENNIES and (MISS) M. A. BENNETT (J. Biol. Chem., 1936, 112, 497—502).—*l*-Cysteine (modified prep.), $[\alpha]_{\text{H}_2\text{O}}^{20} + 9.68 \pm 0.05^\circ$, $[\alpha]_{\text{H}_2\text{O}}^{30} + 7.6 \pm 0.1^\circ$ (*M* solution in *N*- HCl ; $d\alpha/dt = -1\%$ between 23° and 33°), is determined within $\pm 0.25\%$ by oxidation with H_2O_2 (2% excess) in *N*- HCl in presence of 0.003*M*- CuSO_4 and determination of the max. $[\alpha]$ (due to cystine) during 1 hr.

R. S. C.

Detection of cystine in presence of cystine. C. B. DI CAPUA (Boll. Soc. ital. Biol. sperim., 1935, 10, 428—429).—Grothe's reagent can be used for detection of cystine, but the supposed blue cystine (I) coloration appears in acid solution without (I) and is probably due to formation of Prussian-blue.

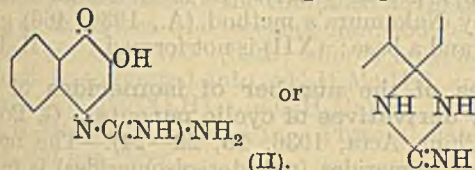
R. N. C.

Highly polymerised compounds. CXXIV. Measurements of the viscosity of amides and anilides of fatty acids. H. STAUDINGER and K. RÖSSLER (Ber., 1936, 69, [B], 61—73).—The m.p. of the normal fatty amides is considerably $>$ that of the corresponding acids; the lower m.p. of *sec.*- and *tert.*-amides may be caused by the presence of branched chains. Correspondingly the methylamides and more particularly the dimethylamides are more freely sol. in C_6H_6 , CCl_4 , or CHCl_3 than the simple amides. The relatively high m.p. of primary amides depends on peculiarities of structure as well as on the formation of co-ordinative mols. Measurements of η_{sp} of dimethylamides in C_6H_6 gives vals. $>$ expected, which do not depend on concn. Since the temp. effect is normal the $\text{CO}\cdot\text{NH}_2$ group causes exaltation; this view is confirmed by the behaviour of the piperidides. Similarly, η_{sp} of amides and methylamides in CHCl_3 is $>$ expected. Methylanilides in C_6H_6 , CCl_4 , or CHCl_3 behave similarly to the dimethylamides. On the hypothesis that mols. in solution assume the longest possible form, the normal mols. of anilides have the structure $\text{Me}\cdot[\text{CH}_2]_n\cdot\overset{\text{O}}{\text{C}}\cdot\text{NHPh}$. Co-ordinative mols. can have the structure $\text{Me}\cdot[\text{CH}_2]_n\cdot\overset{\text{O}}{\text{C}}(\text{O})\cdot\text{NH}\cdot\text{Ph}\cdot\text{HN}(\text{O})\text{C}(\text{O})\cdot[\text{CH}_2]_n\cdot\text{Me}$ or $\text{PhNH}\cdot\text{COR}\cdot\text{HN}\cdot\text{Ph}\cdot\text{COR}$ dependent on whether or not $\text{Me}\cdot[\text{CH}_2]_n\cdot\text{CO}$ is longer than Ph . Support for this view is found in the observation that the m.p. of fatty acid anilides passes through a min. at octoanilide. η_{sp} of anilides in C_6H_6 , CHCl_3 , or $\text{C}_5\text{H}_5\text{N}$ shows progression similar to that of the m.p. In AcOH the viscosity of anilides appears to depend on the ionic groups rather than on the chain length. The following compounds are incidentally described: methylamides of undecenoic, myristic (I), and palmitic (II) acid, m.p. 48—49°, 78—79°, and 86°, respectively; dimethylamides of lauric (III), (I), (II), and stearic acid (IV), b.p. 180°/15 mm., m.p. 18—20°, b.p. 210—213°/15 mm., m.p. 31—32°, m.p. 41° and m.p. 50.5—51.5°, respectively; stearpiperidide, m.p. 37—38°; methylanilides of (III), (I), (II), and (IV), b.p. 187°/0.2 mm., m.p. 15°, b.p. 204.5—206°/0.5 mm., m.p.

29—30°, b.p. 202—203°/0.01 mm., m.p. 40—45° and m.p. 48.5—49.5°, respectively. H. W.

Condensation of carbamide and formaldehyde. G. WALTER (Trans. Faraday Soc., 1936, 32, 377—395).—A summary of work previously published (cf. B., 1931, 357; A., 1932, 150). F. L. U.

Coloured compound formed in Sullivan reaction for guanidine. M. X. SULLIVAN and W. C. HESS (J. Amer. Chem. Soc., 1936, 58, 47—48; cf. this vol., 195).—The compound, decomps. about 250°, formed from guanidine (I) and Na 1:2-naphthaquinone-4-sulphonate in aq. NaOH at 90°, followed by acidification (conc. HCl+conc. HNO₃), is considered to be (II) since it is hydrolysed (conc. H₂SO₄, 95% EtOH) to 2-hydroxy-1:4-naphthaquinone. (II) is



rose-coloured in acid, purple in alkali, and forms NH₄, m.p. 285—288°, and Na, m.p. 297—300°, salts. 1:2-Naphthaquinone, (I), and a little HNO₃ in aq. EtOH give the compound, 1:2-O:C₁₀H₆:N·C(NH)₂, m.p. 265—267° (decomp.), hydrolysed (20% HCl) to α-C₁₀H₇·OH. H. B.

Reduction of nitroguanidine. II. Preparation and properties of nitrosoguanidine. V. J. SABETTA, D. HIMMELFARB, and G. B. L. SMITH. III. Synthesis of aminoguanidine. G. B. L. SMITH and E. ANZELMI. IV. Preparation of nitrosoguanidine by catalytic hydrogenation [of nitroguanidine]. E. LIEBER and G. B. L. SMITH (J. Amer. Chem. Soc., 1935, 57, 2478—2479, 2730, 2479—2480).—II. Slightly impure nitrosoguanidine (I), detonates at 161°, is obtained in 40—60% yield by reduction (Zn dust and aq. NH₄Cl at < 50°) of nitroguanidine (II). Methods for the determination of (I) are given.

III. Methylisothiocabamidesulphate and N₂H₄·H₂O give MeSH and the sulphate (yield 90%) of aminoguanidine (*K_B* 1.1 × 10⁻³), the H carbonate of which is CH₆N₄·H₂CO₃.

IV. Reduction [H₂ (slightly > 1 mol.), PtO₂ or Raney Ni, H₂O] of (II) affords 36—62% of (I). H. B.

Vinyldiazomethane. C. D. HURD and S. C. LUI (J. Amer. Chem. Soc., 1935, 57, 2656—2657).—Vinyl diazomethane (I), obtained from nitrosoallylurethane (modified prep.) by Nirdlinger and Acree's method (A., 1910, i, 341), with BzOH gives allyl benzoate. Appreciable isomerisation of (I) to pyrazole (cf. Adamson and Kenner, A., 1935, 479) occurs during its distillation. H. B.

Parachor and molecular refraction of hydrazine and its aliphatic derivatives.—See this vol., 272.

Dibutylphosphorous acid chloride and preparation of butylpyrophosphorous acid from it. A. E. ARBUSOV and V. S. ABRAMOV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 28—33).—

BuO·PCl₂ is converted by NaOBu into (BuO)₂PCl; this, with (BuO)₂P·ONa, affords *butylpyrophosphorous acid*, b.p. 175—176°, which, with H₂O, yields (BuO)₂P·OH, and, with Br, a Br₄-compound.

CH. ABS. (*r*)

Acetoacetic acid O-phosphoric ester. P. KARRER and H. BENDAS (Helv. Chim. Acta, 1936, 19, 98—99).—Cautious treatment of ONa·CHMe·CH·CO₂Et with POCl₃ give Et₃ acetoacetate O-phosphate, isolated as the salt PO₃Ba·O·CMe·CH·CO₂Et. The corresponding Na₂ salt is hydrolysed to the compound (I), PO₃Na₂·O·CMe·CH·CO₂Na. Hot, dil. acids convert (I) into CH₂Ac·CO₂H or COMe₂; kidney phosphatase readily removes ·OPO₃Na₂ from (I) at *p_H* 9. H. W.

Phosphate transferences by means of phosphopyruvic acid in alcoholic fermentation of sugar.—See this vol., 246.

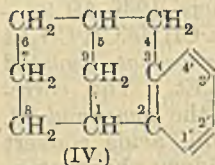
Preparation of boron alkoxy-halides and their reaction with metals. C. R. KINNEY, H. T. THOMPSON, and L. C. CHENEY (J. Amer. Chem. Soc., 1935, 57, 2396—2397).—A mixture of triisomyly borate (I) (2 mols.) and BCl₃ (1 mol.) is kept for 24 hr. and then fractionated; *B diisomyloxy-chloride* (II), b.p. 110—115°/14 mm., is obtained in 45% yield. (II) and Na in C₆H₆ at 70° give HCl, isopentene, H₂, (I), and B₂O₃. BCl(OEt)₂ warmed with Na or Zn dust similarly affords B(OEt)₃ and B₂O₃. H. B.

Colour reaction for detection of cyclopentadiene. B. N. AFANASIEV (Ind. Eng. Chem. [Anal.], 1936, 8, 15).—A violet colour is produced when one drop of cyclopentadiene dissolved in CHCl₃ (1 c.c.) and AcOH (1 c.c.) is treated with conc. H₂SO₄. A similar coloration is obtained with higher terpenes but only when Ac₂O is used. S. C.

Ozonisation of hydrogenated diphenyls. C. R. NOLLER and G. K. KANEKO (J. Amer. Chem. Soc., 1935, 57, 2442—2443).—1-Phenyl-Δ¹-cyclohexene (I) and di-Δ^{1:1}-cyclohexenyl add 1 and 2 mols., respectively, of O₃, indicating that steric hindrance in the 1 and 1' positions is not the factor involved in the failure of Ph₂ to give a hexaozonide (cf. Harries and Weiss, A., 1906, i, 228). Decomp. of the ozonides affords δ-benzoylvaleric and adipic acid, respectively. The tetrahydrodiphenyl obtained (cf. Bamberger and Lotter, A., 1888, 292) by reduction (Na, amyl alcohol) of Ph₂ is mainly (I). H. B.

Dehydration of benzylcyclohexanols. J. W. COOK and C. L. HEWETT (J.C.S., 1936, 62—71).—2-Methylcyclohexanone and CH₂Ph·MgCl (I) give impure 1-benzyl-2-methylcyclohexanol, b.p. 115°/0.8 mm., dehydrated (KHSO₄ at 160—175°) to 1-benzyl-2-methyl-Δ¹-cyclohexene, b.p. 158—160°/19 mm., converted by AlCl₃ in CS₂ at 0° into a saturated hydrocarbon, C₁₄H₁₈, b.p. 141°/18 mm., which could not be dehydrogenated (Se at 300—320°; Pd-C at 300°) and is oxidised (dil. HNO₃ at 180—185°) to o-C₆H₄(CO₂H)₂. Tetrahydrocarvone and (I) afford 1-benzyl-2-methyl-5-isopropylcyclohexanol, b.p. 140—142°/0.6 mm., dehydrated (ZnCl₂ at 160°) to 1-benzyl-2-methyl-5-isopropyl-Δ¹-cyclohexene, b.p. 159°/12 mm., similarly converted into a saturated hydrocarbon, C₁₇H₂₄, b.p. 160—161°/13 mm., which could

not be dehydrogenated. Phenylcyclohexylcarbinol (II) and 1- (III) and 2-benzylcyclohexanol, b.p. 154°/11 mm., m.p. 75.5—76° (prepared by reduction of the hexanone with Na and H₂O in Et₂O), are all converted by P₂O₅ at 150° into 30—70% of 2:3-benz-1:3:3-dicyclo-Δ²-nonene (IV), b.p. 85°/0.3 mm., 123°/15 mm., and not (XII) (below) (see A., 1933, 1042); (IV) is oxidised (dil. HNO₃ at 180°) to *o*-C₆H₄(CO₂H)₂, thus showing that cyclisation involves the attachment of the alicyclic part of the mol. at C2 of the C₆H₆ ring.



(IV) could not be dehydrogenated (Pt-black or -asbestos); it is oxidised (Na₂Cr₂O₇, AcOH) to 2:3-benz-1:3:3-dicyclo-Δ²-nonen-4-one (V), b.p. 108—110°/0.2 mm. (*oxime*, m.p. 123—124°; *semicarbazone*, m.p. 222—224°), which is reduced (Clemmensen) to pure (IV). The complete absence of strain in (IV) is probably the determining factor in its formation. (V) and HNO₃ (*d* 1.5) give the 3'-NO₂-derivative, m.p. 118.5—119.5°, reduced (SnCl₂, conc. HCl, EtOH) to the 3'-NH₂-derivative, m.p. 122.5—123.5°, which is oxidised (CrO₃, AcOH) to *cis*-hexahydroisophthalic acid (VI) and converted (through the diazonium sulphate) into 3'-hydroxy-2:3-benz-1:3:3-dicyclo-Δ²-nonen-4-one, m.p. 160.5—161.5° [oxidised (KMnO₄, aq. KOH) to (VI)]. (V) could not be methylated (MeI, NaNH₂). No reaction occurs between (V) and Br in CS₂, indicating the absence of enol.

1-Benzyl-Δ¹-cyclohexene (VII), obtained (cf. von Auwers and Treppmann, A., 1915, i, 789; Prévost *et al.*, A., 1934, 649) by dehydration (KHSO₄) of (III), is converted into the nitrosochloride, m.p. 116—117° (lit. 110°), and thence by boiling C₅H₅N into 2-benzyl-Δ²-cyclohexenoneoxime, m.p. 138.5—139.5° (lit. 136—138°), which when hydrolysed (6*N*-H₂SO₄) and then reduced (H₂, Pd-black, Et₂O) gives 2-benzylcyclohexanone (VIII). Dehydration (ZnCl₂ at 170—180°) of (II) affords a mixture of (IV) [proved by oxidation to (V)] and unsaturated material, which is not (VII) (cf. von Auwers, this vol., 195) but may be benzylidenecyclohexane. Contrary to von Auwers and Treppmann (*loc. cit.*), there is no evidence of the change CHPh:C< → CH₂Ph:C<. *Et*-2-benzylcyclohexanone-2-carboxylate, b.p. 144—145°/0.4 mm., m.p. 34.5—35° (*semicarbazone*, m.p. 182—183°), prepared from *Et* sodiocyclohexanone-2-carboxylate and CH₂PhCl in C₆H₆, is hydrolysed (EtOH-KOH) to *α*-benzylpimelic acid, m.p. 81—82°, which when distilled (from bath at 360—380°) gives (VIII). *trans*-2-Ketodecahydronaphthalene and (I) give β-decahydronaphthylbenzylcarbinol, b.p. 171°/6 mm. (3:5-dinitrobenzoate, m.p. 162.5—164°), dehydrated (KHSO₄ at 160—170°) to 2-benzyldecahydronaphthalene, b.p. 151°/6 mm., which is reduced (H₂, Pd-black, AcOH) to 2-benzyldecahydronaphthalene (IX), b.p. 173—175°/10 mm., and dehydrogenated (Se at 310—320°) to 2-benzyldecahydronaphthalene [also formed from (IX) and Pt-black at 300—305° but not with Se at 320—330°]. Successive oxidation (CrO₃, cold AcOH) and reduction (H₂, Pd-black, AcOH) of 2-phenyl-Δ³-tetrahydrobenzaldehyde (Lehmann and Pnasche, A., 1935, 978) gives 2-phenylhexahydro-

benzoic acid (X), m.p. 105—107°, better prepared by reduction (Na, amyl alcohol) of *o*-C₆H₄Ph·CO₂H [the acid obtained by catalytic reduction (Raneco and León, A., 1925, i, 665) is not a stereoisomeride of (X) but is *o*-cyclohexylbenzoic acid, m.p. 104°, oxidised (alkaline KMnO₄) to *o*-C₆H₄(CO₂H)₂]. The chloride of (X) with AlCl₃ in CS₂ at 0° affords 1:2:3:4:10:11-hexahydrofluorenone (XI), m.p. 41.5—42° (*oxime*, m.p. 183—185°; *semicarbazone*, m.p. 212—213°), reduced (Clemmensen) to 1:2:3:4:10:11-hexahydrofluorene (XII), b.p. 127°/15 mm., which is readily dehydrogenated (Se at 300—320°; Pt at 250—260°) to fluorene. Oxidation (CrO₃, AcOH) of (XII) gives resinous products but no (XI). The hexahydrofluorenone of Vocke (A., 1934, 189) is probably (XI). Reduction of fluorenone-oxime by Nakamura's method (A., 1930, 466) gives fluorene and a base; (XII) is not formed. H. B.

Tables of the number of isomerides of the simpler derivatives of cyclic parents. G. PÓLYA (Helv. Chim. Acta, 1936, 19, 22—24).—The no. of structural isomerides (not stereoisomerides) is tabulated which can be derived by replacement of H of C₆H₆, C₁₀H₈ (anthraquinone), anthracene (pyrene), phenanthrene or thiophen (furan) by the univalent radicals X, Y, and Z provided that the introduction of X_a, Y_b, and Z_c into the parent does not lead to the same mol. formula as the introduction of X_b, Y_k, and Z_l. The case of alkyl derivatives receives extended treatment. H. W.

Kinetics of nitration of aromatic compounds.

—See this vol., 297.

Direct introduction of deuterium into benzene.

—See this vol., 299.

Reaction of paraffins with aromatic hydrocarbons (destructive alkylation). A. V. GROSSE and V. N. IPATIEV (J. Amer. Chem. Soc., 1935, 57, 2415—2419; cf. A., 1935, 1348).—In presence of suitable catalysts paraffins and aromatic hydrocarbons react thus: C_(m+n)H_{2(m+n)+2} + ArH → C_nH_{2n+2} + Ar·C_mH_{2m+1}. Dry HCl is passed through ββ-trimethylpentane (I), C₆H₆, and AlCl₃ at 25—50° (or ZnCl₂ at 50—75°); isobutane, PhBu^γ, and C₆H₅Bu^γ₂ (only the *p*-compound is isolated pure) [formed by further reaction of PhBu^γ with (I)] are produced. (I) and C₆H₆ do not react in presence of MgCl₂-HCl at 200°/20 atm. or BF₃ (promoted by Ni and H₂O) at 55°. H. B.

Kinetics of Friedel-Crafts reaction and activity of mixed catalysts in the reaction of benzoyl chloride with toluene. L. F. MARTIN, P. PIZZOLATO, and L. S. McWATERS (J. Amer. Chem. Soc., 1935, 57, 2584—2589).—The reaction between PhMe and BzCl in presence of AlCl₃, FeCl₃, and mixtures (I) of AlCl₃ and FeCl₃ is investigated using Steele's method (J.C.S., 1903, 83, 1470). All the (I) are more active than either of the components; the velocity coeff. increases with rise in the % of FeCl₃ (and is a max. with > 50 mols.-%) in (I). For each mol. of total metal chlorides used, < 1 mol. of COPH·C₆H₄Me is produced; evidence showing that this is due to the removal of the catalyst as the complex.

COPH·C₆H₄Me, AlCl₃, FeCl₃, is given. The variation of the velocity coeff. with concn. is of the same order as that found by Olivier (A., 1918, i, 228) for the reaction between C₆H₆ and BzCl. The velocity coeff. for the reaction between PhMe and CH₂PhCl is greatly increased by a small % of FeCl₃; a subsequent decrease occurs when substantial amounts are present. The results support the reaction mechanism proposed by Steele (*loc. cit.*). H. B.

Decomposition of di-*o*-tolylidonium iodide. H. J. LUCAS, E. R. KENNEDY, and C. A. WILMOT (J. Amer. Chem. Soc., 1936, 58, 157—160).—*o*-C₆H₄Me·IO, *o*-C₆H₄Me·IO₂, and Ag₂O [which catalyses the reaction C₇H₇IO + C₇H₇IO₂ → (C₇H₇)₂I⁺ + IO₃⁻] are triturated in CHCl₃ + successive small amounts of H₂O; treatment of the combined aq. extracts with SO₂ or KI gives di-*o*-tolylidonium iodide (I). Decomp. of (I) at 155° (bath) affords only *o*-C₆H₄MeI (which is converted into *o*-C₆H₄Me·MgI and thence into *o*-C₆H₄Me·CO₂H): (*o*-C₆H₄Me)₂I·I → *o*-C₆H₄MeI + *o*-C₆H₄Me⁺ + I⁻. Physical data for the C₆H₄MeI are given. H. B.

Chloro-derivatives of xylene. H. WAHL (Ann. Chim., 1936, [xi], 5, 5—82).—Partly a detailed account of work already reported (A., 1933, 815; 1934, 177, 181, 772, 878; 1935, 739). The following is new. Chloro-*p*-xylene (I) and H₂SO₄ give 2-chloro-*p*-xylene-5-sulphonic acid, +2H₂O, m.p. about 100° (Na, +H₂O, and Ca salts, +3H₂O; chloride, m.p. 50°; amide, m.p. 185°; anilide, m.p. 155°), obtained (diazo-reaction) also from *p*-xylidine-5-sulphonic acid and converted by HNO₃-H₂SO₄ at 50—60° into a mixture of 65—70% of 2-chloro-3-nitro-*p*-xylene-5-sulphonic acid (K, Ca, +4H₂O, and Na, +2H₂O, salts) and 20% of 2-chloro-3:5-dinitro-*p*-xylene (II), m.p. 95° [also obtained from 2-chloro-3- and -5-nitro-*p*-xylene and HNO₃ at about 10° and (diazo-reaction) from 3:5-dinitro-*p*-xylidine]. Reduction (Fe-HCl) affords 3-chloro-*p*-xylidine-6-sulphonic acid, +H₂O. The prep. of the 3-NO₂, m.p. 36° (*Ac* derivative, m.p. 190°), and 5-NO₂-derivatives of acet-*p*-xylidine is described. The third aldehyde (phenylhydrazone, m.p. 145°), obtained by nitration of (I), has m.p. 101°. 2-Chloro-6-nitro-*p*-xylene and HNO₃ at about 10° give 2-chloro-5:6-dinitro-*p*-xylene, m.p. 101°, reduced by Zn and AcOH-EtOH to the (NH₂)₂-compound, m.p. 50°, which affords a phenanthrazine, m.p. 235°. 5-Chloroacet-*p*-xylidine (III) and HNO₃ give 5-chloro-3-nitroacet-*p*-xylidine, m.p. 200—200·5°, hydrolysed (H₂SO₄) to 5-chloro-3-nitro-*p*-xylidine, m.p. 100—101° (*Bz* derivative, m.p. 160°), the structure of which is proved by conversion into 2-chloro-6-nitro-*p*-xylene. The Cl of the chloronitro-*p*-xylenes is unreactive owing to steric hindrance. The K salts, +H₂O, of 2:3- and 2:6-dichloro-*p*-xylenesulphonic acids are described. 2:5-Dichloro-*p*-xylene and HNO₃ give the 6-NO₂-derivative, m.p. 95°, b.p. 155—160°/15 mm., reduced (Fe) to the 6-NH₂-derivative, m.p. 81°, b.p. 155—160°/15 mm. (*Ac*, m.p. 198°, and *Bz* derivative, m.p. 205°). (III) and Cl₂ in AcOH give 3:5-dichloroacet-*p*-xylidine, m.p. 172°, hydrolysed to the *base*, m.p. 48°, b.p. 160—162°/15 mm. (*Bz* derivative, m.p. 179—180°), which (diazo-reaction) yields 2:6-dichloro-*p*-xylene. *p*-Xylidine with Cl₂ in conc.

H₂SO₄ at about 40° affords the 5:6-Cl₂-derivative, m.p. 78—80°, b.p. 165—170°/15 mm. [*Ac*, m.p. 165° (corr.), and *Bz* derivative, m.p. 173° (corr.)], converted (diazo-reaction) into 2:3-dichloro-*p*-xylene. Hot chlorination of (III) affords 3:5:6-trichloroacet-*p*-xylidine, m.p. 220°, and thence the *base*, m.p. 206°. Dyes obtained by coupling each of 10 diazotised xylidines with 9 2-hydroxy-1-naphthylidines and 9 naphthols are described. The fastness of these dyes to light, Cl₂, and washing is good. The following are prepared: 2-hydroxy-1-naphth-xylidine, m.p. 200°, -3', m.p. 230°, -5', m.p. 258°, and -6'-chloro-, m.p. 180°, -3', m.p. 150° (decomp.), -5', m.p. 255° (decomp.), and -6'-nitro-, m.p. 145°, and -3':5', m.p. 223°, -3':6', m.p. 250°, and -5':6'-dichloro-*p*-xylidine, m.p. 233°. R. S. C.

Jacobsen reaction. IV. L. I. SMITH and C. L. MOYLE (J. Amer. Chem. Soc., 1936, 58, 1—10).—The Jacobsen rearrangement is not a general reaction; it is limited (with few exceptions) to C₆H₂Me₄, C₆HMe₅, C₆H₂Et₃, and halogeno-derivatives of C₆H₆ and methylbenzenes. Labile groups are Cl, Br, I, Me, Et, and SO₃H; no rearrangement occurs when NO₂, Ac, OMe, or CO₂H is present. In general, except when Hal is present, < 4 substituents must be in the C₆H₆ nucleus to obtain rearrangement; the course (and ease) of the reaction is determined by the substituents. Results now and previously obtained (A., 1933, 600) show that for all the C₆HMe₄Cl and C₆HMe₄Br, the ease of migration is Br > Me > Cl, whilst for C₆H₂Me₃Cl and C₆H₂Me₃Br the order is Br > Cl > Me (when rearrangement occurs). There appears to be some correlation between the ease of hydrolysis of ArSO₃H and its ability to undergo rearrangement. Whenever rearrangement occurs, side reactions leading to amorphous solids or tars and SO₂ also occur. Attempts to rearrange C₆Me₅·SO₃H, using conditions designed to avoid such reactions, failed; rearrangement could not be effected with reagents [*e.g.*, PhSO₃H, H₃PO₄, CaCl₂, Mg(ClO₄)₂] other than H₂SO₄. The constitutions of the compounds described below are established by conversion into known or proved derivatives.

Chlorodurene (from durene and Cl₂ in CHCl₃ at 0°) and conc. H₂SO₄ at 65° give 99% of chloropentamethylbenzene (I), m.p. 154·5—155° [reduced (red P, 45% HI, 220°) to C₆HMe₅], and 81% of 3-chloro-*ψ*-cumene-5-sulphonic acid (II) [also prepared by short treatment of 3-chloro-*ψ*-cumene (III) with oleum]. Chloroisodurene, b.p. 139°/41 mm., m.p. -1° to 1° (obtained with a little of the Cl₂-derivative, m.p. 188°, from isodurene and Cl₂ in CHCl₃), similarly affords (I) (96·4%), (II) (70%), and a little of a compound, C₂₀H₂₄Cl₂, m.p. 209·5°, whilst chloroprenitene, b.p. 131—132°/24 mm., m.p. 24°, and approx. 14% oleum at 25—30° yield (I) (98%) and (II) [or, by hydrolysis, (III)]. At least two rearrangements are considered to occur with the above C₆HMe₄Cl. 5-Chloro-*ψ*-cumene, m.p. 70·5—71° [formed with (III) from *ψ*-cumene and Cl₂ in CHCl₃ at 0°, and 20% oleum at 65—70° give (II) (71%) and tar. (II) (44%) and a small amount of an unidentified product, m.p. 148—153°, are formed from 6-chloro-*ψ*-cumene (IV), b.p. 127—128°/20 mm. [3:5-(NO₂)₂-derivative, m.p.

162° (lit. 162° and 169—170°), and approx. 15% oleum at 25—30°. Intramol. migration of Cl thus occurs in both cases. (IV) is prepared by deamination of 6-chloro-5-*ψ*-cumidine [from 5-*ψ*-cumidine (V) (in EtOH-I) and Cl₂ (in CHCl₃)]. Chloromesitylene [SO₃H derivative (Na salt +0.5H₂O; *amide*, m.p. 165.5—166°)] and 4-chlorohemimellitene, b.p. 86—87°/16 mm. [5:6-Br₂-derivative, m.p. 229—230°], prepared from hemimellitene and Cl₂ in CHCl₃-I at 0°, do not rearrange; sulphonation occurs with 20% oleum at 70—75°. Bromomesitylene [SO₃H derivative (Na salt +0.5H₂O; *amide*, m.p. 160—160.5°)] and 20% oleum at 25—30° give *dibromomesitylene*, m.p. 65.5°, and 2:4:6-C₆H₃Me₃·SO₃H (not isolated; hydrolysed to *s*-C₆H₃Me₃); at 70°, *tribromomesitylene*, m.p. 223.5—224°, is formed in 68.5% yield. 5-Bromo-*ψ*-cumene [from *ψ*-cumene-5-sulphonic acid (VI) and Br in aq. EtOH] and 20% oleum at 25—30°/6 weeks afford a little *tribromo-ψ*-cumene, m.p. 232°, and 90% of 3-bromo-*ψ*-cumene-5-sulphonic acid [Na salt, also prepared from the Na salt of (VI) in EtOH with Br in CHCl₃], hydrolysed (dil. H₂SO₄ at 145°) to 3-bromo-*ψ*-cumene. The following compounds did not undergo any rearrangement when treated with conc. H₂SO₄ or oleum: (V), hemimellitene, 5-nitro-*ψ*-cumene, 2:3-C₁₀H₆Me₂, *p*-C₆H₄PhBr, pentamethylcyclohexane, b.p. 98—98.5°/38 mm., 188°/730 mm. [prepared by reduction (H₂, Ni-kieselguhr, 225°) of C₆HMe₅], and *Me pentamethylbenzenesulphonate*, m.p. 91—91.5° (from C₆Me₅·SO₂Cl and MeOH-NaOMe).

Reduction (Zn, dil. HCl) of 3-chloro-*ψ*-cumene-5-sulphonamide, m.p. 182°, affords *ψ*-cumene-5-sulphonamide, m.p. 180°. Na 3-chloro-*ψ*-cumene-5-sulphonate (VII) is reduced (Na-Hg, H₂O) to Na *ψ*-cumene-5-sulphonate (nitrated to trinitro-*ψ*-cumene, m.p. 183.5°), is converted by red P and 45% HI into *ψ*-cumene, and is hydrolysed (dil. H₂SO₄ at 135—155°) to 3-chloro-*ψ*-cumene, b.p. 127°/61 mm. [5:6-(NO₂)₂-derivative (VIII), m.p. 173.5—174°, also formed by nitration of (VII)]. 3-Chloro-5:6-diamino-*ψ*-cumene, m.p. 136.5° [from (VIII), SnCl₂, and EtOH-conc. HCl], and phenanthraquinone (IX) in EtOH-AcOH afford 12-chloro-10:11:13-trimethylphenanthrophenazine, m.p. 330.5—331°, whilst reduction (SnCl₂, HCl) of (VIII) in AcOH gives 6-chloro-2:4:5:7-tetramethylbenzimidazole, m.p. 250—251°. 3-Chloro-5:6-dibromo-*ψ*-cumene, m.p. 224°, is obtained from (VII) and Br in AcOH at 70°. 2-Chloro-4:6-diaminomesitylene, m.p. 137—138°, is prepared by reduction (SnCl₂) of the (NO₂)₂-derivative. 3-Bromo-5:6-dinitro-*ψ*-cumene is reduced (SnCl₂, EtOH-HCl) to 5:6-diamino-*ψ*-cumene, which with (IX) yields 10:11:13-trimethylphenanthrophenazine, m.p. 253°; reduction in AcOH affords 2:4:5:7-tetramethylbenzimidazole, m.p. 233°. 6-Bromo-*ψ*-cumene, b.p. 117°/17 mm., 233° (corr.)/724 mm., is obtained by deamination of 6-bromo-5-*ψ*-cumidine, m.p. 69° [from (V) (in dil. HCl) and Br in AcOH]. 4-Chloro-5:6-dinitrohemimellitene, m.p. 183°, is similarly reduced to the (NH₂)₂-derivative, m.p. 137—137.5°, which with Ac₂ and (IX) gives 8-chloro-2:3:5:6:7-pentamethylquinoline, m.p. 160.5°, and 13-chloro-10:11:12-trimethylphenanthrophenazine, m.p. 346.5—347°; reduction in AcOH yields 7-chloro-2:4:5:6-tetramethylbenzimidazole, m.p. 288.5°. The (NO₂)₂-

derivative, m.p. 196.5°, of 4-bromohemimellitene, b.p. 103—103.5°/12 mm., 229.5°/750 mm., m.p. 1°, on reduction (SnCl₂, HCl) and treatment with (IX) gives 10:11:12-trimethylphenanthrophenazine, m.p. 311°. H. B.

Oxidation in benzene series by gaseous oxygen. V. Oxidation of tertiary hydrocarbons. H. N. STEPHENS and F. L. RODUTA (J. Amer. Chem. Soc., 1935, 57, 2380—2381).—Slow oxidation (O₂) of CHPhMeR (R=Et, Pr^a, Bu^a) at 119° (bath) gives COPhMe but no COPhR; CHPh₂Me and CHPh₃ similarly afford COPh₂. These reactions, unlike that with CH₂Ph₂(→COPh₂) (cf. A., 1928, 1233), are not inhibited by H₂O. H. B.

Reactions between organomercury compounds and nitrosyl compounds. L. I. SMITH and F. L. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 2460—2463).—Acetoxymercureidurene (I) (in CHCl₃) and NOCl (from EtO·NO and AcOH-conc. HCl) give *nitroso-durene* (II), m.p. 160° (decomp.) (rapid heating). *Nitroso-isodurene* (III), m.p. 134°, *-pentamethylbenzene*, m.p. 160° (decomp.) (rapid heating), *-prehnitene*, m.p. 72°, *-mesitylene*, and *-ψ*-cumene are similarly prepared: ArHgX + NOCl → ArNO + HgXCl. (I) and (II) are both converted by HNO₃ (*d* 1.26) at 70° into *nitrodurene*, m.p. 112—113°; (III) and acetoxymercureiidurene (IV) similarly afford *nitroisodurene*, m.p. 38—39°, also prepared from (III) and NO₂ in CHCl₃. N₂O₃ distilled into (IV) (in CHCl₃) gives a colourless ppt. of (probably) nitritomercureiidurene contaminated with Hg(NO₂)₂, which subsequently redissolves; a brown ppt. is then formed and the CHCl₃ contains (III) [similarly obtained from (IV) and NO₂]. The reaction between HgPh₂ and N₂O₃ (Bamberger, A., 1897, i, 288; 1900, i, 145) is considered to give PhNO as the primary product; PhN₂·NO₃ is then formed from PhNO and NO. Diazonium nitrates are formed only when N₂O₃+NO (excess) act on Hg compounds. H. B.

Reaction between chlorodiphenylmethane and ethyl alcohol. F. G. KNY-JONES and A. M. WARD (J. Amer. Chem. Soc., 1935, 57, 2394—2396).—Re-examination of the method previously used (A., 1927, 1061) in greater detail again shows that the reaction, CHPh₂Cl+EtOH → CHPh₂·OEt+HCl, is irreversible (cf. Norris and Morton, A., 1928, 1000). H. B.

Polystyrene and the mechanism of polymerisation. G. S. WHITBY (Trans. Faraday Soc., 1936, 32, 315—323).—Evidence is presented for the view that polymerisation of unsaturated compounds is due to successive additions to the double linking present in the monomeride or the preceding polymeric stage, a H atom going to one side of the double linking and the rest of the addendum to the other. F. L. U.

Highly polymerised compounds. CXXI. Insoluble polystyrene. H. STAUDINGER [with W. HEUER and E. HUSEMANN] (Trans. Faraday Soc., 1936, 32, 323—332).—When styrene (I) is polymerised in presence of *p*-divinylbenzene (II) the product, although highly turgescible, is insol. in the usual solvents. The proportion of (II) needed to render the resulting polystyrene (III) insol. decreases as the chain-length of (III) increases, being, e.g. (II)/

(I) = 1/50,000 for a highly polymerised product. The insol. product is thus chemically indistinguishable from sol. (III), and the striking difference in physical properties is due to the relatively small no. of "bridges" effected by (II) between the long chains of (III), converting a linear into a three-dimensional polymeride. The results are discussed with reference to sol. and insol. caoutchouc, and to highly polymerised biological materials.

F. L. U.

Synthesis of diacetylene derivatives. J. S. SALKIND and F. B. FUNDYLER (Ber., 1936, 69, [B], 128—130).—CPh:CH is converted by heating with a feebly acidified solution of NH_4Cl and excess of CuCl into the compound, $\text{C}_{16}\text{H}_{10}\text{CuCl}$, immediately decomposed by Et_2O into $\alpha\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butindine (I), m.p. 86—87°. The change appears to be balanced. (I) is hydrogenated (Pt-sponge) to $\alpha\delta$ -diphenylbutane. The liberated H is involved in the formation of resinous material (? $\text{C}_{16}\text{H}_{14}$). Analogous reactions are given by γ -hydroxy- γ -methyl- Δ^{α} -butinene and hydrocyclohexylacetylene.

H. W.

Rearrangements of polyinenes. VII. Formation of allenenes. J. H. FORD, C. D. THOMPSON, and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 2619—2623).—COPhBu γ (I) (2 : 4-dinitrophenylhydrazone, m.p. 194—195°), prepared in 67% yield from MgPhBr and Bu γ COCl in Et_2O and N_2 , with $\text{C}_6\text{H}_5\text{MgBr}$ gives phenyltert.-butyltert.-butylethinylcarbinol (II), b.p. 125—128°/4 mm., converted by PBr_3 in light petroleum into the carbinyl bromide (III), b.p. 115—117°/1 mm., and by AcOH—conc. H_2SO_4 into γ -phenyl- $\beta\beta\zeta\zeta$ -tetramethyl- Δ^{γ} -hepten- ϵ -one, b.p. 96—97°/1 mm., m.p. 30.5° (2 : 4-dinitrophenylhydrazone, m.p. 150—151°). A hydrocarbon could not be prepared from (II) and TiCl_3 or from (III) and Ag or Cu. (III) and moist Ag_2O in COMe_2 give (II). Decomp. of the Grignard reagent (A) from (III) with H_2O affords the allenic hydrocarbon γ -phenyl- $\beta\beta\zeta\zeta$ -tetramethyl- $\Delta^{\gamma\delta}$ -heptadiene (IV), b.p. 78—80°/1 mm. [ozonolysis products, $\text{Bu}^{\gamma}\text{CO}_2\text{H}$ and (I)]. ClCO_2Me and (A) similarly give Me γ -phenyl- $\beta\beta\zeta\zeta$ -tetramethyl- $\Delta^{\gamma\delta}$ -heptadiene- ϵ -carboxylate, b.p. 116—120°/2 mm. [free acid, m.p. 160—161°, also formed from (A) and CO_2], which is oxidised (O_3) to the Me ester (2 : 4-dinitrophenylhydrazone, m.p. 205—206°) of trimethylpyruvic acid [2 : 4-dinitrophenylhydrazone, m.p. 169—171° (decomp.)]. (III) does not give a stable Na alkyl when treated with 40% Na—Hg in Et_2O and N_2 ; decomp. of the product with H_2O affords (IV) and two isomeric hydrocarbons, $\text{C}_{31}\text{H}_{46}$, m.p. 148—149° and 115—125°. The same mixture is obtained by reduction (Zn dust, EtOH) of (III) or treatment with Li. α -Phenyl- $\beta\beta$ -dimethylbutyric acid, m.p. 105°, is prepared from CO_2 and $\text{CHPhBu}^{\gamma}\text{MgBr}$. The acids and esters formed from metallic derivatives of the type $\text{CR}:\text{C}:\text{R}'_2\text{M}$ may all be $\text{CO}_2\text{R}''\cdot\text{CR}:\text{C}:\text{CR}'_2$. H. B.

Rearrangements of polyinenes. VIII. Formation of diallenes. E. D. FARLEY and C. S. MARVEL (J. Amer. Chem. Soc., 1936, 58, 29—34).—The hydrocarbon obtained (A., 1932, 505) from diphenyltert.-butylethinylcarbinyl bromide and Ag or Cu-bronze is now considered to be $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\gamma\delta$ -ditert.-butyl- $\Delta^{\alpha\beta\zeta}$ -hexatetraene (I), $(\text{C}_6\text{H}_5)_2\text{C}:\text{C}:\text{Bu}^{\gamma}$, since oxidation

(dry O_2 in $\text{C}_6\text{H}_4\text{Me}_2$ at 140°) gives 52% of COPh_2 (apart from products derived from the $\text{C}_6\text{H}_4\text{Me}_2$). (I) could not be oxidised by PbO_2 ; with O_3 the products previously reported (*loc. cit.*) and BzOH are obtained. The hydrocarbon $\text{C}_{42}\text{H}_{46}$ [obtained (*ibid.*, 496) from $\text{CMeEt}_2\text{C}:\text{C}:\text{CPh}_2\text{Br}$] is also oxidised (O_2) to COPh_2 (38%); definite products could not be isolated from the hydrocarbon prepared by Moureu *et al.* (A., 1927, 355) from $(\text{CPh}:\text{C}:\text{CPh}_2)_2$. Reduction of diphenyltert.-butylethinylcarbinol with TiCl_3 gives (I) and a compound, $\text{C}_{38}\text{H}_{39}\text{Cl}$, m.p. 201°. Reduction (Na, amyl alcohol) of (I) affords hydrocarbons, $\text{C}_{38}\text{H}_{42}$ (II), m.p. 132° (II), and $\text{C}_{38}\text{H}_{44}$ [described previously (A., 1932, 505) as $\text{C}_{19}\text{H}_{22}$], m.p. 182°; with red P and 47% HI in AcOH, a hydrocarbon, $\text{C}_{30}\text{H}_{42}$ (III), m.p. 210—211° [which may be the dimeride of 3-phenylindene (Blum-Bergmann, A., 1931, 208)], results. The hydrocarbon, $\text{C}_{38}\text{H}_{38}$, m.p. 176°, obtained (*cf. loc. cit.*) from (I) and AcOH—HCl, is not oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ in AcOH, does not give a Na alkyl with 40% Na—Hg, but is reduced (P, HI, AcOH) to (III). (I) and 40% Na—Hg in Et_2O and N_2 afford a product (A) containing $\text{CNaPh}_2\text{C}:\text{C}:\text{CBu}^{\gamma}$ [since treatment with CO_2 gives a little $\text{CBu}^{\gamma}\text{C}:\text{C}:\text{CPh}_2\text{CO}_2\text{H}$ (A., 1932, 50)] and an additive compound $\text{C}_{38}\text{H}_{38}\text{Na}_2$ [since the action of H_2O affords a hydrocarbon, $\text{C}_{38}\text{H}_{40}$ (IV), m.p. 163° (*loc. cit.*), whilst ClCO_2Me gives an ester, $\text{C}_{38}\text{H}_{38}(\text{CO}_2\text{Me})_2$, m.p. 173°, which when (partly) hydrolysed (MeOH-KOH) and then heated passes into an ester, $\text{C}_{38}\text{H}_{39}\text{CO}_2\text{Me}$, m.p. 162°]. Oxidation of (IV) with KMnO_4 in COMe_2 gives a neutral compound, $\text{C}_{33}\text{H}_{30}\text{O}_2$, m.p. 217—218°; with $\text{K}_2\text{Cr}_2\text{O}_7$ in AcOH, a neutral compound, $\text{C}_{33}\text{H}_{28}\text{O}_3$ (V), m.p. 169°, results. Reduction (Na, amyl alcohol) of (IV) affords a hydrocarbon, $\text{C}_{38}\text{H}_{42}$ (VI), m.p. 197°; and a mixture (B) of (VI) and a more fusible isomeride; the hydrocarbon, $\text{C}_{38}\text{H}_{42}$, m.p. 181—182°, previously described (A., 1932, 505), is identical with (B). (VI) is also obtained by successive treatment of (IV) with 40% Na—Hg and H_2O . The hydrocarbon, $\text{C}_{38}\text{H}_{38}$, m.p. 179—180° (*loc. cit.*), prepared from (A) and $\text{C}_2\text{Me}_4\text{Br}_2$, is oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$, AcOH) to (V), is reduced (Na, amyl alcohol) to (VI) and an isomeride, m.p. 155—156°, and is converted by successive treatment with 40% Na—Hg and H_2O into (IV).

The Na alkyl from $\alpha\alpha$ -diphenyl- $\delta\delta$ -dimethyl- $\Delta^{\alpha\beta}$ -pentadiene (A., 1932, 50) and 40% Na—Hg with $\text{C}_2\text{Me}_4\text{Br}_2$ gives a hydrocarbon, $\text{C}_{38}\text{H}_{40}$, m.p. 143—144°; the dimeride (VII) (*loc. cit.*) similarly regenerates (VII), but decomp. with H_2O affords a hydrocarbon, $\text{C}_{38}\text{H}_{44}$, m.p. 133° [probably formed also by reduction (Na, amyl alcohol) of (VII)], which differs from (II). Reduction (red P, 47% HI, AcOH) of (VII) affords a hydrocarbon, $\text{C}_{38}\text{H}_{42}$, m.p. 134—135°, whilst oxidation ($\text{K}_2\text{Cr}_2\text{O}_7$, AcOH) gives a little of a neutral compound, $\text{C}_{26}\text{H}_{26}\text{O}_2$, m.p. 227°, but no COPh_2 . H. B.

Mol. compounds of polycyclic hydrocarbons and their quinones with polynitro-compounds and with metallic salts. K. BRASS and K. FANTA (Ber., 1936, 69, [B], 1—11).—Examination of many compounds fails to confirm Bruni's view (A., 1906, i, 491) that the power of adding NO_2 -compounds depends essentially on the C_6H_6 nucleus and that the no. of added mols. is in the limit equal to the no. of independent C_6H_6 nuclei present in the hydrocarbon

and that polynuclear condensed mols. add only 1 mol. of NO_2 -compounds. Perylene does not add dipicric acid (I), but with styphnic acid (II) gives a compound (1:1), m.p. 211° . 2:3:10:11-Dibenzperylene affords the compounds, $\text{C}_{28}\text{H}_{16}$, $2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m.p. 240° (decomp.), $\text{C}_{28}\text{H}_{16}$, $2\text{C}_6\text{H}_3\text{O}_8\text{N}_3$, decomp. 236° , $\text{C}_{28}\text{H}_{16}$, SbCl_5 , and $\text{C}_{28}\text{H}_{16}$, SnCl_4 . 1:12-Benzperylene does not add (I), but affords the substances, $\text{C}_{22}\text{H}_{12}$, $\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m.p. 267° , $\text{C}_{22}\text{H}_{12}$, $\text{C}_6\text{H}_3\text{O}_8\text{N}_3$, m.p. 234° , $2\text{C}_{22}\text{H}_{12}$, SbCl_5 , and $\text{C}_{22}\text{H}_{12}$, 2SnCl_4 . 2:3-Benzanthracene does not unite with picric acid (III), dibromopicric acid (IV), (I), or (II), but gives the substances, $2\text{C}_{18}\text{H}_{12}$, SbCl_5 and $\text{C}_{18}\text{H}_{12}$, 2SnCl_4 . Addition of (I), (II), (III), or (IV) to 2:3-benzanthraquinone is not observed, but the compounds, $\text{C}_{18}\text{H}_{10}\text{O}_2$, 2SbCl_5 and $\text{C}_{18}\text{H}_{10}\text{O}_2$, 2SnCl_4 , have been isolated. 1:2-Benzanthracene gives the compounds, $\text{C}_{18}\text{H}_{12}$, $\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m.p. $141.5\text{--}142.5^\circ$, $\text{C}_{18}\text{H}_{12}$, $\text{C}_6\text{H}_3\text{O}_8\text{N}_3$, m.p. 153° , and $2\text{C}_{18}\text{H}_{12}$, SbCl_5 . 1:2-Benzanthraquinone does not add (I), (II), (III), or (IV), but affords the substances, $\text{C}_{18}\text{H}_{10}\text{O}_2$, SbCl_5 and $2\text{C}_{18}\text{H}_{10}\text{O}_2$, SnCl_4 , CHCl_3 . (III) is not added by 3-isopropyl-, m.p. $154\text{--}155^\circ$, 7-isopropyl-, m.p. 114° , 4-methyl-, m.p. $168\text{--}169^\circ$, 5-methyl-, m.p. $173.5\text{--}174.5^\circ$, or 6-methyl-, m.p. 174° , -1:2-benzanthraquinone. Additive compounds of 9:9'-dianthryl with (II), (III), or (IV) could not be isolated; SnCl_4 causes halochromism, whilst SbCl_5 affords the substance, $\text{C}_{28}\text{H}_{18}$, SbCl_5 . 9:9'-Dianthranlyquinone does not add (I), (II), (III), or (IV), but gives the compounds, $\text{C}_{28}\text{H}_{10}\text{O}_2$, 2SbCl_5 and $\text{C}_{28}\text{H}_{10}\text{O}_2$, 2SnCl_4 . H. W.

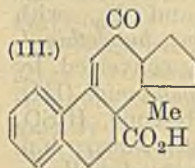
Action of oleum on decahydronaphthalene. E. I. PROKOPETZ (J. Appl. Chem. Russ., 1935, 8, 1214—1215).—When *cis-trans*-decahydronaphthalene is shaken with 20% oleum, only the *cis*-isomeride is oxidised, leaving the pure *trans*-isomeride. R. T.

Rubrene problem. A. SCHÖNBERG (J. Amer. Chem. Soc., 1936, 58, 182; cf. A., 1934, 643).—A question of priority (cf. Eck and Marvel, A., 1935, 1492). H. B.

Attempts to obtain rubenes soluble in water. Hexabromotetraphenylrubene; its transformation into rubenepolycarboxylic acids. C. DUFRAISSE and L. VELLUZ (Bull. Soc. chim., 1936, [v], 3, 254—265).— $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{C}\cdot\text{MgBr}$ and $\text{CO}(\text{C}_6\text{H}_4\text{Br}\cdot p)_2$ give $\alpha\gamma\gamma\text{-tri-}p\text{-bromophenylpropinen-}\gamma\text{-ol}$, m.p. $141\text{--}142^\circ$ (*Me ether*, m.p. $101\text{--}102^\circ$); this with $\text{H}_2\text{SO}_4\text{-Bu}_2\text{O}$ gives $p\text{-C}_6\text{H}_4\text{Br pp}'\text{-dibromohydrindenylmethyl ketone}$, m.p. ($+ \text{C}_6\text{H}_6$) $114\text{--}115^\circ$ and (anhyd.) $135\text{--}136^\circ$, which with PCl_3 in ligroin affords the chloride, m.p. $130\text{--}131^\circ$ (*dimeride*, m.p. $273\text{--}275^\circ$), converted in quinoline at $100^\circ/15\text{--}16$ mm. into 5:5'- (or 5:6'-) *dibromo-1:3:1':3'-tetra-}p\text{-bromophenylrubene} (bisindenyl formulation), m.p. $401\text{--}402^\circ$ (cryst. peroxide loses 75% of its O at $150\text{--}200^\circ$). Four Br readily and the last two very slowly react with Mg; CO_2 then leads to an amorphous acid (H_2O -sol. Na salt), which forms a dissociable peroxide. M.p. are taken on a block. R. S. C.*

Chemical interrelationships in the cholane group. H. JENSEN (J. Chem. Educ., 1935, 12, 559—564).—A review. L. S. T.

Synthesis of compounds related to sterols, bile acids, and oestrus-producing hormones. VIII. C. L. HEWETT. IX. A. COHEN, J. W. COOK, and C. L. HEWETT. X. Ruzicka's hydrocarbon " $\text{C}_{21}\text{H}_{16}$ " from cholic acid. W. E. BACHMANN, J. W. COOK, C. L. HEWETT, and J. IBALL (J.C.S., 1936, 50—52, 52—53, 54—61).—VIII. Dihydroresorcinol (I) (1 mol.) and CH_2PhCl (1 mol.) in EtOH-NaOEt (1 mol.) give some *benzylcyclohexane-2:6-dione*, m.p. $184\text{--}185^\circ$, converted by conc. H_2SO_4 at -15° into a SO_3H derivative ($+\text{H}_2\text{O}$), m.p. $193\text{--}194^\circ$. $\beta\text{-}m\text{-Methoxyphenylethyl bromide}$ (II), b.p. $138^\circ/12$ mm., and (I) similarly afford (mainly) the $\beta\text{-}m\text{-methoxyphenylethyl ether}$, b.p. $205\text{--}207^\circ/0.5$ mm., of (I) and a little $\beta\text{-}m\text{-methoxyphenylethylcyclohexane-2:6-dione}$, m.p. $149\text{--}150^\circ$ (cf. Robinson and Schittler, A., 1935, 1498), which is best converted into 1-keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene (*loc. cit.*) by 80% H_2SO_4 at 100° (bath). $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$ and (I) give 3-keto- $\Delta^1\text{-cyclohexenyl } \beta\text{-1-naphthylethyl ether}$, m.p. $138\text{--}139^\circ$, hydrolysed (aq. EtOH-KOH or $\text{NH}_2\text{OH, HCl}$ in $\text{C}_5\text{H}_5\text{N}$ at 100°) to $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$. Hydrolysis (dil. HCl) of the product from $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$ and $(\text{CH}_2)_2\text{O}$ at 100° (Et_2O removed first) gives $\beta\text{-}m\text{-methoxyphenylethyl alcohol}$, b.p. $150\text{--}155^\circ/18$ mm. (3:5-dinitrobenzoate, m.p. $106.5\text{--}107.5^\circ$), converted by PBr_3 in CCl_4 into (II). Modified preps. of $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$ (from $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$) and $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{OMe}$ are given. 2-Acetyl-1-methyl- $\Delta^1\text{-cyclopentene}$ (from 1-methyl- $\Delta^1\text{-cyclopentene}$ and AcCl in $\text{CS}_2\text{-SnCl}_4$) and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ in EtOH-NaOEt afford a little of (probably) the acid (III), m.p. 242° .



IX. $\beta\text{-}6\text{-Methoxy-1-naphthylethyl bromide}$ and $\text{CHK}(\text{CO}_2\text{Et})_2$ in PhMe at $120\text{--}130^\circ$ give the *Et ester*, b.p. $200\text{--}205^\circ/0.3$ mm., of $\beta\text{-}6\text{-methoxy-1-naphthylethylmalonic acid}$, m.p. 160° (decomp.), decarboxylated at 190° to $\gamma\text{-}6\text{-methoxy-1-naphthylbutyric acid}$, m.p. $150\text{--}151^\circ$ [*Et ester* (I), b.p. $169^\circ/0.2$ mm.]. 1-Keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene (Butenandt and Schramm, this vol., 76) and a little of the 7-OH-ketone are formed from (I) and 80% H_2SO_4 at 100° . The product from (I) and $\text{Et}_2\text{C}_2\text{O}_4$ in $\text{Et}_2\text{O}+\text{KOEt}$ is converted by warm 80% H_2SO_4 into 7-methoxy-3:4-dihydrophenanthrene-1:2-dicarboxylic anhydride, m.p. $217.5\text{--}218.5^\circ$, which is demethylated [HBr (d 1.48) in AcOH] to 7-hydroxy-3:4-dihydrophenanthrene-1:2-dicarboxylic anhydride, m.p. $275\text{--}278^\circ$ (previous sintering), and dehydrogenated (Pt-black at 300°) to 7-methoxyphenanthrene-1:2-dicarboxylic anhydride, m.p. $260\text{--}261^\circ$ (corr.) (cf. this vol., 71).

X (cf. A., 1935, 1359). The carbinol from 2-methylhydrindone and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{MgBr}$ (I) is dehydrated (KHSO_4 at 160°) (general procedure) to 3- $\beta\text{-}1\text{-naphthylethyl-2-methylindene}$, m.p. $99\text{--}99.5^\circ$ (dipicrate, m.p. $161\text{--}161.5^\circ$), which is cyclised by AlCl_3 in CS_2 at 0° (general method) to 10-methyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene (II), m.p. $111\text{--}112^\circ$, dehydrogenated (Se at 310° ; general method) to 2':1'-naphtha-1:2-fluorene, m.p. 328° (*ibid.*, 74). $p\text{-Methylbenzylmethylmalonic acid}$, m.p. $178\text{--}180^\circ$

(decomp.) [the *Et* ester, b.p. 203—210°/26 mm., is prepared from $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Br}$ and $\text{CNaMe}(\text{CO}_2\text{Et})_2$ in EtOH], is decarboxylated at 180° to $\beta\text{-}p\text{-tolyl-}\alpha\text{-methylpropionic acid}$, b.p. 181—182°/23 mm., m.p. 30—31·5°, the chloride, b.p. 139—141°/21 mm., of which with AlCl_3 in ligroin gives 2:6-dimethylhydrindone, b.p. 145—

148°/21 mm. [*phenylhydrazone*, m.p. 173—175° (decomp.)]. This and (I) lead to 3- β -1'-naphthylethyl-2:5-dimethylindene, m.p. 81—81·5° (*dipicrate*, m.p. 144—144·5°), converted into 6:10-dimethyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene, m.p. 106·5—107° (*semipicrate*, m.p. 133·5—134°), and thence into 6-methyl-2':1'-naphtha-1:2-fluorene, m.p. 330° (varies with rate of heating), which is oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$, AcOH) to the -1:2-fluorenone, m.p. 225—226°. *m*-Methylbenzylmethylmalonic acid, m.p. 152—153° (decomp.), is similarly converted through $\beta\text{-}m\text{-tolyl-}\alpha\text{-methylpropionic acid}$, b.p. 178—179°/20 mm. (chloride, b.p. 137—138°/21 mm.), into 2:5-dimethylhydrindone, b.p. 142—144°/21 mm. [2:4-dinitrophenylhydrazone, m.p. 225—226° (decomp.)], which with (I) gives 3- β -1'-naphthylethyl-2:6-dimethylindene, b.p. 184—186°/0·05 mm., cyclised to 7:10-dimethyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene, m.p. 134·5—135° [accompanied by some $\alpha\delta$ -di-1-naphthylbutane, m.p. 101° (*dipicrate*, m.p. 174—175°), which is undoubtedly present as an impurity in the indene; it is now prepared from $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ and Mg]. 7-Methyl-2':1'-naphtha-1:2-fluorene, m.p. 334—336°, is oxidised to the -1:2-fluorenone, m.p. 175—176·5°. *o*-Methylbenzylmethylmalonic acid, m.p. 122·5—123°, similarly yields $\beta\text{-}o\text{-tolyl-}\alpha\text{-methylpropionic acid}$, b.p. 179—180°/20 mm. (chloride, b.p. 137—138°/21 mm.), and thence 2:4-dimethylhydrindone, b.p. 147—149°/20 mm. [*semicarbazone*, m.p. 224—225° (decomp.)]. This and (I) lead to 3- β -1'-naphthylethyl-2:7-dimethylindene, m.p. 96°, resolviding with m.p. 113·5—114°, cyclised to 8:10-dimethyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene, m.p. 121—122° (*semipicrate*, m.p. 130·5—131·5°), dehydrogenated to 8-methyl-2':1'-naphtha-1:2-fluorene (III), m.p. 281—281·5° (corr.) (*fluorenone*, m.p. 237—238°). Hydrolysis (aq. MeOH-KOH) of the product from $\text{CNaMe}(\text{CO}_2\text{Et})_2$ and 4-bromo-3-bromomethyltoluene, b.p. 148—152° (from $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Br}$, Br , and Fe powder at 0°), or a mixture of 4-bromo-2- and -3-chloromethyltoluenes (Fieser and Seligman, A., 1935, 853), gives 2-bromo-5-methylbenzylmethylmalonic acid, m.p. 179—180° (decomp.), converted through $\alpha\text{-}2\text{-bromo-5-methylbenzylpropionic acid}$, m.p. 84—85° (chloride, b.p. 173—174°/20 mm.), into 4-bromo-2:7-dimethylhydrindone, b.p. 115—117°/0·15 mm. This and (I) lead to 7-bromo-3- β -1'-naphthylethyl-2:4-dimethylindene, m.p. 84—85° (*dipicrate*, m.p. 142·5—143·5°), which is cyclised to 8-bromo-5:10-dimethyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene, m.p. 137·5—138·5°, dehydrogenated to 5-methyl-2':1'-naphtha-1:2-fluorene (IV), m.p. 275—276° (corr.) [*fluorenone* (V), m.p. 209—210°]. Hydrolysis (aq. NH_4Cl) of the product obtained from $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ and propylene oxide at 100° (Et_2O first removed)

gives $\alpha\text{-}1\text{-naphthylisopropyl alcohol}$, b.p. 148—155°/25 mm. [3:5-dinitrobenzoate, m.p. 171—172°; chloride (VI), b.p. 131°/6 mm.]. Cyclisation of a fraction, b.p. 195—215°/0·8 mm., obtained from 2-methylhydrindone, the Grignard reagent from (VI), and MgEtBr (1 mol.) gives $\alpha\delta\text{-di-}1\text{-naphthyl-}\beta\gamma\text{-dimethylbutane}$, m.p. 131—132° (removed as picrate), and resinous material, dehydrogenated with Se to a little 4-methyl-2':1'-naphtha-1:2-fluorene, m.p. 202—203° (corresponding fluorenone, m.p. 214—215°). All the methylnaphthafluorenones give intense purple colours, gradually changing to magenta, with conc. H_2SO_4 .

Comparison (m.p.; colour with H_2SO_4) of (V) and the ketone obtained by oxidation of the hydrocarbon, $\text{C}_{21}\text{H}_{16}$ (VII), of Ruzicka *et al.* (A., 1933, 278; 1934, 398) shows their identity. Powder photographs of (IV) and (VII), which are first fused under identical conditions, are very similar; the slight difference is ascribed to impurity in (VII). Crystallographic data for (III) and (IV) are given. The production of (VII) [*i.e.*, (IV)] from cholic acid is due to simple cyclisation of the side-chain during dehydrogenation. H. B.

Alkali fusion. I. Fusion of potassium sulphanilate with alkali. N. N. VOROSCHCOV and M. M. SCHEMJAKIN (Ber., 1936, 69, [B], 148—152).— $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$ when heated with a large excess of KOH at 350—355° in N_2 gives NH_3 (76·7%); the normal exchange of $\cdot\text{SO}_3\text{K}$ for $\cdot\text{OK}$ occurs to only a slight extent since only 1·5% of SO_3'' is observed. At higher temp. (> 400°) the yield of SO_3'' increases but the product becomes carbonised. Although $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$ enters almost quantitatively into reaction the product does not contain NH_2Ph , PhOH , or $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ is formed in 77·53% yield. H. W.

Action of sodium on aromatic nitro- and nitroso-compounds. V. O. LUKASCHEVITSCH (Annalen, 1936, 521, 198—214).—The Na compounds of aryl NO_2 - and NO -derivatives (Schmidt, A., 1900, i, 20) are best prepared by the action of 0·5% Na-Hg on the NO_2 - or NO -compound in dry Et_2O , C_6H_6 , or PhMe (N_2 atm.). The structures $\text{R}\cdot\text{N}(\text{ONa})_2$ (I), and $\text{R}\cdot\text{NNa}\cdot\text{ONa}$ (II), respectively, are suggested. The reactions $(\text{I}) + \text{R}'\text{NO}_2 \rightleftharpoons \text{R}'\text{N}(\text{ONa})_2 + \text{RNO}_2$ (A), and $(\text{II}) + \text{R}'\text{NO} \rightleftharpoons \text{R}'\text{NONa}_2 + \text{RNO}$ (B), are reversible, but the reaction $(\text{I}) + \text{R}'\text{NO} \rightarrow \text{R}'\text{NONa}_2 + \text{RNO}_2$ (C) proceeds only from left to right. These relationships are established by investigation of the products of interaction of (I) or (II) (or mixtures in accordance with equations A, B, or C) with BzCl , dil. H_2SO_4 , or H_2O , numerous examples being given. Thus with BzCl (I) reacts: $(\text{I}) + 2\text{BzCl} \rightarrow \text{RN}(\text{OBz})_2 \rightarrow \text{Bz}_2\text{O} + \text{RNO}$, which then reacts as C to give (II), which with BzCl affords $\text{RN}(\text{Bz})\cdot\text{OBz}$ (III). The isolation of Bz_2O and various dibenzoylarylhydroxylamines in yields closely corresponding with these equations is described. With H_2O or dil. H_2SO_4 (I) gives the corresponding $\text{NHR}\cdot\text{OH}$ (isolated cryst., and determined in the mother-liquor by reduction of 2—3% AgNO_3), and with PhNO_2 , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{MeNO}_2$ the yields of $\text{NHR}\cdot\text{OH}$ are, respectively, 79·1, 90·9, 85·3, and 83·3%. By the action of $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$ on the appropriate $\text{NHR}\cdot\text{OH}$ in dry Et_2O (N_2) are obtained NO -

dibenzoyl-phenyl-, m.p. 118—118.8°, -*o*-, m.p. 137—138°, -*m*-, m.p. 114.5—115.5°, and -*p-tolyl*-, m.p. 127—127.8°, and -*p-chlorophenyl*-, m.p. 86—87°, -*hydroxylamine* [all identical with the derivatives (III)], from which, by hydrolysis with cold NaOH-MeOH, are obtained *N-benzoyl-phenyl*-, m.p. 121—122°, -*p-tolyl*-, m.p. 109—110°, and -*o*- (? -*p*-)*chlorophenyl*-, m.p. 157° (decomp.), -*hydroxylamine*. J. W. B.

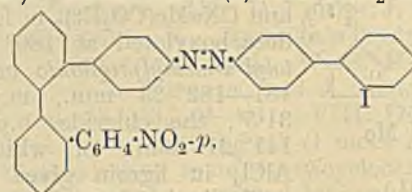
Manufacture of derivatives of *N*-butylaniline.
—See B., 1936, 91.

Synthesis of aromatic nitro-compounds with the azide group in the side-chain. J. JUSCHTSCHENKO (Mem. Inst. Ukrain. Acad. Sci., 1935, 2, 195—205).—*o*-, b.p. 121—122°/2 mm., and *p-Nitrobenzyl azide*, b.p. 144—148°/2 mm., and 2 : 4-*dinitrobenzyl azide*, m.p. 46—47°, have been prepared from NaN₃ or AgN₃ and the appropriate chlorides or iodides in EtOH or Et₂O (8—10 hr. at the b.p.). The azides yield the corresponding aldehydes, NH₃, and N₂ when treated with hot dil. H₂SO₄. R. T.

Interaction of amines and ammonia with di(diphenylene)ethylene. L. A. PINCK and G. E. HILBERT (J. Amer. Chem. Soc., 1935, 37, 2398—2402).—Di(diphenylene)ethylene (I) and NH₂Et at 65° for 2 days give 9-ethylamino-9 : 9'-difluorenyl (II), m.p. 165° [hydrochloride, m.p. 210—215° (decomp.)]; picrate, m.p. 228° (decomp.); *NO*-derivative, m.p. 217°, and small amounts of fluorene (III) and 9 : 9'-difluorenyl (IV). (II) heated with EtOH for 10 days affords (III), 9-ethyliminofluorene (V) [picrate, m.p. 206° (decomp.)], and fluorenone (VI) [formed by hydrolysis of (V)]; in NH₂Et at 85° (sealed tube), (III) and (IV) are produced. (I) and NH₂Me at room temp. similarly afford 9-methylamino-9 : 9'-difluorenyl, m.p. 151° (*Ac*, m.p. 232°, and *NO*-, m.p. 203°, derivatives). 9-Dimethylamino-9 : 9'-difluorenyl has m.p. 215° (decomp.). (I) and CH₃Ph·NH₂ at 100°/6 days give 9-benzylamino-9 : 9'-difluorenyl (VII), m.p. 168° (hydrochloride, m.p. 215—218°; *NO*-derivative, m.p. 217—218°), (III), (IV), a base, C₂₁H₂₂N₂, m.p. 90° (dihydrochloride, m.p. 212°), and a hydrocarbon, m.p. 318°; at room temp./6 months, (VII) appears to be the sole product. (VII) heated in EtOH at 100° (sealed tube) gives (III), (VI), PhCHO, and a little of an unidentified product, m.p. 202°. (I) and liquid NH₃ at 65° for 3 weeks afford (III), 9-iminofluorene, m.p. 123° [hydrochloride, m.p. 303° (decomp.)] [which with NH₂Et at 55° gives (V)], and a compound, m.p. 300°. The rate of addition of amines to (I) is NH₂Me > NH₂Et > NHMe₂ > CH₃Ph·NH₂ > NH₃ > NHEt₂, NH₂Ph. All m.p. are corr. H. B.

Attempted formation of rings attached to the *p*-positions of the phenyl groups in 2 : 2'-diphenyldiphenyl. S. SAKO (Bull. Chem. Soc. Japan, 1935, 10, 585—592).—4'-Nitro-2-aminodiphenyl hydrochloride (improved prep.) is converted by diazotisation-KI into 2-iodo-4'-nitro-, m.p. 100—101.5°, reduced (SnCl₂-HCl-EtOH) to 2-iodo-4'-aminodiphenyl (hydrochloride; *Ac* derivative, m.p. 162—163°), converted by Cu powder (1.4 times the theoretical quantity gives highest yield of 53%) at 220—225° into 2 : 2'-bis-(*p*-nitrophenyl)diphenyl (I), m.p. 290°, and (?) 4-*o*-iodophenyl-4'-(2''''-*p*-nitrophenyl-2''-di-

phenyl)azobenzene (annexed), m.p. 312—313° (dimorphous). Reduction of (I) with SnCl₂-HCl-AcOH



at 60—70°, or with Na₂S-EtOH, affords 2 : 2'-bis-*p*-aminophenyl- (II), b.p. 290°/5 mm., m.p. 163—164°, converted (Sandmeyer) into 2 : 2'-bis-*p*-iodo- (III), m.p. 205—206°, and 2 : 2'-bis-*p*-bromophenyl- (IV), m.p. 170—171°, -*diphenyl*. With Na in boiling Et₂O (III) and (IV) give only 2 : 2'-diphenyldiphenyl, and various other attempts to prepare large rings from (I) and (II) by ring-closure between the substituent groups were unsuccessful. J. W. B.

Synthesis of 2 : 2'-diphenylbenzidine. S. SAKO (Bull. Chem. Soc. Japan, 1935, 10, 593—594).—Diazotised 5-nitro-2-aminodiphenyl with KI affords 2-iodo-5-nitrodiphenyl, b.p. 191—192°/4 mm., m.p. 114°, converted by heating with Cu powder at 215—225° into 4 : 4'-dinitro-2 : 2'-diphenyldiphenyl, b.p. 290°/4 mm., m.p. 218—219°, reduced (SnCl₂-HCl-AcOH) to 2 : 2'-diphenylbenzidine, m.p. 151—152°. J. W. B.

***o*-Quinonephenylhydrazones.** A. BURAWOY (Annalen, 1936, 521, 298—302).—A criticism of the views of Kuhn *et al.* (A., 1935, 613). The author's earlier views regarding the *o*-quinonephenylhydrazone structure of *o*-hydroxyazobenzenes (A., 1934, 401 and references there cited) are maintained. J. W. B.

Diazo-compounds. VII. Diazo-resins. VIII. Coupling and oxidising power of normal diazotates during their decomposition. IX. Reversion of isodiazotates into normal diazotates; its application in dyeing and in negative diazo-type [printing]. X. Rapid preparation of solutions of alkali diazotates from diazonium salts. XI. Constitution of diazonium salts and of alkali diazotates. G. ODDO and R. INDOVINA (Gazzetta, 1935, 65, 1037—1054, 1054—1067, 1099—1104, 1104—1105, 1105—1127; cf. this vol., 199).—VII. The yield of the resins from 32 diazotised amines decomposing in presence of 0.4, 0.8, and 1.6% NaOH (cf. A., 1899, i, 543) varies with the nature of the amine (least from *o*-NO₂·C₆H₄·NH₂; most from halogenated amines, and anisidine), and irregularly with the alkalinity. The resins contain N in varying amount and may be separated into fractions richer and poorer in N by pptn. by light petroleum from C₆H₆ solution. *o*-C₆H₄Me·NH₂ yields indazole and its *o*-tolueneazo-derivative; *p*-xylidine gives 6-methylindazole and its *p*-xyleneazo-derivative; ψ -cumidine, dimethylindazole and its ψ -cumeneazo-derivative; mesidine forms similar products. The resins all contain hydroxyazo- or bisazo-compounds, and are sulphonated by oleum. Some contain diazoamino-compounds. The results are tabulated and discussed; formation of resins is considered due essentially to coupling of diazo-compounds with decomp. products, e.g. phenols, amines, or indazole; autoxidation plays an insignificant part.

VIII. As diazotised amines decompose in presence of NaOH they lose their power to couple with β - $C_{10}H_7OH$, and take progressively longer to give a (delayed) blue coloration with starch-KI paper. Both reactions are negative when N_2 has ceased to be evolved; their progressive decrease with decomp. of 32 diazotised amines is tabulated, and the oxidising action discussed.

IX. *iso*Diazotates (I) are reconverted into normal diazotates (II) by the action of heat or light (sun, ultra-violet, or electric). Azo-pigments are formed when (I) are mixed with 1% β - $C_{10}H_7OH$ in 1% NaOH and exposed to light. The reaction is given by (I) from NH_2Ph , *o*-4-xylydine, and *o*-, *m*-, and *p*- $C_6H_4X \cdot NH_2$ ($X=Cl, Br, \text{ or } I$), but not by those from *o*- $C_6H_4Me \cdot NH_2$, *m*-4-xylydine, ψ -cumidine, or mesidine. The interconversion is represented: $NR_2N \cdot ONa$ (II) \rightleftharpoons $NR_2N \cdot ONa$ (I). Application of (I) to dyeing, and to "diazotype" photographic printing, is discussed; good prints have been obtained using (I) from *p*- $C_6H_4Br \cdot NH_2$, or from *p*- $C_6H_4I \cdot NH_2$.

X. (I) may be rapidly prepared by adding solutions of diazonium salts to 1.6% NaOH heated to 100°, and keeping at 100° until (after a few min.) coupling power is completely lost (β - $C_{10}H_7OH$ paper). Yields are: from NH_2Ph , 29%; from its *m*- and *p*-Me, *p*-Br-, *p*-I-, and *m*- NO_2 -derivatives, 31, 8, 39, 52, and 61%; when 0.4 or 0.8% NaOH is used, yields are smaller.

XI. A historical review, summed up in favour of the structures: $NR_2NCl \rightarrow NR_2N \cdot OH \rightarrow NR_2N \cdot OK \rightleftharpoons NR_2N \cdot OH$ (see Part IX). On this view, "(I)" ("antidiazotates" of Hantzsch) should be renamed "diazotates," and "(II)" ("syndiazotates" of Hantzsch) be renamed "diazoniates." The very small depressions of f.p. of aq. NaOH caused by diazonium salts (A., 1895, i, 661) support the view that slightly hydrolysed diazotates are formed, and are in contrast to the great depressions now observed with methylpyridinium and *o*-tolyltrimethylammonium iodides. An aq. solution of benzeneazoxycarbonamide (III) (A., 1922, i, 1071) [but not anhyd. (III)] reacts with Br to form a substance, m.p. 102–103°, decomposed by boiling H_2O . (III) heated in H_2O with Br, and treated with SO_2 , yields an insol. substance, m.p. 222°, and an acid, m.p. 142° (decomp. to a substance, m.p. 136°), which couples with β - $C_{10}H_7OH$ and is regarded as benzeneazoxycarboxylic acid, $Ph \cdot N_2O \cdot CO_2H$, together with a substance, m.p. 75°. The action of NaOH on (I) is formulated: $NPh \cdot N(O) \cdot CO \cdot NH_2 \rightarrow NPh \cdot N \cdot NH_2O \rightarrow NPh \cdot N \cdot OH \rightarrow NPh \cdot N \cdot ONa$. (I) treated with aq. or conc. H_2SO_4 , or with PCl_5 , does not give $PhNO_2$ [which would be expected if (I) were $NPh(O) \cdot N \cdot CO \cdot NH_2$ as suggested by Angeli (A., 1917, i, 418)], but only, after prolonged action, $PhOH$.

E. W. W.

Identification of phenols with 1-chloro-2:4-dinitrobenzene. R. W. BOST and F. NICHOLSON (J. Amer. Chem. Soc., 1935, 57, 2368–2369).—Aryl 2:4-dinitrophenyl ethers are prepared by heating $NaOAr$ (0.01 mol. in 5 c.c. of H_2O) with 1:2:4- $C_6H_3Cl(NO_2)_2$ (0.01 mol. in 30 c.c. of 95% EtOH). The following are described: Ph, m.p. 69°; *o*-, m.p. 90°; and *m*-, m.p. 74°, -*tolyl*; *p*-*tolyl*, m.p. 93–5°; *thymyl*, m.p. 67°; *o*-*anisyl*, m.p. 97°; α - $C_{10}H_7$, m.p. 128°; β - $C_{10}H_7$, m.p. 95°; *p*-*diphenyl*yl,

m.p. 118°; *m*- $OH \cdot C_6H_4$, m.p. 194° (lit. 184°); *eu*-*genyl*; *isoeugenyl*, m.p. 130°; 2:4-(OMe)(CHO) C_6H_3 ; *o*-, m.p. 142° (lit. 119°), *m*-, m.p. 138°, and *p*-, m.p. 120° (lit. 114°), $NO_2 \cdot C_6H_4$; 6-*chloro*-*m*-*tolyl*, m.p. 112°; *o*- C_6H_4I , m.p. 95°; *p*- C_6H_4I ; *o*-, m.p. 99°, *m*-, m.p. 75°, and *p*-, m.p. 126°, C_6H_4Cl ; 2:4- $C_6H_3Cl_2$, m.p. 119°; 2:4:6- $C_6H_3Cl_3$, m.p. 136°; *o*-, m.p. 89°, and *p*-, m.p. 141°, C_6H_4Br ; 2:4- $C_6H_3Br_2$, m.p. 135°; 2:4:6- $C_6H_2Br_3$, m.p. 135°.
H. B.

m-2-Xylyl α -naphthylcarbamate. C. D. HURD and M. A. POLLACK (J. Amer. Chem. Soc., 1936, 58, 181).—The xylene obtained (A., 1932, 857) by pyrolysis of furfuraldehyde is 2:6- $C_6H_3Me_2 \cdot OH$ (α -*naphthylcarbamate*, m.p. 176.5°).
H. B.

Synthesis of alkyl- and aryl-cryptophenols. M. E. MCGREAL and J. B. NIEDERL (J. Amer. Chem. Soc., 1935, 57, 2625–2627).— $CMe_2Pr^{\beta} \cdot OH$ (1 mol.), $PhOH$ (1 mol.), and $ZnCl_2$ (1.5 mols.) at 180° give β -*p*-hydroxyphenyl- β - γ -dimethylbutane, m.p. 105° (45); $CMe_2Bu^{\alpha} \cdot OH$ similarly affords β -*p*-hydroxyphenyl- β -methylhexane, b.p. 280°/760 mm., but $\beta\delta\delta$ -trimethylpentan- β -ol yields *p*- $C_6H_4Bu^{\alpha} \cdot OH$ (I); the methylcyclohexanols give *p*-2-, m.p. 107° (50), -3-, m.p. 101° (105), and -4-, m.p. 108° (70), -methylcyclohexylphenols, but 4-*tert*-octylcyclohexanol affords (I); $CH_2Ph \cdot OH$ yields *p*-benzylphenol; $CH_2Ph \cdot CH_2 \cdot OH$ or $CHPhMe \cdot OH$ gives α -phenyl- α -*p*-hydroxyphenylethane, m.p. 64° (40) (dehydration of the former presumably preceding addition of the $PhOH$); $CPhMeEt \cdot OH$ affords β -phenyl- β -*p*-hydroxyphenylbutane, b.p. 145–148°/2.5 mm., also prepared (method: A., 1935, 79) from $PhOH$ and β -phenyl- Δ^{β} -butene; $CPhMePr^{\beta} \cdot OH$ yields β -phenyl- β -*p*-hydroxyphenyl- γ -methylbutane, b.p. 157–160°/3 mm., also prepared from the appropriate phenylpentene. The nos. quoted in parentheses are the $PhOH$ -coeffs. (using *Staph. aureus*).
H. B.

Reduction of isosafrole with sodium and ethyl alcohol. K. ONO and M. IMOTO (J. Chem. Soc. Japan, 1934, 55, 991–1001).—A mixture of *m*- and *p*- $C_6H_4Pr \cdot OH$ is produced. Addition of active C increases the yield.
CH. ABS. (r)

Phenols of anthracene oil. O. KRUBER (Ber., 1936, 69, [B], 107–114).—The liquid products obtained by centrifuging a crude phenanthrene fraction, b.p. 320–340°, after extraction with NaOH and distillation of the extracted matter in vac., yielded *p*-hydroxydiphenyl, m.p. 163°. Similar treatment of crude $C_{10}H_8$ press-cake yielded β - $C_{10}H_7 \cdot OH$ and a *diphenol*, $C_{16}H_{18}O_2$, m.p. 135°, b.p. 341°/755 mm. [Me_2 ether, b.p. 200–201°/15 mm., m.p. 85°; *diphenylurethane*, m.p. 199–200°; compound, $C_{42}H_{36}O_4N_2$, m.p. 192–193°, with $CO(NHPh)_2$]. Separation of the phenols of the anthracene oil fraction, b.p. 340–370°, is rendered difficult by the presence of complex, non-phenolic substances with feebly acidic properties; it is best effected by repeated alternate extraction with NaOH and distillation of the extracted matter, whereby the complex materials are extensively decomposed. Distillation of the phenolic fraction over Zn dust or a Mo contact affords diphenylene oxide and fluorene. Further fraction-

ation and prolonged keeping of the individual fractions in PhMe at 0° causes the separation of a solid material which cannot be separated into its components by crystallisation. When treated with NaOH and Me₂SO₄ it yields a mixture of ethers, non-separable by crystallisation, from which 2-methoxydiphenylene oxide (I), m.p. 98°, is isolated after partial oxidation with Na₂Cr₂O₇ in AcOH at 70°. Treatment of (I) with NH₂Ph.HCl at 250° affords 2-hydroxydiphenylene oxide, b.p. 348°/758 mm., m.p. 142—143° (phenylurethane, m.p. 173°). The synthesis of (I) from 2-aminodiphenylene oxide is recorded. Treatment of the mother-liquors from (I) with NH₂OH.HCl and BaCO₃ leads to the isolation of 2-methoxyfluorenoneoxime, m.p. 174° after softening, whence 2-methoxyfluorenone, m.p. 78°. Separation of the crude methylated product into its components can also be effected by Na at 180—200° but is complicated by many by-reactions. H. W.

Phenyl ether series. IV. 4:4'-Dithioldiphenyl ether and related compounds. C. M. SUTER and P. H. SCRUTCHFIELD (J. Amer. Chem. Soc., 1936, 58, 54—55).—Reduction (SnCl₂, AcOH-HCl) of (p-SO₂Cl-C₆H₄)₂O (A., 1931, 616) gives 4:4'-dithioldiphenyl ether, m.p. 103—104° (Me₂ ether, m.p. 81—81.5°), converted by CH₂Cl.CO₂K into the 4:4'-dithioglycollic acid, m.p. 165—166° (chloride, converted by AlCl₃ into a red tar), which could not be cyclised by oleum or ClSO₃H to a thionaphthen derivative. H. B.

(+)- and (-)- γ -Phenyl- α -methylallyl alcohols. J. KENYON, S. M. PARTRIDGE, and H. PHILLIPS (J.C.S., 1936, 85—88).—CHPh.CH₂CHO and MgMeBr give *dl*- γ -phenyl- α -methylallyl alcohol (I), b.p. 129—131°/11 mm., m.p. 33° [p-nitrobenzoate, m.p. 58—59°; H phthalate (II), m.p. 92—93.5°, prepared by the action of o-C₆H₄(CO)₂O on (I) (in C₅H₅N) or the Grignard complex], which could not be separated (distillation; partial fusion; crystallisation) into *cis*- and *trans*-forms. Recrystallisation (from EtOAc) of the cinchonidine salt of (II) affords the cinchonidine salt, m.p. 179° (decomp.), of (+)- γ -phenyl- α -methylallyl H phthalate (III), m.p. 68.5°, [α]₅₄₆₁ +44.71° in CS₂, -15.4° in EtOH (vals. for many solvents and different λ given). Hydrolysis of (III) with aq. Na₂CO₃ gives (I); 5*N*-NaOH and subsequent crystallisation from CH₂Cl₂-light petroleum lead to the (+)-alcohol (IV), m.p. 61°, [α]₅₃₆₁ +28.3° in CS₂ (p-xenylcarbamate, m.p. 179—180°; p-nitrobenzoate, m.p. 41°; acetate, b.p. 132—133°/9 mm.), reduced (Adams) to (-)-CH₂Ph.CH₂CHMe.OH (V) (phenylcarbamate, m.p. 47—48°) (J.C.S., 1914, 105, 1124). The recovered H phthalate [from (III)] gives the brucine salt, decomp. about 110°, of (-)- γ -phenyl- α -methylallyl H phthalate, m.p. 68.5°, [α]₅₄₆₁ -44.53° in CS₂, and thence (as above) the (-)-alcohol, m.p. 61°, [α]₅₄₆₁ -28° in CS₂. Comparison of the rotatory powers of (IV), (V), (-)-CHMeEt.OH, and (+)-CH₂:CH-CHMe.OH shows that introduction of Ph [as in (IV) and (V)] causes [*M*] to be approx. doubled; the introduction of the Δ° -double linking doubles [*M*] and reverses the sign. H. B.

Resolution of phenyl-*n*-propylcarbinol. J. KENYON and S. M. PARTRIDGE (J.C.S., 1936, 128—

129).—CHPhPr.OH (H phthalate, m.p. 90—91°) is resolved through the quinidine salt, m.p. 168—169°, of the *d*-H phthalate, m.p. 53—54°, [α]₅₄₆₁ -11.5° in Et₂O, into the *d*-form, b.p. 115°/14 mm., m.p. 49°, [α]₅₄₆₁ +52.2° in C₆H₆, and afterwards through the strychnine salt, m.p. 184—185° (decomp.), of the *l*-H phthalate, m.p. 52—53°, [α]₅₄₆₁ -11° in Et₂O, into the *l*-form, m.p. 48—49°, [α]₅₄₆₁ -53.5°, [α]₅₈₉₃ -45.9° in C₆H₆ (cf. Levene and Marker, A., 1932, 1027). Vals. for other solvents and λ are given. H. B.

epialloCholesterol, a new isomeride of cholesterol. E. A. EVANS, jun., and R. SCHOENHEIMER (J. Amer. Chem. Soc., 1936, 58, 182).—Reduction of cholestenone with Al(OPr^{*t*})₃ gives epiallocholesterol (I), m.p. 84°, [α]_D +120.8° in C₆H₆ (acetate, m.p. 82.5°), and an isomeride [pptd. by digitonin whereas (I) is not]. (I) is reduced (catalytically) to a mixture of epidihydrocholesterol and epicoprosterol, indicating that (I) contains C³-OH *trans* to C¹⁰-Me; an intense Rosenheim reaction also indicates that the double linking is between C⁴ and C⁵. (I) is dehydrated by dil. HCl in 95% EtOH to a hydrocarbon, C₂₇H₄₄, m.p. 79°, [α]_D -118.2° in C₆H₆, the absorption max. (244, 235, and 229 m μ) of which differ from those of cholesterolene (Heilbron *et al.*, A., 1928, 219). H. B.

Androsterone and related sterols. R. E. MARKER, F. C. WHITMORE, and O. KAMM (J. Amer. Chem. Soc., 1935, 57, 2358—2360).— α -Cholestyl chloride (I), m.p. 112°, is prepared (a) by reduction (H₂, PtO₂, AcOH) of cholesteryl chloride, (b) from epichoestanol (II) and PCl₅, and (c) from β -cholestanol (III) and SOCl₂; Walden inversion occurs in (a) and (c). (I) is hydrolysed (KOAc in valeric acid followed by EtOH-KOH) to (II). β -Cholestyl chloride, m.p. 102—103°, obtained from (II) and SOCl₂ or (III) and PCl₅, is similarly hydrolysed to (III). Oxidation (CrO₃, AcOH) of (I) gives α -chlorocholelanic acid, m.p. 174—175°, and α -chloroandrosterone, m.p. 170—171° (Butenandt and Dannenbaum, A., 1935, 413; cf. Ruzicka *et al.*, *ibid.*, 1125). H. B.

Alkaline halogenation. Bromination of sodium benzoate. P. L. HARRIS and J. C. SMITH (J.C.S., 1936, 168; cf. A., 1934, 405).—BzOH (61 g.) in aq. NaOBr [2 litres from NaOH (40 g.) and Br (80 g.)] at 35°/7 days gives approx. 5 g. each of *o*-, *m*- (I), and *p*-C₆H₄Br.CO₂H; the results vary owing to rapid decomp. of NaOBr. Use of 2 equivs. of NaOH (*i.e.*, NaOBz : NaOBr = 1) almost inhibits bromination. In agreement with Stark (A., 1910, i, 234), (I) is the main product from BzOH and HOBr in H₂O. H. B.

Syntheses in the anæsthetic group. I. G. SANNA (Annali Chim. Appl., 1935, 25, 638—643).—*Et p*-chloroacetamidobenzoate, m.p. 115°, is prepared by treating anæsthesine (I) in C₆H₆ with CH₂Cl.COCl, and is converted (NHMe₂) into *Et p*-dimethylglycylamidobenzoate (II), m.p. 95° (hydrochloride, m.p. 193°) and (NHEt₂) into the corresponding *Et*₂ compound (III), m.p. 115° (hydrochloride, m.p. 211°). (II) and (III) are more sol. than (I) in H₂O, and have anæsthetic properties, which are being examined. E. W. W.

Preparation of α -naphthoic acid. D. J. LODER and F. C. WHITMORE (J. Amer. Chem. Soc., 1935, 57,

2727).— α -C₁₀H₇CO₂Et, obtained in 70% yield from α -C₁₀H₇MgBr and Et₂CO₃, is hydrolysed to the acid (yield > 90%). H. B.

Synthesis of alkeines derived from O-phenyl-lactic and D-mandelic acid. E. PŁAZEK, Z. RODEWALD, and D. KRZYŻANIAK (Rocz. Chem., 1935, 15, 360—364).—O-Phenylmandetyl chloride, b.p. 135°/0.6 mm., yields the *tropyl* ester, b.p. 208°/1 mm. (*picrate*, m.p. 171°; *picrolonate*, m.p. 187°), with tropine, and β -dimethylaminoethyl O-phenylmandelate, b.p. 148—150°/0.2 mm. (*picrolonate*, m.p. 141—142°), with NEt₂·CH₂·CH₂·OH. KOPH and CHMeBr·CO₂Me (2 hr.; 100°), followed by hydrolysis of the product with EtOH-KOH, yield O-phenyl-lactic acid (I), m.p. 114°, the *chloride*, b.p. 115°/20 mm., of which affords the *tropyl*, b.p. 140—150°/0.6 mm. (*picrate*, m.p. 175°; *picrolonate*, m.p. 200—202°), and β -dimethylaminoethyl esters of (I), m.p. 75° (*picrate*, m.p. 113°; *picrolonate*, m.p. 148°). R. T.

Dehalogenation of β -bromo-acids. IV. β -Bromophenylpyruvic acid. B. SOBIN and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 2458—2460).— β -Bromophenylpyruvic acid (I), m.p. 103—104° (from CH₂Ph·CO·CO₂H and Br in CCl₄), is converted by boiling with H₂O or shaking with Ag₂O in H₂O into CH₂Ph·CO₂H (II) (yield 77 and 94%, respectively); the following reactions are considered to occur: CHBrPh·CO·CO₂H → CO₂ + HBr + CHPh·C:O; CHPh·C:O + H₂O → CH₂Ph·CO₂H. CH₂Ph·CO₂Et is similarly obtained in 36% yield from (I) and Ag₂O in EtOH. (I) and aq. Na₂CO₃ give benzoyl-carbinol (III) (by rearrangement of the intermediate OH·CHPh·CHO); with aq. NaHCO₃, a mixture of (II) and (III) and a little of an acid, C₂₃H₁₆O₅, m.p. 218—219° (*Ac* derivative, m.p. 162—163°), result. Tars (free from CHPh·C:O) are produced from (I) and C₂H₅N or NPhMe₂. H. B.

General reaction for the preparation of keto-acids, unsaturated acids, and disubstituted lactones. II. G. KOMPPA and W. ROHRMANN (Annalen, 1936, 521, 227—242).—*apo*Camphoric anhydride (I) (1 mol.) and MgMeI (1 mol.) at -15° (cf. A., 1934, 650) give, after esterification, *Et cis-3-acetyl-2:2-dimethylcyclopentane-1-carboxylate*, b.p. 122—124°/11 mm., isolated as its *semicarbazone*, m.p. 142—142.5°, not identical with the *trans-ester* [*semicarbazone*, m.p. 196—200° (decomp.); *semicarbazone* of the free acid, m.p. 191° (decomp.)] obtained by Winzer's method (A., 1890, 1152) by the action of CHNa(CO₂Et)₂ on (I) in C₆H₆ to give *malonylapo-camphoric anhydride*, m.p. 63.5—64°, b.p. 216°/12 mm., and subsequent hydrolysis with NaOEt-EtOH. With 2 mols. of MgMeI (I) affords *dimethylapo-campholide* (45% yield), m.p. 102—103°, and *3-isopropylidene-2:2-dimethylcyclopentane-1-carboxylic acid* (35% yield), m.p. 103—104° (gives 2:2-dimethylcyclopentanone-3-carboxylic acid on ozonolysis). Similarly *d*-camphoric anhydride (II) with MgMeI (1 mol.) gives *Et cis-3-acetyl-2:2:3-trimethylcyclopentane-1-carboxylate*, b.p. 133—135°/8 mm. (*semicarbazone*, m.p. 177°), hydrolysed to the acid, +H₂O (III), m.p. 76—78° (*semicarbazone*, m.p. 223—224°), probably identical with the acid, m.p. 73°, obtained

by Quadrat-i-Khuda (A., 1930, 471), but different from Winzer's acid (*loc. cit.*), which is *cis-3-acetyl-1:2:2-trimethylcyclopentane-1-carboxylic acid* (IV) (*semicarbazone*, m.p. 218°, indefinite). With 2 mols. of MgMeI (II) gives *dimethylcampholide* and *3-isopropenyl-1:2:2-trimethylcyclopentane-1-carboxylic acid* (V), the m.p., 68.5—70.5°, of which (Komppa. A., 1908, i, 353) is raised to 87—88° by repeated crystallisation, probably by conversion into the *3-isopropylidene acid* (VI); ozonolysis of (V) gives a *3-acetyl-1:2:2-trimethylcyclopentane-1-carboxylic acid* (*semicarbazone*, m.p. 220—221°) not identical with either (III) or (IV), whereas (VI) gives an indefinite oil with O₃. The results of Houben *et al.* (A., 1908, 539) on the interaction of CH₂Ph·MgCl on (II) are confirmed and, in addition, are isolated an *Et phenyl-acetyltrimethylcyclopentanecarboxylate*, b.p. 217—218° [converted into the bicyclic compound (VII) by hydrolysis], and an *Et β -phenyl- α -benzyl-ethylidenetrimethylcyclopentanecarboxylate*, b.p. 230—234°/9 mm. (*acid*, m.p. 166—167°). Santenic anhydride (VIII) with MgMeI gives *cis-3-acetyl-2:3-dimethylcyclopentane-1-carboxylic acid*. m.p. 63—65° (*semicarbazone*, m.p. 218°), not identical with *cis-3-acetyl-1:2-dimethylcyclopentane-1-carboxylic acid*, m.p. 95—96° (*semicarbazone*, m.p. 219°), obtained by Winzer's method. With 2 mols. of MgMeI (VIII) affords *dimethylsantolide*, b.p. 136—138°/15 mm., and a trace of an unsaturated acid.

J. W. B.

Preparation of tetrachlorophthalic acid. J. S. SALKIND and M. BELIKOVA (J. Appl. Chem. Russ., 1935, 8, 1210—1213).—o-C₆H₄(CO)₂O at 240—250° and Cl₂ (in presence of 3% of Fe) yield tetrachlorophthalic acid in 90—95% yield. The product loses H₂O of crystallisation (1.5 mols.) at 100°, and is converted into the anhydride at 110°. R. T.

Lithium phthalate.—See this vol., 282.

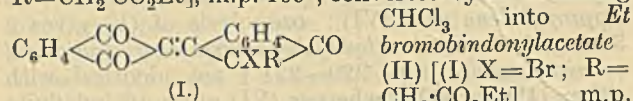
Synthesis of hydrogenated phenanthrenes. E. E. GRUBER and R. ADAMS (J. Amer. Chem. Soc., 1935, 57, 2555—2556; cf. Barnett and Lawrence, A., 1935, 1243).—1:1'-Dihydroxy-1:1'-dicyclohexyl (from cyclohexanone, Mg, and HgCl₂ in C₆H₆) is dehydrated (10% H₂SO₄) to di- $\Delta^{1,1'}$ -cyclohexene, b.p. 101—102°/5.5 mm., which with maleic anhydride in C₆H₆ gives the anhydride, m.p. 122.5—123.5°, of *dodecahydrophenanthrene-9:10-dicarboxylic acid*, m.p. 242° (Maquenne block) (*imide*, m.p. 182—183°), and with CH₂:CH·CHO in C₆H₆ at 50—60° affords *dodecahydrophenanthrene-9-aldehyde*, b.p. 136—137°/4 mm. (*semicarbazone*, m.p. 179—180°). H. B.

Synthesis of 1-methylcyclopentane-1:3-dicarboxylic acid (1-methylnorcamphoric acid). N. J. TOIVONEN, A. JOHN, E. SAINIO, and T. KUUSINEN (Suomen Kem., 1935, 8, B, 46—47).—Et₃ 2-methylcyclopentanone-2:4:5-tricarboxylate with glycerol-H₂O at 170—200° affords *Et₂ 2-methylcyclopentanone-2:4-dicarboxylate*, b.p. 153—156°/11 mm., which with K-Hg in EtOH-dil. H₂SO₄ gives *Et₂ 2-methylcyclopentan-1-ol-2:4-dicarboxylate*, b.p. 126—128°/0.5 mm. [*acid*, m.p. 172—174°, converted by HBr followed by Zn in AcOH-HCl into *cis*- (cf. this vol., 339) and *trans-1-methylcyclopentane-1:3-dicarboxylic acid*, m.p.

114—115°, the former of which with PCl_5 and excess of Br gives the 3-Br-derivative, m.p. 136—138°].

J. L. D.

Condensation of bindone with α -halogeno-carboxylic esters. G. WANAG (Ber., 1936, 69, [B], 189—194; cf. A., 1935, 623).—Bindone [(I) $\text{X}=\text{R}=\text{H}$] condenses with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ in boiling EtOH containing K_2CO_3 to *Et bindonylacetate* [(I) $\text{X}=\text{H}$; $\text{R}=\text{CH}_2\cdot\text{CO}_2\text{Et}$], m.p. 109°, converted by Br in boiling



CHCl_3 into *Et bromobindonylacetate* (II) [(I) $\text{X}=\text{Br}$; $\text{R}=\text{CH}_2\cdot\text{CO}_2\text{Et}$], m.p.

153°, by fuming HNO_3 in boiling AcOH into *Et nitrobindonylacetate* [(I) $\text{X}=\text{NO}_2$; $\text{R}=\text{CH}_2\cdot\text{CO}_2\text{Et}$], m.p. 154—155°, and hydrolysed by acid or alkali to *bindonylacetic acid*, m.p. 242—244°. Treatment of (II) with conc. HCl in AcOH affords (?) *indandionylene- α -naphthaquinone* [(I) with $\text{CH}:\text{CH}$ for CXR], m.p. 310—312°. Analogously, (I) and $\text{CHBr}\cdot\text{Me}\cdot\text{CO}_2\text{Et}$ yield *Et α -bindonylpropionate* [(I) $\text{X}=\text{H}$; $\text{R}=\text{CHMe}\cdot\text{CO}_2\text{Et}$], m.p. 126—127°, whence *Et α -nitrobindonylpropionate*, m.p. 154—155°, and *α -bindonylpropionic acid*, m.p. 230°. *Et bindonylphenylacetate* [(I) $\text{X}=\text{H}$; $\text{R}=\text{CHPh}\cdot\text{CO}_2\text{Et}$], m.p. 153°, *Et nitrobindonylphenylacetate*, m.p. 158—159°, and *bindonylphenylacetic acid*, m.p. 234°, are obtained with $\text{CHBrPh}\cdot\text{CO}_2\text{Et}$. Treatment of (I) with $\text{CHCl}(\text{CO}_2\text{Et})_2$ leads to *trans-dibindonylene*, production of which does not appear to be due to simple dehydrogenation, since it is also formed when $\text{Pr}^{\beta}\text{I}$ or $\text{C}_2\text{H}_4\text{Br}_2$ is used and (in small amount) when MeI is employed; it is suggested that these substances accelerate autoxidation.

H. W.

Mechanism of the Perkin-Oglialoro synthesis.

(SIGNA.) M. BAKUNIN and D. PECCERILLO (Gazzetta, 1935, 65, 1145—1161).—The yield of *o*-nitrocinnamic acid (I) from the reaction (at 90°) between *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (II) and various metallic salts of $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ (III), in presence of Ac_2O , increases in the order $\text{Ba} < \text{Li} < \text{Na} < \text{K} < \text{Rb}$. NH_4 and NH_3Ph salts do not give (I). With (II) and the anhydride of (III), the catalytic action of bases etc. is in the order $\text{NH}_4\text{Et}_2 < \text{C}_5\text{H}_{11}\text{N} < \text{NaOAc} < \text{NMe}_3 < \text{NEt}_3$. From (II) and (III) in absence of Ac_2O , or of catalyst, no (I) is formed; the effects of various bases in presence of Ac_2O , and of various anhydrides in presence of NEt_3 , are tabulated. (II) and (III) react in presence of NaOBz . $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ does not react with (II). *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OAc})_2$ with $\text{CH}_2(\text{CO}_2\text{H})_2$ yields *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{CO}_2\text{H})_2$, but does not react appreciably with (III). The reaction $\text{Ac}_2\text{O} + 2\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{M} \rightarrow (\text{CH}_2\text{Ph}\cdot\text{CO}_2)_2\text{O} + 2\text{MOAc}$ has been shown to take place, and to depend on the nature of M (Na, Li, Ba), and on temp. The effect of inorg. salts as catalysts is ascribed to formation of MOAc ; KI, which does not yield KOAc , is not a catalyst. Mol. compounds are formed between anhydrides or acids, and salts of the same (or perhaps even of a different) acids, e.g., the compound $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ (IV), m.p. 95° (stable in org. solvents). (IV) reacts with (II) in the presence, but not in the absence, of Ac_2O or Bz_2O . $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ and Ac_2O react to form a mol. com-

ound, m.p. 60°, together with (IV); AcCl reacts similarly, as do other substances. It is concluded that the Perkin synthesis depends on the intermediate formation of acid-salt or anhydride-salt compounds (which are decomposed by H_2O), on their stability at the temp. of reaction, and their solubility in the medium, and on the homogeneous presence in the of substances capable of absorbing H_2O . The formation of Ac and imide derivatives of aldehydes impedes the reaction.

E. W. W.

Removal of hydrogen and acid radicals from organic compounds by bases. II. Removal of acetic acid from acetylaldoximes by alkalis. C. R. HAUSER and E. JORDAN (J. Amer. Chem. Soc., 1935, 57, 2450—2456; cf. A., 1934, 73).—Acetyl- α - and - β -araldoximes undergo the same types of reaction with alkalis; the oxime is formed by hydrolysis and the ArCN by elimination (which occurs more readily with the β -derivatives) of AcOH. The yields of products depend on the relative rates of the two (competing) reactions. Acetyl- β -*p*-methoxy-, -3:4-methylenedioxy- (I), and -*p*-nitro-benzaldoximes with 2*N*-NaOH give mixtures of ArCN (predominates at 30°) and the β -oxime (II) (predominates at 0°); the first two with aq. 10% Na_2CO_3 at 0° or 30° give ArCN and a little (II) (cf. loc. cit.). Hydrolysis (2*N*-NaOH) of acetyl- α -*o*- (III), -*m*-, and -*p*-nitro-, -*p*-methoxy-, and -3:4-methylenedioxy- (IV) -benzaldoximes, prepared by a modification of Brady and Dunn's method (J.C.S., 1913, 103, 1619), at 30° and 97—100° gives (usually) the α -oxime (V) and a little ArCO_2H ; at 61—64°, (III) affords an appreciable amount of *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$. (IV) and acetyl- α -*o*-chloro-, -*p*-methoxy-, and -*m*-nitro-benzaldoximes with KNH_2 in liquid NH_3 give ArCN (major product) and (V); the first three with boiling 2*N*-EtOH-NaOEt afford mainly (V) (as Na salts). (I) is hydrolysed more readily than (IV) by an excess of Na_2CO_3 in aq. COMe_2 . H. B.

Reactions of aldoxime derivatives with bases.

II. Reactions of carbethoxy- α -benzaldoximes with sodium hydroxide. C. R. HAUSER, E. JORDAN, and R. O'CONNOR (J. Amer. Chem. Soc., 1935, 57, 2456—2458).—Carbethoxy- α -benzaldoxime and its *o*- (I), *m*- (II), and *p*-nitro-, *o*- and *p*-chloro-, *o*- and *p*-methoxy- (III), and 3:4-methylenedioxy derivatives with 2*N*-NaOH give mixtures of the corresponding α -oxime (IV) [predominates at 30°; except for (I) and ArCN (or ArCO_2H) [the yield at 97—100° is > at 30° and often exceeds that of (IV)]]; the yields of ArCN are generally > those from the acetyl- α -araldoximes (preceding abstract). (II) and (III) with KNH_2 in liquid NH_3 give ArCN and a little (IV). Some of the above CO_2Et derivatives are wrongly described as β -isomerides by Brady and McHugh (J.C.S., 1923, 123, 1190).

H. B.

Derivatives of dihydrovanillin. Catalytic hydrogenation of nitrostyrenes. (A) O. S. CHALES. (B) K. MAURER (J. pr. Chem., 1936, [ii], 1464, 214—215, 216).—Concerning priority (A., 1935, 1232, 1497).

R. S. C.

Iodine substitution products of vanillin and their derivatives. L. C. RAIFORD and E. H. WELLS

(J. Amer. Chem. Soc., 1935, 57, 2500—2503).—2-Aminovanillin is converted (Sandmeyer) into 2-iodovanillin (I), m.p. 155—156° [Ac derivative, m.p. 70—72°; oxime (+0.5H₂O), softens ca. 122°, m.p. (anhyd.) 142.5—143.5°; semicarbazone, m.p. 199—200°; p-nitrophenylhydrazone, m.p. 211—212°; benzidine condensation product, decomp. ca. 232—233°], methylated (Me₂SO₄, aq. KOH) to 2-iodo-3:4-dimethoxybenzaldehyde, m.p. 82°. 5-Aminovanillin (hydrochloride; stannichloride; ON-Ac₂, m.p. 174—176°, and ON-Bz₂, m.p. 161—162°, derivatives), prepared by reduction (SnCl₂, conc. HCl, EtOH) of the NO₂-compound, similarly gives 5-iodovanillin, m.p. 179—180° [Ac (II), m.p. 105—106°, and Bz, m.p. 135.5—136.5°, derivatives; oxime, m.p. 178—179°; semicarbazone, m.p. 205—205.5°; p-nitrophenylhydrazone, m.p. 242—243° (decomp.); benzidine condensation product, m.p. 232° (decomp.); Me ether, m.p. 69—70°], which is identical with the iodovanillin of Carles (A., 1872, 708). (II) or 5-iodo-4-acetoxy-3-methoxybenzylidene diacetate, m.p. 132—133°, with fuming HNO₃ at < 6° gives the Ac derivative, m.p. 124—125°, of 5-iodo-2-nitrovanillin, m.p. 146—147° [oxime, m.p. 128—129°; semicarbazone, m.p. 187—188° (decomp.); p-nitrophenylhydrazone, (+0.5EtOH), m.p. 228—230° (decomp.); benzidine condensation product], reduced [Fe(OH)₂, aq. NH₃] to 5-iodo-2-aminovanillin (III), m.p. 155°. (I) and I in AcOH-NaOAc give 2:5-di-iodovanillin, m.p. 200° [Ac derivative, m.p. 127—128°; oxime, m.p. 174.5—175.5°; semicarbazone, m.p. 235° (decomp.); p-nitrophenylhydrazone, m.p. 252—253° (decomp.); benzidine condensation product; Me ether, m.p. 94°], also prepared (Sandmeyer) from (III). H. B.

Synthesis of dicyclo-[1:2:3]-octanone and dicyclo-[1:2:3]-octane. G. KOMPPA, T. HIRN, W. ROHRMANN, and S. BECKMANN (Annalen, 1936, 521, 242—261).—The following methods of prep. of hexahydrohomoisophthalic acid (I) (A., 1904, i, 60) have been investigated. (a) Homoisophthalic acid (II), m.p. 185° [diamide, m.p. 228°; Et, b.p. 175°/12 mm., and Me, b.p. 152—153°/10 mm., esters; Ba (+2H₂O), Ag, Cd (+2H₂O), and Zn (+0.96H₂O) salts], is reduced by Na-Hg-NaOH to its H₁-derivative (III) (Br₂-derivative, m.p. 193—194°), which with HBr-AcOH at 100° gives the bromohexahydro-acid, m.p. 283° (decomp.) (and a substance, m.p. 157—158°), converted by Ag₂O in EtOH into an unsaturated acid, C₉H₁₂O₄, m.p. 141—143°, and reduced (Na-Hg) to (?) trans-hexahydrohomoisophthalic acid (IV), m.p. 156—158° [diamide, m.p. 277—278° (decomp.); Ag and Ba salts]. (b) Direct reduction of (III) with H₂-Pd, or, better, direct catalytic reduction (Skita) of (II) (85% yield) is the best method of prep. (c) Reduction of (II) with Na-C₅H₁₁-OH gives a mixture, m.p. 120—127°, of stereoisomerides of (I). (d) cycloHexanone-3-carboxylic acid, obtained from m-OH·C₆H₄·CO₂H (Einhorn et al., A., 1896, i, 530), with CH₂Br·CO₂Et-Zn and dehydration of the OH-ester with NaHSO₄ at 120—140°, gives the Et₂ ester, b.p. 151—156°/16 mm., of (III), reduced (Skita) to the Et ester, b.p. 138—144°/8 mm., of (I). (e) (IV) is obtained by condensation of Et 3-bromocyclohexane-1-carboxylate

with either CHNa(CO₂Et)₂ or CN·CHNa·CO₂Et and complete hydrolysis of the products. Reduction of hexahydroisophthalic anhydride with H₂-Ni at 280—290° affords the lactone, b.p. 111—113°/8 mm., f.p. -5° to -10°, of 3-hydroxymethylcyclohexane-1-carboxylic acid, also obtained by the action of I at 150° on the Ag salt of (IV). dicyclo-[1:2:3]-Octanone (V) (loc. cit.) [oxime, m.p. 66—67°; semicarbazone, m.p. 183—183.5° (corr.), and not 189—190° as previously recorded] is best obtained by distillation of the Ca salt of (IV). Oxidation of (V) with HNO₃ at 50° gives cis-hexahydroisophthalic acid, and reduction (Na-EtOH) affords dicyclo-[1:2:3]-octanol, b.p. 200—205°, m.p. 170° (corr.) [phenylurethane, m.p. 133° (corr.)], the chloride, b.p. 73—75°/14 mm., m.p. 43—45°, of which is reduced (Na-EtOH) to dicyclo-[1:2:3]-octane, m.p. 133—134°.

J. W. B.

Preparation of m-nitroacetophenone. V. G. MORGAN and H. B. WATSON (J.S.C.I., 1936, 55, 29—30T).—A method of nitration, using HNO₃-H₂SO₄, is described, differing in some details from the procedure given in "Organic Syntheses," 1930, 10, 74, and leading to a better yield of a very pure product. The m.p. of m-nitroacetophenone is 79.5° (corr.).

Synthesis of mixed acetones by means of ethyl malonate. A. GIACALONE [in part with F. Russo] (Gazzetta, 1935, 65, 1127—1138).—Acyl chlorides react with CHNa(CO₂Et)₂ (I) to form acyl compounds of type R·CO·CH(CO₂Et)₂ (II), and acyl derivatives of the enolic form of these, viz., R·CO₂·CR·C(CO₂Et)₂ (II). (II) and (III) with NH₂Ph, NPh·NH₂, or NH₂OH yield CH₂(CO₂Et)₂ and R·CO·NHR'. BzCl and (I) give Et₂ benzoylmalonate, b.p. 198°/8 mm., and dibenzoylmalonate, m.p. 45°, b.p. 249°/6 mm. With NPh·NH₂ these yield NPh·NHBz, new m.p. 170—171°; both are hydrolysed to CPhMe. 6-Amino-3-methylacetophenone (IV), m.p. 50—51°, is prepared [with a view of synthesising 2-(4'-amino-m-tolyl)-4:6-dimethylquinoline (cf. A., 1935, 758)] as follows. 4-Nitro-m-toluic acid (V) (this vol., 69) is converted into the chloride, m.p. 45—46°, and this combined with (I) to form Et₂ 4-nitro-m-toluoyl- (VI), sol. in aq. NaOH, and di-(4-nitro-m-toluoyl)-malonate (VII), m.p. 106—107°, insol. in aq. NaOH. (V) is hydrolysed (80% H₂SO₄) to 6-nitro-3-methylacetophenone (VIII), and (VI) to (V) and (VIII). (VIII) is then reduced (Sn-HCl) to the stannichloride, (C₉H₄ON₂)₂·H₂SnCl₆, m.p. 187° (decomp.), of (I), with the stannichloride, m.p. 215° (decomp.), of 4-amino-m-tolylmethylcarbinol, m.p. 35°. 2-Nitro-m-toluic acid (IX) similarly yields, through its chloride, m.p. 82—83°, Et₂ 2-nitro-m-toluoyl- (X), m.p. 73°, and di-(2-nitro-m-toluoyl)-malonate (XI), m.p. 134—135°. (X) is hydrolysed to 2-nitro-3-methylacetophenone (XII), m.p. 85°, and (XI) to (IX) and (XII). (XII) is reduced to the stannichloride, m.p. 208°, of 2-amino-3-methylacetophenone.

E. W. W.

Autoxidation of ketones. S. S. JENKINS (J. Amer. Chem. Soc., 1935, 57, 2733).—o-C₆H₄Cl·CO₂H and PhCHO are formed when o-C₆H₄Cl·CO·CH₂Ph is kept. Similar autoxidation occurs with several ketones of the type COR·CH₂Ph. H. B.

Reaction between (A) phenyl $\alpha\beta$ -dibromo- β -phenylethyl ketone and azides, (B) phenyl $\alpha\beta$ -dibromo- β -*m*-nitrophenylethyl ketone and sodium azide. V. A. KUZMIN and N. I. ZEMLIANSKI (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 183—190, 191—194).—(A) NaN_3 and $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{COPh}$ in aq. COMe_2 (12 hr. at 60—65°) yield a Br-containing oil, and a monoazide of Ph styryl ketone, m.p. 64—65°, both decomposed by H_2SO_4 with evolution of N_2 .

(B) $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COPh}$ and NaN_3 in aq. EtOH or COMe_2 (12—14 hr. at 65—70°) afford a monoazide, m.p. 76—77° (decomp.) of Ph 3-nitro-styryl ketone. R. T.

New route to hydroaromatic ketones related to anthracene and phenanthrene. J. W. COOK, C. L. HEWETT, and C. A. LAWRENCE (J.C.S., 1936, 71—80).—2-Chlorocyclohexanol and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ (I) lead (by ring-contraction) to cyclopentylbenzylcarbinol, b.p. 120° (bath)/0.1 mm., m.p. 30° (3 : 5-dinitrobenzoate, m.p. 100.5—101.5°), oxidised (CrO_3 , AcOH) to phenylacetylcyclopentane (semicarbazone, m.p. 117—118°), cyclohexene oxide (II) and (I) give 2-benzylcyclohexanol (III), m.p. 76.5—77.5° (3 : 5-dinitrobenzoate, m.p. 133—135°) (oxidised to 2-benzylcyclohexanone), and a mixture (A) of *cis*- and *trans*-2-chlorocyclohexanols. The $\text{Mg}(\text{CH}_2\text{Ph})_2$ present in the Grignard reagent thus appears to be more reactive than the $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ [responsible for the production of (A)] towards (II). 2-Phenylcyclohexanol (IV), b.p. 153—154°/16 mm., m.p. 56—57° (lit. 54—55°) (3 : 5-dinitrobenzoate, m.p. 121—121.5°), prepared from (II) and LiPh in Et_2O and N_2 , is oxidised (CrO_3 , AcOH) to δ -benzoylvaleric acid and 2-phenylcyclohexanone (V). The poor yield of (IV) from (II) and MgPhBr (Bedos, A., 1926, 508) is due to cyclopentylcarbinol formation. $\alpha\text{-C}_{10}\text{H}_7\cdot\text{Li}$ and (II) afford 2-1'-naphthylcyclohexanol, b.p. 183°/1 mm., m.p. 129—130° (3 : 5-dinitrobenzoate, m.p. 162—163°; phenylcarbamate, m.p. 134—135°), dehydrated (ZnCl_2 at 160—170°) to 1-naphthyl- Δ^1 -cyclohexene, m.p. 46° (lit. 36°), also prepared by Weiss and Woidich's method (A., 1926, 509), and from the alcohol and PBr_3 in cold CCl_4 . $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, (V), and Zn in C_6H_6 give *Et* 1-hydroxy-2-phenylcyclohexylacetate, b.p. 146—154°/0.8 mm. (free acid, m.p. 128—129°), dehydrated (SOCl_2 , Et_2O - $\text{C}_5\text{H}_5\text{N}$ at 0°) to the *Et* ester, b.p. 123—125°/0.8 mm., of 2-phenyl- Δ^1 -cyclohexenylacetic acid (VI), b.p. 150—155°/0.4 mm., m.p. 92.5—93.5°. Reduction (H_2 , Pd-black, AcOH) of (VI) affords 2-phenylcyclohexylacetic acid (VII), m.p. 168—170°, and an impure isomeride (?) (cf. below) [converted by conc. H_2SO_4 at 100° into a ketone, $\text{C}_{14}\text{H}_{16}\text{O}$, m.p. 95—96° (oxime, m.p. 175—177°), which is probably stereoisomeric with (VIII) (below)]. The bromide from (IV) and PBr_3 in CCl_4 with $\text{CHK}(\text{CO}_2\text{Et})_2$ in C_6H_6 gives (after hydrolysis and decarboxylation) a stereoisomeric (?) 2-phenylcyclohexylacetic acid, m.p. 84—85° (cf. Ghose, A., 1935, 1495). The chloride of (VII) with AlCl_3 in CS_2 at 0° gives 9-keto-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (hexahydrophenanthrone) (VIII), b.p. 137—138°/0.5 mm. (oxime, m.p. 123.5—124.5°; semicarbazone, m.p. 195—196°), also formed from (VII) and conc. H_2SO_4 at 100°. Reduction (H_2 , PtO_2 , EtOH) of (VIII) affords the 9-hydroxyoctahydrophen-

anthrene, m.p. 114—115°, dehydrogenated (Pt-black at 310—320°) to 9-phenanthrol and dehydrated (ZnCl_2 at 180°) to hexahydrophenanthrene, b.p. 125—126°/2.5 mm., which is similarly dehydrogenated to phenanthrene. *as*-Octahydrophenanthrene (A., 1933, 1042) is oxidised (CrO_3 , AcOH) to a mixture of (VIII) and an isomeride (?) (oxime, m.p. 186.5—187.5°). The Grignard reagent from impure 1-chloro-2-benzylcyclohexane, b.p. 85—100°/0.2 mm. [from (III) and SOCl_2 in NPhMe_2], and CO_2 give *cis*- (IX), m.p. 86—88°, and *trans*- (X), m.p. 133—134°, 2-benzylhexahydrobenzoic acids. The Grignard reagent from 1-bromo-2-benzylcyclohexane, b.p. 120°/0.4 mm. [from (III) and PBr_3 in cold CCl_4], with ClCO_2Et affords (after hydrolysis with aq. EtOH-KOH) (X), probably 4-benzylhexahydrobenzoic acid, m.p. 140—141° (the formation of which involves a migration), and 2 : 2'-dibenzyl-dicyclohexyl, m.p. 180—181° (cloudy; clear at 191°). $o\text{-CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is reduced by Na and amyl alcohol to (X) and by H_2 and PtO_2 in AcOH to *o*-hexahydrobenzylbenzoic acid, m.p. 95.5—96.5° [oxidised (alkaline KMnO_4) to *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$]. (X) with cold conc. H_2SO_4 , or its chloride with AlCl_3 in cold CS_2 , leads to *trans*-hexahydroanthrone (XI), m.p. 109—109.5° (oxime, m.p. 174.5—175.5°); (IX) similarly gives *cis*-hexahydroanthrone (XII), m.p. 79—80° (cloudy; clear at 85°) (oxime, m.p. 150—151°), and some (XI). Dehydrogenation (Pt-black at 300°) of (XI) and (XII) affords anthracene. A mixture of (XI) and (XII) is formed from either (IX) or (X) and conc. H_2SO_4 at 100°; interconversion of the ketones probably occurs through an intermediate enolic form.

[By R. ROBINSON.] Contrary to the previous statement (A., 1934, 75), cyclohexene oxide and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgBr}$ (XIII) give cyclopentyl- β -phenylethylcarbinol (XIV), also prepared from (XIII) and cyclopentylformaldehyde. The following corrections should be made in the abstract: the chloride and *p*-nitrobenzoate of 2- β -phenylethylcyclohexanol are those of (XIV); the 2- β -phenylethylcyclohexanone is cyclopentyl β -phenylethyl ketone; 2- β -phenylethyl-1-ethylcyclohexanol is cyclopentyl- β -phenylethylethylcarbinol; 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene is 1-cyclopentylhydrindene; 2- β -phenylethyl-1-ethyl- Δ^1 -cyclohexene and ethyloctahydrophenanthrene are best described as hydrocarbons, both $\text{C}_{16}\text{H}_{22}$. The apparent difference between the previous results and those of Bardhan and Sen-Gupta (A., 1932, 1241) no longer exists. H. B.

Preparation of 9 : 10-dihydrophenanthrene and its derivatives. A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1935, 57, 2731—2732).—Reduction of phenanthrene with H_2 at 2000—4000 lb. per sq. in. at 220° in presence of a Cu-Cr-BaO catalyst (Connor *et al.*, A., 1932, 477) gives 60—80% of the 9 : 10- H_2 -derivative, m.p. 31—32°, which with AcCl in CS_2 or PhNO_2 affords 2-acetyl-9 : 10-dihydrophenanthrene (I), m.p. 51—52° (oxime, m.p. 146—147.5°; semicarbazone, m.p. 236—237°). (I) is oxidised by CrO_3 to 2-acetyl-9 : 10-phenanthraquinone, m.p. 223—224°, and by NaOCl to 9 : 10-dihydrophenanthrene-2-carboxylic acid, m.p. 211.5—212.5° [*Me* ester, an oil, dehydrogenated (Se at 300°) to phenanthrene-2-carboxylic acid].

2-Bromoacetyl-9:10-dihydrophenanthrene has m.p. 93.5—95°. 9:10-Dihydroanthracene is obtained in nearly quant. yield by reduction (H_2 ; Cu chromite; 160°) of anthracene. H. B.

Higher benzenoid hydrocarbons. II. Isomeric bromofluorenones. III. Isomeric bromo-9-fluorenols and bromofluorenes. H. F. MILLER and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 2443—2446, 2447—2450).—II. The chloride, m.p. 162—163°, of 4-bromobenzophenone-2'-carboxylic acid (I) is converted by liquid NH_3 into the amide, m.p. 184.5—185°, and thence by alkaline NaOBr into 4-bromo-2'-aminobenzophenone (II), m.p. 108°, also prepared by hydrolysis (90% H_2SO_4 , AcOH) of the reaction product from 2-*p*-toluenesulphonamidobenzoyl chloride, PhBr, and $AlCl_3$, and from (I) and N_3H (method: Oesterlin, A., 1932, 1030). When the diazo-solution from (II) is warmed, 3-bromofluorenene, m.p. 162°, is obtained. The chloride, m.p. 119—120°, of 3-bromobenzophenone-2-carboxylic acid with NH_4HCO_3 affords the amide, m.p. 135—140°, converted (NaOBr) into 3-bromo-2-aminobenzophenone, m.p. 128—130°, and thence (as above) into 4-bromofluorenene, m.p. 190—191°, which is also prepared from 2-bromodiphenyl-2'-carboxylic acid, m.p. 186—187° (from *o*- $C_6H_4I-CO_2Me$, *o*- C_6H_4BrI , and Cu at 260—290°), and conc. H_2SO_4 at 100° (bath).

III. Bromofluorenones (A) are reduced (Zn dust, conc. aq. NH_3 , EtOH) to bromofluorenols (B), which are reduced further to bromofluorenes [also prepared by Clemmensen reduction of (A)] by red P and I in AcOH. (B) with HBr and HCl in EtOH give the dihalogenofluorenes. The following are new: 3-, m.p. 142—145°, and 4-, m.p. 149—150°, -bromo-9-fluorenols; 3- (III), m.p. 90—91°, and 4- (IV), m.p. 165°, -bromofluorenes; 2:9-, m.p. 107.5—108.5°, 3:9-, m.p. 124—125°, and 4:9-, m.p. 194—195°, -dibromofluorenes; 9-chloro-3-, m.p. 116—117°, and 4-, m.p. 141—142°, -bromofluorenes. Fluorene and $Hg(OAc)_2$ give (mainly) the 4-OAc-Hg-derivative [converted by successive treatment with $CaCl_2$ and Br into (IV)]; in the absence of solvent some of the 3-derivative [converted into (III)] is also formed. In the latter case, the intermediate mixture of ClHg-derivatives differs considerably from the product obtained by Goswami and Das-Gupta (A., 1931, 1435). H. B.

ω -Benzyl derivatives of acetophenone and their reduction products. G. A. HILL and A. J. COFRANCESCO (J. Amer. Chem. Soc., 1935, 57, 2426—2428).—Ph α -diphenylisopropyl ketone (I) (*oxime*, m.p. 157°), formed together with $COPh \cdot CH_2 \cdot CH_2Ph$ (II) from $COPhMe$, CH_2PhCl , and $NaNH_2$ in xylene, is reduced (Na, EtOH) to α -diphenyl- β -benzylpropyl alcohol (*phenylcarbamate*, m.p. 185°). (II) is benzylated (above method) to Ph β -phenyl- α -dibenzylethyl ketone (*tribenzylacetophenone*) (III), m.p. 127—128°, which is reduced by Na and EtOH to α -diphenyl- β -*β*-dibenzylpropyl alcohol, decomp. when heated at low pressure, and by red P and 47% HI to $C(CH_2Ph)_4$ (yield 13%). (I)—(III) could not be reduced by Clemmensen's method. H. B.

Structure of metallic derivatives formed by adding Grignard reagents to unsaturated ket-

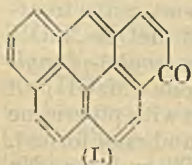
ones. E. P. KOHLER, M. TISHLER, and H. POTTER (J. Amer. Chem. Soc., 1935, 57, 2517—2521).—The compound, $[CHPh_2 \cdot CH \cdot CO \cdot C_6H_2Me_3]MgBr$ (A), obtained from mesityl styryl ketone (I) and $MgPhBr$, with $BzCl$ gives $\approx 96\%$ of γ -diphenyl- α -mesityl- Δ^{α} -propenyl benzoate (II), m.p. 162°. Mesityl β -diphenylethyl (III) or α -bromo- β -diphenylethyl ketones and $MgEtBr$ afford an isomeride (B) of (A); a geometrical isomeride (IV), m.p. 148°, of (II) is obtained from (B) and $BzCl$. (II) and (IV) are both hydrolysed (EtOH-NaOH) to (III). Ability to combine with RCHO is no indication of the structure of such Mg derivatives. Thus, (B) and PhCHO afford β -trimethylbenzoyl- α - γ -triphenylpropyl alcohol, m.p. 132°, oxidised (CrO_3 , AcOH) to α -benzoyl- α -trimethylbenzoyl- β -diphenylethane (V), m.p. 107°, and polymeric material. Acidification of a solution of (V) in MeOH-NaOH gives an enol, m.p. 137°, which reverts to (V) in presence of org. bases; the relative stability of the enol is due to the $C_6H_2Me_3$ group since the enol of $CHBz_2 \cdot CHPh_2$ is mobile. The Mg derivative from $CHPh_2 \cdot CH_2 \cdot COPh + MgEtBr$ with $C_6H_2Me_3 \cdot COCl$ affords (V) and α - γ -triphenyl- Δ^{α} -propenyl trimethylbenzoate, m.p. 93°. The product from (I) + $MgMeI$ treated with $BzCl$ gives (after removal of ester with cold MeOH-NaOH) a little of the enol, m.p. 128°, of α -benzoyl- α -trimethylbenzoyl- β -phenylpropane, m.p. 130°; this enol has the same stability as that of (V). Reduction (Adams) of (I) affords mesityl β -phenylethyl ketone, b.p. 191—192°/about 5 mm.; successive treatment of this with $MgEtBr$, $BzCl$, and MeOH-NaOH gives 12% of α -benzoyl- α -trimethylbenzoyl- β -phenylethane (VI), m.p. 118°, fresh solutions (MeOH) of which contain 4% of enol (equilibration with piperidine gives approx. equal amounts of keto- and enol forms). (VI) is also prepared from CH_2PhCl and the Na derivative of $CH_2Bz \cdot CO \cdot C_6H_2Me_3$ (VII), and by catalytic reduction of α -benzoyl- α -trimethylbenzoyl- β -phenylethylene, obtained in poor yield (method: Knoevenagel and Erler, A., 1903, i, 636) from (VII) and PhCHO. α - β -Diphenyl- γ -mesityl- Δ^{α} -propenyl benzoate (?), m.p. 110°, is formed from Ph trimethylstyryl ketone + $MgPhBr$ and $BzCl$. Decomp. of (A) with cold dil. HCl and treatment of the product (in moist light petroleum) with O_2 gives the peroxide, m.p. 116—117° (decomp.), of γ -diphenyl- α -mesityl- Δ^{α} -propen- α -ol [*i.e.*, the enolic form of (III), stabilised by the $C_6H_2Me_3$ group]. H. B.

Preparation of benzanthrone compounds and benzanthronecarboxylic acids.—See B., 1936, 92.

Additions to conjugated systems in anthracene series. III. Factors influencing mode and extent of reaction of Grignard reagent with ketones. P. L. JULIAN, W. COLE, and T. F. WOOD (J. Amer. Chem. Soc., 1935, 57, 2508—2513).—10-Benzylideneanthrone and $MgMeI$ give (by 1:2-addition) 10-benzylidene-9-methyl-9:10-dihydroanthranol, m.p. 148°, converted by Br in $CHCl_3$ into 10- α -bromobenzyl-9-bromomethylanthracene (I), m.p. 168° (decomp.), which with NaOAc-AcOH affords 10- α -acetoxymethyl-9-acetoxymethylanthracene, m.p. 188°; treatment of the initial reaction product (in solution) with O_2 gives a small amount of a peroxide, decomp. 74° [to anthraquinone (II)]. (I) and Br in $CHCl_3$

afford CH_2PhBr and 10-bromo-9-bromomethylanthracene. The formation of (II) and MeCHO from 10-hydroxy-10-ethylanthrone (III), m.p. 107° [from (II) and MgEtBr in $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$], and AcOH -conc. H_2SO_4 in O_2 supports the view that 10-ethylideneanthrone (IV), b.p. $245-247^\circ/20$ mm. [obtained when (III) is distilled at atm. pressure in N_2], reacts as 9-hydroxy-10-vinylanthracene. The ready oxidation (O_2) of (IV) to (II) and vinyl alcohol through the peroxide, and the oxidative decomp. of (IV) to (II) and C_2H_2 during attempted distillation at atm. pressure, are thus satisfactorily explained. Anthraphenone, which resembles an $\alpha\beta$ -unsaturated ketone, is reduced by MgPhBr to 10 : 10'-dibenzoyl-9 : 10 : 9' : 10'-tetrahydro-9 : 9'-dianthryl; no reaction occurs with MgMeI . 9 : 10-Dihydroanthraphenone similarly affords 9- α -hydroxybenzhydryl-9 : 10-dihydroanthracene, m.p. 173° , dehydrated (AcOH -conc. H_2SO_4) to 9-benzhydrylidene-9 : 10-dihydroanthracene, m.p. 258° , which is oxidised (CrO_3 , AcOH) to COPh_2 and (II). Pure products could not be isolated from 9-benzoyl-10-phenylanthracene (V); the 9 : 10- H_2 -derivative of (V) similarly gives (V), presumably owing to oxidation of the intermediate Mg compound. H. B.

Action of glycerol and sulphuric acid on pyrene: history of benzanthrone. R. SCHOLL and H. K. MEYER (Ber., 1936, 69, [B], 152-158).—Pyrene is converted by H_2SO_4 and glycerol at $100-110^\circ$ into 1 : 9 : 8-diperinaphth-2 : 9-



anthra-2-one (I), m.p. 243° after darkening, which is not further affected by the reactants at 140° and is not transformed into pyranthrone-like substances by $\text{NaCl}-\text{AlCl}_3$ and BzCl . (I) readily gives a (?) Br_2 -derivative and is converted by boiling HNO_3 (d 1.42) into a $(\text{NO}_2)_2$ -derivative, m.p. $>330^\circ$, whence the $(\text{NH}_2)_2$ - and $(\text{NHAc})_2$ -compounds. When treated with red P and boiling HI (d 1.7), (I) is transformed into 1 : 9 : 8-diperinaphth-2 : 3 : 4 : 9-tetrahydroanthracene, m.p. $107-108^\circ$ (picrate), re-oxidised to (I) by H_2SO_4 and glycerol and converted by passage over heated Cu into 1 : 9 : 8-diperinaphth-2 : 9-dihydroanthracene. (I) is oxidised by CrO_3 in boiling AcOH to the quinone, $\text{C}_{19}\text{H}_8\text{O}_3$, m.p. $>330^\circ$ after darkening at 300° . The history of the discovery of benzanthrone is given (cf. A., 1929, 1305). H. W.

cis- and trans-1 : 3-Diketodecahydronaphthalene. C. K. CHUANG and Y. L. TIEN (Ber., 1936, 69, [B], 25-31).—Condensation of cyclohexenyl Me ketone with $\text{CHNa}(\text{CO}_2\text{Et})_2$ by a slight modification of the method of Kon *et al.* (A., 1927, 150) affords Et 1 : 3-diketodecahydronaphthalene-4-carboxylate (I), m.p. 114° (semicarbazone, m.p. 222°), in 87% yield. It is hydrolysed by boiling 20% $\text{KOH}-\text{EtOH}$ to trans-1 : 3-diketodecahydronaphthalene (II), m.p. $152-153^\circ$ (lit. m.p. 142°) [dioxime, m.p. 207° (decomp.); disemicarbazone, m.p. 241° (decomp.)]; trans-1 : 3-diketo-2-benzylidenedecahydronaphthalene, m.p. 229° ; methylenedi-trans-1 : 3-diketodecahydronaphthalene, m.p. $172-173^\circ$. The configuration of (II) follows from its oxidation by NaOBr to trans-*o*-carboxycyclohexaneacetic acid and by KMnO_4 to trans-cyclohexane-

1 : 2-dicarboxylic acid. Treatment of (I) with dil. $\text{KOH}-\text{EtOH}$ at $15-20^\circ$ gives the corresponding acid, which passes with loss of CO_2 into cis-1 : 3-diketodecahydronaphthalene (III), m.p. $124-125^\circ$ (dioxime, m.p. $152-153^\circ$; methylenedi-cis-1 : 3-diketodecahydronaphthalene, m.p. $147-148^\circ$). Oxidation of (III) with NaOBr leads to cis-*o*-carboxycyclohexaneacetic acid, m.p. 146° . (III) is isomerised to (II) by treatment with boiling 20% $\text{KOH}-\text{EtOH}$. Hydrolysis of (I) with boiling 15% HCl (cf. Ruzicka *et al.*, A., 1931, 1302) followed by distillation of the product in vac. gives an acid, *o*- $\text{C}_6\text{H}_{10}\text{Ac}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ or *o*- $\text{CH}_2\text{Ac}\cdot\text{C}_6\text{H}_{10}\cdot\text{CO}_2\text{H}$, m.p. $52-53^\circ$ (Ag salt; semicarbazone, m.p. $158-160^\circ$); the corresponding crude Et ester is converted by NaOEt in Et_2O into (II). H. W.

Preparation of diaryl α -diketones. H. H. HATT, A. PILGRIM, and W. J. HURRAN (J.C.S., 1936, 93-96).— $\text{COAr}\cdot\text{CH}_2\text{Ph}$ (1 mol.) are oxidised by SeO_2 (1.5 mols.) in Ac_2O at $140-150^\circ$ to $\text{COAr}\cdot\text{COPh}$ (I) in almost quant. yields; the following are prepared: benzil; 4-phenyl-, m.p. $104-105^\circ$; 4-chloro-, m.p. 73° ; 4-bromo-, m.p. 86.5° , and 4-methyl-, (II), m.p. 31° ; -benzils; 2 : 4-, b.p. $228^\circ/16$ mm., 2 : 5-, m.p. 41° , and 3 : 4-, m.p. 63.5° ; -dimethylbenzils, oxidised (H_2O_2 , $N\text{-NaOH}$, $\text{C}_6\text{H}_5\text{N}$) to BzOH and 2 : 4-, 2 : 5-, and 3 : 4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}_2\text{H}$, respectively; 2 : 4 : 6-trimethylbenzil, m.p. $136-137^\circ$. (I) and $\text{CO}(\text{NH}_2)_2$ in $\text{EtOH}-\text{KOH}$ give 5-phenyl-5-arylhydantoins and varying amounts of phenylarylacetylenediureide,

$\text{CO}\langle\text{NH}\cdot\text{CPh}\cdot\text{NH}\rangle\text{CO}$. The following are described: 5-phenyl-5-*p*-diphenyl-, m.p. $242-242.5^\circ$, -5-*p*-chlorophenyl-, m.p. 243° , -5-*p*-bromophenyl-, m.p. 239° , -5-*o*-4'-xylyl-, m.p. 225° , -5-*m*-4'-xylyl-, m.p. 269° , -5-*p*-xylyl-, m.p. 226° , and -5-*p*-tolyl-hydantoins; phenyl-*p*-diphenyl-, m.p. $316-318^\circ$, -*p*-chlorophenyl-, m.p. 339° , -*o*-4'-xylyl-, m.p. 333° , and *d*-*p*-tolyl-, m.p. 335° , -acetylenediureides. The compound (m.p. $99-101^\circ$) described as (II) by Weiss (A., 1920, i, 555) is impure *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, m.p. $110-111^\circ$, now shown to be formed [together with (II)] by hydrolysis (EtOH) of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CPhBr}_2$ (*loc. cit.*). (II) undergoes the benzilic acid change (cf. *loc. cit.*) yielding phenyl-*p*-tolylglycollic acid, m.p. 132° . Hydrolysis ($\text{MeOH}-\text{NaOMe}$) of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CHPhBr}$, m.p. $87.5-88^\circ$ (from *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ and Br in boiling CHCl_3), gives *r*-*p*-toluoylphenylcarbinol, m.p. $110-111^\circ$; this prep. is more convenient than those of McKenzie *et al.* (J.C.S., 1914, 105, 1583) and Weissberger *et al.* (A., 1930, 475). H. B.

Constitution of camptospermonol. T. G. H. JONES (Proc. Roy. Soc. Queensland, 1934, 45, 38-40).—Camptospermonol (I) is $\text{C}_{25}\text{H}_{40}\text{O}_2$ and not $\text{C}_{27}\text{H}_{42}\text{O}_2$ or $\text{C}_{28}\text{H}_{44}\text{O}_2$ (Jones and Smith, A., 1928, 291); the structure $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}_2]_7\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_7\cdot\text{Me}$ is assigned to (I). Decomp. of oximinohydrocamptospermonyl Me ether (II) with PCl_5 yields *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ (III) and stearic acid; similarly oximinocamptospermonyl Me ether (IV) yields (III) and oleic acid. Oxidation of (IV) yields suberic, azelaic, nonoic, and *m*-methoxybenzoic acids. The fatty acid previously isolated by oxidation of (II) is

shown to be a mixture of margaric and stearic acids.

CH. ABS. (r)

Hydroxypolyketones. II. Dibenzoylcarbinol. A. H. BLATT and W. L. HAWKINS (J. Amer. Chem. Soc., 1936, 58, 81—84).—Dibenzoylcarbinyl acetate (I), solutions of which in 95% EtOH at room temp. contain 5.1% enol (indirect Br titration), is hydrolysed (a) by aq. Na₂CO₃ to AcOH, BzOH, and CH₂Bz·OH, (b) by aq. 5% NaOH to AcOH and BzOH, (c) by aq. NaHCO₃ in MeOH (EtOH) to AcOH, CH₂Bz·OH, and MeOBz (EtOBz), (d) by short treatment with cold H₂SO₄ to dibenzoylcarbinol (II), m.p. 111—112° (yield 25%) (Bigelow *et al.*, A., 1935, 346). Alkalis and (II) give the same products as (I). (II) is acetylated to (I), is oxidised [Cu(OAc)₂ in 60% AcOH] to benzil, and when distilled at 4 mm. rearranges to CH₂Bz·OBz. (II) is not oxidised by I in neutral or acid solution, indicating the non-formation of OH·CPh:CBz·OH under these conditions. (II) does not give colours with NH₂-acids.

H. B.

Chalkones and chalkone oxides. I. Phenyl 3:4-methylenedioxy-styryl ketone. R. P. DODWADMATH and T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 438—451).—A comparative study of the reactivities of Ph 3:4-methylenedioxy-styryl ketone (I) and of Ph 6-nitro-3:4-methylenedioxy-styryl ketone (II). With Br (1 mol.) (I) yields Ph αβ-dibromo-β-3:4-methylenedioxyphenylethyl ketone (A., 1922, i, 1035), which with EtOH and MeOH gives respectively Ph α-bromo-β-ethoxy-, m.p. 143—144°, and -β-methoxy-, m.p. 115—116°, -β-3:4-methylenedioxyphenylethyl ketone. With Br (2 mols.) (I) gives Ph αβ-dibromo-β-6-bromo-3:4-methylenedioxyphenylethyl ketone, m.p. 174—175°, which yields α-bromo-β-ethoxy-, m.p. 126—127°, and α-bromo-β-methoxy-, m.p. 131—132°, compounds as above, and which with KI in COMe₂ forms Ph 6-bromo-3:4-methylenedioxy-styryl ketone, m.p. 146—147°, which is synthesised from 6-bromopiperonal and COPhMe. Treatment of (I) in AcOH with Cl₂ gives first a product converted by recrystallisation from EtOH into Ph α-chloro-β-ethoxy-β-3:4-methylenedioxyphenylethyl ketone, m.p. 118—119°; on longer treatment, Ph αβ-dichloro-β-6-chloro-3:4-methylenedioxyphenylethyl ketone, m.p. 127—128°, is formed. With KCN-EtOH, (III) forms β-benzoyl-α-3:4-methylenedioxyphenylpropionitrile, m.p. 132—133°, hydrolysed to the acid, m.p. 143—144°. The structure of (III) and of these derivatives is confirmed by the similar formation of β-benzoyl-α-phenylpropionitrile from Ph αβ-dibromo-β-phenylethyl ketone. With Br (1 mol.), (II) yields Ph αβ-dibromo-β-6-nitro-3:4-methylenedioxyphenylethyl ketone, m.p. 174—175°; this does not react with EtOH or further with Br; with KI it regenerates (II). With Cl₂, (II) gives the corresponding αβ-dichloro-compound, m.p. 151—152°. (I) with NaOEt and CH₂Ac·CO₂Et in EtOH yields Et 4-phenyl-2-(3':4'-methylenedioxyphenyl)-Δ⁶-cyclohexen-6-one-1-carboxylate, m.p. 151—152°; (II) does not react. (I) is catalytically reduced (Pd) to α-phenyl-γ-3:4-methylenedioxyphenylpropyl alcohol, m.p. 95—96°, without formation of the saturated ketone; (II) is not reduced. With N₂H₄·H₂O, (I) forms 3-phenyl-5-(3':4'-methylenedioxyphenyl)pyrazoline (?), decomp. on drying

(hydrochloride, m.p. 197—198°; picrate, m.p. 185—186°; Ac derivative, m.p. 153—154°); this substance does not give Knorr's pyrazoline reaction, but its formation of a hydrochloride, and failure to give NH₃ when reduced by Na-Hg, are against its being a hydrazone. With NHPH·NH₂, (I) forms 1:3-diphenyl-5-(3':4'-methylenedioxyphenyl)pyrazoline, m.p. 129—130° (pyrazoline reaction; NO-derivative).

Action of H₂O₂ (6%) on (I) in MeOH and COMe₂ yields Ph 3:4-methylenedioxyphenylstyryl ketone oxide (IV), m.p. 99—100°; with N₂H₄·H₂O this forms a hydrazone, m.p. 173—174° (regarded as such and not as a pyrazoline, since it does not form a NO-derivative), which with NaOEt or Ac₂O condenses to 3-phenyl-5-(3':4'-methylenedioxyphenyl)pyrazole, m.p. 194—195°. With MeOH or EtOH and H₂SO₄, the O-ring opens, and Ph α-hydroxy-β-methoxy- (V), m.p. 117—118°, and Ph α-hydroxy-β-ethoxy-β-3:4-methylenedioxyphenylethyl ketone, m.p. 93—94°, respectively, are obtained. When (V) is heated with NaOAc-AcOH or with aq. NaOH, or (IV) boiled (30 sec.) with aq. NaOH-EtOH, Ph 3:4-methylenedioxybenzyl diketone, m.p. 114—115°, is formed, which with o-C₆H₄(NH₂)₂ yields 2-phenyl-3-(3':4'-methylenedioxybenzyl)quinoxaline, m.p. 137—138°. If (IV) is boiled with aq. NaOH-EtOH for 4 hr., α-phenyl-β-3:4-methylenedioxyphenyl-α-lactic acid, m.p. 149—150°, is produced, oxidised (K₂Cr₂O₇-AcOH) to Ph 3:4-methylenedioxybenzyl ketone (A., 1930, 1041). (II) is oxidised by H₂O₂ (6%) in COMe₂ to Ph 6-nitro-3:4-methylenedioxy-styryl ketone oxide (VI), m.p. 159—160°, but this is not readily isolated, and is better prepared by adding NaOEt to CH₂Br·COPh and 6-nitropiperonal in EtOH at 0°. (VI) does not react with EtOH or MeOH, or with NaOH, but with HCl in AcOH gives Ph β-chloro-α-hydroxy-β-6-nitro-3:4-methylenedioxyphenylethyl ketone, m.p. 183—184°. Action of N₂H₄·H₂O on (II) in AcOH gives Ph 6-nitro-3:4-methylenedioxy-styryl ketone-N-acetylhydrazone, m.p. 244—245°; with NHPH·NH₂, the -phenylhydrazone, m.p. 159—160°, is formed, which is condensed (AcOH) to 1:3-diphenyl-5-(6'-nitro-3'-4'-methylenedioxyphenyl)pyrazoline, m.p. 203—204°, from which AgNO₃ forms the corresponding -pyrazole, m.p. 163—164°, also obtained from (VI) and NHPH·NH₂. Results show that the 6-NO₂ removes the enhanced reactivity which CH₂O₂ confers on one of the Br of the chalkone dibromide, and reduces the reactivity of the oxide towards EtOH or MeOH, but not towards HCl.

E. W. W.

Synthesis of 2:6-dihydroxy-4-methoxyphenyl β-phenylethyl ketone obtained from the oil of *Populus balsamifera*, L. A. GORIS and H. CANAL (Compt. rend., 1935, 201, 1520—1521).—2:4:6-Trihydroxyphenyl β-phenylethyl ketone (cf. A., 1926, 1135) with Me₂SO₄ affords 2:6-dihydroxy-4-methoxyphenyl β-phenylethyl ketone, m.p. 168°, identical with the natural product.

J. L. D.

Organic salts of a diaminobenzoquinonedisulphonic acid. (MLLE.) Y. GARREAU (Compt. rend., 1935, 201, 1515—1517; cf. A., 1935, 338).—Diaminobenzoquinonedisulphonates of the following bases are prepared from the NH₄ salt and the base

in dil. HCl: glycine (+2H₂O, decomp. about 240°), creatine [+2H₂O, 245—248° (decomp.)], adenine (+4H₂O, which at 105—110° is converted into +1H₂O), aliphatic NH₂-acids, uric acid and guanidine bases, and many alkaloids. J. L. D.

Anthragallol esters. M. TANAKA (J. Chem. Soc. Japan, 1935, 55, 196—197).—The methylation of anthragallol with Me₂SO₄-NaOH, and the 1:2:3-Me₃, m.p. 173°; 2:3-Me₂, m.p. 166°, and 3-Me, m.p. 143°, ethers, are described. CH. ABS. (r)

Mechanism of the conversion of 2-aminoanthraquinone into indanthrone. M. TANAKA (J. Chem. Soc. Japan, 1935, 56, 192—195).—Fusion of NH₂Ph with alkali, in the presence of an oxidising agent or PhNO₂, does not give phenazine or the *N*-oxide. Under similar conditions, 2-aminoanthraquinone (I) gives 2-amino-1-hydroxyanthraquinone (II) and dihydro-2'-amino-1:2'-dianthraquinonylamine (III). Alkali fusion of (II) gives, not indanthrone (IV), but a dihydrophenazinecarboxylic acid; (III), treated similarly, affords (IV). A mechanism is advanced for the formation of (IV) from (I), by way of (III). CH. ABS. (r)

Manufacture of derivatives of chrysenequinones.—See B., 1936, 139.

Vat dyes of the benzanthrone series. XV. **Synthesis of 5-methoxybenzanthrone and 5:5'-dimethoxyviolanthrone.** T. MAKI. XVI. **Constitution of dichlorinated violanthrone and preparation of some new Bz-3:3'-violanthrone derivatives.** T. MAKI and T. AOYAMA (J. Soc. Chem. Ind. Japan, 1935, 38, 630—636B, 636—642B; cf. this vol., 206).—XV. 1-Chloro-9-anthrone, m.p. 114° (corr.) (cf. B., 1923, 1216A) (obtained from 1-chloroanthraquinone and H₂SO₄-Al), when heated at 120° during 6 hr. with H₂SO₄ and glycerol and the product boiled with 1% NaOH solution yields 5-chlorobenzanthrone (I), m.p. 181.5°, and a compound, m.p. 121°, probably 4-chlorobenzanthrone. (I) is probably identical with α -chlorobenzanthrone (B.P. 278,496; B., 1928, 9), and is oxidised by CrO₃-H₂O-AcOH to 5-chloroanthraquinone-1-carboxylic acid. (I) with KOH-MeOH at 150° for 7 hr. affords 5-methoxybenzanthrone (II), m.p. 191° (corr.). The OMe is very resistant to HI. (II) when heated at 210° with KOH-PhOH affords mainly 5:5'-dimethoxyviolanthrone (III), sol. in NaOH-Na₂S₂O₄-EtOH-H₂O, and about 35% of a compound (IV), sol. with difficulty in alcoholic alkaline Na₂S₂O₄ and considered to be similar to the *B* dyes described previously (cf. B., 1934, 752). (III) dyes cotton blue, fast to acids and alkalis. (IV) dyes cotton grey-blue. (I) when heated at 220° with KOH, or, better, KOH-PhOH, affords 5:5'-dihydroxyviolanthrone, almost insol. in the ordinary org. solvents and in alkaline Na₂S₂O₄; addition of H₂O to its solution in H₂SO₄ gives a greenish-black ppt.

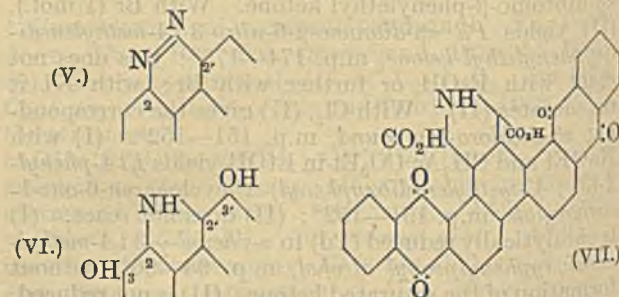
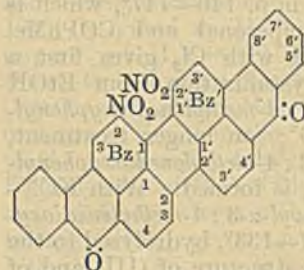
XVI. Careful chlorination of violanthrone in AcOH affords Bz-3:3'-dichloroviolanthrone (V) (cf. A., 1934, 754) and a little of a dark green vat dye, separated by means of PhNO₂. (V) at 150° with KOH-MeOH affords Bz-3:3'-dimethoxyviolanthrone (cf. Jap. P. 109,582), which fairly readily forms a blue hyposulphite vat and dyes cotton fast indigo-blue.

The OMe groups are very resistant to HI. (V) when treated with H₂SO₄-MnO₂-H₃BO₃ at 60° during 1 hr. affords Bz-3:3'-dichloro-Bz-2:2'-dihydroxyviolanthrone, a violet-black cryst. powder, which dyes cotton from a blue Na₂S₂O₄ vat a dull green, similar to that obtained with Bz-2:2'-dihydroxyviolanthrone. (V) with NH₃, H₂O, and Cu at 200° for 7 hr. yields Bz-3:3'-diaminoviolaanthrone, which dyes cotton from a blue Na₂S₂O₄ vat a dark violet-blue, almost unaffected by NaOCl. Similarly (V) when refluxed during 9 hr. with *p*-toluidine, anhyd. NaOAc, and Cu affords Bz-3:3'-di-*p*-toluidinoviolaanthrone, a violet-black cryst. powder, which dyes cotton dark violet-blue from a blue vat. Reasons are given for the constitution assigned to (V).

H. G. M.

Vat dyes of the benzanthrone series. XVII. **Preparation and purification of dinitroviolanthrone.** XVIII. **Constitution of dinitroviolanthrone.** T. MAKI, Y. NAGAI, and Y. HAYASHI (J. Soc. Chem. Ind. Japan, 1935, 38, 710—715B, 715—720B).—XVII. The % of N in the product when violanthrone (I) is nitrated with HNO₃ (*d* 1.48)-AcOH increases with increase in the proportion of HNO₃. Optimum conditions for the formation of the almost pure (NO₂)₂-derivative (II) are the nitration of 3 parts of (I) in 50 parts of AcOH with 30 parts of HNO₃ in 30 parts of AcOH at 60° for 12 hr. The small amount of by-product formed is removed either by crystallisation of (II) from C₂H₂Cl₄, or by extraction with 80% H₂SO₄ in which it is sol. When only 10 parts of HNO₃ at room temp. are used, a mixture of NO₂- and (NO₂)₂-derivatives is formed. Nitration of (I) with HNO₃ (*d* 1.48)-H₂SO₄ at 0—5° does not give (II), but a substance (III), probably a dinitrodihydroxyviolanthrone. The tinctorial properties of these derivatives are described.

XVIII. The following reactions prove that (II) is Bz-2-Bz-2'-dinitroviolanthrone (annexed formula). Reduction with Na₂S₂O₄-NaOH affords the (NH₂)₂-derivative (IV), the green colour of which, on wool, is oxidised by 0.5% NaOCl to a black (V), which is reconverted into (IV) by Na₂S₂O₄-NaOH. Oxidation of (IV) with CrO₃-H₂SO₄ affords first a substance, probably (VI), insol. in aq. NH₃, and finally a substance,



NH₃-sol., to which the structure (VII) is assigned. Oxidation of (II) with MnO₂-H₂SO₄-H₃BO₃ gives

its Bz-3-Bz-3'-(OH)₂-derivative, which is not identical with the Bz-3-Bz-3'-dinitro-Bz-2-Bz-2'-dihydroxy-derivative obtained by nitration of the Bz-2-Bz-2'-(OH)₂-compound (preceding abstract) with HNO₃ (d 1.48)-AcOH at 60°, but appears to be identical with (III).
J. W. B.

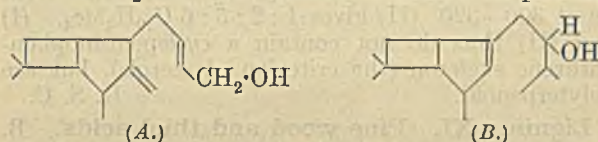
Carbamide derivatives in terpene series. R. L. BATEMAN and A. R. DAY (J. Amer. Chem. Soc., 1935, 57, 2496—2498).—*l*-Menthylcarbamide, m.p. 140.2—140.6° (lit. 134—136°) [Ac, m.p. 118—119°, CH₂Br·CO, m.p. 111.8—112.3°, cinnamoyl, m.p. 144.3—145.1°, *p*-nitro-, m.p. 158.7—159.2°, and *p*-amino-benzoyl, m.p. 208—210° (decomp.), derivatives; additive compound, C₁₀H₁₉·NH·CO·NH·CH(OH)·CCl₃, m.p. 146.2—147.2° [with chloral], *d*-bornylcarbamide, m.p. 165.7—166.3° [Ac, m.p. 129—129.5°, CH₂Br·CO, m.p. 136.1—136.5°, cinnamoyl, m.p. 220.2—220.8°, *p*-nitrobenzoyl, m.p. 230° (decomp.), and *p*-amino-benzoyl, m.p. 233° (decomp.), derivatives; additive compound, m.p. 180° (decomp.), with chloral], and 3-carbamido-2-ketocamphane (+0.5H₂O), m.p. 177.8—178.4° (lit. 169°) (*p*-nitrobenzoyl derivative), are prepared from the appropriate RNH₂·HCl and NO₂·NH·CO·NH₂ in aq. NaHCO₃. All m.p. are corr. Some of the above compounds possess narcotic activity.
H. B.

Anomalous mutarotation of salts of Reychler's acid. IV. Comparison of 2-anilo-*d*-camphane-10-sulphonic acid with *d*-camphor-10-sulphonanilide. H. SUTHERLAND and R. L. SHRINER (J. Amer. Chem. Soc., 1936, 58, 62—63; cf. A., 1935, 1503).—The differences in properties of *d*-camphor-10-sulphonanilide, m.p. 120.5—121°, [α]_D²⁵ +76° in CHCl₃ (no mutarotation in 95% EtOH) [hydrolysed (25% HCl) with difficulty], and the dehydration product (I), [α]_D²⁵ -170.5° in CHCl₃, of NH₂Ph *d*-camphor-10-sulphonate support the view (A., 1935, 1118) that (I) is 2-anilo-*d*-camphane-10-sulphonic acid.
H. B.

Structure of methylsantene obtained by the catalytic dehydration of fenchyl alcohol by weak acids. N. J. TOIVONEN, T. VEJOLA, and S. FRIBERG (Suomen Kem., 1935, 8, B, 44—46).—Mild dehydration of fenchyl alcohol (cf. A., 1930, 348) gives, by intramol. change, 1-methylsantene (A., 1935, 865), which with O₂ gives 1:3-diaceto-1-methylcyclopentane, b.p. 106—109°/6 mm. [semicarbazone, m.p. 230—232° (decomp.)]; this with NaOBr, followed by Zn-AcOH, gives 1-methylcyclopentane-1:3-dicarboxylic acid, m.p. 97° (anhydride, m.p. 81°).
J. L. D.

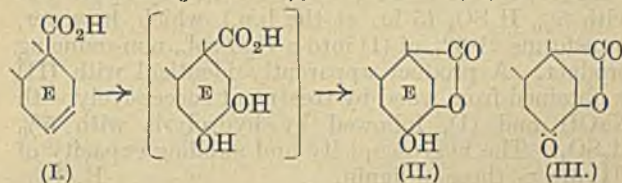
Determination of the constitution of sesquiterpenes by powerful oxidative degradation. III. Betulol. W. TREIBS (Ber., 1936, 69, [B], 41—46).—The unesterified betulol of birch-bud oil (isolated through the non-cryst. H phthalate) has α_D -36°, in agreement with Soden *et al.* (A., 1905, i, 451), whereas that obtained by hydrolysis of the betulyl acetate has α_D -19.5°. Betulol (I) is therefore a mixture of at least two dicyclic, closely related alcohols. The alcoholic group is not exclusively primary, since the oxidation product of tetrahydrobetulol (Semmler *et al.*, A., 1918, i, 301) is only partly aldehydic. Since both components of the oil behave similarly qualitatively, the following work was per-

formed with the mixture. Treatment of the latter with powdered KMnO₄ in COMe₂ affords small amounts of neutral products, H₂C₂O₄ (0.5 mol.), a little AcOH, and an acid mixture (II) oxidised by hot dil. HNO₃ to *betulolic acid* (III) [Me₂ ester, (IV), b.p. 132—136°/18 mm., [α]_D +48°]. The physical properties of (IV) indicate the presence of a 4-C ring, which is confirmed by the stability of (III) towards oxidants. Protracted action of boiling dil. HNO₃ partly converts (III) into H₂C₂O₄ and CO₂H·CH₂·CMe₂·CO₂H without affecting the properties of the unattacked acid, so that (III) is probably a homocaryophyllenic acid belonging to the *trans*-series, since it is not dehydrated by Ac₂O or AcCl. Since (II) is transformed by MeOH-H₂SO₄ and subsequent vac. distillation into the Me₂ ester, b.p. 200—202°/20 mm., α_D +32°, of a saturated OH-dicarboxylic acid, C₁₃H₂₀O₅ (V), and by protracted esterification into the ester of unsaturated acids, and since (V) is oxidised by hot dil. HNO₃ to (III), it follows that the side-chain must have the termination ·CH:CH·CH₂·OH. The structures A and B for primary



and *sec.* (I) are most probable. The portion of the oil which does not react with *o*-C₆H₄(CO)₂O yields *betulene*, C₁₅H₂₂, b.p. 130—132°/20 mm., α_D -78°, a dicyclic sesquiterpene with three double linkings. Treatment of a similar portion with H₂BO₃ yields the unstable, strongly unsaturated compound, C₁₅H₂₂O, b.p. 140°/20 mm., α_D -9.2°. The paraffin of the oil is C₂₀H₄₂, m.p. 49°.
H. W.

Polyterpenes and polyterpenoids. XCIX. Primary products of the oxidation at the double linking of sumaresinolic acid and oleanolic acid. L. RUZICKA, H. HÖSLI, and K. HOFMANN (Helv. Chim. Acta, 1936, 19, 109—114).—Treatment of sumaresinolic acid (I) with O₃ in 80% AcOH at 80° or with H₂O₂ in AcOH at room temp. affords the corresponding OH-lactone (II), m.p. 322—324° (decomp.), [α]_D +8.9° in CHCl₃ with 10% of MeOH. (II) is oxidised



by CrO₃ in AcOH at 50° to *sumaresinonoketolactone* (III), m.p. 311—312°, [α]_D -24.2° in CHCl₃, also obtained from (I) and CrO₃ in H₂SO₄-AcOH. Acetyl-oleanolic acid is oxidised by H₂O₂ in AcOH at 80° to the corresponding OH-lactone (IV), m.p. 292—294°, further transformed into the ketolactone (V), m.p. 279—280° (oxime, m.p. 220—221°) (Kitasato, A., 1932, 1035). (IV) differs from the corresponding compound of Aumüller *et al.* (A., 1935, 865) only in the steric configuration of the OH group, since each yields (V) when oxidised. Hydrolysis of (V) with KOH-MeOH affords *hydroxyketodihydro-oleanolic acid*, m.p. 306—307°.
H. W.

Differentiation of sterols from other polyterpene alcohols. Structure of lanosterol and onocerol. H. SCHULZE (Z. physiol. Chem., 1936, 238, 35—53).—“*iso*Cholesterol” (I) (modified prep.), m.p. 136—137°, $[\alpha]_D^{20} + 61.9^\circ$ in CHCl_3 , or its acetate with Se at 320—335° gives 1 : 2 : 8-trimethylphenanthrene, a hydrocarbon, m.p. 212—213°, and an alkali-sol. substance, (?) a hydroxytrimethylphenanthrene (*Me ether*, m.p. 179—180°, b.p. 215—230°/14 mm.), but (I) is largely unchanged by Pt at 300°. Onocerol (II) (modified prep.), $\text{C}_{30}\text{H}_{50.2}\text{O}_2$, dimorphic, m.p. 232° and 202°, $[\alpha]_D^{20} + 5.04^\circ$ in $\text{C}_5\text{H}_5\text{N}$ [diacetate (III), m.p. 224°, $[\alpha]_D^{20} + 28.3^\circ$; *dibenzoate*, m.p. 237—238°, $[\alpha]_D^{20} + 21.5^\circ$; *dichloroacetate*, m.p. 238—244°, $[\alpha]_D^{20} + 114^\circ$; *di-3 : 5-dinitrobenzoate*, m.p. 291° (decomp.), $[\alpha]_D^{20} + 19.3^\circ$; *dianisate*, m.p. 232—234°, $[\alpha]_D^{20} + 9^\circ$; all $[\alpha]$ are in CHCl_3], gives no PhCHO on ozonisation (cf. lit.) and does not resemble $\text{CH}_2\text{:CHPh}$ or neogosterol in absorption spectrum, reacts with 2 mols. of BzO_2H , and is difficultly reducible. (III), however, readily absorbs 2H (PtO₂ in AcOH). With Se at 300—320° (II) gives 1 : 2 : 5 : 6- $\text{C}_{10}\text{H}_4\text{Me}_4$. (I) and (II) thus do not contain a cyclopentanophenanthrene skeleton (the criterion of sterols), but are polyterpenoid. R. S. C.

Lignin. XI. Pine wood and thiol acids. B. HOLMBERG (Ber., 1936, 69, [B], 115—119; cf. A., 1935, 1502).—The treatment of pine wood with thioacetic, α -thiolpropionic, α -thiolisobutyric, thiolsuccinic, and α -thiol- α -methylsuccinic acid is described, but it is difficult to find a theoretical basis for the interpretation of the results. The change appears to proceed in two stages, during the first of which the lignin reacts with the SH-acid giving acids containing S which in the subsequent stage become sol. in H_2O or alkali. H. W.

Action of ethylene oxide on wood and lignin. II. N. I. NIKITIN and T. I. RUDNEVA (J. Appl. Chem. Russ., 1935, 8, 1176—1183).—Willstätter lignin treated with 18% NaOH and $(\text{CH}_2)_2\text{O}$ (I) (2 hr. at 70°, or 2 days at room temp.) yields amorphous hydroxyethyl-lignin (II), containing 38.76% of $\text{OEt} + \text{OMe}$, and 5.18% of acetylatable OH. (I) is eliminated from (II) by HI at 135—140°, but not by hydrolysis with 5% H_2SO_4 (5 hr. at the b.p.), which, however, transforms 21.6% of (I) into a H_2O -sol., non-reducing product. A product apparently identical with (II) is obtained from wood by treatment successively with NaOH and (I), followed by hydrolysis with 5% H_2SO_4 . The hygroscopicity and swelling capacity of (II) are > those of lignin. R. T.

Elemic acid from elemi resin. VIII. β -Elemionic acid. M. M. MLADENOVIC and I. BERKEŠ (Monatsh., 1935, 67, 36—41; cf. A., 1935, 495).— β -Elemionic acid (I), m.p. 220.5° [modified prep. from α -elemionic acid (II); *oxime*, m.p. 218°, hydrolysed to (I) by HNO_2], gives (Pd-C in AcOH) a H_4 -acid (III), m.p. 244° [oxime, m.p. 245°, hydrolysed to (III)]; also obtained by hydrogenation of crude (II), and is identical with δ -elemic acid (A., 1932, 749). R. S. C.

Toad poisons. VIII. Dehydrogenation of cinobufagin. H. JENSEN (J. Amer. Chem. Soc., 1935, 57, 2733—2734).—Dehydrogenation (Se at

310—340°) of cinobufagin (I), $\text{C}_{25(26)}\text{H}_{32(34)}\text{O}_6$ (cf. A., 1934, 412), gives a little of (probably) methylcyclopentenophenanthrene. (I) and (probably) other bufagins appear to contain the same ring system as the sterols and cardiac aglucones. H. B.

Carotenoids of purple bacteria. II. Rhodoviolascene. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1936, 19, 3—5; cf. this vol., 248).—Rhodoviolascene is $\text{C}_{42}\text{H}_{60}\text{O}_2$. It contains 2 OMe and absorbs 26 H when catalytically hydrogenated. It affords COME_2 when treated with O_3 , and hence is probably a (OMe)₂-derivative of lycopene (I) or similar hydrocarbon. It appears to be optically inactive in C_6H_6 . It does not react with NH_2OH or give a H_2 -derivative by short treatment with Zn-AcOH- $\text{C}_5\text{H}_5\text{N}$. The bacteria contain also *rhodovibrene*, but rhodopurpurin is possibly identical with (I). H. W.

Preparation and reactions of tertiary tetrahydrofurylcarbinols. A. L. DOUNCE, R. H. WARDLOW, and R. CONNOR (J. Amer. Chem. Soc., 1935, 57, 2556—2559).—Reduction (H_2 at 100—130 atm., Raney Ni, 150°) of Et furoate (I) gives 93.3% of Et tetrahydrofuroate (II), b.p. 188—190°/740 mm., which with MgPhBr affords *diphenyl-2-tetrahydrofurylcarbinol* (III), m.p. 79—80°, dehydrated (anhyd. MgSO_4) to 2-benzhydrylidene-tetrahydrofuran (IV), b.p. 195°/10 mm., m.p. 107.5—108.5° [ozonolysis products, COPh_2 and γ -butyrolactone (V)]. Prolonged treatment of (III) with MgPhBr (3 equivs.) in xylene does not cause ring fission; hydrolysis and removal of the xylene gives (IV). 2-Tetrahydrofuryl-diethyl-, b.p. 200—203°/740 mm., and -*di-n-butyl*-, (VI), b.p. 151—152°/24 mm., 251—252°/740 mm., -*carbinols*, best prepared from (II) and MgRBr, are also obtained by reduction of 2-furyl-diethyl-, b.p. 92—95°/14 mm., and -*di-n-butyl*-, b.p. 128—131°/14 mm., -*carbinol*, respectively [from (I) and MgRBr]. Dehydration (MgSO_4 -KOH) of (VI) gives an inseparable mixture. (V) is obtained in 10% yield by reduction (H_2 at 90—130 atm., Cu-Cr-BaO catalyst, 250°) of Et succinate. (V) and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ give a little succinhydrazide and (mainly) γ -hydroxybutyrylhydrazide, m.p. 89—90°. H. B.

Dicarboxylic acid esters of tetrahydrofurfuryl alcohol. J. N. BORGLIN (Ind. Eng. Chem., 1936, 28, 35—36).—Tetrahydrofurfuryl alcohol reacts (48 hr.; 170—190°) with the calc. amount of terpinene, maleic, maleic, or phthalic anhydride to form the corresponding acid ester or di-ester. F. N. W.

Production of furfuraldehyde from xylose solutions by means of hydrochloric acid-sodium chloride systems. E. I. FULMER, L. M. CHRISTENSEN, R. M. HIXON, and R. L. FOSTER (J. Physical Chem., 1936, 40, 133—141).—Xylose-HCl-NaCl mixtures were refluxed with PhMe and the furfuraldehyde (I) yields determined from the *d* of the resulting (I)-PhMe solutions. The yield of (I) diminishes as the concn. of xylose increases, being twice as great for 4% as for 60% xylose. It increases with increasing concn. of NaCl, *i.e.*, it is a linear function of the p_{H} or of the activity coeff. of the acid. M. S. B.

Terpene furoates. J. N. BORGLIN (Ind. Eng. Chem., 1936, 28, 31—32).—Borneol and fenchyl alcohol heated (40 hr.; 160°) with furoic acid give, respectively, *bornyl*, b.p. 275°/760 mm., and *fenchyl furoate*, b.p. 275°/760 mm., hydrogenated (PtO₂) to fenchyl tetrahydrofuroate. F. N. W.

Orientation in the dibenzfuran series. W. G. BYWATER, E. W. SMITH, G. E. BROWN, and H. GILMAN (Proc. Iowa Acad. Sci., 1934, 41, 166).—Sulphonation and chlorination take place at position 2, nitration at position 3, whilst metals attack in position 4. Rules governing the position of entry of a second substituent are given. Sulphonation of *dibenzfuran-2-sulphonic acid* yields the *-2:8-disulphonic acid*; nitration of 2-bromo- and bromination of 3-nitro-dibenzfuran give the same *7-bromo-3-nitro-dibenzfuran*. Bromination of *3-acetamidodibenzfuran* yields *2-bromo-3-aminodibenzfuran*. CH. ABS. (r)

Constituents of *Matteucia orientalis*. II. Constitution of demethoxymatteucinol. S. FUJISE and T. NISHI (J. Chem. Soc. Japan, 1934, 55, 1020—1023, 1024—1027; cf. A., 1935, 91).—II. Condensation of dimethylphloroglucinol with cinnamoyl chloride affords *5:7-dihydroxy-6:8-dimethylflavanone*, m.p. 202.7—203°; although the m.p. is lowered about 1° on admixture with demethoxymatteucinol, the identity of all other properties leads to the conclusion that they are identical. CH. ABS. (r)

General method for synthesis of flavonol derivatives. T. OYAMADA (J. Chem. Soc. Japan, 1934, 55, 1256—1261).—Flavonols are formed when *o*-hydroxychalkones are treated with H₂O₂ in the presence of dil. alkali. Several examples are given. *3-Methoxyflavone* has m.p. 114°. CH. ABS. (r)

Preparation of homogeneous anthocyanins by chromatographic analysis. P. KARRER and F. M. STRONG (Helv. Chim. Acta, 1936, 19, 25—28).—Al₂O₃, activated by cautious treatment with tap-H₂O, is a suitable adsorbent for anthocyanins. Since the slightly basic material partly converts the oxonium salt into colour base, carbinol base, and phenolbetaine, a given pigment does not necessarily produce a homogeneous zone. Pæonin, obtained according to Willstätter *et al.* (A., 1915, i, 288), is found to contain cyanin; the colour of a solution of the pure material and FeCl₃ in EtOH is unchanged by addition of H₂O. H. W.

Pigments of cotton flowers. II.—See this vol., 395.

Bark of *Terminalia arjuna*. I. Arjunin.—See this vol., 395.

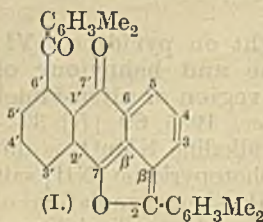
Catalytic chlorination of dioxan. J. J. KUCERA and D. C. CARPENTER (J. Amer. Chem. Soc., 1935, 57, 2346—2347).—Dioxan and Cl₂ in presence of a little SnCl₂ or I at 90° give 96.6% of the 2:3-Cl₂-derivative, chlorinated further (in absence or presence of catalyst) at 145° to 83—85% of a mixture of *s*-(32%) and *as*-Cl₂-derivatives. H. B.

Dioxan series. II. Aryl-substituted dioxans. **Synthesis of *p*-dioxen.** R. K. SUMMERBELL and L. N. BAUER (J. Amer. Chem. Soc., 1935, 57, 2364—2368; cf. A., 1934, 80).—2:3-Diphenyl-, m.p.

49—50°, 2:3-*di-o*-, m.p. 105.7—106.2° (corr.), -*m*-, m.p. 84.2° (corr.), and -*p*-, m.p. 56—57.2° (corr.), -*tolyl*-, 2:3-*di-p-chlorophenyl*-, m.p. 152—153° (corr.), 2:3-*di-p-anisyl*-, m.p. 79—80.2° (corr.), 2:3-*di-α-naphthyl*-, b.p. 255—258°/3—4 mm., 2:3-*dixenyl*-, m.p. 144.5—146° (corr.), and 2:3-*dibenzyl*-, m.p. 62.2° (corr.), -*dioxans* are prepared from 2:3-dichlorodioxan (I) and MgRX. The main product from (I) and MgMeBr, MgEtBr, or MgBuBr is *p-dioxen* (II), O<CH₂·CH₂ / CH=CH>O, b.p. 94.2°/749.9 mm. [ozonolysis products, HCO₂H and C₂H₄(OH)₂]; small amounts of the 2:3-dialkyldioxans (Et₂, b.p. 164—175°/747.9 mm.; Bu₂, b.p. 120—122°/16—17 mm.; not characterised) are also produced. (II) and Hal in CCl₄ at 0° give (I) and 2:3-*dibromodioxan*, m.p. 69—70° (softens at 64°). (I) and HCl at 0° afford *chlorodioxan* (III), b.p. 62—63°/14 mm., which is unstable even at room temp.; in presence of a little BiCl₃, a polymeride of (II) results. (III) and MgPhBr give *phenyldioxan*, m.p. 45—46°. Chlorination of dioxan (IV) to (I) is considered to occur thus: (IV) → (III) → (II) → (I). H. B.

Dimorphism of rotenone. E. L. GOODEN and C. M. SMITH (J. Amer. Chem. Soc., 1935, 57, 2616—2618).—Rotenone exists in two enantiotropic forms, m.p. 163° (stable) and approx. 180° (unstable); optical data are given. H. B.

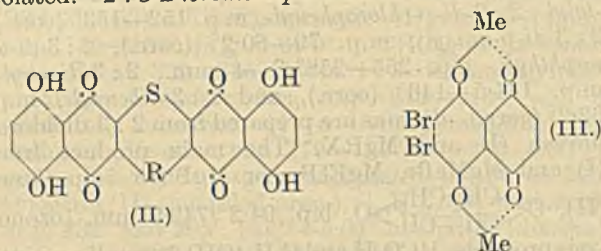
6:7-Benzoylene-ββ'-benzofurans from 1:5-diaroylanthraquinones. R. SCHOLL and S. HASS (Ber., 1936, 69, [B], 194—197).—1:5-Di-*m*-xyloylanthraquinone is transformed by Na₂S₂O₄ in boiling 80—85% EtOH in absence of air into *9-hydroxy-1:5-di-m-xyloylanthr-10-one*, m.p. 230° in a preheated bath (pyridinium salt; *p-bromobenzoate*, m.p. 288°), which in indifferent media or when subjected to pressure passes into an equilibrium mixture with 1:5-di-*m*-xyloylanthraquinol. It is converted by boiling AcOH or conc. H₂SO₄ at 15—20° into *2-m-xylyl-6:7-6'-m-xyloylobenzoylene-ββ'-benzofuran* (I), m.p. 193°, which is not reduced by Na₂S₂O₄ and NaOH and suffers fission of the furan ring with hot C₅H₅N-NaOH. H. W.



and NaOH and suffers fission of the furan ring with hot C₅H₅N-NaOH. H. W.

Tetrahydroxydibenzothianthrenediquinone; chemistry of naphthazarin. K. BRASS, R. PFLUGER, and K. HONSBURG (Ber., 1936, 69, [B], 80—87).—The interaction of Na₂S (1.5 mols.) with dibromonaphthazarin (I) does not proceed as smoothly as with 2:3-dichloro-*α*-naphthaquinone, but gives Na₁, Na₃, and Na₅ derivatives converted by dil. acid into *tetrahydroxydibenzothianthrenediquinone* (II; R=S), m.p. > 300°, best obtained from (I) and Na₂S (1 mol.) at 200°. (II) cannot be acetylated, but is reduced and then benzoylated to *octabenzoyldibenzothianthren*, m.p. 283°. It is not attacked by cold conc. or fuming HNO₃ and is completely oxidised by the hot reactants. The complex course of the prep. is shown by the occasional formation of the *compound* (II; R=S·S). *Dibromonaphthazarin Me₂ ether* (III), m.p. 179—180°, and Na₂S give products containing

Br from which a homogeneous material could not be isolated. 2:3-Dibromonaphthazarin is best obtained



by the action of a slight excess of Br on naphthazarin in AcOH; it does not react with CH_3N_2 or Me_2SO_4 , but is transformed by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ and anhyd. Na_2CO_3 in $o\text{-C}_6\text{H}_4\text{Cl}_2$ at 170° into (III). Under similar conditions naphthazarin affords the Me_2 ether, m.p. 160° . Reasons are advanced for assigning the above constitution to (III) and for considering its reduction product to be 2:3-dibromo-1:4-dihydroxy-5:8-dimethoxynaphthalene. H. W.

Syntheses by means of magnesylypyrroles. Series II. XXI. B. ODDO and G. ACUTO (Gazzetta, 1935, 65, 1029—1036).—Mg 2:5-dimethylpyrrol bromide in Et_2O with AcCl yields 3-acetyl-2:5-dimethylpyrrole, m.p. 89° [semicarbazone, m.p. 234° (decomp.)]. The 3-propionyl, m.p. 102.5° [semicarbazone, m.p. 197° (decomp.)], 3-butyryl, m.p. 60° , and 3-benzoyl, m.p. 132° , compounds are similarly prepared. With $\text{CO}_2\text{Et}\cdot\text{COCl}$, Et 2:5-dimethylpyrrol-3-glyoxylate, m.p. 83.5° , is obtained, hydrolysed to the acid, m.p. $196\text{--}197^\circ$ (decomp.) (NH_4 , Pb^{++} , and other salts); this gives, when heated, an aldehyde, and, with $\text{EtOH}\cdot\text{NH}_3$ at 120° , 2:5-dimethylpyrrol-3-glyoxamide, m.p. 225° (decomp.). E. W. W.

Occurrence of piperidine in black pepper.—See this vol., 395.

Action of ultra-violet light on pyridine. VI. Reactions of photopyridine and behaviour of pyridine derivatives in the region of ultra-violet radiations. H. FREYTAG (Ber., 1935, 69, [B], 32—40; cf. A., 1934, 303).—Dil. alkaline KMnO_4 is unsuitable for the detection of photopyridine [NH_4 salt of enolglutacondialdehyde (I)], since irradiation of H_2O causes formation of H_2O_2 . The applicability of dimedon (I), 1-phenyl-3-methylpyrazol-5-one (II), and indole (III) has therefore been tested with the Na salt of (I); coloured derivatives are obtained which could not be completely purified. Anaesthesin (IV), however, yields glutacondianæstheside, m.p. about $154\text{--}155^\circ$. The effect of irradiation of $\text{C}_5\text{H}_5\text{N}$, 2-, 3-, and 4-methyl-, 2:4- and 2:6-dimethyl-, 2:4:6-trimethyl-, and 2-benzyl-pyridine in presence of (I), (II), (III), and (IV), respectively, is tabulated, whereby it appears that Me in position 3 hinders the photo-reaction. Several $\text{C}_5\text{H}_5\text{N}$ derivatives become coloured yellow to yellowish-brown in H_2O or EtOH, but do not give an aldehydic reaction. Substances with halogen and carbalkoxy-groups become hydrolysed and give halogen ions. 5-Bromo-3-aminopyridine becomes very rapidly discoloured with elimination of Br; since discoloration commences at the boundary of solution and air a photo-oxidative attack on the NH_2 appears to occur. This applies also to 5-amino-

2-methylpyridine, whereas 5-aminopyridine-3-carboxylic acid is unaffected. 4-Chloropicolinic acid and 4-chloro-2-aminopyridine are resistant to irradiation, whilst pyridine-2:3-dicarboxylic acid and -3-carboxydiethylamide are completely unchanged. The behaviour of $\cdot\text{CHO}$ in 5:6-dichloropyridine-3- and 4:6-dichloropyridine-2-aldehyde is uncertain. 4-Iodopyridine-2-carboxylic acid yields I formed by photo-oxidation of primarily-formed HI. Et₂ 2:6-dimethylpyridine-3:5-dicarboxylate is rapidly hydrolysed.

H. W.

Alkylated benzeneazoaminopyridines.—See B., 1936, 124.

Aldehydes of the indole series.—See B., 1936, 140.

Condensation of indolealdehydes with hippuric acid. E. RESTELLI (Anal. Assoc. Quim. Argentina, 1935, 23, 58—62).—Indole-3-aldehyde and hippuric acid, when heated with NaOAc in addition to Ac_2O , give 2-phenyl-4-(1'-acetylindolylidene)oxazolone, m.p. 205° (2'-Me derivative, m.p. 185°). F. R. G.

Catalytic decomposition of ethyl propyl ketone phenylhydrazone. A. E. ARBUSOV and I. A. ZAITZEV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 33—38; cf. A., 1932, 1236).—A substance, $\text{C}_{12}\text{H}_{15}\text{N}$, b.p. $167^\circ/15$ mm. (picrate, m.p. 144°), is obtained, which may be either 2:3-diethyl- or 2-methyl-3-propyl-indole. CH. ABS. (r)

Quinolone-acids from oxindole derivatives. E. ZRIKE and H. G. LINDWALL (J. Amer. Chem. Soc., 1936, 58, 49—50).—Isatin (I) and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$ in $\text{EtOH}\cdot\text{NHEt}_2$ at room temp. for 5 days give 3-hydroxy-3- α -carbethoxybenzylloxindole, m.p. $154\text{--}156^\circ$, converted by warm 1% NaOH into (I) and by conc. HCl-EtOH into 2-keto-3-phenyl-1:2-dihydroquinoline-4-carboxylic acid. 3-(Dicyanomethylene)oxindole (II) (Walter, A., 1902, i, 373) is reduced (aq. $\text{Na}_2\text{S}_2\text{O}_4$) to 3-(dicyanomethyl)oxindole, m.p. $183\text{--}185^\circ$ (darkens about 160°), which is unstable in hot solvents and is converted by 10% NaOH (or acid) into 2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylic acid (III). $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ and (I) in EtOH-piperidine afford 3-(cyanoformamidomethylene)oxindole, m.p. $248\text{--}250^\circ$; this and (II) are hydrolysed (conc. HCl) to a dibasic acid, $\text{C}_{11}\text{H}_7\text{O}_5\text{N}$, m.p. $>340^\circ$ (Ag_2 salt; Et₂ ester, m.p. $150\text{--}151^\circ$), also formed from Et₂ oxindole-3:3-dimalonate (A., 1935, 758) and 10% NaOH, which is reduced (Zn, AcOH or Na-Hg, H_2O) to (III). H. B.

Amino-compounds of the quinoline series.—See B., 1936, 92.

Preparation of 4-alkyl- and 4-aryl-quinolines. J. KENNER and F. S. STATHAM (Ber., 1936, 69, [B], 16—18).—The following % yields of 4-arylquinolines are obtained from the requisite arylamine and Cl₂-ketone (cf. Blaise *et al.*, A., 1907, i, 241) without and with PhNO_2 (1 mol.), As_2O_5 (0.5 mol.), $\text{SnCl}_4\cdot 8\text{H}_2\text{O}$ (1 mol.), and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (2 mols.) as oxidising agent: 4-phenyl (10, —, —, 52.6, —); *p*-tolyl- (7, 9, 14, 36.6, 44.6); 2-methoxy-5-methylphenyl- (5, —, —, 37.5, —), and β -naphthyl- (—, —, —, 41, —) quinoline. The respective % yields of 4-alkylquinolines with PhNO_2 (1 mol.), SnCl_4 (1 mol.), $\text{SnCl}_4\cdot 8\text{H}_2\text{O}$ (1 mol.),

and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2 mols.) as oxidants are as follows: Me- (28, 21, 40, 35—40); Et- (20, —, 40, —); Pr^a- (25, —, 40, —); Bu^a- (28, —, 40, —).

C_{10}H_8 , $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{COCl}$, and AlCl_3 in CS_2 afford β -chloroethyl 2-naphthyl ketone, m.p. 83° , converted by KOH at 280° into 2- $\text{C}_{10}\text{H}_7 \cdot \text{CO}_2\text{H}$ and by $\text{NPh} \cdot \text{NH}_2$ in warm EtOH into 1-phenyl-3- β -naphthylpyrazoline, m.p. 181 — 182° . The picrates, m.p. 200° (decomp.), 205° (decomp.), and 185 — 189° (decomp.), of 4-ethyl-, 4-*n*-propyl-, and 4-*n*-butyl-quinoline, respectively, are described.

H. W.

Tetrahydrocarbazoles with substituents in the 7-position. S. G. P. PLANT and (MISS) K. M. ROGERS (J.C.S., 1936, 40—41).—9-Acetyltetrahydrocarbazole (I), AcBr, and AlCl_3 give 7:9-diacetyltetrahydrocarbazole, m.p. 110° , hydrolysed to 7-acetyltetrahydrocarbazole (II), m.p. 206 — 208° , which is dehydrogenated (S) to 2-acetylarbazole and reduced (Zn—Hg) to 7-ethylhexahydrocarbazole, m.p. 44 — 46° . (I) and BzCl afford 7-benzoyl-9-acetyl-, m.p. 126° , hydrolysed to 7-benzoyl-, m.p. 165° , which is also obtained from 7:9-dibenzoyl-tetrahydrocarbazole, m.p. 121° . 9-Benzoyl-7-acetyltetrahydrocarbazole, m.p. 149° , hydrolysed to (II), is similarly obtained.

F. R. S.

Chemotherapeutic studies in the acridine series. I. 2:6- and 2:8-Diaminoacridines. A. ALBERT and W. H. LINNELL (J.C.S., 1936, 88—93).—Na 2-chloro-4-nitrobenzoate, *m*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, and Cu yield 5:5'-dinitrodiphenylamine-2-carboxylic acid (I), m.p. 263° (Ag salt), reduced (SnCl_2 —HCl) to 3:3'-diaminodiphenylamine, m.p. 94.5 — 95° (Ac_2 derivative, m.p. 211°), also obtained by reduction of 3:3'-dinitrodiphenylamine, m.p. 186.5° . Ring-closure of (I) yields a mixture of 5-chloro-2:6- (II), m.p. 200 — 203° (principally), and 2:8-dinitroacridine (III), with 2:6- and 2:8-dinitroacridone. (II) is hydrolysed (HCl) to 2:6-dinitroacridone, reduced to the 2:6-(NH_2)₂-compound (+0.5 H_2O), m.p. 306° , which with HCl gives 2:6-diaminoacridine, m.p. 213 — 216° (decomp.). 2:8-Diaminoacridine, obtained from (III), forms dibenzylidene, m.p. approx. 370° (decomp.), Ac_2 , m.p. above 350° , and Bz₂ derivatives, m.p. above 350° .

F. R. S.

10-Hydroxyacridone and "acridol." II. A. KIEGL and A. BRÖSAMLE (Ber., 1936, 69, [B], 197—202; cf. A., 1914, i, 867).—Oxidation of acridine (I) in C_6H_6 with BzO_2H affords acridine 10-oxide, identical with "acridol" (loc. cit.; cf. Tanasescu et al., A., 1934, 1010; Lehmstedt, A., 1935, 1251). Similar treatment of 5-methoxyacridine gives 5-methoxyacridine 10-oxide (II), m.p. about 158° (also +1 H_2O), which is not identical with the Me ether obtained by methylation of 10-hydroxyacridone (III) (Kiegl, loc. cit.). Both ethers give 10-hydroxyacridone when treated with HCl and decompose at about the same temp. into CH_2O and (I), but (II) is pronouncedly basic and dissolves readily in 2*N*-HCl at 15 — 20° . (III) is tautomeric, the free compound passing under the influence of alkali into 5-hydroxyacridine 10-oxide.

H. W.

2:8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-groups on the 5-carbon atom. V. Synthesis of 5-amino-2:8-dialkoxy-10-alkylacridinium hydroxides. VI.

Synthesis of 5-amino-2:8-dialkoxy-10-alkylacridinium iodides. VII. Synthesis of 5-amino-2:8-dialkoxy-10-alkylacridinium oxalates. VIII. Synthesis of 5-amino-2:8-dialkoxy-10-alkylacridinium derivatives and 5-(2':8'-dialkoxy-N'-alkylacridonamino)-2:8-dialkoxy-10-alkylacridinium derivatives. IX. Synthesis of (2':8'-dialkoxy-10'-alkyl-10'-substituted-acridine)-5:5'-ethylenediamino-2:8-dialkoxy-10-alkylacridinium derivatives. K. ISHIHARA (J. Chem. Soc. Japan, 1934, 55, 945—958, 1028—1039, 1040—1050, 1185—1206, 1277—1294; cf. A., 1935, 1132).—V. The following 5-anilino-, 5-o-, -m-, and -p-toluidino-, and 5-p-phenetidino-derivatives of substituted-acridinium hydroxides have been prepared by hydrolysis of the chlorides: 2:8-dimethoxy-10-methyl-, m.p. 148 — 149° , 133 — 134° , 137 — 138° , 133 — 134° , 180° ; 2:8-dimethoxy-10-ethyl-, m.p. 145 — 146° , 157 — 158° , 165 — 166° , 167 — 168° , 154 — 155° ; 2:8-diethoxy-10-methyl-, m.p. 164 — 165° , 131 — 132° , 172 — 173° , 158 — 159° , 167 — 168° ; 2:8-diethoxy-10-ethyl-, m.p. 156° , 138 — 139° , 176° , 174 — 175° , 171° .

VI. The acridinium iodide derivatives (as above) are obtained from the hydroxides and AcOH—KI: 2:8-dimethoxy-10-methyl-, m.p. 237 — 238° , 236 — 237° , 243 — 244° , 253 — 254° , 238° ; 2:8-dimethoxy-10-ethyl-, m.p. 249° , 224 — 225° , 243 — 245° , 230 — 231° , 227 — 228° ; 2:8-diethoxy-10-methyl-, m.p. 252 — 253° , 248° , 263° , 257° , 251° ; 2:8-diethoxy-10-ethyl-, m.p. 255° , 248° , 262° , 274° , 234 — 235° .

VII. Similarly the corresponding 20 oxalates are prepared from the hydroxides and $\text{H}_2\text{C}_2\text{O}_4$ in AcOH; respective m.p., in the order given above, are: 232° , 214 — 215° , 220 — 221° , 214 — 215° , 180° ; 206 — 207° , 200 — 201° , 204 — 205° , 184 — 185° , 209° ; 231 — 232° , 210 — 211° , 212 — 213° , 224 — 226° , 202 — 203° , 212° , 234 — 235° , 212 — 214° , 212° , 218 — 219° .

VIII. 5-Amino-2:8-dimethoxy-10-methylacridinium chloride (I), m.p. 324 — 325° , is prepared from the 5-Cl-compound with aq. NH_3 . The corresponding hydroxide, m.p. 74 — 78° , iodide, m.p. 339 — 340° , and oxalate, m.p. 252 — 253° , are described. (I), with AcOH, yields 2:8-dimethoxy-5-(2':8'-dimethoxy-N'-methylacridonamino)-10-methylacridinium chloride, m.p. 269 — 270° . The following are prepared similarly: 5-amino-2:8-dimethoxy-10-ethylacridinium chloride, m.p. 282 — 283° (hydroxide, m.p. 140 — 142° ; iodide, m.p. 294° ; oxalate, m.p. 190°); 2:8-dimethoxy-5-(2':8'-dimethoxy-N'-ethylacridonamino)-10-ethylacridinium iodide, m.p. 295° ; 5-amino-2:8-diethoxy-10-methylacridinium chloride, m.p. 311 — 312° (hydroxide, m.p. 153 — 154° ; iodide, m.p. 312° ; oxalate, m.p. 228°); 2:8-diethoxy-5-(2':8'-diethoxy-N'-methylacridonamino)-10-methylacridinium chloride, m.p. 287 — 288° (iodide, m.p. 288 — 290°); 5-amino-2:8-diethoxy-10-ethylacridinium chloride, m.p. 294 — 295° (hydroxide, m.p. 149 — 150° ; iodide, m.p. 303° ; oxalate, m.p. 237 — 238°); 2:8-diethoxy-5-(2':8'-diethoxy-N'-ethylacridonamino)-10-ethylacridinium chloride, m.p. 218° (iodide, m.p. 269°).

IX. 5-Chloro-2:8-dimethoxy-10-methylacridinium chloride with $(\text{CH}_2\text{NH}_2)_2$ yields (10'-hydroxy-2':8'-dimethoxy-10'-methylacridino)-5:5'-ethylenediamino-2:8-dimethoxy-10-methylacridinium hydroxide, m.p. 230° (tetrapicrate, m.p. 231 — 232°); this with AcOH

affords (10'-chloro-2': 8'-dimethoxy-10'-methylacridino)-5: 5'-ethylenediacetamido-2: 8-dimethoxy-10-methylacridinium chloride, m.p. 250°. The 10'-chloro-chloride, m.p. 231—232°, 10'-iodo-iodide, m.p. 282—283°, and 10'-oxalato-oxalate, m.p. 233—234°, are obtained similarly. The following are described: (10'-hydroxy-2': 8'-dimethoxy-10'-ethylacridino)-5: 5'-ethylenediamino-2: 8-dimethoxy-10-ethylacridinium hydroxide, m.p. 218—220°, and the derived 10'-chloro-chloride, m.p. 253°, 10'-iodo-iodide, m.p. 271—272°, and 10'-oxalato-oxalate, m.p. 235°; (10'-hydroxy-2': 8'-diethoxy-10'-methylacridino)-5: 5'-ethylenediamino-2: 8-diethoxy-10-methylacridinium hydroxide, m.p. 236—238°, and the derived 10'-chloro-chloride, m.p. 267—268°, 10'-iodo-iodide, m.p. 290°, and 10'-oxalato-oxalate, m.p. 253°; (10'-hydroxy-2': 8'-diethoxy-10'-ethylacridino)-5: 5'-ethylenediamino-2: 8-diethoxy-10-ethylacridinium hydroxide, m.p. 204—206°, and the derived 10'-chloro-chloride, m.p. 241—242°, and 10'-oxalato-oxalate, m.p. 249—250°.

CH. ABS. (r)

Action of alkalis and alkali salts on antipyrine. L. E. HARRIS and E. D. TEBOW (J. Amer. Pharm. Assoc., 1935, 24, 1069—1070).—The immiscible liquid obtained on the addition of antipyrine to conc. solutions of alkalis or alkali salts is apparently an isomeride. E. H. S.

Derivatives of 1:3-diaryl-5-pyrazolones and of 1:1'-diaryl-3:3'-arylene-5:5'-bispyrazolones.—See B., 1936, 92.

Alkylglyoxalidines. H. C. CHITWOOD and E. E. REID (J. Amer. Chem. Soc., 1935, 57, 2424—2426).—2-Methylglyoxalidine (I), m.p. 105° (205°), obtained in 68% yield when (·CH₂·NHAc)₂ is heated with Mg powder at 270°, is hydrolysed (aq. alkali) to (·CH₂·NH₂)₂. 2-Ethyl-, m.p. 38.1° (137.1°), 2-propyl-, m.p. 35.3° (129°), 2-butyl-, m.p. 41° (125.8°), 2-amyl-, m.p. 33.8° (128.4°), 2-hexyl-, m.p. 46.2°, 2-heptyl-, m.p. 60° (104.8°), 2-octyl-, m.p. 52.1°, 2-nonyl-, m.p. 71.4° (122°), 2-decyl-, m.p. 79.5° (82°), and 2-undecyl-, m.p. 79.8° (61.5°), -glyoxalidines are similarly obtained (in some cases Mg is replaced by Na) in 5.6—49% yield from the appropriate (·CH₂·NH·COR)₂. The temp. given in parentheses are m.p. of the picrates; the aurichlorides are analysed. The toxicity (towards *Lupinus albus* and animals) of the first 5 compounds decreases with increase in size of the alkyl group. (I) and Br in CHCl₃ give (probably) the N-Br-derivative hydrobromide, hydrolysed (H₂O) to (I).

H. B.

Preparations of methyl β-(ζ-methyl-Δ⁷-heptenyl)amine.—See B., 1936, 124.

Piperazine. VIII. Condensation with aldehydes. W. T. FORSEE, jun., and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 2363—2364).—Piperazine (I) and RCHO in presence or absence of solvent give insol. products of the type (·N<C₂H₄>N·CHR)_n; those where R=H, m.p. > 300° [also formed from (I) and CH₂I₂], Ph, m.p. 270° (decomp.) [also formed from (I) and CHPhCl₂], *o*-OH·C₆H₄·, m.p. 210° (decomp.), *p*-C₆H₄Me·, m.p. 275° (decomp.), *o*-C₆H₄Cl·, m.p. 240° (decomp.), and *p*-OMe·C₆H₄·, m.p. 290° (decomp.), are described. *N*-Phenylpiperazine with

CH₂O, MeCHO, PhCHO, *o*-C₆H₄Me·CHO, and *o*-OMe·C₆H₄·CHO gives di-(*N*-phenyl-*N'*-piperazyl)-methane, m.p. 123—124° (also formed using CH₂I₂), -ethane, m.p. 121—123°, -phenylmethane, m.p. 125—126°, -*o*-tolylmethane, m.p. 144—144.5°, and -*o*-anisylmethane, m.p. 135—136°, respectively. H. B.

Synthesis of 6-amino-4-ethylpyrimidine. W. T. CALDWELL and W. M. ZIEGLER (J. Amer. Chem. Soc., 1936, 58, 78—79).—6-Hydroxy-2-ethylthiol-4-ethylpyrimidine [best prepared from EtCO·CH₂·CO₂Et and SET·C(NH)·NH₂, HBr in MeOH—KOH at 0°] is hydrolysed to 4-ethyluracil, m.p. 204—205°, converted by POCl₃ into 2: 6-dichloro-4-ethylpyrimidine, b.p. 90—95°/4 mm., 103—107°/7 mm., which with red P and HI (b.p. 127°) gives 6-hydroxy-4-ethylpyrimidine hydriodide, m.p. 170.5—171.5° (sinters at 160°). This with POCl₃ affords 6-chloro-4-ethylpyrimidine, b.p. 193°, which with EtOH·NH₃ at 150° gives 6-amino-4-ethylpyrimidine (+3H₂O), m.p. 47.5—48°, m.p. (anhyd.) 87.5—88° (picrate, m.p. 204—205°; hydrochloride, m.p. 198—199°; aurichloride, m.p. 150—151°). H. B.

Reaction products of aromatic amidines with diketones, dialdehydes, and their monoximes. J. B. EKELEY and J. L. ELLIOTT (J. Amer. Chem. Soc., 1936, 58, 163—164).—The following 5-hydroxy-2-phenyl-4-arylpyrimidines are prepared (cf. A., 1936, 1133) from NH₂·CPh·NH (I), (CHO)₂, and the appropriate ArCHO in aq. EtOH—KOH at room temp.: 4-*o*-carboxyphenyl, m.p. 259—260°; 4-*o*-, m.p. 260°, and -*p*-, m.p. 305—306°, -chlorophenyl; 4-2': 4', m.p. 248—249°, -2': 5', m.p. 268—269°, and -3': 4', m.p. 259—260°, -dimethoxyphenyl; 4-*p*-dimethylamino-phenyl, m.p. 277—278°, 4-*p*-phenetyl, m.p. 292—293°; 4-*m*-hydroxyphenyl, m.p. 265—265.5°; 4-dibromo-2'-hydroxyphenyl, m.p. 311°; 4-*o*-hydroxybenzyl, m.p. 287—288°; 4-5'-nitro-2'-hydroxyphenyl, m.p. > 300°; 4-*p*-cumyl, m.p. 246—247°; 4-6'-methoxy-*m*-tolyl, m.p. 253—254°; 4-3': 4'-methylenedioxyphenyl, m.p. 283—287°; 4-*m*-tolyl, m.p. 237—238°. The following 5-hydroxy-2-*m*-tolyl-4-arylpyrimidines are similarly prepared from (CHO)₂, *m*-C₆H₄Me·C(NH)·NH₂ (II), and ArCHO: 4-2': 4', m.p. 250—251°, -2': 5', m.p. 229—230°, and -3': 4', m.p. 238—239°, -dimethoxyphenyl; 4-*p*-phenetyl, m.p. 237—238°; 4-*p*-cumyl, m.p. 263—264°; 4-*o*-, m.p. 272—273°, and -*p*-, m.p. 227—229°, -anisyl; 4-3': 4'-methylenedioxyphenyl, m.p. 249—249.5°, -methoxy-*m*-tolyl, m.p. 237—239°. Phenanthraquinone with (I), (II), and *o*-C₆H₄Me·C(NH)·NH₂ (as hydrochlorides) in 50% alkali gives compounds: C₂₁H₁₄ON₂, m.p. 277—278°, C₂₂H₁₆ON₂, m.p. 269—270°, and C₂₃H₁₈ON₂, m.p. 287.5—288°, respectively. (I) and (II) with CAcMe·N·OH similarly afford compounds, C₁₅H₂₂O₄N₄, m.p. 105—107°, and C₁₆H₂₄O₄N₄, m.p. 94—96°, respectively. Phenanthraquinoneoxime (in amyl alcohol) with (I), (II), and *p*-C₆H₄Me·C(NH)·NH₂ (in CHCl₃+KOH) gives compounds, C₂₁H₁₇O₂N₃, m.p. 186°, C₂₂H₁₉O₂N₃, m.p. 165—166°, and C₂₂H₁₉O₂N₃, m.p. 182—183°, respectively. A compound, C₁₅H₁₆O₂N₃, m.p. 145.8° is described. H. B.

Synthesis of nitrated 2:3-dihydropyrimidazole. O. BREMER (Annalen, 1936, 521, 286—297).—With SOCl₂, 3-nitro-4-β-hydroxyethylaminopyrimidine gives the 4-β-chloroethylamino-compound, m.p. 104°.

reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to 3-amino-4- β -chloroethylamino-pyridine, m.p. 85—80°. 3-Nitro-4- β -hydroxyethoxy-pyridine, m.p. 112—113° [from 4-chloro-3-nitropyridine, Na and $(\text{CH}_2\cdot\text{OH})_2$], similarly affords the 4- β -chloroethoxy-compound, m.p. 70—71°, sinters 44°. 4-Chloro-3-nitropyridine, m.p. 74—75° (lit. m.p. 45°), is reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to the 3- NH_2 -compound, m.p. 82°. 2-Chloro-5-nitropyridine (I) and its 3-Br-derivative with $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ in EtOH at 100° give, respectively, 5-nitro-2- β -hydroxyethylaminopyridine (II), m.p. 131—132° (hydrochloride, m.p. 182°), and its 3-Br-derivative (III), m.p. 136°; 2-chloropyridine gives 2- β -hydroxyethylamino-, m.p. 65° (hydrochloride, m.p. 158.5°), converted by SOCl_2 into 2- β -chloroethylamino-pyridine (IV) (hydrochloride, m.p. 146°). (I) and $(\text{CH}_2\cdot\text{OH})_2\text{-Na}$ give 5-nitro-2- β -hydroxyethoxy-, m.p. 113—114°, converted (SOCl_2) into 2- β -chloroethoxy-pyridine, m.p. 131—132°, converted by NHET_2 into 5-nitro-2- β -diethylaminoethoxy-pyridine, b.p. 170°/3 mm. [reduced by SnCl_2 and condensed with $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ to give the 5- p -dimethylaminobenzylideneamino-derivative, m.p. 163—164° (picrate, m.p. 131°)], also obtained from (I) and $\text{NET}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{ONa}$ in Et_2O . Similarly (I) and the appropriate base afford 5-nitro-2- β -aminoethylamino-, m.p. 123°, 2- β -(diethylamino)ethylamino-, 2- β -hydroxydiethylamino- (V), m.p. 59—60°, and 2-allylamino-, m.p. 97° [converted by HBr to 2- β -bromopropylamino- (VI)], -pyridine. (VI) is converted by warming in H_2O into 5-nitro-3-methyl-2:3-dihydropyriminazole, m.p. 185°. Gentle heat converts (IV) into dihydropyriminazolium chloride, converted by KOH into 2:3-dihydropyriminazole, m.p. 64—65° (picrate, m.p. 213°), also obtained by the action of SOCl_2 and alkali on 1- β -hydroxyethylpyridoneimine (Kunjanjanz, A., 1935, 627). SOCl_2 converts (II), (III), and (V) into, respectively, 5-nitro- (VII), m.p. 258° (decomp.) (chloride, not melting at 280°), 7-bromo-5-nitro-, m.p. 222° (decomp.) [also from (VII) and Br-AcOH at 100°], and 5-nitro-8-hydroxy-1-ethyl-2:3-dihydropyriminazole. J. W. B.

$\alpha\beta$ -Naphthoquinoxaline-2:3-dicarboxylic acid. G. B. CRIPPA and G. PERRONCITO (Annali Chim. Appl., 1935, 25, 618—620).—1-Benzeneazo- β -naphthylamine condenses with $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ at 190° to form *Et*, $\alpha\beta$ -naphthoquinoxaline-2:3-dicarboxylate (I), m.p. 119°, and a substance, m.p. 205—210°. (I) is hydrolysed to the dicarboxylic acid, m.p. 195° (decomp.) (anhydride, m.p. 235°). E. W. W.

Pyrrrole-blues. III. P. PRATESI and A. ZANETTA (Atti R. Accad. Lincei, 1935, [vi], 22, 159—165).—Isatin (1 mol.) in AcOH with 2:3:4-trimethylpyrrrole (1 mol.) yields 3-(3':4':5'-trimethyl-2'-pyrrrolyl)oxindole. Oxidation of opopyrrrole-blue (A., 1935, 1134) with H_2O_2 or CrO_3 affords isatin and methylethylmaleinimide; that of pyrrole-blue B (I) (A., 1905, i, 841; 1907, i, 657) gives maleinimide and isatin. Dry distillation of (I) in a vac. affords oxindole. The production of isatin-5-sulphonic acid indicates that the sulphonic acid of (I) (*ibid.*) is 3-(2'-pyrrrolyl)oxindole-5-sulphonic acid. The constitution of the pyrrole-blues is discussed. F. O. H.

Indoles and isatogens. XXI. Condensation of the three phthalaldehydes with nitrated tolu-

enes and preparation of di-isatogens. P. RUGGLI and E. WOLFF (Helv. Chim. Acta, 1936, 19, 5—15).— $p\text{-C}_6\text{H}_4(\text{CHO})_2$ and 2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$ in presence of piperidine at 160° give 2:4:2':4'-tetranitro-*p*-distyrylbenzene, m.p. 294°, transformed by Cl_2 in AcOH at 110° into the corresponding tetrachloride, m.p. (indef.) 92—99°, which passes in boiling $\text{C}_5\text{H}_5\text{N}$ into 2:4:2':4'-tetranitro-*p*-dichlorostyrylbenzene (I), m.p. 248°. Protracted insolation of (I) suspended in $\text{C}_5\text{H}_5\text{N}$ yields 6:6'-dinitro-2:2'-*p*-phenylenedi-isatogen, $p\text{-C}_6\text{H}_4(\text{C} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{NO} \end{array} \text{C}_6\text{H}_3\cdot\text{NO}_2)_2$, m.p. 294°, reduced by $\text{NHPh}\cdot\text{NH}_2$ in EtOH at 100° to dinitro-*p*-phenylenedi-indoxyl, isolated as the Ac_2 derivative, gradual decomp. > 280°. Similarly, $m\text{-C}_6\text{H}_4(\text{CHO})_2$ gives 2:4:2':4'-tetranitro-*m*-distyrylbenzene, m.p. 243°, the tetrachloride, m.p. (indef.) 90—108°, of which gives 2:4:2':4'-tetranitro-*m*-dichlorostyrylbenzene, m.p. 215°, whence 6:6'-dinitro-2:2'-*m*-phenylenedi-isatogen, m.p. 289° (decomp.), reduced to dinitro-*m*-phenylenedi-indoxyl (Ac_2 derivative, m.p. 304°). Under like conditions *o*- $\text{C}_6\text{H}_4(\text{CHO})_2$ undergoes one-sided condensation giving *o*-2':4'-dinitrostyrylbenzaldehyde, m.p. 186° (phenylhydrazone, m.p. 193°). $p\text{-C}_6\text{H}_4(\text{CHO})_2$ and *o*-nitro-*p*-toluonitrile give 2:2'-dinitro-4:4'-dicyano-*p*-distyrylbenzene, m.p. 350° (decomp.), whence the corresponding tetrachloride, m.p. 278°, 2:2'-dinitro-4:4'-dicyano-*p*-dichlorostyrylbenzene, m.p. 296°, and (?) 6:6'-dicyano-2:2'-*p*-phenylenedi-isatogen, blackens > 300°. 2:2'-Dinitro-4:4'-dicyano-*m*-distyrylbenzene, m.p. 298°, gives a tetrachloride, m.p. (indef.) 80—100°, or cryst. m.p., 248°, and thence 2:2'-dinitro-4:4'-dicyano-*m*-dichlorostyrylbenzene, m.p. 268°, and 6:6'-dicyano-2:2'-*m*-phenylenedi-isatogen, decomp. about 300° after darkening at 270°. *o*-2'-Nitro-4'-cyanostyrylbenzaldehyde, m.p. 210°, and its phenylhydrazone, m.p. 182°, are described. H. W.

Quaternary ammonium compounds of derivatives of the anthracene series [mainly pyrimidines].—See B., 1936, 140.

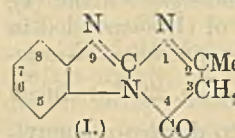
Absorption spectra of 1:2:3-benzotriazoles. A. K. MACBETH and J. R. PRICE (J.C.S., 1936, 111—119).—1:2:3-Benzotriazole and its derivatives absorb in two main regions, the shorter-wave region being attributed to an electron in the C:C system of the C_6H_6 nucleus, and the other being assigned to the N:N of the triazole ring. Introduction of alkyl substituents into the nucleus results in improved separation of the two regions. No absorption characteristic of NO_2 is observed unless an aq. solvent is used or OMe or OH is present in the triazole ring. 1-Hydroxy-1:2:3-benzotriazole and its 6-Me derivative exist in EtOH as equilibrium mixtures of two tautomeric forms, whilst $\text{NO}_2\text{-OH}$ -compounds exist as the stable OH-form in EtOH and aq. solution. Displacements of the max. are found, on change of solvent from EtOH to H_2O , in the $\text{NO}_2\text{-OH}$ -compound. 3-Nitro-4-chlorotoluene with N_2H_4 gives 1-hydroxy-6-methyl-1:2:3-benzotriazole, m.p. 178—179°.

F. R. S.

New soluble derivative of caffeine. G. BARGIONI (Boll. Chim. farm., 1935, 74, 869—871).—Bromocaffeine and $\text{CHNa}(\text{CO}_2\text{Et})_2$ give *Et*, caffeine-

malonate, converted into the acid, and into caffeine-acetic acid, of which the very sol. Na salt has the pharmacological character of caffeine, without toxicity. E. W. W.

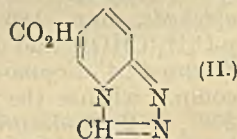
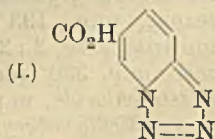
A new heterocyclic grouping: benzopyrimidazole. C. B. CRIPPA and G. PERRONCITO (Gazzetta, 1935, 65, 1067—1070).—2-Aminobenzimidazole and



$\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ give 2-methyl-3:4-dihydrobenzopyrimidazol-4-one (I), m.p. 280° , converted by boiling CH_2 , 25% NaOH into β -2-benzimidazolyl-iminobutyric or -aminocrotonic acid, m.p. $> 300^\circ$. With

Br in AcOH (I) forms a 3:3- Br_2 -derivative, m.p. $> 300^\circ$. E. W. W.

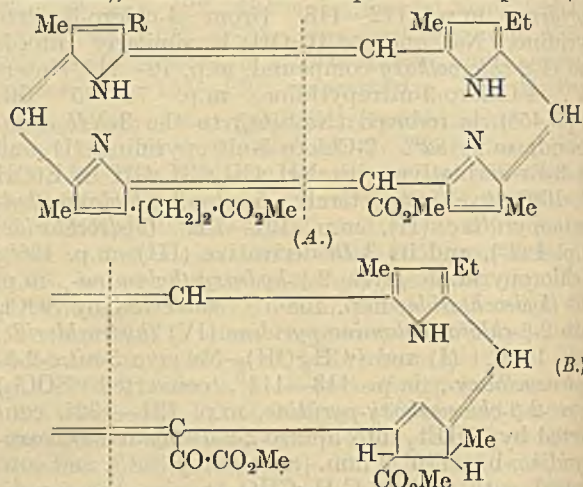
Stereochemistry of trivalent nitrogen. J. KENNER and F. S. STATHAM (Ber., 1936, 69, [B], 187—188).—The *brucine*, m.p. 240 — 244° , $[\alpha]_D^{18} +1.113^\circ$ in CHCl_3 , *quinine*, m.p. 205 — 210° , $[\alpha]_D^{17} -145.2^\circ$ in AcOH, *strychnine*, m.p. 220 — 224° , $[\alpha]_D^{17} -1.559^\circ$ in CHCl_3 and *cinchonine*, m.p. 220° , $[\alpha]_D^{21} +144.0^\circ$ in 10N-AcOH, salts of benzotriazolecarboxylic acid (I)



and the *brucine*, m.p. 218° , $[\alpha]_D^{20} -18.71^\circ$ in 10N-AcOH, and *quinine*, m.p. 135 — 145° , $[\alpha]_D^{17.5} -161.6^\circ$ in AcOH, salts of benzotriazolecarboxylic acid (II) give no indication (I) of the possible resolution of (I) and (II) into optical antipodes; a plane configuration of this type of compound of N^{III} is therefore regarded as established experimentally. H. W.

Chlorophyll. LXV. Synthesis of oxorhodophorphyrin, its conversion into 1:3:5:8-tetramethyl-4-ethyl-2-hydroxyethylporphin-6-carboxylic acid-7-propionic acid; pseudoverdoporphyrin. H. FISCHER and G. KRAUSS (Annalen, 1936, 521, 261—285).—Oxorhodophorphyrin Me_2 ester (I) (A, R=Ac) (A., 1934, 420; improved prep.) (semicarbazone, decomp. 270° ; h aem in, decomp. 287°) with cold Br-HCO $_2$ H affords (by replacement of 2-Ac by Br) the 2-Br-derivative (II), m.p. 300° (Cu complex salt, m.p. 268° , decomp. 278°), of 2-de-ethyl-rhodoporphyrin (III), m.p. 230 — 232° , which is obtained either by the resorcinol fusion of the h aem in of (II) (together with 2-de-ethylpyrroporphyrin) or, better, by KOH-MeOH hydrolysis of (II) and reduction with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -Pd-CaCO $_3$. Reacetylation of the h aem in ester of (III) with Ac_2O -SnCl $_4$ and re-esterification of the product with CH_2N_2 gives [2-de-ethyl]-2-acetyl-rhodoporphyrin Me_2 ester identical with (I), and reduced by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -3% NaOMe to rhodoporphyrin (IV). In agreement with the structure assigned oxidation of (I) with PbO $_2$ -H $_2$ SO $_4$ at 0° gives methylethylmaleimide. 2-Hydroxyethylrhodoporphyrin (V), m.p. 255° (loc. cit.; by MeOH-KOH reduction of the 2-Ac compound) (Cu complex salt, m.p. 222°), is reduced by AcOH-HI (d 1.96) to (IV), and is reoxidised by cold 20% oleum-S to the 2-Ac derivative. With HBr-AcOH at 45° and treatment of the product with KOH-MeOH, AcOH, and CH_2N_2

(V) gives a porphyrin with 3-OMe (partial ether formation), which does not depress the m.p. of (V),



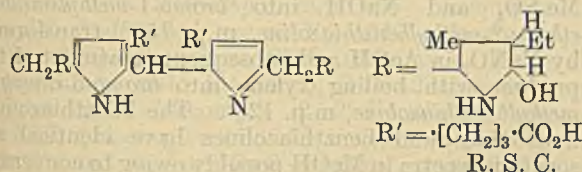
and could not be converted into the 2-vinyl derivative by heating with Cu powder in quinoline. The h aem in ester of (III) with $\text{CHCl}_2\cdot\text{OEt}$ -POCl $_3$ -SnCl $_4$ (cf. A., 1934, 1234) and subsequent re-esterification gives [2-de-ethyl]-2-formylrhodoporphyrin ester, m.p. 283° (VI) (oxime, m.p. 262°), converted by MgMeI in $\text{C}_5\text{H}_5\text{N}$ -Et $_2\text{O}$ into [2-de-vinyl]-2-hydroxyethylpseudoverdoporphyrin (VII), m.p. 250° . Treatment of the HBr-AcOH rearrangement product of pseudoverdoporphyrin Me_2 ester with KOMe-MeOH gives [2-de-vinyl]-2-methoxyethylpseudoverdoporphyrin ester, m.p. 196° , not identical with (VII), but with 20% aq. KOH the Me_2 ester, m.p. 252° , of (VII) is obtained. Pseudoverdoporphyrin (VIII) (A; R= $\text{CH}\cdot\text{CH}_2$) therefore contains a vinyl group and its Me_2 ester with Br-HCO $_2$ H followed by MeOH-KOH gives a Br-derivative, $\text{C}_{35}\text{H}_{46}\text{O}_5\text{N}_4\text{Br}$, m.p. 190° [side-chain $\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{OMe}$ or $\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\text{Br}$]. With $\text{CHN}_2\cdot\text{CO}_2\text{Me}$ the Me_2 ester of (VIII) gives the compound $\text{C}_{37}\text{H}_{46}\text{O}_6\text{N}_4$ (IX), m.p. 247° , and with PhN $_3$ it is converted into (VI). Ph aem purpurin 7 (X) must also contain a $\cdot\text{CH}\cdot\text{CH}_2$ group and its Me_2 ester reacts with $\text{CHN}_2\cdot\text{CO}_2\text{Me}$ to give a liquid product, converted by $\text{C}_5\text{H}_5\text{N}$ -MeOH into (IX). (X) has, therefore, the structure B (R= $\text{CH}\cdot\text{CH}_2$). With AcOH-HI (X) and purpurin 18 give a mixture of (IV) and its γ -carboxylic acid, and chlorin p_6 gives only the latter product. J. W. B.

Optical activity of horse's globin-haemochromogen and of haemoglobin.—See this vol., 221.

Porphyrin-gelatin phosphorescence. F. BANDO and E. J. KLAUS (Z. physiol. Chem., 1936, 238, 1—13).—The absorption and fluorescence spectra of porphyrins in gelatin films closely resemble the absorption spectra of solutions. The fluorescence spectra are less intense and the max. are shifted slightly towards the red. p_{H} has great influence, whether changed by buffering or by variation of the solvent used for the porphyrin. No chemical or physical change occurs during prep. of the films. R. S. C.

Constitution of stercobilin. H. FISCHER and H. HALBACH (Z. physiol. Chem., 1936, 238, 59—83).—Stereobilin (I) (modified prep.), $\text{C}_{33}\text{H}_{46}\text{O}_6\text{N}_4$, m.p. 236° ,

readily absorbs 2H in AcOH (Pd-black), but 4H in 0.05*N*-NaOH; it cannot be converted into or obtained from mesobilirubinogen (II). (II) with O₂ in HCl gives mesobiliviolin and a little urobilin [reduced to (II) by Na-Hg]. (I) and HNO₃ give (·CH₂·CO₂H)₂, but no methylethylmaleinimide which is readily so obtained from mesobilirubin (III) or glaucobilin (IV). (I) and HI-AcOH at 100° give pyrrole bases but no bilirubinic acid. With HBr-AcOH at 180° (I) gives an unidentified porphyrin. With PhN₂Cl (II) and (III) give the ester *hydrochloride*, m.p. 193°, of a dye, stercobilinogen gives an uncrystallisable dye, but (I) does not react; (I) also does not react with PhCHO. With conc. H₂SO₄ at 100° (I), (II), and (III) give (IV). (I) is strongly levorotatory (hydrochloride, [α]_D²⁰ -1733°, [α]_D^{15.500} -1007° in AcOH), but is readily racemised by various reagents. (I) is probably as shown. Opsopyrrole and *p*-C₆H₄Me·N₂Cl give a monoazo-dye, m.p. 238° (*hydrochloride*, m.p. 208°; *hydrobromide*, m.p. 185°; *picrate*, m.p. 182°).



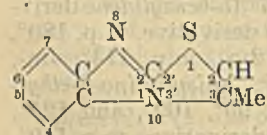
Preparation and tinctorial properties of benzoxazole dyes. V. J. MIKESKA and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 2513—2517).—A series of substantive cotton dyes are prepared from diazotised 4-phenyl-1-*p*-aminophenylbenzoxazole (I) [and its SO₃H derivative (II)] and 4-amino-1:6-diphenylbenzoxazole (III) (and its SO₃H derivative) by coupling with α - and β -C₁₀H₇·OH, PhOH, *m*-C₆H₄(OH)₂, and α -C₁₀H₇·NH₂; those prepared from (I) are more substantive than those from (III). The dyes resemble, but give lighter shades than, the corresponding derivatives from dehydrothio-*p*-toluidine (IV) (A., 1927, 679). Absorption curves for "ingrain red" [from (IV) and β -C₁₀H₇·OH] and "oxazole red" [from (II) and β -C₁₀H₇·OH] are given; the former shows wider absorption. Oxidation (aq. EtOH-NaOCl at 0—10°) of (I) gives pp'-*di*-(4-phenyl-1-benzoxazolyl)azobenzene, decomp. >300° [(SO₃Na)₂ derivative (V); (SO₃Na)₄ derivative, prepared by similar oxidation of 4-phenyl-1-*p*-aminophenylbenzoxaledisulphonic acid]. Similar "chloramine yellow" dyes are prepared from 1-*p*-aminophenyl-4-methylbenzoxazole [resembles (V)] and (III) [inferior to (V)]. Fabrics dyed directly retain (after 5 years) a better colour than those dyed by the "ingrain" process. H. B.

Pyridine and quinoline derivatives of dibenzfuran and their physiological properties. W. H. KIRKPATRICK and H. GILMAN (Proc. Iowa Acad. Sci., 1934, 41, 172).—The physiological properties of a no. of amino- and substituted amino-dibenzfurans and their nuclear reduction products have been studied. In many cases the NH₂-compounds undergo cyclisation, yielding pyridinodibenzfurans. CH. ABS. (r)

Alkyl derivatives of aryl-substituted thiazolidones. J. A. DAVIS and F. B. DAINS (J. Amer.

Chem. Soc., 1935, 57, 2627—2630; cf. A., 1933, 1174).—Alkylation (alkyl halide on Na salt in EtOH) of 2-arylamino-4-thiazolidones [prepared (a) from NHAr·CO·CH₂Cl and KCNS in EtOH, or (b) from NHAr·CS·NH₂ and equimol. amounts of CH₂Cl·CO₂Et and C₅H₅N in EtOH] gives generally a mixture of a little 2-arylimino-3-alkyl-4-thiazolidone (I) [the 5-benzylidene derivatives of which are hydrolysed (EtOH—conc. HCl) to NH₂Ar and 2:4-diketo-5-benzylidene-3-alkyltetrahydrothiazoles] and much 2-*N*-alkylarylamino-4-thiazolidone (II) (the 5-benzylidene derivatives are hydrolysed to NHArAlk and 2:4-diketo-5-benzylidenetetrahydrothiazoles). Certain exceptions are noted. (I) are also synthesised from CH₂Cl·CO₂Et and NHAr·CS·NHAlk. The 3-aryl-2-ethylimino-4-thiazolidones of Beckurts and Frerich (A., 1916, i, 744) are (II). The following are described: (a) substituted *thiocarbamides*: *p*-*cymyl*-, m.p. 152°; *N*-*o*-, m.p. 88°, and *p*-, m.p. 112°, -*ethoxyphenyl*-, *N*-*ψ*-*cumyl*-, m.p. 138°; *N*-*o*-, m.p. 77°, *m*-, m.p. 112°, and *p*-, m.p. 147°, -*anisyl*-, *N*-*p*-*cymyl*-, m.p. 126°, *N*-*p*-*iodophenyl*-, m.p. 147.5°, and *N*-2:4-*di*-*iodophenyl*-, m.p. 164°, -*N*'-*ethyl*-, *N*-*ψ*-*cumyl*-, m.p. 179°, and *N*-*p*-*iodophenyl*-, m.p. 171°, -*N*'-*methyl*-, *N*-*p*-*iodophenyl*-*N*'-*amyl*-, m.p. 130°, and -*N*'-*benzyl*-, m.p. 149°; (b) substituted 4-thiazolidones: 2-*p*-*ethoxyanilo*-3-*ethyl*-, m.p. 93° (5-benzylidene derivative, m.p. 135°); 2-*o*-*ethoxyanilino*-, m.p. 172°; 5-benzylidene derivative, m.p. 210°, of 2-*N*-ethyl-*p*-ethoxyanilino-; 2-*N*-ethyl-*o*-ethoxyanilino-, m.p. 99° (5-benzylidene derivative, m.p. 164°); 2-*o*-ethoxyanilo-3-*ethyl*-, m.p. 79° (5-benzylidene derivative, m.p. 113°); 2-*ψ*-*cumylimino*-3-*methyl*-, m.p. 91° (5-benzylidene derivative, m.p. 136°), and -3-*ethyl*-, m.p. 77° (5-benzylidene derivative, m.p. 141°); 5-benzylidene derivative, m.p. 180°, of 2-*N*-ethyl-*ψ*-*cumylamino*-; 2-*o*-, m.p. 114°, *m*-, m.p. 65—66°, and *p*-, m.p. 83°, -*anisylimino*-3-*ethyl*- (5-benzylidene derivatives, m.p. 99°, 109°, and 125°, respectively); the 5-benzylidene derivatives, m.p. 149°, 135°, and 198°, of 2-*N*-ethyl-*o*-, *m*-, m.p. 112°, and *p*-*anisidino*-, respectively; 2-*m*-*anisidino*-, m.p. 165°; 2-*p*-*cymylamino*-, m.p. 174°; 2-*N*-ethyl-*p*-*cymylamino*-, m.p. 85° (5-benzylidene derivative, m.p. 169°); 2-*p*-*cymylimino*-3-*ethyl*-, m.p. 64° (5-benzylidene derivative, m.p. 73°); 2-2':4'-*di*-*iodoanilino*-, m.p. 233°; 2-2':4'-*di*-*iodoanilo*-3-*ethyl*-, m.p. 173° (5-benzylidene derivative, m.p. 210—211°); 2-*p*-*iodoanilino*-, m.p. 226°; 2-*N*-*methyl*-, m.p. 207°, -*ethyl*-, m.p. 116°, -*amyl*-, m.p. 116°, and -*benzyl*-, m.p. 176°, -*p*-*iodoanilino*- (5-benzylidene derivatives, m.p. 246°, 231°, 202°, and 221°, respectively); 2-*p*-*iodoanilo*-3-*methyl*-, m.p. 152°, -*ethyl*-, m.p. 103°, -*amyl*-, m.p. 57°, and -*benzyl*-, m.p. 137° (5-benzylidene derivatives, m.p. 167°, 172°, 105°, and 162°, respectively); 2-*anilino*-3-*amyl*-, an oil (5-benzylidene derivative, m.p. 78°); 2-*benzylimino*-3-*benzyl*-, m.p. 74° (5-benzylidene derivative, m.p. 109°); (c) miscellaneous: *chloroacet*-2-*p*-*cymidide*, m.p. 85°, and -2:4-*di*-*iodoanilide*, m.p. 153°; *p*-*nitrobenz*-*o*-*phenetidide*, m.p. 155°; *benzenesulphon*-*N*-ethyl-*o*-*phenetidide*, m.p. 61°, -*N*-ethyl-*o*-*anisidide*, m.p. 90°, and -*N*-*methyl*-*p*-*iodoanilide*, m.p. 78°; *N*'-*phenyl*-*N*-*p*-*ethoxyphenyl*-*N*-ethyl-, m.p. 93°, and *N*-*p*-*tolyl*-*N*'-*o*-*ethoxyphenyl*-, m.p. 172°, -*carbamides*; 2:4-*diketo*-5-benzylidene-3-*amyl*-, m.p. 74°, and -3-*benzyl*-, m.p. 134°, -*tetrahydrothiazoles*. H. B.

Aneurine. II. Synthesis of N-arylthiazolium salts; details in the constitution of aneurine and thiochrome. A. R. TODD, F. BERGEL, and KARIMULLAH (Ber., 1936, 69, [B], 217—223).— CH_2PhBr and 2:4-dimethylthiazole at 100° give 3-benzyl-2:4-dimethylthiazolium bromide, m.p. 173°. Addition of thioacetmethylamide to $\text{CH}_2\text{Cl}\cdot\text{COMe}$ at 80° yields 2:3:4-trimethylthiazolium chloride, m.p. 235° (decomp.). Similarly thioacetanilide and $\text{CH}_2\text{Cl}\cdot\text{COMe}$ at 100° afford 3-phenyl-2:4-dimethylthiazolium chloride (I), m.p. 184° (decomp. in sealed capillary; corresponding picrate, m.p. 115°). If reaction is effected at 15—20°, S-acetylthioacetanilide hydrochloride (II), m.p. 112° [corresponding perchlorate, m.p. 130°, unstable free base and its semicarbazone, m.p. 230° (decomp.)], is formed. It passes at 100° into (I) and is hydrolysed by boiling H_2O or dil. acid to NH_2Ph , NHAcPh , and a substance (III), (?) $\text{SH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2)\cdot\text{S}\cdot\text{CH}_2\cdot\text{COMe}$ [semicarbazone, $\text{C}_7\text{H}_{13}\text{ON}_2\text{S}_2$, m.p. 213° (decomp.)]. 3-o-Tolyl-2:4-dimethylthiazolium chloride, perchlorate, m.p. 172°, picrate, m.p. 150°, and iodide, m.p. 217—218° (decomp.), are obtained analogously. S-Acetylthioacet-o-toluidide hydrochloride, m.p. 125°, is more stable than (II); its hydrolysis leads to o- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$, and (III). o- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ is converted by cautious treatment with P_2S_5 into o-nitrothioacetanilide, m.p. 114°, whence 3-o-nitrophenyl-2:4-dimethylthiazolium perchlorate, m.p. 205°. Determination of C-alkyl by oxidation with CrO_3 of thiazolium, pyrimidine, and allied compounds shows that Williams' pyrimidine compound from aneurine (IV) contains only one alkyl; (IV) and thiochrome



(V.)

each contains two alkyls, the higher val. indicated (Kuhn) for (IV) being observed with other compounds which lose CMe quantitatively. o- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ and $\text{CS}(\text{NH}_2)_2$ yield thiobenziminazoline, m.p. 295—300°, converted by $\text{CH}_2\text{Cl}\cdot\text{COMe}$ into 3-methylthiazolo-2':3':2:1-glyoxaline (V), m.p. 164—165°.

H. W.

1-Amino-5-ethoxy-2-methylbenzthiazolium hydroxide and its derivatives. O. BEHAGHEL and E. SCHNEIDER (Ber., 1936, 69, [B], 88—98).—Repetition of the work of Hunter *et al.* (A., 1930, 1452) shows that *p*-ethoxyphenylthiocarbamide is transformed by an excess of Br in CHCl_3 into bromo-1-amino-5-ethoxybenzthiazole (I), m.p. 196°, and by the calc. quantity into 1-amino-5-ethoxybenzthiazole, m.p. 162°. Treatment of (I) with Me_2SO_4 yields the corresponding methosulphate, converted by NaOH into bromo-1-imino-5-ethoxy-2-methylbenzthiazoline, m.p. 144°, also derived from *as-p*-ethoxyphenylmethylthiocarbamide, m.p. 139° (prepared from *N*-methyl-*p*-phenetidine hydrochloride and NH_4CNS), and Br in CHCl_3 . *N*-Methyl-*p*-phenetidine and KCNS in 95% AcOH are transformed by Br in warm AcOH into 1-amino-5-ethoxy-2-methylbenzthiazolium bromide, decomp. 295°, whereas in MeOAc the corresponding thiocyanate, m.p. 187°, is produced. Treatment of the salts with cold Na_2CO_3 affords 1-amino-5-ethoxy-2-methylbenzthiazolium hydroxide (II), m.p. about 64°, which readily loses H_2O when kept over H_2SO_4

giving 1-imino-5-ethoxy-2-methylbenzthiazoline (III), m.p. 98°. 1-Amino-5-ethoxybenzthiazole (III) is transformed by Me_2SO_4 at 100° into 1-amino-5-ethoxy-2-methylbenzthiazolium methosulphate, m.p. 187—189°, converted by NaOH into 1-methylimino-5-ethoxy-2-methylbenzthiazoline, m.p. 86°. 1-Amino-5-ethoxy-2-methylbenzthiazolium iodide, m.p. 245°, results from (II) and HI or from (IV) and MeI in MeOH at 100°, whilst the corresponding chloride, m.p. 308° (decomp.), is obtained from (II) and boiling HCl. The presence of NH in (III) is established by the isolation of 1-nitrosoimino-5-ethoxy-2-methylbenzthiazoline, which evolves N_2 quantitatively when boiled with xylene and gives 5-ethoxy-2-methylbenzthiazolone, m.p. 87°. (III) is converted by boiling Ac_2O , BzCl, or valeric anhydride, respectively, into 1-acetimido-, m.p. 172°, 1-benzimido-, m.p. 191°, and 1-valerimido-, m.p. 119°, -5-ethoxy-2-methylbenzthiazoline, which essentially yield salts with mineral acids. Bromo-1-amino-5-ethoxy-2-methylbenzthiazolium methosulphate is transformed by Me_2SO_4 and NaOH into bromo-1-methylimino-5-ethoxy-2-methylbenzthiazoline, m.p. 158°, transformed by NaNO_2 in AcOH and subsequent treatment of the product with boiling xylene into bromo-5-ethoxy-2-methylbenzthiazolone, m.p. 126°. The benzthiazolium hydroxides and benzthiazolines have identical absorption spectra in MeOH possibly owing to conversion of the former into the latter. The absorption spectra of 2-methylated benzthiazole, benzoxazole, benz-selenazole, and benziminazole are compared. *p*-Chlorophenyl-thioacetic and -selenolacetic acid have closely similar absorption spectra which differ considerably from that of *p*-chlorophenoxyacetic acid.

H. W.

Compounds for treatment of textiles [benzthiazoles].—See B., 1936, 92.

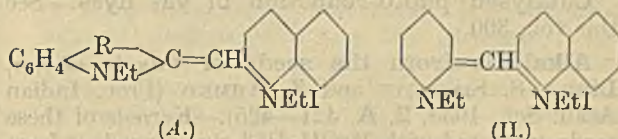
Cyanine dye series. II. Carbocyanines with substituents in the three-carbon chain. L. G. S. BROOKER and F. L. WHITE (J. Amer. Chem. Soc., 1935, 57, 2480—2488).—Substituted thiocarbocyanine iodides, $\text{C}_6\text{H}_4\langle\text{S}\rangle\text{C}\cdot\text{CH}\cdot\text{CR}'\cdot\text{CH}\cdot\text{C}\langle\text{S}\rangle\text{C}_6\text{H}_4$, are prepared from various ortho-esters (I), *e.g.*, $\text{CR}'(\text{OMe})_3$ ($\text{R}'=\text{H}$, Me, Et, Pr, Bu, amyl, CH_2Ph , $\text{OPh}\cdot\text{CH}_2$, Ph) and 1-methylbenzthiazole alkiodides or alk-*p*-toluenesulphonates (followed by aq. KI) in boiling $\text{C}_5\text{H}_5\text{N}$. The following are described: 2:2'-diallyl-, m.p. 264—266° (decomp.); 2:2'-di-*n*-propyl-, m.p. 296—297° (decomp.); 2:2'-di-*n*-butyl-, m.p. 275—277° (decomp.); 8-methyl-2:2'-diallyl-, m.p. 267—268° (decomp.), -2:2'-di-*n*-propyl-, m.p. 295—296° (decomp.), and -2:2'-di-*n*-butyl-, m.p. 236—237° (decomp.); 2:2'-dimethyl-8-ethyl-, m.p. 286—287° (decomp.); 2:8:2'-triethyl-, m.p. 236—237° (decomp.); 8-ethyl-2:2'-diallyl-, m.p. 214—216° (decomp.), -2:2'-di-*n*-propyl-, m.p. 248—250° (decomp.), and -2:2'-di-*n*-butyl-, m.p. 241—243° (decomp.); 2:2'-dimethyl-8-*n*-propyl-, m.p. 268—269° (decomp.), -8-*n*-butyl-, m.p. 168—169° (decomp.), -8-*n*-amyl-, m.p. 217—219° (decomp.), -8-isoamyl-, m.p. 241—242° (decomp.), -8-benzyl-, m.p. 288—289° (decomp.), -8-phenoxyethyl- (bromide), m.p. 255—257° (decomp.), and -8-phenyl-, m.p. 275—277° (decomp.); 2:2'-diethyl-8-*n*-propyl-, m.p. 246—

248° (decomp.), -8-*n*-butyl-, m.p. 233—234° (decomp.), -8-*n*-amyl-, m.p. 237—238° (decomp.), -8-*iso*amyl-, m.p. 219—220° (decomp.), -8-*benzyl*-, m.p. 242—243° (decomp.), -8-*phenoxy*methyl-, m.p. 202—204° (decomp.), and -8-*phenyl*-, m.p. 300—301° (decomp.); 8-*benzyl*-, m.p. 225—227° (decomp.), and 8-*phenoxy*methyl-, m.p. 211—213° (decomp.), -2:2'-*diallyl*-. In the above series introduction of 8-Me (for H) causes a shift in the absorption max. (in MeOH) of about 150 Å. towards the blue; replacement of 8-Me by Et (or higher alkyl) causes a shift of about 50 Å. back towards the red. The following substituted 5:6:5':6'-*dibenzthiacarbocyanine bromides* are similarly prepared from (I) and 1-methyl- α -naphthothiazole meth-*p*-toluenesulphonate, m.p. 232—233°, or etho-*p*-toluenesulphonate followed by aq. KBr: 2:2'-*dimethyl*-, m.p. 285° (decomp.); 2:2'-*diethyl*-, m.p. 280° (lit. 274°) (decomp.); 2:8:2'-*trimethyl*-, m.p. 278—281° (decomp.); 8-*methyl*-2:2'-*diethyl*-, m.p. 261° (decomp.); 2:2'-*dimethyl*-8-*ethyl*-, m.p. 299° (decomp.); 2:8:2'-*triethyl*-, m.p. 296° (decomp.); 8-*phenyl*-2:2'-*dimethyl*-, m.p. 308—310° (decomp.), and -2:2'-*diethyl*-, m.p. 296° (decomp.). 2:2'-*Dimethyl*-, m.p. 237° (decomp.), 2:8:2'-*trimethyl*-, m.p. 240—241° (decomp.), 2:2'-*dimethyl*-8-*ethyl*-, m.p. 230° (decomp.), 2:8:2'-*triethyl*-, m.p. 247° (decomp.), and 8-*phenyl*-2:2'-*dimethyl*-, m.p. 242—244° (decomp.), and -2:2'-*diethyl*-, m.p. 252° (decomp.), -3:4:3':4'-*dibenzthiacarbocyanine bromides* are similarly obtained from 2-methyl- β -naphthothiazole meth-*p*-toluenesulphonate, m.p. 189—190°, or the etho-*p*-toluenesulphonate. 1-Methylbenzselenaazole meth- and etho-*p*-toluenesulphonates lead to 2:8:2'-*trimethylselena*carbocyanine bromide, m.p. 290—291° (decomp.), and 2:2'-*dimethyl*-8-*ethyl*-, m.p. 271—272° (decomp.), 2:8:2'-*triethyl*-, m.p. 146—148°, and 8-*phenyl*-2:2'-*dimethyl*-, m.p. 271—272° (decomp.), and -2:2'-*diethyl*-, m.p. 280—281° (decomp.), -*selena*carbocyanine iodides. 2:8:2'-*Trimethyl*-, m.p. 290—292° (decomp.), 2:2'-*dimethyl*-8-*ethyl*-, m.p. 280—282° (decomp.), and 2:8:2'-*triethyl*-, m.p. 269—270° (decomp.), -*oxa*carbocyanine iodides, prepared from the appropriate benzoxazole salts and (I) in $C_5H_5N \cdot NEt_3$, are sensitizers for the green and blue-green. Absorption curves for many of the dyes are given. The following are new: *Me ortho*-propionate, b.p. 126—128°, -*n*-butyrate, b.p. 145—147°, -*n*-valerate, b.p. 167—170°, -*n*-hexoate, b.p. 187—190°, and -*isohexoate*, b.p. 178—181°; *Et ortho*-phenoxyacetate, b.p. 99—100°/1.5 mm., and -*benzoate*, b.p. 239.5—240.5°; 1-methylbenzthiazole *n*-propionide, m.p. 173—175°, *n*-butiodide, m.p. 186—187°, allyliodide, m.p. 192—193°, and meth-*p*-toluenesulphonate, m.p. 183.5—184.5°.

H. B.

Cyanine dye series. III. Improvements in the 2'-cyanine condensation. L. G. S. BROOKER and G. H. KEYES. **IV. [Thiazolo-2'-cyanines and related compounds.]** L. G. S. BROOKER, G. H. KEYES, and F. L. WHITE (J. Amer. Chem. Soc., 1935, 57, 2488—2492, 2492—2496).—III. 2:1'-*Diethyl*oxa-2'-cyanine iodide (A, R=O), m.p. 290—292° (decomp.), obtained in 43—56% yield from 2-iodoquinoline ethiodide (I) and 1-methylbenzoxazole ethiodide in EtOH-NEt₃, is best prepared using NPhEt₂ (at 100°

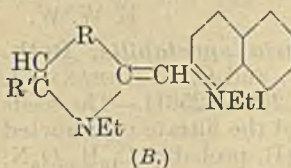
as the condensing agent; EtOH-KOH (cf. Hamer, A., 1928, 307) leads to a 3% yield. The following are prepared in yields of 10—87% usually in Pr^oOH-NEt₃: 2:1'-*diethylselena*-2'-cyanine iodide (A, R=Se), m.p. 280—282° (decomp.), from (I) and 1-methylbenzselenaazole ethiodide; 1:1'-*diethyl*-2-pyrido-2'-cyanine iodide (II), m.p. 237—239° (decomp.), from (I) and 2-methylpyridine ethiodide (III) or from 2-iodopyridine ethiodide (IV) and 2-methylquinoline ethiodide (thus affording further evidence of the virtual tautomerism of the cyanine dyes); 1:1'-*diethyl*-2-pyrido-4'-cyanine iodide, m.p. 194—196° (decomp.), from (IV) and 4-methylquinoline ethiodide;



1:1'-*diethyl*-4-pyrido-2'-cyanine perchlorate, m.p. 211—214° (decomp.), from (I) and 4-methylpyridine etho-*p*-toluenesulphonate (V) followed by aq. KClO₄; 1:1'-*dimethyl*-2:2'-pyridocyanine iodide, m.p. 315—317° (decomp.), from 2-iodopyridine methiodide (VI) and 2-methylpyridine methiodide; 1:1'-*diethyl*-2:2'-pyridocyanine iodide (VII), m.p. 237—239° (decomp.), from (III) and (IV); 1:1'-*dimethyl*-2:4'-pyridocyanine iodide, m.p. 214—217° (decomp.), from (VI) and 4-methylpyridine meth-*p*-toluenesulphonate; 1:1'-*diethyl*-2:4'-pyridocyanine iodide, m.p. 163—166° (decomp.), from (IV) and (V). Absorption curves for the above dyes are given. All the compounds containing the C₅H₅N ring show sensitising action.

IV. 2-Methylthiazole ethiodide, m.p. 195—197°, and 2-iodoquinoline ethiodide (I) in EtOH-NEt₃ give 3:1'-*diethyl*thiazolo-2'-cyanine iodide (B, R=S; R'=H), m.p. 267—269° (decomp.); the 4-*Me*, m.p. 255—257° (decomp.), and 4-*Ph*, m.p. 256—258° (decomp.), derivatives of this are similarly formed from (I) and 2:4-dimethylthiazole ethiodide and 4-*phenyl*-2-methylthiazole ethiodide, m.p. 175.5—176.5°, respectively.

Similarly, (I) with 2:4-dimethyl- (II) and 4-*phenyl*-2-methyl-oxazole etho-*p*-toluenesulphonates affords 4-*methyl*- (B, R=O; R'=Me), m.p. 255—258° (decomp.), and 4-*phenyl*-, m.p. 262—264° (decomp.), -3:1'-*diethyl*oxazolo-2'-cyanine iodide, respectively, whilst (I) and the ethiodide, m.p. 157—158°, of 2:4-dimethylselenaazole, b.p. 54—55°/12 mm. [from selenaacetamide (modified prep.) and COMe·CH₂Cl], give 4-*methyl*-3:1'-*diethylselena*azolo-2'-cyanine iodide (B, R=Se; R'=Me), m.p. 259—260° (decomp.). 2-Iodo- β -naphthquinoline ethiodide and the above S, O, and Se salts [except (II)] afford 3:1'-*diethyl*-, m.p. 268—270° (decomp.), 4-*methyl*-3:1'-*diethyl*-, m.p. 278—280° (decomp.), and 4-*phenyl*-3:1'-*diethyl*-, m.p. 274—276° (decomp.), -5':6'-*benz*thiazolo-, 4-*phenyl*-3:1'-*diethyl*-5':6'-*benz*oxazolo-, m.p. 279—282° (decomp.), and 4-*methyl*-3:1'-*diethyl*-5':6'-*benz*selenaazolo-, m.p. 275—277° (decomp.), -2'-cyanine iodides, respectively. 3:1'-*Diethyl*-, m.p. 260—262°



(decomp.), 4-methyl-3 : 1'-diethyl-, m.p. 255—257° (decomp.), and 4-phenyl-3 : 1'-diethyl-, m.p. 247—249° (decomp.), -thiazolo-, and 4-methyl-3 : 1'-diethylselenazolo-, m.p. 232—233° (decomp.), -2'-pyridocyanine iodides are prepared from 2-iodopyridine ethiodide and the above S and Se salts. All the above dyes are sensitizers; absorption spectra are given.

H. B.

Sensitisation of photographic emulsions.—See B., 1936, 125.

Manufacture of unsymmetrical heptacarbo-cyanine and hexamethine dyes.—See B., 1936, 93.

Catalysed photo-reduction of vat dyes.—See this vol., 300.

Alkaloids from the seeds of *Cassia absus*, Linn. S. SIDDIQUI and Z. AHMED (Proc. Indian Acad. Sci., 1935, 2, A, 421—425).—Kernels of these seeds extracted with MeOH-HCl give a product from which the quaternary alkaloids *chaksine* (I) and *iso-chaksine* (II) are separated through their iodides. *Chaksine iodide* (III), m.p. 168° (decomp.), is converted into the (impure) base, $[\alpha]_D^{25} + 32^\circ$ in EtOH, which absorbs CO₂ from the air to give *chaksine H carbonate*, C₁₂H₂₀ON₃·HCO₃·0.5H₂O, m.p. 167—169° (decomp.). *Chaksine sulphate* (IV), m.p. 316° (decomp.), and *picrate*, m.p. 239—240° (decomp.), are prepared; the *platinichloride*, (C₁₂H₂₀ON₃,HCl)₂PtCl₆, m.p. 232° (decomp.), loses HCl at 120°. *isoChaksine iodide* gives (II); this is also obtained by treating (IV) with Ba(OH)₂, and its *carbonate*, (C₁₂H₂₀ON₃)₂CO₃, m.p. 128° (decomp.), by heating *chaksine H carbonate* in EtOH. *isoChaksine chloride* loses H₂O at 90° to form a *product*, m.p. 250—252°; the *picrate* has m.p. 184°; the *platinichloride*, (C₁₂H₂₀ON₃,HCl)₂PtCl₆, m.p. 172° (decomp.), is stable at 120°. (III) gives no evidence of containing OMe or N-Me; (I) and (II) appear to be quaternary bases, with a second N feebly basic. (IV) is a general depressant (heart, respiration, nerves); lethal dose for frogs, 0.1 g. per kg.

E. W. W.

Alkaloid from *Crotalaria spectabilis*, Roth. W. M. NEAL, L. L. RUSOFF, and C. F. AHMANN (J. Amer. Chem. Soc., 1935, 57, 2560—2561).—The seeds are soaked in 5% aq. NH₃ and the filtrate is extracted with CHCl₃; *monocrotaline* (I), probably C₁₆H₂₆O₆N, m.p. 196—197°, is thus obtained. (I) is the toxic principle of *C. spectabilis*; pharmacological data are given.

H. B.

Alkaloid of *Stemona sessilifolia*. H. SCHILD (Ber., 1936, 69, [B], 74—80).—The isolation from *S. sessilifolia* is described of an alkaloid (I), m.p. 86—87°, b.p. about 220°/0.0006 mm., $[\alpha]_D^{20} - 47.1^\circ$ in CHCl₃, analyses of which together with those of its *perchlorate*, m.p. 243°, and *methiodide monohydrate* (II), decomp. 230—233°, agree most closely with the formula C₂₂H₃₃O₂N. (II) is transformed by AgCl into the *methochloride dihydrate*, m.p. 169°, and by Ag₂O into the *betaine*, C₂₃H₃₇O₅N₂·H₂O, decomp. 227—229°, which re-forms (II) when heated with HI. (I) is a *tert.* base which does not evolve CH₄ with MgMeI. 2 O are present in a lactone group, since it dissolves in 1 mol. of hot KOH. Further groups sensitive to alkali are not present. Catalytic hydrogenation of

(I) in neutral solution yields the *substance*, C₂₂H₃₅O₄N, m.p. 118—120°, $[\alpha]_D^{25} - 10.8^\circ$ in CHCl₃, whereas in acid solution a *compound*, C₂₂H₃₅O₄N, m.p. 134°, $[\alpha]_D^{25} - 13.2^\circ$ in CHCl₃ (*hydrochloride*), is produced. Since (I) does not give an ultra-violet absorption spectrum above 234—313 mμ the presence in it of an aromatic ring is excluded. The presence of a pyrrolidine ring is possible since in conjunction with I, MeI, or EtI it is oxidised by air to a neutral *substance*, C₂₂H₂₉O₄N, m.p. 186°, which retains the lactone ring, readily gives the Ehrlich pyrrole reaction, and has a characteristic ultra-violet absorption spectrum. Electrolytic reduction of (I) yields the di-deoxo-base, C₂₂H₃₇O₂N (*perchlorate*, m.p. 244—245°; *methiodide*, m.p. 261—262°), which does not contain a lactone group; the second replaced O is attributed to the presence of non-reactive CO. (I) is very stable towards HNO₃ and CrO₃ but is oxidised by KMnO₄-H₂SO₄ to *l*-methylsuccinic acid, m.p. 108—109°, $[\alpha]_D^{25} - 9.3^\circ$ in CHCl₃, and by alkaline KMnO₄ to a *substance*, C₁₇H₂₅O₃N, m.p. 134—135° after softening at 130°.

H. W.

Conessine series. I. Isomerisation of conessine and its nor-bases. S. SIDDIQUI (Proc. Indian Acad. Sci., 1935, 2, A, 426—437; cf. A., 1934, 787).—Conessine dissolved in cold conc. H₂SO₄, poured on to ice, and treated with NaOH, AcOH, and KI, gives, with oxidation products, the *hydriodide*, m.p. 325—326° (decomp.), of *isoconessine* (I), C₂₄H₄₀N₂, b.p. 239—241°/3 mm., $[\alpha]_D^{25} + 97^\circ$ in EtOH [*hydrochloride* (+2H₂O), m.p. 318° (decomp.), $[\alpha]_D^{25} + 72^\circ$; *platinichloride*, m.p. 271—273°; *aurichloride*, m.p. 293—295° (decomp.); *picrate*, m.p. 240—242° (decomp.); *hydrobromide* (II), m.p. 318—322° (decomp.); *dimethiodide*, m.p. 316—318° (decomp.)]. (I) with Br in CHCl₃ or AcOH yields (II) and an oily *product*. With H₂SO₄, *isoconessimine* similarly isomerises, to *isonorisocconessine* (III), C₂₃H₃₈N₂, $[\alpha]_D^{25} + 101^\circ$ in EtOH [*hydriodide*, m.p. 239° (decomp.); *hydrochloride*, m.p. 335° (decomp.), $[\alpha]_D^{25} + 72.80^\circ$ in H₂O; *picrate*, m.p. 166°; *platinichloride*, m.p. 290—292° (decomp.)]. (III) with MeI gives an ill-defined *product*, m.p. 280—300°; with CH₂O-HCO₂H followed by KI it furnishes the *hydriodide* of (I). (III) in HCl with NaNO₂ forms a *NO*-derivative (*hydrochloride*, m.p. 282—284°). Conimine in H₂SO₄ gives rise to *isoconimine* (IV), C₂₂H₃₆N₂, $[\alpha]_D^{25} + 89^\circ$ in EtOH [*hydriodide*, m.p. 332° (decomp.); *carbonate*; *hydrochloride*, m.p. 335—336° (decomp.); *picrate*, m.p. 135°; *platinichloride*, m.p. 285—286° (decomp.); (*NO*)₂, m.p. 123—125°, and Ac₂, m.p. 139—140° [*bromination product*, m.p. 185—186° (decomp.)], derivatives). The Me₂ derivative of (IV) (CH₂O-HCO₂H) is identical with (I). *isoConessine* is about three times as active (respiration of frogs) as conessine.

E. W. W.

Alkaloids of *Erythrophloeum guineense*. G. DALMA (Annali Chim. Appl., 1935, 25, 569—571).—From the bark of the West African red-water tree were isolated *cassaine*, C₂₄H₃₉O₄N, m.p. 141°, $[\alpha]_D^{20} - 103^\circ$ in EtOH, *cassaidine*, C₂₄H₄₃O₅N, m.p. 113°, *norcassaidine*, C₂₃H₄₁O₅N, m.p. 131°, and *omofteine*, C₅₆H₉₀O₉N₂. Colour reactions are given.

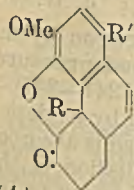
F. O. H.

Reduction in morphine series. VII. ψ -Codeinone. R. E. LUTZ and L. SMALL (J. Amer. Chem.

Soc., 1935, 57, 2651—2656).—The alicyclic double linking in ψ -codeinone (I) [*hydrochloride* (+H₂O) (II), m.p. 201—203° (decomp.)] is considered to be between C6 and C7 [as suggested by Gulland and Robinson (A., 1926, 83)] since treatment with an excess of semicarbazide gives (as with $\alpha\beta$ -unsaturated ketones) *semicarbazinodihydro- ψ -codeinonesemicarbazone* (+H₂O), m.p. 225—227° (uncorr.; decomp.). Condensation of (I), which is prepared by oxidation (method: Knorr and Hörlein, A., 1907, i, 547) of ψ -codeine or *allo- ψ -codeine*, with PhCHO does not indicate the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group since codeine undergoes the same reaction. Reduction (H₂, PtO₂, AcOH) of (II) affords the non-phenolic *dihydro- ψ -codeinone* (III), m.p. 113°, [α]_D²⁵ +37° in EtOH [*hydrochloride* (+H₂O), m.p. 172—173°; *hydriodide*, m.p. 250—255° (decomp.); *H tartrate* (?), m.p. 199—200° (uncorr.); *oxime*, m.p. 244—245°], reduced (Na, EtOH) to *dihydro- ψ -codeine-A* (A., 1933, 170) and converted by Ac₂O-NaOAc into *de-N-acetyldihydro- ψ -codeinone enol acetate*, m.p. 191.5—192°. Reduction (H₂, PtO₂, EtOH) of (I) gives the phenolic *tetrahydro- ψ -codeinone* (+0.5H₂O) (IV), m.p. 137—138.5°, m.p. (anhyd.) 170—171°, [α]_D²⁰ +8° in EtOH [*hydrochloride* (+2H₂O), m.p. 165—166° (decomp.); *hydriodide* (+H₂O), m.p. 154—155°; *Ac derivative*; *oxime*, m.p. 218—219° (lit. 137°)], which differs considerably from Hill's description (Diss., Frankfurt, 1925). (IV) does not react with CH₂N₂; it is reduced, as is (I), by Na and EtOH in N₂ to *tetrahydro- ψ -codeine*. Demethylation (48% HBr) of (III) gives *dihydroisomorphinone* (V), m.p. 198°, [α]_D²⁰ +46° in EtOH. (I) and MgMeI afford the phenolic *methylidihydro- ψ -codeinone* (VI), m.p. 213.5—214.5°, which could not be reduced (various methods); no oxime or semicarbazone could be prepared. (VI) may be formed by 1:2- or 1:4-addition involving fission of the $\cdot\text{O}\cdot$ ring. All m.p. are corr. unless stated otherwise. Pharmacological data for (III) and (V) are given. H. B.

Strychnos alkaloids. LXXXIX. Behaviour of strychninonic acid towards barium peroxide. H. LEUCHS and W. DIELS (Ber., 1936, 69, [B], 47—48).—Treatment of strychninonic acid with Ba(OH)₂ and H₂O₂ at 85—90° gives the *NH₂-acid* (I), C₁₈H₁₈O₄N₂, m.p. 248—255°, [α]_D²⁰ -18.8° in H₂O [*monoperchlorate*, m.p. 240—243° (decomp.) after softening at 230°, [α]_D²⁰ -17.4° (\pm 8°); *semiperchlorate*]. (I) with NaOH-MeOH-MeI gives the *product*, C₁₉H₂₀O₄N₂ (*perchlorate*, decomp. 262°), and a mixture of neutral products. H. W.

Sinomenine. XLIII. K. GOTO and H. SHISHIDO (Bull. Chem. Soc. Japan, 1935, 10, 597—600).—1-Bromodemethoxydihydrosinomenine methiodide (A., 1931, 1171) with hot 2% NaOH affords 1-bromode-N-methyl-demethoxydihydrosinomenine (A; R' = Br), m.p. 130°, [α]_D¹⁵ +7.00° in MeOH (*methiodide*, m.p. 278—279°), which gives a *racemate*, m.p. 148°, with 1-bromode-N-methylidihydro-codeinone, m.p. 132°, [α]_D¹⁵ -8.00° in MeOH. Similarly *de-N-methyl-demethoxydihydrosinomenine* (I) (A; R' = H), m.p. 120°, [α]_D¹⁵ +4.00° in MeOH, gives a



racemate, m.p. 114—116°, with *de-N-methyldihydro-codeinone* (II), [α]_D¹⁵ -4.00° in MeOH (Freund *et al.*, A., 1921, i, 125). Reduction (H₂-Pd-BaSO₄ in 0.3% HCl) of (I) gives its H₂-derivative, m.p. 93—97°, [α]_D¹⁵ +50.00° in EtOH, which gives a *racemate*, m.p. 113—116°, with the H₂-derivative, m.p. 95—98°, [α]_D¹⁵ -50.5° in EtOH, of (II). Catalytic reduction of thebaine in < N-HCl affords dihydrothebaine (III) and a little dihydrothebainone (IV); in 2.5N-HCl (IV), dihydrocodeinone (V), and metathebainone (VI), are obtained, whereas in 5N-HCl a 75% yield of (VI) is obtained (Cahn, A., 1933, 1061). (III) is hydrolysed by cold 2N-HCl to (V). The mixture (A., 1930, 1600) of demethoxydihydrosinomenine [(+)-dihydrothebainone] [*hydrobromide*, m.p. 291° (decomp.); *hydrochloride*, m.p. 293° (decomp.)] and demethoxydihydrosinomeninol [(+)-dihydrothebainol] is separated by dissolution in HBr or HCl, salts of the former crystallising. 1-Bromodemethoxydihydrosinomenine (*oxime*, m.p. 177—178°: the m.p. 263° given in A., 1930, 795, is that of the oxime hydrochloride) has been obtained in a form, m.p. 167°, [α]_D¹⁵ +78.67° in CHCl₃, which gives a *racemate*, m.p. 190—193°, with 1-bromodihydrothebainone. J. W. B.

New alkaloid of ergot. S. SMITH and G. M. TIMMIS (Nature, 1936, 137, 111).—Ergot contains an *alkaloid*, probably C₃₀H₃₅O₅N₅, decomp. approx. 228°, [α]_D²⁰ +522° in CHCl₃. L. S. T.

Dimorphism of ergometrine. R. L. GRANT and S. SMITH (Nature, 1936, 137, 154).—A second *modification*, m.p. 212° (decomp.), of ergometrine, m.p. 162—163° (decomp.), has been cryst. in long needles from COMe₂. The form of low m.p. tends to pass into the less fusible on keeping, and is the more sol. Both forms have [α]_D²⁰ +62.6°, [α]_D²⁰ +42.2° in EtOH. L. S. T.

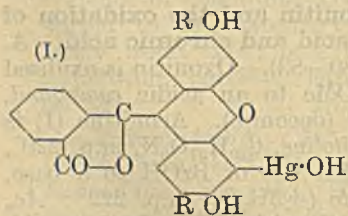
Aconitine. I. Oxonitin and the oxidation of aconitine with nitric acid and chromic acid. A. LAWSON (J.C.S., 1936, 80—83).—Oxonitin is oxidised (HNO₃) with loss of OMe to an *acidic compound*, C₃₁H₃₅O₁₄N₃, m.p. 263° (decomp.). Aconitine (I) is oxidised (CrO₃) to *aconitoline*, C₃₀H₃₇O₉N, m.p. 220°, hydrolysed (NaOEt) with loss of BzOH to a base, C₂₈H₃₃O₈N [*hydrochloride* (+3H₂O), m.p. 222°; *Ac₂ derivative*, m.p. 239°]. (I) with HNO₃ gives an *acid*, C₃₀H₃₅O₁₃N₂, m.p. 268° (decomp.), containing NO, hydrolysed with loss of BzOH and AcOH to a *substance*, C₂₂H₂₉O₁₁N₃, m.p. 201°, and with HCl converted into an *amino-acid*, C₃₁H₃₆O₁₂N₂·HCl·2H₂O, m.p. 218° (decomp.). Aconitine with HNO₃ yields a *nitroso-acid*, C₂₉H₃₃O₁₃N₃, m.p. 186° (decomp.), which with HCl forms an *NH₂-acid*, C₂₉H₃₁O₁₂N₂, m.p. 250° (decomp.), hydrolysed (NaOEt) to an *acid*, C₂₂H₃₀O₁₁N₂·HCl·H₂O, m.p. 218° (decomp.). Oxidation of (I) with HNO₂ gives a *substance*, C₃₁H₄₀O₁₂N₂, m.p. 276° (decomp.). These results are in agreement with the formula for (I) of Späth and Galinovsky (A., 1931, 1313). F. R. S.

Arsenical derivatives of thymol. V. BELLAVITA and M. BATTISTELLI (Annali Chim. Appl., 1935, 25, 631—634).—2-Aminothymol is diazotised and converted by As₂O₃ in NaOH (Cu) into 2-hydroxy-6-methyl-3-propylphenylarsinic acid (I), m.p. 189—190° (decomp.). (I) is resistant to reduction by H₃PO₂; with

$\text{Na}_2\text{CO}_3\text{-KI-SO}_2$ it gives after 10 days 2-hydroxy-6-methyl-3-propylphenylarsinoxide, unaltered at 320° . In EtOH with HCl (or HBr) and SO_2 , (I) yields respectively 2-hydroxy-6-methyl-3-propylphenyldichloro-, m.p. $60\text{--}62^\circ$, and dibromo-arsine, b.p. $140^\circ/12$ mm. With Br in AcOH, (I) forms 5-bromo-2-hydroxy-6-methyl-3-propylphenylarsinic acid, m.p. $204\text{--}205^\circ$; the corresponding 5-I-compound, m.p. 195° , is obtained in alkaline solution using 0.1N-I. (I) gives no colour with FeCl_3 . E. W. W.

Polymethylbenzenes. XIII. Mercuration. L. I. SMITH and F. L. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 2370—2372).—The hydrocarbons are heated with $\text{Hg}(\text{OAc})_2$ in MeOH-AcOH; the resulting OAc-Hg-derivatives (in CHCl_3 , EtOH, or EtOH- CHCl_3) with aq. EtOH-HCl, -NaBr, and -NaI (<1 equiv.) give the HalHg-compounds. The following are described: pentamethylbenzene (OAc-Hg-, m.p. 180° , ClHg-, m.p. 205° , and BrHg-, m.p. $195\text{--}196^\circ$, derivatives); durenene (OAc-Hg-, m.p. $158\text{--}159^\circ$, ClHg-, m.p. $188\text{--}189^\circ$, BrHg-, m.p. 174° , and IHg-, m.p. $161\text{--}162^\circ$, derivatives); isodurenene (OAc-Hg-, m.p. 108° , ClHg-, m.p. 174° , BrHg-, m.p. 160° , and IHg-, m.p. $163\text{--}164^\circ$, derivatives); prehnitene (OAc-Hg-, m.p. 147° , ClHg-, m.p. $216\text{--}217^\circ$, BrHg-, m.p. $213\text{--}214^\circ$, and IHg-, m.p. 200° , derivatives); mesitylene (OAc-Hg- derivative, m.p. $102\text{--}103^\circ$); ψ -cumene (5-OAc-Hg- derivative, m.p. $145\text{--}147^\circ$). $\text{Hg}(\text{C}_6\text{Me}_5)_2$, m.p. 278° (lit. 266°), and Hg diduryl, m.p. $242\text{--}243^\circ$, diisoduryl, m.p. $217\text{--}218^\circ$, and diprehnityl, m.p. 200° , are prepared from the appropriate IHg-derivative and NaI (4 mols.) in EtOH. H. B.

Antiseptics. Mercury salts of alkylfluoresceins. A. NOVELLI (An. Farm. Biochim., 1933, 4, 29—35; Chem. Zentr., 1935, i, 3691).—Mercuration of diacetyl-, dipropionyl-, diethyl-, dipropyl-, dibutyl-, and dihexyl-fluoresceins leads to Hg compounds (I). The antiseptic activity increases with increasing length of the side-chain, R. Presence of :CO in R diminishes antiseptic power.



(I). The antiseptic activity increases with increasing length of the side-chain, R.

H. N. R.

Action of radioactive substances on proteins.—See this vol., 301.

Multivalent amino-acids and peptides. VI.—See this vol., 379.

Influence of neutral salts on the optical rotation of gelatin. III, IV.—See this vol., 288.

Colloid chemistry of edestin. III.—See this vol., 288.

Salting-out and peptisation of edestin by mixtures of two salt solutions.—See this vol., 288.

Reducing groups of proteins. A. E. MIRSKY and M. L. ANSON (J. Gen. Physiol., 1936, 19, 451—459).—Proteins contain, besides SH groups, others which will react with $\text{K}_3\text{Fe}(\text{CN})_6$, and are probably in the tyrosine and tryptophan units. Their activity is enhanced by denaturation and by increase of p_{H} and

temp., but they differ from SH groups in that their activity depends on the concn. and time of exposure to $\text{K}_3\text{Fe}(\text{CN})_6$. F. A. A.

Thiol and disulphide groups of proteins. II. Relation between number of SH and S-S groups and quantity of insoluble protein in denaturation and in reversal of denaturation. III. Thiol groups of native proteins: haemoglobin and the proteins of the crystalline lens. A. E. MIRSKY and M. L. ANSON (J. Gen. Physiol., 1936, 19, 427—438, 439—450).—II. No SH groups are detectable (see A., 1935, 506) in native ovalbumin, but on heat-coagulation as many are found as in the fully hydrolysed protein. The same no. of them appears when ovalbumin is denatured by ultra-violet radiation, or at surfaces. The sol. fraction of partly heat-coagulated ovalbumin shows no SH. When serum-albumin is denatured, S-S groups appear, but disappear when denaturation is reversed.

III. Native haemoglobin and the proteins of the cryst. lens contain SH groups, the no. increasing with rise of p_{H} from 6.8 to 9.5. On denaturation, more SH groups appear; these latter are active at p_{H} vals. so low that those in the native proteins are barely detectable, and thus may be differentiated from them. At p_{H} 6.8, $\text{K}_3\text{Fe}(\text{CN})_6$ oxidises the Fe-porphyrin of haemoglobin without affecting the SH groups; at p_{H} 9.6, the SH groups may be oxidised, by cystine, without affecting the Fe-porphyrin. F. A. A.

Characterisation and determination of the hydrolysis products of elastin. Isolation of the monoamino-acids by a new technique. R. ENGELAND (Bull. Soc. Chim. biol., 1935, 17, 1790—1804).— NH_2 -acids are separated by fractional pptn. of the hydrochlorides from MeOH solution. From elastin two NH_2 -acids, $\text{C}_{11}\text{H}_{22}\text{O}_4\text{N}_2$ and $\text{C}_{17}\text{H}_{38}\text{O}_4\text{N}_2$, are isolated as the Cu salt, $\text{C}_{11}\text{H}_{20}\text{O}_4\text{N}_2\text{Cu}$, and the aurichloride, $\text{C}_{17}\text{H}_{36}\text{O}_4\text{N}_2 \cdot 2\text{AuCl}_4$, respectively. A. L.

Determination of the m.p. of organic substances. F. FRANCIS and F. J. E. COLLINS (J.C.S., 1936, 137—142).—A description of apparatus for setting point and m.p. determination. Setting point gives more accurate experimental vals. for transition temp. from solid to liquid. With the apparatus described, existence of metastable forms fusing within 1° of each other can be detected, transition temp. recorded, and a judgment reached on the purity of the specimen. F. R. S.

Organic micro-analytical practice. C. WEYGAND and H. HENNIG (Chem. Fabr., 1936, 9, 8—10).—The technique of methods of C, H, N, halogen, S, and OMe-determination, as applied to samples of 0.001—0.01 g., is detailed. J. W. S.

Determination of carbon and nitrogen by the action of chromic acid under reduced pressure. C. N. ACHARYA (Biochem. J., 1936, 30, 241—247).—C and N are determined in org. material by oxidation with CrO_3 and H_2SO_4 and the CO_2 evolved is absorbed and weighed. Subsequent direct distillation of the digest with alkali gives low vals. for N owing to the formation of NO_3^- , so that a preliminary reduction is necessary. The disturbing influence of Cl is avoided by addition of HgO. H. D.

Analysis of organic compounds containing H and D. H. ERLÉNMEYER and H. GÄRTNER (Helv. Chim. Acta, 1936, 19, 129—144).—The customary determination of H in org. compounds which contain H and D gives accurate results only when the content of H is very high. In the general case a differentiation between a H- and D-compound cannot thus be effected or only very inexactly. Generally, the differences in the % of C allow an approx. differentiation between H- and D-compounds but for accurate results a high % of C and H is necessary. Suitable relationships exist in hydrocarbons particularly in those of the paraffin series. A method is described in which the substance (0.05 to 0.15 g.) is burnt with CuO and the water is collected in a tube cooled in solid $\text{CO}_2\text{-CCl}_4\text{-CHCl}_3$. It is mixed with 10 c.c. of standard H_2O ; the mixture is distilled and its d is determined. The sensitiveness is such that in a mixture of isotopic benzenes, approx. PhD, it is just possible to discriminate between $\text{C}_6\text{H}_4.995\text{D}_{1.005}$ and $\text{C}_6\text{H}_5.005\text{D}_{0.995}$. H. W.

Determination of organic sulphur by the liquid ammonia-sodium method. F. J. SOWA, V. G. ARCADJ, and J. A. NIEUWLAND (Ind. Eng. Chem. [Anal.], 1936, 8, 49—50).—0.1 g. of substance is dissolved in 175 c.c. of liquid NH_3 with the help if necessary of an inert solvent and Na is added until the blue colour is permanent. The solution is evaporated (25 c.c.), 3—5 g. of NH_4Cl are added, and the mixture is evaporated to dryness. The residue is taken up in H_2O , oxidised with 2 g. of Na_2O_2 , and the S pptd. as BaSO_4 . The method is accurate and of general applicability. S. C.

***p*-Bromobenzhydrazide as a reagent for the identification of aldehydes and ketones.** S. M. WANG, CHENG-HENG KAO, CHUNG-HSI KAO, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1935, A, 3, 279—284).—*p*-Bromobenzhydrazide, m.p. 164° (prep. from *p*- $\text{C}_6\text{H}_4\text{Me-NH}_2$ described), condenses with aldehydes and ketones in boiling 95% EtOH containing a few drops of glacial AcOH yielding *p*-bromobenzoylhydrazones of the following substances: MeCHO, m.p. 192—193°; EtCHO, m.p. 172—173°; PrⁿCHO, m.p. 157—158°, BuⁿCHO, m.p. 153—154°; hexaldehyde, m.p. 144—145°; *n*-heptaldehyde, m.p. 124—125°; PhCHO, m.p. 242—243°; *p*-, m.p. 250—251°, and *m*-, m.p. 217—218°, $\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$; furfuraldehyde, m.p. 218—219°; $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$, m.p. 235—236°; COMe_2 , m.p. 198—199°; Me hexyl ketone, m.p. 131—132°; COPhMe , m.p. 192—193°; *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$, m.p. 212—213°; benzylideneacetophenone, m.p. 219—220°; *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$, m.p. 219—220°; COPh_2 , m.p. 160—161°; lævulic acid, m.p. 158—159°; Et, m.p. 128—129°, and CH_2Ph , m.p. 123—124°, lævulate; $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, m.p. 74—75°. Primary and *sec.* alcohols are oxidised and then identified by this method. H. W.

Determination of thiol and disulphide compounds, with special reference to cysteine and cystine. IV. Accurate determination of thiol compounds. Standardisation of cysteine hydrochloride. V. Cystine determination by sulphite and phospho-18-tungstic acid reagent. K. SHINO-

HARA. VI. Reaction of ascorbic acid and glutathione with phospho-18-tungstic acid reagent. VII. Modified phospho-18-tungstic acid method of determining cysteine, cystine, and ascorbic acid in urine. K. SHINOHARA and K. E. PADIS (J. Biol. Chem., 1936, 112, 671—682, 683—696, 697—708, 709—721; cf. this vol., 60).—IV. Cysteine (I) and $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ are allowed to react with a deficiency of HgCl_2 and the excess is determined colorimetrically by phospho-18-tungstic acid (II). H_2O and a little cystine (III) are the chief impurities in commercial (I). (III) does not interfere with the determination of (I) by this method.

V. (III) is reduced by NaHSO_3 and then determined colorimetrically by (II). NaHSO_3 alone develops little colour; HgCl_2 inhibits formation of colour by (III). Various reducing agents, but not (I), interfere.

VI. Ascorbic acid (IV) is determined colorimetrically by (II), the colour being twice as intense as that due to equimolar amounts of (I). The colour is not affected under specified conditions by HgCl_2 or small amounts of CH_2O . (I), (III), and (IV) are thus determined in the same solution by use of CH_2O , HgCl_2 , and (II). Oxidised (IV) gives no colour. Glutathione gives irregular results, probably due to hydrolysis, and interferes with the methods.

VII. Modifications are necessary for determinations in urine. Fresh normal urine contains 0—0.9 mg. of (I), 1.1—4.8 mg. of (III), and 3.2—26.8 mg. of (IV) per 100 c.c. R. S. C.

Determination of cystine by Sullivan's method: supposed cleavage of cystine from casein by dilute alkali. H. J. LEE (Austral. J. Exp. Biol., 1936, 13, 229—237).—Various factors may interfere with the determination of cystine (I) by Sullivan's method. The conclusion of Jones and Gersdorff (A., 1934, 313) that treatment of casein by dil. alkali destroys some of the (I) is vitiated by their failure to make allowance for the interfering effect of the casein hydrolysate on the determination of (I). W. O. K.

Titration of amino-acids in glacial acetic acid solution. G. F. NADEAU and L. E. BRANCHEN (J. Amer. Chem. Soc., 1935, 57, 1363—1365).— NH_2 -acids (I) (in glacial AcOH) are determined by titration with 0.1N- HClO_4 using crystal-violet, α -naphtholbenzein, or benzoylauramine as indicator; picric acid does not interfere. (I) insol. in AcOH are determined by dissolution in an excess of 0.1N- HClO_4 and back-titration with guanidine acetate. The results agree with potentiometric titration (in AcOH using chlor-anil electrode). H. B.

Colorimetric determination of allantoin. G. MOURROT (Bull. Soc. Chim. biol., 1935, 17, 1845—1850).—The method is a modification of that of Fosse (A., 1931, 976). The allantoinic acid is hydrolysed to glyoxylic acid, which is determined colorimetrically using $\text{NPh}\cdot\text{NH}_2$. A. L.

Weydel reaction for xanthines. G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1934, 72, 345—355; Chem. Zentr., 1935, i, 3162).—Colour reactions for caffeine, theobromine, theophylline, xanthine, and

guanine are described; the underlying mechanism and the influence of constitution are discussed.

H. N. R.

Spectrophotometric determination of chlorophyll *a* and *b*, carotene, and xanthophyll.—See this vol., 396.

Biochemistry.

Effect of respiration of pure oxygen on metabolism. P. BIELCHOWSKY and S. THADDEA (*Z. klin. Med.*, 120, 330—340; *Chem. Zentr.*, 1934, ii, 3399).—Blood-ketones in man, if high, are diminished, and p_{H} is shifted towards the alkaline side as the result of decreased alveolar CO_2 tension. The lactic acid curves obtained by injections of Na lactate and adrenaline in man or the dog lie considerably lower in O_2 respiration.

R. N. C.

Respiration of carbon dioxide in narcosis and in paralysis of the respiratory centre. H. FRANKEN (*Schmerz, Narkose, Anästhesie*, 1934, 7, 26—36; *Chem. Zentr.*, 1934, ii, 3646).

R. N. C.

Simple valveless apparatus for determination of gaseous metabolism in man. F. FÖLDES (*Biochem. Z.*, 1935, 282, 303—307).—The apparatus (cf. the similar apparatus for dogs, A., 1935, 238) is described. The error of duplicate experiments is $\pm 3\%$.

P. W. C.

Respiratory characteristics of the blood of the seal. L. IRVING, O. M. SOLANDT, D. Y. SOLANDT, and K. C. FISHER (*J. Cell. Comp. Physiol.*, 1935, 6, 393—403).—The capacity of the blood for CO_2 and its buffering power are $<$ those of human blood. O_2 capacity vals. and dissociation curves are given.

R. N. C.

Vapour pressure of the blood of arthropods from swift and still waters. H. M. FOX and E. J. BALDES (*J. Exp. Biol.*, 1935, 12, 174—178).—No correlation was apparent between the v.p. of blood and the O_2 consumption.

CH. ABS. (p)

Effect of oxygenation of the external medium on the composition of blood in *Scyllium canicula*. E. A. PORA (*Compt. rend. Soc. Biol.*, 1936, 121, 194—196).—Total osmotic pressure, Na, Ca, proteins, org. substances, and the alkaline reserve are increased, whilst plasma-Cl falls; corpuscular Cl is unaffected. Mineral salts in serum and muscle increase simultaneously, and H_2O passes from the blood to the muscles.

R. N. C.

Variation of blood- p_{H} and blood-gas after injection of sodium silicate. K. DAIKOKU (*Trans. Soc. Path. Japon.*, 1934, 24, 72—76).—Continuous injection caused a decrease in blood- p_{H} and -gas.

CH. ABS. (p)

Regeneration of blood in fish following bleeding. L. BAUDIN (*Compt. rend. Soc. Biol.*, 1936, 121, 330—332).

R. N. C.

Effects of extracts of pituitary gland on sedimentation of red blood corpuscles of normal and hypophysectomised dogs. T. ICHIJO (*Sei-i-Kwai Med. J.*, 1934, 53, No. 6, 123—132).—Data obtained by Kowarski's apparatus are given.

CH. ABS. (p)

Determination of rate of sedimentation of blood corpuscles. Effect of globulin solutions

on the rate *in vitro*. I. BINÉT and I. KRASZNAI (*Biochem. Z.*, 1936, 283, 190—198).—Westergreen's method gives trustworthy results only if const. temp. and p_{H} are maintained in the tubes. *In vitro* the rate of sedimentation of washed red blood corpuscles and to a smaller extent that of blood is diminished by addition of globulin.

W. McC.

"Urea surcharge" (Delaunay) of the erythrocytes of *Sipunculus*: distribution of urea between erythrocytes and plasma in the coelomic liquids charged with erythrocytes. M. FLORKIN (*Compt. rend. Soc. Biol.*, 1936, 121, 158—160).—The erythrocytes of the coelomic liquid of *Sipunculus* are surcharged with urea, but not those of *Echiurus*, *Glycera*, or *Capitella*.

R. N. C.

Effect of heparin on the permeability of the erythrocytes to adrenaline. M. KUCZAROW (*Klin. Woch.*, 1934, 13, 734—735; *Chem. Zentr.*, 1934, ii, 3780—3781).

R. N. C.

Characteristics of the stability of corpuscular glucose subjected to washing with physiological solution. G. PATRASSI and U. TEODORI (*Boll. Soc. ital. Biol. sperim.*, 1935, 10, 525—526).—Repeated washing of erythrocytes with 0.9% NaCl reduces their glucose to a steady min., which in erythrocytes from diabetics is slightly $>$ from normal subjects.

R. N. C.

Corpuscle resistance and bilirubinæmia in young mammals with trychophytia after slow dosage with thallium acetate. I. GATTO and G. MELODIA (*Pediatrics*, 40, 230—235; *Chem. Zentr.*, 1934, ii, 3397).—Corpuscle resistance is increased and bilirubinæmia diminished or abolished.

R. N. C.

Diurnal variations in concentration of red blood cells and hæmoglobin. J. J. SHORT (*J. Lab. Clin. Med.*, 1935, 20, 708—713).

CH. ABS. (p)

Percentage of hæmoglobin compared with the volume of erythrocytes. Importance of this relation in correcting the Van Allen determination of the volume of platelets. K. K. NYGAARD and D. L. DUXBURY (*J. Lab. Clin. Med.*, 1935, 20, 767—772).—The hæmoglobin content expressed as g. per 100 c.c. is closely related to the vol. of erythrocytes expressed as vol.-% of the sample. Tables for intercalculation are given.

CH. ABS. (p)

0.1N-Hydrochloric acid as diluent for combined leucocyte and hæmoglobin determinations. C. A. PONS and W. P. BELK (*J. Lab. Clin. Med.*, 1935, 20, 766—767).—Blood diluted with 0.1N-HCl is suitable for white cell counts and for examination in the Huden-Hausser hæmoglobinometer.

CH. ABS. (p)

Birth pains and the blood of the new-born. Z. HORVÁTH, and C. HOLLÓSI (*Amer. J. Dis. Children*, 1935, 49, 689—694).

CH. ABS. (p)

Determination of hæmoglobin in experimental anæmia in rabbits. R. DAMADE, L. SERVANTIE, and J. FERVILLE (Compt. rend. Soc. Biol., 1936, 121, 229—232).—The methods of Sahli and Autenrieth and of Wong are recommended. R. N. C.

Solutions of hæmoglobin stabilised with time. I, II. W. DUCE (Boll. Soc. ital. Biol. sperim., 1935, 10, 376—379, 379—382).—I. Solutions of hæmoglobin (I) after prolonged dialysis are coagulated by boiling, and by 2*N*-NaCl, or EtOH, are coloured red by slight acidification or alkalis, and pptd. by HNO₃, AcOH, Hg(NO₃)₂-HNO₃, and K₂Fe(CN)₆ (II), but not by CuSO₄, NiSO₄, AgNO₃, basic Pb acetate, or HgCl₂. After prolonged storage at room temp. dialysed (I) is coagulated only by 2*N*-NaCl, is coloured brown by acids and alkalis, and pptd. by all the above reagents except (II).

II. The absorption bands of (I) in the red are displaced towards the red end by prolonged dialysis and storage. The absorption quotient falls.

R. N. C.

Sulphur content of hæmoglobin with special reference to blood-groups. G. BALASSA (Biochem. Z., 1936, 283, 222—228).—In man the hæmoglobin (I) of the blood of some individuals contains 0.611% of S whilst that of others contains 0.662%, the corresponding Fe : S ratios and min. mol. wts. being, respectively, 4 : 13, 4 : 14, and 68,000, 34,000. The blood of individuals belonging to blood-groups A and B contains the second, that of the blood of individuals belonging to blood-group O the first, kind of (I).

W. McC.

Optical properties of acidified solutions of O₂- and CO-hæmoglobin in blood. G. BARKAN (Biochem. Z., 1936, 283, 241—252; cf. A., 1930, 1304).—Spectrophotometric examination indicates that the darker colour of the solutions containing CO is due to a difference in the degree of dispersion.

W. McC.

Analysis of the spectra of hæmoglobin derivatives. D. L. DRABKIN (Amer. J. Med. Sci., 1935, 189, 154).—Absorption curves are represented as summations of a no. of individual bands. Oxy- (I), carboxy- (II), cyano-, and two forms of met-hæmoglobin have certain bands in common. Their position is discussed. The α -bands of (I) and (II) do not belong to this series and probably represent the union of hæmoglobin with a gas.

CH. ABS. (p)

Aliphatic amino-content of the oxyhæmoglobin of animals. K. GERGELY (Biochem. Z., 1936, 283, 229—232).—The average NH₂-N contents of horse-, dog-, and ox-oxyhæmoglobin are, respectively, 11.96—12.48, 13.14, and 13.28%. The vals. are not altered by repeated recrystallisation.

W. McC.

Differentiation of the pigments of human serum. H. SÜLLMANN, E. SZÉCSÉNYI-NAGY, and F. VERZÁR (Biochem. Z., 1936, 283, 263—272; cf. A., 1935, 803).—The pigments may be determined by taking advantage of their differing solubilities in aq. EtOH and light petroleum and may be separated by chromatographic adsorption on Al₂O₃. With the exception of very small amounts of non-diazotisable bilirubin-like pigments the only pigments in normal

human serum are bilirubin (I), carotene, and xanthophyll. (I) in aq. EtOH is determined after treatment with SO₃H·C₆H₄·N₂Cl. The pigments produced by ultra-violet irradiation of (I) are insol. in light petroleum and cannot be diazotised. W. McC.

New crystalline derivative of blood-pigments. M. WAGENAAR (Z. anal. Chem., 1935, 103, 417—418).—The object to be tested for blood is moistened on a microscope slide with COMe₂, and a drop of dil. mineral acid is added. Characteristic crystals of acetone-hæmin are produced with the dried residue from 0.05 mg. of blood.

J. S. A.

Spectrophotometric investigation of cyano-compounds of blood-pigments. S. SCHÖNBERGER and P. BALINT (Biochem. Z., 1936, 283, 210—221; cf. A., 1935, 999).—In the visible part of the spectrum the absorption curves of cyanomethæmoglobin (I), cyano-NH₂-parahæmatin, cyano-C₅H₅N-parahæmatin, and cyanohæmatin are identical and exhibit a max. at 541 m μ . In the ultra-violet (I) and cyanoparahæmatin (but not cyanohæmatin) exhibit an intense well-defined band at 424 m μ . The sp. extinctions in the visible are decreased 15% by increasing the alkalinity. The results throw light on the constitution of blood-pigments.

W. McC.

Variations of osmotic pressure and of the size of hæmocyanin molecules during a long fast (in summer or hibernating) of varieties of Helix. A. ROCHE and J. ROCHE (Compt. rend., 1935, 201, 1522—1524; cf. A., 1934, 673).—The mol. size of hæmocyanin in *H. pisana* and *H. pomatia* is about halved by fasting. This may be the mechanism for H₂O retention within the animal.

J. L. D.

Reticulo-endothelial origin of fibrinogen: comparative study of the fibrinogenetic action of some carioclastics. P. CAMPellone (Boll. Soc. ital. Biol. sperim., 1935, 10, 497—499).

R. N. C.

Micro-Kjeldahl technique for determining fibrinogen. H. R. GARBUTT and R. S. HUBBARD (J. Lab. Clin. Med., 1935, 20, 758—761).—Plasma (0.5 c.c.) is mixed with 24 c.c. of 0.85% NaCl and 0.5 c.c. of 2.5% CaCl₂ solution. The clot is removed centrifugally, washed with 0.05% CaCl₂ solution, digested with the Folin-Wu mixture, and diluted to 10 c.c. N is determined by nesslerisation.

CH. ABS. (p)

Protein and electrolyte contents of the plasma and transudates (serous effusions and subcutaneous fluid). L. ANTOGNETTI (Pathologica, 1935, 27, 182—189).—A progressive and parallel decrease occurs in the [H⁺] and protein concn. in the order erythrocytes, plasma, serous effusions, subcutaneous transudates. Variations in [HCO₃⁻] are in the reverse order. The Donnan membrane equilibrium explains the facts.

CH. ABS. (p)

Protein equilibrium of blood-serum in anaphylactic states. AUBRY, THIODET, and RIBÈRE (Compt. rend. Soc. Biol., 1935, 120, 1257—1259).—Protein equilibrium is disturbed in anaphylactic states, particularly urticaria, albumins remaining steady whilst globulins fall considerably.

R. N. C.

Protein, lipin, and total cholesterol content of the serum of the normal cat. L. BLANCHARD (Bull. Soc. Chim. biol., 1935, 17, 1677—1692).—The vals. for the serum-protein, -serine, -globulin, total serum-lipins, and cholesterol of the normal cat are 73.44 ± 8.64 , 38.35 ± 6.97 , 34.78 ± 8.72 , 8.63 ± 1.92 , and 1.03 ± 0.20 g. per 1000 g., respectively. These vals. are of the same order as those for the dog and for man. A. L.

Influence of ingestion of colostrum on proteins of the blood sera. I. P. EARLE (J. Agric. Res., 1935, 51, 479—490).—Sera of new-born foals, kids, pigs, and lambs are deficient in euglobulin (I) and low in pseudoglobulin I (II). On ingestion of colostrum (I) and (II) increase rapidly. With foals the amounts of (I) and (II) absorbed are related to the quantity of colostrum ingested. E. P.

Determination of the tyrosine index of serum polypeptides. R. LEFAUX (Bull. Soc. Chim. biol., 1935, 17, 1822—1827).—The difference in colour intensity between the $\text{CCl}_3\text{-CO}_2\text{H}$ and phosphotungstic acid filtrates of the material after treatment with conc. HNO_3 and aq. NaOH is measured. A. L.

Polypeptidæmia in anaphylactic shock. M. POLONOVSKI, C. GERNEZ, and J. DRIESSENS (Compt. rend. Soc. Biol., 1936, 121, 37—38).—Blood-polypeptides show no significant modification either in anaphylactic shock or during sensitisation. R. N. C.

Polypeptidæmia during anaphylactic shock. F. MAIGNON (Compt. rend. Soc. Biol., 1936, 121, 225—226).—A reply to Polonovski, Gernez, and Driessens (see above). R. N. C.

Hyperazotæmia of neuro-central origin. P. JEDŁOWSKI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 615—618). R. N. C.

Variation of residual nitrogen in blood after injection of sodium silicate solution. H. AKABANE (Trans. Soc. Path. Japon., 1934, 24, 76—81).—Residual N increased after injection. CH. ABS. (p)

Influence of protein feeding on the nitrogenous blood constituents in the dog. L. SAS (Biochem. Z., 1935, 282, 308—316).—The blood-residual-N is greatly increased by protein feeding, due in the initial stages to increase in blood-urea. The polypeptide-N shows no characteristic changes. In animals receiving a N-free diet, blood-urea decreases, but residual N remains unchanged. P. W. C.

Blood- and urinary nitrogen of a lamelli-branch mollusc (*Anodonta cygnea*). M. FLORKIN and G. BOSSON (Compt. rend. Soc. Biol., 1935, 120, 1368—1369).—Total, protein-, and non-protein-N vals. for blood and urine at different seasons are given. R. N. C.

Non-protein-nitrogen content of blood of healthy Korean adults. H. S. LEE (J. Chosen Med. Assoc., 1934, 24, 1541—1548).—In most cases, vals. varied from 29 to 43 mg. per 100 c.c. of blood (mean for 79 cases 36.11 ± 0.83). CH. ABS. (p)

Adenine nucleotide content of human blood. II. Correlation with hæmoglobin. M. V. BUELL (J. Biol. Chem., 1936, 112, 523—530; cf. A., 1935,

373).—There is a statistically significant correlation between the adenine nucleotide and hæmoglobin contents of the erythrocytes. J. N. A.

Oxidised/reduced glutathione ratio in acute oxidosis. W. LIBBRECHT and A. MASSART (Compt. rend. Soc. Biol., 1935, 120, 1330).—The oxidised/reduced glutathione (I) ratio of rabbits' blood is increased by prolonged exposure to air or O_2 *in vitro*, but is reduced by exposure to pure O_2 at high pressures *in vivo*; the state of (I) depends therefore on oxidation in the tissues. R. N. C.

Liver and glutathione. L. BINET and G. WELLER (Compt. rend., 1935, 201, 992—993).—In fasting dogs, total glutathione (I) (oxidised+reduced) in the blood from the portal vein is 9%, and in the suprahepatic vein 44%, > in blood from the femoral artery. During digestion, the figures are 51% and 27%, respectively, indicating that during fasting the blood absorbs (I) from the liver, and deposits (I) during digestion. F. A. A.

Determination of glyoxalines in serum. A. SCHWARTZ and A. RIEGERT (Compt. rend. Soc. Biol., 1935, 120, 1309—1312).—The method of Loeper *et al.* is unsatisfactory. R. N. C.

Does the blood contain acetylcholine? R. AMMON (Klin. Woch., 1935, 14, 453—456).—Acetylcholine cannot be detected chemically or biologically in the blood. R. N. C.

Arginine as the cause of the non-specificity of analytical methods for blood-guanidine. M. ZAPPACOSTA (Diagnostica tec. lab. [Napoli], 1934, 5, 919—927).—Reagents for colorimetric tests give the same colour intensity with guanidine (I) as with equimol. quantities of arginine (II). (II), like (I), is adsorbed by C and 70% of it may be eluted with 0.02N-HCl in EtOH. CH. ABS. (p)

Indole. II. Effect of indole on blood-sugar, urea-nitrogen, and blood-amino-acids. III. Indolæmia provoked by ligaturing the hepatic peduncle: indican-indole index. E. MACCHIA (Boll. Soc. Ital. Biol. sperim., 1934, 9, 1314—1315, 1935, 10, 528—530).—II. Indole (I) temporarily increases blood-sugar in dogs, but scarcely affects non-protein-N and NH_2 -acids.

III. Ligature of the hepatic peduncle in the dog after injection of (I) increases blood-(I) and reduces blood-indican. The liver is hence concerned in (I) metabolism. The indican-(I) index is defined. R. N. C.

Blood-lipins, -calcium, and -potassium during experimental excitation of the hypothalamus [in dogs]. A. VAN BOGAERT and L. VAN MEEL (Compt. rend. Soc. Biol., 1936, 121, 199—201).—Blood-lipins are temporarily depressed, the fall being almost exclusively due to decrease of fatty acids. Cholesterol and unsaponifiable material are scarcely affected. Ca sometimes shows a slight temporary rise, and K a slight fall. R. N. C.

Serum-lipins by a micro-gravimetric technique. W. R. WILSON and A. E. HANSEN (J. Biol. Chem., 1936, 112, 457—468).—The inorg. P and the wt., total acidity, and I val. of the fatty acids of the saponifiable fraction and the I val. of the unsaponifi-

able fraction of the serum-lipins were determined in 2.5–5 c.c. of serum. The mean total, unsaponifiable, and saponifiable lipins were 0.657, 0.260, and 0.362%, respectively. 81% of the lipin-P is found in the saponifiable fraction.

H. D.

Carotenæmia. E. BOUNIN and M. LÉVINSON (Z. Vitaminforsch., 1935, 5, 12–21).—Carotenæmia is associated with tuberculosis, diabetes, typhus, malaria, metabolic disturbances, spleen and liver diseases, and in normal persons with a carotene-rich diet. The subnormal oxidation of carotenoids is related to the concomitant hypocholesterolaemia.

F. O. H.

Blood-cholesterol in the carotid artery, venæ cavæ, and portal vein. F. H. SHILLITO, E. H. BIDWELL, and K. B. TURNER (J. Biol. Chem., 1936, 112, 551–556).—The level of the blood-cholesterol (I) in these vessels was the same for a given animal, whether the whole blood or serum was used, and whether or not cholesterol was administered previously. Passage through the lungs had no effect on (I). Large doses of KI given for 2–14 days produced no variation in the distribution of (I).

J. N. A.

Variations in blood-cholesterol in man and in animals. L. I. PUTSCHINSKI and T. T. GLUHENKI (Bull. Soc. Chim. biol., 1935, 17, 1836–1844).—The cholesterol (I) content of (fasting) human blood over a 24-hr. period varies between 50 and 130 mg. per 100 g. (I) of rabbit and dog blood varies likewise.

A. L.

Influence of a hyperthermal sulphuretted radioactive environment on some constituents of the blood. A. KRÍJANOVSKY (Compt. rend. Soc. Biol., 1935, 120, 1236–1238).—Blood-sugar, -N, -cholesterol, and plasma-Cl are depressed, whilst corpuscular Cl rises, in man in the Luchon radio-vaporarium.

R. N. C.

Blood-sugar of *Cancer pagurus*: nature of reducing substances and factors of variation of blood-sugar. J. ROCHE and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 120, 1225–1227).—The hæmolymp contains glucose (I) and non-fermentable reducing substances pptd. by Cd(OH)₂. The average normal (I) content is 0.21 g. per 1000; it is temporarily increased by removal from the aquarium, but is unaltered by insulin, adrenaline, or muscular work.

R. N. C.

Hypoglycæmia by conditioned reflex. C. C. PARKON and A. RUDEANU (Compt. rend. Soc. Biol., 1936, 121, 185–186).—Rabbits injected with 0.9% NaCl after 16 daily injections of insulin exhibit a fall of blood-sugar.

R. N. C.

Hourly constancy of phenolæmia in man in normal and pathological states. R. BANFI, E. LIDA, and A. D. MARENZI (Compt. rend. Soc. Biol., 1936, 121, 358–359).—Free phenols (I) in nephropathic blood are > in normal blood, whilst conjugated phenols (II) are more variable. The constancy of (I) in normal blood is > that of (II) over a period of 28 hr.

R. N. C.

Fate of alcohol in the blood in putrefaction *in vitro*. M. NICLOUX (Compt. rend. Soc. Biol., 1935, 120, 1304–1306).—The rate of disappearance

of EtOH from putrefying blood increases with rise of temp.

R. N. C.

Organic phosphorus of the blood studied by the method of prolonged spontaneous hydrolysis, in man and in some domestic animals. G. DE TONI (Arch. Ist. Biochim. Ital., 1935, 7, 303–340).—The autolysis curves at 37° of org. P in infantile and adult human and animal blood are described. The curves are essentially the same in lactating animals of all species. Autolysis is rapid during the first 24 hr., but slackens very considerably afterwards. In the adult animals inorg. P is always < in the corresponding lactating animals, and the autolysis curves show wide variations from each other. Autolysis is most extensive in rabbit blood, moderate in human and horse blood, whilst sheep's and cows' bloods contain little or no org. P.

R. N. C.

Influence of pituitary body and preparations of other endocrine organs on inorganic salts of the blood. S. NISHIDA (Sci-i-Kwai Med. J., 1934, 53, No. 6, 133–175).—Hypophysectomy causes a decrease in blood-Cl, -Na, -K, and -Mg and an increase in -Ca. Pituitrin, antuitrin, and pituglandol produce a reciprocal effect in normal dogs and restoration to normal levels in hypophysectomised animals. Oöphormin, thyroxine, and adrenaline cause a decrease in Mg and K and an increase in Ca. Insulin produces no change in Mg in normal, but a decrease in that of hypophysectomised, dogs.

CH. ABS. (p)

Blood, bile, and liver of animals with permanent biliary fistulas. F. CAVAZZA (Pathologica, 1935, 27, 241–250).—In dogs blood-Ca and alkaline reserve are lowered and blood-K increases. No marked changes occur in Ca content of bile and hepatic tissues.

CH. ABS. (p)

Effect of changes in the concentration of plasma-electrolytes on the concentration of electrolytes in the red blood cells of dogs, monkeys, and rabbits. H. YANNET, D. C. DARROW, M. K. CARY (J. Biol. Chem., 1936, 112, 477–488).—In monkeys and rabbits changes in the plasma-Na, produced by intraperitoneal injection of aq. glucose or NaCl, caused changes in erythrocyte-Na and -K due to shift of H₂O alone. In the dog a certain migration of cations occurred.

H. D.

Bromine in blood and spinal fluid; its relation to blood-iodine. U. C. BONORINO, M. SCHEINGART, and R. FERRAMOLA (Prensa méd. Argentina, 1934, Mar. 7).—Blood-Br varied from 0.6 to 3.6 mg. per 100 c.c. Br and I vary in a parallel manner, I:Br ranging between 70 and 170. Spinal fluid contains 0.2 mg. of Br per 100 c.c.

CH. ABS. (p)

Blood-chloride in healthy Koreans. M. S. KIM (J. Chosen Med. Assoc., 1934, 24, 1537–1540).—Vals. for Koreans who eat excessive amounts of salt fall within normal variations found in occidentals.

CH. ABS. (p)

Effects of hydrochloric acid and sodium hydrogen carbonate administrations on distribution of blood-chlorine. N. MATSUOKA and K. DAITA (Trans. Soc. Path. Japon., 1934, 24, 82–91).—

NaHCO_3 increases blood-Cl and decreases plasma-Cl. Both vals. increase after administration of HCl.

CH. ABS. (p)

Metabolism of iodine. I. Blood-iodine. II. Influence of ascorbic acid on blood-iodine. H. LÖHR (Arch. exp. Path. Pharm., 1936, 180, 332—343, 344—353).—I. Improvements in methods for the micro-determination of I are described. The blood-I (I) of healthy men and women is 20—30 \times 10⁻⁶% and is not influenced by sex or season; it is greatly increased by exercise (rowing) for 1 hr., returning to normal after 1 hr. rest, but increasing again after 24 hr.

II. Ascorbic acid lowers the (I) of normal and thyroidectomised dogs and antagonises the (I)-increasing action of thyroxine. F. O. H.

Diffusible calcium in the serum of laying and non-laying hens. M. W. TAYLOR and W. C. RUSSELL (J. Agric. Res., 1935, 51, 663—667).—No difference in the level of diffusible Ca was apparent. Non-diffusible Ca was much higher in the laying condition. A. G. P.

Variability of non-hæmoglobin iron. T. G. KLUMPP (J. Clin. Invest., 1935, 14, 351—355).—Non-hæmoglobin Fe varies widely and is a significant fraction of the total Fe. CH. ABS. (p)

Chemical and physico-chemical sexual differences in the blood of selachians. E. A. PORA (Compt. rend. Soc. Biol., 1936, 121, 105—107).—Corpuscular vol. and Cl, and κ in the blood of males are > in females, whilst the alkaline reserve is less. The osmotic pressure and inorg. salts in the male are > in the female in *Scyllium canicula*, but less in *Raia undulata*, whilst with blood-proteins and org. substances of the serum the reverse is the case. R. N. C.

Chemical and physico-chemical sexual differences of the blood of *Labrus bergyllia*. E. A. PORA (Compt. rend. Soc. Biol., 1936, 121, 102—105).—The osmotic pressure, κ , blood-, serum-, and corpuscular Cl, serum-Na, and total inorg. substances in the blood of the male are > in the female, whilst K, Ca, proteins, the alkaline reserve, corpuscular vol., and org. substances are less. The fraction of the osmotic pressure due to NaCl in the male is > in the female. R. N. C.

Action of indole on hydræmia, chloræmia, and glycæmia. G. F. DE GAETANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 441—443).—Injection of indole in guinea-pigs increases H_2O and depresses Cl in the blood; blood-sugar behaves variably. R. N. C.

Blood-modifications from administration of indole. G. F. DE GAETANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 439—441). R. N. C.

Composition of the blood of some marine invertebrates and vertebrates. E. A. PORA (Compt. rend. Soc. Biol., 1936, 121, 291—293).—From the analytical data given, the osmotic pressure of poikilosmotic marine animals is slightly > that of the external medium, whilst that of homeosmotic animals is less. κ of the serum of poikilosmotic animals differs from that of the external medium. The % of the osmotic pressure due to NaCl in selachians is

< in teleosteans. Blood-Cl in cephalopods is approx. equiv. to Cl in the sea; in selachians it is half, and in teleosteans a quarter, of the cephalopod val. Proteins are high in cephalopods. R. N. C.

New antagonistic property of normal sera: the cercaricidal action. J. T. CULBERTSON and S. B. TALBOT (Science, 1935, 82, 525—526).—Sera of many animals have a definite cercaricidal action. L. S. T.

Investigations [on sera] in the ultra-violet. W. GRAUBNER (Z. ges. exp. Med., 81, 1—5; Chem. Zentr., 1934, ii, 3397).—The absorption spectra of different human sera vary considerably, but no significant deviation appears in any single serum. Pptn. with EtOH or dialysis shifts the spectrum about 10 $m\mu$ towards the visible, but deproteinisation with $\text{Fe}(\text{OH})_3$ or large p_{H} changes with H_2SO_4 or NaOH are ineffective. The substance responsible for the spectrum is not one of the known serum constituents, and probably contains a CO or a C_6H_6 ring. Urine always shows a band between 260 and 280 $m\mu$; the max. is indefinite. The spectra of both sera and urine are probably due to the same substance, which is also present in cerebrospinal and pathological fluids. R. N. C.

Behaviour of calcium in the electro-dialysis of blood-serum and its dialysate. G. PERETTI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1333—1336).—Ca transport is anodic with small currents and cathodic with large currents in both serum and its dialysate; this confirms the existence in serum of diffusible non-ionisable Ca complexes. R. N. C.

Calcium metabolism in the first phase of blood clotting. III. Mechanism of thrombin formation. H. SCHEURING (Biochem. Z., 1935, 283, 1—11).—The mechanism of the earlier described (A., 1935, 1263) shift of Ca from the ionised to the negative Ca complex condition during thrombin formation is further investigated. The governing reaction results from the affinity of Ca^{++} for prothrombogen (I), the reaction conforming to the mass law and the complex formed being identical with thrombogen (II). The union of thrombokinase (III) with (II) also conforms to the mass law. Normal dog serum contains Ca^{++} corresponding with the (I) content, whilst (I) is present in about twice the amount required by the (III) content. P. W. C.

Action *in vitro* of iron-vitamin-C complexes with different bases on the coagulation of blood. F. ARLOING, A. MOREL, and A. JOSSERAND (Compt. rend. Soc. Biol., 1936, 121, 39—41).—Na ascorbate restrains slightly the coagulation of blood *in vitro*. Ferriscorbone complexes with inorg. and org. bases exhibit greater restraining action, Ca ferriscorbone being the least anticoagulant. With ferrosorbone the time of coagulation is always > 1 hr. R. N. C.

Influence of splenic fractions on blood coagulation. I. Effect of splenectomy, spleen diet, and spleen extract. S. BOKU, I. HIRAI, and K. GON (J. Chosen Med. Assoc., 1935, 25, 48—68).—Splenectomy accelerates coagulation for 2 days and subsequently delays it. Administration of splenic material restores normal conditions. CH. ABS. (p)

Mechanism of the action of anticoagulant substances. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 120, 1181—1185).—The anticoagulant power of compounds of the moranyl group corresponds exactly with, or is slightly $>$, the alexin-destroying power; these compounds therefore affect a coagulant agent, probably prothrombin, the structure of which resembles that of alexin (I). Naphthalenculphonates with high anticoagulant power exert only a feeble effect on (I). The incoagulable plasma exhibits variable characteristics as regards pptn. by acids, and contains "protective colloids." R. N. C.

Toxicity of ricin and body temperature. H. MORIYAMA (Japan. J. Exp. Med., 1934, 12, 591—600).
CH. ABS. (p)

Ricin. II. H. MORIYAMA (Japan J. Exp. Med., 1934, 12, 437—453).—Effects of various substances on the hæmagglutinating power of ricin are recorded. The lyophilic character of the protein is associated with the presence of a double linking, the loss of which causes changes in colloidal state, toxicity, and agglutinating power.
CH. ABS. (p)

Distribution of isoagglutinins in blood-serum fractionated by electrophoresis. A. GRÖNWALL (Biochem. Z., 1935, 282, 257—262).—Human serum of individuals of blood group *O* is fractionated by electrophoresis and the agglutinin titre, protein-N, and precipitability with $(\text{NH}_4)_2\text{SO}_4$ are determined. Isoagglutinin is distributed uniformly through the fractions pptd. by 30% saturation with $(\text{NH}_4)_2\text{SO}_4$.
P. W. C.

Antigenic properties of detoxicated Indian and African venoms: cross-reaction exerted by the respective antivenins. E. GRASSET and A. ZOUTENDYK (Trans. Roy. Soc. Trop. Med. Hyg., 1935, 28, 391—398; cf. A., 1934, 1022).—Venoms were rendered atoxic by 1% CH_2O . The potency of these preps. is compared with that of African viperine and colubrine venoms. Multivalent antivenins of colubrine venoms may be produced either by unmodified venoms or by anavenoms.
CH. ABS. (p)

Toxic and antigenic properties of S. African snake venoms with special reference to multivalency of S. African antivenin. E. GRASSET, A. ZOUTENDYK, and A. SCHAAFSMA (Trans. Roy. Soc. Trop. Med. Hyg., 1935, 28, 601—612).—The potency of horse antivenin can be titrated with venoms of the puff adder and Cape cobra. A sp. flocculation is shown with these venoms and the horse antivenin.
CH. ABS. (p)

Precipitin reaction to phosphatides of tubercle and leprosy bacilli. G. R. DUNCAN, C. C. VAN WINKLE, E. S. MARIETTE, and E. P. K. FENGER (Amer. Rev. Tuberc., 1935, 31, 307—322).—Human phosphatide (Anderson S-1) does not act as an antigen for production of antibodies in rabbits. S-2 is a very poor and bovine, avian, and lepra phosphatides are good antigens. No type specificity among these phosphatides was apparent.
CH. ABS. (p)

Relation between type-specific carbohydrates of pneumococci and blood group-specific substances. E. WITEBSKY, E. NETER, and H. SOBOTKA (J. Exp. Med., 1935, 61, 703—715).—Hæmolysis of

sheep cells is inhibited by human group-sp. *A*-antiserum. Differences between the acetylated and deacetylated polysaccharides of *Pneumococcus* type I are demonstrated by inhibition of hæmolysis, by complement fixation, and by inhibition of group-sp. isoagglutination tests. Destruction of potency of acetylated polysaccharides by fæces filtrates is not due to fission of Ac.
CH. ABS. (p)

Effect of various enzymes on toxin and anatoxin. Y. ANAZAWA (Sei-i-Kwai Med. J., 1934, 53, No. 10, 1—62).—Trypsin detoxicates diphtheric and tetanic toxins and destroys their antigenic property. Anatoxins prepared by heating these toxins with CH_2O are not destroyed by trypsin. Neither diastase nor lipase destroys the toxins or anatoxins.
CH. ABS. (p)

Antibody production through the cutaneous route. Y. HIROSE (Sei-i-Kwai Med. J., 1934, 53, No. 6, 1—73).—The antibody for cholesterol was produced in rabbits by smearing cholesterol or dehydrated lanoline over the skin.
CH. ABS. (p)

Antibody-forming accelerator in spleen. IV. Influence of spleen diet on hæmolysin and agglutinin formation. S. BOKU, I. HIRAI, and K. GON (J. Chosen Med. Assoc., 1934, 24, 1508—1518).—Splentectomy delays hæmolysin and agglutinin formation. Oral administration of spleen counteracts this effect.
CH. ABS. (p)

Chemical composition of pig's stomach.—See B., 1936, 168.

Structure of protoplasm. W. SEIFRIZ (Bot. Rev., 1935, 1, 18—36).
CH. ABS. (p)

Isoelectric point of mucoproteins. A. ROCHE (Compt. rend. Soc. Biol., 1935, 120, 1229—1231).—The isoelectric point of the mucoprotein of the submaxillary of the ox is p_H 2.70.
R. N. C.

Isoelectric point of mucoproteins. A. ROCHE (Compt. rend. Soc. Biol., 1936, 121, 71—73).—The isoelectric points of a no. of mucoproteins from invertebrate tissues are given. That of the vitreous humour is about p_H 3.0, whilst those of the skin are generally higher.
R. N. C.

The myogen volume in relation to the volume of the muscle fibre. W. HAUMANN and H. H. WEBER (Biochem. Z., 1935, 283, 146—152).—The myogen solution of mammalian muscle occupies 35% of the vol. of the minced muscle and may amount to $<$ 20% of the vol. of the intact muscle fibre. Close agreement was obtained by different methods in the determinations of the non-solvent space for myogen.
P. W. C.

Myoglobin. I. Solubility in concentrated ammonium sulphate solutions. V. E. MORGAN (J. Biol. Chem., 1936, 112, 557—563).—The solubility of carboxymyoglobin (I) in conc. solutions of $(\text{NH}_4)_2\text{SO}_4$ at p_H 6.6 and 25° is expressed by $\log S = 8.00 - 0.94(\Gamma/2)$, where S is the solubility in g. and $\Gamma/2$ is the ionic strength per litre. (I) is quite sol. in buffer solutions at p_H 6.6 up to a $[\text{PO}_4^{''}]$ of $\times 3M$.
J. N. A.

Decomposition of tuberculoprotein, starch, and gelatin by dry grinding. C. H. BOISSEVAIN

(Amer. Rev. Tuberc., 1935, 31, 542—546).—Prolonged grinding of starch causes its transformation into erythro-dextrin, and then into achroo-dextrin. Similarly, gelatin is changed to a H₂O-sol. peptone-like compound incapable of forming a gel even at 0°. Tuberculoprotein (I) is decomposed by grinding into H₂O-sol. protein, peptone, and polysaccharide. Boiling with dil. acid or treatment with 4% aq. NaOH produces the same change in (I). CH. ABS. (p)

Factors affecting the affinity of the pulmonary proteins and their degradation products for the lung. P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1935, 10, 459—461).—The proteins of the portion of the lung juice expelled by 400 atm. pressure are able to fix Co and convey it to the lungs, the effect being unaffected by tryptic digestion. The effect is not shared by aq. lung extracts or the proteins of the juice expelled by 200 atm. pressure. R. N. C.

Relation of protein coagulation to oxidation-reduction potential. Y. NAKAMURA (J. Agric. Chem. Soc. Japan, 1935, 11, 1101—1104).—Treatment of ov- and serum-albumin by heat or ultra-violet irradiation and of milk by enzyme action lowers the potential, indicating a relation between coagulation and hydrolysis. F. O. H.

Hydrogen-ion dissociation curve of the crystalline albumin of the hen's egg. R. A. KEKWICK and R. K. CANNAN (Biochem. J., 1936, 30, 227—234).—The H⁺ dissociation curve of ovalbumin has been constructed. The H⁺-combining capacity reaches a max. of 30—32 eqivs. per mol. just below p_H 2. Evidence of a max. dissociating capacity was observed at p_H 8—9 (corresponding with a dissociation of 11 eqivs. of H⁺ per mol.), but not at p_H 11.5—12.0. H. G. R.

Effect of formaldehyde on the hydrogen-ion dissociation curve of ovalbumin. R. A. KEKWICK and R. K. CANNAN (Biochem. J., 1936, 30, 235—240).—H⁺ dissociation curves of ovalbumin (I) in presence of CH₂O indicate the presence of 16—18 NH₂ groups, other than α -NH₂, which are identified with the ϵ -NH₂ of lysine. The action of HNO₂ on (I) indicates the presence of 19—20 NH₂ groups per mol. and the lysine-N of the phosphotungstate ppt., 17—18 mols. of lysine per mol. H. G. R.

Relations between some alkaloids and protein substances. P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1935, 10, 464—467).—Brucine (I) and strychnine in ovalbumin solutions form non-dialysable complexes with the protein. They also form complexes with serum-proteins, the quantity of alkaloid fixed by ox-serum being > by sheep serum. A method of determining (I) is described. R. N. C.

Electric cataphoresis of brucine and strychnine in solutions of ovalbumin or in blood-serum from different animals. P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1935, 10, 461—464).—Brucine and strychnine in the free state in solutions of ovalbumin or animal sera travel to the cathode, but when bound to the protein they travel to the anode. R. N. C.

Bioluminescence. II. Partial purification of Cypridina luciferin. R. S. ANDERSON (J. Gen. Physiol., 1935, 19, 301—305).—The powdered organ-

ism is extracted with MeOH under H₂, Bu^oOH is added, the MeOH removed, and the BuOH solution treated with BzCl. Bz or Ac derivatives of luciferin (I) are more stable to O₂ than is (I) itself. Preps. of (I) 2000 times as active as the starting material are obtained, in yields up to 65%, by two benzoylations followed by hydrolysis with *N*-HCl. F. A. A.

Organic bases, especially spermine, in the muscle of higher animals. K. YOSHIMURA, Y. HIWATASHI, and T. SAKAMOTO (J. Chem. Soc. Japan, 1935, 56, 280—288).—Vals. for creatine, hypoxanthine, carnosine, creatinine, methylguanidine, carnitine, and spermine are given for muscles of cattle, horse, pig, and hen. CH. ABS. (p)

Antianæmic principle of liver. H. B. SREERAN-GACHAR and M. SREENIVASAYA (Current Sci., 1936, 4, 468—472).—A review.

Hæmatin pigments of *Actinia* (actinohæmatin) and cytochrome-*b*. J. ROCHE (Compt. rend. Soc. Biol., 1936, 121, 69—71).—The muscle of *Actinia* is rich in cytochrome-*b* (I), but contains little or no cytochrome-*c* (II). C₅H₅N extracts of (II)-free muscles contain protohæmatin and the hæmatin of (II), with traces of that of cytochrome-*a*. Hence (I) and (II) of *Actinia* contain the same prosthetic group. R. N. C.

Hæmatin of cytochrome-*c* and nature of the combination of hæmatins with globins. J. ROCHE and M. T. BÉNÉVENT (Compt. rend. Soc. Biol., 1935, 120, 1227—1229).—Hæmatin-*c* (I), the prosthetic group of cytochrome-*c* (II), shows absorption bands at 614, 568, 535, 498, and 395 m μ . C₅H₅N transforms it into a parahæmatin (bands at 578 and 538 m μ), which is reduced to a hæmochromogen (bands at 550, 521, and 410 m μ) identical with that formed from (II) by C₅H₅N. (I) and (II) are reduced to the same porphyrin. (I) and natural globin in neutral or slightly alkaline solution form another parahæmatin (bands at 505 and 538 m μ), whereas other hæmatins form methæmoglobins. The results suggest that hæmoglobins and hæmochromogens are not formed by the action of the same group in the hæmatin mol. R. N. C.

Contents of glutathione and vitamin-*C* in anti-anæmic liver preparations. F. G. KOSER (Arch. exp. Path. Pharm., 1936, 180, 183—188).—Glutathione does not occur in several (commercial) liver preps., whilst the vitamin-*C* content varies considerably. F. O. H.

Glycogen in the central nervous system of human embryos. O. FUSEJIMA (Sei-i-Kwai Med. J., 1934, 53, No. 9, 80—93).—A histological study. CH. ABS. (p)

Lardacein from the scale of the insect *Ceroplastes rubens*, Maskell. R. KOYAMA (J. Chem. Soc. Japan, 1935, 56, 365—372).—The wax from insects grown on tea and on citrus trees had d_{20}^{20} 0.69694, 0.99208, m.p. 54—56°, 55—57°, sap. val. 152.8, 126.0, acid val. 22.9, 46.6, I val. 76.3, 130.5, respectively. From the wax were obtained, melissic, ceromelissic, C₃₃H₆₆O₂, m.p. 94°, ceroplastic, C₃₃H₇₀O₂, m.p. 96—98°, and a resin acid, C₂₂H₃₄O₂. The unsaponifiable fraction contained ceromelissyl, cero-

plasyll, and *melissyl* alcohols, all of which are primary. The wax does not contain *ceryl* or *ibotaceryl* alcohols or the corresponding acids. CH. ABS. (p)

Lipin composition and physiological activity in the ovaries of pregnant guinea-pigs. E. M. BOYD (J. Biol. Chem., 1936, 112, 591—595).—Ovaries from guinea-pigs at various stages of gestation showed the same average phospholipin content of about 1.25% as those from non-pregnant controls at the pre-ovulatory stage. Similarly there was no significant variation from the mean (0.30%) for the free cholesterol. There is no increase in physiological activity in the ovaries of gravid guinea-pigs. J. N. A.

Liver-fat and blood determinations after adrenalectomy. J. F. B. BARRETT and A. T. WILSON (J. Physiol., 1934, 81, 43—45P).—In doubly adrenalectomised cats increased blood viscosity causes an increase in residual blood in the liver and a consequent fall in the % of total solids. No correlation is apparent between adrenalectomy and the amount and nature of liver-fat. CH. ABS. (p)

Jaboty fat. Composition of mink fat. New alcohols and hydrocarbons in sperm oil.—See B., 1936, 158.

Hexadecenol and tetradecenol in sperm head oil. Hexadecenol in sperm blubber oil.—See this vol., 311.

Tetradecenoic and dodecenoic acids in sperm oil. I, II.—See this vol., 313.

Change in the solubility of calcium compounds during the autolysis of muscle tissue. I. A. SMORODINCEV and J. N. LASKOVSKAJA (Bull. Soc. Chim. biol., 1935, 17, 1814—1821).—The H_2O -sol. Ca of autolysing beef increases with time in parallel with the lactic acid, but not the $PO_4^{'''}$ content of the extract. A. L.

Analysis of otoliths and endolymphatic sac deposits in *Amblystoma tigrinum*. A. B. HASTINGS (J. Comp. Neurol., 1935, 61, 295—296).—Saccus deposits and otoliths contained 26.7 and 15.9% of $Ca_3(PO_4)_2$ as dahlite and 64.5 and 83.2% of $CaCO_3$ as aragonite, respectively. CH. ABS. (p)

Role of iron and silica in the structure of the radular teeth of certain marine molluscs. E. I. JONES R. A. McCANCE, and L. R. B. SHACKLETON (J. Exp. Biol., 1935, 12, 59—64).—In the *Patellidae* radular teeth consist largely of Si and Fe, the former comprising the skeleton of the teeth. Fe is present as oxide, carbonate, or org. compound. In *Chitonidae* Fe occurs without Si and in *Deutalium* Si, but not Fe, is present. CH. ABS. (p)

Modifications in the quantity of some phosphorus compounds in the muscle of the pigeon deprived of its cerebellum. M. F. DE MIRA and A. DA CRUZ (Compt. rend. Soc. Biol., 1936, 121, 259—261).—Extirpation of the cerebellum diminishes inorg. P, $P_2O_7^{'''}$, and (particularly) phosphagen. R. N. C.

Detection of heavy metals in the retina. E. BARONI (Monatsh., 1935, 67, 129—130).—Traces of Cu have been found in fresh retina and choroid. Zn is absent. F. L. U.

Action of lipins on lacteal secretion and the chemical composition of milk. I. Action of lecithin and cholesterol introduced by the parenteral route in the goat. II. Action of the total lipins of egg-yolk introduced by the parenteral route in the goat. D. TORRISI (Boll. Soc. ital. Biol. sperim., 1935, 10, 443—445, 445—447).—I. Lecithin (I) in small quantities increases, and in larger quantities reduces, body-wt. and lacteal secretion; small quantities increase total milk-lipins (II) and cholesterol (III). Cholesteryl oleate (IV) increases body-wt., (II), and (III) without affecting secretion. Mixtures of (I) and (IV) in small quantities increase body-wt., lacteal secretion, total, inorg., and casein-P, (II), and (III), without affecting acid-sol. and lecithin-P. Larger quantities reduce body-wt. slightly without affecting lacteal secretion or the composition of the milk.

II. Injection of egg-yolk lipins in well-fed animals increases body-wt., lacteal secretion, total, inorg., and casein-P of the milk, (II), and (III); org. acid-sol. P and kephalin-P are unaffected. In sparingly-fed animals body-wt. and lacteal secretion are diminished, whilst small quantities also diminish (II) and kephalin. A succession of small daily doses influences favourably body-wt., lacteal secretion, (II), and the various P fractions in the milk. R. N. C.

Monohydroxypalmitic acid in butter fat. A. W. BOSWORTH and G. E. HELZ (J. Biol. Chem., 1936, 112, 489—492).—A *monohydroxypalmitic acid*, m.p. 16.5—17.5°, $[\alpha]_D^{20} +2.40^\circ$ to 2.47° in $CHCl_3$, was separated from butter fat. H. D.

Biological effects of feeding with the milk of cows in oestrus. F. USUELLI (Boll. Soc. Eustachiana, 1934, 32, 57—64; Chem. Zentr., 1934, ii, 3783). R. N. C.

Detection of oxytocic, pressor, and diuresis-inhibitory components of posterior pituitary secretion in cerebrospinal fluid. S. DELEONARDI (Arch. exp. Path. Pharm., 1936, 180, 135—141).—All three components (oxytocic in amount corresponding with approx. 0.4×10^{-6} g. of fresh pituitary prep. per c.c.) were detected in cerebrospinal fluid (rabbit, dog) and in fluid from the second and third ventricles (man). F. O. H.

Colour reaction of cerebrospinal fluid in cerebrospinal meningitis. R. REITLER (Trans. Roy. Soc. Trop. Med. Hyg., 1935, 28, 405—406).—The centrifuged fluid (1 c.c.) is poured over a layer (1 c.c.) of H_2SO_4 . In pathological, but not in normal, fluids a violet ring is produced in 24 hr. CH. ABS. (p)

Stability of sugar in cerebrospinal fluid. P. G. SCHUBE (J. Lab. Clin. Med., 1935, 20, 752—753).—The sugar content of the fluid stored under sterile conditions at 10° remains unchanged for < 21 days. CH. ABS. (p)

Inorganic phosphorus and sugar of cerebrospinal fluid. P. UJSAGHY (Orvosi Hetilap, 1935, 79, 381—382).—Some proportionality between the two vals. was observed, but no regularities were apparent. The occurrence of high or normal P contents was no indication of the presence or absence of meningitis. CH. ABS. (p)

Modifications of the thiocyanate concentration of the nasal mucus and other secretions, in relation to stimulation of the trigeminum and the olfactorium. P. NICCOLINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 431—432).—Stimulation of the olfactorium with eucalyptus oil increases CNS' in the nasal and lachrymal secretions and the urine, but not in the saliva. R. N. C.

Saliva. A. CASTELLANI, M. DOUGLAS, P. REDAELLI, and G. AMALFITANO (J. Trop. Med. Hyg., 1935, 38, 81—87).—A review. CH. ABS. (p)

Presence of lactic acid in the saliva. R. VLADESCO (Compt. rend. Soc. Biol., 1936, 121, 275—276).—Lactic acid is always present. R. N. C.

Hæmolytic actions and surface tension of human and animal biles and cholates. S. TSUJI (Japan. Z. Mikrobiol. Path., 1934, 28, 1534—1552).—Among various biles examined those of carp and toads had the greatest hæmolytic action and that of chicken the highest surface tension. CH. ABS. (p)

Action of post-pituitary extracts on gastric secretion. L. LANGERON, M. PAGET, and A. DANÈS (Compt. rend. Soc. Biol., 1936, 121, 33—35). R. N. C.

Gastric acidity and its significance. F. L. APPERLY (Lancet, 1936, 230, 5—9). L. S. T.

Urine of the normal cat. L. BLANCHARD (Bull. Soc. Chim. biol., 1935, 17, 1693—1706).—The vol., acidity, and urea, NH_3 , and Cl' content of the urine of the cat are 37 c.c. per kg. wt. per day, 0.060 g. of H, 84.10—89.85, 1.88—2.69, and 3.05—4.67 g. per 1000 g., respectively. The normal urine contains albumin (0.5 g. per 1000 g.), and under certain conditions of feeding small amounts of lipins and cholesterol. A. L.

Modifications of the urinary reaction following renal denervation. E. TRIA and B. CAPALDI (Boll. Soc. ital. Biol. sperim., 1935, 10, 502—504).—Renal denervation induces a fall of the actual and potential acidity of the urine, a slight rise in NH_3 , and a considerable rise of combined CO_2 , free CO_2 being scarcely affected. Conditions tend to return to normal after 10—15 days. R. N. C.

Partition of nitrogenous constituents of urine and its physiological significance. VII. Evolution of specific endogenous nitrogen metabolism during protein inanition. G. MOUROT (Bull. Soc. Chim. biol., 1935, 17, 1741—1789).—In the urine of rats undergoing protein starvation, the total N, after remaining nearly const. for some time, increases before death. Whilst urinary creatinine, uric acid, and purine bases do not, the urea-, NH_4 -, and $\text{NH}_2\text{-N}$, allantoin, and creatine losses do, follow the same course as that of the total N. A. L.

Detection of leucine and tyrosine [in urine]. FISCHER and H. STRALLER (Pharm. Ztg., 1936, 81, 38—39).—A method is given for detecting 0.01% of leucine (I) and tyrosine (II) in urine. In fresh urine containing sediment, (I) and (II) are in the sediment and not in solution. Control tests are advisable when the microscopic test is used. (I) and (II) occur very rarely in urine. P. G. C.

Micro-determination of trimethylamine in the urine. G. MONASTERIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 385—386).—The urine is distilled with alkaline NaOCl , which decomposes all but the *tert.* bases. NMe_3 is collected in 0.02N- H_2SO_4 and excess of H_2SO_4 determined with I. R. N. C.

Histidine in human urine. F. FÖLDES (Biochem. Z., 1936, 283, 199—209).—The frequency of the occurrence of histidine (I) in human urine increases as its *d* increases. (I) is detected more frequently in the urine of pregnant women than in that of non-pregnant, but a test for pregnancy cannot be based on this difference. No (I) could be detected in the urine of non-pregnant animals (dog, horse, cow, elephant, giraffe, tiger, antelope). A method described is more sensitive for the detection of (I) than is that of Kapeller-Adler (A., 1934, 1050). W. McC.

Renal innervation and reducing substances in the urine. E. MARTINI, A. BONSIGNORE, and F. PINOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 474—477).—The oxidised/reduced ascorbic acid ratio in the urine of the dog is increased by congelation of the vagi, renal denervation, or injection of atropine. It is reduced by excitation of the congealed vagi or injection of eserine. R. N. C.

Determination of ascorbic acid in urine by titration. H. VON EULER and D. BURSTRÖM (Biochem. Z., 1935, 283, 153—157).—The ascorbic acid contents of the same samples of urine as determined by the Bezssonoff method (using molybdophosphotungstic acid) are always very much > results on the same urines by the Tillmans method. P. W. C.

Use of Mayer's reagent for detection of quinine in alkaline urine. J. W. FIELD and M. KANDIAH (Trans. Roy. Soc. Trop. Med. Hyg., 1935, 28, 385—390).—Addition of AcOH to the reagent ensures pptn. of albumin (I), and of quinine (II) in clinically significant amounts. If (I) is present, urine and reagent are boiled and filtered while hot. On cooling (II) is pptd. CH. ABS. (p)

Detection of acridine derivatives in urine. G. FERRARI (Diagnostica tec. lab. [Napoli], 1934, 5, 928—932).—The sample (5 c.c.) is treated with 1—2 drops of 20% aq. Na caffeine benzoate. An intense green fluorescence or the enhanced intensity of an existing fluorescence indicates the presence of acridine derivatives. CH. ABS. (p)

Determination of urinary ketones for clinical use. E. MACCHIA (Diagnostica tec. lab. [Napoli], 1934, 5, 908—918).—An application of the nitroprusside reaction is described. CH. ABS. (p)

Paraffin hydrocarbon from urine of pregnancy. W. F. HART and M. A. NORTHUP (J. Amer. Chem. Soc., 1935, 57, 2726—2727).—The material extracted by light petroleum from the adsorbate (fuller's earth) from the acidified, aged urine is separated by warm MeOH into insol. *heptacosane*, m.p. 58—59°, and (probably) sol. *pentacosane*, m.p. 52—54°. H. B.

Urinolysis in fat metabolism. F. J. JIRKA and C. S. SCUDERI (J. Lab. Clin. Med., 1935, 20, 631—633).—Intracystic fat occurs exclusively in the last

few drops of urine excreted. It may be determined directly by centrifuging in a Babcock bottle.

CH. ABS. (p)

Determination of glucose and chlorides in urines containing sodium formaldehydesulphoxylate. E. HUG and R. H. DE MEIO (Compt. rend. Soc. Biol., 1936, 121, 370—372).—Na formaldehydesulphoxylate reduces AgNO_3 and alkaline Cu solutions, and must be oxidised with HNO_3 and KMnO_4 before Cl⁻ can be determined. Glucose can be determined polarimetrically, or by Cu after preliminary deproteinisation with HgSO_4 - H_2SO_4 and BaCO_3 , and removal of Hg with H_2S .

R. N. C.

Enteric coatings. II. Excretion studies with sodium salicylate tablets. M. WRUBLE (J. Amer. Pharm. Assoc., 1935, 24, 1074—1077).—The amounts of salicylate recovered from the urine by a modified Thoburn-Hanzlik method were approx. the same whether coated or uncoated tablets of Na salicylate were administered.

E. H. S.

Approximate rapid determination of the barbital content of urine and drugs. H. OETTEL (Arch. Pharm., 1936, 274, 1—10).—The barbital content of urine is determined within a few mg. by acidifying 10 c.c. with a few drops of 0.1N-HCl, extracting with 20 c.c. of CHCl_3 , and adding small amounts of 0.2% MeOH- $\text{Co}(\text{OAc})_2$ and 0.2% MeOH-LiOH to the extract. Barbitals are detected in urine immediately and several days after administration.

R. S. C.

"Donaggio phenomenon" in the urine of children affected with muscular dystrophy both at rest and after fatigue. E. BOZZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 586—587).

R. N. C.

"Donaggio phenomenon" in the urine of horses in febrile conditions. P. ROCI BITTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 561—563).

R. N. C.

"Donaggio reaction" in the urine of fatigued individuals. A. TORBOLI (Boll. Soc. ital. Biol. sperim., 1935, 10, 548—550).

R. N. C.

"Inhibition phenomena" of Donaggio. T. VITALI (Diagnostica tec. lab. [Napoli], 1935, 6, 9—20).

CH. ABS. (p)

Microdetermination of the p_H of fluid in renal glomeruli and tubules. H. MONTGOMERY and J. A. PIERCE (Amer. J. Med. Sci., 1934, 187, 735).—A colorimetric method for 0.2-c.c. samples and a quinhydrone electrode for 0.02 c.c. are described. Vals. for glomerular, proximal, and intermediate tubular fluids in *Necturus* are the same as that for plasma. The p_H decrease occurs in the distal tubule, in which vals. are always < that of glomerular fluid and > that of the corresponding urine.

CH. ABS. (p)

Determination of total lipins and lipin partition in faeces. H. C. TIDWELL and L. E. HOLT, jun. (J. Biol. Chem., 1936, 112, 605—613).—A method for determining the partition of lipins, unsaponifiable matter, neutral fat, fatty acid, and soap in a single sample is described.

J. N. A.

Calcium precipitation in the pancreas. M. LOEPER, A. LESURE, E. BIOY, and P. PERREAU

(Compt. rend. Soc. Biol., 1936, 121, 22—24).—Pancreatic Ca is 2—5 times as great as hepatic Ca in pathological states, which is probably the cause of its rapid petrification.

R. N. C.

Blood and urinary phosphorus in various diseases. T. IINO (J. Chosen Med. Assoc., 1935, 25, 26—40).—Data are recorded.

CH. ABS. (p)

Carbon disulphide and adrenals (Addison's disease). L. DEVOTO (Arch. Gewerbepath. Gewerbehyg., 1934, 5, 429—432).—A case is reported of Addison's disease following prolonged work with CS_2 .

R. N. C.

Prophylaxis of simple anæmia in infancy with iron and copper. Effect on hæmoglobin, weight, and resistance to infection. S. J. USHER, P. N. MACDERMOT, and E. LOZINSKI (Amer. J. Dis. Children, 1935, 49, 642—657).—Daily administration of Fe^{III} glycerophosphate to infants increased the average hæmoglobin concn. at 1 year by 15%. Simultaneous administration of CuSO_4 enhanced the effect, and increased gains in wt. and resistance to infection.

CH. ABS. (p)

Glutathione and anæmia. G. C. DOGLIOTTI and T. CASTELLANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 521—523).—Total glutathione (I) in the blood is normal or slightly reduced in post-hæmorrhagic or acute infectious anæmia, whilst corpuscular (I) is normal or slightly raised. In other anæmias total (I) is generally normal, whilst corpuscular (I) is raised; in polycythæmia corpuscular (I) is reduced.

R. N. C.

Further evidence for the presence of a toxic factor in pernicious anæmia. G. E. WAKERLIN and H. D. BRUNER (Science, 1935, 82, 494—495).—The urine contains a thermolabile, comparatively toxic, reticulocyte-decreasing factor and a partly thermostable, relatively non-toxic, reticulocyte-stimulating principle for the pigeon. Normal human urine contains the latter, but not the former.

L. S. T.

Non-identity of lactoflavin and the "extrinsic factor" in pernicious anæmia. C. A. ASHFORD, L. KLEIN, and J. F. WILKINSON (Biochem. J., 1936, 30, 218—223).—Lactoflavin is not identical with either the liver anti-pernicious anæmia principle or the "extrinsic factor."

H. G. R.

Effect of transfusion of heterogeneous formolised blood in experimental acetylphenylhydrazine anæmia in the rabbit. O. MALAGUZZI-VALERI (Boll. Soc. ital. Biol. sperim., 1935, 10, 453—455).

R. N. C.

Effect of heterogeneous formolised transfusion in experimental anæmia from bleeding in the rabbit. O. MALAGUZZI-VALERI (Boll. Soc. ital. Biol. sperim., 1935, 10, 546—548).

R. N. C.

Cholesterol content of plasma in arthritis. E. F. HARTUNG and M. BRUGER (J. Lab. Clin. Med., 1935, 20, 675—681).—Plasma-cholesterol (I) decreased in rheumatoid and increased in osteo-arthritis. The ratio of free (I) : (I) esters is normal. Total (I) of the blood and sedimentation rate are not related.

CH. ABS. (p)

Cholesterol-induced atherosclerosis: prevention in rabbits by feeding an organic iodine compound. I. H. PAGE and W. G. BERNHARD (Arch. Path., 1935, 19, 530—536).—Administration of org. I compounds prevents atherosclerosis following feeding of cholesterol (I) in olive oil. Persistent lipæmia also occurring under these conditions is more marked when I compounds are given. The lipæmia differs from that occurring in nephrosis, in that total, free, and ester-(I) are increased relatively $>$ are lipin-N, $-NH_2-N$, or $-P$.
CH. ABS. (p)

Separation of liver substances which are reticulocytogenic in the guinea-pig and therapeutically active in experimental canine black tongue. Y. SUBARROW, B. M. JACOBSON, and C. H. FISKE (New England J. Med., 1935, 212, 663—664).—Approx. 50% of the activity of crude liver extract was due to *l*-tyrosine. A second active substance can be adsorbed on charcoal and eluted by EtOH.
CH. ABS. (p)

Serum-proteins in cancer. W. KOPACZEWSKI (Compt. rend., 1935, 201, 1229—1231).—In cancer serum-globulin and -albumin are $<$ and myxoproteins $>$ normal. The hydrophobic colloid content, and the physical condition of the colloid, are concerned in the acceleration of lactogelatinisation of cancerous sera.
A. G. P.

Schubert-Dannmeyer test for cancer. E. R. HOLIDAY and F. C. SMITH (Amer. J. Cancer, 1935, 23, 339—342).—The method, based on changes in serum-lipin in cancer, is not sufficiently trustworthy for clinical use.
CH. ABS. (p)

Early diagnosis of carcinoma by exact chemical measurement. R. LINKS (Z. Krebsforsch., 1934, 41, 166—206; Chem. Zentr., 1934, ii, 3787—3788).—A formula is given for the diagnosis of carcinoma from serum-K and -Mg determinations.
R. N. C.

Inhibiting the development of tar-carcinoma in mice. J. R. DAVIDSON (Canad. Med. Assoc. J., 1935, 33, 364—366).—A diet rich in vitamin-*E* (and incidentally in $-B_1$ and $-B_2$) increased the resistance of mice to carcinogenic factors in tar. CH. ABS. (p)

Carcinogenic action of 1:2-benzpyrene. C. SANNIÉ, C. OBERLING, M. GUÉRIN, and P. GUÉRIN (Compt. rend. Soc. Biol., 1935, 120, 1196—1198).
R. N. C.

Physiological validity of enzyme [amylase] determinations in tumour tissue. F. H. SCHARLES, P. ROBB, and W. T. SALTER (Amer. J. Cancer, 1935, 23, 322—327).—The method previously described (A., 1934, 1023) determines only the enzymic activity, and not the effect of accelerators or inhibitors.
CH. ABS. (p)

Plasma and erythrocyte glutathione in human cancer. J. W. SCHOONOVER (Amer. J. Cancer, 1935, 23, 315—321).—In cancer the ratio of oxidised glutathione (I) to reduced (I) is increased in plasma and lowered in erythrocytes. The quotient of the ratio in plasma \div the ratio in erythrocytes is $>$ normal.
CH. ABS. (p)

Blood-glutathione in human cancer. J. W. SCHOONOVER (Amer. J. Cancer, 1935, 23, 311—314).—

The average concns. of oxidised and of reduced glutathione (I) remain normal in cancer, but vals. for reduced (I) in erythrocytes were slightly $>$ normal.
CH. ABS. (p)

Aminoethyl phosphate from tumours. E. L. OUTHOUSE (Biochem. J., 1936, 30, 197—201).—Bovine malignant tumours contain aminoethyl phosphate (I) [*Ba* salt; *brucine* salt (one equiv. of brucine); *flavianate*, m.p. 223°] identical with synthetic (I) from aminoethanol (II) phosphate and $POCl_3$. Hydrolysis of (I) with phosphatase gives (II) (flavianate, m.p. 198° and 212°). Probably the formula of (I) is $CH_2 \langle \begin{smallmatrix} NH_3 \cdot O \\ CH_2 \cdot O \end{smallmatrix} \rangle PO \cdot OH$, at least at p_H 5—9.
W. McC.

Biodynamics of the pseudo-proteins. Chemotherapy of carcinoma by redox substances from osteocolla. O. HUPPERT (Wien. med. Woch., 1934, 84, 624—628; Chem. Zentr., 1934, ii, 3788).—A thiogelatin, an org. Fe-heavy-metal complex with a synthetically-introduced thiazole-glyoxal group of the character of glutathione, prepared from osteocolla, has an inhibitory effect on growth of *B. coli*, and is thus a possible therapeutic agent for cancer.
R. N. C.

Effect of bromohexic acid on rat sarcoma 39. W. A. SELLE and M. BODANSKY (Amer. J. Cancer, 1935, 23, 289—296).—No sp. inhibition of growth was observed.
CH. ABS. (p)

Enzymes in rabbit sarcoma. K. MIYAMA (Sei-i-Kwai Med. J., 1934, 53, No. 6, 105—123).—Necrotic and non-necrotic areas in rabbit sarcoma contain amylase and lipase, the latter being greater in necrotic sections. The lipase is resistant to atoxyl and quinine. Small amounts of trypsin and a pepsin-like enzyme occur in both areas.
CH. ABS. (p)

Dental caries. III. Rickets in relation to caries in deciduous and in permanent teeth. A. F. HESS, H. ABRAMSON and J. M. LEWIS (Amer. J. Dis. Children, 1934, 47, 477—487).
CH. ABS. (p)

Mottled enamel in Texas. H. T. DEAN, R. M. DIXON, and C. COHEN (U.S. Publ. Health Repts., 1935, 50, 424—442).—A review.
CH. ABS. (p)

Calcium and phosphorus metabolism of children with mottled enamel. E. M. LANTZ, M. C. SMITH, and R. M. LEVERTON (J. Home Econ., 1935, 27, 236—239).—The Ca and P metabolism is not affected by feeding F. F probably causes mottled enamel by a sp. effect on the enamel-forming organ.
CH. ABS. (p)

Changes in teeth and bone in chronic fluoride poisoning. C. J. SUTRO (Arch. Path., 1935, 19, 159—173).—Changes in the enamel and bone matrix caused by feeding NaF are due to chemical disturbances unrelated to the parathyroid glands.
CH. ABS. (p)

Glutathione and diabetes. G. C. DOGLIOTTI and O. MELONI (Boll. Soc. ital. Biol. sperim., 1935, 10, 523—525).—Total glutathione (I) in the blood of diabetics is normal whether or not insulin (II) has been administered. Corpuscular (I) is slightly $>$ normal in moderate diabetes, and slightly $<$ normal after (II); it is also $<$ normal in severe cases.
R. N. C.

Diabetes mellitus, its differentiation into insulin-sensitive and insulin-insensitive types. H. P. HIMSWORTH (*Lancet*, 1936, 230, 127—130).—One type appears to be caused by a deficiency of insulin (I), and the other to lack of an unknown factor which sensitises the body to (I). L. S. T.

Effect of protein on carbohydrate tolerance of two patients having combined diabetes mellitus and pernicious anæmia. N. JOLIFFE, H. BRAN-DALEONE, and H. MOST (*J. Clin. Invest.*, 1935, 14, 357—365).—High-protein (II) diets reduced carbohydrate (I) tolerance. Use of high-(I) diets counteracted the immediate effects of (II), but loss in tolerance was permanent and not affected by insulin. CH. ABS. (p)

Absorption curve of glucose by the red corpuscles of normal and diabetic subjects *in vitro*. G. PATRASSI and U. TEODORI (*Boll. Soc. ital. Biol. sperim.*, 1935, 10, 527—528).—The absorption curves of the corpuscles are very similar in the two cases, both rising to a steady max., the increases of the glucose contents being equal. R. N. C.

Relations between bilirubinæmia and carbohydrate metabolism. I. Bilirubinæmia in fasting and glucose-fed diabetics. E. SLAVICH (*Boll. Soc. ital. Biol. sperim.*, 1935, 10, 531—532).—Bilirubinæmia in diabetics is considerably > normal. It is not affected by ingestion of glucose. R. N. C.

Effect of thyroidectomy in poisoning by diphtheria toxin. P. LOCATELLI (*Boll. Soc. ital. Biol. sperim.*, 1934, 9, 1317—1318). R. N. C.

Influence of acute infection and artificial fever on plasma-lipins. A. V. STOEISSER and I. Mc-QUARRIE (*Amer. J. Dis. Children*, 1935, 49, 658—671).—Plasma-lipins decrease in acute febrile, but not in afebrile, disorders or induced fevers. Fever, in itself, does not cause lipin changes. CH. ABS. (p)

Experimental goitre: functional, chemical, and histological studies. C. A. HELLWIG (*Arch. Path.*, 1935, 19, 364—371).—A Ca-rich diet induces goitres in rats. The I content of goitres is related to that of the diet. Colloid (I-rich) goitres have a higher thyroid function than do parenchymatous, colloid-rich goitres. The latter induce the higher blood-Ca vals. CH. ABS. (p)

Etiology of enzoötic bovine hæmaturia. I. S. C. A. DATTA (*Indian J. Vet. Sci.*, 1934, 4, 341—361).—Oral administration of Ca lactate or intravenous injection of CaCl₂ caused no appreciable difference in coagulability of blood in affected cases. Serum-Ca was not affected, but serum-PO₄^{'''} increased. CH. ABS. (p)

Hæmoglobin index and jaundice of the newborn. C. HOLLÓSI and Z. HORVÁTH (*Amer. J. Dis. Children*, 1935, 49, 638—641).—The hæmoglobin index is > 100% in normal and < 100% in jaundiced newborn. CH. ABS. (p)

Serum-phosphatase in toxic and hæmolytic jaundice. A. R. ARMSTRONG and E. J. KING (*Canad. Med. Assoc. J.*, 1935, 32, 379—383; cf. A., 1935, 403).—The phosphatase increased markedly in toxic, but not in hæmolytic, jaundice. CH. ABS. (p)

Significance of thiocyanate in hepatic coma. H. INOUE (*J. Chosen Med. Assoc.*, 1934, 24, 1355—1365).—The SCN['] in blood and urine is lowered in hepatic coma. Vals. were also low in rabbits with total biliary obstruction and in dogs with Eek fistula. CH. ABS. (p)

Pathological physiology of the liver. III. Impaired function in relation to nitrogen-containing substances. I. MATSUI and K. INOUE (*Acta Schol. Med. Kioto*, 1935, 17, 417—432).—A review. CH. ABS. (p)

Rôle of fats and cholesterol in the Henry reaction. V. CHORINE (*Compt. rend. Soc. Biol.*, 1936, 121, 297—300).—The intensity of the Henry reaction is reduced by washing the serum with Et₂O, which reduces surface tension and removes fats and cholesterol. The reaction is associated with protein modifications in the serum, the rôle of fats and cholesterol being secondary. R. N. C.

Lipins and melano-flocculation (Henry reaction). F. TRENSZ (*Compt. rend. Soc. Biol.*, 1935, 120, 1268—1270).—The euglobulins of paludic sera that have been freed from fat by pptn. with COMe₂ no longer give positive melano-flocculation reactions. The isolated globulins also lose their melano-flocculability when treated with COMe₂; the reaction is therefore dependent not on the protein part of the globulin mol., but on associated lipins or other COMe₂-influenced substances. R. N. C.

Chemical factors of malaria-flocculation (Henry reaction) in anophelian paludism. E. BENHAMOU and R. GILLE (*Compt. rend. Soc. Biol.*, 1935, 120, 1259—1261).—The three factors controlling malaria-flocculation are euglobulin, serin, and cholesterol; the Henry reaction depends on their ratio (the index of flocculability), but not on any of them separately. R. N. C.

Melano-precipitation serological reaction in malaria. E. D. W. GRIEG, C. O. VAN ROOYEN, and E. B. HENDRY (*Trans. Roy. Soc. Trop. Med. Hyg.*, 1934, 28, 175—191).—The substitution of a colloidal melanin (I) solution (prep. described) for the ochroid antigen (Henry) is suggested. In the course of a benign tertian infection the blood-phospholipin inversely \propto the reacting titre with (I). CH. ABS. (p)

Malaria and blackwater fever. I. Malaria. II. Blackwater fever. Hæmoglobinæmia. III. New blood pigment in blackwater fever and other biochemical observations. N. H. FAIRLEY and R. J. BROMFIELD (*Trans. Roy. Soc. Trop. Med. Hyg.*, 1933—1934, 27, 289—314).—I. Blood destruction in malaria is associated with hyperbilirubinæmia, urea increase, decrease in blood-cholesterol, and normal alkali reserve. Hæmoglobinæmia does not occur. Sp. treatment (quinine etc.) decreases plasma-bilirubin and -urea and increases blood-cholesterol.

II. In blackwater fever blood is brownish-red and contains methæmoglobin (I). Washed red cells do not contain (I). Variations in (I) and oxyhæmoglobin (II) are recorded. (I) arises from (II) which has been liberated from corpuscles after lysis. Drug-methæmoglobinæmia is intracorpuseular in origin and does not

involve presence of (I) in plasma or excretion in urine.

III. The pigment resembles but is not identical with (I). The hæmolytic agent in blackwater fever arises from metabolic breakdown in chronic subtertian malarial infection, is pptd. by quinine, lysing the corpuscle and converting the liberated (II) into (I), or the new pigment. CH. ABS. (p)

Function of the liver in malaria. Overloading with galactose and combined overloading with insulin-glucose-water. K. TSCHELOV and I. MLADENOV (Arch. Schiffs- u. Tropen-Hyg., 1934, 38, 282—287; Chem. Zentr., 1934, ii, 3405).—Galactosuria following overloading with galactose does not indicate liver injury. In some patients blood-sugar (I) is increased without sugar excretion. Combined administration of glucose and H₂O after insulin produces a disturbance of the liver function, with hypoglycæmia and an abnormal difference between (I) in the unaffected and hypoglycæmic states. (I) is frequently delayed in reaching its max. R. N. C.

Experimental chemotherapy in malaria. W. KIRUTH (Deut. med. Woch., 1935, 61, 573—577). R. N. C.

Chlorine metabolism in meningitis. A. PRUNELL (Prensa méd. Argentina, 1935, No. 2).—Bacillary meningitis is usually followed by decreased Cl' in spinal fluid; glucose content is lowered and fibrin is present. Blood-NaCl is correspondingly decreased. CH. ABS. (p)

Diagnostic and prognostic significance of the creatine-creatinine metabolism in various myopathies before and after amino-acid therapy. H. H. BEARD, C. J. TRIPOLI, and J. E. ANDES (Amer. J. Med. Sci., 1934, 188, 706—712).—Clinical improvement is associated with increased creatine excretion (50—200% > that of control period) provided this increased creatinuria soon disappears or returns to the control level. Creatinuria probably has an exogenous origin from the NH₂-acids of the diet. CH. ABS. (p)

Thiocyanate ions in blood and urine of nephritic cases. H. INOUE and M. YAMASHITA (J. Chosen Med. Assoc., 1935, 25, 1—13).—Blood-SCN' increases and urinary SCN' decreases in nephritis. A similar retention of SCN' occurs in experimental nephritis produced in rabbits by cantharidin, U, and HgCl₂. CH. ABS. (p)

Phenol contents of blood of nephritic and hepatic patients. D. YANAGIHARI (J. Chosen Med. Assoc., 1934, 24, 1562—1570).—Vals. for free, combined, and total PhOH in nephritic patients were <, and in hepatic patients >, normal. The free PhOH in blood increases with the gravity of the disease. No relationship was apparent between blood pressure and blood-PhOH. CH. ABS. (p)

An optimal diet in promoting nitrogen gain in nephrosis S. H. LUV and H. I. CHU (J. Clin. Invest., 1935, 14, 293—303).—In Bright's disease of the nephrotic type, N retention was favoured by increasing the carbohydrate, fat, and N in the diet. Optimum

vals. are given. Changes in serum-protein level took place slowly even during N retention.

CH. ABS. (p)
Indican test on blood and urine in renal insufficiency. S. H. POLAYES and E. A. ECKERT (J. Lab. Clin. Med., 1935, 20, 681—688).—High blood-indican (I) is always accompanied by high total non-protein-N (II). In some cases of severe renal disease normal (I) occurs with high (II). A persistent increase in (I), concomitant with a decrease in urinary indican, indicates a fatal prognosis. CH. ABS. (p)

Influence of glycine on creatinuria in peripheral neuritis. M. J. C. ALLISON, H. H. HENSTELL, and H. E. HIMWICH (Amer. J. Med. Sci., 1934, 188, 560—564).—Ingestion of glycine markedly increased creatinuria. Edestin and glutamic acid had no action. CH. ABS. (p)

Nutritional œdema in the dog. II. Hypoalbuminæmia and the augmentation of tissue fluid. A. A. WEECH, E. GOETTSCHE, and E. B. REEVES (J. Exp. Med., 1935, 61, 717—734).—Data relating to N metabolism and wt. changes indicate increasing retention of fluid during the pre-œdema stage. A positive correlation between the duration of œdema and the protein content of the œdema fluid is not demonstrable. CH. ABS. (p)

Polypeptidæmia in pellagra. P. TOMESCO, N. G. IONESCO, and P. CONSTANTINESCO (Compt. rend. Soc. Biol., 1936, 121, 190—192).—Polypeptidæmia is increased in pellagra, particularly in the more pronounced visceral forms. R. N. C.

Behaviour of hepatic lipins in experimental rabies. R. MACCOLINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 580—583).—Hepatic lipins are > normal in the rabbit. R. N. C.

Action of the lung on polypeptides: application to the study of scalds. L. BINET and M. BURNSTEIN (Compt. rend. Soc. Biol., 1936, 121, 287—289).—Perfusion of blood through an isolated scalded lung causes an increase in the polypeptide content of the blood, which is reduced by subsequent perfusion through a normal lung. R. N. C.

Chemotherapy of schistosomiasis. M. KHALIL (J. Egypt Med. Assoc., 1935, 18, 284—295). CH. ABS. (p)

Experimental scurvy. XX. Leucocytes in blood of guinea-pigs on a vitamin-C-free diet. XXII. Amounts of reducing substance and hydrolysed sugar in urine of guinea-pigs on a vitamin-C-free diet. J. SHIMADA. XXIV. Gas metabolism. Y. SONEDA and Y. KATO (Sei-i-Kwai Med. J., 1934, 53, No. 6, 105—123, No. 10, 159—171, 172—186).—XXII. Scurvy does not affect the reducing substances in urine. Partial inanition causes a decrease in the amount and % of these substances.

XXIV Diets free from vitamin-C cause an initial decline (2 days), a return to normal (3 days), and from the tenth scorbutic day till death a steady decline in gaseous metabolism. The O₂ intake of semi-starved guinea-pigs is reduced in abs. val., but is practically unchanged if calc. on a body-wt. basis. CH. ABS. (p)

Complement fixation as related to resistance and allergy in experimental tuberculosis. A. B. BAKER (Amer. Rev. Tuberc., 1935, 31, 54—61).

CH. ABS. (p)

Gastric acidity in pulmonary tuberculosis. I. GRAY and J. MELNICK (Amer. Rev. Tuberc., 1935, 31, 460—465).

CH. ABS. (p)

Vitamin therapy in intestinal tuberculosis. M. M. STEINBACH and M. B. ROSENBLAT (Amer. Rev. Tuberc., 1935, 31, 35—43).—High-vitamin diets neither cured nor prevented intestinal tuberculosis.

CH. ABS. (p)

Effect of applications of irradiated cholesterolised lanoline on the blood-cholesterol in pulmonary tuberculosis. A. DUFOURT and P. LAROUX (Compt. rend. Soc. Biol., 1936, 121, 43—45).

R. N. C.

Standardised tuberculin (purified protein derivative) for uniformity in diagnosis and epidemiology. E. R. LONG, F. B. SEIBERT, and J. D. ARONSEN (Tubercle, 1935, 16, 304—322).

CH. ABS. (p)

Old tuberculin, human tubercle bacillus protein, and trichloroacetic acid precipitate. C. A. STEWART (Amer. J. Dis. Children, 1935, 49, 625—637).—Cutaneous sensitivity to tuberculoprotein (by $\text{CO}_2\text{CO}_2\text{H}$ pptn.) differs with age.

CH. ABS. (p)

Effect of reduced glutathione on the curative action of neosalvarsan in the nagana-infected mouse. C. MONCORPS and R. M. BOHNSTEDT (Arch. Dermatologie, 1934, 170, 26—32; Chem. Zentr., 1934, ii, 3983).—Glutathione (I) increases the virulence of trypanosomes, and detoxifies neosalvarsan (II). In mice infected with *T. nagana* the action of (II) is weakened by small quantities of (I) (subcutaneous), but strengthened by large quantities (intravenous).

R. N. C.

Study of gastric acid secretion by fractional analyses in cases of gastric and duodenal ulcers. V. DELFINO (Pathologica, 1935, 27, 261—268).—Curves representing changes of titratable acidity with time of extraction of the gastric secretion are parabolic in normal cases but not in cases of ulceration.

CH. ABS. (p)

Central regulation of basal metabolism. L. ARMENTANO (Orvosi Hetilap, 1935, 79, 311—314).—Basal metabolism is not influenced by agents affecting cerebral centres. Narcotics cause a change $> 10\%$.

CH. ABS. (p)

Basal metabolism in children of normal and subnormal intelligence. Blood-cholesterol and -creatinine values. H. B. ROTHBART (Amer. J. Dis. Children, 1935, 49, 672—688).—No correlation was apparent between metabolic rates and intelligence quotients.

CH. ABS. (p)

Specific-dynamic action of amino-acids. I. Effect of glucose on the specific-dynamic action of glycine. II. Effect of configuration on specific-dynamic action. III. Dependence of specific-dynamic action on amino-group content. Y. MASAI, H. MABUCHI, and T. FUKIWAKE (Biochem. Z., 1936, 283, 159—168, 169—173, 174—179).—I.

In fasting rabbits, distilled H_2O , orally administered, has no sp.-dynamic action and during the fast that of glucose (I) is very weak. The sp.-dynamic action of glycine (II) gradually decreases and finally disappears as fasting continues. The action of (II) is weakened and curtailed by administration of phloridzin. In both cases previous administration of (I) increases the action of (II). Hence the presence of (I) is essential for the development of the sp.-dynamic action of (II).

II. The sp.-dynamic action of *l*-alanine, *l*-glutamic acid, and *l*-aspartic acid is respectively $>$ that of the corresponding *d*- and *dl*-acids, the action of *dl*-aspartic acid being very weak.

III. For each NH_2 -acid there is an optimal amount which has the most powerful sp.-dynamic action, this being less powerful with larger or smaller amounts. There is no relation between the amount of NH_2 -acid given or its NH_2 content and the magnitude of the action. The action of urea is strong, but weaker than that of (II) and alanine.

W. McC.

Diffusion of nitrogenous compounds from frog muscles in Ringer's solution. W. O. FENN (J. Cell. Comp. Physiol., 1935, 6, 469—485).—Frog muscles in Ringer's solution at 22° lose about 52 ± 6 mg. of N per 100 g. of muscle in 5 hr., half the N lost being protein, and the remainder urea, creatine, and NH_2 -acids. In solutions of varying $[\text{K}^+]$ the loss in protein \propto the gain in Cl^- , with a min. at about 50 mg. of K per 100 g. Protein loss is increased by rise of temp., asphyxia, and frequent renewal of the solution; non-protein-N loss is increased by stimulation and asphyxia. Both N losses are reduced by previous perfusion of the muscle with Ringer's solution. During immersion in Ringer's solution p_{H} falls in the muscles and rises in the solution, owing to loss of K^+ and gain of Cl^- by the muscle. Ringer's solution as a medium for muscle is abnormal.

R. N. C.

Water balance of a marine mammal, the seal. L. IRVING, K. C. FISHER, and F. C. McINTOSH (J. Cell. Comp. Physiol., 1935, 6, 387—391).

R. N. C.

Mechanism by which the acidity of an acid meal is reduced in the stomach. F. C. HILL, L. C. HENRICH, and C. M. WILHELMJ (Surg. Gynecol. Obstet., 1935, 60, 966—968).—The mechanism includes neutralisation and the regurgitation of duodenal fluids. The two factors may be determined by use of phenolphthalein. In dogs vals. were 35 and 65%, respectively.

CH. ABS. (p)

Metabolism of injured tissue. (A) W. FLEISCHMANN. (B) H. DRUCKREY (Naturwiss., 1936, 24, 15; cf. this vol., 102).—The results of Druckrey are in harmony with previous work, e.g., that by Fleischmann on the metabolism of leucocytes.

W. O. K.

Metabolism of injured tissue. H. DRUCKREY (Arch. exp. Path. Pharm., 1936, 180, 231—250; cf. this vol., 102).

F. O. H.

Tissue metabolism. VIII. Effect of fumarate and succinate on tumour respiration. E. BOYLAND and M. E. BOYLAND (Biochem. J., 1936, 30, 224—226).—Respiration of tumour tissue, like

that of muscle, kidney, and liver, is increased by succinate or fumarate and decreased by malonate.

H. G. R.

Exhaustion of the respiratory capacity *in vitro* of some tissues. G. DOMINI and P. PERUZZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 493—496).

R. N. C.

Respiration *in vitro* of some tissues in relation to the growth-curve of the organism. P. PERUZZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 489—493).—O₂ consumption by surviving muscle, spleen, and liver sections of the albino rat rises to a max. during the period when body-wt. has reached 40—60 g., and then falls to a steady val.

R. N. C.

Utilisation of oxygen by *Mya arenaria*. L. VAN DAM (J. Exp. Biol., 1935, 12, 86—94).—The O₂ utilisation coeff. is normally 3—10%, but increases temporarily to 25% after a period of anaërobiosis.

CH. ABS. (p)

Anoxybiosis of the embryo of *Rana fusca* in different stages of development. I. LATINIR-VETULANI (Bull. Acad. Polonaise, 1935, B, 273—278).—The effect of anaërobic conditions on CO₂ production by the embryo varies with the stage of development. The mechanism of these effects is examined.

A. G. P.

Respiratory quotients during embryonic development (Orthoptera). E. J. BOELL (J. Cell. Comp. Physiol., 1935, 6, 369—385).—Bound CO₂ in eggs of *Melanoplus differentialis* increases during development. The O₂ consumption curve reaches a max. in 20 days at 25°. In diapause, respiration is maintained at a min. level, but afterwards it increases steadily. The R.Q. shows that fat is the chief metabolite oxidised during development; it decreases slowly in later stages and is probably converted into chitin.

R. N. C.

Photodynamically-induced oxygen consumption in muscle and nerve. A. J. KOSMAN and R. S. LILLIE (J. Cell. Comp. Physiol., 1935, 6, 505—515).—Exposure of eosin-stained muscle and nerve to visible light increases O₂ consumption by 135—183% and 133—144%, respectively. The increase is unaffected by Ca⁺⁺, Na salt solutions, CN⁻, or boiling. Ovalbumin stained with eosin consumes O₂ in presence of light; glucose-eosin solutions, either alone or in presence of adsorbents, do not. Irradiated fat-free muscle extracts but not protein-free extracts consume O₂. The photodynamic effect in skeletal muscle is possibly associated with the membrane proteins.

R. N. C.

Energy sources in ontogenesis. VIII. Respiratory quotient of developing gastropod eggs. E. BALDWIN (J. Exp. Biol., 1935, 12, 27—35).—Throughout development the R.Q. was 1.05. Fat synthesis is indicated. The increase in CO₂ content of the eggs coincides with the formation of true shell. Synthetic fat is probably not derived from protein. Uric acid is synthesised by the embryo during the later period of development.

CH. ABS. (p)

Nutrition and national health. (SIR) R. McCARRISON (Roy. Soc. Arts., 1936, 56 pp.).—Cantor Lectures.

Nutritive value of canavanine. M. KITAGAWA and M. WADA (J. Agric. Chem. Soc. Japan, 1935, 11, 1083—1088).—Dietary experiments on rats failed to elucidate the growth-promoting action of canavanine (cf. Ogawa, A., 1934, 1391).

F. O. H.

Nutritive value of mustard oil. B. B. BRAHMACHARI (Indian Med. Gaz., 1934, 62, 327—329).—The oil contains no vitamin-A and tends to inactivate -A in other foods. It has a nutritive val. similar to that of other fats provided the -A supply is adequate.

CH. ABS. (p)

Comparison between the nutritive value of some legumes and some cereals. V. ZAGAMI and V. FAMIANI (Arch. ital. Biol., 88, 119—127; Chem. Zentr., 1935, i, 3301).

G. H. F.

Nutritive value of alcohol-extracted animal tissues, and supplements required for growth and lactation. W. H. SEEGER and H. A. MATTILL (Proc. Iowa Acad. Sci., 1934, 41, 173—174).—Extracted tissues (beef heart, kidney, round, and liver) produced inferior growth in rats to that obtained with whole tissues. The deficiency was supplied by the EtOH-extract of liver.

CH. ABS. (p)

Determination of digestibility coefficients. I. Method and computation for directly obtaining coefficients of individual nutrients in a mixed ration. M. CARBERY, I. CHATTERJEE, and M. A. HYE (Indian J. Vet. Sci., 1934, 4, 295—340).—Methods utilising graphical and multiple regression equations are described.

CH. ABS. (p)

Nutritional investigation of the porgy. IV. Fractionation of porgy meat. Y. HATAKOSHI (J. Chem. Soc. Japan, 1935, 56, 221—229).—Max. dissolution of protein from ground meat was obtained with 0.1N-NaCl or 0.02N-NaOH.

CH. ABS. (p)

"Disequilibrating" effect of fructose. R. LECOQ (Compt. rend. Soc. Biol., 1936, 121, 226—228).—Fructose (I) causes disequilibrium when present in the diet to 80—84% of the total carbohydrates. The disequilibrium is not so accentuated as with galactose or lactose. Equilibrium is established with 35% of (I), and with 66% if yeast is added to the diet.

R. N. C.

Metabolism of the lung-fish. II. Effect of feeding meat on metabolic rate. H. W. SMITH (J. Cell. Comp. Physiol., 1935, 6, 335—349).—Lung-fish fed with meat exhibit a rise of O₂ consumption, and fasting causes a logarithmic decrease.

R. N. C.

Organic matter in dissolved and colloidal form as food for *Daphnia magna*. S. S. GELLIS and G. L. CLARKE (Physiol. Zoöl., 1935, 8, 127—137).—The animals require colloidal nutrients.

CH. ABS. (p)

Nutrition: vegetable proteins. L. B. MENDEL and H. B. VICKERY (Carnegie Inst. Wash. Yearbook, 1934, 33, 289—295).—In synthetic rations for rats in P-metabolism trials casein may be replaced by lactalbumin or, less satisfactorily, partly purified ovalbumin. Highly purified vitamin-B₂ preps. are obtained from liver, protein-free milk, or yeast by extraction with 5% HCl, adsorption on activated fuller's earth, and elution with NH₃ or C₅H₅N.

Yellow solutions showing green fluorescence (especially in ultra-violet light) are produced. A yeast constituent other than $-B_1$ or $-B_2$ is required for satisfactory growth of rats. The cystine content of haemoglobin (Cu¹ mercaptide method) is: horse 0.41, sheep 0.61, dog 1.16%. Histidine was completely pptd. from protein hydrolysates by HgCl₂. In addition to nicotine, green tobacco leaves contain *N*-methylpyrrolidine and nornicotine, but no sol. quaternary bases other than volatile alkaloids.

CH. ABS. (p)

Influence of protein on longevity. C. Y. CHEN (Nat. Peiping Univ. Coll. Agric. Nutrition Bull., 1935, B, 2, 12—21).—On a 9% protein level the life span of rats was shortest on a beef diet and the longest on a mixed cereal diet containing maize protein 2, casein or soya-bean protein 1.

CH. ABS. (p)

Protein metabolism and oxidation processes in experimental scurvy. III. Urea and creatinine excretions in experimental scurvy and the effect of iron. L. D. KASCHEVNIK and I. B. FRIDLAND (Biochem. Z., 1935, 282, 265—268).—The urinary creatinine in guinea-pigs increases during the development of scurvy and also by addition of Fe to the diets. Addition of Fe, however, does not affect urea excretion.

P. W. C.

Histochemical studies of the development of fish. I. Vitellogenesis in the gudgeon (*Gobio fluviatilis*) and the carp (*Cyprinus carpio*). B. KONOPACKA (Bull. Acad. Polonaise, 1935, B, 163—182).—Appropriate histological technique is described and the stages of formation of vitellin during the growth of the oocyte are examined.

A. G. P.

Synthesis of creatinephosphoric acid in organ extracts and in living spermatozoa. I. TORRES (Biochem. Z., 1935, 283, 128—133).—The transfer of PO₄^{'''} from phosphopyruvic acid (I) to creatine occurs in many organ extracts, most rapidly in muscle and next in extract of testicles, the activity in the latter case being related to the sperm content. Living sperms on addition of (I) and creatine show a considerable synthesis of creatinephosphoric acid.

P. W. C.

Utilisation of tryptophan administered subcutaneously. V. DU VIGNEAUD, R. R. SEALOCK, and C. VAN ETTEN (J. Biol. Chem., 1936, 112, 451—456).—In view of Alcock's contention (A., 1934, 1392) that tryptophan (I) produces no growth response in (I)-deficient animals, earlier work indicating the contrary (A., 1933, 89) was repeated and confirmed. The discrepancies remained when Alcock's technique was used exactly.

H. D.

Availability of tryptophan derivatives for supplementing diets deficient in tryptophan. C. P. BERG and H. E. HANSON (Proc. Iowa Acad. Sci., 1934, 41, 165; cf. A., 1935, 1405).—Utilisation of tryptophan (I) by rats is prevented by benzoylation, but not by acetylation or esterification (EtOH). The propionyl and phenylpropionyl derivatives of (I) as well as the Ph and CH₂Ph ester hydrochlorides (but not the phenylacetate) were utilisable.

CH. ABS. (p)

Production of a deficiency involving cystine and methionine by the administration of cholic

acid. A. WHITE (J. Biol. Chem., 1936, 112, 503—509).—Rats fed on a diet low in cystine (I) and containing cholic acid (II) lost wt., but addition of either *l*-(I) or *dl*-methionine (III) caused resumption of growth. Taurine and Na₂SO₄ were ineffective. The deficiency in (I) and (III) produced by (II) may be due to the demand for taurine for the synthesis of taurocholic acid, or to a direct detoxication of (II) by (I) and (III).

J. N. A.

Influence of feeding amino-acids and other compounds on the excretion of creatine and creatinine. M. BODANSKY (J. Biol. Chem., 1936, 112, 615—624).—Comparatively large doses of arginine, aspartic acid, glutamic acid, cystine, histidine, tyrosine, choline, betaine, sarcosine, and salts of guanidine had no effect on the excretion of creatine (I) and creatinine in rats. Glycine, guanidinoacetic acid, and to a smaller extent, alanine increased the output of (I). 30—80% of (I) given in doses of 35—120 mg. was recovered in the urine within 48 hr.

J. N. A.

Resorption of bile acids in the small intestine. E. FRÖLICHER (Biochem. Z., 1936, 283, 273—279).—In the small intestine of rats taurocholic acid is more readily absorbed than are cholic and glycocholic acid. The absorption of the acids is more rapid in the lower than in the upper part of the intestine. The differences are not due to variations in *p*_H (5.9, 7.8) or to excretion of bile acids by the upper part of the intestinal mucous membrane.

W. McC.

Indican. IV. Absorption of indoles and indican synthesis in the body. V. Excretion of indican by bile. H. INOUE (J. Chosen Med. Assoc., 1934, 24, 1519—1536; 25, 121—135).—IV. In rabbits and dogs absorption of indoles can be greater in the small than in the large intestine. Some absorbed indole passes into blood by the lymphatics. Synthesis of indican (I) occurs in liver and lungs but not in kidneys or intestines. Emulsions from liver and lungs synthesise (I) *in vitro* (optimum *p*_H 6.8—9.0).

V. Normal bile contains 0.06—0.12 mg. of (I) per 100 c.c., vals. being close to those in blood at the time of excretion.

CH. ABS. (p)

Formation of xanthurenic acid: experiments on man. F. M. CHIANCONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 578—580).—Administration of kynurenine (I) to a healthy man produces the diazo-reaction in the urine, but none of the other reactions of xanthurenic acid. (I) is present in the urine, and is probably responsible for the diazo-reaction.

R. N. C.

Phosphatide metabolism and the influence of thyreoidin. L. PASTERNAK and I. H. PAGE (Biochem. Z., 1935, 282, 282—292).—Phosphatide (I) injected intraperitoneally into white mice is not stored, but is completely utilised. The muscle-(I) in rats after treatment with thyreoidin (II) increases by 96%. This increase is not due to any injury of the (I)-degrading power nor to any infiltration of (I) from other tissues. It is not a relative, but an abs. increase due probably to a synthesis of (I) under the action of (II), possibly as intermediate products in the degradation of fat.

P. W. C.

Choline and dietary production of fatty livers.

C. H. BEST, H. J. CHANNON, and J. H. RIDOUT (J. Physiol., 1934, 81, 409—421).—Fatty liver caused by high-fat diet is due to an increase in the neutral fat fraction. That caused by cholesterol is due to excessive amounts of cholesteryl esters with an increase in neutral fat. The phosphatide (I) content of both types of fatty liver is inversely \propto the total lipin content. Choline prevents the occurrence of both types of fatty liver, and increases the % of (I) in the livers without disproportionate increases in lecithin and sphingomyelin. CH. ABS. (p)

Physiology of lipins and sterols under complete and protein inanition. S. VALLA (Bull. Soc. Chim. biol., 1935, 17, 1715—1740).—A comparison is made of the lipin and sterol content of normal mice and animals undergoing complete and protein starvation. Although the length of life under protein starvation is $>$ that under complete starvation, the continuous carbohydrate intake in the first case does not prevent the complete utilisation of the fatty reserves. Fasting increases both cholesterol and total N of the animals. A. L.

Fat metabolism. I. Effect of ingestion of olive oil on lipin contents of rabbit tissues. II. Effect on lipin contents of splenectomised rabbit tissues. III. Effect on sulphur distribution in rabbit tissues. Y. SONEDA (Sci-i-Kwai Med. J., 1934, 53, No. 8, 49—65, 66—87, 88—91).—I. Daily administration of 10 c.c. of olive oil increased the fat acid (I) and lecithin (II) contents of spleen and adrenals, and the cholesterol (III) in spleen and (slightly) in kidneys. Other organs were unaffected.

II. Splenectomy lowered the (I), (II), and (III) in all organs. Administration of olive oil markedly increased the (I) of the lungs, decreased the (III) : (I) and (III) : (II) ratios of the kidneys, and increased the (II) : (I) ratio in the heart.

III. Feeding of olive oil caused a considerable increase in liver-S, and a slight increase in S of all other organs except lungs (decrease) and kidneys (no change). CH. ABS. (p)

Combustion of odd-numbered fatty acids in the animal organism. S. SKRAUP and E. STREIBER (Verh. Ges. Verdauungs- u. Stoffwechsellkrankh., 1934, 132—136; Chem. Zentr., 1934, ii, 3784).—Saturated C_{11} and C_{13} fatty acids are not oxidised in the body of the dog when administered alone, but the oxidation is catalysed by small quantities of unsaturated fats which are not themselves oxidised. R. N. C.

Central regulation of fat metabolism in the epidermis. A. PERUTZ, B. LUSTIG, and A. E. KLEIN (Arch. Dermatol. Syphilis, 1934, 170, 511—520; Chem. Zentr., 1934, ii, 3784).—Destruction of the mid-brain followed by prolonged feeding with fatty substances in rabbits increases hair-fat and blood- β -hydroxybutyric acid, blood-ketones being unaffected. Fat excretion by the skin is therefore probably regulated by a central mechanism. R. N. C.

Fat metabolism in the course of gestation of *Trygon violacea*. G. STOLEI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1315—1316).—The I vals. of the

fats of the uterine liquid and embryonal tissues are $<$ that of the maternal liver, which hence must undergo a saturation process in order to be utilised by the foetus. R. N. C.

Nutritive effect of plant gums on formation of fat and glycogen. H. IWATA (Bul. Sci. Fak. Terkult. Kjusu, 1933, 5, 352—366).—Feeding gum arabic or starch to rabbits did not increase glycogen formation. Blood-protein-N and hæmoglobin were unchanged but -total sugar increased somewhat. CH. ABS. (p)

Influence of acid-base equilibrium on the glycogen content of the liver. S. KUMAMURA (Trans. Soc. Path. Japan, 1934, 24, 2—5).—Acidosis decreases, and alkalosis increases, liver-glycogen. CH. ABS. (p)

Glycogenic function of the liver in the chicken embryo. A. GUELIN-SCHEDRINA (Compt. rend. Soc. Biol., 1936, 121, 144—146).—Insulin does not cause the premature appearance of liver-glycogen (I) in the developing chick embryo; (I) appears at a later stage than the pancreas. R. N. C.

Glycogen metabolism of the organiser in amphibian gastrula. C. P. RAVEN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1107—1109).—When pieces of ectoderm were inserted in the dorsal lips of the blastopore of the embryo, there was a definite decrease of glycogen (I) in those cells which had involuted. This loss of (I) is closely connected with the involution. J. N. A.

Initial transformations of glycogenolysis: function of hexose monophosphoric ester. P. OSTERN and J. A. GUTHKE (Compt. rend. Soc. Biol., 1936, 121, 282—285).—Glycogen is first broken down to hexose monophosphate, which then reacts with adenosinetriphosphoric acid to form hexose diphosphate. R. N. C.

Utilisation of *d*-mannoheptulose (*d*-manno-ketoheptose) by adult rabbits. J. H. ROE and C. S. HUDSON (J. Biol. Chem., 1936, 112, 443—449).—Rabbits fed with *d*-mannoketoheptose (I) showed an increased blood-sugar which was not accounted for by the blood-(I); (I) is converted into a reducing substance fermentable by yeast. The conversion does not occur in the liver, but during the process of intestinal absorption. Insulin accelerates the oxidation of the reducing substance formed from (I). H. D.

Hydrolysis, oxidation, and energy changes in dogs. IV. Absorption of fructose by the organs of dogs *in vivo*. M. WIERZUCHOWSKI and H. FISZEL (Biochem. Z., 1935, 283, 30—44).—Further work on the utilisation of fructose (I) is described (cf. A., 1935, 1017, 1542). The absorption velocities of (I) by the organs of the dog are, in mg. per g. per hr., for liver 21, organs of the portal system 3.5, motor system 0.4, muscle only 0.8, organs of the head 0.39, other organs 2.0. Simultaneously glucose is being formed by the liver and is being absorbed by the organs of the head with a velocity of 1.3, of the portal system 1.0, motor system 0.02, other organs 0.32. One fifth of the (I) absorbed is returned by the liver to the blood as lactic acid. The organs of

the head and portal system do not appear to give lactic acid in this way. The glucose-forming power of the liver is unchanged during the introduction of inositol, Na lactate, and MeCHO. P. W. C.

Chief method of lactic acid formation in muscle. O. MEYERHOF and W. KIESSLING (Biochem. Z., 1935, 283, 83—113).—Lactic acid (I) arises in muscle chiefly by the oxidation of 1 mol. of triosephosphoric acid to phosphoglyceric acid with simultaneous reduction of 1 mol. of AcCO_2H to (I). This reaction proceeds much more rapidly than does the earlier described reaction in which α -glycerophosphoric acid + AcCO_2H gave 2 mols. of (I). The stages of the new reaction can be separated using NaF and $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ in the same way as with alcoholic fermentation. A complete scheme of the intermediate reactions in muscle is given, and it is seen that in muscle AcCO_2H is the biological equiv. of MeCHO and (I) of EtOH of alcoholic fermentation. PO_4''' changes involve the muscle-adenylic acid system. The scheme is in close agreement with the requirements of the Harden-Young equation. P. W. C.

Effect of hydrazine on the production of ketonic substances in the phloridzin-intoxicated animal. M. M. GREENBERG (J. Biol. Chem., 1936, 112, 431—436).—Phloridzinised rats, treated with N_2H_4 , showed a decreased excretion of ketones which was not due to kidney retention, decreased deamination of NH_2 -acids, or increased glucose or protein metabolism. H. D.

Comparison of the tendencies of different animal species to ketonuria and ammoniuria. E. F. TERROINE and H. TRIMBACH (Arch. int. Physiol., 1934, 39, 377—416; Chem. Zentr., 1934, ii, 3980).—Ketonuria in milk-fed animals is higher in those of smaller body-wt., but is independent of the amount of food ingested per kg. The ratio ($\text{COMe}_2 + \text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$)/ β -hydroxybutyric acid in the excreta is generally 30 : 70, but is less for the cat and hedgehog. NH_3 excretion differs greatly with the species, and is independent of the type or quantity of the food. R. N. C.

Acetaldehyde in muscular work and avitaminosis-B. H. HANDOVSKY (Compt. rend. Soc. Biol., 1935, 120, 1357—1358).—Blood-MeCHO is not modified in the dog by muscular work. Injection of MeCHO in vitamin-B-deficient pigeons delays death. R. N. C.

Fate of alcohol in the corpse of an alcoholised mammal: formation of alcohol in non-alcoholised control animals. M. NICLOUX (Compt. rend. Soc. Biol., 1935, 120, 1306—1309).—The rate of disappearance of EtOH from the corpse of an alcoholised mouse increases with temp. Formation of EtOH occurs in non-alcoholised control animals; the rate of formation increases with temp., but always rises to a max. and then falls. The highest max. occurs at 15—18°. R. N. C.

Mineral metabolism of pullets. II. R. H. COMMON (J. Agric. Sci., 1936, 26, 85—100; cf. A., 1933, 1326).—Heavy P excretion during egg laying is accompanied by increased excretion of $\text{NH}_3\cdot\text{N}$. Probably the excess of P is eliminated as NH_4

phosphate in the urine. Excreted P is not unduly high if the intake of CaCO_3 is adequate. Pullets receiving 5% of CaCO_3 in the ration produced eggs with a higher P content than when the CaCO_3 was omitted. A. G. P.

Renal threshold of potassium. H. GRIFFON (Compt. rend. Soc. Biol., 1936, 121, 47—49).—Theoretical. R. N. C.

Aluminium in nutrition. H. H. KEIL and V. E. NELSON (Proc. Iowa Acad. Sci., 1934, 41, 161—164).—Of the salts examined the order of toxicity was $\text{Al(OH)(OAc)}_2 < \text{K alum}$ and $\text{Al(NO}_3)_3 < \text{AlCl}_3$. CH. ABS. (p)

Influence of lungs on salt metabolism. S. RYU (J. Chosen Med. Assoc., 1934, 24, 1404—1410).—Blood-Cl in the right heart of the rabbit is $>$, and the plasma-Cl $<$, the corresponding amounts in the left. Passage of CO_2 into arterial blood increases plasma-Cl and decreases corpuscular Cl. Reverse effects occur in venous blood. Lungs not only remove Cl from blood but regulate Cl distribution by the gaseous exchange. CH. ABS. (p)

Probable nervous mechanism of the increase of the reducing power of the aqueous humour under the action of light. A. BONSIGNORE (Boll. Soc. ital. Biol. sperim., 1935, 10, 505—509).—The increased ascorbic acid content is probably due to parasympathetic action. R. N. C.

Insolation and acidosis. G. DI MACCO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 437—438).—Administration of HCl to rabbits delays death from insolation. R. N. C.

Increase of cell permeability by mitogenetic irradiation. (Chemical detection of the mitogenetic effect.) I. R. BACHROMEJEV (Biochem. Z., 1935, 282, 297—302).—The small amounts of inorg. P, phosphatide, phosphatase, sugar, and catalase separated from surviving mouse liver into Ringer's solution are very largely increased when the liver is previously subjected to mitogenetic irradiation for $\frac{1}{2}$ hr. P. W. C.

Rôle of the reticulo-endothelial system in the fixation of radiothorium. K. SCHACHOWITZ, D. K. JOWANOWITSCH, and M. WISCHNITSCHewa (Glas Srpske kraljevske Akad., 1933, 78, 65—73; Chem. Zentr., 1934, ii, 3401). R. N. C.

Radioactive effect of potassium on the vegetative nervous system. O. MERCK (Strahlenther., 1934, 50, 471—475; Chem. Zentr., 1934, ii, 3786). R. C. N.

Influence of changes in the medium on the development of eggs of *Bothriocephalus scorpii* (Müller 1776). S. MARKOWSKI (Bull. Acad. Polonaise, 1935, B, 49—58).—Eggs are not susceptible to any but extreme changes in salt concn. in the medium. Light intensity is a more important factor. A. G. P.

Behaviour of the water-flea, *Daphnia pulex*, de Geer, in media of different hydrogen-ion concentrations. K. PASSOWICZ (Bull. Acad. Polonaise, 1935, B, 59—86).—Optimum development occurs at p_H 7.3. With p_H 5.7 and 6.0 the population

of *D. pulex* in a culture is restricted but the parthenogenetic increase of the survivors is not affected.

A. G. P.

Embryonic and larval development in *Saccolina (Rhizocephala)* in media of changed osmotic condition. M. RAMULT (Bull. Acad. Polonaise, 1935, B, 87—109).—Effects of hypo- and hypertonic solutions on the various stages of development are examined.

A. G. P.

Water exchange and fatigue: effect of ingestion of water on tachycardia and hyperpnœa from work. G. DI MACCO (Boll. Soc. ital. Biol. sperim., 1935, 10, 436—437).

R. N. C.

Electromotive force in biological systems. IV. Effect of carbon monoxide on the electromotive force of frog skin. A. B. TAYLOR and E. J. BOELL (Proc. Iowa Acad. Sci., 1934, 41, 316—317; cf. A., 1934, 327).—The e.m.f. of frog skin is depressed by CO in CO-O₂ mixtures. The effect is not due to decreased [O₂]. No additional change occurs in darkness. Aeration causes a return to normal (and sometimes > normal) vals.

CH. ABS. (p)

Sensitisation of animals with simple chemical compounds. K. LANDSTEINER and J. JACOBS (Proc. Soc. Exp. Biol. Med., 1934, 31, 790, 1079).—Positive effects on guinea-pigs are obtained with a no. of substances. The mechanism of the action is discussed.

CH. ABS. (p)

Harmful effect of certain chemicals on the uterus of the rat. F. E. D'AMOUR and N. KIVEN (Amer. J. Obstet. Gynecol., 1935, 29, 503—509).

CH. ABS. (p)

Toxic action of heavy metal salts on the three-spined stickleback (*Gastrosteus acullatus*). J. R. E. JONES (J. Exp. Biol., 1935, 12, 165—173).—Toxic effects of the salts are largely due to the cations, although anions have some influence, e.g., SO₄²⁻ > NO₃⁻ or Cl⁻. Difference in toxicity is closely related to difference in electrical conductivity.

CH. ABS. (p)

Mammalian organism and action of metallic salts. L. E. WALBUM (Z. Immunitäts., 1934, 82, 399—419).

R. N. C.

Influence of neutral salts on the photodynamic stimulation of muscle. R. S. LITTLE, M. A. HINRICHS, and A. J. KOSMAN (J. Cell. Comp. Physiol., 1935, 6, 487—501).—Pure Na salts in solution sensitise eosin-stained muscles to stimulation by light, the efficiencies of the anions being Cl⁻ < Br⁻ < NO₃⁻ < I⁻. Stained muscles irradiated in Ringer's solution are sensitised to subsequent stimulation by Na salts; staining alone has a depressant action. Ca²⁺ inhibits the photodynamic response, which is more sensitive to Ca²⁺ than to Na⁺. O₂ is essential to photodynamic response.

R. N. C.

Effect of iodine on the sexual organs and growth in the rat. A. LIPSCHÜTZ and E. MORALES (Compt. rend. Soc. Biol., 1936, 121, 337—340).

R. N. C.

Iodine compounds and fertilisation. IX. Fertilisation in the starfish, *Asterias rubens*. L. G. S. CARTER (J. Exp. Biol., 1935, 12, 108—118; cf. A., 1932, 1285).—Immature starfish sperm is activated and the fertilisability of unripe eggs is

improved by treatment with thyroxine (I). Ripe sperm and eggs are unaffected. (I) causes a temporary rise in the O₂ consumption of unripe eggs.

CH. ABS. (p)

Interpretation of the [physiological] action of some preparations of bromine. I. SIMON (Boll. Soc. ital. Biol. sperim., 1935, 10, 382—383).—Injection of dibromocholesterol in olive oil in rabbits causes a deposition of Br in the blood, liver, kidney, and adipose tissue, but not in the brain.

R. N. C.

Effect of cupric, manganous, and ferric chlorides on cardiac explants in tissue culture. D. C. HETHERINGTON and M. E. SHIPP (Biol. Bull., 1935, 68, 215—230).—Low concns. of the salts produced stimulatory and higher concns. toxic effects. A combination of the three chlorides was very toxic.

CH. ABS. (p)

The combination of iron and copper and their relation to blood-formation and to general metabolism, and the connexion between their effects and the crystalline state of the metals. S. ODA (Z. ges. exp. Med., 1932, 84, 719—727; Chem. Zentr., 1935, i, 3154).—Active Fe₂O₃ (Siderac) (I) causes no polycythæmia in normal animals, but produces changes in the urinary C/N ratio. Cu-albumin compounds or Cu glycerophosphate cause polycythæmia, are efficacious in experimental anæmia, and affect the urinary ratio. Mixtures of (I) and Cu compounds have the greatest effect on blood and C/N ratio, but cryst. combinations of Cu and (I) have no effect on blood formation.

G. H. F.

Therapeutic action of iron. L. J. WITTS (Lancet, 1936, 230, 1—5).—Factors affecting the requirement, absorption, and utilisation of Fe are discussed. Absorption of Fe from food or drugs ∝ the ease with which Fe²⁺ ions are liberated. Fe is a nutrient and not a stimulant for blood-forming organs.

L. S. T.

Mercurial (novurit) suppository as a diuretic for cardiac œdema. J. PARKINSON and W. A. R. THOMSON (Lancet, 1936, 230, 16—19).

L. S. T.

Action of potassium on formation of lactic acid and breakdown of phosphagen in the isolated muscle of the frog. D. NACHMANSOHN, J. WAJZER, and A. MARNAY (Compt. rend. Soc. Biol., 1936, 121, 141—142).—Excess of K⁺ accelerates lactic acid formation and phosphagen breakdown in the isolated muscle in anaërobiosis.

R. N. C.

Physiological and pharmacological action of sulphur. F. M. CHIANGONE (Boll. Soc. ital. Biol. sperim., 1933, 8, 1511—1513).—S injected subcutaneously in dogs in aq. EtOH-glycerol solution increases the resistance of the erythrocytes, and also augments the alkaline reserve of the plasma, thus favouring the O₂-fixing power of hæmoglobin and increasing the buffering power of the blood. The intracellular oxidation-reduction processes are maintained and accelerated.

R. N. C.

Action of Viterbo sulphurous water on germination and on the activity of the epithelium of frog's œsophagus. A. ROSSINI (Annali Chim. Appl., 1935, 25, 541—557).—The SO₂-containing H₂O (ana-

lyses given), after a brief initial retardation, accelerates the germination and growth of wheat and lentil when compared with controls in normal H₂O or Knop's solution. The movements of ciliated epithelial cells are depressed and finally (1—2 hr.) arrested. F. O. H.

Action of some natural mineral waters on the isolated heart. G. GUIDI (Boll. Soc. ital. Biol. sperim., 1935, 10, 432—434). R. N. C.

Action of hydrocyanic acid on carbon dioxide assimilation and respiration of *Stichiococcus bacillaris*. F. VAN DER PAAUW (Planta, 1934, 24, 353—360).—Small amounts of HCN accelerate assimilation and respiration under conditions of high or low light intensity. The inhibitory effect of larger dosages of HCN is more marked in high light intensity. A. G. P.

Fixation of propyl bromide in the blood and brain of the guinea-pig, after preliminary administration of different poisons of the central nervous system. M. TIFENEAU and D. BROWN (Compt. rend. Soc. Biol., 1935, 120, 1169—1170).—The Pr²Br-fixing capacity of the brain is reduced by hypnotics (chloralose, soneryl, urethane), but increased by stimulants such as caffeine. R. N. C.

Pharmacology of bromoacetic acid. H. FREUND (Arch. exp. Path. Pharm., 1936, 180, 199—208).—The mechanism of the sp. actions of CH₂BrCO₂H on carbohydrate metabolism of animals and bacteria and of the toxic action on ascarides (the muscular contraction of which is compared with that due to santonin) is discussed. F. O. H.

Elimination of sodium formaldehydesulphoxylate by the kidneys. E. HUG (Compt. rend. Soc. Biol., 1936, 121, 365—367).—The kidneys of the dog have a concentrating capacity of 2—2.5% for the compound. The greater part is excreted in 2—3 hr. after injection. R. N. C.

Pharmacology of tetraethylammonium phosphate. I. SIMON (Arch. int. Pharmacodyn. Thé., 1934, 47, 75—95; Chem. Zentr., 1934, ii, 3981). R. N. C.

β -n-Alkylcholine chlorides and their acetyl esters.—See this vol., 319.

Influence of the water vapour content of an odorous gas on the olfactory sense. H. WOERDEMAN (Arch. Néerland. Physiol., 1935, 20, 591—595).—The intensity of the odour of isoamyl acetate when mixed with damp air is > when mixed with dry air. J. N. A.

Relations between simple odorous and odorous irritant stimuli and thiocyanate concentration in the nasal mucus. P. NICCOLINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 429—431).—The [CNS'] of the mucus is increased by non-irritant and decreased by irritant odours. R. N. C.

Organic effects of hydrazine derivatives. W. C. HUEPER (J. Ind. Hyg., 1936, 18, 17—36).—The four derivatives examined produced lesions of the same type and in the same site, differing only in degree. α -Ethyl- β -propylacetaldehydehydrazone was the most toxic. Destruction of erythrocytes and leucocytes occurred in all cases. P. G. M.

Relation between the chemical constitution and pharmacological action of phenylhydrazine derivatives. W. F. VON OETTINGEN and W. DEICHMANN-GRUEBLER (J. Ind. Hyg., 1936, 18, 1—16).—Attempts to preserve the antipyretic action of NPh-NH₂ while decreasing its toxicity have been unsuccessful. Substitution of one or more H by alkyl, aryl, alkoxy, or acyl decreases toxicity, which depends largely on the solubility in H₂O and the ease of hydrolysis. Introduction of Bu, CH₂Ph, or CHO yields compounds which have no effect on blood pressure, respiration, etc. because of their stability at high temp. P. G. M.

Action of indole on the dehydrogenating power of tissues. G. F. DE GAETANI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1291—1294).—The dehydrogenating processes are generally diminished; blood-sugar is raised. R. N. C.

Action of diketopiperazines on fibroblasts cultivated *in vitro*. R. TRUHAUT and D. ODIETTE (Compt. rend. Soc. Biol., 1935, 120, 1198—1201).—Growth is stimulated by 2:5-diketopiperazine, and to a smaller extent by glycine. R. N. C.

Alkylglyoxalidines.—See this vol., 344.

Mercury salts of alkylfluoresceins.—See this vol., 352.

Action of β -dinitrophenol (1:2:6) on respiratory exchange and temperature of homeothermic animals. G. SARZANA and D. ELIA (Boll. Soc. ital. Biol. sperim., 1935, 10, 545—546).—2:6-Dinitrophenol increases O₂ consumption in pigeons and rats by about 100%. R. N. C.

Pharmacology of the vegetative nervous system. IV. Point of attack of 2:4-dinitrophenol. B. DE BIASIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 383—385). R. N. C.

Action of phenylglyoxal on the vasomotor innervation of the kidney. E. MARTINI and G. FRANCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 473—474). R. N. C.

Vagal central action of phenylglyoxal. E. MARTINI (Boll. Soc. ital. Biol. sperim., 1933, 8, 1709—1710).—BzCHO acts similarly to AcCHO, but is effective in smaller concns. R. N. C.

Urinary sulphate determinations as a measure of benzene exposure. W. P. YANT, H. H. SCHRENK, R. R. SAYERS, A. A. HORVATH, and W. H. REINHART (J. Ind. Hyg., 1936, 18, 69—88).—A marked decrease in the % of inorg. SO₄'' in the urine occurs many weeks before symptoms of anæmia etc. P. G. M.

Proliferation-stimulating action of 1:2:5:6-dibenzanthracene on *Obelia geniculata*. S. P. REIMANN and F. S. HAMMETT (Amer. J. Cancer, 1935, 20, 343—349).—Hydranth development was stimulated in sea-H₂O cultures containing this compound. CH. ABS. (p)

Hypoglycæmic action of methylene-blue. G. PIOTROWSKI (Compt. rend. Soc. Biol., 1935, 120, 1215—1216).—Methylene-blue does not reduce normal blood-sugar in rabbits, but apparently reduces hyperglycæmia caused by adrenaline or glucose. R. N. C.

Secretion in tissue cultures. I. Inhibition of phenol-red accumulation in the chick kidney. R. CHAMBERS, L. V. BECK, and M. BELKIN. **II. Effect of sodium iodoacetate on the chick kidney.** L. V. BECK and R. CHAMBERS (*J. Cell. Comp. Physiol.*, 1935, 6, 425—439, 441—455). R. N. C.

Influence of pyocyanine on respiration of sea-urchin's eggs. J. RUNNSTRÖM (*Biol. Bull.*, 1935, 68, 327—334).—Pyocyanine (I) increases the respiration of the eggs, the effect being further increased by HCN in unfertilised, but decreased in fertilised, eggs. The block in division of the egg caused by HCN is not removed by (I). The rate of respiration in presence of (I) is > that in the presence of methylene-blue. Neither the Fe-containing enzyme nor the dehydrase-substrate system acts as a limiting factor for the oxidation rate in the unfertilised or newly fertilised egg. CH. ABS. (p)

Action of acetylcholine on energy exchange. V. BASUNTI (*Minerva med.*, 1935, i, 486—489).—Subcutaneous injection of acetylcholine (0.2 c.c.) during fasting produces a slight but inconst. increase in respiratory exchange and a definite const. increase in the sp. dynamic effect of foods. CH. ABS. (p)

Acetyl- β -methylcholine (mecholine). Action on blood pressure, skin temperature, and the heart as exhibited by electrocardiograms of hypertensive patients. I. H. PAGE (*Amer. J. Med. Sci.*, 1935, 189, 55—64). CH. ABS. (p)

Developmental growth and the amino-acids. II. *l*-Tryptophan. F. S. HAMMETT and M. L. ELLIOTT. **III. *d*-Arginine.** F. S. HAMMETT and N. CHATALBASH (*Protoplasma*, 1935, 23, 457—465, 492—502).—II. Effects of various concns. of *l*-tryptophan (I) on the development of *Obelia* are recorded. The chief function of (I) is that of retarding catabolic activity, hence its indispensability for wt. maintenance. In developmental growth (I) is a sp. determining participant in processes concerned in differentiation or organisation and in the prep. of the tissue reaction basis for new growth initiation.

III. The function of arginine (II) in growth is not the regulation of any particular metabolic activity, but participation in preparatory processes essential for organisation of the tissue reaction basis for new growth initiation. The possible significance of (II) in malignancy is discussed. A. G. P.

Highly active pressor substance from cerebral ventricular fluid of human beings. I. H. PAGE (*Science*, 1935, 82, 550).—Intravenous injection into cats of extract of human cerebral ventricular fluid from malignant hypertension cases produces a sharp rise in arterial pressure. Similar extracts prepared from plasma produce a slower but more prolonged rise. L. S. T.

Vasoconstrictive substance in blood. M. ENOMOTO (*J. Chosen Med. Assoc.*, 1935, 25, 14—25).—The amount of vasoconstrictive substances is increased in pulmonary tuberculosis, typhoid, nephritic and hepatic cases. The substance is not destroyed by O₂, H₂, or CO₂, nor by heating at 60° for 30 min. It is destroyed at 100°. CH. ABS. (p)

Effect of specific substances of the body on blood pressure in man. III. Action of lacarnol, myoston, padutin, "fourth substance" (Lange), and eutonone on intravenous application. H. J. WOLF and H. A. HEINSEN (*Z. klin. Med.*, 1934, 127, 1—14; *Chem. Zentr.*, 1934, ii, 3787). R. N. C.

(A) Antagonistic action of lipins to the toxic action of bile salt. (B) Effect of thyroid gland preparation on formation of gastric ulcer by bile salts, and antagonistic action of cholesteryl oleate. (C) Relationship between toxicity of bile salts and their antagonist. K. ISHII (*Sei-i-Kwai Med. J.*, 1934, 53, No. 9, 94—191, 192—198, 199—211).—(A) Susceptibility to bile salt (I) toxicity in the male is > in the female starfish. The effect is antagonised by cholesteryl oleate (II) or phospholipin, but not by free cholesterol, oleic acid, castor or olive oil, glucose, Na K tartrate, Na citrate or lactate.

(B) Hyperthyroidic guinea-pigs are more susceptible to gastric ulcer formation by (I). (II) antagonises the thyroid effect.

(c) When (I) and diphtheria toxin are simultaneously injected into guinea-pigs the antagonistic ratio of (II) : (I) is 1 : 0.8. CH. ABS. (p)

Influence of cell constituents of the pancreas on the external secretion of the pancreas. I. Influence of parenteral introduction of pancreas cell constituents into dogs with complete pancreatic fistulas. II. Influence of cell constituents of other organs. III. Influence of purified extracts of pancreas and other organs. IV. Mechanism of hypersecretion and nature of the exciting agent. K. TABUCHI (*Japan. J. Exp. Med.*, 1934, 12, 411—418, 419—421, 423—425, 427—435).—Pancreatic cell constituents and their purified extracts stimulate strongly the external secretion of the pancreas, independently of simultaneous secretion of gastric juice and bile. Secretion is not inhibited by atropine. The mechanism of stimulation differs from that of insulin and histamine and is effected by a hormone acting by way of the blood stream on the acinar cells. CH. ABS. (p)

Action of some amines related to adrenaline: methoxyphenylmethoxyethylamines. G. K. ELPHICK and J. A. GUNN (*J. Physiol.*, 1934, 81, 422—433).—The physiological effects of *p*-methoxy-3:4-dimethoxy-, and 3:4:5-trimethoxy-phenyl- β -methoxyethylamines are compared with corresponding compounds lacking OMe. Addition of OMe to the side-chain diminishes the activity. CH. ABS. (p)

Importance of cholesterol in the action of calcium on heart muscle. S. MENTL, J. KÁRASEK, and V. KRUTA (*Arch. int. Physiol.*, 1934, 40, 158—172; *Chem. Zentr.*, 1935, i, 3158).—The heart of cholesterol-treated frogs reacts normally to Ca and adrenaline, although the isolated heart is abnormally sensitive in presence of cholesterol. The right auricle of cholesterol-fed guinea-pigs is more sensitive and contains more cholesterol than normal.

G. H. F.

Action of creatine on the double electric curve of fatigue in man. G. BORGATTI (*Boll. Soc. ital. Biol. sperim.*, 1935, 10, 609—611). R. N. C.

Variations of the dehydroascorbic/ascorbic acid ratio in the liver and adrenals after administration of parasympatheticotropic substances. F. COPELLO (Boll. Soc. ital. Biol. sperim., 1935, 10, 509—515).—The ratio is decreased by parasympathetic excitants, and increased by paralyzers, in the liver, but is not affected by either in the adrenals. R. N. C.

Theory of narcosis. N. V. LAZAREV (Biochem. Z., 1935, 283, 158).—Claim of priority in respect of the work of Meyer and Hemmi (A., 1935, 893).

P. W. C.

Effects of chloral hydrate on maternal and fetal organisms. R. E. CAMPBELL (Amer. J. Obstet. Gynecol., 1934, 28, 83—88).—Chloral hydrate depresses respiration and urinary output.

CH. ABS. (p)

Carbohydrate metabolism under barbiturate narcosis. M. G. MULINOS (Arch. int. Pharmacodyn. Théor., 1934, 47, 111—112; Chem. Zentr., 1934, ii, 3403).—Blood-sugar (I) in rabbits and dogs is raised by amylal, pernocton (II), nembutal (III), and dial. (II) anaesthesia does not affect the action of subcutaneously-injected glucose, adrenaline, or insulin on (I). Oral administration of glucose to anaesthetised rabbits raises (I) to only 60% of the val. reached in unanaesthetised animals. The urine of (III)-anaesthetised cats contains a reducing substance that is not glucose. R. N. C.

Constitution and hypnotic action: bromoethyl- and diethyl-barbituric acid. L. DONATELLI (Arch. Farm. sperim., 1935, 40, 497—516).—The Na salt of 5-bromo-5-ethyl- (I) has a stronger hypnotic action than that of 5:5-diethyl-barbituric acid (II), and is very toxic. In restricting the respiration, and in diminishing the amplitude and the frequency of the cardiac function, and in vasodilatory action the effect of (I) is much > that of (II). E. P.

Effect of oxygen in the prevention of liver necrosis produced by volatile antiseptics. S. GOLDSCHMIDT, I. S. RAVDIN, and B. LUCKÉ (Amer. J. Med. Sci., 1935, 189, 155—156).—In CHCl_3 or divinyl ether anaesthesia, O_2 decreases subsequent necrosis. CH. ABS. (p)

Local anaesthetics with vasopressor action. I. Esters of aryethanolamines. G. A. ALLES and R. K. KNOEFEL (Arch. int. Pharmacodyn. Théor., 1934, 47, 96—110; Chem. Zentr., 1934, ii, 3404). R. N. C.

Effects of drugs on the autonomic nervous system, and on protein metabolism in normal and hypophysectomised dogs. Y. TAKIZAKI (Sei-i-Kwai Med. J., 1934, 53, No. 11, 98—117).—Injection of eserine increased protein and intermediate metabolism. The effect was reversed by administration of nicotine or atropine. CH. ABS. (p).

Action of decamethylenediguanidine bitartrate on blood-sugar. B. L. MONIAS (Illinois Med. J., 1934, 66, 87).—Dosages of 12 mg. administered by stomach tube caused a temporary increase of blood-sugar. Larger amounts (24 mg.) caused convulsions and death even when glucose (I) was given after

convulsions started. Simultaneous injection with (I) was non-toxic. CH. ABS. (p)

Cardiazol as a reviver in animal experiments. M. H. FISCHER and H. LÖWENBACH (Klin. Woch., 1934, 13, 1401; Chem. Zentr., 1934, ii, 3983).

R. N. C.

Carioclastic crisis in the reticulo-endothelial system and endogenous uric acid exchange. G. DOMINI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1297—1300).—Carioclastic substances do not affect blood- or urinary uric acid in the dog, but allantoic excretion is increased. R. N. C.

Comparison of the effect of guanidine, synthalin, and "anticoman" on the muscle of cold-blooded animals. R. RITTMANN and J. MAGERL (Arch. Verdauungskr., 1935, 57, 9—14; Chem. Zentr., 1935, i, 3158).—The fatigue induced in frog sartorius muscle, indicated by the acceleration in rate of production of lactic acid, gives the order: synthalin > guanidine > "anticoman" > "anticoman" + pancreatic enzyme prep. > "anticoman" tablets. G. H. F.

Action of ricin on the isolated heart of the rabbit. R. ATTIMONELLI (Boll. Soc. ital. Biol. sperim., 1933, 8, 1524—1528). R. N. C.

Action of thevetin, a cardiac glucoside, and its clinical application. H. L. ARNOLD, W. S. MIDDLETON, and K. K. CHEN (Amer. J. Med. Sci., 1935, 189, 193—206).—Thevetin from "be-still" nuts (*Thevetia neriifolia*) has a digitalis-like action with potency and toxicity approx. 1/7 of that of ouabain. CH. ABS. (p)

Mechanism and course of chemotherapeutic action. F. AXMACHER (Arch. exp. Path. Pharm., 1936, 180, 142—166).—The action of various chemotherapeutic substances is ascribed to purely physical processes, e.g., changes in permeability and surface action, resulting in exclusion of nutritive substances from the cell and in inhibition of cell-enzymes. The action of germanin (I) on the fermentation of cell macerates does not depend on adsorption-inactivation of zymase, but is possibly related to the presence of $\cdot\text{SO}_3\text{H}$ in (I); that of Sb preps. is due to inhibition or destruction of carboxylase. The mechanism of curative processes is discussed. F. O. H.

Mode of action of chemotherapeutics in spirochaete and protozoan infections. E. SINGER (Med. Klinik, 1935, 31, 380—389). R. N. C.

New antipyretic: isopropylantipyrene. G. ORESTANO (Boll. Soc. ital. Biol. sperim., 1935, 10, 470—473). R. N. C.

Pharmacology of chenopodium oil. II. M. ALAZZI-MANCINI and L. DOVATELLI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1306—1307). R. N. C.

Theosan and its combinations. F. ECKHARDT (Wien. med. Woch., 1934, 84, 1059; Chem. Zentr., 1934, ii, 3787). R. N. C.

Mechanism of the action of ephedrine on gaseous exchange. G. ORESTANO (Boll. Soc. ital. Biol. sperim., 1935, 10, 467—469).—The action of ephedrine on gaseous metabolism is similar to that of

adrenaline, and is effective in the same species, the effect persisting longer. R. N. C.

Octaverine, a new spasmolytic. P. ELLINGER, W. KOSCHARA, and H. SEEGER (Arch. int. Pharmacodyn. Thér., 1934, 48, 50—62; Chem. Zentr., 1934, ii, 3402).—Octaverine, a derivative of phenylisoquinoline, is less toxic and is less rapidly absorbed and detoxicated than papaverine. R. N. C.

Action of bulbocapnine on the frog's heart. F. M. CHIANCONE and U. POPPI (Boll. Soc. ital. Biol. sperim., 1935, 10, 573—575). R. N. C.

Action of bulbocapnine on isolated frog muscle. U. POPPI and F. M. CHIANCONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 570—573). R. N. C.

Action of cocaine on fish. R. DE MARCO (Boll. Soc. ital. Biol. sperim., 1933, 8, 1488—1490). R. N. C.

Pharmacology of physostigmine. C. R. LINEGAR, J. M. DILLE, and T. KOPPANYI (Science, 1935, 82, 497). L. S. T.

New active principle in ergot: effects on uterine mobility. M. E. DAVIS, F. L. ADAIR, G. ROGERS, M. S. KHARASCH, and R. R. LEGAULT (Amer. J. Obstet. Gynecol., 1935, 29, 155—167).—A yellow, stable, non-alkaloidal fraction is isolated. It provokes the characteristic uterine response. CH. ABS. (p)

Physiological action of ergometrine and of ergometrine. R. HAMET (Compt. rend. Soc. Biol., 1935, 120, 1208—1212).—The activity of ergometrine in the dog is the smaller. R. N. C.

Effect of morphine and of heroin on blood-sugar and respiration in rabbits. H. GYOKU (J. Chosen Med. Assoc., 1935, 25, 222—226).—Blood-sugar is increased by injection of morphine hydrochloride (0.05 g. per kg.), reaching a max. in 2—3 hr., and regaining normal in 6—7 hr. Heroin hydrochloride produces similar but smaller changes. CH. ABS. (p)

Antagonism between nicotine and some quaternary hexamethylenetetramine iodides. Curare poisons. J. GAUTRELET and N. HALPERN (Arch. int. Pharmacodyn. Thér., 1934, 47, 4—44; Chem. Zentr., 1934, ii, 3402). R. N. C.

Effect of nicotine on sex and sexual hormone. Y. C. LEE (Trans. Soc. Path. Japon, 1934, 24, 446—449).—Luteo-hormone had a marked antidotic action to nicotine. CH. ABS. (p)

Action of pilocarpine and acetylcholine, introduced into a Vella loop, on enteric secretion. G. SARZANA (Boll. Soc. ital. Biol. sperim., 1935, 10, 542—544). R. N. C.

Action of pilocarpine on formation of lactic acid and breakdown of phosphagen in the isolated frog's muscle at rest. D. NACHMANSOHN, J. WAJZER, and R. LIPPMANN (Compt. rend. Soc. Biol., 1936, 121, 139—141).—Pilocarpine accelerates both lactic acid formation and phosphagen breakdown in the isolated muscle in anaërobiosis. R. N. C.

Tolerance of cells cultivated *in vitro* to the action of quinine dichloride. L. PILATI (Boll. Soc. ital. Biol. sperim., 1935, 10, 414—416). R. N. C.

Influence of quinine derivatives on the iodine contents of endocrine organs. II. A. OHTA (Sei-i-Kwai Med. J., 1934, 53, No. 11, 78—97).—Quinine hydrochloride (10 c.c. of 10% solution per kg.) increased the I content of thyroid, adrenals, liver, ovaries, and testicles, and lowered that of blood, thymus, spleen, pituitary, and pancreas. Both cinchonine hydrochloride and 2-hydroquinine produced smaller increases in I in thyroid, adrenals, and testicle; the former lowered that of spleen, and the latter that of spleen and liver. Optoquin caused no changes (cf. A., 1935, 1396). CH. ABS. (p)

Action of quinic and phenylcinchoninic acids on metabolism. E. BECCARI (Boll. Soc. ital. Biol. sperim., 1935, 10, 402—405).—Injection of quinic (I) and phenylcinchoninic acids (II) in healthy human subjects increases uric acid excretion. (I) produces a negative and (II) a positive balance of N and P. The urinary urea-/total N ratio is reduced by (I) through an increase of non-urea-N excretion, whilst the variations produced by (II) are due to variations of urea. The azoturic coeff. is reduced by both acids. R. N. C.

Alkaloids from the seeds of *Cassia absus*, Linn.—See this vol., 350.

Isomerisation of conessine and its nor-bases.—See this vol., 350.

Variable action of cobra venoms standardised for therapeutic use. P. SIMOMIN and J. BRION (Compt. rend. Soc. Biol., 1935, 120, 1253—1255). R. N. C.

Ultra-violet absorption spectra of snake venoms. H. F. HOLDEN and C. G. SETTER (Austral. J. Exp. Biol., 1936, 13, 223—228).—The venoms of many snakes exhibit an ultra-violet absorption band at about 280 m μ , but no correlation exists between the toxicity of the venom and the position or intensity of the band. W. O. K.

Carbon tetrachloride intoxication. A. NASSAN and M. SALAH (J. Egypt. Med. Assoc., 1935, 18, 207—214).—Poisoning by CCl₄ used as an anthelmintic is not related to the amount used or to Ca deficiency, but is due to constitutional intolerance. CH. ABS. (p)

Arrow poisons. C. G. SANTESSON (Skand. Arch. Physiol., 1934, 70, 102—125; Chem. Zentr., 1935, i, 3310).—An arrow poison of central African pigmies is of the digitalis-strophanthus type. Investigation of two Celebes arrow poisons points to their glucosidic nature, one of them possibly being derived from *Antiaris toxicaria*, Lesch. H. N. R.

Physiology of the treatment of barbiturate poisoning. R. MASSIERE and G. BEAUMONT (Presse Méd., 1935, 43, 4—7; Chem. Zentr., 1935, i, 3310).—The efficacy of strychnine as an antidote for barbiturate poisoning is not due to antagonism, but is an adsorption effect analogous to the toxin-antitoxin reaction. H. N. R.

Toxicity of methyl alcohol. S. KAJIZUKA (J. Soc. Chem. Ind. Japan, 1935, 38, 746—747B).—MeOH stimulates the mucous membranes locally, but is not highly toxic. On a diet containing 10% MeOH,

rats show a turbidity of the urine and an increased excretion of HCO_2H . H. G. R.

Cause of the toxicity of methyl alcohol. I. SIMON (Boll. Soc. ital. Biol. sperim., 1935, 8, 1376—1379).—The toxic effect of MeOH is considered to be due to MeOH itself, no oxidation to CH_2O or HCO_2H occurring in the body. R. N. C.

Distribution of arsenic a few hours after ingestion of small amounts. G. VITTE (Bull. Trav. Soc. Pharm. Bordeaux, 1934, 72, 357—358; Chem. Zentr., 1935, i, 3159).—The distribution of As in the viscera with and without simultaneous dosing with Na_2SO_4 has been investigated. J. S. A.

Effect of Fowler's solution on animals. E. ROBERTS and W. M. DAWSON (Illinois Agric. Exp. Sta. Bull., 1935, No. 413, 187—202).—The practice of feeding Fowler's solution to animals for show purposes diminishes respiratory activity and reproductive functions. In treated animals As may be detected in the urine, faeces, and hair. A. G. P.

Increase in toxicity for mice of solutions of neoarsphenamine on exposure to air. R. WIEN (Quart. J. Pharm., 1935, 8, 631—641).—The toxicity to rats of a solution of neoarsphenamine increased by 17.5 and 23% after exposure to air for 15 and 25 min., respectively, but this increase was prevented if the solution was protected by a layer of liquid paraffin. W. O. K.

Toxicity of sodium cyanide and the efficiency of the nitrite-thiosulphate combination as a remedy for poisoned animals. A. B. CLAWSON, J. F. COUCH, and H. BUNYEA (J. Washington Acad. Sci., 1935, 25, 357—361).—NaCN is less toxic than KCN or HCN, whilst the two latter are similar. The ratio min. toxic/min. lethal doses is 1 : 2 for KCN and HCN, and 1 : 1.25 for NaCN. Intraperitoneal injection of 1 g. of NaNO_2 and 2 g. of $\text{Na}_2\text{S}_2\text{O}_3$ in H_2O 1.5—4 min. after the NaCN effected recovery in 4 out of 7 cases. P. G. M.

Use of sodium tetrathionate in cyanide poisoning. E. MENEGHETTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 386—391).—A criticism of the method of Aurisicchio and de Nito (cf. A., 1935, 1276). R. N. C.

Treatment of cyanide poisoning of sheep and cattle. H. BUNYEA (J. Amer. Vet. Med. Assoc., 1935, 39, 656—661).—Injections of methylene-blue, $\text{Na}_2\text{S}_2\text{O}_6$, NaNO_2 , and $\text{Na}_2\text{S}_2\text{O}_3$ had some val. 10 c.c. of 10% NaNO_2 followed immediately by 20 c.c. of 10% $\text{Na}_2\text{S}_2\text{O}_3$ was preferable to either alone. CH. ABS. (p)

Tannic acid and soaps are not antidotes for mercury. P. BELLECCI (Arch. Farm. sperim., 1935, 40, 517—533).—If intravenous injection of the min. lethal dose of HgCl_2 is followed by injection of tannic acid (I) or Na oleate (II) death is not prevented; it is retarded by small, accelerated by large, doses of (I) or (II). If HgCl_2 is given *per os*, (I) or (II) (*per os*) even in large excess retards but does not prevent death. E. P.

Diagnosis of lead poisoning in children. M. KASAHARA (Klin. Woch., 1934, 13, 1646—1647; Chem. Zentr., 1935, i, 3320).—X-Ray examination,

supplemented by the skin reaction with Na_2S , is best. H. N. R.

Action of electromagnetic waves on enzyme systems. A. DE P. FORJAZ (Biochem. Z., 1935, 283, 53—58).—Electromagnetic waves have no effect on the activity of fumarase, but increase the activity of the phosphatase of takadiastase by 20%. P. W. C.

So-called "blood-group enzyme" content of saliva. O. SIEVERS (Klin. Woch., 1934, 13, 1640—1641; Chem. Zentr., 1935, i, 3148).—The power of saliva to destroy blood-group characteristics is greatest when collected during starvation. G. H. F.

Enzymic reactions in heavy water. D. L. FOX (J. Cell. Comp. Physiol., 1935, 6, 405—424).—Catalase, amylase, and emulsin show no loss of activity in D_2O at the same temp. and p_{H} as controls in H_2O . The activity of amylase appears to be increased in conc. D_2O . R. N. C.

Enzymic hydrolysis of glucosides in heavy water. K. F. BONHOEFFER and F. SALZER (Naturwiss., 1935, 23, 867).—Glucosides with high affinities for emulsin (*e.g.*, salicin) are hydrolysed more slowly in D_2O than in H_2O , whilst for those with low affinities (*e.g.*, methylglucoside) the reverse is the case. D_2O retards the hydrolysis of the enzyme-substrate complex, but may also increase the affinity of the enzyme for its substrate, in which case the higher concn. of the enzyme-substrate complex may compensate for the retardation of the hydrolysis, leading to an increase in the rate of reaction. E. A. H. R.

Hydrogen-transporting co-enzyme, its composition and mode of action. O. WARBURG, W. CHRISTIAN, and A. GRIESE (Biochem. Z., 1935, 282, 157—205).—The co-enzyme (I) from red blood cells, which is designated the H-transporting enzyme, was purified until its catalytic activity could not be further increased. The purest prep. (12.9% N, 12.3% P) was readily sol. in H_2O , did not crystallise, and on hydrolysis yielded 1 mol. each of adenine and nicotinamide together with 3 mols. of H_3PO_4 and 2 mols. of pentose. Assuming that these are united with the loss of $6\text{H}_2\text{O}$, (I) is $\text{C}_{21}\text{H}_{28}\text{O}_{17}\text{N}_7\text{P}_3$. The H_2 transportase of heart-muscle is probably, and that of yeast is certainly, identical with (I). (I) cannot replace cozymase (II) in yeast fermentation nor can (II) replace (I) in oxidation experiments. (I) is however, probably closely related to (II). (I) is active only in association with certain proteins, which are called intermediate enzymes (III). Hexosephosphoric acid (IV) in presence of traces of (I) + (III) + Warburg's yellow enzyme (V) is oxidised to hexosephosphonic acid (VI), (V) being reduced and, in presence of atm. O_2 , reoxidised. (IV) is also oxidised by an equiv. amount of (I) in presence of (III), giving (VI) + (I)- H_2 , the latter then being able to react with (V) to give free (I) + (V)- H_2 . This then reacts with atm. O_2 giving H_2O_2 + (V). (I) can be hydrogenated reversibly by $\text{Na}_2\text{S}_2\text{O}_4$ and irreversibly by $\text{Pt} + 3\text{H}_2$. In the latter reaction the $\text{C}_5\text{H}_5\text{N}$ is converted into a piperidine ring and (I) loses its activity. The reversible hydrogenation of (I) is a partial hydrogenation of the $\text{C}_5\text{H}_5\text{N}$ ring. P. W. C.

Destruction of hydrogen transporting co-enzyme by ultra-violet light. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1935, 282, 221—223).—When 0.001 mg. of co-enzyme (I) in 1 c.c. of H₂O is irradiated in a quartz vessel at a distance of 30 cm., the activity of (I) is lost in 15 min. Irradiation in a glass vessel or of more conc. solutions (1 mg. per c.c.) in quartz vessels does not result in detectable loss in 15 min. Using dil. solutions, the time for half-destruction of (I) increases rapidly with the λ , being 520 times as great at 283 m μ as at 186 m μ .

P. W. C.

Constitution of the prosthetic group of catalase. K. G. STERN (J. Biol. Chem., 1936, 112, 661—669; cf. A., 1935, 1278).—Catalase (I) solutions from horse liver after an Al₂O₃ gel adsorption were further conc. by COMe₂-CO₂ treatment. The (I) solution is then sufficiently conc. to allow the cleavage of (I) by the acid-COMe₂ treatment used for respiratory h \ddot{a} m pigments, which ppt. the protein. On removal of the COMe₂ the prosthetic group of (I) is pptd. The identity of this prosthetic group with the protoh \ddot{a} matin of h \ddot{a} moglobin is established by the prep. from it of a mesoporphyrin Me₂ ester and by its conversion into the h \ddot{a} moglobin of the same species by the substitution of native globin for the enzyme-protein.

E. A. H. R.

Nutritive value of pentosans. V. Digestion by intestinal enzymes. H. IWATA (J. Agric. Chem. Soc. Japan, 1935, 11, 1024—1027).—Xylanase occurs in rabbit's and pig's intestine to an extent < that of co-existing amylase. Optimum temp. and p_H are 38° and 6, respectively.

F. O. H.

Action of lithium, sodium, and potassium bromides and iodides on the activity of the amylase of the fowl's crop. VII, VIII. A. BERNARDI and M. A. SCHWARZ (Giorn. Biol. Appl. Ind. Chim., 1932, 2, 41—52; Chem. Zentr., 1935, i, 3679).—LiBr > KBr > NaBr stimulates the amylase activity; otherwise they behave similarly to the chlorides. LiI < KI < NaI inhibits the activity.

R. N. C.

Technique of diastase determination in blood according to Ottenstein. J. BRINCK (Klin. Woch., 1934, 13, 1686—1688).—The technique is described and possible sources of error are discussed.

R. N. C.

Relation of glycolysis to proteolysis in tissues. V. M. RUBEL (Biochem. Z., 1936, 283, 180—189).—In healthy and diseased (tumour) tissue, glycolysis, increased by addition of glucose, AcCO₂H (I), and MeCHO or decreased by addition of NaF is accompanied, respectively, by increased or decreased proteolysis. Lactic acid (II) increases proteolysis and is probably the link which connects the two processes. When production of (II) is restricted by NaF the extent of proteolysis is restored to normal by addition of (I) and (II).

W. McC.

Conversion of *p*-tolylglyoxal into *l-p*-methyl-mandelic acid by the enzyme of fresh cells. S. FUJISE and M. IWAKIRI (Biochem. Z., 1936, 283, 298—300).—Fresh carp-muscle extract converts *p*-tolylglyoxal almost quantitatively into *l-p*-methyl-mandelic acid. The conversion of BzCHO into *l*-

mandelic acid by the extract is more rapid, but not so complete.

W. McC.

Complete enzymic hydrolysis of chondroitin- and mucoitin-sulphuric acid. C. NEUBERG and W. CAHILL (Atti R. Accad. Lincei, 1935, [vi], 22, 149—155).—Enzyme preps. from *B. fluorescens* hydrolyse chondroitinsulphuric acid to glycuronic acid (I), chondrosamine, AcOH, and H₂SO₄ and mucoitinsulphuric acid to (I), glucosamine, AcOH, and H₂SO₄.

F. O. H.

Glucosulphatase. XII. Purification of the enzyme and the effects of phosphate, sulphate, and fluoride on the enzyme action. T. SODA and F. EGAMI (J. Chem. Soc. Japan, 1934, 55, 1164—1168).—Activity of the enzyme is inhibited by PO₄''' and F' in concns. > 0.0005M (cf. A., 1935, 659).

CH. ABS. (p)

Pancreatic lipase. I. II. Influence of various compounds on the hydrolytic activity. S. S. WEINSTEIN and A. M. WYNNE (J. Biol. Chem., 1936, 112, 641—648, 649—660).—I. The rate of hydrolysis of glycerides and alkyl esters of fatty acids by pancreatic lipase (I) is investigated. The initial rate of hydrolysis of triglycerides decreases in the order tripropionin (II), tributyrin, trihexoin, triacetin, trivalerin. The initial rates of acid formation from mono-, $\alpha\gamma$ -di-, and tri-acetin are in the ratio 1 : 2 : 2.66, indicating that the ester linking on the β -C is more slowly hydrolysed than the two end linkings. The rate of hydrolysis of the alkyl esters of the fatty acids increases with the length of the C chain of the acid radical, but decreases with its length in the alkyl. With phosphate buffers the initial rate of hydrolysis of (II) and of PrCO₂Me is greatest at p_H 7.2, but in glycine buffers the optimum p_H is 9.3. The initial velocity of hydrolysis \propto (I) concn. and (II) concn. (in the range 0.016—0.16M). The vals. did not accord with the Michaelis equation.

II. Ketones and aldehydes markedly inhibit (I). The degree of inhibition depends on the time of preliminary incubation of (I) with the inhibitor, the mol. vol., the no. of CO groups present, and the presence or absence of the C₆H₆ ring. Heavy metals are inhibitory. CN' and .SH compounds activate (I). Phenols and cresols are inert, but a NO₂-group increases the toxicity. Di- but not tri-hydric phenols are inhibitory; the inhibitory action of the former increases with increased separation of the OH groups. Monohalogen derivatives of AcOH inhibit in the order I > Br > Cl, and halides in the order F > I > Br > Cl. Bile salts in neutral solution are without effect. Possible mechanisms of some of the inhibitions and activations are discussed, and it is suggested that NH₂ may be an essential constituent of (I).

E. A. H. R.

Castor bean lipase. VII. Relation between activity of highly active *Ricinus* lipase and some oxidising and reducing substances. E. TAKAMIYA (J. Agric. Chem. Soc. Japan, 1935, 11, 147—156; cf. A., 1935, 1416).—Exposure to air or H₂O₂ retarded the activity of the lipase. Glutathione (I) accelerated activity to extents $\propto p_H$. Larger proportions of (I) or adjustment of p_H to 6.0 had a

retarding action. Cysteine (II), CH_2O , glucose, fructose, and NaHSO_3 produced similar effects, but cystine had no action. Lipase, inactivated by oxidation, was not regenerated by addition of (I) and (II).
CH. ABS. (p)

Inhibitory action of formaldehyde on the activity of blood choline-esterase. E. CORREGIANI, J. GAUTRELET, N. HALPERN, and A. SERFATY (Compt. rend. Soc. Biol., 1936, 121, 316—318).— CH_2O inhibits the action of choline-esterase after a latent period which \propto the dilution of the CH_2O . The inhibition is probably the result of alterations of p_{H} .
R. N. C.

Formation of acetylcholine in the body, and an investigation of the choline-esterase. I—III. F. H. SHAW (Austral. J. Exp. Biol., 1935, 13, 251—260).—Stimulation of the lingual nerve of the dog does not alter the choline content of the tongue. Two esterases exist in serum, of which only one is inhibited by eserine. In presence of pig's serum, acetylcholine (I) is synthesised from choline and NaOAc . Neither this action nor the enzymic synthesis of tributyrin is inhibited by eserine. The synthesis of (I) in the body is probably effected through the synthetic action of tissue-esterase.
W. O. K.

Enzymic histochemistry. I. Distribution of arginase activity in rabbit kidney. L. WEIL and J. O. ELY (J. Biol. Chem., 1936, 112, 565—577).—The micro-method of Linderström-Lang *et al.* (A., 1935, 1163) for determining arginase (I) activity is suitable for histo-enzymic studies if the solution is buffered at p_{H} 9.5. A micro-(I) unit is defined. (I) activity is present in the cortex only of rabbit kidney, and runs parallel with the no. of proximal convoluted tubular cells. The medulla shows no (I) activity, and as addition of inactive medullary tissue to cortical tissue causes no inhibition of (I) activity in the latter, it is concluded that the inactivity of the medulla is not due to inhibitors.
E. A. H. R.

Diffusion of aspartase. K. P. JACOBSON and M. SOARES (Compt. rend. Soc. Biol., 1936, 121, 251—255).—Experiments described do not establish the presence of aspartase in the vegetable tissues examined, nor the amination of fumaric acid as a regular metabolic reaction in plants.
R. N. C.

Action of various salts on the aspartase system. F. B. PEREIRA and M. SOARES (Compt. rend. Soc. Biol., 1936, 121, 255—258).—Synthesis of acid by aspartase is accelerated by $\text{SO}_4^{''}$ and retarded by NO_3^- relative to Cl^- . Atoxyl does not affect the reaction in presence of $\text{PO}_4^{''}$ buffer, but morphine restrains it. $\text{PO}_4^{''}$ buffer alone exerts a restraining action, as does Na^+ in presence of Cl^- .
R. N. C.

Peptic hydrolysis of caseinogen. L. UTKIN (Biochem. Z., 1936, 283, 233—240).—In the early stages of the hydrolysis the liberation, at p_{H} 4.6, of org. P compounds occurs in two (possibly more) sharply defined phases. The P:N ratio of the compounds produced in the first phase differs from that of those produced in the second, the difference being due to differences in the composition of the

compounds, and not merely to differences in the amounts.
W. McC.

Physiology of digestion of plankton Crustaceæ. I. Digestive enzymes of *Daphnia*. A. D. HASLER (Biol. Bull., 1935, 68, 207—214).—The p_{H} of the intestine of *D. magna* varied from 6.8 at the anterior to 7.2 at the posterior end. Tryptic digestion of casein is indicated. Glycerol extracts of the intestine digested gelatin. Hog-pancreas extract gave a similar hydrolysis curve. Extracts of defatted *D. pulex* contained amylase and lipase.
CH. ABS. (p)

Multivalent amino-acids and peptides. VI. Action of proteolytic enzymes on synthetic substrates. J. P. GREENSTEIN (J. Biol. Chem., 1936, 111, 517—522; cf. this vol., 194).—Anhydro-*l*-lysyl-*l*-glutamamide, $[\alpha]_D^{25} - 27.7^\circ$, is unaffected by pepsin, trypsin, or papain-HCN (also without action on anhydro-*dl*-aminotricarballylic tetra-amide), which is inconclusive evidence against the existence of diketopiperazine rings in proteins. *l*-Lysyl-*l*-glutamamide and *l*-histidine are hydrolysed by yeast peptidase, the former more slowly. Glycyl-*dl*-aminotricarballylic acid is slowly split by yeast autolysate and intestinal erepsin, but not by carboxypeptidase.
R. S. C.

Inhibition of enzymic proteolysis by oxidising agents. Nature of the action of potassium bromate and analogous substances as improvers of wheat flour. II. H. JØRGENSEN (Biochem. Z., 1935, 283, 134—145).—The inhibition of proteinases (I) in flour- H_2O suspensions by KBrO_3 and the consequent decrease of solubility of flour-N are greatly emphasised on adding yeast, due to the activation of (I) by the glutathione of the yeast (cf. B., 1935, 1115).
P. W. C.

Action of enzyme extracts on soluble keratin. P. G. CASTELLINO (Arch. Ist. Biochim. Ital., 1935, 7, 417—424).—Extract of rabbit's skin is free from enzymes hydrolysing sol. keratin [prepared by the action of Na thioglycollate (A., 1934, 1238)] at p_{H} 1.5, 3, or 8, but contains a tryptic enzyme hydrolysing caseinogen.
F. O. H.

Enzymic synthesis from thyroid di-iodotyrosine peptone of an artificial protein which relieves myxœdema. W. T. SALTER and O. H. PEARSON (J. Biol. Chem., 1936, 112, 579—589).—A solution of di-iodotyrosine peptone (I) was prepared by peptic digestion of thyroglobulin (II) of human origin, followed by removal of thyroxine (III). (I) was conc. and then subjected to a peptic synthesis, with the formation of an artificial protein containing I, analogous in its properties to a true protein. Clinically, in equiv. I dosage, it relieves myxœdema as effectively as (II). The view is held that di-iodotyrosine is the precursor of (III) and that a naturally occurring protease in the thyroid cells is possibly responsible for the synthesis.
E. A. H. R.

Phosphatase content of blood-serum and tissues in the rat following administration of vitamin-D and -A. P. D. CRIMM and J. W. STRAYER (J. Biol. Chem., 1936, 112, 511—515).—The mean phosphatase (I) content of rat serum is about 20 times that of human serum. Toxic doses of viosterol (II) lead to a marked decrease of (I) activity in blood

and kidney, and a considerable increase in the small intestine. The effect of (II) on the high (I) content of bones is variable. Liver and spleen contain small amounts of (I) both before and after administration of (II). The decrease in serum-(I) with rats deficient in vitamin-A (III) or with hypervitaminosis-A is attributed to impaired nutrition rather to the presence or absence of (III). E. A. H. R.

Plasma-phosphatase in normal and rachitic children. O. ANDERSEN (Jahrb. Kinderheilk., 1935, 144, 206—221; Chem. Zentr., 1935, i, 3148).—Antirachitic treatment of rachitic children (technique of Kay) produces a diminution of plasma-phosphatase. G. H. F.

Intestinal phosphatase. H. G. K. WESTENBRINK (Arch. Néerland. Physiol., 1935, 20, 566—590).—The activity of a solution of intestinal phosphatase (I) is not \propto its concn., and the rate of hydrolysis of Na glycerophosphate continually decreases with time of reaction. This is not due to inhibition by H_3PO_4 or glycerol, or to decreasing substrate concn. or to inactivation by the buffer of p_H 8.8. The activity of (I) \propto concn. if it is previously kept in contact with the buffer for some hr. at 25° . In determining (I) by the hydrolysis of H_3PO_4 from a suitable substrate, it is best to work in a medium containing Ca. J. N. A.

Determination of the phosphatase activity of whole blood, plasma, and serum. J. CAYLA (Bull. Soc. Chim. biol., 1935, 17, 1707—1714).—A modification of the Mo colorimetric method for the determination of phosphatase (I) is described. In the normal adult the (I) content is 15 units per litre of serum, 1 unit of (I) liberating 1 mg. of H_3PO_4 from 10% aq. Na β -glycerophosphate at p_H 7.6. A. L.

Specific pyrophosphatase. E. BAUER (Naturwiss., 1935, 23, 866—867).—Glycerol extracts of yeast retain their ability to act on pyrophosphate after the α -glycerophosphatase activity has largely been destroyed by heat, indicating the separate existence of a sp. pyrophosphatase. E. A. H. R.

Glycerophosphatase of the brain. F. CEDRANGOLO (Boll. Soc. ital. Biol. sperim., 1935, 10, 374—376).—Brain-glycerophosphatase shows optimum activity at p_H 5.32 and 9.16, with a max. in 0.0016M-glycerophosphate. Prolonged electro dialysis abolishes the enzyme activity, which is restored by $MgCl_2$. Activity is inhibited by NaF, CH_2I-CO_2H , As_2O_3 , and phloridzin. The enzyme shows a preference for α -glycerophosphate. R. N. C.

Mode of action of intermediate enzymes. E. NEGELEIN and E. HAAS (Biochem. Z., 1935, 282, 206—220).—In the reaction, co-enzyme (I) + hexosephosphoric acid = (I)- H_2 + phosphohexonic acid, which occurs in presence of intermediate enzyme (II), the velocity of hydrogenation can be determined in terms of the rate of the resulting increase of absorption in the ultra-violet at 345 m μ . A study of the hydrogenation velocities with varying amounts of (I) and (II) shows that (II) functions not as a catalyst, but as the colloidal carrier of (I). (I) and (II) by a reversible reaction are converted into the H-transporting enzyme (III). At a concn. of (I)

of 10^{-5} mol. per litre, half of the (III) is dissociated into (I) + (II). As a result of such dissociation, a small amount of (II) can effect hydrogenation of large amounts of (I). (II) therefore differs from the carrier of the yellow enzyme (IV), since it is combined with (IV), and the oxidational reaction requires therefore a stoichiometric amount of pigment.

P. W. C.

Oxidation, phosphorylation, and fermentation by apozymase in presence of reversible oxidation-reduction systems. A. LENNERSTRAND and J. RUNNSTRÖM (Biochem. Z., 1935, 283, 12—29).—Oxidation and phosphorylation are studied in a system containing apozymase, cozymase, hexose diphosphate, glucose, and either methylene-blue (I) or pyocyanin (II), fermentation being inhibited by NaF. The system absorbs O_2 , but forms practically no CO_2 . Although (I) and (II) belong to the same potential range, the O_2 absorption with (II) is three times that with (I) and moreover using α -naphthol-2-sulphonate-indophenol, which has a much higher potential, the O_2 absorption is $<$ with (II). There is a definite connexion between oxidation and phosphorylation, 1 mol. of glucose being esterified with PO_4 for each mol. of phosphoglyceric acid produced by oxidation from triose phosphate. P. W. C.

Formation of flavin enzyme systems in germinating seeds. H. VON EULER and O. DAHL (Biochem. Z., 1935, 282, 235—241).—The total flavin (I) content of barley in the first 5 days of germination is 3—7 times that of oats. The (I) synthesis is completed in barley by the 2nd day, but continues longer in oats. In extracts of germinated seeds, the ratio of non-dialysable to total (I) is 2 : 3, and is maintained fairly const. during germination. In peas (ungerminated) which contain considerable amounts of (I), almost all the (I) is in the non-dialysable form. Tables summarise the accompanying increases in respiration during germination. P. W. C.

Nicotinamide and luminoflavin. O. WARBURG and W. CHRISTIAN (Ber., 1936, 69, [B], 228; cf. Kuhn *et al.*, this vol., 227).—Nicotinamide has been obtained previously from co-enzyme (I) and luminoflavin by irradiation of an alkaline flavin solution obtained from milk. Since the yellow enzyme and (I) are universal components of cells, Kuhn's discoveries are not fundamentally new. H. W.

Fermentation velocity of hexosediphosphoric acid and phosphate transfer to adenylic acid. P. OHLMEYER (Biochem. Z., 1935, 283, 114—127).—Although muscle-adenylic acid (I) is not identical with and cannot replace cozymase in all its reactions, yet (I) has an activating rôle in some fermentation reactions. Thus hexose diphosphate in yeast maceration juice with added (I) is partly fermented and partly converted into hexose monophosphate (II), whilst (I) is converted into adenylic pyrophosphate (III), which is identical with muscle-(III). The higher is the concn. of (I) in this reaction, the greater is the max. velocity. The fermentation velocity of (II) is also increased, but to a smaller extent by addition of (I), and (III) is again formed. Addition of (III) has no effect on the velocity of fermentation of the diphosphate. P. W. C.

Action of extracts of liver and other organs on fermentation by yeast. J. DADLEZ and W. KOSKOWSKI (Biochem. Z., 1936, 283, 292—297; cf. Zipf *et al.*, 1935, 253).—The stimulating effect on fermentation by yeast of liver extract is > that of extract of other organs (spleen, stomach, lung, heart, muscle, kidney, brain, testes, uterus, mammary gland, bone-marrow, pituitary, thymus, adrenals). With liver and spleen extracts the action does not always run parallel with the anti-anæmic effect. W. McC.

Mechanism of oxidation processes. XLIII. Arrest of the respiration and fermentation processes of yeast. H. WIELAND, K. RAUCH, and A. F. THOMPSON (Annalen, 1936, 521, 214—226).—The inhibiting action of various poisons on the fermentative action (glucose) of "impoverished" yeast is generally smaller than that on the aerobic dehydrogenation of EtOH at 30° and p_H 6.8. 0.0002M-KCN reduces the O₂ consumption to 56%, but 30 times this concentration is necessary to effect an equal retardation of the fermentation process. Na₂S is similar, but NaCNO, which is more potent than KCN, inhibits both processes to approx. the same extent; NaN₃, which inhibits the dehydrogenation as effectively as does KCN, has actually a small accelerating influence on the fermentation, and is equally effective under O₂ as under N₂. The catalase activity is inhibited by NaCNO > NaN₃ > KCN. The inhibiting action of these poisons is largely removed by centrifuging the yeast with H₂O. The O₂ consumption in the aerobic dehydrogenation of EtOH is greatly reduced if the [O₂] is only 2—5% (cf., A., 1932, 303).
J. W. B.

Effect of selenium on cellular metabolism. Rate of oxygen uptake by living yeast in presence of sodium selenite. V. R. POTTER and C. A. ELVEHJEM (Biochem. J., 1936, 30, 189—196).—The uptake in presence of glucose, fructose, and mannose is diminished by 80% when Na₂SeO₃ (min. effective concn. 0.0033M) is added. With lactate and pyruvate as substrates, the diminution is < 10%. The oxidation by yeast of EtOH, AcOH, and possibly succinic acid also appears to be diminished by Na₂SeO₃. The action is in all cases most marked in the acid zone and decreases rapidly at p_H 7.0—7.5. Se appears to act primarily as inhibitor of glycolysis. Na₃AsO₃ (min. effective concn. 0.001M) is more toxic to oxidative systems than is Na₂SeO₃.
W. McC.

Action of *m*-dinitrobenzene and its reduction derivatives on the metabolism of Fleischmann's yeast. P. CREAC'H (Compt. rend. Soc. Biol., 1936, 121, 246—248).—Respiration of liquid-cultured yeast is increased considerably by *m*-NO₂-C₆H₄-NO (I) and feebly by *m*-C₆H₄(NO₂)₂ (II), whilst that of solid-cultured yeast is increased considerably by both (I) and (II), possibly through the reduction of (II) to (I) by the organism. *m*-NO₂-C₆H₄-NH₂·OH does not affect respiration.
R. N. C.

Action of dinitrothiophen on the metabolism of Fleischmann's yeast. P. CREAC'H (Compt. rend. Soc. Biol., 1936, 121, 248—250).—Dinitrothiophen is reduced irreversibly after a period of latency ∝ the concn. Respiration of the yeast

rises temporarily when reduction begins, afterwards falling rapidly to < the initial val.
R. N. C.

Catalytic fermentation of some fructoholosides. R. GUILLEMET (Compt. rend., 1935, 201, 1517—1519).—Raffinose, gentianose, stachyose, and levosin are fermented by yeast juice to the extent of 100, 66, 50, and 30%, but in the absence of von Euler's Z factor fermentation is much reduced and levosin is not fermented.
J. L. D.

Action of methyl and ethyl alcohol on enzymes. I. Action on beer yeast and on the cytoplasm of castor seeds. N. T. DELEANO and D. MEZINCESCO (Bull. Soc. Chim. biol., 1935, 17, 1805—1813).—Small quantities of MeOH and EtOH increase slightly the rate of carbohydrate fermentation by yeast, but larger amounts inhibit the reaction, MeOH being less toxic. The inhibition of lipase action by MeOH and EtOH is almost the same, but is more marked with olive oil than with castor oil as substrate.
A. L.

Yeast lipins. III. Lecithin and kephalin. L. F. SALISBURY and R. J. ANDERSON (J. Biol. Chem., 1936, 112, 541—550).—The mixed phospholipins of yeast have been separated into lecithin (I) and kephalin (II). (I) was obtained free from NH₂-N and all the N of (II) was in the NH₂-form. On hydrolysis (I) gave a mixture of fatty acids, 86% of which were liquid, optically active glycerophosphoric acid (III), and choline, whilst (II) gave a similar mixture of acids, 84% of which were liquid, optically inactive (III), and NH₂-CH₂-CH₂-OH. The liquid component acids of both (I) and (II) gave a mixture of palmitic (IV) and stearic (V) acids on catalytic reduction. The solid acids consisted only of (IV) and (V). Methods of prep. of hydrolecithin and hydrokephalin are given.
E. A. H. R.

Biological value of two *Torula* from the cheese factory. G. GUITTONNEAU and H. SIMONNET (Compt. rend. Soc. Biol., 1935, 120, 1166—1168).—The antineuritic vals. of both *Torula* are < that of brewer's yeast; the *Torula* with lactose-fermenting power is the more active of the two.
R. N. C.

Yeast growth-promoting substances. N. NIELSEN (Compt. rend. Trav. Lab. Carlsberg, 1935, 21, No. 7, 151—183).—The effect of growth-promoting substances (I) (bios) on yeast can be shown by the increase in dry wt. of cultures. The heavier is the inoculation the less is the relative increase in growth. (I) can be quantitatively extracted from yeast with boiling H₂O. The (I) content of yeast cultures is determined by the (I) content of the culture medium. Yeast must contain more than a certain min. amount of (I) to grow on a (I)-free culture medium. Most of the utilised (I) undergoes no great chemical change, as it can be extracted again, but a certain proportion is so transformed that it cannot be extracted.
E. A. H. R.

Buffered and low oxygen content physiological salt solutions. M. RANDALL and T. C. DOODY (Biol. Bull., 1935, 68, 258—262).—Mn(OH)₂ effectively removes O₂ and buffers solutions from p_H 7.0 to 9.0. Its use is convenient in the culture of protozoa.

Nature of crystals found in amœba. R. H. LUCE and A. W. POHL (Science, 1935, 82, 595—596).—The most prominent cryst. inclusions have n 1.668, m.p. approx. 290°; they probably consist of Ca chlorophosphate. L. S. T.

Ultra-violet irradiated amœbæ. W. A. BLACK (Science, 1935, 82, 495—497).—*A. proteus* is negatively phototropic towards ultra-violet light. Irradiation appears to stop the digestion of food. L. S. T.

Infection with *Trypanosoma equiperdum*. D. PERLA (Arch. Path., 1935, 19, 505—523).—Infected but surviving rats acquired a secondary hæmolytic anæmia, and showed increased [Fe], without change in [Cu], in livers. [Fe] and [Cu] in the spleen declined. CH. ABS. (p)

Action of certain derivatives of copper on *Treponema cuniculi* and *Trypanosoma brucei*. R. SAZERAC and N. LARTHE (Compt. rend. Soc. Biol., 1935, 120, 1179—1181).—*T. cuniculi* lesions in the rabbit are cured by injections of $\text{Na}_2\text{Cu}(\text{S}_2\text{O}_4)_2$, but in the case of CuO they recur. *T. brucei* infection in the rat is reduced temporarily by Cu_2O , electrocuprol, or 1% CuSO_4 . R. N. C.

Changes in the nucleus of *Euglena gracilis*, Ehrbg., in chronic arsenical poisoning. S. B. RYBINSKY and L. M. ZRYKINA (Arch. Protistenk., 1935, 85, 334—340).—Chronic As_2O_3 poisoning results in an increase in the thymonucleic acid of the nucleus and changes in morphological characteristics. A. G. P.

Relation of hydrogen-ion concentration to growth of *Chilomonas* and *Chlorogonium*. J. B. LOEFER (Arch. Protistenk., 1935, 85, 209—223).—Total growth ranges of p_{H} and optimum zones are determined for *Chilomonas paramecium*, *Chlorogonium euchlorum*, and *C. elongatum*. NaOAc prevents growth of *Chlorogonium* below p_{H} 5.4 and of *Chilomonas* below p_{H} 8.5. A. G. P.

Influence of heat and storage on electrophoretic migration velocities of various micro-organisms. K. P. DOZOIS and F. HATCHEL (J. Bact., 1935, 30, 473—477).—Migration velocities increased with rising temp. $> 60^\circ$. A. G. P.

Precision photometer for study of bacteria and other micro-organisms. H. MESTRE (J. Bact., 1935, 30, 335—358).—A "densitometer" used in conjunction with a photo-electric cell is described. A. G. P.

Growth and survival of micro-organisms at sub-freezing temperatures. H. F. SMART (Science, 1935, 82, 525).—Many species of bacteria, yeasts, and moulds are able to survive in frozen fruit kept at -9.4° for 3 years; some of these showed slow growth at -8.9° in fresh cultures. L. S. T.

Carbohydrate metabolism of *Aspergillus niger* is a function of the nitrogen source of the nutrient medium. R. BONNET and J. JACQUOT (Compt. rend., 1935, 201, 1213—1215; cf. A., 1935, 1027).—*A. niger* produces citric (I) and oxalic acid (II) when N is supplied as peptone or NH_2 -acids. The wt. of mycelium and its (I) content remained practically const. during 4—20 days, but accumulation of (II)

increased progressively. In NO_3' media (I) and (II) are produced from all sugars examined, except lactose. In no case was (II) formed in NH_4 media. A. G. P.

Assimilation of oxalic acid by *Aspergillus niger*. D. BACH and J. FOURNIER (Compt. rend., 1935, 201, 982—984).—5-day-old cultures of this organism consume $\text{H}_2\text{C}_2\text{O}_4$; the amount diminishes with increasing p_{H} , and is practically zero at $p_{\text{H}} > 5.8$. The acid ion as well as the neutral mol. appears to be utilised. F. A. A.

Proteolytic enzymes of *Aspergillus niger*. H. OTANI (Acta Schol. Med. Kioto, 1935, 17, 317—322).—Aq. or glycerol extracts of *A. niger* exhibit digestive properties typical of pepsin, trypsin, and erepsin. Optimum digestion of fibrin occurs at p_{H} 7.1 or 2.0. CH. ABS. (p)

Mould enzymes splitting nucleic acid. H. OTANI (Acta Schol. Med. Kioto, 1935, 17, 323—329).—Glycerol extracts of a no. of species of moulds hydrolysed nucleic acid. Optimum p_{H} vals. were between 4.2 and 6.2. CH. ABS. (p)

Action of mould enzymes on benzene derivatives of amino-acids and dipeptides. H. OTANI (Acta Schol. Med. Kioto, 1935, 17, 330—333).—Mould enzymes readily decomposed benzoyl-*dl*-leucylglycine. In general hippuric acid was more strongly attacked than benzoyldiglycine. Benzoyl- and benzylglycyl-*dl*-phenylalanine are not attacked. CH. ABS. (p)

Nutrient solution purification for removal of heavy metals in deficiency investigations with *Aspergillus niger*. R. A. STEINBERG (J. Agric. Res., 1935, 51, 413—424).—The solution is treated with CaCO_3 and filtered while hot. Supplementary use of C is unnecessary and lowers experimental precision. Extraction of spores of *A. niger* with aq. KHCO_3 partly removes Fe, Cu, and Mn. Subsequent growth of treated spores leads to accentuated deficiency effects in respect of these metals. A. G. P.

Pharmacodynamic action of zinc in general metabolism. O. KAUFFMAN-COSLA and R. BRÜLL (Bull. Soc. Chim. biol., 1935, 17, 1828—1835).—The absence of Zn from cultures of *Aspergillus niger* leads to a decrease in the synthesis of carbohydrates, lipins, and protein. A. L.

Mould tissue. X. Phospholipins of *Aspergillus sydowi*. D. W. WOOLLEY, F. M. STRONG, W. H. PETERSON, and E. A. PRILL (J. Amer. Chem. Soc., 1935, 57, 2589—2591; cf. A., 1934, 697).—The phospholipins (0.4—0.7% of mycelium), purified by repeated pptn. from Et_2O -solution with COMe_2 , consist of a mixture of lecithin and kephalin. Hydrolysis (5% H_2SO_4) gives glycerophosphoric acid, choline, cholamine [*picrolonate*, m.p. 222—226° (decomp.)], oleic acid, and (probably) traces of palmitic, stearic, and a more unsaturated acid. H. B.

Dissimilation of glucose by heterofermentative lactic acid bacteria. M. E. NELSON and C. H. WERKMAN (J. Bact., 1935, 30, 547—557).—The end-products of fermentation of glucose by three heterofermentative species were lactic acid, AcOH , CO_2 ,

EtOH, and glycerol. The amount of CO₂ produced was equiv. to the EtOH+AcOH (mols.), and that of glycerol to twice the AcOH (mols.). A tentative scheme representing these changes is presented.

A. G. P.

Utilisation of amino-acids as common sources of carbon and nitrogen by soil bacteria: organisms decomposing betaine and valine. H. HEIGENER (Zentr. Bakt. Par., 1935, II, 93, 81—113).—As simultaneous sources of N and C, valine (I), betaine (II), and glycine were but poorly utilised by soil bacteria; leucine, phenylalanine, alanine, and asparagine were rather more effective. Glutamic and aspartic acid were very generally utilised. Organisms decomp. (I) and (II) were isolated and described and their significance in humus formation is discussed.

A. G. P.

Relation of oxidation-reduction potential to growth of an aerobic micro-organism. W. B. WOOD, jun., M. L. WOOD, and I. L. BALDWIN (J. Bact., 1935, 30, 593—602).—Reversible oxidation-reduction indicators positive to, and including, methylene-blue when in oxidised forms inhibit the growth of *B. megatherium*. Indicators negative to this do not inhibit. Substances which are inhibitory in the oxidised form are not bacteriostatic when reduced. Bacteriostatic compounds affect growth only in the lag phase. Addition of inorg. reducing agents to broth renders it more favourable to the growth of the organism.

A. G. P.

Effect of some alkaloids on soil micro-organisms: nitrogen fixers. I. Effect on *B. radicola*. G. MEZZADROLI and L. SGARZI (Giorn. Biol. Appl. Ind. Chim., 1934, 4, 162—174; Chem. Zentr., 1935, i, 3679).—Development is stimulated by caffeine, quinine, and strychnine, the effect in nutrient solution being > that in soil mixture. Glucose can serve as a source of carbohydrate.

R. N. C.

(A) Action of radiation in the extreme ultra-violet on *Bacillus subtilis* spores. (B) Inhibition of growth of *B. subtilis* by ultra-violet-irradiated carbohydrates. I. H. BLANK and W. ARNOLD (J. Bact., 1935, 30, 503—506, 507—511).—(A) Radiation in the region 110—140 m μ has a marked germicidal action.

(B) Radiations of 235.7 m μ modify agar in a manner which prevents the growth on it of *B. subtilis*. A non-volatile, thermostable inhibitory agent, diffusible through agar, is formed. A similar inhibition is caused by irradiation of carbohydrate solutions used in the prep. of media.

A. G. P.

Microbial decomposition of chitin. H. BUCHERER (Zentr. Bakt. Par., 1935, II, 93, 12—24).—Organisms decomp. chitin are isolated from soil and other sources.

A. G. P.

Urea-decomposing microflora of soils. I, II.—See B., 1936, 114.

Mannitol-forming bacteria isolated from (a) sweet potatoes (*Ipomoea edulis*, Makino), (b) "kaki" fruit (*Diospyros kaki*). Y. IWASAKI (Bull. Agric. Chem. Soc. Japan, 1935, 11, 159—164, 164—167).—Both strains produce mannitol from

fructose, but not from glucose, mannose, or galactose. Morphological characteristics are given. F. O. H.

Anaerobic bacteria capable of fermenting waste sulphite liquor. A. M. PARTANSKY and B. S. HENRY (J. Bact., 1935, 30, 559—571).—Five new species of *Clostridium* are described, and their biochemical activities are recorded.

A. G. P.

Production of *d*-lactic acid and of butyric acid.—See B., 1936, 167.

Amylase of *Clostridium acetobutylicum*. W. W. JOHNSTON and A. M. WYNNE (J. Bact., 1935, 30, 491—501).—The amylase shows optimum activity at *p*_H 4.8—5.05. NaOAc retards its action *in vitro*, but when added to the culture media increases the amount of the amylase present in the nutrient at the end of the fermentation. PO₄^{'''} and Cl['] also retard starch hydrolysis at *p*_H 4.95. Temp. effects are examined.

A. G. P.

Effect of synthetic surface-active materials on bacterial growth. I. Effect of sodium di-*sec*-butylnaphthalenesulphonate on growth of *Mycobacterium smegmatis*. J. KATZ and A. LIPSITZ (J. Bact., 1935, 30, 419—422).—In concns. of 1:10,000 the salt inhibits growth. In small proportions (to 1:50,000) involution forms occur frequently. No synergistic action was apparent between the salt and neutral acriflavine.

A. G. P.

Existence in *B. tumefaciens* of an endotoxin capable of causing the formation of tumours in plants. A. BOVIN, M. MARBE, I. MESROBEANU, and P. JUSTER (Compt. rend., 1935, 201, 984—986).—CCl₃·CO₂H extracts a "complete" antigen (I) from *B. tumefaciens* (II), corresponding with 3% of the dry wt. of the bacteria. (I) is a solid, aq. solutions of which are not dialysable. In dil. AcOH at 100° it yields fatty acids and a slowly dialysable polysaccharide (III) ("residual antigen"). Both (I) and (III) are pptd. specifically by serum from rabbits injected with (II). (I) is toxic to mice, whilst (II) is non-toxic. (I) produces tumours in *Helianthus annuus* stems similar to those produced by living (II).

F. A. A.

Bactericidal action of organic acids towards Bang's bacillus. E. ZIMMERMAN (Zentr. Bakt. Par., 1935, I, 215—221).—Lactic, tartaric, citric, and (especially) formic acid have marked toxic action on the bacillus. Lethal dosages are determined. Possible chemotherapeutic uses of org. acids are discussed.

A. G. P.

Presence of hæmolysins in young cultures of cholera vibrios. W. DOORENBOS (Compt. rend. Soc. Biol., 1936, 121, 128—129).

R. N. C.

Cultural requirements of bacteria. VI. Diphtheria bacillus. J. H. MUELLER. VII. Amino-acid requirements for the Park-Williams No. 8 strain of diphtheria. J. H. MUELLER and I. KAPNICK (J. Bact., 1935, 30, 513—524, 525—534).—VI. Animal tissue extracts contain substances essential to the growth of the organism. Considerable amounts of the active substance occur in the 95% EtOH filtrate of aq. liver extract (beef), and may be adsorbed on C and eluted with acidified EtOH. The

filtrate from such C adsorptions also contains growth-stimulating materials, including K and Mg.

VII. This strain grows freely on media containing only *l*-cystine, *d*-glutamic acid, *dl*-valine, *dl*-leucine, *dl*-methionine, glycerol, inorg. salts, and liver "clute." The prep. of the latter is described. A. G. P.

Electrophoretic phenomena of bacteria. II. Electrophoretic velocities of virulent and non-virulent *C. diphtheriae*. III. Electrophoretic velocity in relation to growth, senescence, and death. C. W. BUGGS and R. G. GREEN (J. Bact., 1935, 30, 447—451, 453—463).—II. Although no strict line of demarcation was apparent, the average velocity of all non-toxigenic strains is 18.8% > that of all toxigenic strains.

III. The velocity of cultures was approx. const. from 6 hr. to 10 days, and showed variable changes after killing by heat, but not after treatment with PhOH, CH₂O, or HgCl₂. Extraction of cultures with hot 70% EtOH lowered the velocities approx. to those of cells killed in PO₄''' buffer solution.

A. G. P.

Metabolic activity of various colon group organisms at different phases of the culture cycle. G. MOONEY and C. E. A. WINSLOW (J. Bact., 1935, 30, 427—440).—The presence of a fermentable sugar (glucose) stimulates multiplication of *E. coli* and *Salmonella gallinarum* in aerated media, but tends to inhibit that of *S. pullorum*. Production of CO₂ per cell per hr. by organisms in the same period of culture cycle is independent of species and culture medium. Metabolic rates vary considerably with the phase of the cycle. The period of physiological youth in cultures is characterised by relatively larger cells and by greater metabolic activity per unit of living matter concerned. A. G. P.

***Escherichia coli* and three of its rough variants.** E. H. RENNEBAUM (J. Bact., 1935, 30, 625—638).—As energy sources AcOH, lactic, and malic acids are more readily utilised by the parent cell, whilst tartaric, citric, and salicylic acids are preferentially utilised by one or more of the variants. A typical rough variant has less vigorous enzymes than the parent, in respect of glucose decomp. Injection of the normal strain into the ear vein of rabbits causes a sudden increase in blood-sugar and death in a few hr. Variants have no appreciable action. The fatal action of the normal form is probably due to a sol. exo-toxin which increases the permeability of lung capillaries. A. G. P.

"Complete" somatic antigen contained in some *B. coli*. A. BOIVIN, L. MESROBEANU, G. MAGHERU, and A. MAGHERU (Compt. rend. Soc. Biol., 1935, 120, 1276—1279).—Eight strains of *B. coli* examined fall into six serological types. The "complete" antigens contain 38—48.4% of sugar and 9.9—20.7% of fatty acid (liberated by acid hydrolysis); the chemical composition is not const. for strains of the same type. R. N. C.

"Residual" antigen of *B. coli*. G. MAGHERU, A. MAGHERU, A. BOIVIN, and L. MESROBEANU (Compt. rend. Soc. Biol., 1935, 120, 1279—1282). R. N. C.

Importance of the electric charge in certain aspects of immunity. H. C. BROWN and J. C. BROOM (Trans. Roy. Soc. Trop. Med. Hyg., 1935, 28, 357—376).—*Leptospira* are killed by colloidal Cu when suspended in immune but not when in normal serum. Victoria-blue is toxic in both sera. If the charge on red cells is diminished, a hæmolytic serum becomes inactive. CH. ABS. (p)

Violet agar reaction as a differential characteristic of the *Micrococcus catarrhalis* group. G. H. CHAPMAN (Stain Tech., 1936, 11, 25—26).—The crystal-violet-agar reaction is useful in the study of different strains of this group. P. G. M.

Cultural characteristics of *Pasteurella tularensis*. C. M. DOWNS and G. C. BOND (J. Bact., 1935, 30, 485—490). A. G. P.

Effects of quinine derivatives in experimental *Pneumococcus* studies. W. W. G. MACLACHLAN, H. H. PERMAR, J. M. JOHNSTON, and J. R. KENNEY (Amer. J. Med. Sci., 1934, 188, 699—705).—Toxicity of ethylapoquinine varies considerably, but decreased toxicity does not diminish its protective power. Hydroxyethylapoquinine is less toxic but has greater antipneumococcal power. Hydroxyethylhydrocupreine is the least toxic, and its protective action is < that of other derivatives. CH. ABS. (p)

Anaerobic surface cultures. II. Gaseous products of metabolism of organisms (yeast, *Staphylococcus aureus*, *B. coli*, *B. prodigiosum*): aldehyde content and bactericidal action at a distance. W. BACHMANN and OGAIT (Zentr. Bakt. Par., 1935, I, 134, 281—288).—The inhibitory action (at a distance) of certain yeasts etc. on aerobic and anaerobic bacteria depends on the production of appreciable amounts of MeCHO. A. G. P.

Denaturation of staphylococcal proteins. A. P. KRUEGER and V. C. NICHOLS (J. Bact., 1935, 30, 401—409).—Antigens separated by ultrafiltration contain < 10% of the total bacterial protein in the denatured form. On heating, the native proteins are denatured, become insol. at the isoelectric point, and show a considerable decrease in -SH. The denaturation process obeys the law of mass action. The facts are considered in relation to the prep. of vaccines and the preservation of active antigens. A. G. P.

Organism of European foul-brood of bees. H. L. A. TARR (Nature, 1936, 137, 151—152).—Photomicrographs of two kinds of *Streptococcus apis*, which differ only in that one rapidly liquefies gelatin and coagulates and peptonises the casein of milk, are reproduced. L. S. T.

Donators and acceptors of hydrogen for *Streptococcus hemolyticus*. D. BACH (Compt. rend. Soc. Biol., 1936, 121, 215—217).—Fructose, glucose, mannose, xylose, galactose, lactose, sucrose, maltose, arabinose, glycerol, CH₂:CH·OH, EtOH, MeOH, Bu'OH, lactate, cysteine, fumarate, and pyruvate are active H donators; NaBrO₃ and NaIO₃ are the only active H acceptors. R. N. C.

Lipins of tubercle bacilli. XLI, XLII.—See this vol., 311, 314.

Comparison of antigenic properties of defatted tubercle bacilli and their derived proteins. C. H. BOISSEVAIN (Amer. Rev. Tuberc., 1935, 31, 547—552).—The H₂O-sol. proteins from ground or hydrolysed bacilli or from filtered culture media all have the same tuberculin activity. Guinea-pigs cannot be rendered hypersensitive to 1% tuberculoprotein by injection of 10—100 mg. of any H₂O-sol. protein or peptone derived from the bacillus. CH. ABS. (p)

Preparation of purified tuberculin. A. BOQUET and G. SANDOR (Compt. rend. Soc. Biol., 1936, 121, 99—100).—Tubercle bacilli filtrate is pptd. with phosphotungstic acid and H₂SO₄. The ppt. is collected by centrifuge, washed with 0.2N-H₂SO₄, and eluted with Ba(OH)₂ solution; the residue is washed twice with H₂O and the eluate and washings are combined and filtered. The stable filtrate contains tuberculin. R. N. C.

Cultural characters of *Trichomonas (Trichomastix) colubrorum*. R. CAILLEAU (Compt. rend. Soc. Biol., 1936, 121, 108—110).—*T. colubrorum* ferments glucose, galactose, fructose, maltose, sucrose, raffinose, and lactose with production of acid. Horse serum, but not rabbit serum, can replace whole blood or organs as nutrient. R. N. C.

Nitrogen distribution in the protein of mouse typhoid bacillus. H. OTANI (Acta Schol. Med. Kioto, 1935, 17, 334—337).—Data are given for the dry defatted bacilli and for the fraction pptd. from a conc. H₂SO₄ extract on dilution to 5%.

CH. ABS. (p)

Variation of the hæmolytic power of the El Tor vibrio. W. DOORENBOS (Compt. rend. Soc. Biol., 1936, 121, 130—132). R. N. C.

Microbiological basis of chemotherapeutic action. III. Fixation of therapeutically administered gold compounds by various recurrent spirochætes. N. VON JANCÓS and E. NOVAK (Zentr. Bakt. Par., 1935, I, 134, 159—169).—Fixation of Au by *Sp. obermeiri* is reversible. Washing with serum removes the Au. *Sp. usbekistanica* does not absorb Au to any appreciable extent. A unimol. surface fixation by this organism is postulated. A. G. P.

Bacteriostatic and bactericidal studies of dyes and allied compounds. S. A. PETROFF and W. S. GUMP (J. Lab. Clin. Med., 1935, 20, 689—698).—Azine, oxazine, thiazine, and basic CHPh₃ dyes (I), anil-quinoline derivatives (II), and some alkaloids have bactericidal and bacteriostatic effects on Gram-positive organisms. The order of activity for Gram-negative organisms was (II) > (I) > acridine dyes. CH. ABS. (p)

Study of the relations between bacteria, ultraviruses, bacteriophages, toxins, and enzymes, by means of the action of gonacrine. C. LEVADITI, P. HABER, and G. HORNUS (Bull. Acad. méd., 1934, 112, 573—586).—Gonacrine rapidly suppresses the vitality, virulence, and sp. activity of bacteria, bacteriophages, and ultraviruses (except that of poliomyelitis), but does not affect toxins or enzymes. R. N. C.

Production of a neurotropic strain of Rift Valley fever virus. R. D. MACKENZIE and G. M. FINDLAY (Lancet, 1936, 230, 140—141). L. S. T.

Action of sodium ricinoleate on rabies virus. H. VIOLLE and J. LIVON (Compt. rend. Soc. Biol., 1936, 121, 100—102).—Na ricinoleate injected with rabies virus in rabbits prevents the onset of rabies. R. N. C.

Cultivation of the virus of St. Louis encephalitis. J. T. SYVERTON and G. P. BERRY (Science, 1935, 82, 597). L. S. T.

Apparatus for determining the fermentative properties of aerobic and anaerobic microorganisms. A. P. STRUYK (Chem. Weekblad, 1936, 33, 44—45). S. C.

Hormonal equilibrium and hormonal derangement in the interferometric picture of the serum. A. SCHITTENHELM, F. CHROMETZKA, and W. SPIEKER (Z. ges. exp. Med., 1935, 95, 149—167; Chem. Zentr., 1935, i, 3431). R. N. C.

Gaseous exchange after injection of adrenaline in cocks and owls. A. PAGANO (Boll. Soc. ital. Biol. sperim., 1935, 10, 540—542).—Gaseous exchange, as in pigeons, is scarcely affected. R. N. C.

Adrenal cortex and carbohydrate metabolism. S. THADDEA (Z. ges. exp. Med., 1935, 95, 600—626; Chem. Zentr., 1935, i, 3299).—Adrenal cortex hormone injected into guinea-pigs causes increase of blood-sugar and of liver- and muscle-glycogen; it counteracts the action of insulin. G. H. F.

Modifications of the hypertensive action of adrenaline by certain colloidal products. D. BROWN and A. BEAUNE (Compt. rend. Soc. Biol., 1935, 120, 1202—1204).—The action of adrenaline in the dog is reduced by colloidal lipins, and by certain colloidal metals and proteins. R. N. C.

Physiology of the autonomous nervous system. VI. Action of adrenaline on the blood-calcium of the dog with parathyroid insufficiency. F. MATHIEU and Z. M. BACQ. VII. Phosphagen in the muscle of the sympathectomised cat. W. L. DULIÈRE, Z. M. BACQ, and L. BROUHA (Arch. int. Physiol., 1934, 38, 160—163, 164—171; Chem. Zentr., 1934, ii, 3401).—VI. Serum-Ca falls 10—15 min. after intravenous injection of adrenaline, which therefore has only a secondary rôle in Ca regulation.

VII. P in the muscles affected is increased some time after sympathectomy, owing to the slackening of the process of resynthesis. After 3—5 months P metabolism in the resting state is scarcely affected, whilst in the muscle a compensating or adapting process has taken place. R. N. C.

Action of adrenaline and potassium on the phosphagen of muscle poisoned with iodoacetic acid. J. WAJZER, R. LIPPMANN, and A. MARNAY (Compt. rend. Soc. Biol., 1936, 121, 142—144).—Adrenaline scarcely affects phosphagen (I) in the isolated CH₂I-CO₂H-poisoned frog's muscle in anaërobiosis, no resynthesis occurring even when (I) is almost absent from the muscle. Excess of K⁺ causes a breakdown of (I). R. N. C.

Influence of rapidity of intravenous injection of adrenaline on hyperglycæmic action. Y. SUGANUMA (*Folia Pharmacol. Japon.*, 1935, 19, 412—416).—The longer was the time of injection the stronger was the hyperglycæmic response (max. at 10—30 min.). CH. ABS. (p)

Decomposition of adrenaline in tissues. H. BLASCHKO and H. SCHLOSSMANN (*Nature*, 1936, 137, 110).—Rat-liver tissue accelerates the loss of adrenaline (I) activity in presence of O₂. The O₂ uptake of liver tissue is not markedly influenced by (I), but that of liver extracts is increased when (I) is added. In presence of tissue extracts activity is approx. halved after the uptake of one O and practically abolished after that of 2 O per mol. of (I). L. S. T.

Significance of the vegetative nervous system on the regulation of blood-sugar. E. FILLA (*Minerva med.*, 1935, I, 489—494).—Insulin (I) injection with adrenaline is less effective in producing hypoglycæmia than is (I) alone. Simultaneous injection of atropine and ginegin followed by (I) has a greater effect than (I) alone. CH. ABS. (p)

Action on local glycæmia, *in vivo*, of insulin injected intravenously. D. OLMER, J. OLMER, J. PAILLAS, and J. VAGUE (*Compt. rend. Soc. Biol.*, 1936, 121, 76—78).—Injection of insulin in a section of a limb that has been ligatured off from the circulation causes a local fall of blood-sugar that varies with the subject. The hypoglycæmic action of insulin probably depends on direct glycæmic and muscular glycolysis, but the hepatic factor is excluded. R. N. C.

State of functional reactivity of the endocrine pancreatic tissue in normal dogs subjected to prolonged biquotidian injection of insulin. E. AUBERTIN, A. LACOSTE, and R. SARIC (*Compt. rend. Soc. Biol.*, 1936, 121, 241—244).—The blood-sugar curve after glucose does not exhibit an abnormal rise in animals subjected to prolonged insulin treatment, but the post-hyperglycæmic fall is increased. R. N. C.

Influence of insulin on the liver-glycogen level of frogs. E. GEIGER [with H. HALMOS] (*Arch. exp. Path. Pharm.*, 1936, 180, 251—257).—Continuous electrical stimulation of the muscles in summer and spring (but not winter) frogs diminishes the liver-glycogen (I). Prior administration of insulin (II) inhibits this change. Administration of glucose causes production of (I) in all seasons, but the increase in (I) of summer frogs disappears after a few days unless (II) is injected. Hence the seasonal variation in (I) is due to deprivation of (II), which inhibits glycogenolysis but does not influence (I) formation. F. O. H.

Direct action of glucose on secretion of insulin by the pancreas. V. G. FOGLIA and R. FERNANDEZ (*Compt. rend. Soc. Biol.*, 1936, 121, 355—358).—Injection of glucose in a dog with a pancreatic graft on the neck causes an increase of insulin secretion in the graft, independent of extrinsic innervation. R. N. C.

Effect of repeated injections of insulin on the histological state of the endocrine pancreatic tissue and its insulin content in the normal dog.

A. LACOSTE, E. AUBERTIN, and R. SARIC (*Compt. rend. Soc. Biol.*, 1936, 121, 239—241).—The no. of islets of Langerhans and the insulin content are increased. R. N. C.

Modifications of the cardiovascular action of acetylcholine by insulin. D. BROWN and A. BEAUNE (*Compt. rend. Soc. Biol.*, 1935, 120, 1205—1208).—The action is reinforced by insulin. R. N. C.

Effect on local glycæmia, *in vivo*, of parathyroid hormone injected intravenously. J. OLMER, J. PAILLAS, and B. SICNASTI (*Compt. rend. Soc. Biol.*, 1936, 121, 78—80).—Intravenous injection of parathormone (I) in a section of a limb that has been ligatured off from the circulation does not affect local blood-sugar; the action of (I) is therefore not due to direct glycolytic influence exercised by muscle or blood. R. N. C.

Effect of parathyroid extract on blood coagulation. R. BONNYNS (*Arch. Int. Physiol.*, 1934, 40, 189—208).—Parathyroid extract (I) does not affect coagulation of re-calcified oxalated blood *in vitro*. The time of coagulation of such blood of rabbits is reduced by intravenous injection of (I), reaching its min. 45 min. after injection, and returning to normal in 3 hr. The action takes place principally in the second phase of (I) action. Plasma-scrozyme is increased, and also, very slightly, the fibrinogen and platelet contents of the blood, the p_H and alkaline reserve being unaffected. R. N. C.

Action of hormones on the secretion of digestive enzymes. Effect of (I) thyroid, (II) parathyroidectomy, (III) insulin, on the composition of gastric juice. R. FERRARI (*Boll. Soc. ital. Biol. sperim.*, 1934, 9, 1320—1322, 1323—1325, 1325—1328).—I. Thyroid preps. fed to dogs increase the enzyme content of the gastric juice; thyroidectomy reduces it, whilst subsequent administration of thyroid preps. restores it to the normal val. Total acidity and free HCl are unaffected.

II. Parathyroidectomy increases the enzyme content and free HCl, but does not affect total acidity.

III. Insulin increases the enzyme content, total acidity, and free HCl as the blood-sugar falls, and vice versa; the rate of secretion is also increased. Glucose increases enzyme content and free HCl slightly, but does not affect total acidity. R. N. C.

Rôle of cholesterol in thyroid-ovarian antagonism: ovarian and adrenal cholesterol in thyroidectomised and thyroxine-treated animals. C. I. PARHON, C. PARHON-STEFANESCU, and I. ORNSTEIN (*Compt. rend. Soc. Biol.*, 1936, 121, 187—189).—Thyroidectomy in rabbits and guinea-pigs causes an increase in ovarian cholesterol (I), which is slightly further increased in rabbits and decreased in guinea-pigs by administration of excess of thyroxine (II). Adrenal (I) is decreased in guinea-pigs and increased in rabbits by both thyroidectomy and excess of (II). (I) is apparently concerned in thyroid-ovarian antagonism. R. N. C.

Influence of thyroxine on the oxygen consumption of surviving tissue. W. HAARMANN (*Arch. exp. Path. Pharm.*, 1936, 180, 167—182).—

The O_2 consumption of surviving muscle or liver tissue is increased by addition of 10^{-17} — $10^{-9}\%$ (max. 10^{-12} — $10^{-14}\%$) of thyroxine: higher concns. have an inhibitory action. F. O. H.

Influence of thyroxine on tissue respiration. A. REUTER (Z. ges. exp. Med., 1935, 95, 214—216; Chem. Zentr., 1935, i, 3300).—Thyroxine caused a rise in O_2 consumption of isolated organs of rat and cat (Warburg's method) of 20—35%; the effect vanished after 1—2 hr. Results on isolated organs may not be comparable with those on living organisms. G. H. F.

Pathogenesis of the histological alterations of the myocardium with excessive administration of synthetic thyroxine. C. MANZINI and E. COSTANTINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 597—600). R. N. C.

Mode of toxic action of excessive administration of thyroxine on the liver. C. MANZINI and E. COSTANTINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 594—597). R. N. C.

Histological lesions of the liver with excessive administration of thyroxine. C. MANZINI and E. COSTANTINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 591—594). R. N. C.

Influencing of the thyroxine-catechin balance of different types of blood by a growth-promoting principle. H. EUFINGER and J. B. GOTTLIEB (Klin. Woch., 1934, 13, 1204—1205; Chem. Zentr., 1934, ii, 3396).—The effect of thyroxine (I) on *Rana temporaria* when added to the aquarium- H_2O is restricted by addition of umbilical, retroplacental, or pubertal blood, which contain an inhibitory and growth-promoting substance. Lactic and uric acids increase the effect of (I), probably through shifting of p_H . R. N. C.

Occurrence of thyrotropic hormone in the central nervous system and cerebrospinal fluid. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1935, 95, 121—123; Chem. Zentr., 1935, i, 3434).—Thyrotropic hormone occurs in the mid-brain and cerebrospinal fluid of the cat. The mid-brain contains about 1/3 of the pituitary content. R. N. C.

Transmission of thyrotropic hormone through the placenta and milk. A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1935, 95, 124—125; Chem. Zentr., 1935, i, 3298).—Thyrotropic hormone administered to guinea-pigs, when pregnant or when feeding young, produced no change in the thyroids of the young. G. H. F.

Anti-thyrotropic substance in blood and carbohydrate metabolism of the liver. A. LOESER (Arch. exp. Path. Pharm., 1936, 180, 325—331).—The blood-principle (I) antagonistic to the anterior pituitary thyrotropic hormone (A., 1935, 1543) inhibits the characteristic symptoms of hyperthyroidism. The hepatic carbohydrate metabolism indicates that changes (e.g., glycogenolysis) due to thyroxine acting independently of the thyroid gland are not influenced by (I). The relation of (I) to thyroid activity is discussed. F. O. H.

Effect of pituitary on protein metabolism. I. Pituitary preparations. II. Thyroid preparations. III. Pancreatic preparations. IV. Adrenal preparation. V. Ovarian preparations. Y. TOKIZAKI (Sei-i-Kwai Med. J., 1934, 53, No. 9, 212—242, No. 10, 105—117, 118—129, 130—139, 140—148).—I. Hypophysectomy decreases protein (I) metabolism and only the anterior pituitary prep. can accelerate it.

II. Injection of thyroxine accelerates (I) metabolism in normal and hypophysectomised dogs, the action being less in the latter.

III. Injection of insulin into normal animals increases all N fractions in urine, and the total, non-protein-, NH_3 -, and creatinine-N in blood. Blood-urea, -uric acid, -creatinine, and $-NH_2$ -acid decline. With hypophysectomised dogs all urinary N fractions increase, blood-uric acid increases, and all other N fractions together with HIO_3 decrease.

IV. Adrenaline increases (I) metabolism in normal and hypophysectomised animals.

V. Ovarian prep. (oöphormin) increases (I) metabolism in normal > in hypophysectomised dogs.

CH. ABS. (p)

Influence of pituitary preparations on non-protein-nitrogen and urea in blood, and iodic acid in serum, of normal and hypophysectomised dogs. Y. TOKIZAKI (Sei-i-Kwai Med. J., 1934, 53, No. 10, 149—158).—Pituitrin and pituglandol increased, but hypophorin decreased, the non-protein-N and urea in blood of normal and hypophysectomised dogs. HIO_3 in serum increased in all cases.

CH. ABS. (p)

Difference of response of the pituitary glands of male and female albino rats treated with the growth hormone. H. S. RUBINSTEIN (Anat. Rec., 1934, 61, 131—140). R. N. C.

Significance of the pituitary in kidney disease. H. MARX (Klin. Woch., 1935, 14, 367—372; Chem. Zentr., 1935, i, 3153). G. H. F.

Stability of anterior pituitary extract in aqueous solution. I. W. ROWLANDS (Quart. J. Pharm., 1935, 8, 642—645).—Aq. extracts of anterior pituitary preps. lost about 50% of their gonadotropic activity in 9 days at room temp. and in about 1 year at 0—2°. W. O. K.

Migraine as a pituitary disease and its treatment with ovarian preparations. I. MUELLER (Med. Klinik, 1935, 31, 448—450).—The anterior pituitary hormone content of the urine of women suffering from migraine is frequently > normal. Progynon exerts a curative effect. R. N. C.

Adrenaltropic action of the anterior pituitary. K. J. ANSELMINO, L. HEROLD, and F. HOFFMANN (Klin. Woch., 1934, 13, 1724).—The chrome-pigmentability of the adrenal medulla is almost abolished and vacuole formation increased by injection of anterior pituitary extract in rats or mice. The active principle is sensitive to acids and alkali, but comparatively thermostable; it can be separated from the corticotropic hormone by ultrafiltration through collodion, which retains it. R. N. C.

Influence of hormones of the anterior and posterior lobes of the pituitary, the thyroid, and the adrenals on the spontaneous creatinuria of endocrine disturbances. A. SCHITTENHELM and F. BÜHLER (*Z. ges. exp. Med.*, 1935, 95, 206—213; *Chem. Zentr.*, 1935, i, 3435).—Spontaneous creatinuria in males with gonadal insufficiency is abolished by prolan and orasthin, but not by prähormone. Thyrotropic hormone and thyroxine induce creatinuria in myxœdema. Spontaneous creatinuria in Addison's disease is abolished by small doses of cortical preps.; its appearance is due to increased breakdown of phosphagen in the muscles. R. N. C.

Glyco-chloro-proteinæmic curve in normal and diabetic individuals after injection of posterior pituitary extract. G. DELL'ACQUA (*Boll. Soc. ital. Biol. sperim.*, 1935, 10, 423—447).—Injection of the extract in normal subjects induces a short rise of blood-sugar (I) followed by a prolonged fall and recovery to normal. Proteins (II) show a fall followed by a recovery to almost normal; NaCl falls without recovering. In diabetics (I) shows a marked rise followed by a fall without recovery. (II) rise rapidly at first, fall to vals. < normal, and then rise slowly to > the first max. NaCl rises irregularly. R. N. C.

Determination of the excretion of prolan by mature and by aged men. H. SAETHRE (*Klin. Woch.*, 1935, 14, 376—378; *Chem. Zentr.*, 1935, i, 3153).—The urinary prolan excretion of healthy men is 25—30 mouse units per litre. In old age there may be some increase. G. H. F.

Prepubertal reversal of the sex difference in the gonadotropic hormone content of the pituitary gland of the rat. H. M. CLARK (*Anat. Rec.*, 1934, 61, 175—192).—The prolan content of the pituitary in the immature female rat is > that in the male; at puberty the male gland is more potent. From 4 to 6 months the sex difference is negligible, whilst at 7 months it is reversed. In the female the content rises sharply at 13—20 days, whilst in the male it increases gradually to a const. level at puberty. R. N. C.

Sex difference in the change of potency of the anterior pituitary following bilateral castration in newborn rats. H. M. CLARK (*Anat. Rec.*, 1934, 61, 193—202).—Prolan in the male pituitary increases on castration; it fluctuates in females. R. N. C.

Is there an antagonism of sex hormones? O. O. FELLNER (*Z. ges. exp. Med.*, 1935, 95, 373—377; *Chem. Zentr.*, 1935, i, 3431—3432).—Hormones are extracted from urine by boiling with CaO and pptn. with Na₂C₂O₄, the hormones remaining in the filtrate. The masculin (I) content of pregnancy urine is > that of male urine, (I) probably originating from the placenta. The sex hormone antagonism hypothesis is discarded in favour of one of synergism between the hormones and gonads. R. N. C.

Physiology of Δ^5 -androstenediol. A. BUTENANDT (*Naturwiss.*, 1936, 24, 16).— Δ^5 -Androstenediol in pure condition displays the activities of both testicular and follicular hormones. W. O. K.

Action of the male hormone (androsterone) injected into the chicken embryo: experimental production of intersexuals. E. WOLFF (*Compt. rend. Soc. Biol.*, 1935, 120, 1312—1314).

R. N. C.

Interpretation of the results obtained by injection of synthetic androsterone in the chicken embryo. E. WOLFF (*Compt. rend. Soc. Biol.*, 1935, 120, 1314—1316).

R. N. C.

Influence of sex hormone on the spontaneous creatinuria of endocrine disturbances. A. SCHITTENHELM and F. BÜHLER (*Z. ges. exp. Med.*, 1935, 95, 197—205; *Chem. Zentr.*, 1935, i, 3433).—Spontaneous creatinuria in males with gonadal insufficiency is abolished by "proviron," but not if muscle metabolism has been disturbed by degenerative muscle changes. Similar creatinuria in women at the climacteric is abolished by "progynon," but not so uniformly. In certain cases creatinuria is abolished also by the heterosexual hormone.

R. N. C.

Response of immature rats to various gonadotropic substances. R. DEANESLY (*Quart. J. Pharm.*, 1935, 8, 651—668).—Various gonadotropic preps. were administered to male and female immature rats and their resulting actions observed. A method of assay which employs 10 rats with an error of $\pm 10\%$ is described.

W. O. K.

Relative activity of different gonadotropic preparations on œstrous rabbits, pregnant rabbits, and immature rats. I. W. ROWLANDS (*Quart. J. Pharm.*, 1935, 8, 646—650).—Extracts of pituitary gland (cow, horse) and urine of pregnancy have been assayed on œstrous, 15 days- and 25 days-pregnant rabbits, and on immature rats. For ovulation, pregnant rabbits require more of all extracts tested than do œstrous rabbits. Horse pituitary and urine of pregnancy extracts are relatively equally potent when tested on rabbits and rats, but ox pituitary is less potent in rats.

W. O. K.

Physiology of the corpus luteum. IX. Inhibition of œstrin by progestin-containing extracts of the corpus luteum. W. M. ALLEN and R. K. MEYER (*Anat. Rec.*, 1935, 61, 427—439).—Progestin inhibits cornification by œstrin and the œstrous smear.

R. N. C.

Structure of œstrin in alkaline solution. K. P. BJERGAARD and S. A. SCHOU (*Quart. J. Pharm.*, 1935, 8, 669—673).—In neutral or acid EtOH solution, the max. ultra-violet absorption of œstrin occurs at 282 m μ , whilst in alkaline solution it is at 295 m μ . The shift is probably associated with enolisation of the keto-group.

W. O. K.

Biological activity of theelol. R. K. MEYER, L. C. MILLER, and G. F. CARTLAND (*J. Biol. Chem.*, 1936, 112, 597—604).—Theelol (I) has little biological activity compared with international standard theelin (II) when determined by the vaginal smear method, but it is 4 times as active when determined by the opening of the vagina of the immature rat. (II) is approx. 90 times as active as (I) when administered in oil and 250 times when injected in aq. 10% EtOH containing 0.5% Na₂CO₃.

J. N. A.

Follicular hormone content of eclamptic blood. W. BICKENBACH and H. FROMME (Klin. Woch., 1935, 14, 496—497).—The follicular hormone content of the blood of eclamptic women is \times that of the blood of pregnancy.
R. N. C.

Sexual hormones in domestic animals. KÜST (Klin. Woch., 1934, 13, 1782—1784).—Pregnancy is diagnosed in mares by the Aschheim-Zondek serum reaction from the sixth week to the fifth month, and later by increased follicular hormone (I) excretion in the urine. (I) excretion is increased in the 23rd week in cows, and after 3½ months in goats; in the sow it reaches max. in the fourth week and at the end of pregnancy. (I) is present in the urine of mature boars.
R. N. C.

Sexual hormones in domestic animals. S. KOBER (Klin. Woch., 1935, 14, 381).—Excretion of follicular hormone in the urine of the pregnant mare appears before the 110th day, rises to a max. between the 6th and 8th months, and then falls to a trace at the conclusion of pregnancy (cf. preceding abstract).
R. N. C.

Artificial (hormonal) growth of the oviduct in female carp. K. EHRHARDT and K. KÜHN (Endokrinol., 1934, 15, 1—14; Chem. Zentr., 1935, i, 3433; cf. A., 1935, 413).—The oestrus hormone (I) is apparently not identical with the oviduct hormone (II); crude (I) affects the oviduct more strongly than the cryst. product, whilst (II), although resembling (I) in solubility, thermostability, and adsorbability on C, is difficult to elute from the adsorbate, and is destroyed by 15% NaOH or by AcOH.
R. N. C.

Embryological interpretation of changes induced by oestrogens in the male reproductive tract. S. ZUCKERMAN (Lancet, 1936, 230, 135—136).
L. S. T.

Follicular and luteal hormones and their reaction on the anterior lobe of the pituitary. C. CLAUBERG and W. BREIPOHL (Klin. Woch., 1935, 14, 119—121; Chem. Zentr., 1935, i, 3298).
G. H. F.

Inhibitory effect of follicular hormone on the anterior lobe of the pituitary gland. B. ZONDEK (Lancet, 1936, 230, 10—12).
L. S. T.

Biological determination of corpus luteum extracts. R. COURRIER (Compt. rend. Soc. Biol., 1935, 120, 1263—1266).
R. N. C.

Antigonadotropic hormone in the pineal gland, blood, and organs. P. ENGEL (Z. ges. exp. Med., 1935, 95, 441—457; Chem. Zentr., 1935, i, 3300).—Antigonadotropic hormone (I) of pineal gland is standardised by injecting into immature female rats simultaneously with standardised gonadotropic hormone of the anterior pituitary (II). The amount of (I) required to neutralise the effect of a rat unit of (II) is measured. (I) is found in small amounts in blood, kidney, and spleen.
G. H. F.

Effects of the melanophore hormone and prolans on pigmentation and growth of tadpoles. M. AGLIALORO and U. CIULLA (Boll. Soc. ital. Biol.

sperim., 1935, 10, 538—540).—The melanophore hormone inhibits, whilst prolans stimulates, these.

R. N. C.

Standardisation of the melanophore hormone. M. AGLIALORO and U. CIULLA (Boll. Soc. ital. Biol. sperim., 1935, 10, 537—538).
R. N. C.

Villikin in the human intestine. G. VON LUDÁNY (Klin. Woch., 1935, 14, 123—124; Chem. Zentr., 1935, i, 3301; cf. A., 1934, 331).—Human intestinal mucous membrane when extracted with HCl, neutralised, and the extract injected intravenously into fasting dogs caused great acceleration of the rate of contraction of villi.
G. H. F.

Colour reactions of vitamin-A, -D, and -E, and of some sterols. S. UENO, Y. OTA, and Z. UEDA (J. Soc. Chem. Ind. Japan, 1935, 38, 742—744B).—The colour reactions of these vitamins and of cholesterol, ergosterol, and sitosterol, with fourteen new reagents (mainly PhOH + a second substance) are tabulated and briefly discussed.
J. W. B.

Vitamin-A storage of *Macrurus rupestris*. S. SCHMIDT-NIELSEN, A. FLOOD, J. STENE, and N. A. SØRENSEN (Kong. Norske Vid. Selsk. Forhandl., 1935, 7, 174—177; Chem. Zentr., 1935, i, 3302).—Data for liver-fat and tintometer no. are given and correlated.
H. J. E.

Vitamin-A content of the liver and its variations. A. CHEVALLIER and Y. CHORON (Compt. rend. Soc. Biol., 1935, 120, 1223—1225).—Vitamin-A (I) is decreased in the liver and increased in the blood of the rabbit by anaesthesia. In the guinea-pig, liver-(I) shows marked variations with the animal, whilst blood-(I) is practically const.
R. N. C.

Metabolism of rat liver in avitaminosis-A. O. ROSENTHAL (Arch. Néerland. Physiol., 1935, 20, 539—551).—In about 2/3 of the avitaminotic rats examined, the energy of metabolism decreased considerably, and there was a slight decrease in respiration. These effects appeared as often in fatty as in de-fatted livers. Fatty degeneration, probably as a result of the respiration disorder, is assumed. Changes in metabolism and fatty degeneration of the liver are secondary effects of the vitamin-A deficiency.
J. N. A.

Effect of standard diet on liver metabolism in experimental avitaminosis-A in rats. O. ROSENTHAL (Arch. Néerland. Physiol., 1935, 20, 552—558).—The changes in metabolism and the histological fatty degeneration of the liver are due to an unsp. diet deficiency. The importance of this in the problem of experimental avitaminosis-A is discussed.
J. N. A.

Size and vitamin content of liver of various animals. S. SCHMIDT-NIELSEN, A. FLOOD, and J. STENE (Kong. Norske Vid. Selsk. Forhandl., 1934, 3, 81—84; Chem. Zentr., 1935, i, 2620).—Vitamin-A contents of livers of warm-blooded animals are < those of many fish.
J. S. A.

Effect of vitamin-A on fat and lipin metabolism. P. E. SIMOLA and T. KALAJA (Suomen Kem., 1935, 8, B, 43—44).—Rats and guinea-pigs fed a vitamin-A (I)-free diet show large decreases in the I val. and neutral fat content of the skin, whereas the cholesterol

content is increased, especially in rats. In rats fed on (I)-rich diets, the free cholesterol of the skin and the cholesteryl esters (II) of the liver and kidneys are increased. In guinea-pigs, the changes are indefinite, although the (II) content, the I val., and the neutral fats of the liver are increased.

J. L. D.

Fate of carotene injected into the circulation of the rat. J. C. DRUMMOND and R. J. MACWALTER (*J. Physiol.*, 1934, **83**, 236—242).—Vitamin-A and fat distribution is fairly uniform in the three main lobes of the liver. Carotene injected into the portal circulation is taken up uniformly by the lobes, and tends to disappear after a few days, -A not increasing simultaneously, but in some cases falling. Removal of one lobe may cause a fall in the -A of the other lobes.

R. N. C.

Vitamin-A in the red corpuscles of the blood of vertebrates. A. MAGNAN and H. GIRERD (*Compt. rend.*, 1935, **201**, 1219—1221).—Vitamin-A occurs in certain of the red corpuscles of the blood of the ray and is localised on the chondriome.

A. G. P.

Determination of vitamin-A. A. L. BACHARACH, J. C. DRUMMOND, and R. A. MORTON (*Nature*, 1936, **137**, 148—149).—A crit. discussion of the three approved methods of standardisation which may give three different results.

L. S. T.

Effects of vitamin-B on female genital organs of white rats. J. UENO (*Japan. J. Obstet. Gynecol.*, 1934, **17**, 388—411).

CH. ABS. (p)

Deficiency of vitamin-B and endocrine glands of female white rats. J. UENO (*Japan. J. Obstet. Gynecol.*, 1934, **17**, 267—278)

CH. ABS. (p)

Effect of arginine and of liver and stomach extracts on vitamin-B deficiency in pigeons. A. VON JENEY (*Klin. Woch.*, 1935, **14**, 379—380; *Chem. Zentr.*, 1935, **i**, 3155).—The length of life of pigeons on a vitamin-B-free diet was increased by administration of extracts from yeast, liver, or pig's stomach, or of arginine. The -B complex appears to contain an antianæmic factor resembling arginine.

G. H. F.

Assay of vitamin-B₁ by the "beri-beri" quotient (Q_b). G. AMANTEA (*Atti R. Accad. Lincei*, 1935, [vi], **22**, 173—176).—Further details of the technique are given (cf. A., 1934, 460, 706).

F. O. H.

Vitamin-B₁ and -B₂. J. F. FEASTER and V. E. NELSON (*Proc. Iowa Acad. Sci.*, 1934, **41**, 149—152).—Autoclaved yeast supplies a factor, probably vitamin-B₂, enhancing lactation in rats.

CH. ABS. (p)

Interrelationship of vitamins. C. A. ELVEHJEM and A. ARNOLD (*Nature*, 1936, **137**, 109—110).—The cure of certain symptoms in experimental animals even with cryst. preps. of vitamin does not necessarily mean that the deficiency is due to a lack of the factor fed. Rats showing -B₄-deficiency may be relieved by administration of -B₁. The latter appears to relieve accompanying anorexia, and food consumption increases to a level which supplies adequate -B₄. Synthetic diets used for -B₁ studies must be

amply supplied with -B₄, especially when growth is used as a criterion of potency. The improved growth often obtained by adding large amounts of -B₁ to rats on a low -B₁ diet may be due to the additional effect of traces of -B₄ present as an impurity.

L. S. T.

Objective method for fluorescence determination, with special application to the determination of vitamin-B₂. F. H. COHEN (*Acta Brev. neerl. Physiol.*, 1935, **5**, 18—19; *Chem. Zentr.*, 1935, **i**, 3306).—The apparatus previously described (A., 1935, 466) is applied to the determination of vitamin-B₂.

H. N. R.

Effect of adenine fed to rats on a diet deficient in vitamin-B₄. T. Y. LO (*Nat. Peiping Univ. Coll. Agric. Nutrition Bull.*, 1934, **B**, **1**, 40—46).—Pure adenine from yeast does not serve as a source of vitamin-B₄ for rats.

CH. ABS. (p)

Influence of some food factors on pellagra-like symptoms in rats. F. J. GORTER (*Z. Vitaminforsch.*, 1936, **5**, 1—11).—The incidence and type of pellagra-like disease in rats depend on the composition of the basal diet. There exists an anti-pellagic growth-promoting factor other than flavin and perhaps identical with vitamin-B₆. This factor is separated from caseinogen by hydrolysis. Factors causing dermatitis in rats are discussed.

F. O. H.

Antiscorbutic activity of dehydroascorbic acid: its storage and that of ascorbic acid by the guinea-pig at different levels of intake. F. W. FOX and L. F. LEVY (*Biochem. J.*, 1936, **30**, 211—217).—The antiscorbutic val. of dehydroascorbic acid has been confirmed (Hirst *et al.*, A., 1933, 1091). After reduction to ascorbic acid (I) it is stored in small amounts in the liver. Storage of (I) in the liver is dependent on the level of intake, being small at the min. protective dose and reaching an upper limit at higher levels.

H. G. R.

Does vitamin-C affect the occurrence of normal pigmentation? F. TENCHIO (*Klin. Woch.*, 1934, **13**, 1511—1512; *Chem. Zentr.*, 1934, **ii**, 3644—3645).

R. N. C.

Reversibility of oxidation of ascorbic acid. R. WURMSER and N. MAYER (*Compt. rend. Soc. Biol.*, 1936, **121**, 3—5).—Oxidation of ascorbic acid by 2:6-dichlorophenol-indophenol is as reversible as oxidation by I.

R. N. C.

Reversible oxidation of ascorbic acid by norite charcoal. F. W. FOX and L. F. LEVY (*Biochem. J.*, 1936, **30**, 208—210).—The C (and to a smaller extent other kinds) rapidly (10—15 min.) converts ascorbic acid almost quantitatively into dehydroascorbic acid. With small amounts of C, the effect ∝ the amount of C. Probably the oxidation results from direct transfer of O₂ from the C surface.

W. McC.

Biological oxidations. V. Copper and haemochromogens as catalysts for the oxidation of ascorbic acid. Mechanism of the oxidation. E. S. G. BARRON, R. H. DEMEIO, and F. KLEMPERER (*J. Biol. Chem.*, 1936, **112**, 625—640).—Ascorbic acid (I) is not autoxidisable in solutions free from Cu when the p_H is < 7.6. Above p_H 7.6 the rate of

autoxidation increases rapidly with the p_H . KCN slightly accelerates the rate of O_2 consumption. In neutral and acid solution Cu^{++} (alone of metallic ions) catalyses the oxidation of (I) in concns. as low as 0.046 mg. of Cu per litre. The O_2 uptake is 1 O per mol. of substrate. The optimum p_H of the Cu-catalysed oxidation is 6.95. The haemochromogens of nicotine, C_5H_5N , and pilocarpine can also act as catalysts. 0.001M-KCN completely inhibits the catalytic effect of Cu, and CO, by combining with Cu_2Cl_2 and thus inhibiting its reoxidation to $CuCl_2$, also considerably retards the reaction. The low val. of 1.65 for the temp. coeff. suggests that the reoxidation of Cu_2Cl_2 is the reaction governing the rate of oxidation of (I). The oxidation product can be completely reduced by H_2S up to p_H 5.0, but above this the amount of (I) recovered gradually decreases until at p_H 7.6 the oxidation is mainly irreversible. E. A. H. R.

Diagnosis of vitamin-C subnutrition by urine analysis. M. A. ABBASY, L. J. HARRIS, S. N. RAY, and J. R. MARRACK (Lancet, 1935, 229, 1399—1405).—Data obtained by the method previously described (A., 1935, 417), together with its specificity, are discussed. The urinary excretion of vitamin-C by adults receiving graded doses of -C over long periods reaches levels \propto the intake. Little variation occurs between individual subjects; the same daily dose of -C soon produces an almost identical rate of excretion. During fever, output falls, and an additional dose is needed to restore the original level. A diet appears to be unduly low in -C whenever the daily excretion is $<$ a titration val. of 10—15 mg. per day per 10 stone body-wt., or when the standard dose of 700 mg. produces no response on the second day. In England, the average daily excretion of normal adults receiving small allowances of fruit or other source of -C is approx. 20 mg. per day. L. S. T.

Effect of vitamin-C on the growth of plants. S. VON HAUSEN (Suomen Kem., 1935, 8, B, 50; cf. A., 1935, 1036).—Removal of the cotyledons of young pea seedlings reduces their ascorbic acid (I) content to a low val. and growth is almost completely retarded. Addition of (I) causes increased (approx. normal) growth; the (I) content of the treated plants is much $>$ that of the untreated. J. L. D.

Antiscorbutic value of dandelion. I. S. KLEINER and H. TAUBER (Science, 1935, 82, 552).—The ascorbic acid (I) content varies between 0.08 and 0.10 mg. per g. of fresh greens. Compared with the greens of other vegetables it is not a good source of (I). L. S. T.

Ascorbic acid content of plant tissue. L. RANDOIN, A. GIROUD, and C. P. LEBLOND (Bull. Soc. Chim. biol., 1935, 17, 1649—1676).—Equal quantities of tissue containing chlorophyll and that containing no chlorophyll of the carrot, turnip, vipers-grass, endive, lettuce, leek, and beetroot are administered to guinea-pigs in addition to a diet containing no vitamin-C. The chlorophyll tissue has a much higher antiscorbutic val., as is shown by the wt. curves and the ascorbic acid content of the adrenal glands, the kidney, liver, and testicles. A. L.

Sources of vitamin[-C]. XI—XVI.—See B, 1936, 121.

Vitamin-D requirements in relation to the calcium and phosphorus content of the diet. A. QUERIDO (Arch. Néerland. Physiol., 1935, 20, 487—538; cf. A., 1935, 1431).—The daily requirement for rats varies between 0 and 1×10^{-6} g. of calciferol. It is influenced by the salt level of the ration, and diminishes with increase of the abs. concn. of P. Influence of vitamin-D on the ash content of bone is seen only with diets having a Ca : P ratio of 4. Unpreventable rickets produced by some diets can be changed into a preventable form by preliminary feeding with a diet rich in minerals. Rickets produced by a diet containing 0.2% of P and Ca : P = 1 resembles the human form $>$ that produced with a Ca : P ratio of 4. J. N. A.

Evaluation of the relative toxic effects of large doses of calciferol and the crystalline antirachitic preparation substance L. J. VAN NIEKERK (Arch. Néerland. Physiol., 1935, 20, 559—561).—The ratio of toxic to antirachitic activity of the substance L of Reerink and van Wijk is identical with that of calciferol. J. N. A.

Anti-infective power of vitamin-D. G. SPAGNOL (Rev. sudamer. endocrinol., 1935, 18, 163—166).—Irradiated ergosterol prevented infection of rats with *Salmonella typhimurium*. CH. ABS. (p)

Changes in composition of blood in rabbits by irradiated food. A. FALASCHINI (Boll. Soc. Eustach., 1934, 32, 1—15; Chem. Zentr., 1934, ii, 3782—3783). R. N. C.

Irradiation and growth. F. ROGOZIŃSKI and Z. GŁOWCZYŃSKI (Bull. Acad. Polonaise, 1935, B, 123—136).—Ultra-violet irradiation had no apparent influence on the growth, food utilisation, or bone composition of rats receiving a complete diet, but afforded marked protection when a rachitogenic diet was used. A. G. P.

Cereals and rickets. VI. Comparative rickets-producing properties of different cereals. B. H. THOMAS and H. STEENBOCK (Biochem. J., 1936, 30, 177—188; cf. Green *et al.*, A., 1928, 333).—Rolled oats, patent flour, whole wheat, polished rice, and yellow maize fed to rats as 75% of a low-Ca diet do not differ as regards the severity of the rickets produced. W. McC.

Hypervitaminosis-D. L. THATCHER (Lancet, 1936, 230, 20—22).—Young infants may have idiosyncrasy to the vitamin-D (I) in cod-liver oil as well as to artificially-prepared calciferol. The current tendency to increase the (I) potency of cod-liver oil is deprecated. L. S. T.

Vitamin-D content of calf, beef, lamb, and hog livers. G. M. DEVANEY and H. E. MUNSELL (J. Home Econ., 1935, 27, 240—241).—Ox and hog livers have 0.5—0.4, lamb 0.2, and calf liver $<$ 0.1 international units per g. CH. ABS. (p)

Vitamin-D content of New Zealand fish oils : prophylactic method of biological assay. M. M. CUNNINGHAM (New Zealand J. Sci. Tech., 1935, 17, 563—567).—Vals. for a no. of oils are recorded.

That for proper-liver oil was exceptionally high. The trustworthiness of the prophylactic method of assay is confirmed. A. G. P.

Vitamin-E. IV. Influence on fertility and condition of the young. L. SCHIOPPA (Z. Vitaminforsch., 1936, 5, 22—26).—Administration of large doses of wheat-germ oil to doe rabbits increases their fertility and body-wt. F. O. H.

Chemical properties of vitamin-E. H. S. OLCOTT (Proc. Iowa Acad. Sci., 1934, 41, 173; cf. A., 1935, 1431).—The inactive product obtained by bromination of vitamin-E concentrates is reactivated by boiling with Zn and HCl in MeOH. Catalytic hydrogenation at 200°/200 atm. does not destroy -E.

CH. ABS. (p)

Newly-discovered nutritional factor in milk. G. VON WENDT (Z. Volksernähr., 1935, 10, 116—118; Chem. Zentr., 1935, i, 3686).—The milk of cows fed with green food contains a nutritional factor that stimulated growth and lacteal secretion in rats and in a nursing woman. It is not stored in the organism, nor bound to the milk fat. It is stable to drying of the milk, but not to drying for hay of the grass fed to the cows. R. N. C.

Relationships between the chemistry of chlorophyll and its function in photosynthesis. A. STOLL (Naturwiss., 1936, 24, 53—59).—A lecture.

Photosynthesis in *Grimmia montana*. E. MCKAY (Plant Physiol., 1935, 10, 803—809).—Photosynthesis begins within 10—20 min. of moistening the dry moss, and reaches equilibrium with respired CO₂ in 30 min. The reducing sugar contents of the plant increase from the beginning of photosynthesis and reach a steady level after 30 min.

A. G. P.

Photochemical responses of wheat plan to spectral regions. E. J. LEASE and W. E. TOTTINGHAM (J. Amer. Chem. Soc., 1935, 57, 2613—2616).—Elimination of $\lambda < 390$ or 520 m μ from artificial sunlight decreases the assimilation of NO₃' (I) and conserves carbohydrates in young wheat plants. The chlorophyll and SH-compounds in the tissue also decrease; these appear to influence the reducing power of the press sap. Increased assimilation of (I) is accompanied by a reduction in the pentosans. Most of the compositional effects in the tissue are associated with variations in the proportion of blue-violet light. Reduction of (I) to NO₂' is, however, associated with long ultra-violet radiation. H. B.

Histological variations in *Cosmos* in relation to photoperiodism. O. BIDDULPH (Bot. Gaz., 1935, 97, 139—155).—Short-day treatment of *C. sulphureus* causes rapid initiation of flower primordia (7 days). Transition of foliar to flower primordia is accompanied by marked accumulation of carbohydrates and protein in the growing tip, and by hydrolysis of these at the base of the stem. The glutathione content of the tip shows diurnal variations during the short-day treatment, but remains permanently high from the time of the actual anatomical change from vegetative to flower primordia. Flower-bud formation is associated with somewhat higher asparagine and lower NH₄' contents in the stem tip. A. G. P.

Modification of [plant] leaf structure by X-rays. Y. NOGUCHI (Plant Physiol., 1935, 10, 753—762).—Localised modifications of cellular structure and of the distribution of chloroplasts follow exposure to X-rays. A. G. P.

Theory of assimilation. H. GAFFRON and K. WOHL (Naturwiss., 1936, 24, 81—90, 103—107).—A discussion.

Metabolism of certain *Chlorella* and allied forms. T. D. BECKWITH (Publ. Univ. Calif. Biol. Sci., 1933, 1, No. 1, 1—34).—Three among 8 examined species of unicellular algæ produced NO₂' from NO₃'. None effected the reverse change, although several species grew well on NO₂' media. As source of N urea was generally unsuitable, asparagine had a depressive action, peptone was favourable to some species, and in one case (NH₄)₂CO₃ was satisfactorily utilised. The end-products of N metabolism were bases. Neither indole nor tryptophan was formed. Complete protein was not essential to these organisms. In diffuse light only maltose and glucose favoured proliferation. The end-products of carbohydrate metabolism were alkaline whether grown in darkness or in light. The antigenic protein structure of *Chlorella* varies with the species. A. G. P.

Phosphorus metabolism in leaves of persistent-foilage plants, during yellowing. E. MICHEL-DURAND (Compt. rend., 1935, 201, 1215—1217; cf. A., 1935, 265).—Fractionation of the P compounds of end-of-season green leaves and of yellowed leaves is recorded. Small amounts of phytin-P occurred in all green leaves. On yellowing this migrated completely in Algerian ivy and *Aucuba* (but not in cherry-laurel) before actual leaf-fall. Other forms of P declined in varying proportions at this stage. A. G. P.

Lipin metabolism in germinating mung bean. H. C. KAO (Biochem. J., 1936, 30, 202—207).—During germination the N and ash contents of the whole bean (*Phaseolus aureus*) remain const., the amounts of Et₂O and EtOH extracts increase, the chief constituents of the cotyledon are gradually transferred to the germinating portion, the sterols increase, and the phosphatides decrease. The total fatty acids first decrease and then increase. In the cotyledon the amount of fatty acids remains const., but the amount in the growing portion increases. The degree of saturation of the fatty acids in the sprouting portion increases. W. McC.

Effect of an atmosphere enriched in oxygen on development of plants. M. MOLLARD (Compt. rend., 1935, 201, 1160—1162).—Dry matter production by radish plants decreased with rising [O₂] (20—80%) of the atm., probably as a result of chlorophyll injury. *A. niger* was similarly affected, but to a relatively smaller extent. In a current of O₂, conidia produced after exhaustion of sugar in the medium were coloured brick-red. A. G. P.

Structure of the walls of higher plants. D. B. ANDERSON (Bot. Rev., 1935, 1, 52—76).—A review.

CH. ABS. (p)

Physiological characteristics of frost-resistant winter grains. M. T. TIMOFEEV (Bull. Appl. Bot.

U.S.S.R., 1934, Ser. A, No. 9, 17—24).—The significance of the proteins, the p_{H} of the sap, and other physicochemical properties, in addition to the sugar and H_2O contents, is emphasised. CH. ABS. (p)

Distribution of plant constituents in capillary form. II. Fluorescence of chlorophyll. A. KUHN and G. SCHÄFER (Pharm. Zentr., 1936, 77, 33—35).—With capillary formation, the green zone of chlorophyll (e.g., from tinctures) as viewed by daylight becomes black or red by filtered ultra-violet light. This is due to presence of essential or fatty oils. F. O. H.

Cause of cold-resistance in plants. W. KESSLER (Planta, 1935, 24, 312—352).—No causal relationship exists between cold-resistance and the osmotic pressure or $[H^+]$ of the cell sap. The winter resting period of the plant is associated with changes in the condition of the plasma resulting in increased viscosity and hydration of the colloids and probably with greater d of the plasma. A. G. P.

Course of stone cell formation in pear fruits. W. W. SMITH (Plant Physiol., 1935, 10, 587—611).—Changes in the lignin, cellulose, reducing substances, and H_2O -, alkali-, and EtOH-extractives during the development of the fruit are recorded. The decrease in the % of lignocellulose (I) during growth of certain varieties of apple and pear is due not to a decline in abs. amounts present, but to a relatively rapid increase in EtOH-extractives. There is no evidence of a breakdown of (I) to simpler substances. Sugars are probably elaborated to form lignified tissue. Hemicellulose disappears during storage of fruit and probably serves as a source of respirable matter. A. G. P.

Osmotic pressure and water content of prairie plants. L. A. STODDART (Plant Physiol., 1935, 10, 661—680).—The osmotic pressure of plant saps is characteristic of environment, i.e., the resultant of soil forces which supply H_2O and transpiration effects. A close inverse relationship is established between the osmotic pressure and H_2O contents of individual plants. The osmotic pressure in new was > that in old tissue. A. G. P.

Comparison of the plasmolytic and cryoscopic methods for determining osmotic values in plants. A. BUHMANN (Protoplasma, 1935, 23, 579—612).—Appropriate technique is described. The two methods yield comparable results. Extensive experimental data are recorded and discussed. A. G. P.

Unfreezable and freezable water equilibrium in plant tissues as influenced by sub-zero temperatures. G. A. GREATHOUSE (Plant Physiol., 1935, 10, 781—788).—The conception that normally "unfreezable" H_2O in plant tissues does actually freeze at a definite low temp. (-18° to -20°) applies to hardened but not to unhardened clover-root tissue or to potato tubers. A. G. P.

Streamline flow and the movement of solutes in the transpiration stream. R. C. MCLEAN and L. R. HUTCHINGS (Plant Physiol., 1935, 10, 773—780).—The diffusion of solutes in plants may be explained by consideration of the radical velocity

gradient due to streamline flow in tubes. Movement of solutes in the H_2O stream of the xylem may be considerably more rapid than that indicated by transpiration data. A. G. P.

Temperature regulation of the dry matter production in marine algæ as a plasmatic adjustment. H. LAMPE (Protoplasma, 1935, 23, 534—578).—Respiration rates and the assimilation/respiration quotient of several species of marine algæ are examined in relation to temp. and seasonal changes and to the distribution of species. A. G. P.

Influence of the carbohydrate-nitrogen relation on nodule production by red clover. C. E. GEORGI (J. Agric. Res., 1935, 51, 597—612).—The inhibitory action on nodulation of combined-N feeding of clover plants is partly counteracted by increasing carbohydrate synthesis, e.g., by CO_2 -enrichment. The inhibitory influence is associated with increased concn. of sol. carbohydrates, and decreased % of N and concn. of inorg. N in the sap. A. G. P.

Possible structure of chlorophyll granules in the plastid. J. G. WAKKIE (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1082—1086).—Additional support is given for the granular model of the plastid. Anisotropic colloidal chlorophyll (I) models were made, which fluoresced in a hydrophilic environment by association with a "carrier-mol." Owing to the low concn. of (I) the models did not possess the required band spectrum. The results are in agreement with data for the diffusion of (I) in paraffin and MeOH. J. N. A.

Formation of cell-wall substance [in plants]. A. KIESEL and R. JATZINA (Planta, 1935, 24, 308—311).—Both H_2O - and EtOH-sol. galacturonic acids occur on the cell wall. The EtOH-sol. form is probably stored within the cell. A transition into EtOH-insol. and probably into H_2O -insol. forms in the cell wall is indicated. A. G. P.

Slime flux [of trees]. E. F. GUBA (10th Nat. Shade Tree Conf. Proc. Ann. Meet., 1934, 56—60).—Exudates from heartwood of shade trees become gritty through deposition of $CaCO_3$ dissolved from cell walls. Exudates are alkaline and favour growth of numerous organisms. Exudates from wounds in inner bark or sapwood are usually acid and rich in sugars, proteins, and starch: many contain BzOH, $H_2C_2O_4$, cinnamic acid, and traces of MeCHO and PhCHO. CH. ABS. (p)

Digitalis lanata and D. purpurea: comparative biological investigation. E. BERTONASCO (Giorn. Farm. Chim. Sci. aff., 1934, 83, 421—424; Chem. Zentr., 1935, i, 3690). R. N. C.

Plant pigments and reproduction. R. H. ROBERTS and N. LIVINGSTON (Science, 1935, 82, 596).—With apple leaves, no correlation between fruitfulness and the carotenoid pigments could be detected (cf. A., 1934, 1045). L. S. T.

Assimilation and respiration of Mediterranean macchia plants in rainy and dry seasons. H. VON GUTTENBERG and H. BUHR (Planta, 1935, 24, 163—265).—Daily and seasonal changes in assimilation

ation and respiration rates and in the starch and sugar contents of leaves are recorded. The influence of temp., light conditions, and H_2O supply is examined.

A. G. P.

Gaseous exchange in aquatic plants during photosynthesis. F. GÓRSKI (Bull. Acad. Polonaise, 1935, B, 177—198).—Factors affecting the results of the "bubble" method are examined. Most of the O_2 produced (70%) diffuses in the H_2O , the balance escaping in bubbles. Relatively less N passes from the H_2O into the intercellular spaces at higher rates of assimilation, since the rate of diffusion is slow. The size of the plant has little influence on the relative amounts of gases evolved.

A. G. P.

Kinetics of an intracellular system for respiration and bioelectric potential at fluxequilibrium. G. MARSH (Plant Physiol., 1935, 10, 681—697).—Mathematical.

A. G. P.

Absorption and accumulation of potassium bromide by *Elodea* as related to respiration. R. S. ROSENFELS (Protoplasma, 1935, 23, 503—519).—In *Elodea* tissue immersed in aq. KBr, artificially induced changes in respiration rate were paralleled by similar changes in Br' absorption. The mechanism of these effects is discussed.

A. G. P.

Hormones in relation to root formation on stem cuttings. W. C. COOPER (Plant Physiol., 1935, 10, 789—794).—Application of β -indolyacetic acid to leafy or leafless cuttings of lemon and other species stimulates root formation. The hormone is translocated in the phloem.

A. G. P.

Chemical nature of some growth hormones as determined by the diffusion method. A. N. J. HEYN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1074—1081).—The growth hormone from root tips of *Vicia faba* is identical with auxin, and the latter is probably present in the regenerated tip of the coleoptile of *Avena*. The hormone obtained from the sporangiophore of *Phycomyces nitens* is probably β -indolyacetic acid.

J. N. A.

Follicular and other hormones and plant growth. M. A. H. TINCKER and S. E. JACOBS (Ann. Appl. Biol., 1935, 22, 619—629).—Administration of ketohydroxyœstrin and theelol to plants, by the roots, by injection, or by application to cut surfaces failed to produce any growth response or acceleration of flowering. Auxin stimulated the growth of *Bacterium auxinophilum* (nov. sp.) isolated from gelatin cultures of greenhouse cuttings.

A. G. P.

Influence of ovarian hormone on plant development. G. TEODORO and R. ZAMPETTY (Arch. Ist. Biochim. Ital., 1935, 7, 425—440).—The cryst. hormone tends to inhibit germination of some plants, but stimulates the subsequent growth especially of the roots (e.g., with *Lens esculenta*). Variations occur with different plants and also with different culture media.

F. O. H.

Effect of artificial wind on growth and transpiration in *Helianthus annuus*. E. V. MARTIN and F. E. CLEMENTS (Plant Physiol., 1935, 10, 613—636).

A. G. P.

Action of sulphurous mineral waters on germination and plant development. P. TESTONI (Annali Chim. Appl., 1935, 25, 558—563).—Mineral H_2O (analyses given) of Tivoli and Telesse produces more rapid germination and growth of wheat and lentil than does normal H_2O .

F. O. H.

Growth and seasonal changes in composition of oak leaves. A. W. SAMPSON and R. SAMISCH (Plant Physiol., 1935, 10, 739—751).—Protein (I) and fibre accumulate in the leaves at an early stage of growth. Assimilation of N ceases for a considerable period during active leaf expansion. Fibre production proceeds, only very slowly. Resorption of (I) of older leaves occurs in the late growth stage. The Et_2O -extractives increase steadily throughout growth. Accumulation of N-free extractives varies with the location. Rates of intake of Ca, Si, K, and P varied individually with advancing growth.

A. G. P.

Formation of ethylene by plant tissues and its significance in the ripening of fruit. R. GANE (J. Pomology, 1935, 13, 351—358).—Ripe apples generate gaseous products which produce epinastic effects on petioles and leaves of plants and abnormal growth of seedlings similar to those produced by C_2H_4 . Esters evolved by ripe apples do not affect seedlings. C_2H_4 is isolated from the "active substance" of apples (cf. A., 1935, 265).

A. G. P.

Effects of ethylene on plant-growth hormone. H. D. MICHENER (Science, 1935, 82, 551—552).—Experiments in which C_2H_4 acts on plant growth in a manner different from heteroauxin are described. Action of C_2H_4 on growth may be explained, not as direct effects of C_2H_4 alone, but as effects of C_2H_4 on a growth hormone.

L. S. T.

Germination experiments with peas in heavy water. J. BRUN and L. TRONSTAD (Kongl. Norske Vid. Selsk. Forh., 1935, 7, 171—173; Chem. Zentr., 1935, i, 3242).—Germination occurred in H_2O containing $\gt 40\%$ D_2O , but was inhibited at higher concns. Algal growth occurred up to 94% D_2O .

J. S. A.

Effect of the pyrrole nucleus on the formation of chlorophyll. G. POLACCI, B. ODDO, and M. GALLOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 565—567).—Growth of algæ and formation of chlorophyll are not opposed by Mg pyrrole-2-carboxylate.

R. N. C.

Influence of sulphur deficiency on the metabolism of soya bean. S. V. EATON (Bot. Gaz., 1935, 97, 68—100).—External symptoms of S deficiency resemble those of N, P, or K deficiency in many respects, and are probably the immediate effect of inferior assimilation of NO_3' within the plant. Stem elongation is only slightly reduced by S deficiency, largely because of the ability of the soya bean to break down and re-utilise protein. Plants lacking S produce harder stems. Cell-wall thickness is more closely related to the accumulation of starch and hemicellulose (I) than to that of total carbohydrates. (I) probably acts as a reserve material. S-deficient plants contain much sol. org. N, but have a low sugar content. Proteolysis is active but resynthesis is incomplete through inadequacy of the S supply.

A. G. P.

Biochemical modifications in phytopathology: carbohydrate substances of the leaf of *Ampelopsis vitifolia*, Hort. R. SALGUES (Compt. rend. Soc. Biol., 1935, 120, 1212—1214).—Sol. polysaccharides in the healthy leaf increase during the late summer and fall in autumn, whilst insol. polysaccharides fall rapidly in summer and more slowly in autumn. In the leaf affected with *Phyllosticta altescheri*, Syd., the changes are similar but retarded. R. N. C.

Effect of titanous chloride on the formation of chlorophyll in *Zea mays*. O. L. INMAN, G. BARCLAY, and M. HUBBARD (Plant Physiol., 1935, 10, 821—822).—In chlorophyll formation Ti cannot replace Fe. Addition of Fe to nutrient media increases root formation. A. G. P.

Calcium deficiency effects on *Pisum sativum*. D. DAY (Plant Physiol., 1935, 10, 811—816).—Insufficient supplies of Ca are associated with shorter and less succulent growth, high % of dry matter in the tops and low % in the roots, and low Ca content in the whole plant. A. G. P.

Serological studies of plant viruses. J. M. BIRKELAND (Ann. Appl. Biol., 1935, 22, 719—727).—Precipitin reactions with plant viruses cultivated in serologically unrelated hosts show that the virus is, in itself, antigenic. Viruses of cucumber mosaic, tobacco ringspot, and tobacco mosaic are serologically distinct, whereas tobacco mosaic, aucuba mosaic, and probably tomato streak virus are indistinguishable. A. G. P.

Properties of virus causing degeneration diseases of beet. G. VERPLANCKE (Sucrerie belge, 1935, 54, 118—127, 142—151, 162—168; Chem. Zentr., 1935, i, 3210).—The properties of the virus causing yellowing and mosaic diseases of beet leaves, and its resistance towards temp. and chemical agents, are reviewed. The virus in purified solutions is more sensitive than that in the juice. J. S. A.

Chlorosis of hortensia (*Hydrangea hortensis*) in relation to iron.—See B., 1936, 165.

Effects of fuel oil on plants. G. D. FULLER and M. R. LEADBETTER (Plant Physiol., 1935, 10, 817—820).—Oil injures plants when brought into contact with roots, the effect becoming fatal when the quantity reaches a level crit. for each species. Penetration may or may not occur, but if oil enters the root it appears principally in the primary xylem. A. G. P.

Chemical composition of grasses in pure cultures at different stages of growth.—See B., 1936, 169.

Radium content of plants and water. B. K. BRUNOVSKI and K. G. KUNASHEVA (Trav. lab. biogeochim. Acad. Sci. U.S.S.R., 1935, 3, 31—41).—The Ra content of plants varied from 0.89 to 20.5 × 10⁻¹²%. Plankton contained 10 times as much Ra as the sea-H₂O from which they were obtained. Yeast contained amounts of the same order. CH. ABS. (p)

Comparative sulphur and phosphorus content of plants grown in the same soil. G. BERTRAND and L. SILBERSTEIN (Compt. rend., 1935, 201, 1449—1453).—The S/P ratio in the foliage of many plants grown under the same conditions varies from 0.377

to 4.021, which indicates that the S or P content depends on the physiological requirements of the plant. The capacity to "fix" S, probably present in org. combination, is more variable than for P. J. L. D.

Constituents of *Orthosiphon stamineus*, Benth. R. DIETZEL and E. SCHMIDT (Arch. Pharm., 1936, 274, 10—16).—Cold and hot aq. extracts of *O. stamineus* are treated with urease at p_{H} 7.2 and the CO₂ (modified Barcroft method) and NH₃ liberated determined. 100 g. of air-dried drug contain 14 mg. of free and a further 26 mg. of combined urea. R. S. C.

Occurrence of piperidine in black pepper. E. SPÄTH and G. ENGLAENDER (Ber., 1935, 68, [B], 2218—2221).—Distillation of a mixture of finely divided black pepper and MgO with steam in vac. at 35° affords an alkaline distillate which after neutralisation with HCl gives a mixture of NH₄Cl and piperidine hydrochloride separable by CHCl₃. Under these conditions piperine is not hydrolysed. Since similar results are obtained with an aq. extract of pepper free from piperine the presence of piperidine (0.0086%) as such or as a simple salt is established. The presence of 3-methylpyrrolone could not be confirmed. H. W.

Odoriferous constituent of *Periploca graca*, L. T. SOLACOLU, A. MAVRODIN, and G. HERRMANN (J. Pharm. Chim., 1935, [viii], 22, 548—556).—The bark contains 2-hydroxy-4-methoxybenzaldehyde, which is distributed fairly widely in the *Asclepiadaceae*. J. L. D.

Acids contained in the wood of *Libocedrus formosana*, Florin. VII. N. ICHIKAWA (J. Chem. Soc. Japan, 1934, 55, 1124—1133).—Oxidation experiments with dihydroshonanic acid indicate the presence of the 3-carboxy-6-methylene- Δ^4 -cyclohexyl grouping in shonanic acid. CH. ABS. (r)

Bark of *Terminalia arjuna*, Bedd. I. Isolation of arjunin. R. R. AGARWAL and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 5, 50—54).—C₆H₆ extracts arjunin, C₂₆H₃₂O₁₁, m.p. 192° (decomp.) [Pb, Ag, and Na salts; Ac₂ and Bz₂ derivatives, m.p. 103° and 207°, respectively; (NO₂)₅-derivative, m.p. 118°], from the bark. The substance is sol. in NaHCO₃ and gives many colour reactions. J. L. D.

Lichen substances. LXII.—See this vol., 314.

Colouring matter of flowers of *Kerria japonica*, DC. T. ITOUGH, H. SUGINOME, and K. UENO (J. Chem. Soc. Japan, 1934, 55, 1101—1105).—In the colouring wax the palmitate with smaller amounts of the oleate of lutein was the chief constituent. CH. ABS. (p)

Pigments of cotton flowers. II. Uppam (*Gossypium herbaceum*). K. NEELAKANTAM, T. R. SESHADRI, and R. H. R. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 490—496).—Petals of *G. herbaceum* from Coimbatore, South India, differ from those (from North India?) studied by A. G. Perkin (A., 1916, i, 280) in containing gossypitrin and quercetin (instead of isoquercetin), and a new flavonol monoglucoside, m.p. 247—249°, with small quantities of gossypetin (cf. A., 1929, 326). E. W. W.

ation and respiration rates and in the starch and sugar contents of leaves are recorded. The influence of temp., light conditions, and H₂O supply is examined.

A. G. P.

Gaseous exchange in aquatic plants during photosynthesis. F. GÓRSKI (Bull. Acad. Polonaise, 1935, B, 177—198).—Factors affecting the results of the "bubble" method are examined. Most of the O₂ produced (70%) diffuses in the H₂O, the balance escaping in bubbles. Relatively less N passes from the H₂O into the intercellular spaces at higher rates of assimilation, since the rate of diffusion is slow. The size of the plant has little influence on the relative amounts of gases evolved.

A. G. P.

Kinetics of an intracellular system for respiration and bioelectric potential at flux equilibrium. G. MARSH (Plant Physiol., 1935, 10, 681—697).—Mathematical.

A. G. P.

Absorption and accumulation of potassium bromide by *Elodea* as related to respiration. R. S. ROSENFELS (Protoplasma, 1935, 23, 503—519).—In *Elodea* tissue immersed in aq. KBr, artificially induced changes in respiration rate were paralleled by similar changes in Br⁻ absorption. The mechanism of these effects is discussed.

A. G. P.

Hormones in relation to root formation on stem cuttings. W. C. COOPER (Plant Physiol., 1935, 10, 789—794).—Application of β-indolylacetic acid to leafy or leafless cuttings of lemon and other species stimulates root formation. The hormone is translocated in the phloem.

A. G. P.

Chemical nature of some growth hormones as determined by the diffusion method. A. N. J. HEYN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1074—1081).—The growth hormone from root tips of *Vicia faba* is identical with auxin, and the latter is probably present in the regenerated tip of the coleoptile of *Avena*. The hormone obtained from the sporangiphore of *Phycomyces nitens* is probably β-indolylacetic acid.

J. N. A.

Follicular and other hormones and plant growth. M. A. H. TINCKER and S. E. JACOBS (Ann. Appl. Biol., 1935, 22, 619—629).—Administration of kojohydroxycastrin and theelol to plants, by the roots, by injection, or by application to cut surfaces failed to produce any growth response or acceleration of flowering. Auxin stimulated the growth of *Bacterium auxinophilum* (nov. sp.) isolated from gelatin cultures of greenhouse cuttings.

A. G. P.

Influence of ovarian hormone on plant development. G. TEODORO and R. ZAMPETTI (Arch. Ist. Biochim. Ital., 1935, 7, 425—440).—The cryst. hormone tends to inhibit germination of some plants, but stimulates the subsequent growth especially of the roots (e.g., with *Lens esculenta*). Variations occur with different plants and also with different culture media.

F. O. H.

Effect of artificial wind on growth and transpiration in *Helianthus annuus*. E. V. MARTIN and F. E. CLEMENTS (Plant Physiol., 1935, 10, 613—636).

A. G. P.

Action of sulphurous mineral waters on germination and plant development. P. TESTONI (Annali Chim. Appl., 1935, 25, 558—563).—Mineral H₂O (analyses given) of Tivoli and Telesse produces more rapid germination and growth of wheat and lentil than does normal H₂O.

F. O. H.

Growth and seasonal changes in composition of oak leaves. A. W. SAMPSON and R. SAMISCH (Plant Physiol., 1935, 10, 739—751).—Protein (I) and fibre accumulate in the leaves at an early stage of growth. Assimilation of N ceases for a considerable period during active leaf expansion. Fibre production proceeds, only very slowly. Resorption of (I) of older leaves occurs in the late growth stage. The Et₂O-extractives increase steadily throughout growth. Accumulation of N-free extractives varies with the location. Rates of intake of Ca, Si, K, and P varied individually with advancing growth.

A. G. P.

Formation of ethylene by plant tissues and its significance in the ripening of fruit. R. GANE (J. Pomology, 1935, 13, 351—358).—Ripe apples generate gaseous products which produce epinastic effects on petioles and leaves of plants and abnormal growth of seedlings similar to those produced by C₂H₄. Esters evolved by ripe apples do not affect seedlings. C₂H₄ is isolated from the "active substance" of apples (cf. A., 1935, 265).

A. G. P.

Effects of ethylene on plant-growth hormone. H. D. MICHENER (Science, 1935, 82, 551—552).—Experiments in which C₂H₄ acts on plant growth in a manner different from heteroauxin are described. Action of C₂H₄ on growth may be explained, not as direct effects of C₂H₄ alone, but as effects of C₂H₄ on a growth hormone.

L. S. T.

Germination experiments with peas in heavy water. J. BRUN and L. TRONSTAD (Kongl. Norske Vid. Selsk. Forh., 1935, 7, 171—173; Chem. Zentr., 1935, i, 3242).—Germination occurred in H₂O containing > 40% D₂O, but was inhibited at higher concns. Algal growth occurred up to 94% D₂O.

J. S. A.

Effect of the pyrrole nucleus on the formation of chlorophyll. G. POLACCI, B. ODDO, and M. GALLOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 565—567).—Growth of algae and formation of chlorophyll are not opposed by Mg pyrrole-2-carboxylate.

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