## BRITISH CHEMICAL ABSTRACTS

## A.-PURE CHEMISTRY

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## General, Physical, and Inorganic Chemistry.

Theory of hyperfine structures. E. FERMI and E. SEGRÈ (Mem. R. Accad. d'Italia Sci. fis., 1933, 4, 131-158).—A theoretical discussion of the hyperfine structure of the spectral lines of Li, Na, Cu, Ga, Rb, Cd, In, Cs, Ba, Au, Hg, Tl, Pb, and Bi. The theory of the nuclear magnetic moment is discussed.

O. J. W.

Spectrum of atomic nitrogen, N I. D. SEFERIAN (Compt. rend., 1934, 198, 68—69).—An arc is struck between parallel W wires 3 mm. diam. and 2—3 mm. apart,  $N_2$  at the rate of 800—1000 litres per hr. being passed around them. With a.c. of 46—50 amp. at 110 volts the spectrum of N I is obtained (cf. A., 1929, 1116; 1932, 103), and also two different continuous spectra, one due to W, the other to either W or N. C. A. S.

Spectrum of atomic nitrogen (N I) in ammonia and in mixtures of hydrogen and nitrogen. D. SÉFÉRIAN (Compt. rend., 1934, 198, 358—460; cf. preceding abstract).—N<sub>2</sub> was replaced by (a) H<sub>2</sub>, (b) NH<sub>3</sub>, (c) N<sub>2</sub>-H<sub>2</sub> mixtures, (d) air. (a) confirms previous results (cf. A., 1930, 387) and gives the "raies ultimes" of W; (b) and (c) give identical spectra of N I, whilst (d) shows that the two continuous spectra are due one to the incandescent electrodes, the other to the W atom. C. A. S.

Continuous spectrum of neon. N. T. ZE and V. S. LING (Compt. rend., 1934, 198, 356-358).— The intensity of the continuous spectrum of Ne relatively to that of H<sub>2</sub> (cf. A., 1931, 275), and hence absolutely, increases with  $\lambda$ , to  $\lambda$  3400, remains approx. stationary to  $\lambda$  4200, and afterwards increases again. With increase in pressure of Ne the intensity of the continuous spectrum increases, that of the line spectrum diminishes. C. A. S.

Effect of pressure on high terms of alkaline spectra. E. AMALDI and E. SEGRE (Nature, 1934, 133, 141). L. S. T.

Remarkable optical properties of the alkali metals. R. DE L. KRONIG (Nature, 1934, 133, 211-212).—A discussion based on Zener's interpretation (this vol., 124). L. S. T.

Seeing in sodium-vapour light. M. LUCKIESH and F. K. Moss (J. Opt. Soc. Amer., 1934, 24, 5–13). —The relation of the spectral quality of Na vapour and W filament light to physiological effects is examined. N. M. B.

Band spectrum of magnesium hydride. A. GUNTSCH (Z. Physik, 1934, 87, 312-322).-Rotation and dissociation consts. are given for various levels. A. B. D. C. Infra-red grating spectra and spectral series (Al II, Al I, He I and II, Zn I and II). F. PASCHEN and R. RITSCHL (Ann. Physik, 1933, [v], 18, 867— 892).—A comprehensive analysis of the grating spectrum of Al II is made. With a specially luminous hollow eathode arrangement new infra-red lines beyond l  $\mu$  are tabulated and an extended analysis is given for Al I, He I and II, Zn I and II. W. R. A.

Arc spectrum of silicon in the red and infrared. C. C. KIESS (Bur. Stand. J. Res., 1933, 11, 775-782).—130 new lines have been measured in the arc spectrum of Si between 6125 and 11,290 Å. These include the strongest previously unidentified Fraunhofer line (6155 Å.) and other solar spectral lines. Most have been classified as combinations, including terms arising from 4p, 4f, and 5f electron configurations. J. W. S.

New calculation of the term system of Si IV. B. EDLÉN and J. SÖDERQVIST (Z. Physik, 1933, 87, 217-219). A. B. D. C.

Absorption spectra due to excitation of inner electrons. V. The doublet in potassium vapour due to excitation of the  $(3p)^6$ -shell. (K I<sup>b</sup> resonance lines.) H. BEUTLER and K. GUGGENHEIMER (Z. Physik, 1933, 87, 188—191). A. B. D. C.

Relative intensities of the components of the  $a^3F-y^3F^0$  multiplet of Fe I. J. PIERAND (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 16-19).-The intensities of the weaker components relative to those of the stronger members of this multiplet are > would be anticipated from the Sommerfeld formulæ (cf. Proc. Nat. Acad. Sci., 1932, 18, 590).

J. W. S.

Ionisation potential of Fe II. J. C. DOBBIE (Physical Rev., 1934, [ii], 45, 76-78).—New high terms  $e^6D$  (77861·4) and  $e^4D$  (79439·3) are reported in the spark spectrum of Fe. Combination multiplets with low terms are tabulated. The val. 16·16 volts is found for the principal ionisation potential of Fe II. N. M. B.

**Spectrum of fluorine.** F II, F III, F IV. I. S. BOWEN (Physical Rev., 1934, [ii], 45, 82-86).—Full data and classifications for the region 125-620 Å. and corr. classifications of additional lines in the longer wave-length regions are tabulated. The ionisation potentials are : F II 34.81, F III 62.35, F IV 87.34 volts. N. M. B.

Absorption spectra due to excitation of inner electrons. IV. Zn spectrum from 1150 to 700 A. due to excitation of the  $(3d)^{10}$ -shell (Zn I<sup>b</sup>). Comparison of terms and their values for Hg I<sup>b</sup>,

R

Cd I<sup>b</sup>, and Zn I<sup>b</sup>. H. BEUTLER and K. GUGGEN-HEIMER (Z. Physik, 1933, 87, 176–187; cf. this vol., 124). A. B. D. C.

Fine structure in the spectrum of arsenic II. S. TOLANSKY (Z. Physik, 1933, 87, 210–217).—Lines reported by Rao to have fine structure (A., 1933, 880) are single. A. B. D. C.

Mechanical moment of the nucleus of cæsium. D. A. JACKSON (Proc. Roy. Soc., 1934, A, 143, 455— 464).—The hyperfine structure of the lines 4555 and 4593 Å. of Cs has been examined. The intensity ratio is  $1.27 \pm 0.02$  for both doublets, which establishes the val. 7/2 for the mechanical moment of the Cs nucleus. L. L. B.

Continuous absorption of light in cæsium vapour. H. J. J. BRADDICK and R. W. DITCHBURN (Proc. Roy. Soc., 1934, A, 143, 472-481).—A detailed account of work already noted (A., 1933, 200). L. L. B.

Temperature of the mercury arc. W. ELEN-BAAS (Physica, 1934, 1, 211–224).—The calc. temp. at the centre of a contracted discharge (5.5 amp., 8.8 volts per cm.) was  $6000^{\circ} \pm 800^{\circ}$  abs. H. J. E.

Hyperfine structure absorption in optically excited mercury vapour. M. L. POOL and S. J. SIMMONS (Physical Rev., 1933, [ii], 44, 997–1001).— The absorption, with high and low dispersion, of the Hg 4047, 2967, and 2752 Å. lines in optically excited Hg vapour was investigated for various lengths of excited vapour, and various pressures of admixed N<sub>2</sub>. N. M. B.

Structure of the band spectrum of mercury vapour. S. MROZOWSKI (Z. Physik, 1934, 87, 340-355).—The variation of structure of the Steubing band series with exciting wave-length is due to deviation of the rotational energy distribution from that of Maxwell's law. Polarisation and other effects are investigated on this hypothesis. A. B. D. C.

Multiplet and hyperfine structure analyses of Bi IV. Discussion of perturbation effects. A. B. McLAY and M. F. CRAWFORD (Physical Rev., 1933, [ii], 44, 986—996).—Classifications of 360 lines of Bi IV excited in an electrodeless discharge are tabulated. Hyperfine structure intervals of several terms are evaluated, and agree with theoretical separations consistent with the multiplet analysis. N. M. B.

Stark effect of the Lyman series. R. FRERICHS (Ann. Physik, 1934, [v], 19, 1—8).—The Stark effect was investigated for the first three lines of the Lyman series. The no., position, and polarisation of the components agree with conclusions based on quantum mechanics. The intensities of the components, however, show some deviations from theory. A. J. M.

Wave-lengths and spectral laws. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1933, No. 30, 12 pp.).—The accuracy of wave-lengths and wavenos. is discussed. A. J. M.

Emission spectrum of the night sky in the ultra-violet. J. DUFAY (Compt. rend., 1934, 198, 107-109).-67 emission bands observed in the night sky at Courbons (Basses-Alpes) by exposure of 24 hr. on 13—18 Sept., 1925, are tabulated; of these 27 are new, and 29 referrable to  $N_2^+$  or  $N_2^-$  (cf. A., 1932, 105). C. A. S.

Spectral analysis of the night sky at the Pic du Midi. J. CABANNES and J. DUFAY (Compt. rend., 1934, 198, 306—309).—With a new form of spectroscope 91 lines, 36 new and 8 found only on reexamining an old plate (see above), were measured between  $\lambda\lambda$  3891 and 5204, and their relative intensities shown in many cases to vary from night to night and in different parts of the sky. Some of the lines indicate O, N, A, para- and ortho-He. C. A. S.

Explosive potentials in argon. H. GUIMIOT (Ann. Guébhard-Séverine, 1933, 9, 306-311).—The current flowing in a discharge tube containing A, at various potentials, has been measured for different gas pressures and electrode separations. A. J. M.

Significance of broadening effects of spectral lines due to foreign gases. M. KULP (Z. Physik, 1933, 87, 245—254).—These effects are qualitatively explained by means of potential curves.

A. B. D. C.

Gas discharge with diffusion and transverse forces. W. FUCKS (Z. Physik, 1933, 87, 139-153). --Equilibrium conditions for steadily burning discharges are given, and are discussed with respect to min. cross-section and current. A. B. D. C.

Vibrational isotope effects in three-particle systems. I. A. ADEL (Physical Rev., 1934, [ii], 45, 56-58).—Mathematical. N. M. B.

Anomalous dispersion and absorption of X-rays. E. J. WILLIAMS (Proc. Roy. Soc., 1934, A, 143, 358–376).—The anomalous dispersion of X-rays is calc. from the experimental data for photoelectric absorption. The results for Fe and Cu are compared with experiment. The theoretical reasons for the observed val. of the oscillator strength are considered, and in particular the equivalence of the 2K electrons to about 1.3 classical electrons. L. L. B.

Spectroscopy of ultra-soft X-rays. II. M. SIEGBAHN and T. MAGNUSSON (Z. Physik, 1934, 87, 291—310; cf. A., 1930, 1229).—Wave-lengths are given for C, N, and O  $K\alpha$  lines, for Li, Be, and B K lines, and L lines from K to Na. A. B. D. C.

Quantum scattering of X-rays. H. HULUBEI (Ann. Physique, 1934, [xi], 1, 5—71).—Bands due to multiple scattering with change of wave-length, additional to normal and Compton scattering, when  $K_{x}$ radiation of Mo and Rh was scattered by paraffin or Li, were investigated for the angular range 0—130°. An expression is found for the displacement limits of bands for *n*-fold scattering. Double scattering (n=2) was found in all cases, with some indications of triple scattering. An electronic Raman effect (partial absorption) on the direction of the primary beam was not confirmed. N. M. B.

Spatial distribution of photo-electrons ejected from the atomic K shell. J. A. VAN DEN AKKER (Physical Rev., 1934, [ii], 45, 49—55).—The longitudinal space-distribution of electrons ejected from the K level of Cu by Mo  $K\alpha_1$  radiation shows asymmetries differing by 10% from the wave-mechanical asymmetries. N. M. B. K absorption discontinuities of the elements zirconium to iodine. P. A. Ross (Physical Rev., 1933, [ii], 44, 977–983).—All except Cd showed, on the high-frequency side of the discontinuity, faint fine structure appearing as narrow bands of slightly decreased absorption. The width of the main discontinuity increased with at. no. The wave-lengths of the discontinuity, accurate to  $\pm 0.02$  Å., corresponding with the inflexion point in the main absorption curve are tabulated. N. M. B.

Quadrupole transitions and other new weak lines in the K spectra of elements 48 Cd and 50 Sn. III. E. C. INGELSTAM (Z. Physik, 1934, 87, 283-291; cf. Carlsson, A., 1933, 881).

A. B. D. C.

Relative intensities of certain L-series X-ray satellites in cathode-ray and in fluorescence excitation. F. R. HIRSH, jun., and F. K. RICHT-MYER (Physical Rev., 1933, [ii], 44, 955—960).— Using a special X-ray tube the relative intensities of satellites and their parent  $L\alpha_1$  line were measured for cathode-ray excitation by 20-kv. electrons and for fluorescence excitation by the radiation from a Ag target bombarded by 20-kv. electrons for Zr, Mo, Ru, Rh, Pd, and Ag. Fluorescence results indicate LM ionisation as the origin of  $L\alpha$  satellites, but cathoderay excitation indicates peripheral electron structure influence on satellite production. N. M. B.

Natural widths of the *L*-series lines in the *X*-ray spectra of elements 74—83. J. H. WILLIAMS (Physical Rev., 1934, [ii], 45, 71—75).—Data for the widths at half-max. of the  $L\alpha_1$ ,  $\beta_1$ ,  $\beta_2$ ,  $\gamma_2$  lines of Bi, Pb, Tl, Au, Pt, Ir, and W and for the relative wavelengths of neighbouring lines are given. Relations with the at. no. and electron transitions, and the effects of alloys of the elements, are discussed.

N. M. B.

Measurement of X-ray emission wave-lengths in the M-series by means of the ruled grating. E. G. PURDOM and J. M. CORK (Physical Rev., 1933, [ii], 44, 974—976).—Results are tabulated for Hf, Ta, W, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U. Wave-lengths are > those found by the crystal method. N. M. B.

Townsend coefficients for ionisation by collision. F. H. SANDERS (Physical Rev., 1933, [ii], 44, 1020—1024).—The photo-electric current between parallel plates in dry air was measured as a function of plate distance for const. field strength and pressure for plate distances of 1—7 cm. at 1 mm. pressure of Hg. The relation of results to the Townsend coeffs. is discussed. N. M. B.

Effect of alkali ions on the photo-electric emissivity of tungsten. A. K. BREWER (Physical Rev., 1933, [ii], 44, 1016—1019; cf. A., 1931, 1106).— Curves are given for the effect on photo-emission of W excited by various Hg lines and the fraction of W surface covered by Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> ions. Effect of temp. and variation of the work function are discussed. N. M. B.

Production of secondary electrons by argon positive ions and by argon atoms. C. J. BRASE-FIELD (Physical Rev., 1933, [ii], 44, 1002-1005).-- Positive A ions of energy up to 150 equiv. volts were much less efficient than A atoms of equal kinetic energy in producing secondary electrons from a lampblacked Ni collector. The efficiency of production by these probably metastable atoms was approx.  $3\cdot5\%$ . It is concluded that positive ions have negligible influence in producing electrons for the maintenance of a cold cathode discharge in gases. N. M. B.

Electron orbits in crossed electric and magnetic fields. A. E. SHAW (Physical Rev., 1933, [ii], 44, 1006—1011).—Focussing properties were investigated. Polarisation layers form on the plates of the electric field, reducing the effective deflecting potential. The abs. magnitude of the layers, measured for Au and bronze, depends on plate material, gas pressure, and electron intensity. Permanent insulating layers, vitiating e/m determinations, may be formed if electrons bombard a metal surface.

N. M. B.

Elastic scattering of high-velocity electrons by mercury atoms and the agreement with Mott's theory. E. B. JORDAN (Physical Rev., 1934, [ii], 45, 47—48; cf. A., 1933, 202).—The distribution in the angular range 8—48° of electrons scattered elastically by single Hg atoms for electron volt energies of 900, 1160, 1600, and 2000 gave curves differing widely from Mott's curve in the 900-volt case, but showing progressively closer agreement at the other voltages. N. M. B.

Study of the transformation of metals by [measuring] secondary electron emission. K. HAYAKAWA (Sci. Rep. Töhoku, 1933, 22, 934—958).— At the A3 transformation point of Fe the secondary electron emission-temp. curve shows a break which is independent of the voltage of the exciting electrons. The variation in electron emission during the magnetic transformation depends on the exciting voltage, changing sign at a certain "crit." val. of the latter. Similar changes are observed in the magnetic transformation of Co, Ni, and Fe–Ni alloys. The existence of the crit. voltage is explained on the basis of Richardson's structure electrons. F. L. U.

Light excitation in hydrogen canal rays. R. DÖPEL (Z. Physik, 1934, 87, 356—360).—Balmer series emitted by canal rays are due to direct excitation, neutralisation of the proton being probably radiationless. A. B. D. C.

Atomic collision. I. Production of slow atomic rays by recharging, and their determination by the thermo-element. O. BEECK. II. Ionisation of argon by neutral argon. O. BEECK and H. WAYLAND (Ann. Physik, 1934, [v], 19, 121– 128, 129–142).—I. A method of producing a bundle of monochromatic, slow at. rays of considerable intensity is described. The construction and calibration of a thermo-element, suitable for determining the intensity of neutral rays, are described.

II. The above method is used to find the ionisation function, N, of A, by A rays of 350—650 ion-voltequivs. In this range, N increases from 4.5 to 6.5. The efficiency is four times that for collisions of K<sup>+</sup> with A, and exceeds to an even greater extent the efficiency of collisions of A with A. The effective cross-section of A<sup>+</sup> in A is const. over the velocity range 350—650 volts. A. J. M.

Masses of the proton and electron. (SIR) A. EDDINGTON (Proc. Roy. Soc., 1934, A, 143, 327–350; cf. A., 1933, 107).—The mass *m* of a proton or electron is given by  $10m^2$ —136 $mm_0$ + $m_0^2$ =0, where  $m_0$ =  $h\sqrt{N/2\Pi c\rho}$ , N being the no. of such particles in the universe, and  $\rho$  the radius of curvature of an empty region, = $\sqrt{(3/\lambda)}$ , where  $\lambda$  is the cosmical const.

L. L. B.

Thermal data and the at. wt. of krypton. W. HEUSE and J. OTTO (Physikal. Z., 1934, 35, 57-59; cf. A., 1929, 1226; 1931, 1004).--Using a gas-thermometric method, previously described, the 0° isotherm, and the expansion and compressibility coeffs. for Kr in the region of 1 m. pressure, have been determined. The density of Kr determined by direct weighing is  $3.743\pm0.001$  g. per litre, and its at. wt.,  $83.66\pm0.01$ .

A. J. M.

Periodic system of chemical compounds of the type  $A_m B_n$ . H. G. GRIMM (Angew. Chem., 1934, 47, 53—58).—Binary compounds are divided into the classes salts, at. mols., diamond-like substances, metallic compounds, noble gases, and substances with two types of linking. Starting from the periodic arrangement of the elements it is shown that these various types of compounds recur at corresponding places in the table. The table provides new assumptions for the study of the relation between the properties of atoms and those of their compounds, and suggests fresh problems. A. G.

Names for the hydrogen isotopes. H. C. UREY, F. G. BRICKWEDDE, and G. M. MURPHY (Science, 1933, 78, 602—603, and Nature, 1934, 133, 173).— Wood's nomenclature (this vol., 127) is considered unsatisfactory owing to the difficulty in naming the three waters, four ammonias, and thirteen benzenes now possible. Objections to the name diplogen (cf. this vol., 156) are discussed. Deuterium is the name and H<sup>2</sup> the symbol preferred for heavy H. L. S. T.

Suggested nomenclature for heavy hydrogen and its compounds. F. C. WHITMORE (Science, 1933, 78, 603).—Deuterium is preferred to the "bar" nomenclature suggested by Wood (this vol., 127).

L. S. T.

Designation of heavy hydrogen. H. E. ARM-STRONG (Nature, 1934, 133, 173).—Deuthydrogen is suggested. L. S. T.

Isotope report. Chemical elements and types of atoms according to isotope investigation. (Report on the work from end of 1932 to end of 1933.) O. HAHN (Ber., 1934, 67, [4], 1-8).—The work on H, Li, Be, B, C, O, F, Ne, Cl, Ga, Ge, Rb, Cd, and Hg is reviewed. H. W.

Distribution of the radioactive thallium isotope Th-C" in thallium salt solutions. J. ZIRKLER (Z. Physik, 1934, 87, 410).—Th-C" distributes itself in Tl' ions in proportion to the [Tl'], but does not distribute itself equally between Tl' and Tl''' ions. A. B. D. C.

Periodic series of biogenetic elements in the periodic system. K. HRYNAKOWSKI (Rocz. Chem., 1933, 13, 541-545).—Certain numerical relationships between the biologically active elements N, O, Na, Mg, P, S, K, and Ca are pointed out. R. T.

Amendment to the law of multiple proportions. E. A. VUILLEUMIER (Science, 1934, 79, 13). L. S. T.

New type of radioactivity. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1934, 198, 254-256; cf. A., 1933, 762).—The emission of positive electrons as previously described continues after removal of the source of  $\alpha$ -particles for times that vary according to the irradiated element; the intensity of such emission decreases exponentially, the periods for Al, B, and Mg being respectively 3.25, 14, and 2.5 min. The initial intensity increases with the time of irradiation up to an approx. equal limit. No such effect is observed with H, Li, C, Be, N, O, F, Na, Ca, Ni, or Ag. Absorption by Cu screens indicates energies of  $2.2 \times$  $10^6$  ev. for the positive electrons from Al, and  $0.7 \times 10^6$ ev. for those from B and Mg. The emission is probably explained by Al<sup>27</sup>+He<sup>4</sup>=P<sup>30</sup>+n<sup>1</sup><sub>0</sub>, P<sup>30</sup> being radioactive with period 3.25 min. ( $P^{30}=Si^{30}+\epsilon^+$ ); B and Mg would yield similarly N13 and Si27 of similar short C. A. S. periods.

Radioactivity of samarium. M. CURIE and F. JOLIOT (Compt. rend., 1934, 198, 360–363; cf. A., 1933, 4, 442).—When examined in a Wilson's expansion chamber a thick layer of  $\text{Sm}_2(\text{C}_2\text{O}_4)_3$ ,  $10\text{H}_2\text{O}$  emits per sq. cm. approx. 7  $\alpha$ -particles per min., with path probably  $\Rightarrow 1.5$  cm.; the period of Sm is about  $10^{12}$  years. The disintegration suggested is  $^{148}\text{Sm} = ^{144}\text{Nd} + {}^4\text{He} + 0.0030$ . C. A. S.

Recoil atoms in gaseous media. L. GOLDSTEIN (Compt. rend., 1934, 198, 363-365; cf. A., 1933, 761).—With an electrode negatively charged in an atm. of Rn and (a)  $H_2$ , (b) Br vapour, the % of atoms of Ra-A remaining charged at the end of their recoil path varied, in (a) from 36 to 32.5 when pressure varied from 140 to 250 mm. Hg, or, deducting the activation of the electrode by direct recoil, 32%, as for the rare gases; in (b) the % was 79, or approx. the same as in air or  $O_2$  (83). C. A. S.

Radium-uranium ratio and the number of actinouranium isotopes. A. E. RUARK and F. WESTERN (Physical Rev., 1934, [ii], 45, 69-70).—An expression for the ratio is found. Evidence indicates the existence of only one Ac-U isotope. N. M. B.

Gamow's theory of radioactive decomposition. H. CASIMIR (Physica, 1934, 1, 193–198).—Theoretical. H. J. E.

Measurement of natural  $\alpha$ -particles ejected from solids. R. D. EVANS (Physical Rev., 1934, [ii], 45, 29—37).—Mathematical. From an analysis of empirical ionisation curves, expressions and their graphical integration for ionisation due to  $\alpha$ -particle emission are given. N. M. B

Complex radiation excited in aluminium by  $\alpha$ -particles. P. SAVEL (Compt. rend., 1934, 198, 368—370).—When the radiation produced from Al by the impact of  $\alpha$ -particles from Po is examined in a high-pressure (A or H<sub>2</sub>, 25 atm.) ionisation chamber (cf. A., 1933, 659), both the  $\gamma$ -radiation and neutrons are found to be complex. The  $\gamma$ -radiation (mainly photons) consists of two varieties with  $\mu/\rho_{Pb}=0.17$ ,

energy  $0.55 \times 10^6$  ev., and  $\mu/\rho_{Pb}=0.045$ , energy  $2.10 \times 10^6$  ev. Similarly the neutrons include two varieties the intensities of which are reduced to half by 1.7 mm. and 1.53 cm. Pb, respectively, the energy of the more rapid being  $2 \times 10^6$  ev. To excite the  $\gamma$ -radiation the min. energy of the incident  $\alpha$ -particles is  $3-3\cdot1\times10^6$  ev., and for the neutrons  $4-4\cdot3\times10^6$  ev., penetration to the Al nucleus being by a resonance level. The softer  $\gamma$ -radiation is attributable to the annihilation of + electrons of Al (cf. this vol., 126, 127), the harder to disintegration of the Al atom (cf. A., 1932, 318).

Ionisation curves of  $\alpha$ -rays. R. NAIDU (Ann. Physique, 1934, [xi], 1, 72—122).—Using a new apparatus to eliminate the effect of multiple scattering, normal Bragg curves are constructed for  $\alpha$ -rays of Po and Ra-C'. A proportionality between energy loss and ionisation energy is shown for Po rays, but rather less so for Ra-C' rays. Regarding energy transformation into ionisation energy as complete in He the same was found true for Ne, but for A and air there is a loss of 20 and 50%, respectively, due to excitation or dissociation of atoms or mols.

N. M. B.

Suggested explanation of β-ray activity. M. N. SAHA and D. S. KOTHARI (Nature, 1933, 132, 747; 1934, 133, 99).—Theoretical. L. S. T.

Radioactive radiations from the surfaces of solids and the measurement of the thorium content of rocks. R. D. EVANS (Physical Rev., 1934, [ii], 45, 38-42).—Ionisation due to  $\alpha$ - and  $\gamma$ -radiation from granite and representing the combined effect of the U, Ac, and Th series can be corr., by emanation measurements, for contributions due to U and Ac; hence the Th content of rocks can be obtained.

N. M. B.

Zero method for the  $\gamma$ -radiation strength of radium preparations. A. PICCARD and L. MEYLAN (J. Phys. Radium, 1933, [vii], 4, 715—718).—An improved precision form of Rutherford's method is described, in which the position on a graduated scale is found at which the sample neutralises the ionisation due to a standard sample, using two identical ionisation chambers. N. M. B.

 $\gamma$ -Rays of radium-B+C and of thorium-C+C'. C. D. ELLIS (Proc. Roy. Soc., 1934, A, 143, 350—357). —A re-measurement has been made of the Ra-B+C spectrum, and all the energies have been recalc. using  $C=2.9980+10^{10}$  and  $e/m=1.760\times10^7$ . The results are in excellent agreement with the  $\alpha$ -ray measurements (A., 1933, 1224). Certain measurements on the Th-C+C' spectrum are described. L. L. B.

Slow neutrons emitted by beryllium under the action of  $\alpha$ -rays. P. AUGER (J. Phys. Radium, 1933, [vii], 4, 718—724).—Photographs of tracks, due to the action on a chamber of moist H<sub>2</sub>, when Be was bombarded by  $\alpha$ -rays were obtained. Tracks for high-speed protons under the action of high-energy neutrons, and others for slow protons arising from collisions with slow neutrons were distinguished. The slow neutrons are attributed to excitation of the Be nucleus by  $\alpha$ -particles, without capture of the latter, emission being due to excitation energy. N. M. B.

Combination of proton and neutron. D. E. LEA (Nature, 1934, 133, 24).—Scattering experiments with paraffin wax suggest that in some of the collisions between neutron and proton the particles combine to form H<sup>2</sup> with emission of energy in the form of  $\gamma$ -radiation. L. S. T.

Radiative collisions of neutrons and protons. H. S. W. MASSEY and C. B. O. MOHR (Nature, 1934, 133, 211).—Calculation of the probability of a radiative combination of a neutron (I) and proton (II) to form a diplon shows that for the range of energies involved in the experiments of Lea (see above) combination should not take place more frequently than 1 in  $10^3$  collisions, which is < the observed frequency of 1 in 4. The calc. probability of a (II) radiating in the impact without combination taking place is even smaller. Assuming (I) to be a complex particle consisting of (II) and electron and that there are exchange forces between (I) and (II) of the type suggested by Heisenberg, a smaller probability (1 in 10<sup>6</sup>) of combination is obtained. These results indicate the need for additional information concerning the (I)–(II) collision. L. S. T.

 $\gamma$ -Rays produced by passage of neutrons across hydrogenated substances. P. Auger (Compt. rend., 1933, 198, 365-368; cf. Lea, above).-If a proton and neutron unite to form a deuton, the latter should move off in nearly the direction of the initial motion of the neutron, but this is not the case (cf. A., 1933, 551; but cf. also ibid., 1100). Measurements of e/m by a magnetic field also give no indication of the presence of deutons. It is therefore suggested that the mass of the neutron is > that of the proton (1.011 or 1.009), the proton being a combination of a neutron and a positron with loss of mass= $2-4 \times 10^6$  ev. The impact of a neutron on such a proton would excite the proton and cause emission of a  $\gamma$ -ray of energy 2-4× 10<sup>6</sup> ev., whilst the trajectory of the proton would be more inclined to the initial direction of the neutron than in the case of an elastic collision. C. A. S.

Action of X-rays on atomic nuclei. G. I. POKROVSKI and V. K. KORSUNSKI (J. Exp. Theor. Phys., U.S.S.R., 1932, 2, 141-153).—Theoretical conclusions regarding conditions for disintegration of unstable nuclei agree with results obtained with Pb, Sn, W, and Al. CH. Abs.

Cloud photographs of cosmic-ray stosse. G. L. LOCHER (J. Franklin Inst., 1933, 216, 673-682).—The large instantaneous increments in the ionisation by cosmic rays were photographed stereoscopically in ionisation chambers containing A and surrounded by a large mass of metal, the chamber being operated automatically. The origin and mechanism of production of the stosse are discussed. Neutrons arising from disintegration processes appear to be generated or liberated. N. M. B.

Hoffmann stösse and the origin of cosmic-ray ionisation. W. F. G. SWANN (Physical Rev., 1933, [ii], 44, 1025—1027).—Mathematical. It is shown that nearly the whole of observed cosmic-ray intensity may be attributed to bursts of Hoffmann stösse in the atm., but, as observed by Geiger counters, the effect will be only that of single rays at random.

N. M. B.

Ionisation by cosmic-ray particles and swift  $\beta$ -particles. G. L. LOCHER (J. Franklin Inst., 1934, 217, 39—58).—Suggestions are put forward to account for the discrepancies between the results of the Geiger counter and cloud-chamber methods of determination of the ionisation along cosmic-ray tracks. J. W. S.

Ionisation per centimetre of path by individual secondary cosmic rays. W. F. G. SWANN (Physical Rev., 1933, [ii], 44, 961—968).—Results for A,  $N_2$ , and  $O_2$  are 89, 61, and 57 ions per cm., respectively, at atm. pressure. The existence of multiple rays, contributing 2/3 of the total ionisation, is verified. N. M. B.

Distribution of low-energy cosmic rays in the atmosphere. W. E. DANFORTH and M. R. LIPMAN (J. Franklin Inst., 1934, 217, 73—78).—By using thin-walled Geiger counters it has been found that the energy spectrum of cosmic-ray secondaries extends at least as far as  $5 \times 10^6$  ev., and that the intensity between  $5 \times 10^6$  and  $10^7$  ev. is about one eighth of the total intensity above  $10^7$  ev. J. W. S.

Dematerialisation of pairs of electrons. F. JOLIOT (Compt. rend., 1933, 198, 81-83; cf. this vol., 126).—Positrons from an Al plate irradiated by  $\alpha$ -particles from Po and conc. magnetically fell on a Pb radiator placed above a Geiger-Müller counter. All such are stopped by 1.5 mm. Pb with production of  $\gamma$ -rays, of  $\mu/\rho = 0.19 - 0.32$ , whilst the average energy of a photon is  $485\pm60$  ekv. in agreement with Dirac's theory. There are three possible methods of dematerialisation : (i) an electron and a positron meet, resulting in production of two photons of equal energy  $(0.5 \times 10^6 \text{ ekv.})$ . This can occur only when the positron has been stopped in absorbing material, and implies an average life for a positron in  $H_2O$  of  $4 \times 10^{-10}$  sec. (ii) A positron meets an electron strongly bound in an at. nucleus, resulting in production of one photon of energy 10<sup>6</sup> ekv. These are both in accordance with Dirac's theory. Comparison with the emission from Ra implies the production of 1.6-3 photons per positron, *i.e.*, favours (i). (iii) A neutrino (cf. this vol., 127), which, having no intrinsic mass, has no effect on the counter, and one photon of energy  $0.5 \times 10^6$  are produced, which Thibaud's results seem to favour. As positrons dematerialise only when they have lost most of their velocity, their average life may be much > supposed by Thibaud. C. A. S.

Materialisation of æther. V. POSEJPAL (Compt. rend., 1934, 198, 59—61).—The discovery of the positron has extended the author's theory (cf. A., 1932, 1187) of the ether as consisting of inert mass of at. no. zero, with nucleus of combined proton and electron, to include any pair of such particles provided they are of opposite sign; the formation of an ether particle in this way is accompanied by production of two photons of quanta  $h_v = m_{\rm R}c^2/2$ . Conversely, access of photons of at least similar energy should split an ether particle into its constituents, materialising it into a proton and an electron; such separation should become complete in vac. in presence of a sufficiently powerful electric field. This has been demonstrated by maintaining an intense field between a cylindrical electrode and a Pd wire along its axis as cathode, the whole in vac. Production of protons was inferred from the increase of 1.7-7.5% (increase greatest with wire of least diam.) in the resistance of the Pd wire caused by their absorption, the process being unaccompanied by production of light, whereas when the field was reversed the Pd wire was ruptured with emission of sparks (cf. A., 1932, 892). C. A. S.

[Materialisation of æther.] A. COTTON (Compt. rend., 1934, 198, 61–62; cf. preceding abstract).—It is suggested that in spite of all precautions the protons thought to be produced were really present *ab initio* in the tube, as, *e.g.*, a trace of  $H_2O$ . C. A. S.

The photon. L. DE BROGLIE (Compt. rend., 1934, 198, 135—138; cf. A., 1932, 1184; this vol., 7). —It is shown mathematically that the photon is not simple, but consists of a "corpuscle of light" accompanied in its movements by an "anticorpuscle" related to it as the positive to the negative electron in Dirac's theory of holes. In presence of matter the photon would yield to the matter energy  $h_{\nu}$ , the corpuscle of light falling into the hole that accompanies it. Such corpuscle of light would be identical with the neutrino (cf. this vol., 127). C. A. S.

Quantum mechanics of photons. A. PROCA (Compt. rend., 1934, 198, 54—56).—Regarding the photon as a particle of zero mass and charge, the limitations of the application thereto of a method analogous to the relativistic form of Schrödinger's mechanics are considered. C. A. S.

Representation of radiation reaction in wave mechanics. W. F. G. SWANN (J. Franklin Inst., 1934, 217, 59-71).—Mathematical. J. W. S.

Energy distribution of a surface lattice of atoms with electronic orbital angular momentum. H. LUDLOFF and G. REYMANN (Z. Physik, 1933, 87, 154—175).—The total angular momentum is on the average zero, and does not contribute to ferromagnetism. The "proper" val. spectrum is discussed in relation to degeneracy and zero point entropy.

A. B. D. C.

Negative result of an attempt to combine light quanta. C. J. GORTER (Physica, 1934, 1, 199— 200).—Sunlight (5000—6000 Å.) was conc. on  $H_2O$  or aq. NiCl<sub>2</sub>. No indication of light of twice the incident frequency was found in the radiation scattered at right angles. H. J. E.

Electron theory of metals. A. SOMMERFELD (Naturwiss., 1934, 22, 49—52).—Theoretical. The Thomson effect for the alkali metals, and the Richardson effect, are considered. A. J. M.

Isotope of hydrogen. III. P. ZEEMAN and J. DE GIER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 2—3; cf. A., 1933, 1099; this vol., 4).—The mass differences between He and H<sub>2</sub>H<sup>2</sup>, HeH<sup>1</sup>, and H<sup>1</sup>H<sub>2</sub><sup>2</sup>, HeH<sup>2</sup>, and H<sup>2</sup> as measured by the parabola method using a mixture of He with H<sub>2</sub> containing 10% H<sup>2</sup>, agree to 1—1.5% with the vals. calc. from the data of Bainbridge (cf. A., 1933, 203). Parabolas corresponding with m/e vals. of 41 and 42 are attributed to AH<sup>1</sup> and AH<sup>2</sup>, respectively. J. W. S. Existence of negatively-charged proton; constitution of the nucleus of the isotope  $H^2$ . I. I. PLACINTEANU (Bul. Soc. Române Fiz., 1933, 35, 95— 102; cf. A., 1933, 995).—Theoretical. The nucleus of  $H^2$  of mass 2.013 is formed by the union of two neutrons and a positive electron. H. J. E.

"Mottled "hydrogen. W. GERLACH (Z. Physik, 1934, 87, 409).—A criticism of Günther-Schulze and Betz (A., 1933, 759), particularly with regard to introduction of this term. A. B. D. C.

Equilibrium between the three hydrogens. D. RITTENBERG, W. BLEAKNEY, and H. C. UREY (J. Chem. Physics, 1934, 2, 48—49; cf. this vol., 30).— Mass-spectrographic analysis of H<sub>2</sub> made by the decomp. of HI (used previously) at 25°, 397°, and 468° gave abundance ratios of H<sub>2</sub>, H<sup>1</sup>H<sup>2</sup>, and H<sub>2</sub> at these temp. of approx. 1:21:134, 1:13·3:46, and 1:2·69:1·93, respectively. The observed and calc. vals. for the equilibrium H<sub>2</sub>+H<sub>2</sub>=2H<sup>1</sup>H<sup>2</sup> agree.

H. J. E.

Atomic and molecular radii. V. POSEJPAL (J. Phys. Radium, 1933, [vii], 4, 741-748).—A theory previously developed (cf. A., 1932, 1187) is applied to the calculation of the at. radius and mean at. collision durations of H, He, N, O, Ne, Cl, A, Br, Kr, I, and Xe. Results are in good agreement with available data. N. M. B.

Value of c/m from the Zeeman effect. L. E. KINSLER and W. V. HOUSTON (Physical Rev., 1934, [ii], 45, 104–108).—A high-precision repetition of previous work (cf. A., 1932, 444) gives the val.  $1.7570 \pm$ 0.0010. N. M. B.

Approach to an explanation of the surface work functions of pure metals. J. F. CHITTUM (J. Physical Chem., 1934, 38, 79—84).—A formula is deduced for the net surface work function of a metal. The intrinsic potentials are calc. for many metals and compared with the arbitrary experimental vals. The agreement is satisfactory. M. S. B.

Electron terms of the nitrogen molecule. A. RECKNAGEL (Z. Physik, 1934, 87, 375–398).—An approx. solution is obtained for the Schrödinger equation; this gives good approximations to the lower terms as determined empirically, and is applied to allocation of the higher terms. A. B. D. C.

Quantised molecules formed of excited mercury atoms and methane molecules. G. GLOCK-LER and F. W. MARTIN (J. Chem. Physics, 1934, 2, 46).—Four diffuse fluorescence bands between 2554.2and 2542.6 Å., attributed to quantised states of a CH<sub>4</sub>-Hg complex, were observed on illuminating a mixture of CH<sub>4</sub> (1 atm.) and Hg vapour with a Hg (Ne) discharge tube. Raman scattering is excluded. Oldenberg observed similar bands with excited Hg and rare gas atoms (A., 1928, 346). H. J. E.

Large electronic isotope effects in molecular spectra. H. L. JOHNSTON (Physical Rev., 1934, [ii], 45, 79—81).—Measurements of fine structure in the isotopic OH bands confirm a large electronic isotope effect in the spin coupling of  $2\Pi$  terms. For BO and OH the observed increase in the doublet spacings, in the mol. with the heavier isotope, agree with theory. A large electronic isotope effect in A doubling is also observed for OH. N. M. B.

Rotation-vibration coupling in diatomic molecules. C. L. PEKERIS (Physical Rev., 1934, [ii], 45, 98—103).—Mathematical. N. M. B.

Zeeman effect for the absorption lines of the ruby. H. LEHMANN (Ann. Physik, 1934, [v], 19, 99—117).—The transverse Zeeman effect for the absorption lines  $R_1$  and  $R_2$  is dependent on the orientation of the crystal lattice with respect to the magnetic field and plane of polarisation down to  $-190^{\circ}$ . The variation of the splitting follows the symmetry of the crystal lattice. The optic axis is one of six-fold symmetry. A. J. M.

Photometric and spectrophotometric studies. X. Influence of adsorption on the absorption spectra. K. SCHAUM and K. MAENNCHEN (Z. wiss. Phot., 1934, 32, 201–221).—The extinction coeff. of aq. KMnO<sub>1</sub> does not decrease uniformly with dilution, and other anomalies are found; the absorption curve is flattened somewhat but not shifted on addition of SiO<sub>2</sub> sols. Detailed results are given of the changes in absorption of various dyes (methylene-blue, rhodamine, pinacyanol, etc.) in admixture with hydrophile colloids (gelatin, agar, etc.), in acid and alkaline solutions. J. L.

Predissociation in the Angström bands of CO. D. COSTER and F. BRONS (Physica, 1934, 1, 155—160). —Predissociation of the upper level of the Ångström bands occurs at v=0 and J=38. The dissociation energy of normal CO is 9.82 ev. H. J. E.

Absorption spectra of the sulphides of zinc, cadmium, and mercury, from 7000 to 1900 Å., and the heat of dissociation of sulphur. P. K. SEN-GUPTA (Proc. Roy. Soc., 1934, A, 143, 438-454). -The vapours of ZnS, CdS, and HgS absorb light continuously from a long-wave limit, resulting in photochemical dissociation into two normal atoms, thus:  $MS + hv_1 = M + S$  (<sup>3</sup>P). After the first absorption there is a re-transmitted patch and a second absorption corresponding with  $MS + h\nu_2 = M + S (^1D_2)$ . For HgS there is another re-transmitted patch and a third absorption corresponding with  $MS + hv_3 =$  $M+S(^{1}S_{0})$ . It is postulated that in the vapour state these compounds are ionic in nature, of the type  $M^{++}S^{--}$ . The heat of dissociation of  $S_2$  into S atoms is 102.9 kg.-cal. L. L. B.

Temperature dependence of the absorption spectrum of chromium oxychloride. P. K. PEERLKAMP (Physica, 1934, 1, 150—154; cf. A., 1933, 997).—With rise of temp. the diffuse bands between 6000 and 5300 Å. weaken, and disappear at 220°, whilst the general absorption increases. Between 5300 and 2300 Å. absorption is continuous. Predissociation occurs in all vibrational levels of the upper electronic state. SO<sub>2</sub>Cl<sub>2</sub> shows diffuse absorption bands between 3200 and 2800 Å., and continuous absorption at greater frequencies (cf. this vol., 129). H. J. E.

Ultra-violet absorption of binary liquid mixtures. III. System propaldehyde-ethyl alcohol. M. PESTEMER and (FRL.) P. BERNSTEIN (Monatsh., 1933, 63, 236-243).—Although the absorption spectrum of a EtCHO-EtOH mixture shows BRITISH CHEMICAL ABSTRACTS .--- A.

no distinctive absorption bands due to acetal formation, the deviations of the val. of  $\varepsilon$  from the additive law are a max. for an equimol. mixture and indicate that OH•CHEt•OEt is formed, but not CHEt(OEt)<sub>2</sub>. D. R. D.

Spectral differentiation of pure hydrocarbons : near infra-red absorption study. U. LIDDEL and C. KASPER (Bur. Stand. J. Res., 1933, 11, 599—618).— The absorption spectra of 36 hydrocarbons have been measured over the range 5500—9000 cm.<sup>-1</sup> by means of an automatic recording infra-red glass spectrograph, the results being recorded in graphical form. The absorption bands are correlated and discussed with reference to the mol. structures. J. W. S.

Absorption spectra of monohalogen derivatives of saturated aliphatic hydrocarbons. J. LECOMTE (Compt. rend., 1934, 198, 65–67).—The infra-red spectra ( $\lambda 20.4$ —6.9  $\mu$ ,  $\nu 490$ —1450 cm.<sup>-1</sup>) of 20 compounds have been determined. Where comparison is available, agreement with Raman spectra is good. Differences *inter se* in homologous series are sufficient to make the method suitable for analysis. Frequencies in corresponding bands are in the order Cl>Br>I, a pair of fundamental frequencies characteristic of the halogens in straight-chain derivatives with C  $\leq$  3 lying, respectively, between 650 and 725, 560 and 645, and 505 and 595 cm.<sup>-1</sup> (cf. A., 1933, 208). C. A. S.

Structure of the ultra-violet absorption spectrum of formaldehyde. I. G. H. DIEKE and G. B. KISTIAKOWSKY (Physical Rev., 1934, [ii], 45, 4–28). —Wave nos., intensities, rotational analyses, and combination relations are tabulated for the 3530, 3430, 3390, 3370, 3295, and 3260 Å. bands.

N. M. B.

Absorption and fluorescence of alcoholic solutions of phenanthrene. R. TITEICA (Bul. Soc. Române Fiz., 1933, 35, 149—155).—The absorption and fluorescence spectra in solutions of various concens. have been measured. New bands were found with max. at 3096 and 2420 Å. H. S. P.

Effect of ultra-violet rays of the ultra-violet absorption spectrum of aqueous methylene-blue solution. C. E. NURNBERGER and L. E. ARNOW (J. Physical Chem., 1934, 38, 71–77).—Max. absorption in the ultra-violet by methylene-blue occurs at 2920 and 2460 Å., but on continuous exposure there is a decrease in the absorption bands in both visible and ultra-violet regions, the most active wave-lengths in decreasing the bands being those < 2700 Å., so that this absorption cannot be used to measure radiation intensity in the "physiologically active" region 2900—3100 Å.  $p_{\rm H}$  change has no effect on the spectrum, but irradiation causes the greatest change in solutions of highest  $p_{\rm H}$ . M. S. B.

Ultra-violet absorption of thin blown glass. S. CRISTESCU and S. VENCOV (Bul. Soc. Romane Fiz., 1933, 35, 75–87).—The transmission of Jena and Thuringer glass,  $2 \cdot 5$ —300  $\mu$  thick, has been measured. For very thin plates it extends to 2300—2500 Å.

H. J. E.

Infra-red bands and molecular constants of HBr. E. K. PLYLER and E. F. BARKER (Physical Rev., 1933, [ii], 44, 984-985).-Vals. obtained by remeasurement of the fundamental band and examination of the harmonic band under high resolution are :  $v_0=2649.74$  cm.<sup>-1</sup>,  $I_0=3.2634\times10^{-40}$  g.-cm.<sup>2</sup>,  $r_0=1.4096\times10^{-8}$  cm. Separations of isotopic components were in agreement with those calc. from the isotopic masses of Br. N. M. B.

Harmonic and combination bands in CO<sub>2</sub>. E. F. BARKER and T. Y. WU (Physical Rev., 1934, [ii], 45, 1-3).—The 5·0, 1·43, 2, and 1·6  $\mu$  bands have been resolved. N. M. B.

Influence of foreign gases on the intensity of infra-red absorption. P. C. CROSS and F. DANIELS (J. Chem. Physics, 1934, 2, 6—10).—The effect of He, A,  $O_2$ ,  $N_2$ ,  $C_2H_6$ ,  $CO_2$ , and  $H_2$  on the  $N_2O$  and CO bands at 4.5  $\mu$  and 4.66  $\mu$ , respectively, and on infra-red absorption by EtBr, has been measured. The foreign gas enhances the absorption. To explain the effects, collision diameters related linearly to the gas-kinetic diameters must be assumed. The vals. are not related to those which must be taken for explaining the influence of the same gases on the thermal decomp. of  $N_2O$  (cf. Volmer and Froehlich, A., 1933, 30). The applicability of Beer's law is discussed. H. J. E.

Infra-red absorption of benzene vapour. R. TITEICA (Bul. Soc. Romane Fiz., 1933, 35, 89–91).— Bands between 1  $\mu$  and 17  $\mu$  resemble closely the absorption bands of liquid  $C_6H_6$  in the same region, but have a different intensity distribution. The C-H distance in  $C_6H_6$  is 1.04 Å. The C-C and the C:C linkings are both indicated. H. J. E.

Infra-red absorption of organic substances. III. A. ROTH (Z. Physik, 1933, 87, 192–204).—  $Pr^{\alpha}Cl$ ,  $Pr^{\alpha}Br$ ,  $Pr^{\beta}I$ ,  $HCO_{2}H$ ,  $HCO_{2}Me$ ,  $HCO_{2}Et$ , PhCCl<sub>3</sub>, BzCl, MeOBz, anisole, and anisaldehyde were investigated from 0.8 to 2.6  $\mu$ . A. B. D. C.

Infra-red absorption spectra of some plant pigments. R. STAIR and W. W. COBLENTZ (Bur. Stand. J. Res., 1933, 11, 703—711).—The infra-red absorption spectra of chlorophyll, carotene, xanthophyll, ethylchlorophyllide, phytol, phæophytin, and Cu phæophytin have been measured as far as  $15 \mu$ , and the changes in absorption spectrum accompanying the oxidation of carotene examined in detail.

J. W. S.

Raman spectrum of water. J. CABANNES and J. DE RIOLS (Compt. rend., 1934, 198, 30—32).—This consists of (1) a large band around 3450 cm.<sup>-1</sup>, with max. at 3224, 3436 (most intense), and 3525, all three polarised,  $\rho$  for 3436=0.3; (2) a narrow band at 1650, also polarised,  $\rho=0.4$ ; and (3) a weak band at 350—750. Lines or bands corresponding with (1) and (2) occur in aq. NaNO<sub>3</sub>, and in H<sub>2</sub>O vapour, those in the latter (3654 and 1648) being the symmetrical lines  $n_2$  and  $n_3$  of the angular mol. H<sub>2</sub>O, whilst the antisymmetric line  $n_1$  is probably concealed by 3654, with which 3625 in liquid H<sub>2</sub>O corresponds. 3411 and 3495 in gypsum are attributed to the double mol. (H<sub>2</sub>O)<sub>2</sub>. C. A. S.

Raman spectrum of heavy water. R. W. WOOD (Nature, 1934, 133, 106; cf. this vol., 129).

L. S. T.

The OH Raman band of nitric acid. L. MÉDARD and (MLLE.) T. PETITPAS (Compt. rend., 1934, 198, 88—89).—Using pure HNO<sub>3</sub> renowed every 3 hr. to avoid photochemical decomp., and exposing for 30 hr. to Hg  $\lambda$  4046.5 filtered through aq. CoCl<sub>2</sub>, a dissymmetric band around 4685 Å. (*i.e.*, 3215—3485 cm.<sup>-1</sup>) was observed (cf. A., 1931, 1111; A., 1933, 1228). A similar band occurs in a solution of NH<sub>4</sub>NO<sub>3</sub> in HNO<sub>3</sub>, the Raman spectra of which and of a HNO<sub>3</sub> solution of KNO<sub>3</sub> resemble each other. C. A. S.

Molecular spectra of some indium and gallium halides. E. MIESCHER and M. WEHRLI (Z. Physik, 1934, 87, 310—311).—A criticism of Petrikaln and Hochberg (this vol., 7). A. B. D. C.

Molecular spectra of some indium and gallium halides. A. PETRIKALN and J. HOCHBERG (Z. Physik, 1934, 87, 311).—A reply to the above.

A. B. D. C.

Raman effect. XXVIII. Isomeric paraffin derivatives. IV. K. W. F. KOHLRAUSCH and F. KOPPL (Monatsh., 1933, 63, 255—270).—Data are recorded and discussed for five *n*-paraffin halides, three mercaptans, six alcohols, and one amine with branched chains. D. R. D.

[Raman] spectra of some acetylenic alcohols. (MLLE.) B. GRÉDY (Compt. rend., 1934, 198, 89—91). —The Raman spectra of CR:C·CH<sub>2</sub>·OH and CR:C·CHMe·OH (R=n-C<sub>5</sub>H<sub>11</sub>, n-C<sub>6</sub>H<sub>13</sub>, cyclo-C<sub>6</sub>H<sub>11</sub>·CH<sub>2</sub>, and Ph) have been determined. Replacement of R' (not Me) in CR:CR' by CH<sub>2</sub>·OH has practically no effect on the characteristic frequencies (cf. A., 1933, 886), but replacement by CHMe·OH increases them by 20—25 cm.<sup>-1</sup>, greatly reducing the intensity of the second line. Ph has its usual effect. The following are described:  $\Delta^{\gamma}$ -decinen- $\beta$ -ol, b.p. 110— 112°/16 mm.,  $\delta$ -cyclohexyl- $\Delta^{\beta}$ -butinen- $\alpha$ -ol, b.p. 134°/17 mm.,  $\varepsilon$ -cyclohexyl- $\Delta^{\gamma}$ -pentinen- $\beta$ -ol, b.p. 133°/17 mm.  $\Delta^{\gamma}$ -Noninen- $\beta$ -ol (Moureu, Bull. Soc. chim., 1905, 33, 155) has b.p. 100°/16 mm. C. A. S.

Raman effect of furan and furfuraldehyde. G. GLOCKLER and B. WIENER (J. Chem. Physics, 1934, 2, 47).—Data are given. A Raman line 1567 cm.<sup>-1</sup> due to the C:C linking occurs for furfuraldehyde, but not for furan, thus favouring a centric formula for the latter mol. H. J. E.

Raman effect of multiple linkings between C and N in organic molecules. G. B. BONINO and R. MANZONI-ANSIDEI (Mem. R. Accad. d'Italia Sci. fis., 1933, 4, 759—776).—The Raman spectra of various aliphatic and aromatic aldoximes and ketoximes have been measured. The aliphatic oximes have a characteristic frequency about 1650—1660 cm.<sup>-1</sup>, and the aromatic oximes about 1625 cm.<sup>-1</sup>, attributed in both cases to the C:N linking. In the Na salts of the aromatic compounds the C:N frequency is displaced to 1540—1550 cm.<sup>-1</sup> The nature of the C:N linking in oximes and in other compounds is discussed. O. J. W.

Raman spectra of some unsaturated nitriles. M. DE HEMPTINNE and J. WOUTERS (Ann. Soc. Sci. Bruxelles, 1933, 53, B, 215-218).—Vinylaceto-, crotono- (I), and *iso*crotono-nitriles (II) all show an intense Raman frequency of about 2250 cm.<sup>-1</sup>, attributed to the ·C:N vibration, as well as the frequencies 1407 and 2921 cm.<sup>-1</sup> of the ·CH<sub>2</sub> and :CH groups. The C:C vibration frequency is higher for (I) (1645) than for (II) (1628 cm.<sup>-1</sup>). J. W. S.

Photoluminescence of sodium and potassium hydroxides. A. GRUMBACH and (MLLE.) M. RIBAL-LIER (Compt. rend., 1934, 198, 70—72).—The fluorescence of freshly cut KOH is green, of NaOH blue; after heating to fusion the fluorescence is at first more brilliant, but changes to yellow, and on prolonged heating disappears. The blue and green fluorescence appears to be due to formate, the change to yellow to formation of carbonate in addition. The fluorescence is restored to the calcined product on addition of formate, but not by carbonate. C. A. S.

Phosphorescence of eosin solutions. Influence of temperature. J. CHLOUPEK (Chem. Listy, 1933, 27, 493—497).—The duration of luminescence of eosin dissolved in glycerol is diminished by addition of  $H_2O$ or by raising the temp., to an extent proportionate to the change in viscosity of the medium, indicating that the phenomenon is one of true phosphorescence.

Extinction of fluorescence by organic compounds. K. WEBER and M. L. SAVIC (Z. physikal. Chem., 1934, B, 24, 68—74).—The extinction of the fluorescence of solutions by foreign substances and the part played by the solvent in the extinction have been studied. For a given foreign substance and fluorescing substance change of the solvent usually causes a parallel shift of the extinction curve in a direction which is the same whatever the foreign substance, X. The order of increasing effectiveness of a group of foreign substances varies with the fluorescing substance, Y. The order of magnitude of the dimensions of the sphere of action is determined by the properties of Y and is independent of X. R. C.

Coloration of fluorides of different elements by cathode rays. H. NAGAOKA, Y. SUGIURA, and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1933, 9, 486-489).-The colours observed when Ca, Li, Na, Mg, Al, Ti, Mn, Cr, Zn, and Pb fluorides are subjected to the radiation from a heated W filament are described. The curves relating the ratio of intensities of reflected and incident light to voltage  $V^{2/3}$  are almost linear at low voltages, but change slope abruptly at 660 volts owing to the excitation of the K radiation of F, and subsequently when the M and K radiations of the cations appear. No direct evidence was obtained of dissociation, since when, e.g., Ca and CaF<sub>2</sub> are heated at 800° colorations similar to those caused by bombardment are produced. H. F. G.

Thermo-luminescence spectra of fluorites. III. Thermo-luminescence spectra of fluorites from Wilberforce. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 153—161; cf. this vol., 10, 130).—Three specimens of different appearance each gave eleven bands in almost identical positions. The bands at wave-lengths > 3840 Å. are attributed to Tb and those in the ultra-violet region to Gd, the proportions of these impurities varying in the three specimens. J. W. S.

Artificial production of the blue fluorescence of fluorite. H. HABERLANDT, B. KARLIK, and K. PRZIBRAM (Nature, 1934, 133, 99-100).—Experi-

R. T.

ments with synthetic materials show that a rare-earth element, probably Eu, is responsible for the blue fluorescence band shown by fluorite. L. S. T.

Polarised photoluminescence of adsorbed molecules of dyes. A. JABŁOŃSKI (Nature, 1934, 133, 140).—The degree of polarisation of fluorescence and phosphorescence from Cellophane films coloured by Kautsky's method has been investigated.

L. S. T.

Rectification. W. C. VAN GEEL and H. EMMENS (Z. Physik, 1933, 87, 220—230).—Experiments on electrolytic rectifiers show that these act according to the emission theory, although electron emission is complicated by electrons having to be freed from hydrated ions before passing into the barrier layer.

Rôle of intervening layer in rectification by imperfect contact. QUINTIN (Compt. rend., 1934, 198, 347-349).—A plate of polished Si in contact with graphite shows no rectifying effect, but if separated by a thin mica plate with a hole so that a film of air  $10^{-3}$ — $10^{-5}$  cm. thick intervenes such effect appears. Current-p.d. curves are given and also for similar contacts with Si and Cu and Si and Sn. With Si–C and Si–Cu the current passes most easily with Si +; with Si–Sn and Si–Cd, which are less stable, the reverse is the case. C. A. S.

Mechanism of the cupric sulphide-magnesium rectifier. J. CAYREL (Compt. rend., 1934, 198, 64–65).—The author has shown that in a Cu sulphide rectifier the rectifying action is due mainly to CuS,  $Cu_2S$  being responsible only for subsidiary effects.

C. A. S.

Crystal photo-effect. H. TEICHMANN (Z. Physik, 1933, 87, 264—272).—Experiments on the temp. variation of the crystal photo-effect indicate that a purely electronic theory (cf. A., 1933, 209) is untenable. A. B. D. C.

Influence of water on some rectifying contacts. R. AUDUBERT and J. ROULLEAU (Compt. rend., 1934, **198**, 344—346).—Current-p.d. curves for the couple Si|SiO<sub>2</sub>|PbO<sub>2</sub>|C show that for low p.d. the current passes most easily with Si +, but for higher p.d. is reversed; the inversion p.d. rises greatly if the intervening substance, PbO<sub>2</sub>, etc., is dried, being initially 0.5—3 volts for PbO<sub>2</sub>, CuI, Fc<sub>2</sub>O<sub>3</sub>+CuI, Ag<sub>2</sub>S, MnO<sub>2</sub>, or PbS, but 12 volts with thoroughly dried PbO<sub>2</sub> (cf. A., 1927, 1145). C. A. S.

Conductivity of thin layers of insulating or slightly conducting liquids: variations with temperature. (MLLE.) T. MEYER (Compt. rend., 1934, 198, 160—163).—Working with layers of liquid 20  $\mu$  thick the following conductivities were determined: (10<sup>-12</sup> ohm<sup>-1</sup>) vaseline 0.8, decalin 0.8, C<sub>6</sub>H<sub>6</sub> 1, CCl<sub>4</sub> 1, PhMe 1.3, xylene 1.8, Et<sub>2</sub>O 2, C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> 2, C<sub>2</sub>HCl<sub>3</sub> 2, pinene 3, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> 400, PhCl 500, CHCl<sub>3</sub> 600; (10<sup>-8</sup> ohm<sup>-1</sup>) NH<sub>2</sub>Ph 2, glycol 4.5, glycerol 5, COMe<sub>2</sub> 600; EtOH (95%)  $2 \times 10^{-4}$  ohm<sup>-1</sup>. Resistivity increases with the current; it also increases slowly as temp. falls and rapidly at the f.p., abruptly where this is definite (e.g., NH<sub>2</sub>Ph), more gradually where there is a pasty stage (e.g., from  $-10^{\circ}$  to  $-40^{\circ}$  for glycol). The conductivity is probably due to impurities. Heating in the high-frequency condenser field on account of abnormal absorption. H. HAASE (Physikal. Z., 1934, 35, 68—76).—A method is described for determining the heating caused in dipole liquids by abnormal absorption in the high-frequency condenser field. The substances used in various conens. were  $C_6H_{13}$ ·OH in  $C_6H_6$ , and  $C_5H_{11}$ ·OH in  $C_6H_6$  and in xylene. The pure alcohols and their bromides were also used. The extent of the absorption decreases, and the max. is displaced towards the higher frequencies, with increasing dilution. In general the results agree with Debye's theory, but the wavelength of the max. for the pure alcohols was twice the theoretical val., and the displacement of the max. due to change of viscosity was smaller than expected.

A. J. M.

Electrical properties of liquid hydrocarbons. C. SALCEANU and D. GHEORGHIU (Bul. Soc. Romane Fiz., 1933, 35, 103—116).—The electrical conductivity of "petroleum spirit" and its mixtures with paraffins,  $C_6H_6$ ,  $C_{10}H_8$ , and  $Ph_2$  has been measured by the electroscope leak method. No connexion exists between the vals. for the liquid fuels and their antiknock characteristics. H. J. E.

Determination of dielectric constant and electric moment by electrical-resonance method. (Preliminary test.) K. S. CHANG and Y. T. CHA (J. Chinese Chem. Soc., 1933, 1, 107—115).—The dielectric consts. of dil. solutions of PhNO<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> have been determined to  $\pm 2.5\%$ . The calc. mol. polarisation and electric moment of PhNO<sub>2</sub> are 32.77 c.c. and  $3.82 \times 10^{-18}$  e.s.u., respectively. E. S. H.

Relation between dipole moment and cohesive forces. V. A. E. VAN ARKEL and J. L. SNOEK (Rec. trav. chim., 1933, 53, 91—94).—The dipole moments of pyrazine, 2:5- and 2:6-dimethyland tetramethyl-pyrazine, 2:3-dimethyl- and 2:3dichloro-quinoxaline, and 2-methylquinazoline are, respectively, < 1, 0, 0.53, < 0.45, < 0.3, 3·2, and 2·2 10<sup>-18</sup> e.s.u. The measured vals. are compared with those obtained by the vectorial addition of the group moments. 2:6-Dimethylpyrazine has b.p. 155·6°, m.p. 39°. H. S. P.

Free rotation [in molecules]. P. C. HENRIQUEZ (Chem. Weekblad, 1934, 30, 2—15).—The theoretical aspects, and means of experimental investigation of the problem of the relative rotation of two parts of a mol. are discussed. Measurement of the dipole moment and X-ray determination of interat. distances are regarded as the most promising methods of attack. H. F. G.

Molecular polarisations of nitrobenzene in various solvents at 25°. H. O. JENKINS (Nature, 1934, 133, 106).—Data for dil. solutions of PhNO<sub>2</sub> in  $n \cdot C_6 H_{14}$ , cyclohexane, dekalin, CCl<sub>4</sub>,  $C_6 H_6$ , CS<sub>2</sub>, and CHCl<sub>3</sub> are recorded. L. S. T.

[Variation with time of] properties of liquids. J. R. POUND (Chem. and Ind., 1934, 71-76).—The changes of d and n of liquids stored in bottles in the dark for 11 years are small except for esters and BzCl (where change is ascribed to absorption of H<sub>2</sub>O and hydrolysis) and for fatty oils and terpene oils, where change is due to polymerisation and oxidation.

A. B. Ď. C.

CHCl<sub>3</sub> is stable in presence of  $H_2O$  but not when dry. [ $\alpha$ ] varies for terpenes but not for amyl esters.

D. R. D.

[Refractive] index of water by interferometric method. (MLLE.) O. JASSE (Compt. rend., 1934, 198, 163—164).—Measurements have been made for  $\lambda\lambda$  5790, 5770, 5460, and 4360 Å., at some 30 temp. between 0° and 94°, accuracy  $\pm 2$ —8×10<sup>-6</sup>.

C. A. S.

Refractive index of water for waves of length 3-3.6 mm. M. M. ALIMOVA and N. S. NOVOSILZEV (Ann. Physik, 1934, [v], 19, 118—120; cf. A., 1929, 1129).—The previous work has been extended up to waves of length 3.6 mm. There is no anomalous dispersion over the wave-length range  $2\cdot2-3\cdot6$  mm.

A. J. M.

Refractive indices of *l*-ascorbic acid. S. B. HENDRICKS (Nature, 1934, 133, 178; A., 1932, 987). *l*-Ascorbic acid from pepper has  $n_a$  1.465,  $n_{\beta}$  1.600 $\pm$ 0.006, and  $n_{\gamma}$  1.747 for 5780 Å.; m.p. 188°. The results substantiate Cox's deduction of a plane configuration for the mol. in accord with the accepted furanose ring structure. L. S. T.

Rule of shift (Verschiebungsgesetz). P. A. LEVENE and G. M. MEYER (J. Amer. Chem. Soc., 1934, 56, 244—245).—Data for the max. mol. rotations of the free acid, Et ester, and *p*-nitrophenyl esters of configuratively related acids are inconsistent with the rule of shift: CHMeEt·CO<sub>2</sub>H series  $-18\cdot0$ ,  $-22\cdot9$ ,  $-52\cdot5$ , CHMeBu·CO<sub>2</sub>H  $-24\cdot3$ ,  $-30\cdot7$ ,  $-65\cdot7$ , CHMeEt·CH<sub>2</sub>·CO<sub>2</sub>H  $-10\cdot4$ ,  $-11\cdot5$ ,  $-20\cdot0$ , CHMePr·CH<sub>2</sub>·CO<sub>2</sub>H  $+3\cdot6$ ,  $+0\cdot7$ ,  $+5\cdot0$ , C<sub>5</sub>H<sub>11</sub>·CHMe·CH<sub>2</sub>·CO<sub>2</sub>H  $+8\cdot1$ ,  $+4\cdot2$ ,  $+11\cdot2$ .

E. S. H.

Optical rotation of unpolarised light. I. A. LANGSDORF, jun., and L. A. DU BRIDGE. II. R. W. WOOD (J. Opt. Soc. Amer., 1934, 24, 1-3, 4).—I. One part of an unpolarised beam was passed through a dextrorotatory and the other through a lævorotatory solution, the sum of the rotations being 90°; the emergent beams showed no interference fringes, in agreement with theory.

II. A note on the above. N. M. B.

Rotatory dispersion of sparteine in aqueous solution. C. LAPP and (MLLE.) G. ZALC (Compt. rend., 1934, 198, 177—178).—[ $\alpha$ ] at 18° for a solution containing, as sulphate, 1.09% sparteine was plotted against  $p_{\rm II}$  (2—11) for  $\lambda\lambda$  5890, 5780, 5460, 4920, and 4360. The curves show the two base functions at  $p_{\rm II}$ 4—5 and > 7. To determine sparteine the solution is brought to  $p_{\rm II}$  4 (bromocresol-green) or  $p_{\rm II}$  5 (bromocresol-purple) and [ $\alpha$ ] determined. For the above  $\lambda\lambda$  and 1.242% sparteine solution it is, respectively,  $-34.2^{\circ}$ ,  $-37.0^{\circ}$ ,  $-41.3^{\circ}$ ,  $-49.6^{\circ}$ , and  $-64.0^{\circ}$ . Agreement with results of the silicotungstic acid method is within 1%. C. A. S.

Thermal variation of magnetic birefringence and dispersion of ethyl phenylsuccinate. R. LUCAS, M. SCHWOB, and A. GOLDET (Compt. rend., 1934, 198, 72-74).—Thermal variation ( $-6^{\circ}$  to 107.5°) of the magnetic birefringence, and the dispersion thereof for  $\lambda\lambda$  5461 and 4358, of Et phenylsuccinate indicate the presence of  $\leq$  three isomerides, the birefringence of one or more being negative (cf. A., 1933, 765, 1103). C. A. S.

Magnetic investigation of organic radicals. H. KATZ (Z. Physik, 1933, 87, 238–244).—Magnetic susceptibilities have been measured for org. compounds containing N<sup>III</sup>, N<sup>IV+</sup>, N<sup>II</sup>, N<sup>III+</sup>, and N<sup>IV</sup>, and these are in agreement with Lewis' electron pair theory and Bose's theory of magnetism (A., 1927, 805). A. B. D. C.

Anomalies in the variation with temperature of the magnetic susceptibilities of salts. G. Bozza (Gazzetta, 1933, 63, 778–786).—Mainly mathematical. In view of the large deviations from Curie's law exhibited by most salts, it is suggested that two forms of these compounds, of different magnetic properties, coexist; that a majority of the mols. are mutually compensated magnetically, and that Curie's law is applicable to each form. H. F. G.

Structure and magnetic susceptibility of complex ferric salts. L. CAMBI and A. CAGNASSO (Gazzetta, 1933, 63, 767—778).—The susceptibilities at temp. between 84° and 350° abs., and the temp. coeffs., have been determined for a no. of Fe<sup>III</sup> derivatives of oximinoketones (anhyd., and with  $H_2O$ and  $C_5H_5N$  of crystallisation), glyoximes, and pyridine-, quinoline-, and quinoxaline-carboxylic acids. The following *compounds* are described :

 $K_2Fe_3(C_3H_4O_3N_3)_2$  and  $Fe(C_3H_4O_3N_3)_2, 3C_5H_5N$ , from isooximinomalonamide;  $Fe(C_4H_2O_4N_3)_2, 3.5C_5H_5N$ , from violuric acid; and  $Fe(C_{10}H_6O_2N_2)_2, H_2O$ , from quinoline-2-carboxylic acid. H. F. G.

Effect of crystalline electric fields on the paramagnetic susceptibility of cupric salts. O. M. JORDAHL (Physical Rev., 1934, [ii], 45, 87–97).— The paramagnetic susceptibility of the Cu ion in  $Cu(NH_4)_2(SO_4)_2, 6H_2O$  and  $CuK_2(SO_4)_2, 6H_2O$  is calc., assuming for the cryst. field monoclinic symmetry deviating only slightly from cubic symmetry. The cale. variation of the magnitudes of the principal susceptibilities with temp. agrees with experimental data. The observed and cale. variations of the direction of the principal axes with temp. are discussed. N. M. B.

Interaction between the magnetogenic atoms in a paramagnetic crystal. H. A. KRAMERS (Physica, 1934, 1, 182—192).—Theoretical.

H. J. E.

Weiss constant of paramagnetic ions in the S-state. A. Bose (Nature, 1934, 133, 213).—In aq. solutions of  $MnCl_2$  (I) and  $Mn(NO_3)_2$  (II) the susceptibility of  $Mn^+$  obeys the simple Curie law. The Curie consts. of  $Mn^{++}$  in (I) and (II) are 4.19 and 4.11 per g. ion, respectively, corresponding with 28.8 and 28.5 Weiss magnetons. L. S. T.

States of aggregation. K. F. HERZFELD and M. GOEPPERT-MAYER (J. Chem. Physics, 1934, 2, 38-45). —Theoretical. H. J. E.

Theory of the structure of  $CH_4$  and related molecules. III. J. H. VAN VLECK (J. Chem. Physics, 1934, 2, 20—30; cf. this vol., 13).—The <sup>5</sup>S state of C is probably 5—8 ev. above the ground state. A formula is derived for the energy of the "valency state" of the C atom, characteristic of C<sup>IV</sup> compounds with four electron pair linkings. It involves an increase of about 7 ev. in the internal energy of C over that in the ground state. Consequently the observed linking energy is < the gross or true interat. val. The gross energy per linking is probably greater in CH<sub>3</sub> than in CH<sub>4</sub>, although the reverse is true of the observed vals. The Slater-Pauling theory of directed valency and the Heitler-Rumer non-directional theory are compared. It is shown to be accidental that the linking energy in CH<sub>4</sub> is almost exactly four times that in CH. H. J. E.

Symmetric states of atomic configurations. F. SEITZ and A. SHERMAN (J. Chem. Physics, 1934, 2, 11-19).—Theoretical. H. J. E.

Form of molecules. H. J. BACKER (Chem. Weekblad, 1934, 31, 71-73).-Substances with spherical or compact mols. are characterised by stability of the cryst. phase, high m.p., low b.p., low heats of fusion and vaporisation, small temp. range and high mobility of the liquid phase, volatility, penetrating camphoraceous odour, and relatively high density. These properties are most marked with radial compounds, CX4, the compactness depending on the size and shape of X. Similar properties are shown by some s-polysubstituted, chain mols. (C2H6 derivatives) and tricyclic, cage-like mols. (camphor). Long-chain mols. have opposite characteristics. Rigid, long-chain mols. of limited but definite length tend to orient themselves in parallel directions with the formation of liquid crystals. S. C.

Oxygen molecules as radicals. W. STEINER (Trans. Faraday Soc., 1934, 30, 34—39; cf. A., 1933, 5).—Existing data relating to absorption spectra of gaseous, liquid, and solid O disclose the occurrence of spin-interaction between  $O_2$  mols. which is not, however, associated with sufficient energy to justify their being regarded as free radicals. F. L. U.

Relation between chemical and physical theories of the source of stability of organic free radicals. C. K. INGOLD (Trans. Faraday Soc., 1934, 30, 52-57; cf. A., 1933, 1151).-Applying the rule that, in neutral dissociations, coupled electrons move in divergent directions, it is shown that perturbation mechanisms analogous to all those involved in the degeneracy of either ion must co-exist in the degeneracy of a CAr<sub>3</sub> radical. The relative stability of such radicals may be predicted with a knowledge of the degree of complexity of the degeneracy, as is illustrated by a series of triarylmethyls. This chemical theory is closely related to the physical theories of Huckel and of Pauling, and, although qual., is of wider scope. F. L. U.

Nature of the covalent linking, and formation of free radicals. M. W. TRAVERS (Trans. Faraday Soc., 1934, 30, 100–102).—It is suggested that the changes involved in the (chemical) condensation of  $B_2H_6$  may be similar to those which  $C_2H_6$  undergoes on pyrolysis. There is no evidence for dissociation of the latter into CH<sub>3</sub> radicals, nor for production of CH<sub>2</sub> from  $C_2H_4$ . The structure of  $B_2H_6$  is discussed.

F. L. U.

Applications of molecular rays technique to the study of free radicals. R. G. J. FRASER (Trans. Faraday Soc., 1934, 30, 182–184).—The possibility of carrying out a qual. analysis of mol. rays is indicated, the constituents being characterised by their ionisation potentials and/or magnetic properties. F. L. U.

Electronic levels of polyatomic molecules. I. Levels of the C:C double linking. C. P. SNOW and C. B. ALLSOPP (Trans. Faraday Soc., 1934, 30, 93— 99).—The fine structure observed in spectra of vapours of  $C_2H_4$ ,  $C_2HMe_3$ , and cyclohexene indicates a common origin for the band system of  $C_2H_4$  derivatives at about 2100 Å. and for the  $C_2H_4$  band at slightly shorter wave-lengths. It is probable that the effective permitted states of C:C derivatives of lower symmetry than  $V_h$  are in general the same as for  $C_2H_4$ .

F. L. U. Potassium superoxide and the three-electron linking. E. W. NEUMAN (J. Chem. Physics, 1934, 2, 31-33).—The oxide is paramagnetic, the susceptibility corresponding with a Bohr magneton no. of 2.04. The formula must therefore be  $KO_2$ , containing  $O_2'$  ions in a <sup>2</sup>II state (:0:0:') and not  $K_2O_4$ , which probably contains the  $O_4''$  ion (:0:0:0:0:').

H. J. E. Hydrides of lithium, boron, and beryllium. J. TUTIN (Chem. and Ind., 1934, 65).—In  $B_2H_6$  the assumption of  $H^{II}$  is preferred to that of  $B^{IV}$ . E. S. H.

Thallic oxide. [Lead suboxide.] F. HALLA, H. TOMPA, and L. ZIMMERMANN (Z. Krist., 1934, 87, 184; cf. A., 1933, 1106).—Two corrections concerning  $Tl_2O_3$ . Regarding the existence of Pb<sub>2</sub>O, the grey layer formed on the slow oxidation in air at room temp. of a saturated Pb amalgam consists of PbO and Hg. C. A. S.

Carbon-halogen linking energy and the molecular structure as related to halogen alkyls. Y. HUKUMOTO (J. Chem. Physics, 1934, 2, 46; cf. this vol., 8).—From absorption spectra the C-halogen linking energy increases in the order I<Br<Cl, and increases with the length of the C chain. It diminishes with multiple substitution of halogens. Results harmonise with Raman spectra data. H. J. E.

Energy relations in the dissociation of the water molecule into its atoms. O. RIECHEMELER, H. SENFTLEBEN, and H. PASTORFF (Ann. Physik, 1934, [v], 19, 202-217).-A mixture of water vapour and Hg was irradiated with Hg (2537 A.) with an energy of 4.9 volts, causing dissociation. The extent to which the process has occurred can be found by determining the partial pressure of H<sub>2</sub> after other products have been removed by cooling in liquid air. The increase in dissociation with temp. to be expected since the no. of effective collisions of energy > 4.9volts increases with temp. has been observed. The difference between the heat of dissociation of the  $H_2O$  mol. and the energy imparted to the mol. by the radiation is  $0.21 \pm 0.04$  volts. The heat effect of the reaction  $H_0O = H + OH$  is  $5 \cdot 11 \pm 0.04$  volts  $(117.9\pm0.9 \text{ kg.-cal. per mol.})$ , agreeing with previous vals. The heat of dissociation of the OH mol. (OH= H+O) is 5.29+0.14 volts. A. J. M.

Atomic parachors of carbon and hydrogen. A. I. VOGEL (Chem. and Ind., 1934, 85).—The Me and Et esters of *n*-dibasic acids yield a mean parachor increment of 40.3 units per  $CH_2$ ; the val. 39.0 was deduced by Sugden from other series (cf. A., 1924, ii, 662). D. R. D.

Electron diffraction and the imperfection of crystal surfaces. L. H. GERMER (Physical Rev., 1933, [ii], 44, 1012—1015).—Bragg reflexions were obtained by scattering fast electrons (0.05 Å.) from the etched surfaces of (100) Fe, (111) Ni, and (110) W single crystal faces. A given reflexion is found for glancing angles varying up to 1° from the calc. Bragg val. The accuracy with which this glancing angle must be adjusted is a measure of the degree of crystal imperfection. Widths of half max. of electron rocking curves are  $0.8^\circ$ ,  $1.5^\circ$ , and approx. 1° for the Fe, Ni, and W crystals, respectively. Corresponding X-ray rocking curves are much narrower. It is concluded that the degree of misalignment is much greater at the surface than deep down in the crystal.

N. M. B.

Scattering of electrons by stibnite and galena. A. G. EMSLIE (Physical Rev., 1934, [ii], 45, 43-46).— The patterns for 20-60-kv. electrons are discussed. Results indicate that the stibnite crystal has relatively large mosaic units, and that collisions with atoms, involving small energy losses, cause high absorption of the primary beam as it penetrates the crystal.

N. M. B.

Fine structure of X-ray absorption edges and the influence of the polar character of the compound. D. COSTER and G. H. KLAMER (Physica, 1934, 1, 145—149).—Fine structure of the K edge of K and Cl in KCl and KClO<sub>3</sub> has been photographed. There is no resemblance between that of K and Cl, although they are in the same crystal lattice. For metal alloys the type of fine structure depends mainly on the lattice (cf. Veldkamp, A., 1932, 979; 1933, 760). H. J. E.

Determination of Debye-Scherrer X-ray structure of non-cubic systems. V. NESKUCHAEV (J. Tech. Phys., U.S.S.R., 1931, 1, 105—110).—Formulæ are given for tetragonal, hexagonal, and rhombohcdral systems. CH. ABS.

Crystal lattice of nickel and the sudden change in magnetic properties. B. DEL NUNZIO (Atti R. Ist. Veneto Sci. Lett., 1933, 92, 541-549; Chem. Zentr., 1933, ii, 1850).—Ni is face-centred, with a 3.56 Å. X-Ray analysis does not elucidate changes in magnetic behaviour. A. A. E.

Crystal structure of  $\alpha$ -( $\beta$ -)tungsten. E. EBERT and H. HARTMANN (Z. Krist., 1934, 87, 183; cf. A., 1933, 665).—Neuberger's work is criticised, and the proposed interchange of the names of  $\alpha$ - and  $\beta$ -tungsten is deprecated. C. A. S.

Crystal structure of NdAl. C. W. STILLWELL and E. E. JUKKOLA (J. Amer. Chem. Soc., 1934, 56, 56-57).—NdAl has the CsCl type of structure and  $a_0$  3.73 $\pm$ 0.01 Å. E. S. H.

Structure of calcium boride. L. PAULING and S. WEINBAUM (Z. Krist., 1934, 87, 181–182; cf. A., 1933, 116, 891).—CaB<sub>6</sub> is cubic with a 4·145 Å., and one mol. in the unit cell; each B is equidistant, 1.716 Å., from each of five other B, forming a rigid 3-dimensional network in the interstices of which are the Ca atoms. C. A. S.

Crystal structure of copper sulphate. C. A. BEEVERS and H. LIPSON (Nature, 1934, 133, 214).— CuSO<sub>4</sub>,5H<sub>2</sub>O has a 6·12, b 10·7, c 5·97 Å.,  $\alpha$  82° 16',  $\beta$  107° 26',  $\gamma$  102° 40', 2 mols. per unit cell. The Cu atoms lie on the centre of symmetry at (000) and ( $\frac{1}{2}$ 10) and the S atoms on the general position (0·01, 0·29, 0·64). Each Cu is surrounded by an octahedron consisting of 4 H<sub>2</sub>O and 2 O, suggesting direct linkings from Cu to O. The odd H<sub>2</sub>O touches 2 O of different SO<sub>4</sub> groups and 2 H<sub>2</sub>O of different octahedra, and appears to play an important part in maintaining the structure. L. S. T.

Crystal structure of  $CaSO_4, 4CO(NH_2)_2$ . S. B. HENDRICKS (J. Physical Chem., 1933, 37, 1109– 1122).—The crystallographic and optical consts. of triclinic crystals of  $CaSO_4, 4CO(NH_2)_2$  have been measured and the crystal structure has been partly determined from X-ray diffraction data. M. S. B.

Crystal structure of cadmium hydroxychloride. J. L. HOARD and J. D. GRENKO (Z. Krist., 1934, 87, 110—119).—CdCl·OH, prepared by heating CdO in a solution of CdCl<sub>2</sub> for several days at 210°, is hexagonal, a 3.66, c 10.27 Å., with 2 mols. in the unit cell, space-group  $C_{ss}^4$ —C6mc. Each Cd<sup>\*\*</sup> is surrounded octahedrally by 3 Cl' and 3 (OH)', each of which is shared among 3 Cd<sup>\*\*</sup>, the whole forming neutral layers parallel to the basal plane of composition CdCl·OH. C. A. S.

Structure of the hypophosphite group as determined from the crystal lattice of ammonium hypophosphite. W. H. ZACHARIASEN and R. C. L. MOONEY (J. Chem. Physics, 1934. 2, 34—37).— NH<sub>4</sub>H<sub>2</sub>PO<sub>2</sub> is orthorhombic-holohedral (a 3.98, b 7.57, c 11.47 Å.; 4 mols. in unit cell; space-group Acmm  $V_{h}^{2}$ ). The H<sub>2</sub>PO<sub>2</sub> group forms a distorted tetrahedron, with O atoms at two corners and H at the other two. The P-O distance is 1.51 Å., and the P-O linkings are at 120°. The P-H distance is 1.5 Å., with the linkings at 92°. Each NH<sub>4</sub> is surrounded by 4 O at 2.81 Å. and by 4 H at 3.08 Å. The NH<sub>4</sub> group probably is not rotating and its H atoms are probably linked to the surrounding O atoms.

H. J. E.

Structure of thallous and potassium thiocyanates. W. BÜSSEM, P. GÜNTHER, and R. TUBIN (Z. physikal. Chem., 1934, B, 24, 1—21; cf. A., 1933, 666).—TICNS crystallises in the rhombic system, and probably has the space-group  $V_h^{11}$  and a 6.80, b 6.78,  $c \ 7.52$  Å.; the unit cell contains 4 mols. KCNS has the space-group  $V_h^{11}$  and a 6.67, b 6.65, c 7.54 Å.; unit cell contains 4 mols. From the at. arrangements in both salts the SCN chain is probably bent, making an angle of 125—130°, but the possibility of a straight chain is not excluded. R. C.

Crystal structure of potassium osmyl chloride. J. L. HOARD and J. D. GRENKO (Z. Krist., 1934, 87, 100–109).—K<sub>2</sub>OsO<sub>2</sub>Cl<sub>4</sub> is face-centred tetragonal, a 6.99, c 8.75 Å., with 2 mols. in the unit cell, spacegroup  $D_{45}^{11}-I4/mmm$ . The structure is ionic, with a fluorite-like grouping, in which 2K° and  $[OsO_2Cl_4]''$ are situated as F'<sub>2</sub> and Ca°, respectively;  $[OsO_2Cl_4]''$ , symmetry  $D_{4h}$ , is octahedral with Os in the centre and Os-Cl=2.28, Os-O=1.85 Cl-Cl=3.22, and O-Cl=2.94 Å. C. A. S.

Crystal morphology of ammonium tetroxalate. H. HIMMEL (Zentr. Min. Geol., 1933, A, 209–214; Chem. Zentr., 1933, ii, 1867).—16 forms have been measured. a:b:c=0.5995:1:0.6860. A. A. E.

Сгузtal structure of enargite (Cu<sub>3</sub>AsS<sub>4</sub>). К. Такамб (Proc. Imp. Acad. Tokyo, 1933, 9, 524—527). —The cell dimensions are  $a_0 6.39 \pm 0.05$ ,  $b_0 3.68 \pm 0.03$ ,  $c_0 6.15 \pm 0.05$  Å.; 1 mol. per unit cell; space-group  $V_{h^2}^{h^2}$ . H. F. G.

The Si<sub>3</sub>O<sub>8</sub> chains in space-groups  $V_{h}^{16}$  and  $C_{2^{J_{k}}}^{5}$ . T. IBO (Proc. Imp. Acad. Tokyo, 1933, 9, 528—530).— The structure of eudidymite (rhombic HNaBeSi<sub>3</sub>O<sub>8</sub>) may be derived from that of epididymite (the monoclinic form) on the assumption that both are built of Si<sub>3</sub>O<sub>8</sub> groups connected by centres of symmetry. Epididymite has a 12.63, b 7.32, c 13.58 Å.; spacegroup  $V_{h}^{18}$ ; 8 mols. per unit cell. H. F. G.

New determination of the lattice constant of carbon dioxide. W. H. KEESOM and J. W. L. KOHLER (Physica, 1934, 1, 167–174).—The lattice is cubic (space-group  $T_{h}^{c}$ ). At -190° the lattice const. is  $5 \cdot 575 \pm 0.005$  Å. The C-O distance is  $1 \cdot 13 \pm 0.02$  Å. H. J. E.

X-Ray diffraction in long-chain liquids. B. E. WARREN (Physical Rev., 1933, [ii], 44, 969—973).— Mathematical. Vals. are calc. by the Zernicke-Prins method for the fatty acid, *n*-alcohol, and *n*-paraffin series. N. M. B.

X-Ray diffraction by gaseous benzene derivatives. W. C. PIERCE (J. Chem. Physics, 1934, 2, 1-5).—The scattering of X-rays by o- and p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> vapours has been studied. Correction was made for C-C and C-Cl scattering from measurements on PhCl, and vals. of the Cl-Cl distance of 3.0 and 6.25 Å., respectively, were deduced. The structure of C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> forms a planar hexagon, with the Cl atoms in or near the plane. H. J. E.

X-Ray behaviour of sodium cellulose II, washed with dilute sodium hydroxide and when dehydrated. C. TROGUS and K. HESS (Cellulosechem., 1934, 15, 1—3).—Na-cellulose II produced by treating cellulose fibres with > 21% aq. NaOH give somewhat diffuse X-ray diagrams, but if subsequently treated with more dil. (6.6—15%) aq. NaOH the spots are sharper. It is proposed to restrict the name Nacellulose II to the latter product. This substance is changed by dehydration with NaOH in MeOH to Nacellulose II'. A. G.

X-Ray investigation of elastic tissue. H. KOLPAK (Naturwiss., 1934, 22, 72).—Submicroscopic changes in the fine structure of elastic tissue, with and without stretching, have been investigated. On stretching, extensive orientation occurs. The diagram for damp, unstretched tissue shows two " amorphous " rings, of which the inner shows four max. A. J. M.

Orientation of the micelles in unstretched agar films. I. SAKURADA and K. HUTINO (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1934, 23, 162– 163; cf. A., 1933, 1235).—Debye–Scherrer photographs of hydrated agar films suggest that the micelle is of needle or plate form. J. W. S.

Limits of validity of the law of electric forces in metals; Volta's second law. O. SCARPA (J. Phys. Radium, 1933, [vii], 4, 725—731).—It is shown theoretically and experimentally that Volta's law for metallic circuits is not valid when, in addition to electrons, the metals contain mobile ions; this is the case for liquid metals, and probably also for solid metals at high temp. Cu-Cd-Hg-Pt-Cu and Cu-Zn-Hg-Pt-Cu contacts were investigated. N. M. B.

Non-conducting modifications of metals. J. KRAMER (Ann. Physik, 1934, [v], 19, 37-64).-Modi-fications of certain metals (Fe, Ni, Pt, Zn, Sn, Cd, and Sb) which possess very low conductivity can be made by vaporisation or cathodic sputtering. The temp. (t) at which the abnormal changes to the normal form are Fe 440°, Ni 336°, Pt 510°, Zn 133°, Sn 180°, Cd 150°, and Sb 446° (all temp. abs.). The normal conductivity is determined by t and the no. of conductivity electrons. It is supposed that the poorly conducting layers are amorphous phases, which are formed from the above metals when the atoms come together at < t. The change to the normal metal takes place with the formation of the lattice, and liberation of conductivity electrons. With Sb the transition can be followed experimentally by the Debye-Scherrer method. The large temp. coeff. of conductivity of amorphous metals is due to the increase in the no. of free conductivity electrons at the higher temp. The conductivity of the amorphous forms of Fe, Ni, and Sb can be increased by light. With Sb the increase is related to the absorption spectrum. After transition, the layers are no longer sensitive to light.

A. J. M.

Electrical properties of thin metallic layers obtained by cathode sputtering. Y. MASLAKOVETZ (J. Tech. Phys., U.S.S.R., 1931, 1, 401–427).—Vals. are tabulated. Layers of Pt, Au, Ag, Cu, and Ni swell on absorption of  $H_2O$ ,  $Et_2O$ , or benzine. CH. ABS.

Hardening phenomena in compressed metal powders. W. TRZEBIATOWSKI (Z. physikal. Chem., 1934, B, 24, 75-86).-The hardness, H, and d of specimens prepared by compressing Au and Cu powders in moulds under pressures up to  $30 \times 10^3$  atm. have been studied. Max. hardnesses of 180 Brinell with Cu and 145 Brinell with Au have been observed. X-Ray examination showed widening of the interference lines and increase of the diffuse scattering due to the compression, but the fibre diagrams showed that in the compressed mass the crystallites retained the same random orientation as in the loose powder. On heating the compressed material H falls rapidly above about 200°, which is ascribed to recovery and recrystallisation. At about 400° the internal strains in the lattice have disappeared. It is concluded that hardening and recrystallisation effects play a decisive part in the production of synthetic masses of metal (cf. A., 1933, 450). The changes in d on heating such masses depend on the loss of gas sorbed by the powder, the ease of which decreases with increasing compression, and on sintering. **R**. C.

Electrical conductivity of compressed masses of metal powder. W. TRZEBIATOWSKI (Z. physikal. Chem., 1934, B, 24, 87-97).—The resistance, R, of specimens prepared by compressing powdered Au and powdered Cu has been measured at 18-600°. The temp. coeff. of R is positive up to about 100°, negative between about 100° and 300°, and positive above about 300°. Dilatometric measurements show that between 100° and 300° there is only slight sintering; the principal cause of the fall in R seems to be the evolution of adsorbed gas, which is continuous at 100° and a max. at the temp. between 350° and 500° at which the X-ray diagram shows the first signs of grain growth. In the variation of R with temp. compressed metal powders resemble thin films of metal (cf. A., 1933, 893). R. C.

Electric resistivity of peranthracites. P. LEBEAU and P. CORRIEZ (Compt. rend., 1934, 198, 170—172).—Using material powdered to pass 120mesh, subjected to 50 kg. per sq. cm. pressure, the resistivity of ten samples varied from 0.65 to 556.0 ohms, the order of increase being the same as that in amount of gas (21.78-147.51 cu. m.) evolved at 1000°, and almost the same as that in H content (0.67— 1.93%). Similarly determined resistivities of graphites varied from 0.030 to 0.036 ohm. C. A. S.

Cause of the increase of the electrical conductivity of crystalline substances on approaching the m.p. M. LE BLANC and E. MÖBIUS (Z. Elektrochem., 1934, 40, 44—46).—The rise in conductivity of AgNO<sub>3</sub> on approaching the m.p. becomes sharper and occurs closer to the m.p. with progressive purification. Firmly-held  $H_2O$  causes the phenomenon. 0.1% Ag<sub>2</sub>SO<sub>4</sub> gives a similar effect. The increase in the sp. heat of AgNO<sub>3</sub> just below the m.p. is also due to impurities. H. J. E.

Electrical conductivity of nickel oxide. H. H. von BAUMBACH and C. WAGNER (Z. physikal. Chem., 1934, B. 24, 59—67).—At 800—1000° the conductivity,  $\kappa$ , of NiO varies with the O<sub>2</sub> pressure, p, in the surrounding gas atm., when p lies between  $2 \times 10^{-4}$  and 1 atm., according to  $\kappa = kp^{1/n}$ , where n is about 4 and k is a const. The conduction is nearly all electronic. It is inferred that the conduction is of the electron deficiency type (cf. A., 1933, 888), a conclusion confirmed by thermo-c.m.f. measurements. The excess of O<sub>2</sub> over the stoicheiometric proportion is too small for direct determination, but is estimated from data for diffusibility and the rate of formation of surface oxide films. R. C.

Conduction of electricity in solid silver sulphide, selenide, and telluride. C. TUBANDT and H. REINHOLD (Z. physikal. Chem., 1934, B, 24, 22— 34).—Experiments have been made on the combination of Ag with X (X=S, Se, or Te) in an arrangement in which Ag is separated from X by layers of two or three of the corresponding compounds. The results in conjunction with those of new transport measurements show that  $\alpha$ -Ag<sub>2</sub>S, -Ag<sub>2</sub>Se, and -Ag<sub>2</sub>Te are mixed conductors and that < 1% of the total conduction is electrolytic (cf. A., 1933, 467). R. C.

Presence of a negative minimum in the resistance hysteresis loop of nickel in longitudinal magnetic fields. M. S. ALAM (Z. Physik, 1933, 87, 255–257).—This min. does not appear with fields of max. 200 gauss, and cannot be due to incomplete initial demagnetisation as suggested by Stierstadt (A., 1931, 898). A. B. D. C.

Change in magnetic susceptibility in metals and alloys caused by internal stress. Y. SHIMIZU (Sci. Rep. Tohoku, 1933, 22, 915—933; cf. A., 1931, 154; B., 1931, 1054).—The paramagnetic susceptibility of Cu, Ag, Au, Al, Pt, and of their binary alloys decreases, and the diamagnetic susceptibility increases, with increasing residual internal stress, the latter being measured by the decrease in density caused by working. F. L. U.

Stern-Gerlach experiment with iron. W. KLABUNDE and T. E. PHIPPS (Physical Rev., 1934, [ii], 45, 59-61).—The at. ray trace was found to be widened when the ray was subjected to a magnetic field, indicating that Fe in the vapour state has a magnetic moment. N. M. B.

Refraction and dispersion of crystals. VIII. Refraction measurements of crystals; comparison of isomorphous salts with cations similar to and dissimilar from inert gases. P. WULFF and D. SCHALLER. IX. Molecular refraction, dispersion, and absorption of isomorphous salts of strontium, barium, lead, and thallium. P. WULFF and A. KING (Z. Krist., 1934, 87, 43-71, 72-99; cf. A., 1933, 765).—VIII. The regularities in  $\Delta R$  (difference between the additively calc. and the experimental vals. of the mol. refractivity) existing in the case of salts with inert gas-like ions (cf. A., 1924, ii, 372; 1929, 13), and due to the electrostatic effect of neighbouring ions, are shown to be present in the Ag halides of NaCl type, but not in the TI<sup>I</sup> halides. Revised vals. of d and n are given for NaBr, Na<sub>2</sub>SO<sub>4</sub>, NaOAc, 3H<sub>2</sub>O, CsCl, Ag<sub>2</sub>SO<sub>4</sub>, TIClO<sub>4</sub>, CaCl<sub>2</sub>, 6H<sub>2</sub>O, CaSO<sub>4</sub>, and CaSO<sub>4</sub>, 2H<sub>2</sub>O.

IX.  $\Delta R$  are compared for sulphates and nitrates of Pb, Ca, Sr, and Ba, some halides of these and of Rb, Cs, and Tl<sup>I</sup>. The connexion of  $\Delta R$  and of the dispersion and absorption curves of some of the salts with the structure of the salts and the electronic structure of their cations is discussed.  $\Delta R$  for Pb(NO<sub>2</sub>)<sub>2</sub> agrees with the results for salts with inert gas-like ions (cf. A., 1931, 24, 669), but for PbSO<sub>4</sub> and the Pb halides  $\Delta R$  is greater, indicating increased influence of the stronger electrostatic field due to the double charge of the cation. The non-ionic lattice of PbCl<sub>2</sub> is confirmed. Revised vals. of  $d^{25}$  and  $n_{11}^{25}$  are given for Ba(NO<sub>3</sub>)<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub>. C. A. S.

Latent energy remaining in a metal after coldworking. G. I. TAYLOR and H. QUINNEY (Proc. Roy. Soc., 1934, A, 143, 307—326).—Measurements have been made of the latent energy remaining in metal rods after severe twisting. As the total amount of cold work which has been done on a specimen increases, the proportion which it absorbs decreases. Although saturation was not completely reached even with twisted rods, the experimental results for Cu show that it would have been reached at a plastic strain very little > the strain of fracture. The cold work necessary to saturate Cu with latent energy at  $15^{\circ}$  is slightly > 14 g.-cal. per g. L. L. B.

Indifferent and critical points. E. JOUGET (Compt. rend., 1934, 198, 218—222; cf. this vol., 133).—A previous investigation is extended to the case of n independent constituents in one phase, or in two phases, the constituents passing from one to the other. C. A. S.

Effect of high-frequency currents on the transition point of superconductors. E. F. BURTON, J. O. WILHELM, A. PITT, and A. C. YOUNG (Canad. J. Res., 1933, 9, 630-636).-The modified technique shows that the temp. of transition to superconductivity of thin films of Sn does not vary within the frequency range  $0-3 \times 10^7$  cycles with small currents, but the min. of a.c. resistance (I) is nearer 0° abs. than is that of d.c. resistance (II). D.c. has no effect on the a.c. point, but a.c. superimposed on d.c. lowers the temp. at which (II) suddenly falls, and this effect depends on the strength of the a.c. only (cf. A., 1932, 684, 1193). With solid Ta wires, the initial change of (I) at the transition point is a slight increase which is absent with thin films of metal. The phenomena are related to variation, with frequency, of current distribution in the wire and J. G. A. G. magnetic effects.

Current stability in a superconductor. L. BRILLOUIN (J. Phys. Radium, 1933, [vii], 4, 677—690; cf. A., 1932, 1005).—Difficulties arising from the effect of perturbations on electron distribution in the interpretation of superconductivity are discussed. The influence of inductive forces for electrons in metals (cf. Frenkel, A., 1933, 769), and conditions for transition from the resistant to the superconductive state, are considered. N. M. B.

Measurements with liquid helium. XXIII. Superconductivity of vanadium. W. MEISSNER and H. WESTERHOFF (Z. Physik, 1933, 87, 206–209). —Superconductivity sets in between  $4\cdot3^{\circ}$  and  $4\cdot4^{\circ}$ abs.; resistance measurements are given between this and  $0^{\circ}$ . A. B. D. C.

New methods of attaining low temperatures. E. JUSTI (Z. Physik, 1933, 87, 273—276).—Simon's isothermal adsorption and subsequent adiabatic desorption method (A., 1927, 100) does not work in practice, but might be used to obtain uniform intermediate temp. A. B. D. C.

Dependence of the volume and f.p. of carbon tetrachloride on the thermal pretreatment. W. BRULL (Z. Elektrochem., 1934, 40, 8–10; cf. A., 1932, 1194).—Retention of air by CCl<sub>4</sub> and hysteresis of the Beckmann thermometer caused the change in physical properties with pretreatment previously reported. Nieuwenhuis' method is criticised (A:, 1933, 1109). H. J. E.

Transition point of carbon tetrachloride as a fixed point in thermometry. M.p., heats of transition and of fusion. H. L. JOHNSTON and E. A. LONG (J. Amer. Chem. Soc., 1934, 56, 31–35).— Data obtained with CCl<sub>4</sub> containing  $< 1 \times 10^{-3}$  mol.-% of impurities are: transition point  $-47.66\pm0.05^{\circ}$ , m.p.  $-22.87\pm0.05^{\circ}$ , heat of transition  $1080.8\pm3$  g.-cal. per mol., heat of fusion  $577.2\pm1$  g.-cal. per mol. The transition in solid  $CCl_4$  is sharp and reproducible and provides a satisfactory secondary fixed point for the calibration of thermometers.

E. S. H. F.p. and triple points with water. W. P. WHITE (J. Amer. Chem. Soc., 1934, 56, 20–24).—An ice point at atm. pressure, const. to 0.0001°, can be made with good commercial ice by carefully protecting against melting from external sources and removing impurities in the ice from the surfaces by washing with thoroughly chilled  $H_2O$ . This ice point is more convenient for continuous work than the triple point. E. S. H.

Atomic heats and heats of fusion and of transformation of gallium, indium, and thallium. W. A. ROTH, I. MEYER, and H. ZEUMER (Z. anorg. Chem., 1934, **216**, 303—304).—Corrections to a previous paper (A., 1933, 1237). F. L. U.

Specific heat of thallium at liquid helium temperatures. W. H. KEESOM and J. A. KOK (Physica, 1934, 1, 175-181).—Measurements have been made from  $1\cdot3^{\circ}$  to  $4\cdot2^{\circ}$  abs. The at. heat falls from 0.01325 to 0.01177 at the transition point. No latent heat was observed at this point. H. J. E.

Series of coefficients occurring in some phenomena dependent on thermal agitation. P. WEISS (Compt. rend., 1934, 198, 302—304).—The vals. of  $\zeta$  in the equation of state of fluids (cf. A., 1918, ii, 354); of the factor F (or  $T_1$ ) in the law of discontinuous distribution of Curie and of m.p. (cf. A., 1932, 449, 452); and of the temp. at which discontinuous increases occur in the resistance of Pt-black (cf. A., 1933, 893) are all expressible with fair accuracy by the terms of arithmetical progressions with common difference approx. 0.0465. No explanation is suggested. C. A. S.

Thermodynamic derivation of the Boltzmann equation. N. BARBULESCU (Bul. Soc. Române Fiz., 1933, 35, 69—73).—Theoretical. H. J. E.

Isothermals of helium at temperatures of 0°, 20°, and 100° and pressures from 5.5 to 16.5 atmospheres. W. H. KEESOM and J. J. M. VAN SANTEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 813—821).—The second virial coeffs. of Onnes' equation of state for He, deduced from p-v data, are  $B_{0^*} 0.5028 \times 10^{-3}$ ,  $B_{20^*} 0.4989 \times 10^{-3}$ , and  $B_{100^*} 0.4814 \times 10^{-3}$ , from which  $B_{100^*} - B_{0^*} = -0.0214 \times 10^{-3}$  and hence, in conjunction with  $\alpha_A 0.00366130$ , 0° abs.=  $-273.127^\circ$ . J. G. A. G.

Relation between the maximum vapour tensions in some organic series. I. E. LUCATU (Bul. Soc. Romane Fiz., 1933, 35, 127–128).—At fixed temp. between 0° and 130° the ratio of the saturation v.p. for neighbouring members in various homologous series (e.g., hydrocarbons, alcohols, or esters) is approx. const. It increases linearly with rise of temp. H. J. E.

Density discontinuities at the critical temperature. [Propylene and methyl ether.] C. A. WINKLER and O. MAASS (Canad. J. Res., 1933, 9, 613—629; cf. A., 1933, 1237).—With an improved technique it was found that in a vertical tube of either  $C_3H_6$  or Me<sub>2</sub>O a sharp discontinuity (I) of *d* persisted above the crit. temp. in the zone from which the meniscus vanished. (I) became sharper and its magnitude decreased as the ratio of the vol. of the container to the wt. of fluid increased. In general, (I) was not changed by stirring, but was eliminated by appropriate thermal treatment. The results are discussed. J. G. A. G.

Density of propylene in the liquid and vapour phases near the critical temperature. C. A. WINKLER and O. MAASS (Canad. J. Res., 1933, 9, 610-612; cf. A., 1933, 1105).—The data refer to the range 66-92°. J. G. A. G.

Barometric formula for real gases and its application near the critical point. R. RUEDY (Canad. J. Res., 1933, 9, 637-640).-Theoretical. From equations of state (e.g., van der Waals) it is shown that in a short column of fluid maintained throughout its length at the crit. temp. marked variations of d may exist, especially near the layer which is at the crit. d, and to obtain uniform d a temp. gradient must be applied. These phenomena are not necessarily inconsistent with the theory of the continuity of state (cf. A., 1933, 1237). With isotopes, e.g., Ne, of almost identical crit. temp., the concn. of heavier mols. tends to rise near the layer which is at the crit. point. Vals. of crit. temp. derived from experiments in closed tubes are not, in general, J. G. A. G. trustworthy.

Physical properties of compressed gases. IV. Entropies of nitrogen, carbon monoxide, and hydrogen. W. E. DEMING and (MRS.) L. S. DEMING (Physical Rev., 1934, [ii], 45, 109—113).— Previous work is extended (cf. A., 1932, 799) to the calculation of the change of S and abs. S along isotherms for the temp. range  $-75^{\circ}$  to 600° and pressure range 25—1200 atm. Full data for N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub> are tabulated and deviations from results for an ideal gas are discussed. N. M. B.

Entropy diagram of liquid helium. W. H. KEESOM and (MISS) A. P. KEESOM (Physica, 1934, 1, 161-166).—The diagram is described and discussed. H. J. E.

Specific volumes of saturated vapours. C. H. MEYERS (Bur. Stand. J. Res., 1933, 11, 691—701).—A formula is derived for the sp. vol. of a saturated vapour in terms of the v.p., sp. vol. of the liquid, and two empirical consts., one of which is the same for all the 23 substances tested. The formula holds for pressures up to one fourth of the crit. pressure. An equation of state, for a limited range, for superheated vapours is developed from this formula. J. W. S.

Thermal expansion of bismuth by X-ray measurements. A. H. JAY (Proc. Roy. Soc., 1934, A, 143, 465-472).—X-Ray measurements on the expansion of the Bi lattice from  $18.5^{\circ}$  to  $268^{\circ}$  have been made. The vals. are compared with those given by optical methods. No evidence is found of the discrepancy recorded by Goetz and Hergerrother (A., 1932, 681, 796), and the lattice expansion agrees with that of the specimen as a whole. The characteristics of the expansion curve are a steady expansion from 20° to 70°, a sudden rise between 70° and 80°, a linear expansion up to 240°, and a decrease above 250°. L. L. B. Glass. VIII. Coefficient of thermal expansion of boron trioxide. M. E. SPAGHT and G. S. PARKS (J. Physical Chem., 1934, 38, 103—110).— The cubical coeff. of thermal expansion for viscous liquid  $B_2O_3$  is > ten times that for the glassy state. Between these there is a state of transition extending over the temp. range 200—260°, approx. The form of the expansion coeff.-temp. curve in this region depends mainly on the extent of annealing during the initial formation of the glass. M. S. B.

Density and viscosity of titanium tetrachloride. T. SAGAWA (Sci. Rep. Tõhoku, 1933, 22, 959—971).— The viscosity has been measured at 20° and 25° (0.007921 and 0.007458 e.g.s. unit, respectively), and d in the range  $-18\cdot1^{\circ}$  to 109.6°. F. L. U.

Viscosity of air at 200 atmospheres pressure. A. G. NASINI and G. PASTONESI (Gazzetta, 1933, 63, 821-832).—The viscosity  $\eta$  of air has been determined at 14° and pressures (p) up to 200 atm. in a new form of apparatus. The error is  $\geq 0.5\%$ .  $\eta = [185.6+0.295(p-70)] \times 10^{-6}$ . H. F. G.

Thermal conductivity of gaseous mixtures. O. RIECHEMEIER, H. SENFTLEBEN, and H. PASTORFF (Ann. Physik, 1934, [v], 19, 218–224).—The thermal conductivity (I) of pure H<sub>2</sub>O vapour is increased by irradiation with  $\lambda 2537$  Å., when some of the H<sub>2</sub>O is dissociated. (I) of the H<sub>2</sub> in the dissociated mixture is < that of H<sub>2</sub>O vapour at the same pressure. It is thus not possible to determine (I) of a mixture from a knowledge of the partial pressures of the constituents. A. J. M.

Viscosity, heat conductivity, and diffusion in gas mixtures. XXIV. Viscosity laws in binary mixtures. M. TRAUTZ (Ann. Physik, 1933, [v], 18, 833-866).—Theoretical. W. R. A.

**Density of aqueous hydrofluoric acid.** L. DOMANGE (Compt. rend., 1934, **198**, 469-471).--New vals. have been obtained for solutions with the use of a bakelite container. The wt.-% and  $d^{15}$  vals. recorded are: 5.06, 1.017; 10.1, 1.035; 15.3, 1.054; 20.25, 1.072; 26.4, 1.097; 29.8, 1.1085; 36.4, 1.134; 39.9, 1.149; 42.4, 1.1595; 47.3, 1.179; 53.8, 1.205 (cf. B., 1898, 578; A., 1902, ii, 287). C. A. S.

Specific gravity of acetone-water mixtures. W. YOUNG (J.S.C.I., 1933, 52, 449–450T).—COMe<sub>2</sub>. purified by repeated drying and distillation had b.p.  $56\cdot25^{\circ}/760 \text{ mm.}, d_4^{\circ\circ} 0.79061$ . Further purification by the NaI method followed by drying and distillation gave a product of b.p.  $56\cdot25^{\circ}\pm0.05/760 \text{ mm.}, d_4^{\circ\circ}$ 0.79053. A table gives the d of COMe<sub>2</sub>-H<sub>2</sub>O mixtures from 0 to 100% COMe<sub>2</sub>.

Densities of molten inorganic nitrate mixtures. K. LAYBOURN and W. M. MADGIN (J.C.S., 1934, 1—7).—The densities of various molten binary mixtures of K, Na, Sr, Ba, and Pb nitrates and of ternary mixtures of K, Ba, and Sr nitrates have been determined at a no. of temp. to an accuracy of  $\pm 0.001$ . The T-d and sp. vol.-composition curves are almost linear. D. R. D.

F.p. of mixtures of waters HO and HO. V. K. LA MER, W. C. EICHELBERGER, and H. C. UREY (J. Amer. Chem. Soc., 1934, 56, 248-249).—Vals. of f.p. and d are recorded. F.p. is a linear function of d

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up to 20% of  $H_2^*O$ , but a deviation is perceptible at 40%. E. S. H.

Partial pressures of water in equilibrium with aqueous solutions of sulphuric acid. E. M. COLLINS (J. Physical Chem., 1933, 37, 1191–1203).— An isoteniscope is described which permits the measurement of v.p. of solutions without change in the conen. This has been used to determine aq. partial pressures for 0-70% H<sub>2</sub>SO<sub>4</sub> at  $20-140^{\circ}$ . The heats of vaporisation of H<sub>2</sub>O from solutions of the same range of conen. and temp. have been calc. M. S. B.

Azeotropic mixtures in the system hydrogen chloride-water-chlorobenzene-phenol. W. PRAHL and W. MATHES (Angew. Chem., 1934, 47, 11-13).—The following const.-boiling mixtures are recorded :  $H_2O$  90.79%, PhOH 9.21% (b.p. 99.57°); HCl 5.3%,  $H_2O$  20.2%, PhOH 9.21% (b.p. 96.90°); HCl 15.8%,  $H_2O$  64.8%, PhOH 19.4% (b.p. 107.3°). Apart from these and the binary mixtures of HCl and PhCl with  $H_2O$ , there are no other azeotropic mixtures in the system HCl-H<sub>2</sub>O-PhCl-PhOH. The application of these results to the separation of PhOH manufactured by catalytic hydrolysis of PhCl is discussed. H. F. G.

B.-p. curves of systems  $TiCl_4-CCl_4$ ,  $TiCl_4-SiCl_4$ , and  $TiCl_4-SnCl_4$ . N. NASU (Sci. Rep. Tohoku, 1933, 22, 987-996, and Bull. Chem. Soc. Japan, 1933, 8, 392-399; cf. A., 1933, 1012).-B.p.-composition curves are of simple type for all three systems. F. L. U.

Vapour pressure of fused mixtures of aluminium and sodium chlorides. V. A. PLOTNIKOV, N. S. FORTUNATOV, and V. S. GALINKER (J. Appl. Chem. Russ., 1933, 6, 1025–1028).—Data are recorded for 700°. R. T.

Electrical conductivity and related properties in binary aggregates. K. LICHTENECKER (Z. Elektrochem., 1934, 40, 11–14).—A discussion of the applicability of the logarithmic mixture law.

H. J. E.

Structure of gold-copper alloys. W. BRONEW-SKI and K. WESOLOWSKI (Compt. rend., 1934, 198, 370—372).—Curves relating composition to m.p., electric conductivity, temp. coeff. of resistance, thermoelectric power and its temp. coeff., and elongation all indicate that slowly cooled alloys contain AuCu and AuCu<sub>3</sub>, both of which form solid solutions. Mixtures occur only with 62—65.5% Au in which AuCu has a martensitic and other Au-Cu alloys have a polyhedric structure. Alloys cooled suddenly from 650° give no indication of either compound. There is no evidence for the existence of Au<sub>2</sub>Cu<sub>3</sub> (cf. A., 1931, 1224, 1364; 1932, 989). C. A. S.

X-Ray analysis of the crystal structure of the thallium-tin alloys. H. J. C. IRETON, J. P. BLEWETT, and J. F. ALLEN (Canad. J. Res., 1933, 9, 415–418).—The Sn lattice const. shows a max. at the eutectic point. Addition of Sn to Tl induces the change  $\alpha$ -Tl  $\longrightarrow \beta$ -Tl (cf. A., 1928, 1181). Unusual superconductivity phenomena have been observed at low temp. R. S.

System copper-lead. M. NISHIKAWA (Suiyokaishi, 1933, 8, 239-243).—The system has been studied by thermal and microscopical methods. At 13-48%Cu a monotectic reaction, liquid+Cu  $\Longrightarrow$  liquid, occurs at 957°. CH. ABS.

Rontgenographic determination of the phase boundaries in the copper-zinc diagram. A. JOHANSSON and A. WESTGREN (Metallwirt., 1933, 12, 385-387; Chem. Zentr., 1933, ii, 1747).—The results in general confirm those of Owen and Pickup (A., 1932, 990) except where the latter differ from those obtained microscopically. A. A. E.

Mechanism of age-hardening of silver-copper single crystals. P. WIEST (Z. Metallk., 1933, 25, 238-240).—Measurements of the hardness (H) and lattice parameter (a) of 5% Ag-Cu single crystals during ageing at 350-470° after quenching from 780° show that the ageing process passes through three stages, in all of which H first increases and then decreases with time of ageing. In the first stage a remains unchanged, in the second a slight broadening of the interference points in the X-ray photograph occurs, and in the third this becomes more marked and a large decrease in a takes place due to the rejection of the dissolved Ag atoms from the Cu lattice. The increase of H in the first two stages is attributed to at. movements preparatory to pptn. A. R. P.

Behaviour of graphitic silicon in aluminium at high temperatures. C. SCHAARWACHTER (Z. Metallk., 1933, 25, 250–251).—Owing to its slow rate of diffusion graphitic Si does not dissolve in Al at temp.  $< 540^{\circ}$ , even after prolonged annealing, but above the eutectic temp. (577°) it dissolves rapidly. A. R. P.

Active oxides. LXIX. Variation of the magnetic properties of mixtures of ferric and beryllium oxides on heating. G. F. HUTTIG and H. KITTEL (Gazzetta, 1933, 63, 833—844).—Neither the variations of susceptibility nor the X-ray diagrams afford any evidence of the formation of a compound when an equimol. mixture of BeO and Fe<sub>2</sub>O<sub>3</sub> is heated (for 200 hr.) at temp. up to 1000°. The susceptibility of a CaO-Fe<sub>2</sub>O<sub>3</sub> mixture passes through a max. at about 400°, and a min. at about 475°, and with further rise of temp. increases very rapidly. H. F. G.

Dia- and para-magnetism in metallic mixed crystal series. II. E. VOGT and H. KRUEGER. III. Atomic magnetic moments of the transition metals in dilute mixed crystal solutions. E. VOGT (Ann. Physik, 1933, [v], 18, 755-770, 771-790).—II. The magnetism of Au-Ni mixed crystals containing 1, 2, 4, and 6% Ni has been examined. Ni occurs in the Au lattice up to the solubility limit, with a paramagnetism which is const. between 200° and 300° abs., and equal to  $+380 \times 10^{-6}$  per g.-atom of Ni. Below 200° abs. there is an increase in the paramagnetism, the rate of which increases with falling temp. If this is ascribed to Ni<sup>+</sup> ions, these form at the most 1% of the dissolved Ni. The superstructure and magnetism of the alloys CuPd, Cu<sub>3</sub>Pd, and Cu<sub>3</sub>Pt after various heat-treatments were also examined.

III. The magnetic properties of mixed crystal series of the transition metals dissolved in Cu, Ag, and Au

have been examined at various temp. The strong interaction between the ionic moments of the transition metals gives rise to ferromagnetism or causes the effect of temp. on paramagnetism to be very small. When, however, the transition metals are dissolved in the diamagnetic noble metals to form dil. mixed crystals the presence of free, or almost free, moments is found. The Curie-Weiss law for paramagnetism is obeyed only when the dissolved transition metal has a d-shell of < 10 electrons. Diamagnetism is shown with Pd alloys and with Cu-Pt; in other cases the addition of foreign metal produces little or no change in the effect of temp. on paramagnetism. Ni dissolved in Au shows an increase in paramagnetism at low temp., and the results agree with the fact that at  $-185^{\circ} < 1\%$  of the Ni exists as Ni<sup>+</sup>. The results of Linde, which show that the at. resistance of the noble metals is increased by addition of the transition metals, are in agreement with the magnetic observations. A. J. M.

Lattice dimensions of some solid solutions in the system MgO-Al<sub>2</sub>O<sub>3</sub>. G. L. CLARK, E. E. Howe, and A. E. BADGER (J. Amer. Ceram. Soc., 1934, 17, 7-8).-MgO, Al<sub>2</sub>O<sub>3</sub> (I) has  $a_0 \otimes 0.64 \pm 0.002$  Å., and for solid solutions of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in (I) this decreases progressively with increase in Al<sub>2</sub>O<sub>3</sub> content. MgO does not form a solid solution and therefore does not distort the lattice. Attempts to ppt. (I) by mixing solutions of K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and Mg(OH)<sub>2</sub> were unsuccessful. J. A. S.

Approximate composition of the lowest fusing mixture of barium oxide, magnesium oxide, and silica. C. H. TURNER (J. Amer. Ceram. Soc., 1934, 17, 14—15).—The mixture with the lowest softening point (pyrometric cone equiv. 1115°) corresponds approx. with BaO 46, MgO 8, SiO<sub>2</sub> 46%. J. A. S.

Does the change in lattice constant in mixed crystal formation depend on particle size? E. SCHMID and G. SIEBEL (Metallwirt., 1932, 11, 685; Chem. Zentr., 1933, i, 1733).—Data for Al-Mg, Zn-Mg, and Mg-Al alloys do not support a particle-size effect, whilst a Cu-Al alloy (5% Cu) shows no difference between single and poly-crystals. The effect described by Wiest (A., 1932, 330) for Ag-Cu alloys could not be observed. L. S. T.

Does the change in lattice constant in mixed crystal formation depend on particle size? U. DEHLINGER and P. WIEST (Metallwirt., 1933, 12, 2-3; Chem. Zentr., 1933, i, 1733; cf. preceding abstract).—The difference in lattice consts. (I) of single and poly-crystals of Ag-Cu is confirmed by additional data; it exists also for the system Ag-Au (II). Further, (I) are different for cast and recryst. particles in (II). L. S. T.

Foreign material which added to a solution is able to modify the form of crystals of the solute. L. ROYER (Compt. rend., 1934, 198, 185—187; cf. A., 1932, 682; 1933, 369).—The spacing characteristics of the added substance must be related to those of the solute if the cryst. form of the latter is to be affected. C. A. S.

Separation and rate of growth of crystals of inorganic salts in extracts and other colloidal media of so-called second consistency. H. KUNZ-KRAUSE (Apoth-Ztg., 1933, 48, 57–60; Chem. Zentr., 1933, i, 1732). L. S. T.

Crystallisation of eutectic mixtures. G. TAM-MANN (Z. Metallk., 1933, 25, 236-238).-The linear rate of crystallisation (R) of eutectic mixtures (I)depends on the degree of undercooling as is the case with homogeneous melts (II). In (II) the flow of heat from the ends of the crystal filaments (F) determines R, whereas in (I) the separation of the con-stituents into individual F, which proceeds by diffusion, affects R. By increasing R the thickness of the F may be decreased until they cannot be detected by the microscope. Thus, even with a high R, the relatively slow rate of diffusion is sufficient to cause separation of the constituents, and therefore the max. val. of R for (I) must be much < that of either of the constituents. This has been proved for the NHPhAc-OH·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub> and azobenzene-benzil eutectics. A. R. P.

Accelerated and retarded diffusion in aqueous solution. J. W. MCBAIN and C. R. DAWSON (J. Amer. Chem. Soc., 1934, 56, 52-56).—The mutual influence of ions in altering the usual rates of diffusion is illustrated by experiments on the KCl-HCl system. Very high rates of diffusion were found for all constituents when glycine diffused against HCl.

E. S. H.

Diffusion of water in a zeolite crystal. A. TISELIUS (Nature, 1934, 133, 212–213).—The diffusion of  $H_2O$  in heulandite has been determined by observation of the change in optical properties of dehydrated crystals in an atm. of  $H_2O$  vapour.

L. S. T.

Diffusion of potassium into glass. B. VON LENGYEL (Z. physikal. Chem., 1933, 167, 295-311).— The diffusion of K from various molten K salts into glass has been studied. Irrespective of the Na content of the glass, the amount of K diffusing into the glass and the resulting increase, R, in the resistance of the glass are both proportional to the square root of the time of diffusion, t. This result may be deduced theoretically, assuming the validity of Fick's law, and shows the mobilities of Na' and K' in the glass to be independent of the concn. The temp. coeff. of  $R/\sqrt{t}$  is small and negative, which agrees with theoretical deductions. No diffusion occurs from K<sub>2</sub>SO<sub>4</sub> dissolved in conc. H<sub>2</sub>SO<sub>4</sub>. R. C.

Exchange of heavy hydrogen atoms between water and molecular hydrogen. K. F. BON-HOEFFER and K. W. RUMMEL (Naturwiss., 1934, 22, 45; cf. A., 1933, 1233; this vol., 37).—Heavy  $H_2O$ and ordinary  $H_2$  were shaken together, under pressure, in the presence of Pt-black. The equilibrium attained agrees with theory. A. J. M.

Solubility of hydrogen in water at 0°, 50°, 75°, and 100° from 25 to 1000 atmospheres. R. WIEBE and V. L. GADDY (J. Amer. Chem. Soc., 1934, 56, 76—79).—Data for the range indicated show a min. similar to that of  $N_2$  in  $H_2O$ . E. S. H.

Solubility equation of hydrated salts. J. PERREU (Compt. rend., 1934, 198, 172-174; cf. A., 1889, 752).—Evidence for certain relations shown by hydrated salts is discussed in reference to the data for  $MnCl_2, 4H_2O$  and  $Na_2S_2O_3, 5H_2O$ . C. A. S.

Aqueous solubility of salts at high temperatures. II. Ternary system Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub>-H<sub>2</sub>O from 100° to 200°. W. F. WALDECK, G. LYNN, and A. E. HILL (J. Amer. Chem. Soc., 1934, 56, 43-47; cf. A., 1932, 457).—Four solid phases are involved : (1) Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, (2) NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, 2H<sub>2</sub>O (stable up to  $195\pm5^{\circ}$ ), (3) 3NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> (stable over this temp. range), (4) NaHCO<sub>3</sub>. The solubility of NaHCO<sub>3</sub> under the natural pressure of the system increases from  $19\cdot1\pm0\cdot2\%$  at 100° to  $43\cdot0\pm1\cdot0$  at 200°. E. S. H.

Solubility of silver bromate in mixtures of alcohols and water. E. W. NEUMANN (J. Amer. Chem. Soc., 1934, 56, 28–29).—The solubilities of AgBrO<sub>3</sub> in binary mixtures of MeOH, EtOH,  $Pr^{\circ}OH$ , and  $Pr^{\beta}OH$  with H<sub>2</sub>O have been determined at 25°. The data are incompatible with the Born electrostatic formula. E. S. H.

Solubility of inorganic salts in liquid ammonia at  $-33.9^{\circ}$ . W. C. JOHNSON and O. F. KRUMBOLTZ (Z. physikal. Chem., 1933, 167, 249–259).—Solubilities of alkali salts have been determined with a special apparatus permitting direct measurement. With the more sol. salts the results are reproducible to 0.5%. R. C.

Solubility of glucose in methyl alcohol. J. GILLIS and H. N. NACHTERGAELE (Rec. trav. chim., 1933, 53, 31–33).—The solubility of glucose in MeOH has been measured from 0° to 128.5°. The transition temp.  $S_{aabh} \longrightarrow S_{\beta abh} + L$  is 108°.

H. S. P.

Solubility of acet-o-toluidide in various solvents. J. L. HALL, A. R. COLLATT, and C. L. LAZZELL (J. Physical Chem., 1933, 37, 1087—1094).— The solubility of  $o \cdot C_6 H_4 Me \cdot NHAc$  (I) in MeOH, EtOH, Pr<sup>o</sup>OH, Pr<sup>o</sup>OH, Bu<sup>o</sup>OH, Bu<sup>o</sup>OH, COMe<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, Et<sub>2</sub>O, and H<sub>2</sub>O has been determined by the synthetic method between 25° and the m.p. (110·3°). With H<sub>2</sub>O two liquid phases are obtained over a wide range of temp. and a triple point is shown at approx. 79·6°. According to the solubility data the mol. heat of fusion of (I) is approx. 5700 g.-cal. From this val. the ideal solubility curve has been plotted.

M. S. B.

Solubility of trinitrotrimethylenetriamine. T. URBAŃSKI and B. KWIATKOWSKI (Rocz. Chem., 1933, 13, 585—587).—The solubility in MeOH, EtOH, *iso*- $C_5H_{11}$ ·OH, COMe<sub>2</sub>, Et<sub>2</sub>O, CCl<sub>4</sub>,  $C_6H_6$ , and PhMe has been determined between 0° and the b.p. of the solvent. R. T.

Solubility of pentaerythritol tetranitrate. T. URBAŃSKI and B. KWIATKOWSKI (Rocz. Chem., 1933, 13, 740-741).—Data are given for MeOH, EtOH,  $Et_2O$ ,  $COMe_2$ ,  $C_6H_6$ , and PhMe, between 0° and the b.p. R. T.

Validity of mass law. II. Determination of solubility of radium sulphate in sodium sulphate solutions and in water. B. NIKITIN and P. TOLMATSCHEV (Z. physikal. Chem., 1933, 167, 260—272; cf. A., 1932, 223).—The solubility at 20° of RaSO<sub>4</sub> in  $H_2O$  and in 10<sup>-4</sup> to 10<sup>-2</sup>N-Na<sub>2</sub>SO<sub>4</sub> shows that in all these

solutions the solubility product in terms of activities of RaSO<sub>4</sub> has approx. the same val.,  $4 \cdot 25 \times 10^{-11}$ . The solubility of RaSO<sub>4</sub> is  $2 \cdot 1 \times 10^{-4}$  g. per 100 c.c. of H<sub>2</sub>O. R. C.

Influence of conditions of precipitation of zinc sulphide on its solubility in hydrochloric acid. T. KROKOWSKI (Rocz. Chem., 1933, 13, 561–568).— The solubility of ZnS (I) increases in the order : (I) pptd. by  $H_2S$  from aq.  $ZnSO_4$  (II) at  $75^\circ <$  at  $25^\circ <$ from aq.  $Zn(OAc)_2 <$  (I) pptd. by  $(NH_4)_2S$  from (II) <from ammoniacal (II). R. T.

Diffusion of hydrogen through palladium. V. LOMBARD and C. EICHNER (Bull. Soc. chim., 1933, [iv]. 53, 1176—1206; cf. A., 1933, 218).—The diffusion of H<sub>2</sub> through heated Pd for pressures varying from 1 atm. to a few mm. into a vac. has been shown in three cases to be expressed by the formula D (rate of diffusion)= $K.P^{0.56}$  and in a fourth by  $D=K.P^{0.5}$  at 493°, 470°, and 617°. The latter is the formula found for other metals. For the same sample the rate of diffusion from a high to a low pressure is given by  $D=K(P^{0.5}-p^{0.5})$ . The influence of temp. on the normal sp. rate of diffusion,  $D_{SN}$ , for 350—850° is expressed by  $D_{SN}=20.73T^{0.5}e^{-2022/T}$  ( $D_{SN}$  is the val. of Dfor 1 mm. thickness of Pd). The permeability of Pd is strongly influenced by its state of purity.

M. S. B. Measurement of diffusion velocities in dissolution of gases in solids. H. DÜNWALD and C. WAGNER (Z. physikal. Chem., 1934, B, 24, 53-58).— The formulæ used are reviewed. R. C.

Chemisorption on charcoal. II. Acid constituent of charcoal. A. KING (J.C.S., 1934, 22-26; cf. A., 1933, 898). - The quantity of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> formed is independent of the pressure of O<sub>2</sub> or time of treatment, and proportional to the mass of charcoal. Repetition of the treatment on the same C without drying the C yields less  $H_2C_2O_4$ , but, if dried in air at 120°, the normal yield is obtained. No  $H_2C_2O_4$  is produced when dried org. liquids replace H<sub>2</sub>O, but with 5% or more  $H_2O$  in EtOH the yield is the same as with pure  $H_2O$ . Activated birch C gives a slightly higher yield. Intensively dried C saturated with dry O<sub>2</sub> yields almost pure CO on heating in vac., the greater part being evolved at 370°. Such C yields little  $H_2C_2O_4$  with air-free  $H_2O$ , and after shaking with dil.  $H_2SO_4$ , the latter gives no coloration with starch-KI solution. It is suggested that O2 is adsorbed in two different ways. D. R. D.

Adsorption of carbon tetrachloride on carbon and the activation of carbon. W. LEMCKE and U. HOFMANN (Angew. Chem., 1934, 47, 37–43).—The adsorption isotherms for CCl<sub>4</sub> on activated carbons, lampblacks, graphites, and CO carbon have been determined with an automatic apparatus. Capillary condensation occurs only when the air is nearly saturated with CCl<sub>4</sub>; at lower pressures a two-dimensional film is formed. The effect of activation on the adsorption of CCl<sub>4</sub> is parallel to its effect on the adsorption of methylene-blue and PhOH from aq. solution, and the increase is due to a reduction in the crystal size. Adsorption by Ceylon graphite is less after activation, which smooths the surface and destroys the smaller sizes. A. G. Sorption of vapours by activated, highly evacuated sugar charcoal over long periods of time. J. W. MCBAIN and R. F. SESSIONS (J. Amer. Chem. Soc., 1934, 56, 1—4).—Sorption experiments with 10 vapours show that, when evacuation of the C is adequate, sorption is nearly complete at infinitesimal pressures. Equilibria are established rapidly and then remain almost const. for periods of 4-5years. E. S. H.

Absorption of gases at low pressure by active carbon and silica gel. O. WINKLER (Z. tech. Physik, 1933, 14, 319–332; Chem. Zentr., 1933, ii, 1853).—Measurements have been made with N<sub>2</sub> and H<sub>2</sub> at  $10^{-2}$  and  $10^{-5}$  mm. and at the temp. of liquid O<sub>2</sub> or N<sub>2</sub>. A. A. E.

Adsorption. Relation of water held by charcoal at zero pressure to the ash content. L. J. BURRAGE (J. Physical Chem., 1933, 37, 1095—1101). —The ash content of a no. of different charcoals has been compared with the amounts of  $H_2O$  held at zero pressure. To explain this and other data it is suggested that the ash plays no part in the retention of the  $H_2O$  at zero pressure, but that the latter is held in a quasi-chemical manner by the active centres and  $C_zO_y$  complex. M. S. B.

Adsorption of hydrogen atoms and iodine on calcium fluoride. J. H. DE BOER and J. J. LEHR (Z. physikal. Chem., 1933, B, 24, 98–102).—Under favourable conditions thin vac.-sublimed films of  $CaF_2$ can adsorb twice as many H atoms as  $I_2$  mols. With larger amounts of  $CaF_2$  the adsorbability of H atoms seems to decline. Owing to the lamellar structure of thicker films (cf. A., 1933, 672) it is possible that the inner parts of the salt surface become inaccessible to H atoms but not to other gases. R. C.

Adsorption of neon on glass at liquid hydrogen temperatures. W. H. KEESOM and G. SCHMIDT (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 825-832).—The fraction of wall covered, q, increases regularly with increasing pressure, p, until at about the saturated v.p.,  $p_s$ , a complete unimol. layer is produced. The adsorption isotherms in the range  $14\cdot45-20\cdot28^\circ$  abs. are given, approx., by  $q^3=p/$  $[0\cdot7(p_s-p)+p]$ . J. G. A. G.

Adsorption of helium on glass at liquid helium temperatures. W. H. KEESOM and G. SCHMIDT (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 832—835).—In the range  $3\cdot 56-1\cdot 13^{\circ}$  abs., the adsorption isotherms of He on glass are given by  $q^4=p/[0\cdot 26(p_s-p)+p]$ , where q is the fraction of wall covered at pressure p and  $p_s$  is the saturated v.p. Below  $0\cdot 8^{\circ}$  abs. the error in the temp. determined by the He thermometer is liable to be > 1% owing to adsorption; this is not adequately diminished by previously forming a unimol. layer of Ne.

J. G. A. G.

Thermodynamic basis of adsorption of gas mixtures. I. KRITSCHEVSKI (Z. anorg. Chem., 1934, 216, 253—262).—Three-component systems (two gases+adsorbent) are treated. F. L. U.

Base-exchange equilibria in clays. C. E. MARSHALL and R. S. GUPTA (J.S.C.I., 1933, 52, 433-443T).—The various methods of formulation of base-

exchange reactions are discussed. Putnam clay (beidellite) and bentonite (montmorillonite) have been examined in relation to the systems : Na clay+KCl; Na  $clay+CaCl_2$ ; Na  $clay+AgNO_3$ ; H  $clay+AgNO_3$ ; H clay+Tl<sub>2</sub>SO<sub>4</sub>. The results show little agreement with the equations proposed. In the Na clay+AgNO, and H clay+AgNO3 systems electrometric measurements of Ag' activities were made and the dissociation of Ag clays in absence of electrolyte was studied. It is shown that bentonite has a comparatively high dissociation. In the H clay+Tl<sub>2</sub>SO<sub>4</sub> systems electrometric measurements of both H<sup>+</sup> and Tl<sup>+</sup> were made. The results confirm those of the Ag' measurements. It is inferred that the substitution of ionic activities for concns. does not suffice to make valid the formulations of base-exchange reactions so far proposed. The dissociation of clays is shown to present certain important anomalies, when compared with ordinary electrolytes.

Adsorption of copper sulphate by sphalerite and its relation to flotation. S. F. RAVITZ and W. A. WALL (J. Physical Chem., 1934, 38, 13-18).-With sphalerite (I) particles larger than  $37 \mu$  the amount of CuSO<sub>4</sub> giving the best flotation recovery is that required to form a unimol. film of CuS. For smaller particles it is less. This probably depends on the fact that the wt. of a particle decreases more rapidly than its surface area. The amounts of Cu adsorbed by (I) of various particle size from a 0.02M. CuSO<sub>4</sub> solution are equiv. to surface films of CuS many mols. thick. This layer decreases in thickness as the particles become smaller. The results are explained by the mosaic theory of the structure of crystals and agree with the assumption that the unit blocks of (I) are approx.  $0.37 \ \mu$  in length. M. S. B.

Capillary activity and association of aqueous solutions. H. CASSEL (Naturwiss., 1934, 22, 60).— Measurements of adsorption at the interface water/air, by the bubble method, give vals. for solutions of  $p-C_6H_4Me\cdot NH_2$  and isoamyl alcohol which are about double those obtained by calculation from the Gibbs equation. The activity of the solute does not correspond with the simple osmotic equation. The effect of association in the aq. phase on the Gibbs equation is considered. A. J. M.

Interfacial tension at the surface of two nonmiscible liquids. III. C. BELCOT (Bul. Soc. Romane Fiz., 1933, 35, 119–125; cf. A., 1928, 472).— The author's drop method has been applied to measure the surface tension of aq. HCl. The vals. are correlated with the ionic concus. The surface tension method can be used to measure salt hydrolysis (e.g., for PhONa or NaHCO<sub>3</sub>). H. J. E.

Surface tension at the surface of two nonmiscible liquids. IV. C. BELCOT (Bul. Soc. Române Fiz., 1933, 35, 157—159; see preceding abstract).—Theoretical. From a study of aq. solutions of  $NH_3$  and KOH, evidence is adduced that the activity coeffs. are not equal to the degree of ionisation except at low conces. H. S. P.

Effect of dissolved electrolytes on the boundary tension of water. W. G. EVERSOLE and D. S. DEDRICK (J. Physical Chem., 1933, 37, 1205-1214).-- An apparatus for the very accurate measurement of interfacial tensions (I) by the drop vol. method is described. At low conces. NaOAc and  $HCO_2Na$  tend to lower (I) of oil-H<sub>2</sub>O systems, but this is probably due to the formation of free acid by hydrolysis. At higher concess. (I) is raised and this latter effect has been explained on the basis of the Langmuir theory of mol. orientation and the increased interionic attraction in the interface due to the dielectric const. gradient in the interfacial layer. The effect of strong electrolytes in general on boundary tension may be similarly explained. M. S. B.

Effect of sodium acetate on the interfacial tension of the benzene-water system at 40°. D. S. DEDRICK and M. H. HANSON (J. Physical Chem., 1933, 37, 1215—1221).—A very high conen. of NaOAc in the system  $C_6H_6-H_2O$  produces a secondary lowering of the tension not previously observed (cf. preceding abstract). The effect is considered to be due to the tendency of the electrolyte as a whole to pass through the boundary layer into the non-aq. phase as doublets or undissociated mols. M. S. B.

Unimolecular films of polyesters. S. A. Moss, jun. (J. Amer. Chem. Soc., 1934, 56, 41-43).—Polymeric acid and neutral ethylene succinates, when dissolved in CHCl<sub>3</sub> and spread on 0.01*N*-HCl, form stable unimol. films, which are similar to vapourexpanded films of fatty acid esters. The mol. chains are flexible and can be packed closely before immersion on compression occurs. The closeness of approach is 5.85 Å. E. S. H.

Spreading of ovalburnin. G. T. PHILIPPI (Rec. trav. chim., 1933, 53, 81–90).—The spreading of ovalburnin has been studied in relation to the potential differences at an air-H<sub>2</sub>O interface. For certain  $p_{\rm H}$  ranges a coherent unimol. layer of surface 1.3 sq. m. per mg. is formed, but for others a compressed film of surface 0.7 sq. m. per mg. is obtained. In the latter the polypeptide backbones lie tightly packed in the surface, whilst in the coherent films (I) also lie tightly packed in the surface. H. S. P.

Spreading of insulin and of zein. E. GORTER and J. VAN ORMONDT (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 922—926).—Max. spreading is found at the isoelectric point. C. W. G.

Origin of osmotic pressure and its theoretical calculation. K. FREDENHAGEN (Z. Physik, 1933, 87, 62-77).—The kinetic conception of osmotic pressure is criticised, and shown to be self-contradictory. Solvation of the solute mols. is supposed to be the primary cause of osmotic pressure. A. B. D. C.

Microcryoscopic measurements by Rast's method. II. Cryoscopic constant of retene. T. W. JEZIERSKI (Rocz. Chem., 1933, 13, 720—724).— Retene has m.p. 100.5°; the mol. depression for a no. of substances is 12.16. Certain modifications of Rast's method are proposed. R. T.

[Cryoscopic] determination of hydration of ions of calcium chloride. F. BOURION and E. ROUYER (Compt. rend., 1934, 198, 175–176; cf. A., 1933, 777).—The hydration of the ions in 0.5*M*- and 0.25M-CaCl<sub>2</sub> corresponds with CaCl<sub>2</sub>,27H<sub>2</sub>O and CaCl<sub>2</sub>,30.6H<sub>2</sub>O, respectively. C. A. S.

Structure of arginine in aqueous solution. G. DEVOTO (Z. physiol. Chem., 1933, 222, 227–228).— The dielectric coeff. of d-arginine (+62) indicates that it is  $\delta$ -polar in aq. solution. J. H. B.

Apparent molecular volume of dissolved electrolytes. II. Pressure coefficient of apparent molecular volume. W. GEFFCKEN (Z. physikal. Chem., 1933, 167, 240–244).—The relation between apparent mol. compressibility,  $\beta$ , and concn. pointed out by Gucker (A., 1933, 901) is derived theoretically. The order of magnitude of  $\beta$  at infinite dilution may also be calc. R. C.

Influence of concentration on the compressions of aqueous solutions of certain sulphates. Representation of the compressions of aqueous solutions as a function of pressure. R. E. GIBSON (J. Amer. Chem. Soc., 1934, 56, 4-14).-Compressions of aq. solutions of the sulphates of Li, Na, Cs, Mg, Zn, Cd, Be, NH<sub>4</sub>, Cu, Ce<sup>III</sup>, and H have been determined over a pressure range of 1-1000 bars and over the entire range of possible concns. The bulk compressions of solutions of the same mol. concn. are approx. equal, when the sulphates are not greatly hydrolysed. A deviation function, A, giving the difference between the sp. compression of H<sub>2</sub>O alone and  $H_2O$  in any solution is expressed by A = am + $bm^{32}$ , where m is the mol. concn. and a and b are consts., which vary with the solute. The sp. compressions of H<sub>2</sub>O and aq. solutions are discussed as a function of pressure. E. S. H.

Polarimetric examination of complex ferritartrates. PARISELLE and DELSAL (Compt. rend., 1934, 198, 83–85).—Polarimetric observations indicate the formation of the compounds :  $H[C_4H_2O_6Fe]$ , which is pptd. as an ochre-coloured powder in neutral solution;  $Na[C_4H_2O_6Fe]$ ;  $Fe[C_4H_5O_6]_3$ ;  $Fe[C_4H_4O_6Na]_3$ ;  $Fe[C_4H_3O_6Na_2]_3$ ;  $Fe[C_4H_4O_6Na]_3$ ; and  $H[C_4H_2O_6Fe]$ . C. A. S.

Brownian movement according to Fermi statistics. M. SATÔ (Z. Physik, 1933, 86, 667— 674).—Theoretical. A. B. D. C.

Action of electric field on stratified diffusion of alkali carbonates in gelatin. (MLLE.) S. VEL. (Compt. rend., 1934, **198**, 258–260; cf. A., 1929, 1382; 1933, 224).—The rings formed by a drop of aq.  $K_2CO_3$  placed on a sheet of gelatin some 10 cm. sq., when subjected to an electric field, move towards the anode and the rings on the cathode side gradually disappear. The effect is due to the action of the field on both the gelatin and the electrolyte, and varies with the nature of the latter. C. A. S.

Congruence of colloid correlation principle and a recognised relationship. S. C. BLACKTIN (Chem. and Ind., 1934, 64-65).—Theoretical. The increased freedom of disperse particles on rarefaction of a gaseous dispersion medium is compared with the relation between mean free path and life-tendency of particle size comprehended under the colloid correlation principle. E. S. H.

New theory of ferric oxide hydrosols. W. F. FAIR, jun. (J. Physical Chem., 1934, 38, 19-34).-

The purities of Fe hydrosols at incipient pptn., as measured by the ratio Fe/equiv. anion, are in agreement with the hydrolytic definition of sols, but the val. for weak acids is not much > 1, whilst for strong acids it may be 20—30. A chemical theory of sol pptn., based on the solubility product concept, is developed mathematically and shown to be supported by experimental data. The results are in agreement with the chemical complex theory of hydrosols.

M. S. B.

Colloidal properties of coconut milk. A. CLEMENTE and M. VILLACORTE (Univ. Philippines Nat. Appl. Sci. Bull., 1933, 3, 7—10).—The fresh milk is an emulsion of coconut oil (I) in  $H_2O$ ; the emulsifying agents are colloidally dispersed proteins, adsorbed at the oil- $H_2O$  interface, and sugar, chieffy dissolved in the aq. phase. The average diam. of the oil globules is 0.72  $\mu$ . The surface tension of the fresh milk is about 46.65 dynes per cm. Starch or gelatin coagulates the emulsion. Pure (I) can be extracted from the milk by a centrifugal method. CH. ABS.

Coagulation of colloids. VI. Viscosity variations during coagulation. S. S. JOSHI and T. M. MENON (J. Indian Chem. Soc., 1933, 10, 599— 609; cf. A., 1933, 1011).—Rates of change of viscosity of  $As_2S_3$  sols when coagulated by different electrolytes in the "slow" region are recorded. F. L. U.

Electric double layer of colloids. IV. Sorption of ions of flocculating electrolytes by par-ticles of silver iodide sol. E. J. W. VERWEY and H. R. KRUYT (Z. physikal. Chem., 1933, 167, 312-328; cf. this vol., 143) .- In general the amount of cation, x, taken up from an indifferent electrolyte by colloidally dispersed AgI is equiv. to the amount of counter-ion (I) displaced. With increase in the concn. of electrolyte x rises, but in many cases attains a const. val., corresponding with complete displacement of (I), before the amount of electrolyte is sufficient to cause pptn. In such instances, pptn. does not occur when the amount of cation taken up is equiv. to the total charge on the disperse phase. Metal cations can be displaced again by a large excess of H'. The cation adsorption by a mass m of adsorbent may be represented by x/m = f(c/m), where c is the equilibrium concn. The sorption of oppositely charged ions by colloidal AgI thus belongs to the class of exchange phenomena, and is of no significance for a general theory of pptn. Each member of the series Ce<sup>···</sup>> UO<sub>2</sub><sup>•</sup> ≅Pb<sup>··</sup>>Ba<sup>··</sup>>H<sup>•</sup>>Cs<sup>•</sup>>K<sup>•</sup> is adsorbed more readily and displaced less readily than the one follow-ing it. The older Freundlich theory of pptn. is untenable. Exchange will lead to pptn. only if the ion taken up is completely incorporated in the immobile part of the outer coating of the double layer, as may occur with large highly polar (organic) ions. This mode of pptn. is thus restricted to ions constituting exceptions to the Hardy-Schultze rule.

Lecithin. III. Electrophoretic behaviour of lecithin-cholesterol dispersions. C. W. PRICE (Biochem. J., 1933, 27, 1789–1792).—Since the mobility- $p_{\pi}$  relationship and the position of the iso-electric point are const., the formation of the lecithin-

R. C.

cholesterol complex is not attributable to the amphoteric groups of the lecithin or to those on which ion adsorption occurs. H. G. R.

Electro-deposition of shellac. N. MURTY and M. SREENIVASAYA (Chem. and Ind., 1934, 35–36).— Colloidal particles of shellac in NaOH, Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, or aq. NH<sub>3</sub> are negatively charged and can be electrodeposited, preferably on a Pt anode. Ni, Cu, or Pb anodes are attacked during the deposition. Anions such as Cl' and SO<sub>4</sub>" have a polymerising effect on the deposit. E. S. H.

Summary of the isoelectric points of proteins. A. W. THOMAS (J. Amer. Leather Chem. Assoc., 1934, 29, 3—16, 52).—A list of proteins with the isoelectric points, the method of determination, and a bibliographical reference to the source of information is given. D. W.

Interaction of boron compounds with lyophilic colloids. S. I. INOZENTZEV (Chemis. Social. Agric., Russia, 1933, No. 3, 214—216).—Na borate, and particularly  $H_3BO_3$ , causes gelatin to congcal more rapidly than Na<sub>2</sub>SO<sub>4</sub> or NaI. The swelling is lowest with  $B_4O_7''$ , and highest with I'. CH. ABS.

Nature and amount of non-diffusible calcium in protein sols. W. G. EVERSOLE, L. A. FORD, and G. W. THOMAS (J. Biol. Chem., 1934, 104, 107—114). —Gelatin (I) decreases the activity of Ca<sup>\*\*</sup> in a solution of Ca(OAc)<sub>2</sub> as measured by a Corten-Esterman electrode (A., 1928, 1205), the amount of Ca bound increasing with [Ca<sup>\*\*</sup>]. A solution of NaCl and Ca(OAc)<sub>2</sub> was dialysed against an identical solution containing (I), and Cl' and Ca determinations were made for both solutions. The [Ca<sup>\*\*</sup>] in the (I) solution was calc. and the bound Ca obtained by difference. Vals. obtained by the latter method are > those given by the former unless a correction is made for the vol. occupied by (I). H. D.

Interrelationships between the effect of electrolytes on the swelling of, and their permeability through, gels. M. VON DELLINGSHAUSEN (Planta [Z. wiss Biol.], 1933, 21, 51-97).-In permeable, homogeneous gels, e.g., gelatin, agar, adsorbed ions favour swelling according to their hydrophilic character (" direct ion effect "). The reverse effect of non-adsorbed ions corresponds with their  $H_2O$  affinities ("indirect effect"). The action of adsorbed ions on swelling effects is controlled by the hydro-philic nature of the micelles. Increasing concn. of electrolyte solutions intensifies the "direct ion effect " in permeable gels and the "indirect effect" in imper-meable gels. The mobility of ions in gelatin follows the same order as that in free solutions, unless the gel is in equilibrium with the electrolyte solution, when the order of mobility becomes KCl<NaCl<LiCl and AlCl<sub>3</sub> < MgCl<sub>2</sub> < CaCl<sub>2</sub>. The effect of varying concns. of electrolytes on a no. of other membranes A. G. P. is examined.

Aggregation of gelatin. W. GIEDROYC (Rocz. Chem., 1933, 13, 686-703).—The optical rotation of gelatin (I) sols is at 40° proportional to the concn. of (I) over the range  $p_{\rm H}$  1—10. Mutarotation does not take place at any  $p_{\rm H}$  at > 40°. The val. of  $\alpha$  for a given  $p_{\rm H}$  and concn. varies inversely with the temp.

At 20° the increment in the val. of  $\alpha$  after 20 hr. increases from  $p_{\rm II}$  2 to  $p_{\rm II}$  4.8, then falls to a min. at  $p_{\rm II}$ 6.6, and rises to a second max. at  $p_{\rm II}$  7.35. The velocity of fall of a steel sphere in 1% sols and gels previously kept at 20° during 20 hr. falls with increasing  $p_{\rm II}$  to a min. at  $p_{\rm II}$  4.4, then rises to  $p_{\rm II}$  5, again falls to  $p_{\rm II}$  6.23, rises abruptly to  $p_{\rm II}$  7.5, and falls sharply to a third min. at  $p_{\rm II}$  7.7, above which it rises continuously. Solutions of (I) are regarded as polydisperse sols, in which (I) exists in two forms, differing only in their degree of dispersion. The transition point varies for different samples of (I) from 35° to 40°. R. T.

Rhythmic precipitation with organic precipitants. J. E. HECK and M. G. MELLON (J. Physical Chem., 1934, 38, 85-93).-The formation of ppts. in  $SiO_2$  (I) and agar (II) gels by the action of org. precipitants on metal salts has been investigated under different conditions of acidity and alkalinity. Different types of structure were obtained, bands being formed in certain cases only. 8-Hydroxyquinoline gave very good bands with ZnSO<sub>4</sub>, CdSO<sub>4</sub>, and  $CuSO_4$  in (II) but less good in (I). In other cases there was either no ppt. or a continuous structure. Discrete structures or fern-like growths were also obtained. Nitron nitrate was the only ppt. not giving noticeable bands in at least one type of gel. Better results were always obtained by putting the org. compound in the gel. Light had no influence on the type of structure. M. S. B.

Harmony [between ionic concentrations]. J. STRAUB [with KLOPPERT] (Chem. Weekblad, 1933, 30, 790—792).—The mechanism of the biological processes which lead to "harmony," as opposed to equilibrium, between ionic systems on either side of a membrane, as in white and yolk of egg, yeast cells and their culture media, and blood corpuscles and serum, is discussed. The distribution of the ions is not altered by the diffusion of non-electrolytes, and is rc-established after being disturbed by addition of, e.g.,  $H_2O$ ; if  $NH_4NO_3$  is added to the white of an egg, it undergoes "harmonious" distribution between the white and yolk. H. F. G.

Dissociation constant of nitrogen-nitrogenase in azotobacter.—See this vol., 329.

Calculation of equilibrium constants for the reaction  $C_2H_4+H_2=C_2H_6$  from spectroscopic data. A. V. FROST (Compt. rend. Acad. Sci. U.R.S.S., 1933, 4, 161–164).—The equilibrium consts. calc. for the range 300–1000° abs. assuming free rotation of the Me groups in  $C_2H_6$  are consistent with existing experimental data. Considerable deviations occur if absence of free rotation is assumed.

J. G. A. G.

Electrostatic theory of ionic equilibria. I. Chemical equilibrium in aqueous solution as an electrostatic problem. J. V. CHODAKOV (Z. physikal. Chem., 1934, B, 24, 35—52).—The theory developed is mathematically similar to Kossel's theory of complex compounds, but differs from it fundamentally in its primary postulates, the principal one of which is that a complex ion of approx. spherical symmetry is electrostatically equiv. to an elementary ion of the same radius. By means of the theory, a quantity P, characteristic of the potential energy, may be derived for a system of ions or mols. from at. radii data. From vals. of P ionic equilibria may be qualitatively calc., examples of the application to the strength of acids and bases being reproduced. Ionic radii calc. from dissociation consts. agree within 3-4% with the vals. obtained from considerations of crystal structure. R. C.

Theory of concentrated solutions of strong Theoretical considerations. electrolytes. I. G. B. BONINO. II. Calculation of activity coefficients. G. B. BONINO and G. CENTOLA. III. Calculation of the lowering of the v.p. of the solvent. G. B. BONINO and M. ROLLA (Mem. R. Accad. d'Italia Sci. fis., 1933, 4, 415-444, 445-464, 465-479) .-- I. The Debye-Hückel theory and its limitations are discussed, and the expression for the activity of an ion is modified by substituting for  $D_0$ (the dielectric const. of the solvent) a function which depends on  $D_0$ , on temp., and on the nature of the solvent and of the ions present. The activity of an ion,  $f_i$ , is then given by an expression of the form  $\log f_i = \log f_i^0 + \log f_i^*$ , where  $f_i^0$  is the activity on the Debye-Hückel theory and  $f_i^*$  is the correction term due to the theory put forward.

II. The activity coeffs. of LiCl, NaCl, KCl, CaCl<sub>2</sub>, SrCl<sub>2</sub>, and BaCl<sub>2</sub> calc. from the above formula agree well with experimental data, even for conc. solutions.

III. The v.p. of conc. aq. solutions of LiCl, NaCl, and KCl are calc. and shown to agree very well with experimental data. O. J. W.

**Dissociation constant** of hippuric acid. B. A. JOSEPHSON (Biochem. Z., 1933, 267, 74–76; cf. A., 1933, 1012; this vol., 28).— $K=15.7\times10^{-5}$ .

W. McC.

Dissociation constants of glycine at various temperatures. B. B. OWEN (J. Amer. Chem. Soc., 1934, 56, 24–27).—E.m.f. determinations give the following vals. for the acid and basic dissociation consts.:  $K_{\rm A}$  4·47×10<sup>-3</sup>,  $K_{\rm B}$  6·04×10<sup>-5</sup>. The calc. heats of dissociation are 1159 and 2765 g.-cal., respectively. E. S. H.

Approximate ionisation constant of pantothenic acid as determined by fractional electrolysis. R. J. WILLIAMS and R. MOSER (J. Amer. Chem. Soc., 1934, 56, 169—170).—Fractional electrolysis of pantothenic (I), gallic (II), and salicylic acids and pyrogallol, using the apparatus previously described (A., 1933, 982), shows that (I) is slightly weaker than (II). (I) cannot be an  $\alpha$ -OH-acid; it may contain  $\beta$ - or  $\gamma$ -OH groups. H. B.

Hydrolysis of solutions of stannic chloride. J. GUERON (Compt. rend., 1934, 197, 473-476; cf. A., 1933, 910).—The hydrolysis of aq. SnCl<sub>4</sub> of conen. >0.3N is complete after 80 days at  $20\pm5^{\circ}$ . The micelles consist of granules of hydrated SnO<sub>2</sub> positively charged with Sn<sup>+4</sup> ions, and surrounded by an atm. of anions, mainly Cl<sup>-</sup>, forming the negative charge of the double layer. C. A. S.

Physico-chemical properties of sulphitechromic salt solutions. A. L. ZAIDES (Ovlad. Tekhn. Kozhev. Proiz., 1931, No. 2, 24–25).—The electrical conductivity (I) of aq. (violet) Cr<sup>III</sup> salt increases on addition of increasing amounts of sulphite. In green Cr<sup>III</sup> solutions containing SO<sub>3</sub>" (I) increases with time. The same holds for light absorption (extinction) in the yellow. The max. of absorbed light moves towards the red with increase in SO<sub>3</sub>" content. The  $p_{\mu}$  curve (glass electrode; quinhydrone and indicator methods unsuitable) of solutions containing green Cr<sup>111</sup> salt is similar to the acid neutralisation curve with an inflexion at 5 mols. of SO<sub>3</sub>" per atom of Cr at which the viscosity is max. On keeping, the solutions form gels, which later liquefy. The green solution obtained on boiling the violet Cr<sup>III</sup> solution is considered to contain both positive and negative Cr complexes. On adding 5 mols. of sulphite per atom of Cr to a neutral solution of  $Cr_2(SO_4)_3$ CH. ABS. the mixture has tanning properties.

Dissociation pressure of silver carbonate. M. WATANABE (Sci. Rep. Tõhoku, 1933, 22, 1229—1239). —Dissociation pressures, between 120° and 201°, are given by log p (atm.)= $-3855 \cdot 9/T + 7 \cdot 9040$ . Various thermodynamic quantities have been calc.

F. L. U.

Thermal dissociation of normal manganous and cobalt carbonates. J. KRUSTINSONS (Z. Elektrochem., 1933, 39, 936–939).—Dissociation pressures are recorded for  $MnCO_3$  between 367° and 401° and for  $CoCO_3$  between 317° and 341°. The calc. heats of dissociation are 25,030 and 22,940 g.-cal., respectively. Solid solutions appear to be formed in the dissociation of  $MnCO_3$  (cf. A., 1932, 1204) and  $CoCO_3$ seems to decompose in stages. D. R. D.

Hydrates of nickel sulphate. A. CHRÉTIEN and R. ROHMER (Compt. rend., 1934, 198, 92—94).— The following characteristic points are recorded : ice and NiSO<sub>4</sub>,7H<sub>2</sub>O at  $-3\cdot15^{\circ}$ ; NiSO<sub>4</sub>,7H<sub>2</sub>O and  $\alpha$ -NiSO<sub>4</sub>,6H<sub>2</sub>O at 29·1°;  $\beta$ - and  $\alpha$ -NiSO<sub>4</sub>,6H<sub>2</sub>O at  $60\cdot3^{\circ}$ ;  $\beta$ -NiSO<sub>4</sub>,6H<sub>2</sub>O and NiSO<sub>4</sub>,5, 4, 3, and 2H<sub>2</sub>O at 98°, 97·2°, 96·4°, and 90·3°, respectively. The equilibria in the last four cases are metastable, the monohydrate being the only stable solid phase above the transition point of  $\beta$ -NiSO<sub>4</sub>,6H<sub>2</sub>O and NiSO<sub>4</sub>,H<sub>2</sub>O at 84·3°. The metastable equilibria, especially with the di-, tri-, and tetra-hydrates, are very persistent, and true equilibrium is attained in some cases only after several weeks. The b.p. of saturated solutions of the hydrates with 6, 5, 3, 2, and 1 H<sub>2</sub>O are, respectively, 107·7°, 107·2°, 106·6°, 105·9°, 105·1°, and 103·9°.

C. A. S. Phase diagrams of the systems mercuric sulphate-mercuric iodide, bromide, and chloride. M. PAIĆ (Arh. Hemiju, 1933, 7, 161-169).—Thermal and X-ray data indicate the formation of a 1:1 compound, m.p. 332° (decomp.), in the system HgSO<sub>4</sub>-

two systems. The mutual solubility of the fused salts diminishes in the order  $HgI_2$ ,  $HgBr_2$ ,  $HgCl_2$ . R. T. Phase equilibria in the systems  $TiO_2$ ,  $TiO_2$ -  $SiO_2$ , and  $TiO_2$ -Al<sub>2</sub>O<sub>3</sub>. E. N. BUNTING (Bur. Stand. J. Res., 1933, 11, 719—725).—The stable form of  $TiO_2$ above 400° is rutile, m.p. 1825°. It forms no compounds with SiO<sub>2</sub>; the eutectic, m.p. 1540°, contains 89.5 wt.-% SiO<sub>2</sub>. With Al<sub>2</sub>O<sub>3</sub>,  $TiO_2$  forms a compound  $TiO_2$ , Al<sub>2</sub>O<sub>3</sub>, m.p. 1860°. The eutectics, m.p.

HgI<sub>2</sub>; no compounds appear to be formed in the other

1715° and 1850°, contain 15 and 62 wt.-% Al<sub>2</sub>O<sub>3</sub>, respectively. J. W. S.

System sodium disilicate-sodium fluoride. H. S. BOOTH, B. A. STARRS, and M. J. BAHNSEN (J. Physical Chem., 1933, 37, 1103-1107).-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> has been prepared by fusing together the calc. amounts of Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O and SiO<sub>2</sub>. The binary system Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>-NaF gives a simple cutectic curve, the cutectic composition being  $39.5\pm0.1$  mol.-% NaF and the temp.  $797\pm1.0^{\circ}$ . Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> has m.p. S74°. M. S. B.

System cadmium bromide-ethyl alcohol. F. ISHIKAWA, I. MORI, and T. MUROOKA (Sci. Rep. Tõhoku, 1933, 22, 1163—1178; cf. A., 1933, 905).— The alcoholate has 2 mols. EtOH, not 1.5 as reported by Lloyd (A., 1928, 479). Solubilities in EtOH between 0° and 60°, and v.p. for the systems  $CdBr_2$ - $CdBr_2$ , 2EtOH and  $CdBr_2$ , 2EtOH-saturated solution are recorded. The transition temp. is 37°. Thermodynamic quantities have been calc. from the results of e.m.f. measurements. F. L. U.

Thermal analysis of binary systems of sulphonal with certain organic compounds. K. HRYNAKOWSKI and F. ADAMANIS [with K. TOKAR-ZÓWNA, J. WAWRZYNIAK, S. WESEŁA, and M. BRONIS-ZÓWNA] (Rocz. Chem., 1933, 13, 736—739).—Sulphonal (I) does not form compounds with NHAcPh, phenacetin, resorcinol, salipyrine, or  $CO(NH_2)_2$ . (I) is completely miscible with all the above substances except  $CO(NH_2)_2$ . R. T.

Thermal equilibrium in the binary systems of phenacetin, carbamide, ethylurethane, antipyrine, menthol, salol, and quinine. K. HRYNA-KOWSKI and E. ADAMANIS (Bull. Soc. chim., 1933, [iv], 53, 1168—1175).—B.-p. data are recorded for all the possible binary systems and represented as a function of mol. composition. M. S. B.

Effect of pressure on the binary system monomethylaniline-dimethylaniline. J. C. SWALLOW and R. O. GIBSON (J.C.S., 1934, 18—21).—Over the range investigated (0-61.4% NHPhMe, 1 to about 2000 atm.) the m.p. rises linearly with pressure, the effect being greatest (1° per 40 atm.) with pure NPhMe<sub>2</sub>. D. R. D.

Basic salts. III. Equilibria in system CuO-CrO<sub>3</sub>-H<sub>2</sub>O. E. HAYEK (Z. anorg. Chem., 1934, 216, 315-320; cf. A., 1933, 360).—The system has been studied at 40°. The salts  $2\text{CuCrO}_4$ , $3\text{Cu(OH)}_2$  (and with 1 H<sub>2</sub>O) and CuCrO<sub>4</sub>,Cu(OH)<sub>2</sub> are described. F. L. U.

Complex lead halides. (MME.) N. DEMASSIEUX and E. J. GRELIS (Compt. rend., 1934, 198, 179–180). —Examination of the system  $PbBr_2-NH_4Br-H_2O$ indicates the existence of  $2PbBr_2,NH_4Br$  and  $PbBr_2,2NH_4Br$  at all temp. (cf. A., 1893, ii, 523; 1898, ii, 512). C. A. S.

Systems acetone-sodium hydroxide-water and acetone-potassium hydroxide-water at 0°. C.W. GIBBY (J.C.S., 1934, 9–10).—The complete phase diagrams at 0° indicate that COMe<sub>2</sub> can be salted out from any mixture with H<sub>2</sub>O by addition of NaOH or KOH, the COMe<sub>2</sub> layer containing < 0.5% of alkali. D. R. D. Invariant thermodynamics of elastic systems. (MLLE.) Y. DUPONT (Bull. Acad. roy. Belg., 1933, [v], 19, 1167—1179).—Mathematical. J. W. S.

Thermochemistry of aluminium. A. MEICHS-NER and W. A. ROTH (Z. Elektrochem., 1934, 40, 19-26).—The heats of formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Al<sub>4</sub>C<sub>3</sub> at 20° are 393·3±0·3 and 20±3 kg.-cal., respectively (cf. A., 1929, 1389). H. J. E.

Thermochemistry of thallium. W. A. ROTH and A. MEICHSNER (Z. Elektrochem., 1934, 40, 19; cf. A., 1932, 341).—A correction. H. J. E.

Heat capacity and entropy of potassium chlorate from  $13^{\circ}$  to  $300^{\circ}$  K. Entropy of chlorate ion. W. M. LATIMER, P. W. SCHUTZ, and J. F. G. HICKS, jun. (J. Amer. Chem. Soc., 1934, 56, 88-89).  $-C_p$  increases from 0.44 g.-cal. per mol. at 13.95° abs. to 22.84 at 293.35° abs. The entropy of KClO<sub>3</sub> at 298.1° abs. is 34.17 c.u. The entropy and free energy of formation of ClO<sub>3</sub>' at 298.1° abs. are 39.3 e.u. and 3700 g.-cal., respectively. E. S. H.

Thermodynamic constants of chlorine monoxide. D. M. YOST and R. C. FELT (J. Amer. Chem. Soc., 1934, 56, 68-69).—Partial v.p. of Cl<sub>2</sub>O solutions in CCl<sub>4</sub> have been determined at 0° and 25°. The free energy of the reaction  $Cl_2+0.5O_2 \longrightarrow Cl_2O$ (all gaseous) at 25° is 21,210 g.-cal. The entropy at 25° and 1 atm. is 67.9 g.-cal. per degree. E. S. H.

Thermochemical measurements with oxides of copper, rhodium, palladium, and iridium. L. WOHLER and N. JOCHUM (Z. physikal. Chem., 1933, 167, 169—179).—The heats of formation are :  $IrO_2$ , 40·14; CuO, 33·02; Cu<sub>2</sub>O, 43·00; PdO, 20·40; Rh<sub>2</sub>O<sub>3</sub>, 68·30; RhO, 21·72; Rh<sub>2</sub>O, 22·70 kg.-cal. The mean mol. heats of these oxides and of Ir have been determined at 16—1000°. The dissociation pressures calc. from these data agree with the observed vals. R. C.

Heats of dissolution and heats of reaction in liquid ammonia. I. C. A. KRAUS and J. A. RIDDERHOF. II. C. A. KRAUS and R. F. PRESCOTT (J. Amer. Chem. Soc., 1934, 56, 79-86, 86-88).-I. A calorimeter, in which the heat effect is determined by the amount of NH<sub>3</sub> vaporised, is described. Heats of dissolution in liquid NH<sub>3</sub> have been determined as follows (g.-cal. per mol.): NaNO<sub>3</sub> 3600, NaBr 9500, NaI 17,500, KNO3 -400, KBr 2900, KI 5900, NH,Cl 6400, NH4NO3 5700, NH4Br 8100, NH I 11,000, LiNO3 10,800, AgNO<sub>3</sub> 22,400, AgI 6700, Na -1450. The heat effects for a no. of reactions have been determined. Heats of formation calc. from these are in agreement with published vals. By direct reaction of S and Te with Na in liquid  $NH_3$  the following heats of reaction have been obtained for the first time : Na<sub>2</sub>S<sub>2</sub> 96,200, Na<sub>2</sub>Te 82,500, Na<sub>2</sub>Te<sub>2</sub> 101,800 g.-cal. per mol.

II. Improvements in technique are described. The following heats of dissolution (g.-cal. per g. mol.) in liquid  $NH_3$  have been determined :  $AgNO_3 21,400$ ,  $Hg(CN)_2 13,200$ ,  $PbI_2 29,100$ ,  $Pb(NO_3)_2 26,900$ ,  $NaClO_3 2200$ , NaBr 8000. E. S. H.

Heats of dissolution of sugars in water. B. C. HENDRICKS, W. H. STEINBACH, jun., R. H. LE ROY, and A. G. MOSELEY, jun. (J. Amer. Chem. Soc., 1934, 56, 99-101).—The data (in g.-cal. per g.) refer to dilutions of 0.00035 mol. of sugar per mol. of  $H_2O$ : d-galactose -21.4,  $\alpha$ -methyl-d-glucoside -3.13,  $\alpha$ methyl-d-mannoside -11.0, d-glucose -14.5,  $\beta$ -dglucose -5.65, d-glucose hydrate -25.2. Heats of mutarotation of d-galactose and d-glucose are zero. E. S. H.

Carbon tetrachloride synthesis. C. G. FINK and C. F. BONILLA (J. Physical Chem., 1933, 37, 1135—1167).— $C_p$  for CCl<sub>4</sub> vapour at 1 atm. between 0° and 300°, calc. from available data, is 14.0+ 0.0233T. Two or more of the thermodynamic quantities  $C_p$ ,  $\Delta F^0$ , and S at 298° have been calc. for C (graphite),  $Cl_2$ ,  $CCl_4$ ,  $COCl_2$ ,  $CO_2$ ,  $SiCl_4$ ,  $SnCl_4$ ,  $AlCl_3$ ,  $SiO_2$  (quartz),  $SnO_2$ , and  $Al_2O_3$ . The equilibrium const. for the reaction  $2CCl_4 = C_2Cl_4 + 2Cl_2$  has also been derived from known experimental data. Free energy calculations show that the reaction COCl<sub>2</sub>+  $2MCl = CCl_4 + M_2O$ , where M is the equiv. of Si, Al, or Sn, cannot be carried out to an appreciable extent. This has been confirmed experimentally. Ordinary animal charcoal is a good catalyst for the reaction  $CCl_4 =$ C+2Cl<sub>2</sub>, but the reverse reaction could not be observed. Attempts to obtain CCl<sub>4</sub> by the reaction  $2COCl_2=CO_2+CCl_4$ , using different catalysts, were also unsuccessful. A quant. study of the reverse reaction shows that the theoretical equilibrium is not attained. Methods for the volumetric determination of  $CCl_4$  and of the proportions of  $Cl_2$ ,  $COCl_2$ , and  $CO_2$ in a mixture are described. M. S. B.

Heat of formation of mixed crystals of potassium chloride and bromide. II. M. M. POPOV and S. F. JAVOROVSKAJA (Z. physikal. Chem., 1933, 167, 180—182; cf. A., 1930, 703).—In order to obtain homogeneous mixed crystals from the molten mixture, crystallisation must occur slowly. The heat of formation, Q, of mixed crystals which have received the same annealing treatment is the same, independent of the duration of cooling. With increasing duration of annealing Q passes through a min. It proved impossible to obtain by grinding mixed crystals for which Q is comparable with that of crystals separated from a molten mixture. R. C.

Electrolytic transport of water in certain bromide and iodide solutions. A. WAGNER (Chem. Listy, 1933, 27, 481–484).—Measurements of the electrolytic transport of  $H_2O$  in N- and 0.1N-NaI and 0.1N-KI indicate that I' is associated with 2.55 mols.  $H_2O$ . Viktorin's results (A., 1933, 1247) are confirmed for 0.1N-KBr and -NaBr. R. T.

Hydration of ions Mg", Ca", Sr", and Ba" in normal solutions. J. BABOROVSKY and O. VIKTORIN (Coll. Czech. Chem. Comm., 1933, 5, 518—526).—The true transport nos. of the cations in N-MgCl<sub>2</sub>, -CaCl<sub>2</sub>, -SrCl<sub>2</sub>, and -BaCl<sub>2</sub>, as measured by Baborovsky's method (A., 1928, 244, 954), are 0.262, 0.299, 0.279, and 0.289, respectively. The mols. of H<sub>2</sub>O associated with the respective cations are Mg" 20, Ca" 17—16, Sr" 16, and Ba" 11. These results are compared with previous data. In all cases H<sub>2</sub>O is also transported to the anode. M. S. B.

Conductivity in the transition region between strong and weak electrolytes. R. M. Fuoss. (Physikal. Z., 1934, 35, 59-68).—Theoretical.

A. J. M.

Measurement of electrolytic conductivities. W. FINK and P. GROSS (Monatsh., 1933, 63, 271– 284).—Data for Na<sub>2</sub>SO<sub>4</sub> from  $1 \times 10^{-2}$  to  $2 \times 10^{-4}M$ , and o-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H from  $2 \times 10^{-2}$  to  $1 \times 10^{-3}M$ , are discussed in terms of Onsager's theory. The electrostatic capacity of a cell is shown to be independent of the nature of the solution if the conductivities are equal. D. R. D.

Electrolyte mixtures. II. Measurement of conductivity. V. K. SEMENTSCHENKO, B. V. JERO-FEJEV, and V. V. SERPINSKI. III. Conductivity of mixtures of electrolytes. V. K. SEMENT-SCHENKO and V. V. SERPINSKI (Z. physikal. Chem., 1933, 167, 188—196, 197—208; cf. A. 1932, 570).— II. Conductivity measurements with 0-0001—2N aq. KCl, using an apparatus similar to that of Shedlowsky (A., 1930, 862), have given results in agreement with the latter's and with the Debye-Onsager equation. The attainable precision with this apparatus is 0.02%.

III. Measurements have been made with aq. solutions of NaN<sub>3</sub>, NaBr, and MgSO<sub>4</sub>, and mixtures of KCl and NaN<sub>3</sub>, of KCl and MgSO<sub>4</sub>, and of KCl, NaBr, and MgSO<sub>4</sub>. The results for the single electrolytes agree with the Debye-Hückel-Onsager theory better than existing data. For the mixed solutions at low concess, the conductivity agrees with the val. calc. by the additive principle, probably owing to mutual compensation of opposing effects. R. C.

Simultaneous conduction by electrolytes in resistance measurements on palladium wires containing hydrogen. C. A. KNORR and E. SCHWARTZ (Z. Elektrochem., 1934, 40, 36–38).—A reply to Smith (A., 1933, 1014). H. J. E.

Absolute determination of the absorption of solutions of electrolytes in glycerol and aqueous glycerol, in high-frequency electric fields. J. HIEGEMANN (Physikal. Z., 1934, 35, 91-93; cf. Whitmore, A., 1933, 1015).—The conductivities of glycerol (I), aq. (I), and solutions of KCl and  $MgSO_4$  in (I) and aq. (I) have been measured for wavelengths 23, 46, and 92 m. A. J. M.

Magnesium electrode in ether solution and free energy of formation of magnesium bromide. G. A. SCHERER and R. F. NEWTON (J. Amer. Chem. Soc., 1934, 56, 18—20).—The e.m.f. of the cell Mg| saturated  $Et_2O$  solution of MgBr<sub>2</sub>,2Et<sub>2</sub>O|Hg<sub>2</sub>Br<sub>2</sub>,Hg at 25° is  $1.561\pm0.004$  volt. The v.p. of etherates of MgBr<sub>2</sub> at 25° have been determined. The free energy of formation of MgBr<sub>2</sub> at 25° is -114,000 g.-cal. per mol. E. S. H.

Standard quinhydrone electrode. F. HOVORKA and W. C. DEARING (J. Amer. Chem. Soc., 1934, 56, 243-244).—The quinhydrone electrode is said to excel the 0.1N or saturated calomel electrode in both reproducibility and constancy. E. S. H.

Temperature coefficients of the electromotive force of the cell Cd (metal), CdSO<sub>4</sub>, Cd (satd. amalgam). W. G. PARKES and V. K. LA MER (J. Amer. Chem. Soc., 1934, 56, 90—91).—From e.m.f. measurements at 0—30° the free energy, entropy, and heat content changes for the process Cd(metal)  $\rightarrow$ Cd(s, saturated with Hg) are calc. Corresponding data, calc. for the reaction Cd(s)+PbSO<sub>4</sub>(s)=  $CdSO_4(a=1)+Pb(s)$ , are 3153 g.-cal., -45.20 e.u., and 16,536 g.-cal., respectively. E. S. H.

Potential of an electrode in a solution with no common ion. O. ESSIN and M. LOZMANOVA (Z. physikal. Chem., 1933, 167, 209-220).—The potential of a Au electrode,  $E_1$ , in aq. CuSO<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, or AgNO<sub>3</sub> is a linear function of the potential,  $E_2$ , of the metal contained in the electrolyte. The vals. of a and b in  $E_1=a+bE_2$  seem to be determined principally by the cation of the electrolyte. It is possible that the establishment of a p.d. between Au and the solution involves a small transfer of charge from the cations of the solution to the Au. R. C.

Dependence of metal-salt equilibria on the nature of the anions. G. TAMMANN and H. O. VON SAMSON-HIMMELSTJERNA (Z. anorg. Chem., 1934, 216, 288—302).—The relation between the electrode potential of metals in contact with their molten salts and the heats of formation of the latter is approx. linear for salts having the same anion. Thus the displacement of one metal by another in a molten salt may be predicted from thermal data. The influence of the anion may be considerable; e.g., K is nobler than Na in the fluorides, baser in the other halides; Pb is almost as noble as Ag in the iodides, and Fe as Cu in the sulphides. F. L. U.

Liquid junction potentials. II. J. B. CHLOU-PEK, V. Z. DANES, and B. A. DANESOVA (Coll. Czech. Chem. Comm., 1933, 5, 527-534).-A discussion of the experimental data previously obtained (this vol., 150). The liquid junction potential difference in the cell Hg|HgCl, 0.1N-KCl| junction solution 0.1N-HCl|Hg is a logarithmic function of the concn. of the bridge electrolyte for solutions of a dilution at which the Debye-Hückel theory is valid. In more conc. solutions, 0.1N and upwards, the individual character of the electrolyte becomes more marked, but certain regularities appear. Salts with multivalent anions, such as Na2SO4, ZnSO4, K2CrO4, K4Fe(CN)6, form a class apart from the salts with univalent anions such as KCl, MgCl, and NaNO3, but there is no such distinction between multi- and uni-valent cations. This is attributed to the simpler electronic structure of the multivalent metallic cations as compared with the multivalent anions. M. S. B.

Electrometric titration curves of imino-dibasic acids. A. LITZINGER and L. W. PICKETT (J. Amer. Chem. Soc., 1934, 56, 124—126).—The curves for NH(CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, tyrosine-N-acetic and -phenylacetic (I), and phenylalanine-N-acetic and -phenylacetic (II) acids (A., 1933, 166) are all similar; all show the greatest change in [H'] with 1 equiv. of KOH. Evidence of a second end-point (2 equivs. of KOH) is found with (I) and (II). The dissociation consts. of the acids are very similar and indicate that they are weak acids. H. B.

Phenanthroline-ferrous ion. II. Oxidation potentials at high acidities and determination of vanadium. G. H. WALDEN, jun., L. P. HAMMETT, and S. M. EDMONDS (J. Amer. Chem. Soc., 1934, 56, 57-60; A., 1933, 924).—Relative oxidation potentials of Fe<sup>\*\*\*</sup>/Fe<sup>\*\*</sup>, the phenanthroline-ferrous indicator (I),  $V^{V}/V^{IV}$ , and  $V^{IV}/V^{III}$  have been determined in 1, 3, and 5M-H<sub>2</sub>SO<sub>4</sub>. V can be determined in presence of Fe, Cr, and Mo by titrating the solution in 5M-H<sub>2</sub>SO<sub>4</sub> with dil. FeSO<sub>4</sub> in presence of (I). E. S. H.

Influence of substituents in the nucleus on the energy of reduction of benzaldehyde. G. SEME-RANO and A. CHISINI (Gazzetta, 1933, 63, 802-818).-Measurements with the dropping Hg cathode of the reduction potential (I) of PhCHO and various nuclearsubstituted derivatives in 0.1N-HCl and -NH<sub>4</sub>Cl solutions in 50% EtOH are recorded. The influence of the substituents is independent of the nature of the electrolyte present. (I) is increased by a Cl atom in any position and by an o-Me group; it is lower for the p- and m-Me-substituted aldehydes, and for salicylaldehyde, anisaldehyde, etc. The change is greatest when a substituent enters the o-position, and least when it enters the p-position. The results do not support the theory of induced alternate polarity, but may be qualitatively explained on the basis of Robin-H. F. G. son's hypothesis.

Relation of life to electricity. VIII. Mechanism of oxidation-reduction potentials of living tissues.—See this vol., 327.

Thermodynamics of the electrocapillary curve. I. General equations. F. O. KOENIG (J. Physical Chem., 1934, 38, 111—128).—The theory of electrocapillary curves is re-developed on the single assumption of perfect polarisability, which is defined as the impermeability to electrically-charged particles of the boundary layer between two conducting phases. This corresponds closely with the actual physical conditions in the Lippmann electrometer. The Lippmann-Helmholtz equation holds for all perfectly polarisable systems regardless of composition. M. S. B.

Hydrogen overvoltage and adsorption at the dropping mercury cathode. G. SEMERANO (Gazzetta, 1933, 63, 786–801).—The deposition potential of H at the dropping Hg cathode from 0.002N solutions of HCl containing various salts has been determined, together with the diffusion and adsorption currents in similar solutions to which fuchsin has been added. Progressive addition of fuchsin increases the current which flows at potentials < that required for the liberation of H, and, above a certain concn., reduces the quantity of H evolved. The deposition potential is reduced by addition of the dye; pronounced peaks also appear on the polarograph curve, and the diffusion wave is considerably depressed. The results are discussed at some length. H. F. G.

Catalytic activity of palladium and the hydrogen overvoltage. C. A. KNORR and E. SCHWARTZ (Z. Elektrochem., 1934, 40, 38–43).—Overvoltage data for H on Pd are correlated with its catalytic activity measured by the rate of absorption of  $H_2$ (followed by changes in the electrical resistance of the Pd). At const. c.d. the overvoltage increases with decreasing rate of absorption. A relation between the c.d. and overvoltage is deduced. H. J. E.

Catalytic hydrogen replacement and the nature of overvoltage. J. HORIUTI and M. POLANYI (Nature, 1934, 133, 142).—A reply to criticism (this vol., 150). L. S. T. Electrolytic oxidation. IV. Anodic polarisation in halide solutions. S. GLASSTONE and A. HICKLING (J.C.S., 1934, 10–18).—In electrolysis of halide solutions at const. c.d. with a Pt anode, two anode potentials are observed : the first is due to reversible discharge of halide ions and the higher one to the formation of  $H_2O_2$ , which decomposes causing  $O_2$  evolution when the anode surface is saturated. The presence of catalysts for decomp. of  $H_2O_2$  hastens attainment of this condition, whilst the increased surface of platinised Pt takes far longer to saturate. D. R. D.

Properties of the layer of oxide formed by anodic polarisation at the surface of oxidisable metals. M. MARINESCU (Bul. Soc. Române Fiz., 1933, 35, 135—142).—The anodic resistance of certain oxidisable metals such as Al and Ta is high owing to the adsorption of O by the layer of oxide formed at the anode. A mathematical explanation is advanced of experimental results which have been obtained with a.e. of high and low e.d. H. S. P.

Poisoning of hydrogen electrodes by dichlorochromyl chloride. J. LISIECKI (Rocz. Chem., 1933, 13, 552—559).—Aq. [CrCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>]Cl (I) depolarises and permanently inactivates H electrodes. The electrode should be freshly platinised before each determination of  $p_{\rm H}$  in solutions of (I). R. T.

Passivity of iron and aluminium. W. H. CONE and H. V. TARTAR (J. Amer. Chem. Soc., 1934, 56, 48—52).—The presence of  $PO_4^{\prime\prime\prime}$  (excepting small quantities with Al) or  $SO_4^{\prime\prime}$  accelerates the rate of dissolution of Fe or Al in HNO<sub>3</sub> to a degree which is approx. proportional to the concn. Simultaneously the metal becomes more electronegative to the solution. A gradual transition from activity to passivity is obtained, according to the  $[SO_4^{\prime\prime}]$  or  $[PO_4^{\prime\prime\prime}]$ . The assumption of a film of adsorbed  $O_2$  is preferred to the oxide-film theory. Fe is passive in dil. HNO<sub>3</sub> containing AgNO<sub>3</sub>. E. S. H.

Film theory of passivity. W. J. MÜLLER (Z. Elektrochem., 1934, 40, 18–19).—Schwabe's results (A., 1933, 1248) are discussed in relation to the author's film theory. H. J. E.

Flame temperatures in carbon monoxide and air mixtures. W. T. DAVID and J. JORDAN (Phil. Mag., 1934, [vii], 17, 172—181; cf. A., 1932, 25).— Temp. was measured with a Pt-Rh thermometer in a spherical explosion vessel. A max. was recorded for equimol. proportions of CO and  $O_2$ . The deviation from the calc. temp. was greatest for this mixture. A surface action between the hot wire and the freshly burnt gas is suggested. H. J. E.

Ignition of some explosive mixtures by modified coil discharges. B. W. BRADFORD, G. I. FINCH, and (MISS) A. M. PRIOR (J.C.S., 1934, 75—79). —Previous results are summarised and extended. In a spark, the high-frequency condensed discharge (capacity component) is relatively inefficient as a source of ignition as compared with the inductance component. The igniting power is determined to a greater extent by the discharge duration than by the total energy or its max. rate of dissipation, contrary to the thermal theory of ignition. It is suggested that ignition is occasioned by the production in the discharge of mols. with the correct excitation energies. R. S.

Decomposition of complex molecules at high pressures. C. C. COFFIN and A. L. GEDDES (J. Chem. Physics, 1934, 2, 47–48; cf. A., 1932, 1094).— The velocity of the thermal decomp. of gaseous paraldehyde to MeCHO slowly diminishes as the initial pressure is increased (e.g., at  $254^{\circ}$  it is  $6 \times 10^{-4}$  at several mm. and  $3 \times 10^{-4}$  at 18 atm.). It is suggested that at an activating collision the most probable distribution of internal energy is not that most favourable to decomp. The adjustment of internal mol. energy requires a finite time. Hence, the shorter is the time between collisions (e.g., before deactivation), the smaller is the chance of reaction.

H. J. E.

Vapour-phase oxidation of hydrocarbons. I. Amount and rate of oxidation of n-heptane as a function of temperature. II. Relative oxidisability of *n*-heptane,  $\Delta^{\circ}$ - and  $\Delta^{\gamma}$ -heptenes, and mixtures of *n*-heptane and  $\beta\beta\delta$ -trimethylpentane. III. Chemiluminescence of *n*-heptane. H. A. BEATTY and G. EDGAR (J. Amer. Chem. Soc., 1934, 56, 102–106, 107–111, 112–114).–I. The effect of temp. on the amount and rate of oxidation of *n*-heptane (I) in "air" [(I) is vaporised in  $N_2$  and mixed with sufficient  $O_2$  for complete combustion; the concn. of (I) is 1.9%] is studied by the method previously described (A., 1929, 906, 1036). Reaction is slow and (probably) heterogeneous at  $< 250^{\circ}$ . At 250-270°, reaction is homogeneous and is accompanied by visible chemiluminescence; so-called "ignition " begins at about 270°, but this does not cause any marked increase in the  $O_2$  consumption. These "ignitions" become continuous at about 305°. The reaction occurring at 250-350° involves 3 mols. of  $O_2$  per mol. of (I) and is termed the primary reaction (A); marked local evolution of heat and a rapid increase in reaction velocity take place. The O2 consumption increases from 3 to 4.7 mols. at 350-380° and is considered to be due to a subsequent reaction (B). The velocities of (A) and (B) decrease with rise in temp. at  $380-470^{\circ}$  and the temp. coeff. for  $10^{\circ}$  is about 0.85. At 470-510°, the velocity of (A) continues to decrease, whilst that of (B) increases. Inflammation, followed by complete combustion, occurs at 500-525°.

II. Under the same experimental conditions, oxidation of (I),  $\Delta^{\alpha}$ -heptene (II), and  $\Delta^{\gamma}$ -heptene (III) begins at 244°, 300°, and 300°, respectively; the relative reaction velocities increase in the order (III), (11), (1), but the general course of reaction and max.  $O_2$  consumption (about 40% of the theoretical) are the same in each case. Oxidation of (II) and (III) does not appear to begin at the double linking. β38-Trimethylpentane (IV) is oxidised to a slight extent at about 250°; the main reaction begins at 500° (cf. loc. cit.) and increases rapidly up to about 550° (at which temp. inflammation occurs). (IV) exerts a slight inhibitory effect on the oxidation of (1), but undergoes induced oxidation; these effects appear to be more pronounced with relatively high concns. of (IV). A marked negative temp. coeff. of reaction velocity is observed for (I), (II), and (III) at about  $400-500^{\circ}$ .

III. The chemiluminescence phenomena occurring during the oxidation of (I) and (III) are described. H. B.

Influence of pressure on the spontaneous inflammation of hydrocarbons. M. NEUMANN and V. ESTROVICH (Nature, 1934, 133, 105—106).—The pressure-temp. curves for the spontaneous inflammation of  $C_5H_{12}+8O_2$  mixtures in an Fe bomb and in a bomb coated internally with Au have sharp breaks near 60 cm. pressure. Oxidation thus proceeds in two different ways each prevailing in a definite region of pressure. Bone's hydroxylation theory explains the facts, and the existence of a sudden lowering of the inflammation temp. at any crit. pressure is considered to be general for the inflammation of complex hydrocarbons. L. S. T.

Free radicals in thermal decompositions and combustion of hydrocarbons. W. A. BONE (Trans. Faraday Soc., 1934, 30, 148—152).—In the pyrolysis of  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$  it is necessary to assume the primary formation of free radicals such as  $CH_2$ , CH, and possibly  $CH_3$ . There is no evidence, other than spectrographic, of their formation in combustion, the primary products being oxygenated. F. L. U.

Kinetics and mechanism of the thermal decomposition of hydrocarbons. A. I. DINTSES (Compt. rend. Acad. Sci. U.R.S.S., 1933, 4, 153-157). -The two principal primary reactions in the thermal decomp. of  $n - C_6 H_{14}$  (I),  $n - C_8 H_{18}$  (II), and  $\beta \epsilon$ -dimethylhexane (III) involve the formation of  $CH_4$  and  $C_2H_6$ together with the appropriate olefines which rapidly decompose into lower olefines. The course of the later reactions only are affected by the temp. and The velocity coeffs., K, are: time of contact. (I)  $\log_{10} K = 14.58 - 14,100/T \pm 0.06 (525 - 565°)$ , (II)  $\log_{10} K = 14.70 - 14,100/T \pm 0.09 (495 - 570°)$ , and (III)  $\log_{10} K = 6.553 - 7215/T \pm 0.05 (490 - 575°)$ , from which the respective energies of activation of the primary decomp. are 64,500, 64,500, and 33,000 g.-cal. (cf. A., 1933, 1017). Rice's theory of free radicals affords the best explanation of the data, and the difference between the activation energies of n- and iso-hydro-J. G. A. G. carbons is emphasised.

Kinetic study of reaction between potassium iodide and hydrogen peroxide in acid solution. (MME.) P. RUMPF (Compt. rend., 1934, 198, 256– 258).—Using a spectrographic method (determination of amount of  $I_3'$  by its absorption in solutions buffered by  $KH_2PO_4-K_2HPO_4$ , of  $p_H$  5—6) and equal concn. of KI and  $H_2O_2$ , the velocity of interaction for C=0.004-0.008 and  $\propto C^3$ , but is greater if C is smaller. It varies directly with  $p_H$  for  $p_H=5.6-5.9$ , and C=0.006N. The reaction at very low conen. is independent of  $p_H$ , at higher according to  $2I'+H_2O_2+2H'=I_2+$  $2H_2O$ ; the latter predominates, the final conen. of  $I_5'$  being proportional to  $p_H$  for  $p_H=5.25-6.05$  (cf. A., 1932, 1212). C. A. S.

Kinetics of the action of iodine on hydrazine and hydroxylamine hydrochlorides. A. BERTHOUD and D. PORRET (Helv. Chim. Acta, 1934, 17, 32-43). --In each case the velocity of the "dark" reaction  $\infty$  [salt] and [I]. With N<sub>2</sub>H<sub>4</sub>,2HCl the velocity  $\propto$  1/[H<sup>\*</sup>] and 1/[I']<sup>n</sup> (n < 2), and is decreased by NaCl, KBr, and KNO<sub>3</sub>. With NH<sub>2</sub>OH,HCl it  $\propto$  1/[H<sup>\*</sup>]<sup>2</sup> and 1/[I']<sup>2</sup>. The temp. coeffs. for 20—30° are, respectively, 3.4 and 4.0. A mechanism of reaction is suggested. Conclusions of Bhattacharya and Dhar (A., 1930, 1384) are criticised. F. L. U.

Velocity of esterification of alcohols by formic acid. III. A. KAILAN and F. ADLER (Monatsh., 1933, 63, 155—185).—The velocity of esterification (V) of benzyl,  $\beta$ -phenylethyl,  $\gamma$ -phenylpropyl, allyl, o-, m-, and p-nitrobenzyl alcohols and phenyl-methyl-, -ethyl-, and -propyl-carbinols by HCO<sub>2</sub>H at 15° under various conditions has been determined cryoscopically and unimol. velocity coeffs. have been calc. therefrom. Dilution with H<sub>2</sub>O reduces the val. of V. The increase of V produced by addition of HCl is approx.  $\infty$ [HCl]. Neutral salts may have a positive or negative catalytic effect, varying with [HCO<sub>2</sub>H], [HCl], and the alcohol and salt employed. Ph groups reduce V the more, the nearer they are to the OH group. The mol. depression of the f.p. of cone. and dil. HCO<sub>2</sub>H by its esters is much < the val. calc. from its latent heat. D. R. D.

Velocities of hydrolysis of the methyl esters of the two crotonic acids. A. SKRABAL and W. STOCKMAIR (Monatsh., 1933, 63, 244—254).—The high-boiling Me ester hydrolyses more rapidly than the low-boiling ester under either acid or alkaline conditions. Comparison with related compounds indicates a relation between rate of hydrolysis and constitution. D. R. D.

Stability of fructose in aqueous solutions of varying  $p_{\rm H}$ . J. A. MATHEWS and R. F. JACKSON (Bur. Stand. J. Res., 1933, 11, 619-633).—The decomp. of fructose at 4—100° and in solutions of  $p_{\rm H}$  —2.6 to 14.2 is unimol. in its earlier stages and approaches an equilibrium, the val. of which is a function of the  $p_{\rm H}$ . In acid solutions it is dehydrated to form lævulosans of negative rotation, whilst in alkaline solutions the Lobry de Bruyn-van Ekenstein transformation occurs; at intermediate  $p_{\rm H}$  both changes take place. Fructose shows max. stability at  $p_{\rm H}$  3.3, independent of temp. The temp. coeff. of the decomp. at const.  $p_{\rm H}$  is high, and is greatest in acid solutions. J. W. S.

Determination of acidity in ethyl alcohol by velocity of acetal formation. A. J. DEYRUP (J. Amer. Chem. Soc., 1934, 56, 60—64).—The rate of formation of Et<sub>2</sub> acetal is suitable as a measure of acidity in abs. EtOH. HCl, HBr, HI, and HClO<sub>4</sub> are completely ionised strong acids, whilst HNO<sub>3</sub> and pieric acid are weak acids of about the same strength in EtOH. The effect of change of electrolyte concn. and solvent on the dissociation consts. of weak acids and bases has been determined. The reaction is inhibited by traces of H<sub>2</sub>O. Catalysis in presence of CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, and LiCl is due to traces of strong acids. E. S. H.

Optical activity in relation to tautomeric change. II. Comparison between the rate of racemisation of a tautomeric substance and the rate of its tautomeric interconversion. C. K. INGOLD and C. L. WILSON (J.C.S., 1934, 93–97; cf. this vol., 64).—The velocity and equilibrium consts. of the isomerisation of optically inactive *p*-chlorobenzhydrylidene- $\alpha$ -phenylethylamine (I) have been measured and compared with the rate of racemisation of optically active (I) in the same process. The results agree with the hypothesis that the optical activity of (I) is retained in its ions but destroyed by the subsequent isomerisation, and render the view that racemisation occurs in the preliminary ionisation improbable. R. S.

Reactions between chlorine and solid carbonates. I. Sodium carbonate. F. ISHIKAWA, T. MUROOKA, and H. HAGISAWA. II. Potassium, lithium, and magnesium carbonates. III. Velocity of decomposition of sodium and potassium perchlorates. F. ISHIKAWA and H. HAGISAWA (Sci. Rep. Tôhoku, 1933, 22, 1179-1196, 1197-1206, 1207-1228).-I, II. See A., 1932, 349.

III. NaClO<sub>4</sub> begins to decompose at about  $450^\circ$ , KClO<sub>4</sub> at about  $550^\circ$ . The decomp.-time curves are S-shaped. Admixture of carbonate or of chloride accelerates the decomp. The f.-p. curve of NaClO<sub>4</sub>-NaCl has been determined. The eutectic has m.p. 417°. Expressions representing the isothermal decomp. of NaClO<sub>4</sub> are given. F. L. U.

Corrosion and co-ordination. H. L. RILEY (Proc. Roy. Soc., 1934, A, 143, 399–410).—Measurements have been made of the rates of dissolution of Cu and Ni, respectively, in aq. solutions of the Na salts of the following acids :  $H_2C_2O_4$ ,  $CH_2(CO_2H)_2$ ,  $(CH_2 \cdot CO_2H)_2$ ,  $o \cdot C_6H_4(CO_2H)_2$ ,  $H_2CO_3$ , ACOH, BZOH,  $(OH \cdot CH \cdot CO_2H)_2$ ,  $OH \cdot C(CO_2H)(CH_2 \cdot CO_2H)_2$ , and  $o - OH \cdot C_6H_4 \cdot CO_2H$ . The results support an explanation depending on the electrolytic solution pressure of the metal, the tendency which the metal ions possess to form stable complex ions, and the co-ordinating tendency of the anions. L. B.

Corrosion of tin-silver amalgams. N. BRECHT (Z. Elektrochem., 1933, 39, 927–935).—Five amalgams in the three-phase field Ag<sub>3</sub>Sn Sn-Hg mixed erystal (I)-Ag<sub>3</sub>Hg<sub>4</sub>+trace of Sn (II) behaved identically as regards rate of loss of wt. in and potential against 0.1N-HClO<sub>4</sub>, -citric acid, -NaOH, and -NaCl. From such amalgams Sn dissolves anodically in 0.1N-HClO<sub>4</sub> at all c.d. up to 15 ma. per sq. cm., whilst in the other solutions, gas evolution occurs above about 3 ma. per sq. cm. The rate of dissolution at known current shows that the Sn dissolves as Sn<sup>\*\*</sup>, and examination of the depth of corrosion gives an indication of the degree of porosity. D. R. D.

Corrosion-time relationship of iron.—See B., 1934, 148.

Rate of reduction of carbon dioxide by graphite. M. A. MAYERS (J. Amer. Chem. Soc., 1934, 56, 70– 76).—The experimental procedure involves eliminating conen. gradients by increasing the velocity of gas across the reacting surface until the velocity coeff. of the observed rate of reaction disappears. The rate of reduction of CO<sub>2</sub>, in terms of c.c. of CO at n.t.p. produced per sec. from CO<sub>2</sub> at 1 atm. in contact with 1 sq. cm. of graphite surface, is given at 950–1300° by  $\log A_1 = 5.07 - (38,700/4.575T)$ , and at 850–950° by  $\log A_2 = 3.40 - (32,360/4.575T)$ . The significance of the two stages is discussed. E. S. H.

Determination of surface activity of wood charcoal. B. G. ŠIMEK and R. KASSLER (Chem. Listy, 1933, 27, 484–487).—The temp. initiating combustion and the flash point of wood C (I) are unaffected by exposing (I) to air during 7 days. The heat of adsorption of  $H_2O$  is insufficient to initiate combustion. R. T.

Effect of water vapour on ignition temperatures of methane-air mixtures. G. W. JONES and H. SEAMAN (Ind. Eng. Chem., 1934, 26, 71–72).— The addition of  $H_2O$  vapour (aq. v.p.  $22 \cdot 15$ — $26 \cdot 5$  mm. Hg) raises the ignition temp. of  $CH_4$ -air mixtures ( $CH_4 4$ —9% on dry basis) 7—11°; smaller quantities of  $H_2O$  vapour raise it by smaller amounts.  $H_2O$ vapour has no appreciable effect on the lag on ignition. D. K. M.

Mechanism of gaseous reactions. I. Thermal decomposition of methyl ethyl ether. II. Homogeneous catalysis in the decomposition of methyl ethyl ether. W. URE and J. T. YOUNG (J. Physical Chem., 1933, 37, 1169—1182, 1183—1190).—I. The decomp. of MeOEt is a complex process consisting of a unimol. decomp. into MeCHO and CH<sub>4</sub> followed by a bimol. decomp. of MeCHO, the first predominating at low temp. (457°) and the second at high temp. (565°). A mathematical treatment for intermediate conditions is given.

II. The decomp. of MeOEt is catalysed by small quantities of EtI, the catalytic process consisting chiefly of the unimol. decomp. of MeOEt followed by the unimol. decomp. of MeCHO. By increasing the surface of the reaction vessel by glass-wool packing or Pyrex rods the rate of reaction is decreased.  $C_2H_6$  is also a primary product, and its decomp. to give an equilibrium mixture with  $C_2H_4$  and  $H_2$  is catalysed by EtI. M. S. B.

Stabiliser for hydrogen peroxide. I. R. KONDO and H. HONAMI (Bull. Imp. Hyg. Lab., 1933, 42, 187—189).—Effectiveness is in the order : 0.1%barbituric acid > 0.1% Me *p*-hydroxybenzoate > 0.1% hippuric acid > uric acid. CH. ABS.

Acid catalysis in non-aqueous solvents. I. Rearrangement of N-bromoacetanilide. R. P. BELL (Proc. Roy. Soc., 1934, A, 143, 377–399).—The catalysis by acids of the unimol. transformation of NBrAcPh to  $p \cdot C_6H_4Br$ ·NHAc has been studied in several solvents. The relation between the catalytic coeffs.  $\alpha_0$ , of ten acids in PhCl is expressed by  $\alpha_0 =$  $0.45K_d^{0.80}$ , where  $K_d$  is the dissociation const.  $C_6H_2(NO_2)_3$ ·OH does not obey this relation. The medium has only a small effect on  $\alpha_0$ , and the results in  $C_6H_6$ , although less accurate, also obey the above relationship. Measurements of the temp. coeffs. for catalysis by five acids in PhCl show that the velocity of reaction is  $1/10^4$ — $10^5$  times the val. calc. from the simple collision formula. L. B.

Oxidation of solutions of iodoform. R. DUBRISAY and G. EMSCHWILLER (Compt. rend., 1934, 198, 263-265; cf. A., 1932, 1215).—Addition of I and acid to a solution of  $CHI_3$  in pure  $C_6H_6$  is unnecessary to ensure its oxidation in the cold and dark,

although the velocity is diminished, and independent of the conen. of CHI<sub>3</sub>. There is also a slight delay in starting if the conen. be < 10%. Oxidation is hindered if to the pure C<sub>6</sub>H<sub>6</sub> is added 10<sup>-6</sup> of PhOH, NH<sub>2</sub>Ph, quinol, pyrrole, or of the C<sub>6</sub>H<sub>6</sub> extract of cork; 10<sup>-5</sup> of vanillin or carbazole; or 10<sup>-4</sup> of C<sub>5</sub>H<sub>5</sub>N, azobenzene, or coniferin, but thiophen has no effect. PhMe behaves similarly to C<sub>6</sub>H<sub>6</sub>, although the proportions of retarding agents required are different.

C. A. S.

Mechanism of the Kolbe reaction. S. GLAS-STONE and A. HICKLING (Nature, 1934, 133, 177).— Relatively small amounts of Pb", Mn", Cu", Fe", or Co" ions markedly affect the Kolbe reaction (I) in the electrolysis of acetate solutions. The addition of 0.001M-Pb(OAc)<sub>2</sub> to a solution containing N-KOAc and N-AcOH reduces the efficiency for C<sub>2</sub>H<sub>6</sub> formation from 70% to approx. zero. The effects of the ions are Pb">Mn">Cu">Co"=Fe". The parallelism with their catalytic influence on the decomp. of H<sub>2</sub>O<sub>2</sub> suggests that H<sub>2</sub>O<sub>2</sub> is the effective agent in the formation of C<sub>2</sub>H<sub>6</sub> by (I). L. S. T.

Optical activity in relation to tautomeric change. III. Constitutional and catalytic influences on the rates of racemisation of prototropic compounds. C. L. WILSON (J.C.S., 1934, 98—99; cf. this vol., 260).—The connexion between racemisation and isomerisation in optically active compounds with coincident centres of asymmetry and prototropy is illustrated by examples from the lit.

R. S. Acetylation of cellulose. D. KRÜGER and W. ROMAN (Angew. Chem., 1934, 47, 58-61).—The widely different catalytic activities of HI, HCl,  $HClO_4$ ,  $H_2SO_4$ , and  $H_3PO_4$  on the acetylation of cellulose by AcOH and Ac<sub>2</sub>O are explained on the basis of Brönsted's protolytic theory of catalysis. The greatly increased activity when NaClO<sub>4</sub> is added to  $H_3PO_4$  is similarly explained. A. G.

Catalytic effect of ferricyanide in oxygen absorption of oleic acid. B. F. CHOW and S. E. KAMERLING (J. Biol. Chem., 1934, 104, 69–79; cf. A., 1932, 128).— $O_2$  is necessary for the reduction of K<sub>3</sub>Fe(CN)<sub>6</sub> (I) by oleic acid in HPO<sub>4</sub>" buffer, 5—6 mols. of  $O_2$  being required for the reduction of 2 mols. of (I). With varying Fe<sup>TT</sup>: Fe<sup>TT</sup> ratios and with K<sub>3</sub>Mo(CN)<sub>6</sub>, Cu-glycine, Cu-C<sub>5</sub>H<sub>6</sub>N (II), and indophenol the  $O_2$  absorption was proportional to the redox potential. The reaction with (I) as catalyst was inhibited by phenol, (III), NPhMe<sub>2</sub> (IV), OH-C<sub>2</sub>H<sub>4</sub>·NH<sub>2</sub>, and eugenol, and with (II) as catalyst by (III), (IV), and *p*-C<sub>6</sub>H<sub>4</sub>Br·OH, the inhibition being > could be accounted for by reduction of the catalyst. H. D.

Micro-heterogeneous catalysis of hydrogen peroxide by cholesterol sols. I. REMESOV (Ber., 1934, 67, [B], 134—140).—Mol. disperse cholesterol (I) does not cause decomp. of  $H_2O_2$ , by which it is unaffected under the experimental conditions. Sols of (I) have a catalytic action towards  $H_2O_2$  which is not shared by cholesteryl esters or by lecithin. The change is observed only when the sol is sufficiently conc., and its rate depends on the degree of dispersion of (I). Optimum conditions are given by about 10% H<sub>2</sub>O<sub>2</sub> at  $p_{\rm H}$  6·4–8·04. The catalyst is indifferent towards CN', but is poisoned by Hg and its salts. Reaction is unimol. and resembles the kinetics of catalases and Pt sols. H. W.

Decomposition of nitric oxide by platinum catalysts. J. ZAWADZKI and G. PERLINSKI (Compt. rend., 1934, 198, 260—262).—The decomp. of NO over Pt between 854° and 1055° is unimol. (cf. A., 1929, 520). The reaction is represented according to the state of the Pt surface by  $dx/dt = K_1(a-x)/(1+bx)$ or  $=K_2(a-x)/x$ , where x is % of NO decomposed, a its initial concn., t time of contact,  $K_1$ ,  $K_2$ , and b are consts. The results agree with or lie between those calc. according to one or other of these equations. O<sub>2</sub> added previously has only 0.48—0.56 of the effect of the same amount formed by decomp. The apparent heat of activation is 22,000—25,000 g.-cal. C. A. S.

Catalytic activity of zinc oxide.—See B., 1934, 93.

Catalytic polymerisation of ethylene.—See B., 1934, 135.

Catalytic hydrogenation of nitro-compounds. --See B., 1934, 85.

Catalysts for methane conversion.—See B., 1934, 82.

Adsorption of nitrogen by iron synthetic ammonia catalysts. P. H. EMMETT and S. BRU-NAUER (J. Amer. Chem. Soc., 1934, 56, 35–41).— Rates of adsorption of N<sub>2</sub> by Fe, Fe-Al<sub>2</sub>O<sub>3</sub>, and Fe-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O catalysts have been determined at 273-450°. The energy of activation is about 16,000 g.-cal. and the heat of adsorption about 35,000 g.-cal. Adsorption isotherms at --189° are linear with respect to pressure at 100-760 mm. The rate of adsorption is of the right magnitude to be the slow step in the catalytic synthesis of NH<sub>3</sub>.

E. S. H.

Heterogeneous combustion of carbonic oxide on quartz: water as a negative catalyst. B. W. BRADFORD (J.C.S., 1934, 73-75).—Whilst  $H_2O$  is a positive catalyst on Au surfaces, the reverse is the case on quartz. With dry  $2CO+O_2$  mixtures up to 600° the activation energy is 20,000 g.-cal. and with  $2CO+O_2+15$  mm.  $H_2O$ , 40,000 g.-cal. The absence of a homogeneous reaction in both cases is attributed to long drying of the quartz vessel at 600°. R. S.

Energetics of catalysis. II. Poisoning coefficients and energies of activation of hydrogenation processes. E. B. MAXTED and V. STONE (J.C.S., 1934, 26—29; cf. A., 1933, 680).—The poisoning coeff. is a const. for the hydrogenation of crotonic, oleic, and benzoic acids on a Pt catalyst using Hg<sup>--</sup> ions as poison, whilst the activation energies increase in the order named. R. S.

Vapour-phase esterification. F. E. DOLIAN and H. T. BRISCOE (Proc. Indiana Acad. Sci., 1933, 42, 101-107).—For EtOH+AcOH,  $Al_2(SO_4)_3$  and K alum have little effect on the yield;  $Cr_2(SO_4)_3$  increases the yield slightly and K Cr alum markedly. MgSO<sub>4</sub> promotes esterification above the dehydration temp. With CaCl<sub>2</sub> esterification activity is a min. at 275°. The activity of other salts increases in the order:  $Na_2SO_4$ , NaOAc,  $NaPO_3$ ,  $CdSO_4$ ,  $ZnSO_4$ ,  $MnSO_4$ ,  $ZnCl_2$ ,  $NiSO_4$ . CH. Abs.

Increase in the life-period of  $\beta$ -chloro- $\beta$ -phenylethylamine by carbon. H. FREUNDLICH and G. SALOMON (Helv. Chim. Acta, 1934, 17, 88-98) .---Conversion of CHPhCl·CH<sub>2</sub>·NH<sub>2</sub> (I) into styreneimine hydrochloride in presence of blood charcoal (II) and carboraffin (III; acid-free) (A., 1933, 1112) has been studied kinetically at temp. between 0° and 38°. With (II) for similar initial concns. of (I) max. retardation (1/60-80) times as fast as in homogeneous solution) at 0°, 25°, 30° and 37° occurs with a proportion of (II) 1, 3, and 10, respectively, and the temp. coeff. of the heterogeneous reaction (IV) is = or slightly > that of the homogeneous reaction (V). With (III) (which gives identical absorption of both cation and anion) the retardation is much smaller and the temp. coeff. of (IV) is much < that of (V). As suggested (loc. cit.) with (II) the reaction occurs in the interior of the liquid phase, the acid present in (II) fixing a large proportion of (I) in the form of a salt, but with (III) reaction occurs on the C surface. In agreement with this view the decrease (approx. 5 kg.-cal.) in the heat of activation for the reaction of (I) in presence of (III) compared with that in presence of (II) [which is approx. the same as for (V) is approx, the same as the decrease for the reaction of CH<sub>2</sub>Br·CH<sub>2</sub>·NH<sub>2</sub> (A., 1930, 551) in homogeneous solution compared with that in presence of (II) (surface reaction). J. W. B.

Electrolytic concentration of heavy hydrogen. H. ERLENMEYER and H. GÄRTNER (Helv. Chim. Acta, 1934, 17, 30–31).—Preliminary. Electrolysis of 0.1N-H<sub>2</sub>SO<sub>4</sub> at Pb electrodes is at least as effective as that of aq. KOH at Ni electrodes in concentrating H<sup>2</sup>H<sup>2</sup>O in the residues. F. L. U.

Swelling of graphite at the anode and the mechanical disruption of carbon anodes. H. THIELE (Z. Elektrochem., 1934, 40, 26–33).— Absorption of O by graphite anodes ("swelling") occurs on electrolysis in presence of  $H_2SO_4$ , HClO<sub>3</sub>, HNO<sub>3</sub>, and HF (or their salts); the amount of combined O increases with the acid concn., and is large (e.g., 0.5 c.c. O<sub>2</sub> per g. of C) only at high concn. (e.g., > approx. 30% for  $H_2SO_4$ ). A min. c.d. is necessary. The C acquires a steel-blue colour. "Swollen" C contains both O and acid. On adding  $H_2O$  or aq. NaOH, O<sub>2</sub> is evolved, but not quantitatively. Amorphous C swells less readily than graphite. Swollen C has the properties of a peroxide. The mechanism of the process is discussed. Surface deterioration of graphite anodes can occur without swelling (e.g., in aq.  $H_3PO_4$ ), but swelling is much more disruptive. H. J. E.

Electrolytic separation of metallic niobium. II. N. A. ISGARISCHEV and G. E. KAPLAN (Z. Elektrochem., 1934, 40, 33–36; cf. A., 1933, 681).— The optimum concn. of KOH for dissolving the  $Nb_2O_5$ -Ta<sub>2</sub>O<sub>5</sub> mixture is 20%. In the alkaline or  $H_2O_2O_4$  electrolysis the rate of deposition falls to zero or becomes very small while deposition is still incomplete. This occurs in citric acid solution also, but the solution recovers on keeping, and deposition may be completed. H. J. E.

Number of centres of crystallisation of copper during electrolysis of cupric sulphate. A. GLAZUNOV and J. JANOUŠEK (Chem. Listy, 1933, 27, 457-461).—The no. of centres (I) of crystallisation of Cu appearing during unit time on the cathode increases with increasing c.d. and with diminishing [CuSO<sub>4</sub>]. The velocity of growth of (I) increases rapidly with increasing [CuSO<sub>4</sub>]. R. T.

Velocity of crystallisation during electrolysis of aqueous cadmium acetate and nitrate. A. GLAZUNOV and C. B. KOUŘIL (Chem. Listy, 1933, 27, 489–493).—The velocity of crystallisation of Cd at the cathode increases with the c.d., and diminishes with increasing concn. of Cd(OAc)<sub>2</sub> or Cd(NO<sub>3</sub>)<sub>2</sub>. R. T.

Electrolysis of silver acetate in acetic acid and pyridine. (Silver diacetate and the Kolbe reaction.) C. SCHALL and B. M. SCHALL (Z. Elektrochem., 1934, 40, 5—8; cf. A., 1922, i, 87).—In electrolysing AcOH saturated with AgOAc, a brown colour observed near the anode was attributed to  $Ag(OAc)_2$ . O, produces the same colour. On electrolysing 95% C<sub>5</sub>H<sub>5</sub>N saturates with AgOAc, the dark red compound Ag(OAc)\_2,2.7C<sub>5</sub>H<sub>5</sub>N crystallised, decomp. rapidly when isolated. With aq. NaOH it formed AgO. With I in AcOH it yielded Ag(OAc)\_2I. The mechanism of the Kolbe reaction is discussed. H. J. E.

Electrolytic preparation of isopropyl alcohol. G. A. KIRKHGOF and A. D. STEPANOV (Khim.-Farm. Prom., 1932, No. 1, 21).—A glass cell, 85 sq. cm. in cross-section, and a porous cup diaphragm are used. The anode is Pb in 15% H<sub>2</sub>SO<sub>4</sub>, and the cathode Hg in a mixture of 150 c.c. of 15% H<sub>2</sub>SO<sub>4</sub> and 37.5c.c. of COMe<sub>2</sub>. 8 amp. at 6—7 volts is used for 9 hr. The cathode liquid is then neutralised with conc. aq. NaOH and the Pr<sup>g</sup>OH distilled (yield 33% of theory). CH. ABS.

Electrolytic reduction of aromatic nitro-compounds. I. Preparation of ethyl *p*-aminobenzoate. G. KAWATA (J. Electrochem. Assoc., Japan, 1933, 1, 51—54).—The optimum temp. is 58—60°. When 7.5% HCl+*p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Et (Sn cathode) and 5% H<sub>2</sub>SO<sub>4</sub> (Pb anode) are used, the highest current efficiency (75%) is attained with the best yield (77%). Sb, Cu, and Ni cathodes lower the yield. CH. ABS.

Gaseous combustion in electric discharges. IX. Cathodic water-gas equilibrium. G. I. FINCH, B. W. BRADFORD, and R. J. GREENSHIELDS (Proc. Roy. Soc., 1934, A, 143, 482-486).—An investigation has been made of the cathodic equilibrium between steam and CO. The observed vals. of  $K_p$  vary continuously with the pressure throughout the range studied. The results indicate that equilibrium is approached from the CO side in two ways, pressure being favourable to the one but not to the other (cf. A., 1931, 44). L. L. B.

Free radicals and photochemistry of solutions. J. FRANCK and E. RABINOWITSCH (Trans. Faraday Soc., 1934, 30, 120-130).—See A., 1933, 1255.

T

Photo-oxidation of nitrite to nitrate. N. R. DHAR, S. P. TANDON, N. N. BISWAS, and A. K. BHATTACHARYA (Nature, 1934, 133, 213—214).— Dil. solutions of NaNO<sub>2</sub> or KNO<sub>2</sub> are oxidised to nitrate by exposure to sunlight and air. The photochemical oxidation is accelerated by the presence of TiO<sub>2</sub>, ZnO, and Fe<sub>2</sub>O<sub>3</sub>. The equilibrium  $2\text{KNO}_3 \implies$  $2\text{KNO}_2 + O_2$  is probably obtained and in dil. solutions with excess of O<sub>2</sub>, most of the nitrate (I) is oxidised to nitrate (II) in light. Ammonification, nitrification, and the conversion of (I) into (II) in soil are photochemical rather than bacterial processes. L. S. T.

Photochemistry of phosgene. L. S. KASSEL (J. Amer. Chem. Soc., 1934, 56, 243).—Recent work (A., 1933, 1255) is criticised. E. S. H.

Oxidation of mercury vapour under the action of ultra-violet light. J. M. FRANK (Compt. rend. Acad. Sci. U.R.S.S., 1933, 4, 146—148).—At  $p_{0_3}$ < 1 cm., the formation of HgO initiated by excited Hg is proportional to the intensity of incident light of  $\lambda 2537$  Å., and independent of shorter  $\lambda$ . With  $p_{0_3} > 1$  cm., HgO is formed when  $O_2$  mols. alone are excited by  $\lambda 1860$ , 1935, and 1990 Å., which produce  $O_3$ , and hence excited Hg is not necessary for HgO synthesis in the presence of  $O_3$ . Consistently with the mechanism (1) Hg\*+ $O_2$  —> Hg+ $O_2$ \*, (2)  $O_2$ \*+ $O_2$  $\longrightarrow O_3$ +O, (3)  $O_3$ +Hg  $\longrightarrow$  HgO+ $O_2$ ,  $O_3$  is always produced during these reactions (cf. A., 1929, 155, 777). J. G. A. G.

Photographic sensitivity, latent image, and development. S. E. SHEPPARD (Ber. VIII Int. Kongr. Phot., Dresden, 1931, 13—28; Sci. Publ. Kodak Res. Labs., 1931—1932, 15, 203—213).— Current theories of latent image formation, sensitisation, and desensitisation are discussed. The theory of the production of photo-Ag and the existence of sensitive Ag<sub>2</sub>S nuclei is supported. J. L.

*p*-Aminophenol standard developer for sensitometry. S. E. SHEPPARD and A. P. H. TRIVELLI (Ber. VIII Int. Kongr. Phot., Dresden, 1931, 113—116; Sci. Publ. Kodak Res. Labs., 1931—1932, 15, 200— 202).—The "M20" formula [OH·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>,HCl7·275, Na<sub>2</sub>SO<sub>3</sub> (anhyd.) 50, Na<sub>2</sub>CO<sub>3</sub> (anhyd.) 50 g., H<sub>2</sub>O to 1000 c.c.] is proposed as a standard for sensitometric comparisons. This developer gives the same speed vals. for different emulsions as with pyro-soda, elon, or elon-quinol developers. Nitrobenziminazole (M/3750) could be used as an efficient anti-fogging agent to be added when the developer was used for photographic photometry, normalisation of reciprocity failure, etc. J. L.

Spontaneous growth of the latent image between exposure and development. III, IV. E. R. BULLOCK (Sci. Ind. Phot., 1932, [II], 3, 201-206, 241-244; 1933, [II], 4, 6-10, 33-40; Sci. Publ. Kodak Res. Labs., 1931-1932, 15, 45-48; cf. B., 1932, 129).—The growth val. (defined as the max. % density increase of the developable image, corresponding with two different exposure ages) is apparently independent of temp., wave-length of the exposing light, or the effect of a slight general pre-exposure. The max. observed with increasing development time is very marked with process film. The influence of humidity, intensity of light, and composition of the developer is described. It is suggested that the latent image is formed by stages, one of which is slow in propagation. J. L.

Grainless photographic silver. F. WEIGERT (Naturwiss., 1934, 22, 71—72).—The Ag formed on an exposed and developed photographic plate, after drying, shows dichroism. A portion of the Ag must be grainless. A. J. M.

Solarisation of photographic plates. A. SMAKULA (Z. Physik, 1933, 87, 231–237).—Solarisation of AgBr photographic plates varies rapidly with wave-length, showing a max. near 400 m $\mu$ , the region of max. sensitivity for light of normal intensity. It is due to the re-forming of AgBr mols. by excited Br atoms. A. B. D. C.

Law for [photographic] density curves with mixed coloured lights. A. VAN KREVELD (Z. wiss. Phot., 1934, 32, 222—230).—The *D* curves for red (6500 Å.) and violet (4500 Å.) lights and mixtures of these two on a variety of emulsions have been measured. The energy relation of the coloured lights was:  $E_r: E_v=25:1$ . For a given const. *D*, the law  $1/I_{r+v}=1/I_r+1/I_v$  (where  $I_r$ ,  $I_v$ , and  $I_{r+v}$ are the intensities of red, violet, and mixed light, respectively, required to produce the const. *D* with const. exposure) is theoretically derived and shown, in practice, to be correct within experimental error. The corollary law  $E'_{+e}/E_r+E'_{+e}/E_v=1$  ( $E'_{+e}$  and  $E'_{+e}$  are the red and violet portions of the total energy of the mixed light) is also shown to be experimentally correct. Hence the curve for mixed light can be derived from the curves of the separate lights, and other special relations are deduced. J. L.

Photographic properties of silver sulphide. III.—See B., 1934, 123.

Action of ultra-violet light on glycine. V. HENRI, C. WEIZMANN, and Y. HIRSCHBERG (Compt. rend., 1934, 198, 168—170).—0·1*N*-Aq. glycine irradiated by Hg light for 15 hr. showed the following changes : conductivity  $1.54 \rightarrow 71.20 \times 10^{-3}$ ,  $p_{\rm fl} 4.80 \rightarrow 7.45$ ; % possible NH<sub>3</sub> formed  $0 \rightarrow 13.1$ . Comparison with non-irradiated aq. glycine and NH<sub>3</sub> showed that the NH<sub>3</sub> formed accounted almost entirely for the changes in conductivity and  $p_{\rm fl}$ . The main decomp. is NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H + H<sub>2</sub>O = OH·CH<sub>2</sub>·CO<sub>2</sub>H+NH<sub>3</sub>, but the presence of glycollic acid and absence of AcOH were proved. C. A. S.

Ultra-violet radiation in the photochemical oxidation of toluene. A. CASTIGLIONI (Gazzetta, 1933, 63, 818—820).—Experiments with a Hg-vapour lamp screened by ordinary glass and by glass transparent to ultra-violet radiation show that the short wave-lengths accelerate the photochemical oxidation of PhMe to BzOH. H. F. G.

Photochemical reaction between *m*-dinitrobenzene, ethyl alcohol, and ammonia. G. SOLLAZZO (Boll. Chim. farm., 1933, 72, 913—915).— Vessels containing the reactants were exposed to sunlight at an altitude of 2812 m. above sea level. After 13 min. the reaction had commenced, and it was completed within 52 min.; the colour was then stable, and did not change after 2 months in the dark. Under similar conditions of exposure a mixture of m- $C_6H_4(NO_2)_2$ , amyl alcohol, and  $NH_3$  became yellow on the surface within 2 min., and later violet, and subsequently a yellow ppt., becoming red, was formed. The reaction was completed in 60 min., the mixture being then brown; after about 3 hr. the whole of the coloration had vanished. The influence of altitude on photochemical reactions is discussed. H. F. G.

Photochemistry of fluorescein dyes. H. F. BLUM and C. R. SPEALMAN (J. Physical Chem., 1933, 37, 1123—1133).—The peroxide formed when fluorescein dyes are irradiated in  $H_2O$  in presence of  $O_2$  is probably  $H_2O_2$ , and the bleaching of the dye is probably due to oxidation by this  $H_2O_2$  after the activation of the dye mol. by light. M. S. B.

Effects of  $\alpha$ -particles on aqueous solutions. I. Decomposition of water. II. Oxidation of ferrous sulphate. C. E. NURNBERGER (J. Physical Chem., 1934, 38, 47-69) .- A direct and an indirect method of irradiating liquids with a-rays from radon are described and the decomp. of H2O by a-rays is suggested as a method for the determination of the transmission of a-ray tubes. The gas yields deviate to some extent from the general law of Cameron and Ramsay, owing to recombination of ions in the  $H_2O$ . When aq.  $FeSO_4$  is irradiated by either method the gas obtained is nearly 100% H<sub>2</sub>. The ratio  $M_{\text{FeSO}_4}/N$ , where M is the no. of FeSO<sub>4</sub> mols. transformed and N the no. of ion pairs formed in  $H_2O$  by the absorption of the radiant energy employed, increases in solutions of high concn. (up to 0.5000M) without a corresponding increase of  $M_{\rm H_2}/N$ , and becomes considerably > 2, so that reactions other than the simple oxidation of FeSO4 with the liberation of H2 must take place.

M. S. B.

Ion yield in decomposition of ammonia by  $\alpha$ -rays. H. ESSEN and D. FITZGERALD (J. Amer. Chem. Soc., 1934, 56, 65-67).—The ion yield is 1.09 at 22° and 1 atm. E. S. H.

Heavy hydrogen. C. GROENEVELD (Chem. Weekblad, 1934, 31, 54-60, 118-124).—A review.

Chemical separation of diplogen from hydrogen. A. FARKAS and L. FARKAS (Nature, 1934, 133, 139).—The H<sub>2</sub> liberated by the dissolution of Zn in 0.1N-H<sub>2</sub>SO<sub>4</sub> containing 25% of H<sub>2</sub> contains only 8% of H<sub>3</sub>, *i.e.*, the rates of production are in the ratio of 4:1 approx. For Al, Na, and Ca the approx. ratios are 2, 1.2, and 1.5, respectively. Reactions of this type may serve as an alternative method for the production of H<sup>2</sup> and its compounds. L. S. T.

Interchange between deuterium gas and hydrogen in compounds. A. J. GOULD and W. BLEAKNEY (J. Amer. Chem. Soc., 1934, 56, 247–248). —The composition of  $H_2^3$ – $H_2^1$  mixtures in contact with  $H_2O$  remains const. in absence of preferential solubility, diffusion, and metallic surfaces (cf. this vol., 37). Greased stopcocks may be used without risk of reaction with  $H_2^3$ . E. S. H.

Formation of alkali-metal hydrides by atomic hydrogen. (MISS) E. FERRELL, T. G. PEARSON, and P. L. ROBINSON (J.C.S., 1934, 7-8; cf. A., 1933, 1257).—At. H from a discharge tube converts mirrors of Li, K, and Na into the white hydrides. R. S.

Dark reaction between sodium formate and iodine. S. S. DOÔSAY and W. V. BHAGWAT (Z. anorg. Chem., 1934, 216, 241–252; cf. A., 1931, 802). —The "dark" reaction between aq. I and  $HCO_2Na$ is bimol. both in presence and in absence of KI, but in the latter case the velocity is several hundred times greater. The influence of K halides has been studied. The reaction is retarded by H<sup>\*</sup>. The temp. coeff. has been determined. F. L. U.

Action of solutions of alkaline bases on mercuric iodide. (MLLE.) M. L. DELWAULLE (Bull. Soc. chim., 1933, [iv], 53, 1295-1307).-Dil. solutions of KOH with HgI<sub>2</sub> give yellow HgO and alkaline aq. HgI<sub>2</sub>,2KI with the transitory formation of a wine-coloured oxyiodide HgI<sub>2</sub>,HgO. More conc. solutions, 2-6M, give practically pure red HgO, but as the concn. is gradually increased a white compound, content. Is gratularly increased a white composition, 3HgI<sub>2</sub>,HgO,3KOH, is formed in increasing proportion until it alone remains. Very conc. aq. KOH (above 7M) gives, according to the amount of HgI<sub>2</sub> present, two oxyloides, HgI<sub>2</sub>,3HgO, and HgI<sub>2</sub>,2HgO, contain-ing some KOH. With aq. NaOH on HgI<sub>2</sub> there is a inclusion of HgI HgO at compute  $\leq 6M$  At similar formation of  $HgI_2$ , HgO at conces. < 6M. At concns. < 3M yellow HgO is formed and above this concn. red HgO and also a red oxyiodide, if some unchanged HgI, is present. Very conc. solutions give a pale yellow oxyiodide,  $HgI_2, 2HgO$ , containing chemically combined NaOH. The action of LiOH on  $HgI_2$ is not very marked. A small proportion of yellow HgO is formed and HgI<sub>2</sub> dissolves in the aq. LiI produced in the proportion of HgI<sub>2</sub> to 2LiI. M. S. B.

Compounds of hexamethylenetetramine. L. DEBUCQUET and L. VELLUZ (Bull. Soc. chim., 1933, [iv], 53, 1288–1291).— $(CH_2)_2N_4$  (=hex) with  $K_2CrO_4$  and MgSO<sub>4</sub> in H<sub>2</sub>O during 24 hr. affords 2MgCrO<sub>4</sub>, 3 hex, 15H<sub>2</sub>O, whereas with  $K_2Cr_2O_7$  and MgSO<sub>4</sub> (or CaCl<sub>2</sub>), it gives MgCr<sub>2</sub>O<sub>7</sub>, 2 hex, 5H<sub>2</sub>O and CaCr<sub>2</sub>O<sub>7</sub>, 2 hex, 7H<sub>2</sub>O, respectively. Interaction of MgSO<sub>4</sub> with CaKFe(CN)<sub>6</sub>, 2 hex, 6H<sub>2</sub>O and

 $CaK_{2}Fe(CN)_{6}$ , hex,6H<sub>2</sub>O in H<sub>2</sub>O-hex leads to Mg<sub>2</sub>Ca[Fe(CN)<sub>6</sub>]<sub>2</sub>,4 hex,24H<sub>2</sub>O and 3MgCaFe(CN)<sub>6</sub>,4 hex,40H<sub>2</sub>O, respectively.

Reactions between dry inorganic salts. E. B. THOMAS and L. J. WOOD (J. Amer. Chem. Soc., 1934, 56, 92—97).—Examination by the X-ray method has established double decomp. of the fused mixtures KCl-NaBr, KCl-NaI, and KCl-NaNO<sub>3</sub> in absence of a solvent. Equimol. mixtures of KF and NaCl give KCl and NaF when melted, whilst equimol. mixtures of AgCl and KBr yield AgBr and KCl. Double decomp. has been observed in KCl-NaBr mixtures at temp. < the m.p. All the reactions go to completion and the final products are insol. in each other in the solid state. E. S. H.

Solubility of copper hydroxide in ammonia. G. ETTISCH, E. HELLRIEGEL, and D. KRÜGER (Ber., 1934, 67, [B], 22—24).—The graph showing the relationship between mol.  $NH_3$ : mol. dissolved Cu and concn. of  $NH_3$  passes through a min. between 4N- and 6N- $NH_3$ . H. W. Constitution of Strömholm's double salts:  $2MCI,M_2Cr_2O_7,4HgCl_2,2H_2O$ . G. SPACU and C. G. MACAROVICI (Z. anorg. Chem., 1934, 216, 263–272).— The constitution

Graphitisation process. V. S. VESSELOVSKI and V. N. PERTZOV (Z. anorg. Chem., 1934, 216, 228– 240).—The course of graphitisation of different varieties of C has been studied. The process is regarded as a thermal recrystallisation of graphite crystallites present in the original material. The latter is classified with respect to its "disperse structure," which determines the character of the resulting graphite.

F. L. U.

Oxidation of graphite. V. SIHVONEN (Suomen Kem., 1934, 7, 75—76B).—A summary of the various reactions described in lit.

Formation of refractory metal carbides by a carbon filament glowing in the vapour of a halogen compound of the metal. W. G. BURGERS and J. C. M. BASART (Z. anorg. Chem., 1934, 216, 209–222).—C filaments glowed at  $1600-2500^{\circ}$  in vapours of TiCl<sub>4</sub> and ZrCl<sub>4</sub> are converted into TiC and ZrC, respectively. TaCl<sub>5</sub> vapour with H<sub>2</sub> yields TaC, Ta<sub>2</sub>C, or Ta, according to the temp. The products usually contain excess of metal in solid solution, and can be purified by glowing at a high temp. in a vac. The following lattice consts. have been determined : TiC, ZrC, and TaC (face-centred cubic) a 4.320, 4.687, and 4.445 Å., respectively; Ta<sub>2</sub>C (hexagonal close-packed) a 3.091, c 4.93 Å. F. L. U.

Action of carbon disulphide on alumina gel. L. A. MUNRO and J. W. MCCUBBIN (Canad. J. Res., 1933, 9, 424–431; cf. A., 1926, ii, 191).—The yellow coloration produced when  $CS_2$  is adsorbed by  $Al_2O_3$  gel is due to a mixture of  $Na_2S$ , NaHS, and  $NaS_x$ .  $CS_2$ reacts primarily with  $H_2O$  contained in the gel and the products react further with NaOH which is present in small amount, to give the yellow colour. R. S.

Zirconium sulphides. M. PICON (Bull. Soc. chim., 1933, [iv], 58, 1269—1277; cf. A., 1933, 918).— Cold conc.  $H_2SO_4$  attacks all three sulphides slowly in the order  $ZrS_2 < Zr_2S_5 < ZrS_3$ .  $H_2S$  is evolved and a sulphate formed. Aq.  $H_2C_2O_4$  reacts slowly and incompletely, whether hot or cold, producing  $H_2S$ . Neutral  $H_2O_2$  reacts rapidly with  $ZrS_2$  giving  $H_2S$ ,  $H_2SO_4$  and a basic sulphate. The other sulphides react only slowly. M. S. B.

Quaternary intermetallic compounds. A. S. RUSSELL (Nature, 1934, **133**, 217).—Zn and the simplest ternary compound of Sn and Cu which forms in Hg, viz., SnCu<sub>3</sub>Hg<sub>7</sub>, yield quaternary compounds (I) of the following approx. formula:  $Sn_4Cu_{12}Zn_4Hg_3$ ,  $Sn_5Cu_{15}Zn_5Hg_9$ ,  $SnCu_3ZnHg_6$ ,  $SnCu_3ZnHg_9$ ,  $Sn_4Cu_{12}Zn_4Hg_{45}$ ,  $Sn_4Cu_{12}Zn_7Hg_{21}$ , and  $Sn_4Cu_{12}Zn_7Hg_{33}$ . Sn and ZnCu yield  $Zn_8Cu_8SnHg_7$ ,  $Zn_6Cu_8SnHg_9$ ,  $Zn_{40}Cu_{40}Sn_5Hg_{14}$ , and  $Zn_{40}Cu_{40}Sn_{12}Hg_{21}$ . Quaternary compounds including Cd could not be prepared. The

J. L. D.

derivation of (I), and rules connecting the nos. of valency electrons and atoms, are discussed.

L. S. T.

Reactions of anhydrous thorium tetrabromide with organic liquids. R. C. YOUNG (J. Amer. Chem. Soc., 1934, 56, 29–31).—ThBr<sub>4</sub> reacts with the corresponding org. liquids at temp. up to the b.p., forming  $ThBr_4$ , 4EtOH,  $ThBr_4$ , 2EtOAc,  $ThBr_4$ , 4MeCN, and  $ThBr_4$ ,  $3C_5H_5N$ . In other cases mol. compounds are formed at room temp., but hydrated ThOBr<sub>2</sub> org. complexes are formed at the b.p. Such compounds

are  $ThBr_4, 4PhCHO, 2Th\dot{B}r_4, 7COPhMe,$   $ThBr_4, 4NH_2Ph, ThOBr_2, 2PhCHO, H_2O,$  $ThOBr_2, 0.5COPhMe, H_2O,$  and

 $ThOBr_{2,0} \cdot 5COPhEt, H_2O.$  At room temp. ThBr<sub>4</sub>, 3EtOBz is formed, but yields Th(OBz)<sub>2</sub> at the b.p. E. S. H.

Chemical reactions involving active nitrogen. R. H. EWART and W. H. RODEBUSH (J. Amer. Chem. Soc., 1934, 56, 97–98).—Active N and HBr or HI react to form NH<sub>4</sub>Br or NH<sub>4</sub>I, accompanied by luminous phenomena. The mechanism is discussed.

E. S. H.

Reactions in liquid ammonia. I. Germanium sulphides. W. C. JOHNSON and A. C. WHEAT-LEY (Z. anorg. Chem., 1934, 216, 273–287; cf. A., 1932, 1205).—Cryst. and amorphous GeS and GeS<sub>2</sub> have been prepared and their properties are described. Solubilities of GeS, GeS<sub>2</sub>, Na<sub>2</sub>S, and Na<sub>2</sub>S+NH<sub>4</sub>Br in NH<sub>3</sub> at  $-33^{\circ}$  have been determined. GeS and GeS<sub>2</sub> do not undergo ammonolysis. The solutions are acted on by Na, forming Na<sub>2</sub>S and Ge, and ultimately NaGe<sub>x</sub>. F. L. U.

Reaction of nitrous oxide with hydrogen atoms. J. K. DIXON (J. Amer. Chem. Soc., 1934, 56, 101–102). —H<sub>2</sub>O is formed by reaction of N<sub>2</sub>O and H atoms at 25° under low pressures. No O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> was detected. E. S. H.

Phosphoric acid and phosphates. V. Hydrolysis of dicalcium and tricalcium phosphates. A. SANFOURCHE and J. HENRY. VI. Superphosphates. A. SANFOURCHE. VII. Decomposition of monocalcium phosphate by water in presence of calcium sulphate. VIII. Action of water on iron and aluminium phosphates. IX. Determination of free phosphoric acid in superphosphate. **X**. Determination of water-soluble phosphoric acid in superphosphate. A. SAN-FOURCHE and B. FOCET (Bull. Soc. chim., 1933, [iv], 53, 1210-1217, 1217-1221, 1221-1226, 1226-1232, 1232-1239, 1239-1242).-V. The hydrolysis of CaHPO<sub>4</sub> takes place only in presence of  $Ca_3(PO_4)_2$ , one of the products of hydrolysis. Both substances are then hydrolysed together, giving ultimately  $3Ca_{s}(PO_{4})_{2}$ ,  $Ca_{3}(PO_{4})_{2}$  cannot be isolated by a wet method.

VI. A discussion of the possible constitution of superphosphate (I), its physical condition, and the difficulties encountered in attempts to determine its constitution.

VII. The decomp. of  $CaH_4(PO_4)_2$  by  $H_2O$  is abnormal in that the fraction dissociated increases with concn. Addition of  $CaSO_4$  increases the total amount of decomp., but alters its course so that in presence

of 50% CaSO<sub>4</sub> it becomes normal. This behaviour is attributed to the formation of an insol. double salt.

VIII. FePO<sub>4</sub> is hydrolysed in solution forming basic phosphate, the extent depending on the free acid present. The action is generally rather slow and continues during the washing of the phosphate ppt. The effect on the analysis of (I) is to give too high a free acidity and to diminish the amount of  $P_2O_5$  sol. in  $H_2O$ . AlPO<sub>4</sub> in solution in  $H_3PO_4$  is not hydrolysed by dilution. When treated directly by  $H_2O$  it is attacked similarly to FePO<sub>4</sub>, but the products are sol. and do not affect the (I) analysis.

IX. The most satisfactory liquid for the extraction of free  $P_2O_5$  from (I) is HCO<sub>2</sub>Et.

X. Total acidity in (I) is determined volumetrically by NaOH and phosphate by AgNO<sub>3</sub>. The various causes of error and the possibility of correcting some of them are discussed. M. S. B.

[Explosive] phosphonium perchlorate. F. FICHTER and H. ARNI (Helv. Chim. Acta, 1934, 17, 222—224).—Direct analysis of phosphonium perchlorate, prepared from PH<sub>3</sub> and 70% HClO<sub>4</sub> at  $-20^{\circ}$ , shows it to have the composition 2PH<sub>3</sub>,3HClO<sub>4</sub>. The compound is dangerously explosive. F. L. U.

Hydroxo-compounds. H. BRINTZINGER and J. WALLACH (Angew. Chem., 1934, 47, 61-63).—The rate of diffusion through Cellophane indicates the presence of the following anions in complex hydroxides containing KOH<sub>4</sub>: Sb(OH)<sub>6</sub>', Sb(OH)<sub>4</sub>', Ge(OH)<sub>6</sub>'', Al<sub>2</sub>(OH)<sub>8</sub>'', Ga<sub>2</sub>(OH)<sub>8</sub>'', Zn<sub>2</sub>(OH)<sub>8</sub>'', Be<sub>10</sub>(OH)<sub>40</sub>(?). Plumbites and stannates gave irregular results. A. G.

Preparation of ductile tantalum by thermal dissociation of tantalum pentachloride. W. G BURGERS and J. C. M. BASART (Z. anorg. Chem., 1934, 216, 223—227).—The Ta deposited on a Ta filament glowed in TaCl<sub>5</sub> vapour is highly ductile if foreign gases are rigorously excluded. Lattice consts. for Ta and Nb prepared in this way are, respectively,  $3\cdot296\pm0\cdot0005$  and  $3\cdot294\pm0\cdot001$  Å. F. L. U.

Action of chlorine on chromite in the presence of reducing substances. V. S. JATLOV and A. V. POPOVA (J. Appl. Chem. Russ., 1933, 6, 1049–1053).—• The entire metal oxide content of chromite is converted into Fe, Al, and Cr chlorides by passing  $Cl_2$ during 30 min. at 800°; this process cannot be applied to the separation of these metals. The velocity of formation of chlorides from the metals is > from their oxides, for which reason conversion is obtained at lower temp. in presence of C. Admixture of CO to the  $Cl_2$  retards reaction, owing to dilution of  $Cl_2$ . R. T.

Class of tartaric acid compounds. J. B. MATHIEU (Compt. rend., 1934, 198, 251-253).—The tartrates of the apparently simple formula RT,2 or  $2 \cdot 5H_2O$  (R=Cr<sup>II</sup>, Mn<sup>II</sup>, Fe<sup>II</sup>, Ni, Co, or Zn; T=  $C_4H_4O_6^{(\prime)}$ ) are really complex, [RT(OH<sub>2</sub>)<sub>2</sub>] and nonelectrolytic. If to a solution of one of them excess of aq. Na<sub>2</sub>T is added a true double salt, R<sup>II</sup>T,Na<sub>2</sub>T is formed. The reaction  $0 \cdot 4$ - $1 \cdot 7NaOH$ +RSO<sub>4</sub>+Na<sub>2</sub>T (all in aq. solution) gives ppts. of varying composition : R=Zn, ZnO; R=Mn<sup>II</sup>, Fe<sup>II</sup>, or Co, R<sub>2</sub>T, and with R=Fe<sup>II</sup> also Fe<sup>II</sup><sub>3</sub>T<sub>2</sub> (cf. A., 1931, 823); R=Ni, indefinite and gelatinous. The same compounds are
obtained by digesting  $2R(OH)_2$  with tartaric acid. Mixed solutions containing  $2NaOH+RSO_4+Na_2T$  remain clear for some time, but finally give a ppt. of  $[R(OH)_2T]Na_2$ . The Co and Cu<sup>II</sup> compounds show circular dichroism, the Ni compound slightly so in the red, the Mn<sup>II</sup> and Fe<sup>II</sup> not at all, whilst the Zn compound exhibits normal rotatory dispersion. C. A. S.

Fluorine. I. F. ISHIKAWA and T. MUROOKA (Sci. Rep. Tôhoku, 1933, 22, 1155—1162; cf. A., 1933, 1251).—The preservation of F in glass bulbs has been studied. The % of F in a gas mixture needed to cause ignition of some inorg. and org. substances varies from 7.5 ( $C_6H_6$ ) to 30 (wood C). F. L. U.

Bromine. J. D'ANS and P. HÖFER (Angew. Chem., 1934, 47, 71—74).—The existence of  $Br_{2,8}H_{2}O$ is confirmed; it is converted into Br and  $H_{2}O$  at 5.84°. The v.p. of Br in  $H_{2}O$  and in a solution containing NaCl, KCl, MgCl<sub>2</sub>, and MgSO<sub>4</sub> have been determined at different temp. The iodometric determination of Br' by van der Meulen's method is accurate in presence of a large excess of Cl'. E. S. H.

Formation of carbonyls and related compounds. A. A. BLANCHARD, J. R. RAFTER, and W. B. ADAMS, jun. (J. Amer. Chem. Soc., 1934, 56, 16—17).—Ni(CO)<sub>4</sub> and Co(CO)<sub>4</sub> are prepared at room temp. by treating alkaline suspensions of the sulphide or cyanide with CO. Using a mixture of CO and NO, Co(CO)<sub>3</sub>NO (I) is formed. The v.p. and v.d. of (I) have been determined. E. S. H.

Iridium hydroxopentammines. B. E. DIXON (J.C.S., 1934, 34-36).—The action of  $Ag_2O$  on  $[Ir(NH_3)_5Cl]Cl_2$  gives the light buff compound  $[Ir(NH_3)_5Cl](OH)_2, H_2O$ , which absorbs  $CO_2$  slowly from the atm. and constitutes the most stable of the simple ammine hydroxides. The compounds  $[Ir(NH_3)_5(OH)]Cl_2, H_2O$  and  $[Ir(NH_3)_5(OH)](NO_3)_2$  are obtained as colourless crystals by treatment of the corresponding aquo-salts with aq.  $NH_3$ . R. S.

General theory of the contamination of solid systems. D. BALAREV (Z. anal. Chem., 1934, 96, S1-91).—Cryst. ppts. are composed of minute elementary structural units (I) (cf. the Smekal blocks) which must deviate from the stoicheiometric composition (II) in proportion to the fineness of the mosaic structure. (II) is attained by a compensating preponderance of one or other ion in the interstitial "cement" (III). Impurities may be included (a) as foreign ions in (III), (b) as adsorbed layers on (I), or (c) as solid solutions within the lattice of (I).

J. S. A.

Electrometric methods in physical and analytical chemistry. S. GLASSTONE (Inst. Chem., 1934, 39 pp.).—A lecture.

Methods of "photo-electric titrations." F. MÜLLER (Z. Elektrochem., 1934, 40, 46—51).—A review of the use of photo-electric cells in automatic titrations and colorimetric measurements.

H. J. E.

Fluorescence and its use as a method of testing and analysis. J. GRANT (Nature, 1934, 133, 124– 126).—A summary. L. S. T.

Standardisation of volumetric solutions. J. GRANT (Chem. and Ind., 1934, 76-77).-A system in which the normalities of all commonly used volumetric solutions may be determined in relation to a primary standard of 0.5N-HCl is described. D. R. D.

Qualitative analysis of insoluble substances (insoluble residue). A. FOSCHINI (Annali Chim. Appl., 1933, 23, 522—527).—Procedure is described for the qual. examination of inorg. substances not dissolved by boiling cone. HCl. Pptn. of S during the separation of AgCl from AgBr and AgI by means of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> may be avoided, and the detection of Sn and Sb is simplified, by treatment with HCl instead of H<sub>2</sub>SO<sub>4</sub>. T. H. P.

Spot methods for the determination of  $p_{\rm H}$ . F. R. McCrumb (J. Lab. Clin. Med., 1933, 18, 1174— 1178).—A discussion of advantages and sources of error. CH. Abs.

Cymyl-orange, a new indicator. A. S. WHEELER and J. H. WATERMAN (J. Elisha Mitchell Sci. Soc., 1933, 49, 36).—Aminocymene sulphate is dehydrated and sulphonated with fuming  $H_2SO_4$  at 165°. The purified sulphonic acid is diazotised and coupled with NMe<sub>2</sub>Ph, forming  $SO_3H \cdot C_6H_2MePr \cdot N_2 \cdot C_6H_4 \cdot NMe_2$ , which, yellow in acid and pink in alkaline solutions, is preferred to Me-orange as an indicator. CH. ABS.

 $\psi$ -Cumenesulphonic acid as a standard in alkalimetry. D. TISCHTSCHENKO (J. Appl. Chem. Russ., 1933, 6, 1182—1186).— $\psi$ -Cumene-5-sulphonic acid (2H<sub>2</sub>O) (I) has m.p. 114·5—115°, and may be dried at 40° without loss of H<sub>2</sub>O of crystallisation. (I) is a strong acid, behaving as HCl in the titration of alkalis. It is recommended as a standard in alkalimetry.

R. T.

New type of antimony electrode for  $p_{\rm H}$  measurements. T. R. BALL, W. B. SCHMIDT, and K. S. BERGSTRESSER (Ind. Eng. Chem. [Anal.], 1934, 6, 60-61).—Sb coated with sulphide instead of oxide may be used as an Sb electrode. Five methods for the prep. of such electrodes are described. When prepared by suspending sticks of Sb in hot 0.30N-HNO<sub>3</sub> for 1 hr., followed by saturation with H<sub>2</sub>S, they may be used to determine a  $p_{\rm H}$  range of 2—10 with an agreement within 3 mv. The presence of starch, sugar, or NO<sub>3</sub>' has no effect on the results but OH-acids render them valueless. The electrode may be used to determine the sap. val. of oils, but offers no advantage over the ordinary Sb electrode. M. S. B.

Determination of  $p_{II}$  values with the antimony electrode. J. DI GLERIA (Proc. 2nd Internat. Cong. Soil. Sci., 1933, 2, 17—19).—Results were closely comparable with those obtained with the quinhydrone electrode. A. G. P.

Glass and other electrodes for measuring  $p_{\rm H}$ values of very dilute buffers and of distilled water. J. O. BURTON, H. MATHESON, and S. E. ACREE (Ind. Eng. Chem. [Anal.], 1934, 6, 79, and Bur. Stand J. Res., 1934, 12, 67–73).—The quinhydrone and H electrodes are not satisfactory for distilled H<sub>2</sub>O and dil. buffers. The glass electrode and isohydric indicator methods give approx. the same  $p_{\rm H}$ vals. for clear colourless solutions and are equally satisfactory. For samples which are coloured, turbid, or possess oxidising or reducing properties the glass electrode is preferable. M. S. B. Volumetric determination of chlorates by induced reduction in presence of osmium tetroxide as catalyst. K. GLEU (Z. anal. Chem., 1933, 95, 385-392).—Oxidation of  $As_2O_3$  by KClO<sub>3</sub> is catalysed by traces of  $OsO_4$  (I), but proceeds only slowly. The powerful induced reducing action accompanying Ce(SO<sub>4</sub>)<sub>2</sub> oxidations in presence of (I), which keeps the [Fe(o-phenanthroline)<sub>3</sub>] indicator (II) in the Fe<sup>\*</sup> state, enables KClO<sub>3</sub> to oxidise  $As_2O_3$  quantitatively, provided  $\leq 2$  c.c. excess of 0.1N- $As_2O_3$  are present. Excess  $As_2O_3$  is added to the acid ClO<sub>3</sub>' solution,  $O_2$  expelled by addition of NaHCO<sub>3</sub>, 3 drops each of 0.01M-(I) and (II) are added, and the solution is titrated directly with Ce(SO<sub>4</sub>)<sub>2</sub>. J. S. A.

Determination of small amounts of bromine in presence of larger amounts of chlorine and iodine. S. H. BERTRAM (Biochem. Z., 1933, 266, 417).—In the author's method (A., 1933, 686) the slight losses of I can be avoided by addition of a few drops of starch solution during distillation.

P. W. C.

Potentiometric determination of halogens in mineral water and in saline water.—See B., 1934, 174.

Iodometric micro-determination of  $IO_3'$  and  $Cr_2O_7''$  in low concentrations. Application of silver catalysis. S. K. HAGEN (Z. anal. Chem., 1933, 95, 414—418).—Suspended AgI catalyses the formation and reaction of the starch–I complex, permitting  $Cr_2O_7''$  and  $IO_3'$  in very dil. solutions (down to about  $2 \times 10^{-4}N$ ) to be accurately determined iodometrically. 10 c.c. of 0.001N-AgNO<sub>3</sub> should be added to each titration. Since the liberation of I by O<sub>2</sub> is also catalysed, and is a photo-reaction, solutions must be freed from dissolved air by passing  $CO_2$ , and titrated in red or orange light. J. S. A.

Application of complex-forming and buffer substances in iodometric determinations. J. D'ANS (Z. anal. Chem., 1934, 96, 1–6).—Examples of the above processes are discussed. PhOH may be determined iodometrically by pptn. as  $C_6H_2I_3$ ·OH by excess of I in presence of a NaOAc or NaH<sub>2</sub>PO<sub>4</sub> buffer, or of NaHCO<sub>3</sub>+Na<sub>2</sub>CO<sub>3</sub>. Salicylic acid may be similarly determined in Na<sub>2</sub>CO<sub>3</sub> solution. J. S. A.

Colorimetric determination of fluorine. O. M. SMITH and H. A. DUTCHER (Ind. Eng. Chem. [Anal.], 1934, 6, 61–62).—The determination of F in natural  $H_2O$  by the formation of a colour lake, using a Zrquinalizarin mixture, is described. Al, Fe, SO<sub>4</sub>", and PO<sub>4</sub>"' may be disturbing factors. They are, however, effective only above certain limits and can be removed. The amount of F present in natural  $H_2O$  is usually < 2 p.p.m. M. S. B.

Rapid colorimetric detection and determination of small quantities of oxygen in gases. H. R. AMBLER (Analyst, 1934, 59, 14–15).—The method depends on the brown colour produced by adsorption of the  $O_2$  in alkaline pyrogallol; the depth of colour is matched against standard I–KI solution. An apparatus for making the test is described and illustrated. A. R. P.

Volumetric determination of sulphate. V. R. DAMERELL and H. H. STRATER (Ind. Eng. Chem.

[Anal.], 1934, 6, 19—21).—Standard BaCl<sub>2</sub> is added to the SO<sub>4</sub>" solution using  $Hg(NO_3)_2$  as an outside indicator. A yellow basic Hg sulphate is formed. Most of the BaCl<sub>2</sub> can be added rapidly because a preliminary end-point is reached several c.c. before the final endpoint. Other salts present as impurities cause appreciable errors, but can be corr. for in standardising the BaCl<sub>2</sub>. NH<sub>4</sub> compounds must not be present, nor any ions which ppt. Hg" or Ba" or give a colour.

M. S. B.

Detection of hyposulphite, ferrous salts, hypochlorites, and dichromates with resorufin. H. EICHLER (Z. anal. Chem., 1934, 96, 98–99; see below).—Fc(OH)<sub>2</sub> or Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, but not Na<sub>2</sub>SO<sub>3</sub>, Na<sub>3</sub>AsO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, or CH<sub>2</sub>O, reduces resorufin (I) in NaOH solution to non-fluorescent products. OCl' in the cold, and Cr<sub>2</sub>O<sub>7</sub>" in hot H<sub>2</sub>SO<sub>4</sub> solution, oxidise (I). J. S. A.

Colorimetric determination of nitrogen. R. VON DER HEIDE, jun. (Z. anal. Chem., 1934, 96, 7— 16).—The sample, containing 2—7 mg. N, is treated with  $H_2SO_4$  in presence of a known amount of Hg to avoid losses through volatilisation. The Hg is converted into Nessler's reagent *in situ*, and the colour produced, stabilised by addition of gum arabic, matched against standards. The Hg is added as 2 c.c. of standard aq. HgSO<sub>4</sub> to each analysis; after heating, the  $H_2SO_4$  is neutralised against diamond-fuchsin, HCl being added to prevent pptn. of basic Hg salts. The solution is cooled to room temp. and the calc. vol. of standard KI, made alkaline with NaOH, then added. J. S. A.

Use of aeration in Kjeldahl distillations. W. B. MELDRUM, R. MELAMPY, and W. D. MYERS (Ind. Eng. Chem. [Anal.], 1934, 6, 63-64).—With fairly rapid aeration at the b.p. a Kjeldahl distillation may be completed in < 15 min. Bumping is also obviated.

M. S. B.

Nitron as a precipitant for nitrates. J. E. HECK, H. HUNT, and M. G. MELLON (Analyst, 1934, 59, 18-25).—No entrainment of precipitant or metallic cations occurs in the determination of  $NO_3'$ with nitron acetate; the results are accurate and reproducible considering the solubility of the ppt.

A. R. P.

Identification of nitrates, nitrites, and nitrosylsulphuric acid by formation of resorufin, orcirufin, and indophenols. H. EICHLER (Z. anal. Chem., 1934, 96, 17—21).—Resorufin (I) (violet-red with strong yellow red fluorescence in alkaline solution, disappearing on acidifying or reducing with  $Na_2S_2O_4$ ) is formed by heating resorcinol (II) in conc.  $H_2SO_4$ with material containing  $NO_2'$  or  $NO_3'$ , and subsequently neutralising with  $Na_2CO_3$ . Orcinol similarly yields orcirufin, PhOH and thymol bluish-green, nonfluorescent indophenols. Fe or S'' interferes; oxidising agents must be removed by heating with  $H_2SO_4$ before adding (II).  $NO_3'$ , in presence of  $NO_2'$ , may be detected in the residue after evaporating with AcOH. Dissolved NO, or NO·SO<sub>3</sub>H, gives (I) in the cold. J. S. A.

Colorimetric determination of nitrate in water. —See B., 1934, 174. Detection of nitrites with Magdala-red. H. EICHLER (Z. anal. Chem., 1934, 96, 99–100).— Magdala-red in dil. acid solution is converted by  $NO_2'$ , but not  $NO_3'$ , into blue non-fluorescent products.  $SO_3''$  and  $S_2O_3''$  also destroy the fluorescence.

## J. S. A.

Determination of small quantities of arsenic. G. A. QUINCKE and M. SCHNETKA (Z. Unters. Lebensm., 1933, 66, 581—585).—The method combines the electrolytic process of Mai and Hurt (A., 1905, ii, 284) with the colorimetric procedure of Flückiger (cf. A., 1918, ii, 240). Deposition of As with PbO<sub>2</sub> is prevented by enclosing the anode in a porous pot.  $H_2S$ is removed with Pb(OAc)<sub>2</sub> or CdCO<sub>3</sub>. Development of the coloration of the Hg halide paper gives incorrect results. Sb and Cu must be removed, since SbH<sub>3</sub> gives a yellow colour and Cu forms Cu<sub>2</sub>As<sub>3</sub> which is pptd. in the anode chamber. If when < 12% aq.  $H_2SO_4$  is used the reaction vessel is cooled, and the gases evolved from the cathode are dried,  $H_2S$  does not interfere. E. C. S.

Separation of arsenic and antimony from tin. P. E. WINKLER (Bull. Soc. chim. Belg., 1933, 42, 503-518).-The separation of Sb from Sn (A., 1932, 591) has been modified for determining As, Sb, and Sn in mixtures. The solution of 0.03-0.3 g. of As, 0.04-0.4 g. of Sb, and 0.04-0.2 g. of Sn containing 10 c.c. of 20% tartaric acid, 10 c.c. in excess of 20% KOH, and 5 c.c. of  $H_2O_2$  is gently boiled until all  $H_2O_2$  is decomposed. Before passing  $H_2S$  at the b.p., the solution is neutralised with HCl, 10 g. of  $H_2C_2O_4$  in  $H_2O$ , and 10 c.c. of conc. HCl are added, making the vol. 110 c.c. The pptd. As and Sb sulphides are separated, and in determining Sn in the filtrate, the conversion of Na<sub>2</sub>SnS<sub>3</sub> into Na<sub>2</sub>SnO<sub>3</sub> by alkaline H<sub>2</sub>O<sub>2</sub> is completed by adding KMnO<sub>4</sub> dropwise to the solution acidified with HCl, using Me-orange as indicator. The Sn found is systematically 2-3 mg. low, whilst the As and Sb J. G. A. G. are generally < 1 mg. in error.

Silver iodide test for hydrocyanic acid. D. L. Fox (Science, 1934, 79, 37).—Air is drawn through the system or culture under test and passed into freshlyprepared alkaline suspension of AgI obtained by mixing 1 drop of 5% KI, 1 of 0.001M-AgNO<sub>3</sub>, and 1 c.c. of 5% KOH. When HCN is present the KCN formed clears the solution by dissolving the AgI. H<sub>2</sub>S, NH<sub>3</sub>, and HCNS (NaCNS) have no visible effect on the AgI. 1 part of HCN in  $2 \times 10^6$  can be detected when 0.00025M-AgNO<sub>3</sub> is used under ordinary laboratory conditions, and with special precautions a greater sensitivity should be possible. Roe's method can be used for determination by continuing aëration in the same system after the detection of HCN.

## L. S. T.

Platinised silicagel as a catalyst in gas analysis. II. Oxidation of the methane hydrocarbons. K. A. KOBE and E. B. BROOKBANK (Ind. Eng. Chem. [Anal.], 1934, **6**, 35—37).—No oxidation over commercial platinised SiO<sub>2</sub> gel occurs with CH<sub>4</sub> at 350°,  $C_2H_6$  at 230°,  $C_3H_8$  at 130°, or  $C_4H_{10}$  at 120°. It takes place, however, at temp. 20—25° higher, but is not complete even at 400°. H<sub>2</sub> and CO can be oxidised simultaneously at 300° in presence of CH<sub>4</sub>, but not of higher hydrocarbons. CuO and Pt-SiO<sub>2</sub> gel are compared, both as regards errors due to catalytic oxidation of hydrocarbons and errors introduced through adsorption of gases. M. S. B.

Mercurometric determination of cyanides and thiocyanates. A. IONESCU-MATIU and (MME.) A. POPESCO (J. Pharm. Chim., 1934, [viii], 19, 54—61).— The stoicheiometric mixture of Hg and Hg(CN)<sub>2</sub> [or Hg(CNS)<sub>2</sub>] obtained by the addition of Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> is dissolved in hot H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> and the Hg determined volumetrically by pptn. with Na nitroprusside followed by titration to a clear end-point with 0.1N-NaCl.

W. S. Determination of helium and argon in natural gases from their thermal conductivity. E. K. GERLING (J. Appl. Chem. Russ., 1933, 6, 1153— 1158).—Apparatus for the rapid analysis (45—60 min.) of He and A in natural gases is described. The method, which is based on the difference in thermal conductivity of He and A, is as accurate as is that of fractional distillation. R. T.

Micro-determination of potassium. L. JEN-DRASSIK and J. SZEL (Biochem. Z., 1933, 267, 124– 127).—K is determined with an average error of  $< \pm 1\%$  by pptn. as KNa[Co(NO<sub>2</sub>)<sub>6</sub>] (I) with NaNO<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, and AcOH (added separately), collection on asbestos, dissolution of (I) in H<sub>2</sub>SO<sub>4</sub>, oxidation of the liberated HNO<sub>2</sub> with 0.02*N*-KMnO<sub>4</sub>, addition of 10% aq. KI and titration of the liberated I with 0.02*N*-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Org. matter in biological matter must first be destroyed. W. McC.

Colorimetric determination of potassium. S. N. ROSANOV and V. A. KASARINOVA (Z. anal. Chem., 1934, 96, 26–29).— $K_2Na[Co(NO_2)_6]$  is pptd. by Kramer and Tisdall's cobaltinitrite reagent (A., 1921, ii, 412) from 1 c.c. of solution containing 0.025–0.10 mg.  $K_2O$ . NH<sub>4</sub> salts must first be removed. The ppt. is dissolved in 5 c.c. of 0.1N-NaOH, and 1 c.c. of a solution of sulphanilic acid and PhOH in aq. NH<sub>4</sub>Cl added. HCl is added, then the solution made alkaline with aq. NH<sub>3</sub>. The tropæolin formed is matched against that yielded by standard NaNO<sub>2</sub> solution. Large amounts of PO<sub>4</sub>" interfere. J. S. A.

[Determination of] the alkali content of commercial lime.—See B., 1934, 93.

Determination of potassium as hydrogen tartrate. I. I. TSCHERNJAEVA and R. V. KRAS-NOVSKAJA (J. Chem. Ind. Russ., 1933, 10, No. 10, 57-59).—10—20 c.c. of 0.33N-Na H tartrate (I) are added to 1—2 c.c. of solution, containing > 0.2 g. of neutral K salt, the solution is filtered after 12 min., and excess of (I) is titrated with 0.1N-NaOH.

R. T.

Triple acetate of uranyl, magnesium, and sodium. E. KAHANE (Bull. Soc. chim., 1933, [iv], 53, 1312).—A correction (cf. A., 1933, 1024).

M. S. B.

Reaction for beryllium in minerals and rocks. H. L. J. ZEEMATTEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 899–900).—A fusion bead of the mineral with NaKCO<sub>3</sub> is dissolved in 5N-HCl. Addition of morin and NaOH produces a yellowishgreen fluorescence. C. W. G. Loss of magnesium in systematic qualitative analysis. L. J. CURTMAN and N. MERMELSTEIN (Rec. trav. chim., 1933, 53, 34—36).—In the conventional scheme of qual. analysis losses of Mg occur in groups III and IV. Some of the Mg may be recovered by repptn. H. S. P.

Micro-determination of magnesium as the triple ferrocyanide of magnesium, calcium, and hexamethylene tetramine. L. DEBUCQUET and L. VELLUZ (Bull. Soc. chim., 1933, [iv], 53, 1291—1292).—The Mg solution is evaporated to dryness, and the residue treated with a 10% solution of CaK<sub>2</sub>Fe(CN)<sub>6</sub>,(CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>,6H<sub>2</sub>O in (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>. Pptn. of the Mg compound [MgCaFe(CN)<sub>6</sub>]<sub>3</sub>.4(CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>,40H<sub>2</sub>O, is complete in 1 hr. This is washed with (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> and COMe<sub>2</sub>, dried, dissolved in H<sub>2</sub>O, and determined colorimetrically as Prussian blue by adding aq. FeCl<sub>3</sub> in presence of gum arabic. Quantities of Mg of the order of 0.1 mg. can be determined with an accuracy of always < 5% and often < 3%. M. S. B.

Micro-determination of magnesium by means of 8-hydroxyquinoline. G. GLOMAUD (J. Pharm. Chim., 1934, [viii], 19, 14—29).—A micro-analytical modification of Berg's volumetric method (A., 1927, 639) serves to determine 1 mg. of Mg to an accuracy of 1%. Procedures are described for its determination in presence of Ca or PO<sub>4</sub><sup>'''</sup>, and in biological media. D. R. D.

Detection of cations with resorufin. H. EICHLER (Z. anal. Chem., 1934, 96, 22; cf. this vol., 268).—Resorufin in aq. NH<sub>3</sub> gives with the heavy metal cations violet ppts., readily visible in small quantity against the yellowish-red fluorescent solution. J. S. A.

Determination of lead as di-lead hydrogen arsenate. C. L. DUNN and H. V. TARTAR (Ind. Eng. Chem. [Anal.], 1934, 6, 64).—Pptn. should take place in a solution of  $p_{\rm H}$  4.6. The method is not so satisfactory as the PbSO<sub>4</sub> and PbCrO<sub>4</sub> methods.

M. S. B.

Effect of acetic acid on traces of lead chromate. L. T. FAIRHALL and K. AKATSUKA (J. Amer. Chem. Soc., 1934, 56, 14—15).—AcOH induces a good cryst. habit in PbCrO, and does not impair its quant. pptn. E. S. H.

Sensitive drop reaction for copper. A. S. KOMAROVSKY and N. S. POLUEKTOV (Z. anal. Chem., 1934, 96, 23—25).—The  $(CN)_2$  liberated by Cu salts +KCN gives with 8-hydroxyquinoline (I) a raspberryred coloration (II). A solution containing Cu<sup>\*\*</sup>, added to a spot of (I) on filter paper and moistened with 25% aq. KCN, gives (II), sp. for Cu<sup>\*\*</sup> in the absence of oxidising agents. Hg<sup>\*\*</sup>, Cd<sup>\*\*</sup>, and Pb<sup>\*\*</sup> do not interfere. Fe and U, which give coloured oxinates, should first be pptd. by NH<sub>3</sub>. The limit is  $0.4 \times 10^{-6}$  g. Cu.

J. S. A.

Quinaldinic acid as an analytical reagent. Determination and separation of copper, zinc, cadmium, and uranium. Colorimetric determination of iron. P. RAY and M. K. BOSE (Z. anal. Chem., 1933, 95, 400–414).—Quinaldinic acid (I) gives insol. salts with Cu, Hg, Pb, Ag, Cd, Zn, Mn, Ni, Co, and Fe<sup>\*\*</sup>, basic salts with Fe<sup>\*\*\*</sup>, Cr, Al, and  $UO_2^{***}$ . The Hg, Pb, Ni, and Co salts are readily sol. in acid. Cu is quantitatively pptd. by aq. (I) from hot acid solution as  $(C_{10}H_6O_2N)_2Cu,H_2O$  (14.96% Cu); Zn from dil. AcOH solution as  $(C_{10}H_6O_2N)_2Zn,H_2O$ (15.29% Zn, m.p. 170°); Cd as  $(C_{10}H_6O_2N)_2Cd$  (24.63% Cd, m.p. 150°) on neutralisation with aq. NH<sub>3</sub>. Solutions of Fe<sup>\*\*</sup> give first a silky red ppt., which is transformed rapidly into the bluish-violet  $(C_{10}H_6O_2N)_2Fe,5H_2O$ ; the change is attributed to

Determination of mercury content of the atmosphere. A. STOCK and F. CUCUEL (Ber., 1934, 67, [B], 122-127).-300-500 litres of air, not freed from CO<sub>2</sub> and moisture, are drawn at the rate of about 60 litres per hr. through a U-tube immersed in liquid air, the arms of which are sufficiently long to prevent ingress of volatilised air. Towards the end of the experiment, about 50 c.c. of  $Cl_2$  are drawn into the tube which, after removal of the cooling bath, is allowed to reach room temp. slowly. The U-tube is rinsed with Cl-H<sub>2</sub>O and Hg is determined electrolytically. The process is applicable to air containing much  $CO_2$  provided that the final evaporation occurs very slowly. If liquid N2 is available, air is condensed thereby in a glass vessel until the required vol. of liquid is obtained, Cl<sub>2</sub> being allowed to be drawn into the vessel periodically. The liquefied air is allowed to volatilise very slowly and the analysis is completed as described above. Free air has a Hg content lying on the boundary line of analytical detection. The use of Au for determining minute amounts of Hg is not recommended. If liquid air is not available, Moldav-ski's method (A., 1931, 589), modified by introduction of the micrometric determination of Hg, may be used. H. W.

Potentiometric determination of mercuric salts. G. SPACU and I. G. MURGULESCU (Z. anal. Chem., 1934, 96, 109—114).—Hg<sup>••</sup> is converted by excess of KI into HgI<sub>4</sub><sup> $\prime\prime$ </sup>, and pptd. as [Cu en<sub>2</sub>][HgI<sub>4</sub>] by titration with [Cu en<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> solution, using a Hg-coated Pt wire as comparison electrode.

J. S. A.

Volumetric and gravimetric determination of mercury. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 96, 30–34).—Hg<sub>2</sub>(IO<sub>3</sub>)<sub>2</sub> is pptd. from a hot neutral or dil. HNO<sub>3</sub> solution of Hg<sup>II</sup> salts by excess of KIO<sub>3</sub>. After cooling to room. temp. the ppt. is washed with EtOH and Et<sub>2</sub>O, and dried in vac. By the use of excess of standard KIO<sub>3</sub> solution, the excess of KIO<sub>3</sub> may be determined iodometrically in the filtrate, giving Hg by difference. The solubility of Hg<sub>2</sub>(IO<sub>3</sub>)<sub>2</sub> in H<sub>2</sub>O is 33·1 mg. per litre. J. S. A.

Separation and determination of mercury in presence of elements of the hydrogen sulphide

and ammonium sulphide groups. G. SPACU and G. SUCIN (Bul. Soc. Stiinte Cluj, 1933, 7, 183—189; Chem. Zentr., 1933, ii, 2166).—Hg is pptd. in neutral or slightly ammoniacal solution, in presence of KI and excess of Na K tartrate, as  $[HgI_4][Cu en_2]$ .

A. A. E.

Reactions for distinguishing red and yellow mercuric oxides. I. C. RITSEMA (Pharm. Weekblad, 1934, 71, 58-63).—The reactivities of yellow (I) and red (II) HgO depend both on the method of prep. and subsequent history. The  $H_2C_2O_4$  reaction of the Pharmacopœia is not satisfactory but the two forms can be differentiated by the following reagents, which react, under the conditions described, only with (I):  $(NH_4)_2SO_4$ , white ppt.; fresh  $K_4Fe(CN)_6$ , Prussian blue; 10% NH<sub>3</sub>, ppt. of Millon's base; MgCl<sub>2</sub> and phenolphthalein, red colour (III); NH<sub>4</sub>CNS, brownishgreen basic NH4 Hg salt; CH2O and Na2CO3, reduction to Hg; NH<sub>4</sub> acetylsalicylate, grey ppt.; (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, Millon's base; K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, blood-red solution and ppt. containing Cr and Hg; ZnCl<sub>2</sub>, dark green ppt.; MnCl<sub>2</sub>, ppt. of Mn oxides and Hg passes into solution, [(II) gives MnO<sub>2</sub> but no Hg in solution]; HgCl<sub>2</sub>, black oxychloride; 10% CaBr<sub>2</sub>, cryst. ppt. of Ca(OH)<sub>2</sub> (IV) (not given with  $CaCl_2$ );  $NH_4$  salicylate, cryst.  $NH_4$  Hg salicylate. (II) settles more rapidly than (I). Reactions (III) and (IV) are best for assessing quality. S. C.

Colorimetric determination of aluminium with eriochromecyanin. F. ALTEN, H. WEILAND, and E. KNIPPENBERG (Z. anal. Chem., 1934, 96, 91–98; cf. A., 1929, 531).–-0·1% eriochromecyanin is added to the dil. HCl solution, which is made just alkaline, neutralised with AcOH, and brought to  $p_{\rm II}$ 6·0 by addition of a NaOAc–NH<sub>4</sub>OAc–AcOH buffer. The Al content is evaluated from the extinction coeff. for light of 531 mµ. PO<sub>4</sub><sup>'''</sup> interferes, and must first be removed as Li<sub>3</sub>PO<sub>4</sub> from strongly alkaline solution. KH<sub>2</sub>PO<sub>4</sub> is first added to carry down small amounts. Interference due to pptn. of an Fe lake may be avoided by addition of glycerol. J. S. A.

Electrometric determination of manganese in phosphorite. N. N. SOLOVEVA (Udobr. Uroz., 1931, 1092—1093).—Erich and Müller's method is as accurate as Walters' colorimetric method.

CH. ABS.

Determination of iron and basicity in solutions of ferric salts. A. L. ZAIDES and V. N. SVESHNI-KOVA (Ovlad. Tekh. Kozh. Proiz., 1932, No. 4, 45— 47).—When 3 NaOH are required for 1 Fe<sup>\*\*\*</sup> (electrometrically with the glass electrode or by titration using bromothymol-blue as indicator) the "basicity" is 100%. CH. ABS.

Determination of the basicity of ferric salts in presence of ferrous salts. A. A. SOROKINA (Ovlad. Tekh. Kozh. Proiz., 1932, No. 4, 47–48).—Fe<sup>••</sup> is converted into Fe<sup>•••</sup> with  $H_2O_2$  and the hot solution is titrated with 0.1N-NaOH using bromothymol-blue. CH. ABS.

Volumetric determination of chromium. I. JUMANOV (J. Chem. Ind. Russ., 1933, 10, No. 9, 61).— The substance is fused with 4 parts of 3:1 Na<sub>2</sub>O<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub>, the melt is extracted with boiling H<sub>2</sub>O, and H<sub>2</sub>SO<sub>4</sub> is added. Standard aq. FeSO<sub>4</sub> (I) is added to an aliquot part of the solution, and excess of (I) is titrated with 0.5N-KMnO<sub>4</sub>. R. T.

Determination of molybdenum and copper in special steels.—See B., 1934, 149.

Reaction for tungsten in minerals. J. VER-SLUYS and H. L. J. ZERMATTEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 868-870).—A phosphate bead containing W is dipped while still hot into 5N-HCl. On adding Zn powder the liquid turns violet, distinguishing from Ti, Mo, and Nb.

Rapid determination of titanium in steels.— See B., 1934, 100.

Determination of small amounts of bismuth in copper.—See B., 1934, 150.

Separation of gold from tellurium. V. LEN-HER, G. B. L. SMITH, and D. C. KNOWLES, jun. (Ind. Eng. Chem. [Anal.], 1934, 6, 43–45).—Au may be separated from Te by reduction with HNO<sub>2</sub> in a solution of 0.45*N*-HCl buffered with Rochelle salt to  $p_{\rm fr} > 1$  or by reduction with FeSO<sub>4</sub> in 0.3— 0.6*N*-HCl. Au and Te may be determined in presence of each other by pptg. together and separating Au by reduction with HNO<sub>2</sub>. M. S. B.

Microanalytical determination of palladium with dimethylglyoxime, benzoylmethylglyoxime, and salicylaldoxime. H. HOLZER (Z. anal. Chem., 1933, 95, 392—400).—Hot saturated aq. dimethylglyoxime (I), benzoylmethylglyoxime (II), and salicylaldoxime (III) ppt. Pd quantitatively from dil. acid solution (HCl). The ppts. should be cooled to room temp. before filtering, washed with 30% (not conc.) EtOH, and, with (II) and (III), dried at 110°. With (I), in presence of Pt a few drops of  $H_2O_2$ should be added. The ppt. should be reduced to Pd by covering with  $HCO_2NH_4$  and igniting in  $H_2$ . With (II), the ppt. contains 20.64% Pd. (III) yields ( $C_7H_6O_2N$ )<sub>2</sub>Pd, containing 28.17% Pd. Pt is not pptd. by these reagents, and may be determined in the filtrate by reduction with  $N_2H_4$ . J. S. A.

Thermostat for higher temperatures. B. G. ŠIMEK and J. ZAMRZLA (Mitt. Kohlenforschungsinst. Prag., 1933, 1, 485—489).—A thermostat is described in which as heating medium the vapour of a liquid boiling under const. (reduced) pressure is used.

H. A. P. Eddy-current cryostats. E. JUSTI (Physikal. Z., 1934, 35, 3—6).—The temp. fall in the metal-block cryostat is discussed, and the results show the possibility of constructing such an instrument with eddycurrent heating for low-temp. work (60—160° abs.). The quant. theory of the instrument agrees with experiment. A. J. M.

Use of the Thyratron for temperature control. R. M. ZABEL and R. R. HANCOX (Rev. Sci. Instr., 1934, [ii], 5, 28—29).—A photo-electric cell illuminated by a galvanometer controls the current through a Thyratron in parallel with the furnace windings.

C. W. G.

Cryoscopy of small volumes of liquid. D. Тномаs (Z. ges. exp. Med., 1933, 87, 635—644; Chem. Zentr., 1933, ii, 2164).—The method is applicable to

C. W. G.

the determination of f.p. of 0.1-0.15 c.c. and gives results accurate to  $0.01-0.02^{\circ}$ . A. A. E.

Electrical water heater with thermo-regulating thermometer for refractometry. F. LORENZOLA (Annali Chim. Appl., 1933, 23, 528–529).—The temp. of the  $H_2O$  is readily adjustable between 20° and 70° by the arrangement described. T. H. P.

Unit of light. L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 764—769).—Methods are described for rapid calibration of substandards for total radiation and for radiation in a given direction. By definition of a given energy distribution as a "lumen" and fixation, by definition, of an eyesensitivity curve, these methods can be applied to the measurement of the lumen value of any lamp. The unit is unsuitable for a lighting practice standard.

J. W. S.

Selenium unidirectional layer photo-cells, with special reference to their use in the measurement of meteorological radiations. W. GRUND-MANN and L. KASSNER (Physikal. Z., 1934, 35, 16-20).—The effect of age, duration and intensity of illumination, and temp. on the properties of the Se unidirectional layer cell were investigated. No ageing effect without illumination was found, although such an effect was manifest on long illumination, a limiting current being reached, which is dependent on the light intensity and the characteristics of the cell. Regeneration takes place on keeping in the dark for about 30 min. After this process, each exposure to light results in the recurrence of the ageing process, although the time taken is much shorter, usually < 30min. By decreasing the light intensity, a partial regeneration can be effected. The photo-current for a given light intensity is independent of variations in temp.  $< \pm 10^{\circ}$ . It follows that such cells are unsuitable for meteorological work. A. J. M.

Determination of densities and refractive indices of solutions at higher temperatures. G. PESCE and P. HÖLEMANN (Z. Elektrochem., 1934, 40, 1-5).—Pyknometric *d* determination between 25° and 85° with an accuracy of  $\pm 0.00002$  is described. The pyknometer has one end closed and the other sealed with Hg. The Hg expelled at different temp. is weighed. Improvements in the temp. control of the Pulfrich refractometer are described (cf. A., 1931, 1122). H. J. E.

Precision and accuracy of a photo-electric method for comparison of the low light intensities involved in measurements of absorption and fluorescence spectra. F. P. ZSCHEILE, jun., T. R. HOGNESS, and T. E. YOUNG (J. Physical Chem., 1934, 38, 1—11).—By the use of a monochromator, photo-electric cell, electrometer, and high-resistance leak, with a 900-watt Mazda lamp as the source of light, sp. absorption coeffs. and opacities may be determined with errors of < 1.5% and 1.0%, respectively. Photo-electric current sensitivities of  $2 \times 10^{-17}$  amp. per mm. permit the use of slits so narrow that spectral regions varying in width from 3 Å. at  $\lambda 4000$  Å. to 13 Å. at  $\lambda 7000$  Å. may be investigated with a small standard monochromator without amplification of the photo-electric current. Spectral measurements of fluorescent light from strongly fluorescent solutions such as chlorophyll in  $Et_2O$  can be made. M. S. B.

Reflexion densitometer. J. W. McFARLANE (J. Opt. Soc. Amer., 1934, 24, 19—24).—An instrument, primarily for investigations on photographic printing papers, is described. N. M. B.

Pfund parallel plate refractometer. M. A. COUNTRYMAN and W. KUNERTH (J. Opt. Soc. Amer., 1934, 24, 25—28).—The construction of the instrument and its use in studying the time rate of change of n for drying oils, varnishes, and lacquers are described. N. M. B.

Cell for absorption measurements at various temperatures. C. SALCEANU (Bul. Soc. Române Fiz., 1933, 35, 129—131).—The substance is heated electrically in a cell with two quartz windows.

H. J. E.

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Determination of radiant energy by means of the thermophotometer. M. PLOTNIKOV (Arh. Hemiju, 1933, 7, 170—186).—Apparatus is described, consisting of an air chamber containing a non-reflecting screen, which converts incident radiant energy into thermal energy, measured by the expansion of the air in the chamber. R. T.

Electrical instrument for detecting invisible faults in non-magnetic conductors such as tungsten. D. W. DANA (Rev. Sci. Instr., 1934, [ii], 5, 38-41).—The conductor is passed axially through a coil forming part of the tuned circuit of an oscillator. Flaws cause a change in the tuning. C. W. G.

Investigation of electron counters. C. BOSCH (Ann. Physik, 1933, [v], 19, 65-98).-In investigating the irregular behaviour of some electron counters, the general occurrence of "counts" in discharge tubes (irregular discharge collisions, separated from each other by periods of no current flow) was studied. The existence of these irregularities is due to impurities in the electrodes, and in the cathode particularly. After purification of the electrodes by heating, the discharge in He,  $H_2$ ,  $N_2$ , and, to a certain extent, dry  $O_2$  showed no irregularities. The chief impurity is  $H_2O$ . The size of the electrodes is important. A tube with pure Au electrodes of normal size showed no irregularities in the discharge in He, but with point or wire electrodes the effect was noticed. It is due to a positive space-charge. The method of working of normal electron counters can be based on these observations. On the impure cathode there are places where the discharge can easily occur. A. J. M.

Continuous, self-registering gas analysis. H. ULLRICH (Naturwiss., 1934, 22, 11).—Apparatus is described. A. J. M.

Gas absorption apparatus. R. T. DILLON (Ind. Eng. Chem., 1934, 26, 111).—Gas passes down an inner tube (A) sealed at its upper end to an outer tube (B), the lower end of which extends beyond that of A, and upwards through the annular space between A and B, carrying with it a stream of absorbing liquid (C) in which the apparatus is immersed, and out through holes in B just below the seal of A to B which is below the surface of C. D. K. M.

Vacuum distillation apparatus. G. W. ELLIS (Chem. and Ind., 1934, 77-78).—A simple apparatus in which the vapour is condensed on a cooled surface within a large test-tube in which the material is evaporated is described. The condensate is driven into the receiver through a capillary tube, and a simple device is figured for collecting several fractions separately. D. R. D.

Inverted fractional distillation. R. A. J. BOSSCHART (Ind. Eng. Chem. [Anal.], 1934, 6, 29– 33).—An apparatus for the rapid rectification of gases or liquids at normal pressure between 200° and  $-170^{\circ}$ is described. The analysis can be stopped at any point. This is especially useful in the determination of the fractions of highest b.p. which is chiefly required in the petroleum industry. M. S. B.

Electrical distillation apparatus and other electrical laboratory apparatus. A. H. W. ATEN (Pharm. Weekblad, 1934, 71, 139—143).—A description of electrical laboratory appliances obtainable on hire from the Municipal Electrical Works, Amsterdam. S. C.

Vacuum-leak hunting with carbon dioxide. D. L. WEBSTER (Rev. Sci. Instr., 1934, [ii], 5, 42-43). —Advantages over the use of EtOH are discussed. C. W. G.

Correct construction and handling of the Bunsen burette valve. P. FUCHS (Z. anal. Chem., 1934, 96, 101-103). J. S. A.

Drying of solids. I, II. S. KAMEI and T. SEDOHARA (J. Soc. Chem. Ind. Japan, 1933, 36, 645— 654B).—In the apparatus described the wt. of a solid is continuously recorded while it is being dried by a current of air of controlled temp., humidity, and velocity. A. G. Finger-print detection [on coloured objects]. H. L. BROSE (Analyst, 1934, 59, 25—27).—The article to be tested is dusted with phosphorescent ZnS or anthracene powder, the excess of which is blown off, irradiated with ultra-violet light through a sheet of Wood's glass to cut out visible light, and finally photographed through a thick plate of Super-protex Pb glass which eliminates ultra-violet light and allows only the visible light to enter the camera. An exposure of 40 min. is required with Ilford rapid process panchromatic plates. A. R. P.

Production of collodion thimbles. Apparatus for ultra-filtration. P. KALLÓS and G. HOFFMANN (Biochem. Z., 1933, 266, 128—131).—The thimbles are formed by dipping test-tubes, coated with caramel, in collodion [6% solution in  $EtOH-Et_2O$  containing Bu<sup>o</sup>OH (3%)]. They may be used for dialysis or for ultrafiltration in the simple apparatus described. W. McC.

Cleaning platinum wire for flame tests. W. G. LEIGHTON (Ind. Eng. Chem. [Anal.], 1934, 6, 84).— The hot wire is dipped in KHSO<sub>4</sub> which affords a bead of pyrosulphate on heating in the flame. M. S. B.

Materials for photo-elastic investigations. R. B. CARLETON (Rev. Sci. Instr., 1934, [ii], 5, 30— 32).—The synthetic resins Phenolite, Bakelite, and L'Orca are the most suitable. C. W. G.

Höppler viscosimeter.—See B., 1934, 79.

Apparatus for determining bulk density of powders.—See B., 1934, 127.

Measurement of humidity in closed spaces.— See B., 1934, 127.

Mendeléeff (1834—1907) and the periodic law. ANON. (Nature, 1934, 133, 161). L. S. T.

## Geochemistry.

Cosmic and solar activity. Observations on cosmic rays at Scoresby Sound during the Polar year. A. DAUVILLIER (Compt. rend., 1933, 197, 1741— 1744).—Measurements of cosmic rays were made with (a) Wulf and Kolhörster's and (b) Claude's highpressure (100 atm. A) apparatus. 20% variation was observed during winter storms.  $\mu/\rho$  in air=(a) 2.58, (b) 1.66; in Zn (a) 2.1, (b)  $2.0 \times 10^{-3}$  per g. per sq. cm. I (b)=2.81 ion pairs per c.c. of air. Cosmic activity was independent of magnetic-auroral or solar activity. The observations support the author's theory (cf. *ibid.*, 1931, **193**, 348), and point to the cosmic rays, like the zodiacal light, being due to the internal equatorial corona. C. A. S.

Utah Lake water. L. B. DECKER and C. E. MAW (Proc. Utah Acad. Sci., 1933, 10, 35-40).—Dissolved solids vary from 1060.97 to 5089.47 p.p.m. at different points. Na and Ca sulphates, chlorides, and H carbonates predominate. CH. ABS.

Variations in a hot spring: Les Dames des Plombières. R. DELABY, R. CHARONNAT, and M. JANOT (Compt. rend., 1933, 197, 1739–1741).—The variations in the Rn content (11.4—14.0 mµc in the  $H_2O$ , 123.9—150.6 mµc in the gases), the  $O_2$  in the gases (6-7%), temp. of H<sub>2</sub>O (51.6-52°), and amount of solid matter (277.5-294.9 mg. per litre) were determined at intervals during September 1931, 1932, and 1933. No definite connexion *inter se* or with atm. pressure or rainfall was detected; the source is probably deep-seated and from several depths. C. A. S.

Examination of a water of Bonifica Diamantina, and application of the thermodynamic theory of real solutions. G. BRAGAGNOLO and B. M. FREG-NANI (Annali Chim. Appl., 1933, 23, 546—556).—For this  $H_2O$ , from a spring in the neighbourhood of borings for petroleum, the activity coeffs. for the separate ions have been determined. The f.-p. depression calc. therefrom agrees well with the experimental val. T. H. P.

Radioactivity and composition of waters, minerals, and rocks of Lurisia. L. FRANCESCONI and R. BRUNA (Annali Chim. Appl., 1933, 23, 534— 546).—Results are given of the examination of ten wells, some of which show marked radioactivity.

T. H. P.

Are there granitic and basaltic shells in the earth? A. N. WINCHELL (Science, 1934, 79, 32-33).—A discussion. L. S. T. Weathering of andesite from Mt. Csódi, Hungary. A. VENDL and T. TAKATS (Tsch. Min. Petr. Mitt., 1933, 44, 437—462).—The fresh blue rock contains much glass in the groundmass, and in the weathered yellow rock this has been oxidised and hydrated with devitrification. Analyses are given of the two rocks and of the altered groundmass. Determinations were also made of their porosity and the action of reagents. L. J. S.

Occurrence of gold in King Cassilis ore. F. L. STILLWELL (Proc. Austral. Inst. Min. Met., 1933, No. 90, 227—236).—The Au occurs as minute particles or flakes attached to chalcopyrite or galena veins in arsenopyrite, or disseminated irregularly throughout the pyrite crystals. Characteristic photomicrographs are given to show the Au distribution in various types of ore. A. R. P.

Gold telluride minerals from the Suzaki mine. M. WATANABE (Proc. Imp. Acad. Tokyo, 1933, 9, 621-622).—Au and Te are present, but little Ag.

C. W. G.

Auriferous zone of E. Urega (Kivu, Belgian Congo). R. VAN AUBEL (Compt. rend., 1933, 197, 1732—1734).—The Au occurs in quartz veins penetrating schists of the metamorphic series of the lower stage of the Muva—Ankole–Urundi–Kibada system; it is associated with pneumatolytic minerals, tourmaline, etc., mispickel, pyrite, galena, blende, and graphite, with traces of Bi. The occurrences are connected with granitic and diorite-diabase intrusions and radiate out from Mt. Kibukira. C. A. S.

Andradite rich in titanium. O. ZEDLITZ (Zentr. Min. Geol., 1933, A, 225–239; Chem. Zentr., 1933, ii, 1496).—Melanite from Oberrotweil contains  $12 \cdot 10\%$ TiO<sub>2</sub>;  $a=12 \cdot 104 \pm 0.008$  Å., which is > for a normal andradite. Livaarite, with an even higher TiO<sub>2</sub> content, has a  $12 \cdot 139 \pm 0.008$  Å., whilst melanite from Perlerkopf (Eifel), containing  $8 \cdot 3\%$  TiO<sub>2</sub>, has a  $12 \cdot 060$  $\pm 0.008$  Å. A. E.

Sulphide minerals of the Tsurneb mine. H. MORITZ (Neues Jahrb. Min., 1933, A, 67, Bl.-Bd., 118— 154; Chem. Zentr., 1933, ii, 1498).—" Green enargite" is Cu As fahl ore. Three new forms of Cu glance are described. Germanite contained Fe 7.80, Cu 42.12, Zn 3.93, Ge 10.19, Ga 1.85, Pb 0.96, As 1.37, S 31.27%; corresponding with  $Cu_8(ZnFeGa)_2(AsGe)_2S_{11-12}$ . A. A. E.

Tektites. E. DITTLER (Zentr. Min., 1933, A, 214– 219; Chem. Zentr., 1933, ii, 1496–1497).—Billitonite from Dendang contained SiO<sub>2</sub> 70·30, TiO<sub>2</sub> 0·50, Al<sub>2</sub>O<sub>3</sub> 12·77, Fe<sub>2</sub>O<sub>3</sub> 0·53, FeO 5·43, MnO 0·13, MgO 3·74, CaO 2·37, BaO 0·01, Na<sub>2</sub>O 1·73, K<sub>2</sub>O 2·48, P<sub>2</sub>O<sub>5</sub> 0·06, S 0·08, H<sub>2</sub>O-0·08, GeO<sub>2</sub> < 0·0005, Ga<sub>2</sub>O<sub>3</sub> 0·001, Sc<sub>2</sub>O<sub>3</sub> 0·0005, Y<sub>2</sub>O<sub>3</sub> 0·001, C trace; Ni, Ca, Cl, and H<sub>2</sub>O+ were absent; d' 2·4395. A. A. E.

Radium content of rocks of the Gleinalpe, Styria. H. ROSSNER (Tsch. Min. Petr. Mitt., 1933, 44, 495–504).—Diorite, granite, etc., with SiO<sub>2</sub> 60·01—75·36%, contained  $1\cdot63-2\cdot45\times10^{-12}$  g. of Ra per g. of rock, the amount increasing with the acidity of the rock and also with the % of alkalis, especially K. An exception to this rule was a tourmalinepegmatite with SiO<sub>2</sub> 72·10% and Ra  $2\cdot80\times10^{-12}$ . These amounts are < those given by other observers on similar rocks from other localities. Results obtained by decomposing the rocks by carbonate fusion or with HF are in agreement. L. J. S.

Abundance of zirconium. G. VON HEVESY and K. WÜRSTLIN (Z. anorg. Chem., 1934, 216, 305– 311).—The % of Zr, determined X-radiographically in 1175 rock samples, varies from an average of 0.03 in granites to 0.006 in peridotites. F. L. U.

Abundance of strontium. G. VON HEVESY and K. WÜRSTLIN (Z. anorg. Chem., 1934, 216, 312–314; cf. preceding abstract).—The Sr content of 1046 rock samples varied from an average of 0.011% in volcanic to 0.002% in sedimentary rocks.

F. L. U.

Presence of platinum in mineral sulphides. O. E. ZVAGINTSEV, V. V. LEBEDINSKI, and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1933, 4, 165—169).—Existing data and samples of varied origin show that the presence of Pt in sulphides of hydrothermal origin is due to acid intrusions. High content of Pt is found in some of the minerals analysed. J. G. A. G.

X-Ray investigation of clays. I. X-Ray diagrams of minerals occurring in clays. II. Mineral constituents of clay from Malliss. G. NAGELSCHMIDT (Z. Krist., 1934, 87, 120–145).— Powder diagrams of quartz, nacrite, dickite, kaolinite, halloysite, montmorillonite, muscovite, and calcite are critically examined. The method of differentiation based thereon is exemplified by application to four fractions (< 0.05  $\mu$ , 0.05–1, 1–5.5, and 5.5–30  $\mu$ ) obtained by centrifuging clay from Malliss in Mecklenburg, showing the increase of quartz and decrease of kaolin or halloysite with increasing size of grain (cf. A., 1933, 1030; B., 1930, 832; 1931, 359).

C. A. S.

Chemical composition of clays in a vertical profile through layers of different ages. A. SALMINEN (Suomen. Kem., 1933, 6, 71B).—The composition was independent of the depth and age of the layer. E. S. H.

Natural thermoluminescence of minerals and rocks. A. KÖHLER and H. LEITMEIER (Z. Krist., 1934, 87, 146-180).—The thermoluminescence (I) of numerous samples of each of over 100 minerals, and of many rocks was examined. It is comparatively rare, and markedly shown only by (in decreasing order of intensity) fluorite, danburite, calcite, apatite, zircon, topaz, orthoclase, scheelite, anhydrite, harmotome, pectolite, gypsum, strontianite, phenacite, aragonite, witherite, quartz, cryolite, and barytes. The cause is connected with the presence of impurities and probably with that of radioactive material. This view is supported by a comparison between the (I) and U, Ra, and Th content of 50 specimens of granite; high (I) is apparently associated with a mean content of radioactive material. (I) appears to be less intense in very young and in archaic rocks. C. A. S.

Titanaugite of hour-glass structure. J. HOLZNER (Z. Krist., 1934, 87, 1-42; cf. A., 1933, 1030).—In crystals of titanaugite showing hour-glass structure the difference of the growth-cone is in structure rather than in composition, the structure being looser and the d consequently lower. Relations between replacement of elements by one another (usually in pairs to compensate valency differences) and variations in optical properties are traced.

C. A. S.

Aegirite-augite bearing riebeckite quartz schist from Kamuikotan and some other localities in Hokkaido, Japan. J. SUZUKI (Proc. Imp. Acad. Tokyo, 1933, 9, 617—620).—Analyses are given. C. W. G.

Orbicular rock from Minedera-yama, Japan. Y. KAWANO (Proc. Imp. Acad. Tokyo, 1933, 9, 613— 616).—Analyses are given. C. W. G.

Orbicular rock from Minedera-yama, Japan. B. YOSHKITI (Proc. Imp. Acad. Tokyo, 1933, 9, 609– 612).—Mineralogical details are given. C. W. G.

Genesis of lithium pegmatite, S.E. Manitoba. C. H. STOCKWELL (Trans. Roy. Soc. Canada, 1933, [iii], 27, IV, 27-36).—A pegmatite body on the Bear mineral claim consists on the footwall of albitegranite grading into albite-aphite, and on the hangingwall of quartz and muscovite. The middle is occupied by a spodumene zone with a central zone of lepidolite, After the crystallisation of the albite-granite and the quartz and muscovite on the walls, the remaining magma crystallised in various stages in the middle. L. J. S.

Genesis of pegmatites, S.E. Manitoba. C. H. STOCKWELL (Trans. Roy. Soc. Canada, 1933, [iii], 27, IV, 37-51).—The pegmatites are believed to be mainly of magmatic origin and later replacements by solutions to be of minor importance. L. J. S.

Correlation studies of the central and south central Pennsylvanian bentonite occurrences. R. R. ROSENKRANS (Amer. J. Sci., 1934, [v], 27, 113-134).—Analyses and correlations are given. C. W. G.

Spilite and the average metabasalt. H. W. FAIRBAIRN (Amer. J. Sci., 1934, [v], 27, 92-97).-Spilite is chemically transitional to low-soda metabasalt. C. W. G.

Nepheline syenite from Solwezi, N. Rhodesia. F. D. ADAMS and F. F. OSBORNE (Amer. J. Sci., 1934, [v] 27, 135-145).—Mineralogical details and analyses are given. C. W. G.

Weathering of felspars in relation to soil formation. P. ZEMIACHENSKY (Trans. Dokuchaiev Soil Inst., 1933, 8, No. 1, 1—42).—Atm. action on felspars in N.W. U.S.S.R. and the Murman coast gives rise to a product similar to muscovite (I) in optical properties, but its chemical composition differs from that of (I) in H<sub>2</sub>O content, which is much higher. A. M.

Soil reaction and forest types in the Duke forest [N. Carolina]. T. S. COLE (Ecology, 1933, 14, 323-333).—The litter, fermentation, and humus layers of a large no. of samples show characteristically different ranges of  $p_{\rm ff}$  vals. Decomp. and incorporation of the products into the mineral stratum was more rapid in litters of low than of high [H']. Different types of trees yield litter having fairly characteristic reaction. Differences in soil reaction

between different forest types were insufficient to constitute a factor limiting the distribution of species. A. G. P.

Microflora of soils of varied structure. N. P. KORNEEVA (Agrophysikal. Lab. Kiev, 1933; Proc. Internat. Soc. Soil Sci., 1933, 8, 202).—Higher proportions of structural units > 3 mm. in soils are associated with larger total nos. of micro-organisms, an increased proportion of *Azotobacter*, and a smaller no. of *Clostridium*. A. G. P.

Titanium in Moravian soils. II. B. MALAC (Vestník. Českoslov. Akad. Zeměd., 1932, 111—114; Bied. Zentr., 1933, A, 4, 34; cf. B., 1933, 560).—The satisfactory character of the Neumann-Murphy method for determining Ti in 20% HCl extracts of soils, without pre-removal of org. matter, is confirmed. A. G. P.

Biology and biodynamics of saline, alkali, and solodised soils. F. N. GERMANOV (Pedology, 1933, 28, 203-208).—A general discussion. A. M.

Alkali soils of Spain: classification, composition, and vegetation. E. H. DEL VILLAR (Mezög. Kutat., [Spec. No.], 1933, 6, 510-521).--Types of vegetation associated with gypseous and saline soils are recorded. Ligneous types predominate in the former and herbaceous in the latter soils. A. G. P.

Systematic cartography of Sumatra. J. SZEMIAN (Soil Res., 1933, 3, 202–221).—A system of soil classification is described. Relationships between parent material, weathering, and soil formation are discussed. A. G. P.

Local soil types. A. TILL (Soil Res., 1933, 3, 163—195).—A system of classification of localised soil types in Austria is given. A. G. P.

Volcanic soils from the province of Tottori, Japan. M. HARADA (Soil Res., 1933, 3, 147—162).— Analyses of the three principal horizons of these soils are given and their formation is discussed. A. G. P.

Claypan soils. I. C. BROWN, T. D. RICE, and H. G. BYERS (U.S. Dept. Agric. Tech. Bull., 1933, No. 399, 42 pp.).—In nearly all soils examined the ratios  $SiO_2$ : sesquoxide and  $SiO_2$ :  $Al_2O_3$  and the  $H_2O$  of combination of the soil complex show the colloids to be of similar composition in all horizons. The claypan layer has a higher proportion of bases than has the A horizon. Evidence is advanced indicating that the soils were formed by similar processes, the colloid being translocated as a whole from the surface layer downward to a stratum of higher  $p_{\rm H}$ . The original surface probably contained CaCO<sub>3</sub> which was transported downward as  $Ca(HCO_3)_2$  and redeposited as  $CaCO_3$  in the stratum of max.  $H_2O$  penetration. Sol. salts immediately above this layer tended to flocculate the clay, forming ultimately a layer of low permeability. Differences in properties of actual claypan layers are attributable to differences in parent material. The composition of the colloids examined conforms to that of salts of pyrophyllic acid (B., 1932, 1002) of the type  $MH_5(AlSi_2O_7)_2$ . A. G. P.

Salt domes. R. V. BROWNE (J. Inst. Petroleum Tech., 1934, 20, 73—93).—The geology of salt domes is discussed. D. K. M. Oxidation-reduction reactions between natural hydrocarbons and oil-filled waters. C. H. BEHRE, jun., and R. K. SUMMERBELL (Science, 1934, 79, 39— 40).—Unpublished experiments by other workers show that sulphates can be reduced to sulphides by heating with paraffin-base crude petroleum under pressure at approx. 150°. Sulphate reduction is most pronounced in the presence of FeSO<sub>4</sub> and clay as catalysts.

L. S. T.

Petroleum deposits of Syria and the Lebanon. L. DUBERTRET (Compt. rend., 1934, 198, 379—381).— Throughout the coastal zone there are porous lime-

Number of structural isomerides of the more important types of aliphatic compounds. H. R. HENZE and C. M. BLAIR (J. Amer. Chem. Soc., 1934, 56, 157; cf. A., 1932, 495, 597; 1933, 254).—Theoretical. The nos. of isomerides of various types are calc. H. B.

Thermal decomposition of organic compounds from the viewpoint of free radicals. V. Strength of linkings in organic molecules. F. O. RICE and W. R. JOHNSTON (J. Amer. Chem. Soc., 1934, 56, 214—219).—The extent of decomp. of  $C_2H_6$ ,  $C_3H_8$ , n- $C_4H_{10}$ , n- $C_5H_{12}$ , n- $C_6H_{14}$ , EtOH, COMe<sub>2</sub>, MeCHO, Me<sub>3</sub>CO<sub>3</sub>, Me<sub>2</sub>O, Et<sub>2</sub>O, (CH<sub>2</sub>)<sub>2</sub>O (I), NHMe<sub>3</sub>, and NMe<sub>3</sub> into free radicals is determined by the method previously described (A., 1932, 1108; 1933, 1270) using Sb mirrors. The activation energies of the decomp. are thus found (cf. *loc. cit.*) and show that the C-O (ether) linking is stronger than C-C. The C-N linking is relatively weak. (I) is the least stable compound examined. There appears to be a definite diminution in stability with ascending members of a homologous series. H. B.

Kolbe hydrocarbon synthesis in liquid ammonia. R. A. FULTON and F. W. BERGSTROM (J. Amer. Chem. Soc., 1934, 56, 167—168).—Electrolysis of NH:CR·NHK (I) (R=Me, Et, Pr<sup>a</sup>, Bu<sup>a</sup>) (from R·CN and KNH<sub>2</sub>) in conc. solution in liquid NH<sub>3</sub> using a high c.d. gives  $CH_4$  and  $C_2H_6$  (at anode) in each case; N<sub>2</sub> is also formed [probably by decomp. of (I) at the anode] and is practically the sole anodic gas using dil. solutions and low c.d. H. B.

Determination of ethane by combustion over platinum in the presence of excess oxygen. M. SHEPHERD and J. R. BRANRAM (Bur. Stand. J. Res., 1933, 11, 783—797).—The slow combustion of  $C_2H_6$ over a hot Pt spiral in presence of excess of  $O_2$  does not give theoretical results, the vol. contraction and  $O_2$ consumed being always high and the CO<sub>2</sub> formed low The best volumetric equation to represent the reaction is  $C_2H_6+3\cdot513O_2=1\cdot994CO_2+2\cdot520\times$  contraction. Results are explained by losses of  $C_2H_6$  and CO<sub>2</sub> in the distributor, dissolution of CO<sub>2</sub> in the H<sub>2</sub>O produced in the reaction, and deviations of CO<sub>2</sub> and  $C_2H_6$  from their theoretical mol. vols. J. W. S.

Vapour-phase oxidation of hydrocarbons. I-III.—See this vol., 259. stones and marls impregnated with bitumen. In the Yarmuk ravine a boring showed 50 m. of asphalt in the lower Meastrichian. A little dark petroleum occurs at Latakia in the Nahr-el-kalb, and a true source (the only one so far known) of a petroleum containing much paraffin at Tchenguène, 17 km. S.W. of Alexandretta. In the E., desert, zone the formation resembles that of Iraq. Bituminous limestone and sandstone occur in W. Jebel Bichri and near Jaffraria. There are indications of domes increasingly evident eastwards, the most promising being in the Karatchok Dagh in the extreme N.E. C. A. S.

## Organic Chemistry.

Characterisation of ethylenic linkings by antimony trichloride. R. DELABY, S. SABETAY, and M. JANOT (Compt. rend., 1934, 198, 276-278).— The colours given by SbCl<sub>3</sub> (best in CHCl<sub>3</sub>) with ninetynine compounds of various types are recorded and certain non-reactive compounds named. HgNO<sub>3</sub>, AsCl<sub>3</sub>, and SbBr<sub>3</sub>, but not SbCl<sub>5</sub>, give colours with ethylenic compounds, but are less sensitive. R. S. C.

Ozonolysis of purely aliphatic olefines. Behaviour of the five simplest n-alkyl radicals in the dehydration of tert.-alcohols. J. M. CHURCH [with F. C. WHITMORE and R. V. McGREW] (J. Amer. Chem. Soc., 1934, 56, 176-184; cf. A., 1933, 255).-Dehydration of the following tert.-carbinols by boiling with a little I occurs without rearrangement and more casily with rise in the b.p.; the olefines produced (and % yields) are quoted in parentheses :  $CEt_3 \cdot OH$  ( $\gamma$ -ethyl- $\Delta^{\beta}$ -pentene; 100);  $CPr^a_3 \cdot OH$  ( $\delta$ -*n*-propyl- $\Delta^{\gamma}$ -heptene; 100);  $CBu^a_3 \cdot OH$  ( $\varepsilon$ -*n*-butyl- $\Delta^{\delta}$ -nonene; 100); 100); tri-*n*-amylcarbinol ( $\zeta$ -*n*-amyl- $\Delta$ <sup>c</sup>-undecene; 100); CMe<sub>2</sub>Et·OH ( $\beta$ -methyl- $\Delta^{\alpha}$ - and - $\Delta^{\beta}$ -butene; 22, 78); CMe<sub>3</sub>Bu<sup>a</sup>·OH ( $\beta$ -methyl- $\Delta^{\alpha}$ - and - $\Delta^{\beta}$ -hexene; 55, 45); dimethyl-*n*-amylcarbinol ( $\beta$ -methyl- $\Delta^{\alpha}$ - and - $\Delta^{\beta}$ -heptene; 40, 60); CMeEt<sub>2</sub>·OH (mainly  $\gamma$ -methyl- $\Delta^{\beta}$ -pentene and trace of  $\beta$ -ethyl- $\Delta^{\alpha}$ -butene); CEt,  $Pr^{\alpha}$ ·OH ( $\gamma$ -ethyl- $\Delta^{\beta}$ - and  $-\Delta^{\gamma}$ -hexene; 80, 20); CEt<sub>2</sub>Bu<sup> $\alpha$ </sup>·OH ( $\gamma$ -ethyl- $\Delta^{\beta}$ - and - $\Delta^{\gamma}$ -heptene; 90, 10); diethyl-*n*-amylcarbinol ( $\gamma$ -ethyl- $\Delta^{\beta}$ - and  $-\Delta^{\gamma}$ -octene; 85, 15); CEtPr<sup>a</sup><sub>2</sub>·OH ( $\gamma$ -*n*-propyl- $\Delta^{\beta}$ -hexene and  $\delta$ -ethyl- $\Delta^{\gamma}$ -heptene; 50, 50); di-*n*-propyl-*n*-amyl-carbinol ( $\delta$ -*n*-propyl- $\Delta^{\gamma}$ - and  $-\Delta^{\delta}$ -nonene; 60, 40); CEtHyl- $\Delta^{\gamma}$ - between and  $\Delta^{\delta}$ -nonene; 60, 40); CEtBu<sup>a</sup><sub>2</sub>·OH  $(\gamma - n$ -butyl- $\Delta^{\beta}$ -heptene and  $\varepsilon$ -ethyl- $\Delta^{\delta}$ nonene; 40, 60); CPr<sup>a</sup>Bu<sup>a</sup><sub>2</sub>·OH ( $\delta$ -*n*-butyl- $\Delta^{\gamma}$ -octene and  $\varepsilon$ -*n*-propyl- $\Delta^{\delta}$ -nonene; 25, 75); di-*n*-butyl-*n*-amylcarbinol ( $\varepsilon$ -*n*-butyl- $\Delta^{\delta}$ - and - $\Delta^{\epsilon}$ -decene; 60, 40); methyldi-n-amylcarbinol (ζ-methyl-Δ<sup>c</sup>-undecene and  $\beta$ -*n*-amyl- $\Delta^{\alpha}$ -heptene; 90, 10); *n*-propyldi-*n*-amylcarbinol ( $\zeta$ -*n*-propyl- $\Delta^{\alpha}$ -undecene and  $\delta$ -*n*amyl- $\Delta^{\gamma}$ -nonene; 67, 33); CMeEtBu<sup>a</sup>·OH ( $\beta$ -ethyl- $\Delta^{\alpha}$ -hexene and  $\gamma$ -methyl- $\Delta^{\beta}$ - and  $-\Delta^{\gamma}$ -heptene; 15, 55, 30); methylethyl-*n*-amylcarbinol ( $\beta$ -ethyl- $\Delta^{\alpha}$ heptene and  $\gamma$ -methyl- $\Delta^{\beta}$ - and  $-\Delta^{\gamma}$ -octene; 20, 50, 30); methyl-*n*-propyl-*n*-amylcarbinol ( $\beta$ -*n*-propyl- $\Delta^{a}$ heptene and  $\delta$ -methyl- $\Delta^{\gamma}$ - and  $-\Delta^{\delta}$ -nonene; 20, 50, 30); methyl-n-butyl-n-amylcarbinol ( $\beta$ -n-butyl- $\Delta^{\alpha}$ heptene and  $\varepsilon$ -methyl- $\Delta^{\delta}$ - and - $\Delta^{\epsilon}$ -decene; 15, 45, 40). The same olefines are also obtained by heating

the corresponding  $CR_3 \cdot OMgX$ . The order of decreasing ease with which the groups supply the H for dehydration is Et,  $Pr^{\alpha}$ ,  $Bu^{\alpha}$ , *n*-amyl, Me. The structures and amounts of the olefines are determined by ozonolysis (apparatus described), usually in light petroleum, b.p.  $0-30^{\circ}$ , at  $-10^{\circ}$ ; the ozonides (freed from solvent) are best decomposed by  $H_2O$  and Zn dust in presence of traces of Ag and quinol (cf. A., 1932, 1109). H. B.

Addition of hydrogen bromide to  $\delta\delta$ -dimethyl-  $\Delta^{\alpha}$ -pentene. M. S. KHARASCH, C. HANNUM, and M. GLADSTONE (J. Amer. Chem. Soc., 1934, 56, 244).— Addition of HBr to  $\delta\delta$ -dimethyl- $\Delta^{\alpha}$ -pentene in presence of air or peroxides gives  $\delta\delta$ -dimethyl-*n*-amyl bromide, b.p.  $68\cdot8^{\circ}/34$  mm. (cf. Whitmore and Homeyer, this vol., 55), which is considered to be the "abnormal" product. The "normal" adduct, formed in presence of good anti-oxidants in a vac., is  $\beta$ -bromo- $\delta\delta$ -dimethylpentane, b.p.  $59\cdot4^{\circ}/34$  mm.; 50%of this is formed when addition is carried out in a vac. H. B.

Catalytic hydrogenation and polymerisation of acetylene under pressure to yield benzene. A. D. PETROV and L. I. ANTSUS (J. Appl. Chem. Russ., 1933, 6, 1145—1147).—In presence of Ni 1:5 mixtures of  $C_2H_2$  and  $H_2$  at 170°/18 atm. yield quantitatively  $C_2H_6$ , whilst under similar conditions 1:1:4 mixtures of  $C_2H_2$ ,  $H_2$ , and  $N_2$  yield  $C_2H_4$  5%,  $C_2H_6$  7%,  $H_2$  6%, and liquid hydrocarbons 80%, containing 40% of naphthenes, b.p. < 160°. R. T.

Reactions of anhydrous thorium tetrabromide with organic liquids.—See this vol., 266.

Dehydration of alcohol. G. A. FESTER, A. ABBATE, and J. MAROSO (Rev. fac. quím. ind. agric., Univ. nac. litoral, 1932, 2, 141—148).—100 c.c. of 84 wt.-% EtOH are shaken with 100 c.c. of gasoline and 5 g. of anhyd.  $K_2CO_3$ . The top layer is mainly gasoline, the middle EtOH and gasoline, and the bottom conc. aq.  $K_2CO_3$ . The EtOH recovered contains 90.7% EtOH. Removal of the  $K_2CO_3$  layer and repetition gives (1) 94.0, (2) 95.5% EtOH.

CH. ABS. Electrolytic preparation of *iso*propyl alcohol.— See this vol., 263.

Acetylenic alcohols.—See this vol., 239.

Unsymmetrical tetramethylene glycols. C. F. H. ALLEN, C. V. WILSON, and W. L. BALL (Canad. J. Res., 1933, 9, 432–435).—Reduction (Na-ROH) of the appropriate arylsuccinic ester affords  $\beta$ -phenyl-, m.p. 70° (Na derivative, +EtOH) (cf. Manske, A., 1931, 619),  $\beta$ -(2:4-dimethoxyphenyl)-, m.p. 89° (affords no solid derivatives), and  $\beta$ -methyl-(I) -butane- $\alpha\delta$ -diol, of which only (I) gives a pure dibromide. With the Ac<sub>2</sub> derivatives of n-butane- $\alpha\gamma$ -diol HBr replaces only I Ac group giving a bromobutyl acetate, b.p. 92—94°/27 mm. The halogen compounds do not give Grignard reagents, although with CH<sub>2</sub>Cl·CH<sub>2</sub>·CH<sub>2</sub>Br and Mg an 8% yield of acids is obtained after treatment with CO<sub>2</sub>. J. W. B.

Two constituents of Charon's dipropenyl glycol: isolation of one in a crystalline form. WIEMANN (Compt. rend., 1933, 197, 1654–1656).— When heated with PhNCO and  $Et_2O$  at 60° Charon's

dipropenyl glycol (I) affords a mixture of a *phenyl-urethane* (II), m.p. 190°, and another of lower m.p. not yet obtained pure. Hydrolysis of (II) with aq.  $Ba(OH)_2$  at 150° gives a cryst. *dipropenyl glycol*, m.p. OH OH

48°, to which the configuration  $\begin{array}{cc} R\dot{C} & \dot{C}R \\ H & H \end{array}$ 

•CH:CHMe) is assigned; it causes further crystallisation of the same form when added to (I) at 0°. J. W. B.

Syntheses of dulcitol and allodulcitol. R. LESPIEAU and J. WIEMANN (Compt. rend., 1934, 198, 183—184; cf. this vol., 169).—Slightly impure  $\alpha\beta\epsilon\zeta$ tetrahydroxy- $\Delta^{\gamma}$ -hexinene, m.p. 116—117°, gives, when hydrogenated, an oily olefinic compound, the Ac<sub>4</sub> derivative, b.p. 190—191°/12 mm., of which with AgClO<sub>3</sub> and a little OsO<sub>4</sub> gives an oily  $\alpha\beta\epsilon\zeta$ -tetraacetoxycrithrytol, whence an Ac<sub>6</sub> derivative was obtained which yielded a little ducitol hexa-acetate. R. S. C.

Etherification. I. Preparation of some higher aliphatic ethers with sulphuric acid. G. F. HENNION, H. D. HINTON, and J. A. NIEUWLAND (Proc. Indiana Acad. Sci., 1933, 42, 109—111).—The dry alcohol (2 mols.) is treated slowly with conc.  $H_2SO_4$  (15—20 g.) and the mixture is heated for 1 hr. to remove  $H_2O$ ;  $H_2SO_4$  (15 g., and after 1 hr. a further similar quantity) is added. When the temp. of the mixture is midway between the b.p. of the alcohol and the ether the mixture is cooled and 150 c.c. of  $H_2O$  are added. The separated ether is washed with NaOH, dried, and distilled. CH. ABS.

Reactions of  $\beta$ -halogeno-ethers. I. Action of magnesium on alkyl  $\beta$ -bromoethyl ethers. R. C. TALLMAN (J. Amer. Chem. Soc., 1934, 56, 126-129).-OR·CH<sub>2</sub>·CH<sub>2</sub>Br, where R is Me, b.p. 111-111.4°/746 mm., Et, b.p. 127.3-127.7°/743 mm., Pra, b.p. 146.9-147.3°/743 mm.,  $Pr^{\beta}$ , b.p. 139.9—140.2°/743 mm.,  $Bu^{a}$ , b.p. 67—67.5°/25 mm.,  $Bu^{\beta}$ , b.p. 56.5—57°/21 mm., sec.-Bu, b.p. 47—47.5°/15 mm., and n-amyl, b.p. 75-76°/14 mm., are prepared from OR·CH<sub>2</sub>·CH<sub>2</sub>·OH and PBr<sub>3</sub> in  $C_5H_5N$ . With Mg in Et<sub>2</sub>O, these give  $C_2H_4$ , OR·MgBr, and  $(\cdot CH_2 \cdot CH_2 \cdot OR)_2$  (except when R=Me; the amount increases with the size of R). ad-Diethoxy-, b.p. 59-60°/18 mm., -di-n-propoxy-, b.p. 94-95°/20 mm., -diisopropoxy-, b.p. 77-78°/18 mm., -di-n-, b.p. 117-118°/16 mm., -iso-, b.p. 107-108°/19 mm., and -sec.-, b.p. 102-103°/16 mm., -butoxy-, and -di-n-amyloxy-, b.p. 134-135°/12 mm., H. B. -butanes are described.

Mobility of organic radicals in their bromosulphites. P. CARRÉ (Compt. rend., 1934, 198, 181-182).—The following are the temp. of decomp. of the bromosulphites OR·SOBr in  $C_5H_5N$  to SO<sub>2</sub> and alkyl bromide : Et 13-14°, Pr<sup>a</sup> 30-31°, Bu<sup>a</sup> 39-40°, *n*-heptyl 54°, *n*-decyl 38°, Pr<sup>β</sup> 13-14°, CH<sub>2</sub>Cl·CH<sub>2</sub> 39-40°, and Ph 80°. The compounds are less stable than the corresponding chlorosulphites, but the order of the radicals is the same. R. S. C.

Reaction of substances containing the thiol radical. A. GIROUD and H. BULLIARD (Protoplasma, 1933, 19, 381-384).—The violet coloration produced by the reduction of Na nitroprusside by •SH compounds is changed to a stable red colour by the addition of Zn salts. A. G. P.

Detection and determination of methyl mercaptan and carbon disulphide in air containing hydrogen sulphide. J. F. REITH (Rec. trav. chim., 1934, 53, 18–23).—The gas is bubbled through 0.5Naq. NaOH, dried with CaCl<sub>2</sub>, and then passed through NaOH in EtOH. The aq. solution is then acidified with HCl, a slow stream of air is passed through, and the evolved gases are dried and passed over cryst. Pb(OAc)<sub>2</sub>; this absorbs H<sub>2</sub>S, but not MeSH, which is detected by isatin–H<sub>2</sub>SO<sub>4</sub> or determined colorimetrically by PdCl<sub>2</sub>. CS<sub>2</sub> is determined by pptn. of CuO·CS·SCu from the alcoholic absorbent with Cu(OAc)<sub>2</sub> and AcOH or, if very small in amount, detected by the yellow coloration given with a little Cu(OAc)<sub>2</sub>. H. A. P.

Production of organo-metalloidal compounds by micro-organisms. II. Dimethyl selenide. F. CHALLENGER and H. E. NORTH (J.C.S., 1934, 68-71).—Strains A and D (cf. A., 1933, 266) growing on sterile bread-crumbs containing  $Na_2SeO_3$  or  $Na_2SeO_4(I)$ evolve a gas (II) which affords with Biginelli's solution Me2 selenide mercurichloride, m.p. 153-154° (Et2 selenide mercurichloride has m.p. 92.5°), with HgBr,-H<sub>2</sub>O the corresponding bromide, m.p. 99-100°, with HNO<sub>3</sub>, Me<sub>2</sub> hydroxyselenonium nitrate, with K<sub>2</sub>PtCl<sub>4</sub>, Me<sub>2</sub> sclenide platinichloride (A., 1912, i, 71), and with CH<sub>2</sub>PhCl, benzyldimethylselenonium chloride (A., 1930, 1302). (II) is free from  $H_2$ Se or McScH. Strain D grown on bread-crumbs containing (I) forms much Se, which is not easily methylated (cf. Proc. C.S., 1902, 138; A., 1902, ii, 629). A and C grown on bread do not afford Me2S with many S compounds, but Et2S is formed when SOEt<sub>2</sub> (but not SO<sub>2</sub>Et<sub>2</sub>) is added.

J. L. D. Electrolysis of silver acetate in acetic acid and pyridine.—See this vol., 263.

Modes of addition to conjugated unsaturated systems. VI. Addition of halogens and hydro-Interaction of  $\beta$ -vinylacrylic acid (I) (A., 1929, 1270) and  $Cl_2$  in  $H_2O$  at 50° affords  $\delta$ -chloro- $\gamma$ -hydroxy- $\Delta^{\circ}$ pentenoic acid, m.p.  $73-74^{\circ}$  (cf. A., 1931, 1148), ozonised to HCl,  $H_2C_2O_4$ , and AcCHO [2:4-dinitro-phenylosazone, m.p. 299-300° (decomp.)]. (I) with aq. HOCl (2 mols.) affords a dichlorodihydroxyvaleric acid, m.p. 166° (lit., 143°). Similarly prepared, 8bromo-y-hydroxy-∆<sup>a</sup>-pentenoic acid has m.p. 92—93° [also obtained from (I) and HOBr]; O3 affords products similar to the above. Similar conditions,  $\delta$ initiation and  $\gamma\delta$ -orientation, should hold in all analogous butadiene-a-monocarboxylic acids. Bromination of sorbic acid (II) in CS<sub>2</sub> affords the  $\gamma\delta$ -dibromide (cf. A., 1924, i, 8) [which with O<sub>2</sub> gives  $\alpha$ -bromocrotonaldehyde (III) and CHO-CO<sub>2</sub>H] and a liquid (IV) which, contrary to Farmer and Healey (A., 1927, 646), contains the  $\alpha\beta$ -dibromide. (IV) with boiling EtOH containing 5% H<sub>2</sub>SO<sub>4</sub> during 3 hr. affords sorbic acid tetrabromide and Et sorbate dibromide which with O3 affords MeCHO, (III), H2C2O4, and dibromosuccinic acid. Interaction of

(II) with ICl in AcOH at room temp. affords y-chloroδ-iodo-β-ethylacrylic acid, m.p. 88°, which when treated with weak bases affords (II) and  $\gamma$ -chlorosorbic acid (cf. A., 1909, i, 550) (Et ester, m.p. 31-32°), the structure of which is confirmed by ozonolysis. Interaction of (II) and H<sub>0</sub>O containing Cl<sub>2</sub> at 85° affords  $\delta$ -chloro- $\gamma$ -hydroxy- $\Delta^{\alpha}$ -hexenoic acid (V), m.p. 97°, also obtained by interaction of (II) in Et<sub>2</sub>O with HOCl in H<sub>2</sub>O (cf. A., 1932, 930). The structure of (V) is confirmed by (a) ozonolysis, which affords CHO·COEt (2: 4-dinitrophenylosazone, m.p. 247°), and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; (b) oxidation with  $KMnO_4$  at room temp. in neutral solutions affords  $H_2C_2O_4$  and  $\alpha$ -chloropropionic acid; (c) reduction ( $H_2$ -Adams' catalyst) affords  $\delta$ -chloro- $\gamma$ hexolactone. (II) affords with Br in  $H_2O$  at  $85^{\circ}$ mainly o-bromo- $\gamma$ -hydroxy- $\Delta^{\alpha}$ -hexenoic acid (VI), m.p. 110°, and an oil, which after esterification affords Me bromohydroxyhexenoate and a product, C7H11O4Br, m.p. 154-155°. (II) with HOBr also affords (VI), the structure of which is confirmed by ozonolysis. Me sorbate and Br in  $H_2O$  afford mainly Me  $\gamma\delta$ dibromo- $\Delta^{\alpha}$ -hexenoate, ozonised to (III) [2:4-dinitrophenylhydrazone, m.p. 220° (decomp.)]. (II) with Br in EtOH affords y-bromosorbic acid, m.p. 135° (lit. 140°) (also obtained from  $\gamma\delta$ -dibromo- $\Delta^{\alpha}$ hexenoic acid with dil. EtOH-KOH), ozonised to MeCHO [2:4-dinitrophenylhydrazone, m.p. (less stable form) 146° (cf. A., 1933, 1005)]. The αβ-addition of 2Br to Me cinnamylideneacetate (A., 1904, i, 1012), practically to the exclusion of  $\gamma\delta$ -addition, is in support of the present work, as an unsaturated substituent in the  $\delta$ -position tends to dissipate  $\delta$ -polarisation, and so inhibit primary halogen attack at this point. Similarly, de-activation of a C<sub>a</sub>-polarisation is increased by another  $\alpha$ -CO<sub>2</sub>H, so that cinnamylidenemalonate shows mainly γδ-addition of Br (cf. Å., 1904, i, 1012). Et muconate (VII) affords a dibromide (cf. J.C.S., 1922, 121, 1306), ozonised to Et β-bromo-βaldehydoacrylate (2:4-dinitrophenylhydrazone, m.p. 193-194°),  $H_2C_2O_4$ , and Et *i*-dibromosuccinate. (VII) with ICl in AcOH at room temp. during 12 hr. affords Et  $\beta$ -chloro- $\alpha$ -iodo- $\Delta^{\gamma}$ -dihydromuconate (?), m.p. 68°, converted by dil. Na<sub>2</sub>CO<sub>3</sub> into Et muconate and by boiling dil. EtOH-KOH into muconic acid. (II) with dry HCl during several days at room temp. affords mainly  $\delta$ -chloro- $\Delta^{\beta}$ -hexenoic acid, an oil, ozonised to AcCHO. The orientation of hydrohalide addition cannot always be predicted, because after a-attack by H<sub>2</sub> the CO<sub>2</sub>H is separated from the anionotropic system, which leaves in doubt whether orientation of the halogen atom is determined before or after the J. L. D. prototropic rearrangement.

Esters of tiglic, angelic, and  $\alpha$ -ethylacrylic acids. M. NASTER and A. GAVRLOV (Bull. Soc. chim. Belg., 1933, 43, 519—530).—OH•CMeEt•CN and SOCl<sub>2</sub> give a mixture which with dry HCl at  $< 35^{\circ}$ gives much  $\beta$ - (I), b.p. 62—63°/10 mm., little  $\alpha$ -chlorodl-isovaleronitrile, b.p. 33—34°/10·5 mm., and much  $\alpha$ -chloromethyl-n-butyronitrile (II), b.p. 70—71°/10 mm. With HCl-MeOH (I) gives Me  $\beta$ -chloro-dl-isovalerate (III), cryst., b.p. 54—55°/12 mm. (50% yield), and a little Me tiglate (IV), b.p. 37—38°/12 mm. (amide, m.p. 75—76°), a substance, m.p. 170°, dl- $\beta$ -chloroisovaleric acid, m.p. 63·4—63·8°, and its amide, m.p.

120—120.4°. With quinoline at  $125^{\circ}$  (I) gives (IV), but no Me angelate. Angelamide (V) is stable to  $NH_3-C_6H_6$ . (II) and MeOH-HCl give much  $Me \alpha$ -chloromethylbutyrate, b.p. 57–58°/12 mm., and acidic products, but no unsaturated ester; with quinoline at  $130^{\circ}$  it gives Me a-ethylacrylate (VI), b.p.  $122-123^{\circ}/$ 761 mm., and (IV). Dry distillation of dl- $\alpha$ -hydroxy-isovaleric acid, m.p. 71—72°, gives lactide and tiglic acid (separated by distillation) and a mixture, b.p.  $74-77^{\circ}/10$  mm., whence by fractionation of the Ca salts were obtained angelic (Ca salt,  $+2H_{2}O$ , more sol. in cold than in hot  $H_2O$  and  $\alpha$ -ethylacrylic acid, the K salts of which with MeI in EtOH give Me angelate, b.p.  $127.6 - 127.8^{\circ}/765$  mm. [gives ( $\overline{V}$ )] and (VI) [together with (IV)], respectively. (IV) was also obtained from the acid by MeOH-H<sub>2</sub>SO<sub>4</sub>. The identity of the amides with authentic specimens confirms the structures of the esters and intermediates. Physical data are recorded for the compounds. R. S. C.

Composition of fatty acid mixtures. II. Further development of Twitchell mixed-m.p. method for determination of individual saturated fatty acids. R. N. WENZEL (Ind. Eng. Chem., [Anal.], 1934, 6, 1—7).—An improved form of electrically heated m.-p. apparatus is described. In the analysis of fatty acid mixtures by the Twitchell method palmitic (I) and stearic (II) acids as solvents give normal depression const. ( $K_m=1.82, 1.61$ ), which hold also with glycerides as solute, but myristic acid (III) gives anomalous results with (II) as solute. The m.p. is taken as the point at which the last trace of solid disappears, and is unaffected by previous melting and re-solidification. Results are accurate within a few %. The prep. of pure (I), (II), (III), and oleic acid is described. H. A. P.

Determination of pyruvic acid. G. CARPENI-SEANU (Compt. rend., 1934, 198, 272–274).—Simon's method (A., 1924, i, 632) is modified so as to detect  $AcCO_2H$  in concess. of 1 in 50,000 and to determine it within  $\pm 5\%$  in 0.002% solution. R. S. C.

α- and β-Cinenic acid. Constitution of β-cinenic acid. H. RUPE and H. HIRSCHMANN (Helv. Chim. Acta, 1934, 17, 98–105).—Ozonolysis of β-cinenic acid (I) in CCl<sub>4</sub> gives α-methylparaconic acid, identical with a synthetic specimen. (I) is therefore α-hydroxyαz-dimethyl-Δ<sup>8</sup>-n-heptenoic acid, the isomeric α-acid (II) being 2: 6: 6-trimethyltetrahydropyran-6-carboxylic acid. Oxidation of (I) with 4% KMnO<sub>4</sub> at room temp. gives COMe<sub>2</sub>, small yields of HCO<sub>2</sub>H, AcOH, and (?) valeric acid, (II), and a mixture of (I) and cinogenic acid (az-dihydroxy-az-dimethyl-n-heptoic acid) (separated as its Co salt). J. W. B.

Tartaromanganic salts. G. LEJEUNE (Compt. rend., 1933, 197, 1650—1652).—Dissolution of either hydrated  $MnO_2$  or the green complex manganitartrate of Job (A., 1911, i, 176) in a conc. solution of tartaric acid affords (after pptn. of Na H tartrate in the latter case) a red complex salt

HO·Mn[·C(OH)·CO<sub>2</sub>H]<sub>2</sub>,H<sub>2</sub>O, slowly decomposed by  $H_2O$  to give MnO<sub>2</sub>, and liberating I from KI. The corresponding brown Na H salt +4H<sub>2</sub>O is obtained by dissolving MnO<sub>2</sub> in Na H tartrate solution.

J. W. B.

Vitamin-C. VIII. Constitution of vitamin-C. F. MICHEEL and K. KRAFT (Z. physiol. Chem., 1933, 222, 235—249; cf. A., 1933, 1213).—Mainly a review. Catalytic hydrogenation (PtO<sub>2</sub>) at 35—40°/60 mm. of ascorbic acid affords a mixture from which was isolated *l*-idonic acid [brucine salt, m.p. 192°, [ $\alpha$ ]]<sub>0</sub><sup>m</sup> -16·5° in H<sub>2</sub>O; phenylhydrazide, m.p. 115° (sinters at 102°), [ $\alpha$ ]<sub>0</sub><sup>m</sup> +10·5° in H<sub>2</sub>O; dibenzylidene compound I, m.p. 225°, II, m.p. 209°, [ $\alpha$ ]<sub>10</sub><sup>m</sup> +57·3°]. *d*-Idonic acid also gives two dibenzylidene derivatives: I, m.p. 227°, [ $\alpha$ ]<sub>10</sub><sup>m</sup> -57·8°, II, m.p. 208°, [ $\alpha$ ]<sub>10</sub><sup>m</sup> -57·3°. With 0·1*N*-NaOH, dimethylascorbic acid neutralises I mol.; the Na salt gives the p-nitrobenzoyl derivative, m.p. 181°, inactive towards O<sub>3</sub>, NH<sub>2</sub>OH,HCl, p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·NH<sub>2</sub>, and NH<sub>2</sub>·CO·NH·NH<sub>2</sub>.

J. H. B.

Ascorbic acid and synthetic analogues. D. K. BAIRD, W. N. HAWORTH, R. W. HERBERT, E. L. HIRST, F. SMITH, and M. STACEY (J.C.S., 1934, 62-67).-Glucoascorbic acid (I) [named 3-keto-d-glucoheptonofuranolactone in A., 1933, 1275 (improved prep.)] has  $[\alpha]_{1}^{so} - 14^{\circ}$  in H<sub>2</sub>O (+1H<sub>2</sub>O) (II), m.p. 138° after sintering at 128° (Na salt  $[\alpha]_{1}^{so} - 80^{\circ}$ ). When heated, (II) gives the anhyd. form, m.p. 191° (decomp.) (cf. loc. cit.), which after treatment with I and NHPh·NH<sub>2</sub> (III) yields a compound,  $C_{19}H_{20}O_5N_4$ , m.p. 222°, which corresponds with an osazone, m.p. 210°, obtained similarly from ascorbic acid (IV). dor l-(IV) in H<sub>2</sub>O (loc. cit.) affords with (III) (cf. *ibid.*, 1143) after oxidation with I in theoretical amount, a product m.p. 210° (decomp.), identical with that obtained from (IV). A product, C7H11O6N, probably  $\begin{array}{c} C(:NH) \longrightarrow \\ C(OH):C(OH) \end{array} O CH \cdot [CH(OH)]_2 \cdot CH_2 \cdot OH, \text{ is an inter-} \end{array}$ mediate in the prep. of (I) and is hydrolysed by 20% AcOH at  $80^{\circ}$  to (I). Arabinosazone in H<sub>2</sub>O-EtOH-AcOH with PhCHO at  $90-95^{\circ}$  in N<sub>2</sub> affords CHPh.N.NHPh and arabinosone, which with KCN and CaCl<sub>2</sub> in neutral solution gives  $\psi$ -araboascorbic acid, converted by 8% HCl during 48 hr. into l-arabo-ascorbic acid, m.p. 168° (decomp.),  $[\alpha]_{10}^{20} + 19°$  in H<sub>2</sub>O (Na salt  $[\alpha]_{10}^{20} - 94°$ ), oxidised with I and HI to a product with  $[\alpha]_{10}^{20} + 12°$  after 90 hr. (cf. *ibid.*, 1143). Maurer and Schiedt's product (cf. *ibid.*, 936) is d-araboascorbic acid, for which a furan structure was suggested (cf. ibid., 489). This must now be amended. Similarly prepared, d-galactoascorbic acid has m.p. 109° (decomp.),  $[\alpha]_{11}^{20}$  0° (Na salt,  $[\alpha]_{12}^{20}$  -77°).  $\psi$ -Lactoascorbic acid when heated with 8% HCl at 50° is hydrolysed to (II), and is used as a source of (II). Maltosone (cf. A., 1902, i, 745) is converted quantitatively into  $\psi$ -maltoascorbic acid. In dil. aq. solutions all these substances (except the  $\psi$ -compounds) show an intense band at 265 mµ. In more conc. solution, the band is at  $240-245 \text{ m}\mu$ . J. L. D.

Preparation and properties of aldonic acids and their lactones and basic calcium salts. H. S. ISBELL and H. L. FRUSH (Bur. Stand. J. Res., 1933, 11, 649-664).—The prep. of the commoner aldonic acids and their lactones in the cryst. condition is facilitated by the use of their basic Ca salts, and of dioxan as a solvent. J. L. D.

Micro-method for determination of uronic acids. B. BUCKHART, L. BAUR, and K. P. LINK

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(J. Biol. Chem., 1934, 104, 171—181).—The methods of Buston (A., 1932, 602) and Clark (*ibid.*, 867) have been modified to give either a volumetric or a gravimetric determination of uronic acid and its derivatives. The accuracy of the method is of the same order as that of the best micro-modification.

H. G. R.

Polarimetric determination of gluconic acid. T. A. BENNET-CLARK (Biochem. J., 1934, 28, 45–47).  $-[\alpha]$  of d-gluconic acid (I) is enhanced about 40-fold by formation of complex salts with molybdate (II). The relationship between  $[\alpha]$  and (I) is almost linear, but, in presence of carbohydrate, special procedure is necessary owing to oxidation by (II).  $[\alpha]$  of complexes of (I) with (II) and with UO<sub>2</sub> salts are in the same direction, in contrast to the behaviour of malates. H. G. R.

Synthesis of hexuronic acids. III. Synthesis of *dl*-alluronic acid from *allo*mucic acid. C. NIEMANN, S. KARJALA, and K. P. LINK. IV. Synthesis of *d*-galacturonic acid from *d*-galactose. C. NIEMANN and K. P. LINK (J. Biol. Chem., 1934, 104, 189—194, 195—204; cf. A., 1933, 595).— III. The authors' method (A., 1932, 367) of isolating uronic acids is inferior to that of Fischer (A., 1891, 677). The lactone of *allo*mucic acid, m.p. 170—172°, with Na-Hg gives dl-*alluronic acid*, m.p. 145—146°, decomp. 148—149° [*lactone*; *Ba* and *brucine*,  $+H_2O$ , m.p. 172—173°, (anhyd.) 180—181°,  $[\alpha]_D^{\pm} - 25^{\circ} \pm 1^{\circ}$  in H<sub>2</sub>O, salts; *Ba* salt of p-bromophenylosazone, m.p. 209—211° (decomp.); *Me* ester of *methylglucoside*,  $+H_2O$ ]. The Ba salts of *s*-aldohexuronic acids give osazones, whereas those of *as*-acids give hydrazones.

IV. d-Galactose diisopropylidene ether and KMnO<sub>4</sub> give K diisopropylidene-d-glucuronate (71% yield),  $+0.5H_2O$ ,  $[\alpha]_D^n - 66^\circ \pm 2^\circ$  in H<sub>2</sub>O (also prepared in 30% yield from d-galacturonic acid by COMe<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>), whence were obtained successively (a) the free acid, m.p. 157.5—158°,  $[\alpha]_D^n - 84^\circ \pm 2^\circ$  in CHCl<sub>3</sub>, Ba d-galacturonate,  $[\alpha]_D^n + 24^\circ \pm 1^\circ$  in H<sub>2</sub>O, and the corresponding acid,  $+H_2O$ , m.p. 157—159°,  $[\alpha]_D^n + 51^\circ \pm 1^\circ$  in H<sub>2</sub>O, and (b) the Me ester of  $\alpha$ -methyl-dgalacturonide,  $+H_2O$ , m.p. 137—138°,  $[\alpha]_D^n + 121^\circ \pm 2^\circ$ in H<sub>2</sub>O, and  $\alpha$ -methyl-d-galacturonide (71% yield),  $+2H_2O$ , m.p. 111—111.5°,  $[\alpha]_D^n + 129^\circ \pm 1^\circ$  in H<sub>2</sub>O, also obtained in 3.3% yield by electrolytic oxidation of  $\alpha$ -methyl-d-galactoside (whereby the ring-structure is proved) (cf. A., 1926, 150).  $\alpha$ -Methyl-d-glucoside does not give  $\alpha$ -methyl-d-glucuronide by electrolytic oxidation or with NaOBr or H<sub>2</sub>O<sub>2</sub> (cf. A., 1924, i, 10). R. S. C.

Composition of an aldobionic acid from flaxseed mucilage. C. NIEMANN and K. P. LINK (J. Biol. Chem., 1934, 104, 205–206).—The aldobionic acid from flax-seed mucilage with hot  $2 \cdot 5\%$  H<sub>2</sub>SO<sub>4</sub> gives *u*-galacturonic acid, m.p. 157–158°,  $[\alpha]_{\rm D}^{25}$  +54° (brucine salt, m.p. 188–189°,  $[\alpha]_{\rm D}^{25}$  -7.5°), and *l*-rhamnose (cf. A., 1930, 1408). R. S. C.

Preparation of calcium lactobionate and  $\delta$ -lactobionolactone. H. S. ISBELL (Bur. Stand. J. Res., 1933, 11, 713—717).—When Ca lactobionate (cf. A., 1931, 1038) and CaCl<sub>2</sub> in H<sub>2</sub>O are evaporated, Ca(C<sub>12</sub>H<sub>21</sub>O<sub>12</sub>)<sub>2</sub>,CaCl<sub>2</sub>,6H<sub>2</sub>O, [ $\alpha$ ]<sup>b</sup><sub>D</sub>+20·0° in H<sub>2</sub>O separates; this is converted by CaO in hot H<sub>2</sub>O into Ca(C<sub>12</sub>H<sub>21</sub>O<sub>12</sub>)<sub>2</sub>,5H<sub>2</sub>O,  $[\alpha]_{10}^{30}$  +23.7° in H<sub>2</sub>O, which affords, after treatment with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>,  $\delta$ -lactobionolactone, m.p. 195–196°,  $[\alpha]_{10}^{30}$  +54° to +22° in H<sub>2</sub>O. J. L. D.

Determination of methoxyl in pectin. G. ROMEO (Annali Chim. Appl., 1933, 23, 530–534). l g. of the powdered pectin is dissolved on the waterbath in 250 c.c. of  $H_2O$ . The cooled solution is made up to the initial vol. and neutralised with 0.5*N*-NaOH. This gives the acid val., which is comparatively high for altered or poor material; 20 c.c. of 0.5*N*-NaOH are then added with vigorous stirring and after 15 min., the liquid is treated with 20 c.c. of 0.5*N*-H<sub>2</sub>SO<sub>4</sub>, and titrated with 0.5*N*-NaOH : 1 c.c. of 0.5*N*-NaOH used in the hydrolysis  $\equiv$ 0.0155 g. OMe. T. H. P.

Condensation of chloral and bromal with diamides. F. D. CHATTAWAY and E. J. F. JAMES (J.C.S., 1934, 109–113; cf. A., 1932, 151).-Interaction of  $NH_2$ ·CO·NHMe (I) and  $CCl_3$ ·CH(OH)<sub>2</sub> (2 mols.) in  $H_2O$  affords N-methyl-N'-( $\beta\beta\beta$ -trichloro- $\alpha$ hydroxyethyl)carbamide, m.p. 140° (decomp.) [Ac2 derivative, m.p. 90—91° (decomp.)], the Na derivative of which in aq. NaOH with  $Ac_2O$  affords di-( $\beta\beta\beta\beta$ -trichloro-a-N'-methylcarbamidoethyl) ether (II), m.p. 230° (decomp.)  $[Ac_2 \text{ derivative, m.p. 131° (decomp.)]}.$ (II) in EtOH containing NaOEt during 24 hr. affords N-methyl-N'-  $(\beta\beta\beta$ -trichloro -  $\alpha$  - ethoxyethyl)carbamide, m.p. 145° (decomp.). The following are prepared similarly: N-ethyl-N'-  $(\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethyl)carbamide, m.p. 138° (decomp.) [Ac<sub>2</sub> derivative, m.p. 60° (decomp.)], di-(βββ-trichloro-α-N'-ethylcarbamidoethyl) ether, m.p. 226° (decomp.) [Ac2 derivative, m.p. 145° (decomp.)]; N-ethyl-N'-(βββ-trichloro-α-methoxyethyl)carbamide, m.p. 150° (decomp.) [corresponding OEt., m.p. 135° (decomp.); OPra., m.p. 140° (decomp.); OBu<sup>a</sup>-derivative, m.p. 95° (decomp.)]. Interaction of NH2 CO NHMe and CBr3 CHO in H2O affords similar, though less stable, products. The following similar, though less stable, products. The following are described : N-methyl-, m.p. 189° (decomp.)  $[Ac_2$ derivative, m.p. 119° (decomp.); *OEt*-compound, m.p. 162° (decomp.)], and N-phenyl-N'-( $\beta\beta\beta$ -tribromo- $\alpha$ -hydroxyethyl)carbamide, m.p. 167° (decomp.)  $[Ac_2$ derivative, m.p. 142° (decomp.); *OMe*-, m.p. 158° (decomp.) *OEt* m.p. 145° (decomp.) are proved by *i* (decomp.), OEt-, m.p. 145° (decomp.), -compound]; di-(βββ-tribromo-α-N'-methyl-, m.p. 200° (decomp.) [Ac2 derivative, m.p. 180° (decomp.)], and -phenyl-carbamidoethyl) ether, m.p. 185° (decomp.)  $[Ac_2 \text{ derivative, m.p.} 163° (decomp.)]$ . Interaction of CCl<sub>3</sub>·CHO with  $NH_2 \cdot CO \cdot NAlk_2$  gives the following, which are un-changed by cold  $Ac_2O$  in NaOH : *NN*-dimethyl-, m.p. 157° (decomp.) (lit., 153°); NN-diethyl-, m.p. 146° (decomp.) (lit., 142°), and NN-diphenyl-N'-(βββ-trichloro-a-hydroxyethyl)carbamide, m.p. 170° (decomp.) [Ac derivative, m.p. 108° (decomp.)]; NN-dimethyl-, m.p. 165° (decomp.) [ $+H_2O$ , m.p. 96° (decomp.)] and  $NN - diphenyl - N' - (\beta\beta\beta - tribromo - \alpha - hydroxyethyl)carb$ amide, m.p. 168° (decomp.). (·CO·NH<sub>2</sub>)<sub>2</sub> and CCl<sub>3</sub>·CHO (excess) when boiled during 8 hr. afford NN'-di-(βββtrichloro-a-hydroxyethyl)oxamide (III), decomp. >190° (Ac<sub>2</sub> derivative, m.p. 192°), but no monochloraloxamide, which also is not formed by interaction of Et N-( $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethyl)oxamate (IV) (A., 1914, i, 666). (IV) with NH<sub>2</sub>Ph in EtOH at 100° during 0.5 hr. gives N-phenyl-N'-(BBB-trichloro-a-hydr-

oxyethyl)oxamide, decomp. > 180° into CCl<sub>3</sub>·CHO and CO<sub>2</sub>H·CO·NHPh (Ac derivative, m.p. 185°). (III) with PCl<sub>5</sub> at 100° during 0.5 hr. affords NN'-di-(αβββtetrachloroethyl)oxamide, m.p. 170°, converted by boil-ing EtOH into NN'-di- $(\beta\beta\beta$ -trichloro- $\alpha$ -ethoxyethyl)-oxamide (V), m.p. 176°. The  $(NH_2)_2$ - and  $(\cdot NHPh)_2$ -compounds corresponding with (V) have m.p. 213°, and 193° (decomp.), respectively. CH<sub>2</sub>(CO·NH<sub>2</sub>)<sub>2</sub> and CCl<sub>3</sub>·CHO (excess) at 100° during 12 hr. afford CNN'-tri (0.0° trichloro a badronethyl)malanamide (VI) tri- $(\beta\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethyl)malonamide (VI), polymorphic forms m.p. 180° (labile) and 180° (decomp.) (stable) [Ac<sub>3</sub> derivative, m.p. 165° (de-comp.)]. Reaction between substituted malonamides and CCl<sub>3</sub>·CHO occurs only at unsubstituted positions. The following, prepared similarly to (VI), are described : NN'-diphenyl-(βββ-trichloro-α-hydroxyethyl), malonamide, m.p. 187° (decomp.); N-phenyl-N'-(βββ $trichloro-\alpha-hydroxyethyl)-(\beta\beta\beta-trichloro-\alpha-hydroxyethyl)$ malonamide, m.p. 170° (decomp.) [Ac, derivative, m.p. 175° (decomp.)]; NN'-di-, m.p. 163° (decomp.) (Ac<sub>2</sub> derivative, m.p. 132°), and N-phenyl-N'-(βββ-trichloro-a-hydroxyethyl)ethylmalonamide, m.p. 164° (decomp.) [Ac derivative, m.p. 185° (decomp.)]. Malonanilic acid and CCl3 CHO afford yyy-trichloro-B-hydroxybutyranilide, m.p. 146° (decomp.) [Ac derivative, m.p. 149° (decomp.)]. CN·CH<sub>2</sub>·CO·NH<sub>2</sub> and CCl3 CHO afford cyanoaceto-βββ-trichloro - α - hydroxyethylamide, m.p. 155° (decomp.) [Ac derivative, m.p. 108° (decomp.)]. J. L. D.

Isomerisation of hydroxyaldehydes. V. Oxidation-reduction transformations of  $\alpha$ -hydroxyisobutaldehyde. S. DANILOV and E. VENUS-DANILOVA (Ber., 1934, 67, [B], 24—35).—Previously reviewed (A., 1933, 1277).  $\alpha$ -Hydroxyisobutaldehydesemicarbazone and -p-nitrophenylhydrazone have m.p. 164—165° and m.p. 153—159° (decomp.), respectively. H. W.

δ-Hydroxyvaleraldehyde. R. PAUL (Compt. rend., 1933, 197, 1652—1654).—0.015*N*-HCl converts 2:3-dihydropyran (I) (A., 1933, 831) into the cyclic form of δ-*hydroxyvaleraldehyde* (II), b.p. 80—81°/16 mm., which is tautomeric with the open-chain aldehyde, since it slowly gives a colour with Schiff's reagent, reacts with NHPh·NH<sub>2</sub>, and is oxidised by Ag<sub>2</sub>O to Ag δ-hydroxyvalerate. (II) is reconverted into (I) by distillation at 760 mm. with a trace of HCl. The (static) *Me ether* O<CH(OMe)·CH<sub>2</sub>>CH<sub>2</sub>, b.p. 128— 129° is obtained by holing (I) with MeOH=HCl

129°, is obtained by boiling (I) with MeOH-HCl (trace). J. W. B.

Photopyridine reaction. F. FEIGL and V. ANGER (J. pr. Chem., 1934, [ii], 139, 180—182).— Photopyridine is identified by its colour reactions, presence of  $\cdot$ CHO, and reconversion into  $C_5H_5N$  by heat as CHO $\cdot$ CH:CH:CH:ONH<sub>4</sub> (cf. this vol., 303). With 2(m-NH<sub>2</sub> $\cdot$ C<sub>6</sub>H<sub>4</sub> $\cdot$ NO<sub>2</sub>),H<sub>2</sub>SO<sub>4</sub> (I) it gives  $\varepsilon$ -m-nitroanilino- $\Delta^{\beta\beta}$ -pentadienal-m-nitroanil sulphate, m.p. 116°, also obtained from (I) and

CHO-CH:CH-CH:CH-ONa. H. A. P.

Condensations of furan compounds. II. Determination of small amounts of acetone. V. V. TSCHELINCEV and E. K. NIKITIN (Bull. Soc. chim., 1933, [iv], 53, 1130—1139; cf. A., 1932, 1140). —COMe<sub>2</sub> is determined in concns. >0.0001% by condensation with furfuraldehyde and NaOH, acidification with  $H_2SO_4$ , and matching of the violet-red colour produced. The method is valid in presence of aromatic aldehydes, COMeEt, or  $CH_2Ac \cdot CO_2H$ , but not in presence of sugars; aliphatic and arylaliphatic aldehydes must be removed previously by  $KMnO_4-H_2SO_4$ . R. S. C.

Exchange of heavy hydrogen atoms between water and organic compounds. K. F. BON-HOEFFER and R. KLAR (Naturwiss., 1934, 22, 45; cf. A., 1933, 1242).—The exchange of heavy H atoms from heavy  $H_2O$  with the H of the Me in NaOAc does not take place. If the H atom of a Me is mobile, as in keto-enolic tautomerism, exchange takes place with the H of OH of the enolic form. Pure aq. COMe<sub>2</sub> (keto-form) does not exchange, but after the addition of a small amount of Na exchange takes place. A. J. M.

Action of hydrogen peroxide on acetone. Proof of the existence of a trimeric peroxide of acetone which depolymerises to the monomeride. H. LEcoq (Bull. Soc. chim. Belg., 1933, 43, 531-536). --Mol. wt. determinations show that the peroxide,  $(C_3H_6O_2)_x$ , obtained from  $COMe_2$ ,  $H_2O_2$  (3 parts), and a few drops of  $H_2SO_4$  is trimeric when first dissolved in cold  $C_6H_6$ , but dissociates completely in 2 hr. (cold), or instantly when boiled, into the monomeride (I). The trimeride, m.p. 97-98°, gives (I), m.p. 90°, when kept molten for 2-3 min. or when distilled in steam. It liberates I quantitatively from aq. EtOH-HCl-KI. R. S. C.

Stability of fructose in aqueous solutions of varying  $p_{\mu}$ .—See this vol., 260.

Fructofuranose tetrabenzoate. P. BRIGL and R. SCHINLE (Ber., 1934, 67, [B], 127-130; cf. A., 1933, 378).—Fructofuranose 1:3:4:6-tetrabenzoate (I), m.p. 124-125°,  $[\alpha]_{\rm p}$  -6·1° to -13·7° in CHCl<sub>3</sub>, is readily obtained by successive additions, without cooling, of BzCl (0·5 mol.) to fructose (0·1 mol.) in C<sub>5</sub>H<sub>5</sub>N. The furanoid structure of (I) is confirmed by its formation from the fructose 1:6-dibenzoate (II) of Zervas and Sessler (this vol., 58) (improved prep.) by the action of BzCl and C<sub>5</sub>H<sub>5</sub>N without cooling or of BzCl and C<sub>5</sub>H<sub>5</sub>N in CHCl<sub>3</sub> at -15°. The cyclie nature of (II) is also established. H. W.

Methylglucosides of naturally occurring hexuronic acids. II. Kinetics of the hydrolysis of  $\alpha$ -methyl-*d*-galacturonide. S. MORELL and K. P. LINK (J. Biol. Chem., 1934, 104, 183—188; cf. A., 1933, 595).—In the hydrolysis of  $\alpha$ -methyl-*d*-galacturonide (I) (+2H<sub>2</sub>O, m.p. 112°, decomp. 120°, [ $\alpha$ ]<sub>15</sub><sup>\*</sup> +127.8° in H<sub>2</sub>O) and -*d*-galactoside (II) (+H<sub>2</sub>O, m.p. 114—116°, [ $\alpha$ ]<sub>15</sub><sup>\*</sup> +199.4° in H<sub>2</sub>O) in N-HCl k is 1.56 and 2.01×10<sup>-3</sup> min.<sup>-1</sup> at 70° and E 29,000 and 35,000 between 60° and 80°, respectively. By analogy with (II), (I) thus has a pyran structure. R. S. C.

Ononin. II. F. WESSELY, F. LECHNER, and K. DINJAŠKI (Monatsh., 1933, 63, 201–209).—Fractional crystallisation of crude ononin (Merck) (I) separates diadzein, (I) being purified as its  $Ac_4$  derivative, m.p. 182.5°. Similarly, the specimen of formononetin (II) previously used contained impurities partly separated by fractional crystallisation or sub-

limation, but the identity of (II) with the synthetic specimen (A., 1933, 614) is confirmed. With  $\alpha$ -acetobromoglucose and NaOH in H<sub>2</sub>O-COMe<sub>2</sub> at 0°, 2 : 4dihydroxyphenyl 4'-methoxybcnzyl ketone (A., 1931, 738) affords, after deacetylation, its 4-glucoside, identical with natural onospin, the structure being confirmed by methylation (MeI-McOH-K<sub>2</sub>CO<sub>3</sub>) and hydrolysis to 4-hydroxy-2-methoxyphenyl 4'-methoxybenzyl ketone, sinters 171°, m.p. 173°, identical with a specimen synthesised from m-C<sub>6</sub>H<sub>4</sub>(OH)·OMe and p-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CN with anhyd. ZnCl<sub>2</sub>-HCl in Et<sub>2</sub>O. J. W. B.

Preparation and enzymic fission of basic glycosides. B. HELFERICH, E. GÜNTHER, and S. WINKLER (Annalen, 1934, 508, 192-205).-o-Cresolβ-d-glucoside tetra-acetate, m.p. 142-144° (corr.),  $[\alpha]_{p}^{a} = -27.5^{\circ}$  in CHCl<sub>3</sub>, obtained by the method pre-viously described (A., 1933, 379) from *o*-cresol,  $\beta$ -glucose penta-acetate, and p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H at 120– 130°, is converted by Br in CHCl<sub>3</sub> in presence of NaHCO3 and strong irradiation into w-bromo-o-cresol- $\beta$ -d-glucoside tetra-acetate, m.p. 158—160° (corr.),  $[\alpha]_{p}^{1}$  +35.2°. Prolonged interaction of this with cold aq. MeOH-NH3 gives the hydrobromide of o-aminomethylphenol- $\beta$ -d-glucoside, m.p. 182–185° [ $\alpha$ ]<sup>22</sup> – 64·2° in aq. AcOH (calc. amount), acetylated (Ac2O-C5H5N) to the Ac<sub>5</sub> derivative, m.p. 140-142° (corr.), [a] -64.5° in CHCl<sub>3</sub>, which is hydrolysed (N-NaOH in COMe<sub>2</sub>) to the N-Ac derivative (I), m.p. 195-196°,  $[\alpha]_{1}^{19}$  +33.3° in H<sub>2</sub>O. p-Cresol- $\beta$ -d-glucoside tetraacetate, m.p. 116-118° (corr.), [a]18 -17.6° in CHCl3, is brominated similarly to the  $\omega$ -Br-derivative (II), m.p. 155-158° (corr.), [a]<sup>23</sup> -19° in CHCl<sub>3</sub>, which is In p. 155–155 (corr.),  $[\alpha]_{1}^{\alpha}$  =19 in CHCl<sub>3</sub>, which is converted (as above) into p-aminomethylphenol-β-d-glucoside, m.p. about 140° (sinters at 90°), decomp. 147°,  $[\alpha]_{2}^{\alpha}$  =70·1° in aq. AcOH [N-Ac derivative (+H<sub>2</sub>O), m.p. 130–132° (corr.) (sinters at 119°),  $[\alpha]_{2}^{\alpha}$ =53·8° in H<sub>2</sub>O; Ac<sub>5</sub> derivative, m.p. 123–125° (corr.),  $[\alpha]_{1}^{\alpha}$  =14·9° in CHCl<sub>3</sub>]. Successive treatment of (I) with Ac CO in ac COMe, and MOCH NoOME of (II) with Ag<sub>2</sub>CO<sub>3</sub> in aq. COMe<sub>2</sub> and MeOH-NaOMe gives p-hydroxymethylphenol-β-d-glucoside, dimorphous, m.p. 114-118° (corr.) and 136-138° (corr.),  $[\alpha]_{\rm D} = -65.8^{\circ}$  in H<sub>2</sub>O. o-Aminomethylphenol- $\beta$ -d-galactoside, m.p. 218-220° (corr.) (decomp.), [a]<sup>20</sup> -35° in H<sub>2</sub>O [N-Ac derivative (III), m.p. 211-212° (corr.),  $[\alpha]_{10}^{\infty}$  -19.7° in H<sub>2</sub>O]; p-cresol- $\beta$ -d-galactoside tetra-acetate, m.p. 105-107°,  $[\alpha]_{10}^{\infty}$  +3.9° in CHCl<sub>2</sub> ( $\omega$ -Br-derivative, m.p. 104-107°,  $[\alpha]_{10}^{\infty}$  -1.2° in CHCl<sub>3</sub>), and p-aminomethylphenol-B-d-galactoside, m.p. 206-208° (corr.) (decomp.),  $[\alpha]_{10}^{22} - 45.7^{\circ}$  in aq. AcOH [N-Ac derivative, m.p. 166–168° (corr.); Ac<sub>5</sub> derivative, m.p. 131–132°], are similarly prepared. Hydrolysis of the above NH2- and NHAc-glucosides and -galactosides by emulsin (IV) and acid (V) is studied. (I) and (III) are hydrolysed by (IV) [not by (V)] to a much greater extent than any of the other compounds. In general the -glucosides are hydrolysed more rapidly by (IV) and the -galactosides more readily by (V). In both cases, presence of the NH<sub>2</sub> retards fission. Acet-p-hydroxybenzylamide has m.p. 135-137°.

H. B. Lusitanicoside. H. HERISSEY (Compt. rend., 1934, 198, 265–266).—Lusitanicoside,  $C_{21}H_{30}O_{10}$ , and boiling 2.5%  $H_2SO_4$  give chavicol, *d*-glucose, and rhamnose. The biose (not isolated) is named *lusit*anicose. R. S. C.

Glucosides of Digitalis lanata. C. MANNICH (Arch. Pharm., 1934, 272, 5-8).—In part polemical against Stoll and Kreis (A., 1933, 1146). Various samples of lanata glucoside II (A., 1930, 1561; 1933, 877) contain, respectively, 50—56%, 11—17%, and 31-34% of digilanid A, B, and C, and are identical with the "total digilanids" of Stoll and Kreis, whereas lanadigin is mainly digilanid C (about 45%) contaminated with A (30%) and B (25%). J. W. B.

Preparation and properties of nitric acid esters of starch. I, II. J. HACKEL and T. URBANSKI (Z. ges. Schiess- u. Sprengstoffw., 1933, 28, 306-310, 350-354, 378-382; 1934, 29, 14-16, 16-17).-I. The properties of potato-starch nitrates (I) depend on the conditions of nitration. With 10 parts of  $HNO_3$  (58.08–93.3%) alone for 2 hr. at 20° the yield of (I) and the N content (II) of the product increase with increasing HNO<sub>3</sub> concn., almost no reaction occurring with < 67% HNO<sub>3</sub>. Viscosity ( $\eta$ ) and solubility (s) decrease with increasing (II). Washing the product with cold  $H_2O$  and 1% aq.  $Na_2CO_3$  gives products of low stability, and heating with  $H_2O$  causes partial hydrolysis, increase in s, and reduction of yield. With 96.26% HNO<sub>3</sub> for 2 hr. at 10° (II) increases, at first rapidly, with increase in the HNO<sub>3</sub>/starch ratio up to 80/1. The decrease in (II) caused by decreasing this ratio is greater the greater is the dilution of the HNO<sub>3</sub>. At first (II) increases rapidly with increasing reaction time, then more slowly to a max., but development of yield-reducing side-reactions is correspondingly favoured. Between 0° and 30° rise in temp. causes diminution in (II) and  $\eta$ , and increase in s. Pptn. of the product with H<sub>2</sub>SO<sub>4</sub> instead of H<sub>2</sub>O increases (II) consequent on further nitration. The effect of varying concn. of H<sub>2</sub>O, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> on (II) in mixed acid nitrations is expressed in ternary diagrams, a max. val. for (II) being reached when equimol. proportions of H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> are used, the results corresponding with those for cellulose nitrate (Saposchnikov), but with mixed acids poor in H<sub>2</sub>SO<sub>4</sub> considerable deviations from the latter results occur, due, probably, to the solubility of (I) in the mixed acids. With high  $H_2SO_4$  concn. sulphuric esters are formed giving  $H_2O$ -sol. products. With > 20%  $H_2O$ nitration is irregular, and small yields are obtained.

II. Contrary to some statements in the lit., repetition of the above investigations using maize, rice, wheat, tapioca, and sol. starch gives results and products closely similar to those obtained with potato starch. J. W. B.

Highly polymerised compounds. LXXXV. Cellulose. XI. Mol. wt. of methylcellulose. H. STAUDINGER and H. SCHOLZ (Ber., 1934, 67, [B], 48—91).—The deduction of the mol. wt. of cellulose from observation on the tetra- and tri-methylmethylglucosides (Haworth *et al.*) is not valid, since their trimethylcellulose (I) is derived from a cellulose actate (II) in the formation of which the cellulose suffers acetolysis. Their results, however, give an indirect confirmation of the authors' determinations of the mol. wt. of (II) if it is admitted that further degradation of the mol. does not occur during the transition from

(II) to (I). Evidence on this point is sought in observation of the viscosity of (I) and (II) in *m*-cresol (III). The vals. found for the ethers are almost double those for the esters; the result is attributed to the coordinative union of (I) and (III) to oxonium compounds. Suitable, non-combining solvents for (I) and (II) could not be discovered. High vals. for the viscosity of (I) in AcOH and C<sub>5</sub>H<sub>5</sub>N are recorded. It is considered that the investigations show that the chain-length is not altered during the transformation of polymeric homologous (II) into polymeric analogous (I). The constitution of cellulose and the identity of the colloid particles with the macro-mols. are regarded as established, since it is possible to perform chemical reactions with the macro-mols. of cellulose and its derivatives without alteration of the mean degree of polymerisation just as with the simpler, homogeneous oligosaccharides without change in their degree of polymerisation. H. W.

Preparation of propyl-, butyl-, and amylcelluloses by the action of alkyl halides. N. I. NIKITIN and I. M. ORLOVA (J. Appl. Chem. Russ., 1933, 6, 1093—1104).—The reactivity of alkyl halides with alkaline cellulose increases in the order Cl < I < Br, and  $iso - C_5H_{11} < n - C_5H_{11} < Bu^{\beta} < Bu^{\alpha} < Pr^{\beta}$  $< Pr^{\alpha} < Et$ . In the case of isoalkyl halides considerable quantities of gas are evolved during the reaction. The no. of alkyl groups introduced increases with increasing temp. R. T.

Highly polymerised compounds. LXXXVI. Validity of the viscosity law. H. STAUDINGER (Ber., 1937, 67, [B], 92-101).—Reasons are given for considering the viscosity method particularly valuable in the examination of highly polymerised compounds. Objection is raised to the work of Büchner et al. (A., 1933, 261), on the ground that technical cellulose acetate was used, whereas trustworthy data can be obtained only by use of as homogeneous material as possible; re-calculation of their results shows them to confirm rather than to refute the law of viscosity. In reply to Kraemer et al. (A., 1933, 218) it is pointed out that in the less highly polymerised i-hydroxydecoic acids thread mols. of double length are formed by the co-ordinative union of 2 CO2H. With increasing degree of polymerisation, the co-ordinative forces become weakened, so that normal y vals. are observed. The contention that the polyhydroxydecoic acids are more suitable models than the polystyrenes (Corothers et al., this vol., 56) is disputed for the reason that they do not yield a sufficient range of polymerides.

H. W.

Structure of organic compounds of high mol. wt. H. STAUDINGER (Naturwiss., 1934, 22, 65-71, 84-89).—A review.

Hydrogenation of amides to amines. H. ADKINS and B. WOJCIK (J. Amer. Chem. Soc., 1934, 56, 247).—Reduction of laur-, hepto-,  $\alpha$ -phenylbutyr-, furo-, and tetrahydrofuro-amide with H<sub>2</sub> (100—300 atm.) at 175—205° in dioxan using a Cu-Cr oxide catalyst gives 40—70% of the corresponding primary amine (and 25—50% of the sec.-amine); R·CO·NH<sub>2</sub>+ H<sub>2</sub>—— CH<sub>2</sub>R·NH<sub>2</sub>+H<sub>2</sub>O. Substituted amides (e.g., N-lauryl- and sebacyl-piperidine; laur-mono- and -di- $\beta$ -phenylethyl- and -amyl-amides; laur-cyclohexyl-

amide and -anilide; hepto- $\beta$ -phenylethylamide) are similarly reduced to the corresponding sec.- and tert.amines in 70–95% yield. High yields of amines are obtained by hydrogenation of NH<sub>4</sub> laurate. H. B.

Preparation of diaminobutanes. II.  $dl-\alpha\gamma$ -Diamino- $\beta$ -methylpropane, dl- $\alpha\gamma$ -diaminobutane, and  $\alpha\delta$ -diaminobutane. E. STRACK and H. SCHWANEBERG (Ber., 1934, 67, [B], 39-45; cf. A., 1933, 1148).-(·CH<sub>2</sub>·CH<sub>2</sub>·NH<sub>2</sub>)<sub>2</sub> is obtained in 76·4% yield by reduction of succinonitrile (Pd-80% EtOH, 0.125% by vol.) at room temp. Methylmalononitrile (improved prep. from CHMeBr CO2Et) is hydrogenated (Pd-98-99% MeOH) to dl-αγ-diamino-β-methylpropane in 92% yield; the hydrochloride, m.p. 201° (corr.), sulphate, m.p.  $\geq 300^{\circ}$ , platinichloride, m.p. 201 (corr.), sulphate, m.p.  $\geq 300^{\circ}$ , platinichloride, de-comp. 237° (corr.), aurichloride, m.p. 203—205° after softening at 195° or (+2H<sub>2</sub>O) m.p. 142° (corr.) after softening at 130°, compound C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>(HgCl<sub>2</sub>)<sub>2</sub>, de-comp. 196—198° (corr.), picrate, decomp. 252° (corr.) ofter softening at 240° microlevete, decomp. 260° 271° after softening at 249°, picrolonate, decomp. 269-271° (corr.), Bz<sub>2</sub> derivative, m.p. 145° (corr.), and di-m-nitrobenzoyl derivative, m.p. 187° (corr.), are described. *β*-Iminobutyronitrile (improved prep. from MeCN and Na) is reduced by Na and abs. EtOH or by  $H_2$  (Pd-98% MeOH) to dl- $\alpha\gamma$ -diaminobutane in 90% or 93.1% yield, respectively. It yields a hydro-chloride, m.p. 117° (corr.), sulphate, m.p. > 300°, platinichloride, decomp. 250°, aurichloride, m.p. 210– 212° after softening at 200° or  $(+1 \text{ H}_2\text{ O}) \text{ m.p. } 208-$ 210°, compound C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>(HgCl<sub>2</sub>)<sub>2</sub>, m.p. about 200° (corr.), picrate, decomp.  $251^{\circ}$  (corr.) after softening at 248°, *picrolonate*, decomp. about 260° (corr.) after darkening at 245°,  $Bz_2$  derivative, m.p. 170° (corr.) after softening at 168°, and *di*-m-*nitrobenzoyl* compound, m.p. 201° (corr.). **H.** W.

Preparation of isobutylenediamine. H. D. K. DREW and F. S. H. HEAD (J.C.S., 1934, 49–50).—  $\alpha$ -Chloroisobutaldoxime, m.p. 104° (lit., 96–97°), in saturated EtOH–NH<sub>3</sub> during 10 min. affords  $\alpha$ -aminoisobutaldoxime (I), m.p. 89° [hydrochloride (II), m.p. 210° (decomp.); :CHPh derivative, m.p. 110°]. Reduction of (I) or (II) in EtOH–AcOH at 30° with Na–Hg affords isobutylenediamine (isolated as the dihydrochloride) and 2:2:5:5-tetramethylpiperazine. Acetylation of (I) affords  $\alpha$ -acetamidoisobutyronitrile (cf. A., 1904, i, 563) together with Nacetyl- $\alpha$ -aminoisobutaldoxime, m.p. 198 199°.

J. L. D Compounds of hexamethylenetetramine.—See this vol., 265.

Reaction of aliphatic imino-ethers with hydrazine. W. OBERHUMMER (Monatsh., 1933, 63, 285—300).—Imino-ethers (as their hydrochlorides) react with  $N_2H_4$  to give either amidrazones (new nomenclature suggested) NH:CR:NH:NH<sub>2</sub>+EtOH, or hydrazino-ethers NH<sub>2</sub>:N:CR:OEt+NH<sub>3</sub>, or, probably as a secondary reaction, hydrazidines

 $NH_2 \cdot N:CR \cdot NH \cdot NH_2 + EtOH + NH_3$ , the product depending on reaction conditions, especially on the order of addition of the reactants. Thus addition of acetimido-ether hydrochloride (I) (1 mol.) to  $N_2H_4$ -EtOH at 0° gives a 50% yield of acetamidrazone hydrochloride (II) (R=Me), m.p. 131-132° (free base stable only in H<sub>2</sub>O or EtOH), and with 2 mols. of (I) acethydrazidine hydrochloride (III) (picrate, decomp. 126– 128°; platinichloride; sulphate, altered at 130°, clear melt at 192–193°; free base stable only in solution), decomp. at 140–150° to give 4-amino-3 : 5-dimethyl-1 : 2 : 4-triazole (IV). Addition of N<sub>2</sub>H<sub>4</sub> in EtOH to a solution of (I) in EtOH at 0°, however, gives (IV) and di-( $\alpha$ -ethoxyethylidene)hydrazine (OEt•CMe:N•)<sub>2</sub>, sinters 26°, m.p. 28°. With HNO<sub>2</sub> (II) gives only N<sub>3</sub>H, NH<sub>4</sub>Cl, and AcOH, but with EtO•NO in EtOH at 0°, 5-methyltetrazole  $N \cdot NH = NH = NH$ 145–146°, is obtained. With HNO<sub>2</sub> (III) affords only N<sub>3</sub>H, N<sub>2</sub>H<sub>4</sub>, HCl, and AcOH. J. W. B.

Oxidation of organic compounds by potassium permanganate under the conditions of the Kubel-Tiemann method. M. L. COMPERNOLLE (Natuurwetensch. Tijds., 1934, 15, 237-243).—In the oxidation of org. substances with dil. acid KMnO<sub>4</sub> solution the ratio of O consumed to the theoretical quantity for complete oxidation is termed the oxidation no. (I). (I) approaches a max. as the dilution is increased. With hydroxybenzoic acids (I) is a max. (equal to unity) at a concn. of  $5 \times 10^{-3}$  and as regards case of oxidation, o - m - pr. The following vals. for (I)<sub>max</sub>. are recorded, the optimum concns. being given in parentheses: aminobenzoic acids 0.12 ( $1 \times 10^{-5}$ ); nitrobenzoic acids 0.12 - 0.14 ( $5 \times 10^{-4}$ ); carbamide 0; hippuric acid 0.01 ( $5 \times 10^{-3}$ ); asparagine 0.11( $5 \times 10^{-4}$ ); aminosuccinic acid 0.4 ( $1 \times 10^{-3}$ ); glycine 0.55 ( $1 \times 10^{-2}$ ); phenyldimethylpyrazolone 0.85 ( $5 \times$  $10^{-5}$ ); uric acid 0.85 ( $1 \times 10^{-4}$ ). S. C.

Action of ultra-violet light on glycine.—See this vol., 264.

Action of ammonia and amines on unsaturated esters. III. Action of ammonia, methylamine, and diethylamine on methyl acrylate. K. MORSCH (Monatsh., 1933, 63, 220-235).-Me acrylate (I) with NH<sub>2</sub>-MeOH at room temp. affords successively NH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Me (hydrochloride, m.p. 102.5°; lit. m.p. 95°), di-, b.p. 132·5°/10·5 mm. (hydrochloride, m.p. 136·5—137·5°), and its diamide (II), m.p. 144·5— 145.8° [platinichloride, m.p. 200.5° (decomp.)], tri-, b.p. 171—174°/9 mm. [hydrochloride, m.p. 93°; platini-chloride, m.p. 172.5° (decomp.)], and its monoamide [as platinichloride, m.p. 178—178.5° (decomp.)] and triamide (III), m.p. 185.5-186° [platinichloride, m.p. 196.5° (decomp.)], -( $\beta$ -carbomethoxyethyl)amine, the proportions (recorded) of these products varying with the concn. and excess of NH<sub>3</sub>, and reaction time. With liquid NH<sub>3</sub> the same products are obtained, prolonged action giving mainly (II) and (III). Similarly with NH, Me-MeOH, Me B-methylaminopropionate, b.p. 50°/11 mm. (acid +H<sub>2</sub>O, m.p. 66.5-67.5°, and anhyd., m.p. 144.5-146°), and its methylamide, b.p. 131-132°/9 mm. (hydrochloride, m.p. 134.5°), and methyldi-(β-carbomethoxyethyl)amine, b.p. 123-124°/9 mm. (hydrochloride, m.p. 120.5-121.5°), are isolated. With NHEt2 at room temp. (I) gives a quant. yield of Me  $\beta$ -diethylaminopropionate, b.p. 66.5°/8 mm., but at 190-200° its tetraethyldiamide, b.p. 123.5-124.5°/10 mm., is obtained. J. W. B.

Tastes of glutamic acid and related compounds. II. Tastes of derivatives of *dl*-glutamic acid. C. L. TSENG and E. J. H. CHU (J. Chinese Chem. Soc., 1933, 1, 188—198; cf. A., 1932, 503). dl-Glutamic acid is best (71% yield) obtained from the d-acid (10 g.), Ba(OH)<sub>2</sub> (23·32 g.), and H<sub>2</sub>O (100 c.c.) at 160—170° (9 hr.) (cf. A., 1909, i, 368). NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, and Ca(OH)<sub>2</sub> do not cause racemisation. The tastes of the following derivatives are recorded : Na, K, hygroscopic, Ca, Li, Ba, Mg, Sr, NH<sub>3</sub>Me, hygroscopic, m.p. 75° (hydrochloride, m.p. 168·9°), and NH<sub>2</sub>Me<sub>2</sub> (hydrochloride, m.p. 178·5°) salts; hydrochloride, m.p. 198·5°; sulphate, m.p. 164·6°; Et ester hydrochloride, m.p. 113·1°; formyl, m.p. 181·7°, Ac, m.p. 187·5°, propionyl, m.p. 173·1°, n-butyryl, m.p. 179°, and isovaleryl, m.p. 180·6°, derivatives. M.p. are corr. R. S. C.

Intermediate oxidation product of cystine. T. F. LAVINE, G. TOENNIES, and E. C. WAGNER (J. Amer. Chem. Soc., 1934, 56, 242—243; cf. A., 1933, 598).—A disulphoxide is probably formed when cystine is oxidised with  $BzO_2H$  (= rather > 2 O). H. B.

Triethylsilicyl group. C. A. KRAUS and W. K. NELSON (J. Amer. Chem. Soc., 1934, 56, 195-202). -SiHEt<sub>3</sub> (I) (from SiHCl<sub>3</sub> and MgEtBr) and KNH<sub>2</sub> in liquid NH<sub>3</sub> give K di(triethylsilicyl)amide, (SiEt<sub>3</sub>)<sub>2</sub>NK, converted by NH<sub>4</sub>Br in liquid NH<sub>3</sub> into di(triethylsilicyl)amine, b.p. 100°/1 mm., which is readily hydrolysed  $(H_2O)$  to  $(SiEt_3)_2O$ . (I) and Li in NH2Et afford triethylsilicylethylamine, SiEt3. NHEt (II), hydrolysed readily to SiEt<sub>3</sub>·OH; the Li acts as catalyst. (II) is also obtained from SiEt<sub>3</sub>Br (III),  $NH_2Et$ , and Li. (III) and NaGePh<sub>3</sub> in  $C_6H_6$  give tri-phenylgermanyltriethylsilane, GePh<sub>3</sub>·SiEt<sub>3</sub>, m.p. 93·5°, which is converted by Br into (III) and GePh<sub>3</sub>Br; Li in NH<sub>2</sub>Et gives LiGePh<sub>3</sub> and LiSiEt<sub>3</sub> [treatment of the mixture with NH<sub>4</sub>Br affords (I) and GeHPh<sub>3</sub>; with EtBr, SiEt<sub>4</sub> and GePh<sub>3</sub>Et result]. Si benzyl Et<sub>3</sub>, b.p. 267-269° (corr.), is obtained from CH<sub>2</sub>Ph·SiCl<sub>3</sub>. and MgEtBr or, better, from (III) and CH<sub>2</sub>Ph·MgCl. SiPhEt<sub>3</sub> is prepared from SiPhCl<sub>3</sub> and MgEtBr [not from (III) and MgPhBr or ZnPh2], whilst ('SiEt3)2, b.p. 255° (corr.), is readily obtained from (III) and Na at 140-145°. H. B.

Structural and stereochemical relationships among the disulphines and diammines of platinum and palladium. H. D. K. DREW and G. H. WYATT (J.C.S., 1934, 56-62).-Interaction of diamino)ethylenediethyldisulphineplatinous chloride, [Pt es en]Cl<sub>2</sub> [+ $H_2O$ ; plato-salt, decomposed by  $H_2O$  to give (I) and Pt enCl<sub>2</sub> (II); pallado-salt, decomposed by hot H<sub>2</sub>O into Pd esCl<sub>2</sub> and (II); but with boiling 16% HCl gives (I) and (en H2)PdCl4, converted by warm H<sub>2</sub>O into Pd enCl<sub>2</sub> (cf. A., 1900, i, 209)] (also formed by interaction of (II) and es-H<sub>2</sub>O at 100° during 2 hr.), which is decomposed by dil. HCl to give (I) and en. When [Pt es en]Cl, is heated with dil. HCl, en, the more stable group, is lost from *cis*-positions to give (I). This, together with the decomp. of the plato- and pallado-salts, indicates that the cation [Pt es en] has positive charges located on the N atoms (cf. A., 1933, 1040). (I), m.p. 188°, scarcely depresses the m.p. of Pd esCl., m.p. 182°, which indicates their

structural and stereochemical similarity and, from the foregoing, (I) and (II) are similar, but it is uncertain whether (II) corresponds structurally with Pd esCl<sub>2</sub> and (I). Interaction of  $\beta$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O-en at room temp. during 2 hr. affords a solution of [Pt(Et<sub>2</sub>S)<sub>2</sub> en]Cl<sub>2</sub> [plato-salt, decomposed by hot H<sub>2</sub>O into (II),  $Pt(Et_2S)Cl_2$  (III),  $Pt(Et_2S)_2Cl_2$  (IV) ( $\alpha$ - and  $\beta$ -forms), and (V) (below)], which easily loses Et<sub>2</sub>S to give ethylenediaminomono(diethylsulphine)platinous chloride (V), [Pt(Et<sub>2</sub>S) enCl]Cl, [plato-salt, isolated as the monohydrate, is decomposed by boiling H<sub>2</sub>O into (V), (IV), (III), and (II)], and some  $[Pt en_2]Cl_2$ . (V), together with [Pt en<sub>2</sub>]Cl<sub>2</sub> and (II) is formed from (II) and  $H_2O-Et_2S$  at 100° during 0.5 hr., whereas  $\alpha$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O-en affords only [Pt en<sub>2</sub>]Cl<sub>2</sub>, which is attributed to the difficulty of accommodating the entering chelate grouping; hence the  $\beta$ -platinous disulphines are given a planar cis-structure (cf. A., 1933, 1282; A., 1930, 559), which differs stereochemically and structurally from the configuration of the  $\alpha$ -isomerides. Because  $\beta$ -(IV) and  $\beta$ -Pt(Et<sub>2</sub>S)<sub>2</sub>Br<sub>2</sub> react with Br and  $Cl_2$ , respectively, to give  $Pt(Et_2S)_2Cl_2Br_2$  (VI) (cf. A., 1930, 559), which probably exists in easily interconvertible  $\alpha$ - and  $\beta$ -forms, (VI) must have a symmetrical structure with the entering halogens added in the trans-positions, a facile migration similar to that which occurs in the  $\beta \rightarrow \rightarrow$  $\alpha$ - (IV) change] of one SEt<sub>2</sub> group and one or both halogens accounting for the  $\alpha \rightarrow \beta$ -change. The platinous tetrammines are planar (cf. A., 1932, 797; A., 1933, 1040), whence the conclusion that  $\alpha$ - $Pt(NH_3)_2Cl_2$  has a trans-planar structure; the  $\beta$ isomeride has a cis-structure. Contrary to Werner, the  $\alpha$ -disulphines correspond with the  $\alpha$ - and not the β-diammines. The m.p. of Pd(Et<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub> (VII) is depressed on admixture with  $\beta$ -(IV), but not with the isomorphous  $\alpha$ -isomeride; hence (VII) has a transplanar formula. The behaviour of Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with en, and the decomp. of  $[Pd(NH_3)_2 en]Cl_2$  by HCl, indicate that it has a *trans*-planar structure. The cryst. chelate platinous and palladous disulphines and diammines have (provisionally) halogen attached to the metal (cf. A., 1933, 1282). Interaction of palladous diammines or disulphines in H<sub>2</sub>O with a sulphide or amine affords the following results : Et<sub>2</sub>S and  $Pd enCl_2$  (VIII) give  $[Pd en_2]Cl_2$  and (VII) probably through the unstable [Pd(Et,S)<sub>2</sub> en]Cl<sub>2</sub>; es and (VIII) give Pd esCl<sub>2</sub> (IX) and (VIII); es and  $Pd(NH_3)_2Cl_2$  give (IX) and  $[Pd(NH_3)_4]Cl_2$ ; es and (VII) give (IX) and (VII); en and (IX) give II D J. L. D. [Pd en<sub>2</sub>]Cl<sub>2</sub> and (IX).

Slow oxidation of cyclopentanes with one substituent below their b.p. P. DUPONT and G. CHAVANNE (Bull. Soc. chim. Belg., 1933, 43, 537— 543).—cycloPentanone and MgPhBr give cyclopentylidenecyclopentanone (semicarbazone, m.p. 222°), phenylcyclopentene (I), and 1-phenylcyclopentanol, b.p. 121—121·1°/6 mm., dehydrated by 85% HCO<sub>2</sub>H to (I), m.p. 23°, b.p. 109°/14 mm., which is rapidly hydrogenated (Pt-black) in AcOH to phenylcyclopentane, b.p. 102—102·6°/18 mm. This, when oxidised at 130° under the conditions previously described (A., 1930, 1035), gives benzoylbutyric acid, BzOH, and COPhBu. Ethylcyclopentane gives similarly HCO<sub>2</sub>H, AcOH,  $EtCO_2H$ ,  $\delta$ -keto-*n*-heptoic acid (also prepared by KMnO<sub>4</sub> from 1-ethylcyclopentene), COEtBu (also prepared by CrO<sub>3</sub> from CHEtBu·OH) (semicarbazone, m.p. 110°). Methylcyclopentane gives BuCO<sub>2</sub>H, PrCO<sub>2</sub>H,  $\delta$ -ketononoic acid, b.p. 142°/2 mm., m.p. 40° [semicarbazone, m.p. 133° (block)], and a ketone, C<sub>9</sub>H<sub>18</sub>O [semicarbazone, m.p. 151° (block), 142—145° (capillary)][not COBu<sub>2</sub> (semicarbazone, m.p. 90°)]. All three cyclopentanes give also CO<sub>2</sub>, H<sub>2</sub>, and a little CO, but no ethylenic or OH-compounds. Oxidation thus ruptures the ring at the tert. C. R. S. C.

Determination of constitution by measurement of the mol. depression of the m.p. Constitution of polymerides of cyclopentadiene. J. PIRSCH (Ber., 1934, 67, [B], 101-104; cf. A., 1933, 770).--The argument is based on the observations (loc. cit.) that dicyclic compounds of which the mol. structure is almost equally developed in all three spatial directions have very high mol. m.-p. depressions. In this sense the vals. of  $\alpha$ -dicyclopentadiene, its H<sub>2</sub>- and H<sub>4</sub>-derivatives confirm the structure assigned to these substances by Alder et al. (A., 1933, 941). Tricyclopentadiene and its H<sub>2</sub>- and H<sub>4</sub>-compounds in which the addition of the third cyclopentadiene mol. has caused lengthening in one direction have vals. for E, 8·1-10·4. H. W.

Action of sodium on 1: 4-dibromocyclohexane. N. D. PRIANISCHNIKOV and S. I. SCHUJKINA (Ber., 1934, 67, [B], 64—67).—Evidence of the formation of a dicyclic hydrocarbon by the action of Na on 1: 4dibromocyclohexane in diisoamyl ether is not obtained. The product adds Br, is readily oxidised by KMnO<sub>4</sub> to succinic and adipic acids, and is dehydrogenated (Pd-asbestos) to  $C_6H_6$ . These reactions and the physical consts. indicate that it is a mixture of cyclohexadiene (I), cyclohexene, and cyclohexane (II). (I) and (II) form an azeotropic mixture, b.p. 79.2°.

H. W.

Carbon rings. XXVII. 26-, 28-, 30-, 32-, and 33-Membered carbon rings and the physical properties of large carbon rings. L. RUZICKA, M. HÜRBIN and M. FURTER (Helv. Chim. Acta, 1934, 17, 78-87).-Revised physical data for further purified samples of cyclo-hexacosane, m.p. 43-44°, -octacosane, m.p. 47-48°, -triacontane, m.p. 57-58°, b.p. 230°/0·2 mm., -triacontanone, m.p. 56°, b.p. 230°/ 0.25 mm., -triacontane-1: 16-dione (dipicrate of aminoguanidine compound), and -dotriacontane-1: 17-dione (I), m.p. 77-78°, are given. Clemmensen reduction of (I) affords cyclodotriacontane, b.p. 230°/high vac., m.p. 59-60°. From the boiling EtOH-insol. portion of the semicarbazone from the distillation residue of cycloheptadecanone is obtained (as its disemicarbazone) cyclotetratriacontane-1: 17-dione (II), b.p. 260-280°/ 0.1 mm., m.p. 83-84°, reduced (EtOH-Na) to the -1:17-diol, b.p. 250-260°/0.1 mm., m.p. 110-111°. Clemmensen reduction of (II) affords cyclotetratriacontanone, b.p. 250°/0.3 mm., m.p. 64-64.5°, and cyclotetratriacontane, b.p. 230-240°/0.3 mm., m.p. 66-67°. The relationships of d,  $M_{\rm D}$ , and m.p. of large C rings with the no. of C atoms are discussed. J. W. B.

Ultra-violet radiation in the photochemical oxidation of toluene.—See this vol., 264.

Electrolytic reduction of aromatic-nitro-compounds.—See this vol., 263.

Identification of nitrobenzene and phenol by formation of resorufin. H. EICHLER (Z. anal. Chem., 1934, 96, 21–22; cf. this vol., 268).— PhNO<sub>2</sub> (I), but not other NO<sub>2</sub>-compounds, yields resorufin (II) (yellowish-red fluorescence in alkaline solution) when heated with resorcinol in conc.  $H_2SO_4$ . PhOH also yields (II) when heated with (I) and  $H_2SO_4$ . J. S. A.

Photochemical reaction between *m*-dinitrobenzene, ethyl alcohol, and ammonia.—See this vol., 264.

Nitration of alkylbenzenes. I. Nitration of p-ethyltoluene. O. L. BRADY and J. N. E. DAY. II. Nitro-derivatives of *n*-propylbenzene. O.L. BRADY and R. N. CUNNINGHAM (J.C.S., 1934, 114-121, 121-124; cf. A., 1933, 1153).-I. 4-Methylacetophenone (I) [2:4-dinitrophenylhydrazone, m.p. 256° (decomp.)] is reduced by Zn-Hg in boiling dil. HCl to p-C<sub>6</sub>H<sub>4</sub>MeEt (II), b.p. 160—161°/748 mm. (II) affords with hot HNO<sub>3</sub> (d 1·42—1·5) and H<sub>2</sub>SO<sub>4</sub> (d 1.84) during 2—3 hr. a product which contains  $p-C_6H_4Me\cdotCO_9H$  (III), (I), (I), 2-nitro-p-ethyltoluene (IV), b.p. 248°/760 mm. [oxidised with boiling HNO<sub>3</sub> to 2-nitro-p-toluic acid (V) identical with a specimen prepared from (III)], and 3-nitro-p-ethyltoluene isolated as 3(?)-benzamido-p-ethyltoluene, m.p. 131° (different from the 2-Bz compound), after reduction with Sn-HCl. The amine affords an Ac derivative (VI), m.p. 118°, which consists probably of mixed crystals of 2- and 3-acetamido-p-ethyltoluene. Dinitration of (VI) affords a compound which only slightly depresses the m.p. of the (NO2)2-compound from 2-acetamido-p-ethyltoluene; the m.p. of the hydrolytic product of either is 183°. 2:4-Dinitrophenylhydrazine also yields p-tolylacetaldehyde-dinitrophenylhydrazone, m.p. 206°, when nitration occurs under less severe conditions, but sufficiently severe to mononitrate PhMe completely. (II) with HNO3 (d 1.5) at 20° during 1 hr. affords 2 : 3-dinitro-pethyltoluene, m.p. 51.5°, oxidised (K2Cr2O7) to 2: 3-dinitro-p-toluic acid (cf. A., 1890, 52). (II) by a threestage nitration affords 2:3:6-trinitro-p-ethyltoluene (VII), m.p. 93°, and an oil, which affords with  $N_2H_4,H_2O$  in EtOH the hydrazine of (V), but not of the 2:3:5-compound. (VII) with  $N_2H_4,H_2O$  in boiling EtOH in 10 min. affords 2:6-dinitro-3-hydrazino-p-ethyltoluene, m.p. 171° (decomp.), converted by Cu(OAc)<sub>2</sub> in AcOH at 100° during 0.5 hr. into 2 : 6dinitro-p-ethyltoluene (VIII), m.p. 60° [oxidised by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to 2 : 6-dinitro-p-toluic acid (Me ester, m.p. 87-88°), identical with a specimen obtained by nitrating p-toluic acid]; with warm EtOH-NH3 during 3 hr. (VII) affords 2 : 6-dinitro-3-amino-p-ethyltoluene, m.p. 143°, converted by NaNO<sub>2</sub> in hot EtOHoleum into (VIII). (VII) in boiling EtOH with NH2Me during 0.5 hr. affords 2:6-dinitro-3-methylamino-pethyltoluene, m.p. 168°, whereas with N2H4,H2O in boiling EtOH in 1.5 hr., it affords 6-nitro-1-hydroxy-7methyl-4-ethyl-1:2:3-benztriazole, m.p. 224° (decomp.). (VIII) with (NH<sub>4</sub>)<sub>2</sub>S in boiling EtOH during 1 hr. affords 2-nitro-6-amino-p-ethyltoluene, m.p. 96° (Ac derivative, m.p. 166°). Interaction of (I) and

HNO3 (d 1.5) at 5-10° affords 3-nitro-4-methylacetophenone (IX) (A., 1891, 1020) [oxime, m.p. 133°; semicarbazone, m.p.  $262^{\circ}$  (decomp.); 2:4-dinitrophenyl-hydrazone, m.p.  $232^{\circ}$ ], oxidised by boiling HNO<sub>3</sub> to (V), and reduced (Fe-HCl) to 3-amino-4-methylacetophenone, m.p. 80° {2 : 4-dinitrophenylhydrazone, m.p. 265° (decomp.); Ac derivative, m.p. 142° [semicarb-azone, m.p. 252° (decomp.); 2:4-dinitrophenylhydr-azone, m.p. 280° (decomp.)]}, further reduced (Clemmensen) to 2-amino-p-ethyltoluene, the Ac derivative of which is identical with that from (IV) after reduction. This orients (IV). Reduction of (IX) (Hg-Zn, boiling HCl) during 6 hr, affords a product, b.p. 220-228°/768 mm., acetylated to 2-acetamido-p-ethyltoluene (X), m.p. 137°, identical with the product obtained by reduction and acetylation of 2-nitro-p-ethyltoluene. 2-Benzamido-p-ethyltoluene has m.p. 119°. (X) with HNO<sub>3</sub> ( $d \ 1.5$ ) at  $-5^{\circ}$  to  $-10^{\circ}$  during 15 min. affords 3: 5-dinitro-2-acetamido-p-ethyltoluene, m.p. 176°, hydrolysed ( $H_2SO_4$ -EtOH) to 3:5-dinitro-2-amino-p-ethyltoluene, m.p. 183°. 2- and 3-Methyl-acetophenone afford 2:4-dinitrophenylhydrazones, m.p. 159° and 207°, respectively. II. Interaction of PhPr<sup>a</sup> (XI) with  $H_2SO_4$  and  $HNO_3$ 

(d 1.42) below 40° affords crude 2 : 4-dinitro-n-propylbenzene (XII), reduced by  $(NH_4)_2S$  in boiling EtOH during 0.5 hr. to 2-nitro-4-amino-n-propylbenzene, m.p. 59° [Ac derivative (XIII), m.p. 90°], which with NaNO2 in H2SO4-EtOH at 100° during 15 min. affords o-nitro-n-propylbenzene, b.p. 133-136°/26 mm. oxidised by KMnO<sub>4</sub> during 2 hr. to o-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H. (XII) with SnCl<sub>2</sub> in hot EtOH during 2 hr. affords 4-nitro-2-amino-n-propylbenzene, m.p. 73°. Nitration of (XIII) at 0° gives 2 : 3-dinitro-4-acetamido-n-propylbenzene, m.p. 130°, hydrolysed by hot 50% H<sub>2</sub>SO<sub>4</sub> to 2:3-dinitro-4-amino-n-propylbenzene, m.p. 124°; removal of NH<sub>2</sub> affords 2:3-dinitro-n-propylbenzene, m.p. 64° which is oxidised ( $K_2Cr_2O_7-H_2SO_4$ ) to 2:3-( $NO_2$ )<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H. (XI) in H<sub>2</sub>SO<sub>4</sub> (d 1·8)-HNO<sub>3</sub> (d 1·42) containing a little H<sub>2</sub>O affords a NO<sub>2</sub>-compound. The mixture of amines obtained on reduction (Sn-HCl) is acetylated and the NHAc-compounds (XIV) are nitrated at  $-5^{\circ}$  to give 3:5-dinitro-n-propylbenzene, m.p. 51°, oxidised  $(K_2Cr_2O_7-H_2SO_4)$  to 3:5-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H. Interaction of (XIV) with HNO<sub>3</sub> (d 1.5) in AcOH at 0° during 1 hr. gives a product hydrolysed to an amine; the NH<sub>2</sub> is removed with NaNO<sub>2</sub> to give m-nitro-n-propylbenzene, b.p. 136°/16 mm., oxidised to m-NO2·C6H4·CO2H. Nitration of (XI) gives an impure  $(NO_2)_2$ -compound which appears not to be further nitrated, although energetic nitration of (XII) followed by reduction with (NH<sub>4</sub>)<sub>2</sub>S affords a little 2:6-dinitro-4-amino-n-propylbenzene, m.p. 162°. J. L. D.

Catalytic reduction of arylsulphonyl chlorides with palladium. P. DE SMET (Natuurwetensch. Tijds., 1934, 15, 215—226).—The following have been prepared by reducing the corresponding sulphonyl chloride with Pd-H<sub>2</sub> in aq. COMe<sub>2</sub>: phenyl- (Na salt, +2H<sub>2</sub>O), p-bromo- (Na salt, +2H<sub>2</sub>O), and p-chlorophenyl-,  $\beta$ -naphthyl-, and m-phenylenedi-sulphinic acids. The rapid reaction of zero order is followed by a very slow reduction to the corresponding disulphides. 1:3:5-C<sub>6</sub>H<sub>3</sub>(SO<sub>2</sub>Cl)<sub>3</sub> is completely decomposed.

S. C.

Mobility of groups containing a sulphur atom. III. D. W. COWIE and D. T. GIBSON (J.C.S., 1934, 46-48).—The *p*-directing influence of the SMe group is confirmed (cf. A., 1932, 837). Interaction of cyclohexylsulphonylacetone (I), d-camphorylthiolsulphonate (II), and Na<sub>2</sub>CO<sub>3</sub> affords anhydrocamphorsul-phonylacetone (III) and an oil, which after hydrolysis and oxidation affords cyclohexylsulphonylmethylsulphonylmethane (IV), m.p. 119°, also formed from methylsulphonylacetone (V), m.p. 54° (prepared from MeSO<sub>2</sub>Na and CH<sub>2</sub>Cl·COMe), cyclohexyl cyclohexane-thiolsulphonate, m.p.  $38^{\circ}$  (lit., b.p.  $184^{\circ}/0.1$  mm.), and NaOEt followed by hydrolysis and oxidation. Similarly, ethylsulphonylacetone (VI) and (II) afford d-camphorsulphonic acid, (III), and camphorsulphonylmethylsulphonylmethane (VII), m.p. 123°. (I) with Et ethanethiolsulphonate (VIII) affords a product oxidised to MeSO<sub>2</sub>Et; also a-ethylsulphonyl-a-ethylthioacetone [converted into bisethylsulphonylmethane (IX)] and  $\alpha$ -cyclohexylsulphonyl- $\alpha$ -ethylthioacetone, b.p. 132°/0.2 mm., hydrolysed to cyclohexylsulphonylethylthiomethane, m.p. 38°. Camphordisulphoxide (X), (V), and NaOEt afford (VII), but with (VI) and Na<sub>2</sub>CO<sub>3</sub> after hydrolysis and oxidation, (X) gives camphorsulphonylethylsulphonylmethane, m.p. 85°. (V), (VIII) in excess, and Na<sub>2</sub>CO<sub>3</sub> after hydrolysis and oxidation give (IX), but with equimol. quantities afford methylsulphonylethylsulphonylmethane, m.p. 95°, different from (IX). Benzyl benzylthiolsulphonate, (V), and Na<sub>2</sub>CO<sub>3</sub> give after hydrolysis methylsulphonylbenzylthiolmethane, m.p. 54°, different from (V). (V), p-tolyl p-toluenethiolsulphonate, and NaOEt afford methylsulphonyl-p-tolylthioacetone, m.p. 50°, hydrolysed and then oxidised to p-tolylsulphonylmethylsulphonylmethane. CH2Bz·CN in the theoretical amount of NaOH gives with Me p-toluenethiolsulphonate (XI) in EtOH, w-cyano-w-methylthioacetophenone, m.p. 50°. 4-Chlorophenylsulphonylacetone (1 mol.), (XI) (1 mol.), and KOAc (1 mol.) in EtOH during 5 days afford a 50:50 mixture of the "exchanged" and "normal" material. *m*-Nitrophenylsulphonyl-acetic ester and -acetophenone are not obtained from the Na sulphinate and CH2Cl·CO2Et or COPh-CH<sub>2</sub>Br (cf. A., 1912, i, 389); Na o-nitrophenyl-sulphonylacetate and PhSNa afford o-nitrodiphenyl sulphide, a smoother replacement than those of Levi and Smiles (A., 1932, 735). Interaction of CH<sub>2</sub>O and PhSH affords a product which when oxidised gives bisphenylsulphonylmethane, m.p.  $121-122^{\circ}$ , methylated to bisphenylsulphonylethane (XII), identical with the products of Steinkopf *et al.* (A., 1930, 1566), and 66 bisphenylsulphonylethane (A. 1920, 000). and \$3-bisphenylsulphonylpropane (A., 1930, 900). (XII) is also obtained from PhSO<sub>2</sub>F and MgEtI.

J. L. D.

Action of air in determining the course of bromination. J. HANNON and J. KENNER (J.C.S., 1934, 138).—Bromination of 2:2'-ditolyl is increased by accession of dry air. o-*Iodocyanobenzene*, m.p. 54—55°, with Cu powder gives 2:2'-dicyanodiphenyl, m.p. 176—177°. F. R. S.

Reaction of potassamide in liquid ammonia with chloroethylenes. G. H. COLEMAN and R. D. MAXWELL (J. Amer. Chem. Soc., 1934, 56, 132–134). —CAr<sub>2</sub>:CHCl (I) and CHAr·CHCl<sub>2</sub>, prepared by the

methods of Buttenberg (A., 1894, i, 502) and Wiechell (*ibid.*, 507), react rapidly with  $\text{KNH}_2$  in liquid  $\text{NH}_3$  to give CAr;CAr (II). The following are new :  $\beta$ -chloro- $\alpha\alpha$ -di-p-ethylphenyl-, b.p. 165—166°/1 mm., -di-p-n-propylphenyl-, b.p. 178—181°/1 mm., -di-p-n-butyl-phenyl-, b.p. 190—192°/1 mm., and -di-m-4-xylyl-, b.p. 166—170°/1 mm., -ethylene;  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-diphenylylethane, m.p. 139—140° [all m.p. (and b.p.) except this are corr.]; 4 : 4'-diethyl-, m.p. 71·5—72·5°, -di-n-propyl-, m.p. 69·5—70·5°, -di-n-butyl-, m.p. 41—42°, and -diphenyl-, m.p. 243—244° [oxidised (O<sub>3</sub>) to p-C<sub>6</sub>H<sub>4</sub>Ph·CO<sub>2</sub>H], and 3 : 4 : 3' : 4'-tetramethyl-, m.p. 143—144°, -tolane. (I) show non-selective absorption in the region 200—280 mµ; (II) show two characteristic absorption bands. H. B.

Indirect hydrolysis of hexaphenylethane. W. E. BACHMANN (J. Amer. Chem. Soc., 1934, 56, 239-240).—Addition of a solution of  $CPh_3+MgI_2$  in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> to H<sub>2</sub>O and subsequent aëration gives  $CPh_3$ ·OH, CHPh<sub>3</sub>, and a little  $(CPh_3·O·)_2$ ; I is liberated during the hydrolysis and the following reactions probably occur: (i)  $CPh_3+I\longrightarrow CPh_3I$ ; (ii)  $CPh_3I+H_2O\longrightarrow CPh_3·OH+HI$ ; (iii)  $2CPh_3+$  $HI\longrightarrow CHPh_3+CPh_3I$ . In agreement with this view, equiv. amounts of CHPh<sub>3</sub> and  $CPh_3·OH$  are obtained when  $CPh_3$  in C<sub>6</sub>H<sub>6</sub> is shaken with H<sub>2</sub>O containing a little I. Treatment of  $CPh_3·OH$ ,  $CHPh_3$ , and a little ( $CPh_3·O·)_2$ ;  $2CPh_3·MgBr+I_2\longrightarrow 2CPh_3+MgI_2+$  $MgBr_2$ .  $CPh_3·CO_2H$  is not obtained from CO<sub>2</sub> and  $CPh_3+MgI_2$  in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> unless Mg is present (cf. Gorski, A., 1913, i, 1341). CPh<sub>3</sub> promotes oxidation of MgI<sub>2</sub> by atm. O<sub>2</sub>; the active agent is probably the  $CPh_3O_2$  radical (cf. Ziegler and Ewald, A., 1933, 943). H. B.

Transformation of α- into β-naphthalene derivatives under the influence of catalysts. F. MAYER and R. SCHIFFNER (Bcr., 1934, 67, [B], 67— 69).—1-Phenyl-3: 4-dihydronaphthalene is converted by passage over SiO<sub>2</sub> gel (I) at 350° into  $2-C_{10}H_7Ph$ (II).  $1-C_{10}H_7Ph$  is isomerised to (II) in presence of (I), Co, or Cu silicate at about 350°.  $1-C_{10}H_7Me$  and  $1-C_{10}H_7Et$  are similarly isomerised when passed over (I) at about 420°, whilst 1: 6- affords 2:  $6-C_{10}H_6Me_2$ .  $1-isoPropenyInaphthalene affords essentially <math>C_{10}H_8$ .  $1- passes into <math>2-C_{10}H_7Br$ . H. W.

Synthesis of polynuclear hydrocarbons by cyclodehydration of aromatic alcohols. M. T. BOGERT, D. DAVIDSON, and R. O. ROBLIN, jun. (J. Amer. Chem. Soc., 1934, 56, 248; cf. A., 1933, 153, 599, 601).—1-Ethyl-1:2:3:4-tetrahydronaphthalene is obtained by the action of  $H_2SO_4$  on  $\varepsilon$ -phenyl- $\alpha$ methylamyl alcohol or  $\zeta$ -phenyl- $\Delta^{\alpha}$ -hexene.  $\gamma$ -Phenyl- $\alpha$ methyl- $\alpha$ -ethylpropyl alcohol similarly gives 1:2dimethyl-1:2:3:4-tetrahydronaphthalene and 1methyl-1-ethylindane. H. B.

Synthesis of nine chloroiodonaphthalenes. R. W. BEATTIE and F. C. WHITMORE (J.C.S., 1934, 50-52).—Interaction of  $1: 4-C_{10}H_6Cl$ ·HgCl (I) (cf. A., 1933, 619), I, and NaI in boiling EtOH affords 1chloro-4-iodonaphthalene, m.p. 54·5° (90%) (cf. A., 1900, i, 282). The following are prepared similarly: 1-chloro-5-, m.p. 89° (73%), -6-, m.p. 57° (70%), -7-, m.p. 39° (63%), and -8-iodonaphthalene, m.p. 80·5° (84%); 2-chloro-1-, m.p. 63° (64%), -6-, m.p. 141° (70%), -7-, m.p. 129° (70%), and -8-iodonaphthalene, m.p. 55.5° (71%). (I) and Br in boiling CCl<sub>4</sub> during 2.5 hr. afford  $1: 4-C_{10}H_0ClBr$ , free from isomerides, and identical with a sample obtained by brominating  $1-C_{10}H_7Cl$ . 2- $C_{10}H_7$ ·HgCl and I afford 2- $C_{10}H_7$ I, which demonstrates the validity of the synthetic method. J. L. D.

Dehydrogenation of cholesterol and ergosterol and non-identity of the hydrocarbon  $C_{18}H_{16}$  with 1:2-cyclopentenophenanthrene. O. DIELS and H. KLARE (Ber., 1934, 67, [B], 113-122).-Ruzicka's assumption (A., 1933, 820) that the hydrocarbons  $C_{25}H_{24}$  (I) from cholesterol (II) and ergosterol (III) are different is refuted. The dehydrogenation of (III) by Se is described in detail, together with the purification of (I). The supposed identity of 1: 2-cyclopentenophenanthrene (IV) (Cook et al., ibid., 1042) with  $C_{18}H_{16}$  (V) cannot be maintained. (V) and (IV) have m.p. 125-126° and 137-138°, respectively, and differ appreciably in the compounds they form with picric acid and  $s - C_6 H_3(NO_2)_3$ . Further, (IV) does not show the reaction towards  $N_2O_3$  which is particularly typical of (V). The absorption spectra of (I) from (II) or (III) are practically identical, whereas that of (IV) is closely similar, but exhibits divergencies outside the limits of experimental error. Possibly (V) is identical with the 3-methyl-1: 2-cyclopentenophenanthrene of Kon (A., ibid., 1153), but differs from the compound thus described by Bergmann (ibid., 1154). H. W.

Polycyclic compounds related to the sterols. II. Diels' hydrocarbon, C<sub>18</sub>H<sub>16</sub>. S. H. HARPER, G. A. R. Kon, and F. C. J. RUZICKA (J.C.S., 1934, 124—128).—Interaction of Mg  $\beta$ -( $\alpha$ -naphthyl)ethyl bromide and 2-methylcyclopentanone in warm Et<sub>2</sub>O during 0.5 hr. affords 2-methyl-1-3-(a-naphthyl)ethylcyclopentanol (I), b.p. about 190°/3 mm., and  $\alpha\delta$ -di-( $\alpha$ -naphthyl)butane, m.p. 102° (bistrinitrotoluene compound, m.p. 131°). (I) with P<sub>2</sub>O<sub>5</sub> at 140° during 40 min. affords 1-methyl-1: 2-cyclopentano-1:2:3:4tetrahydrophenanthrene (II), b.p. 155°/0.4 mm., dehydrogenated to cyclopentenophenanthrene (III) (cf. A., 1933, 601, 1153). Interaction of  $2-\beta-(\alpha-naphthyl)$ ethylcyclopentanone and MgMeI in Et<sub>2</sub>O affords an undistillable product, dehydrated  $(P_2O_5)$  to (II) and then dehydrogenated to (III) (trinitrotoluene compound, m.p. 102°) (cf. A., 1933, 820), but no byproduct is formed in this reaction. Interaction of  $\hat{2}$ : 5-dimethylcyclopentanone (cf. A., 1924, i, 1203) and MgMeI affords 2:5-dimethyl-1- $\beta$ -( $\alpha$ -naphthyl)-ethylcyclopentanol, b.p. 190–195°/0.2 mm., converted (P2O5) into 1:3'-dimethyl-1:2-cyclopentano-1:2:3:4tetrahydrophenanthrene, b.p. 160°/0.4 mm., and dehydrogenated to a mixture containing a hydrocarbon, m.p. 230°, the trinitrobenzene derivative of which, m.p. 145–146°, affords, after treatment with  $SnCl_2$  in boiling HCl (cf. A., 1933, 1042), 3'-methyl-1: 2-cyclopentenophenanthrene (IV), m.p. 125-126° [picrate (V), m.p. 118-119°; trinitrotoluene compound (VI), m.p. 93°]. (IV), (V), and (VI) are identical (mixed m.p.) with the corresponding compounds prepared from Dicls' hydrocarbon (VII). The ultra-violet absorption spectrum and cryst. form of (IV) agree closely

with those of (VII). Bergmann and Hillemann's product (cf., A., 1933, 1154) is prepared according to their directions and shows significant differences in physical properties from (IV). J. L. D.

Isomerisation of the hydrocarbon  $C_{42}H_{30}$ , isomeric with 1:3:1':3'-tetraphenyl-1:1'-dihydrorubene. Ninth isomeride. Oxidative scissons. A. WILLEMART (Compt. rend., 1933, 197, 1659—1661).—When heated in xylene with  $K_3$ Fe(CN)<sub>6</sub> (or HgO, PbO, etc.) the colourless hydrocarbon  $C_{42}H_{30}$ (I), m.p. 179° (this vol., 180), affords another yellow *isomeride*, m.p. 225°. Repetition of Halley and Marvel's oxidation (A., 1933, 57) of (I) with CrO<sub>3</sub> gives 30—40% of COPh<sub>2</sub>, in addition to BzOH and  $o-C_6H_4Bz\cdotCO_2H$ , so that only partial cyclisation of  $\alpha\gamma\gamma\delta\delta\zeta$ -hexaphenyl- $\Delta^{\alpha\epsilon}$ -hexadi-inene can occur during rearrangement to (I). Similar oxidation of the yellow isomeride, m.p. 249° (loc. cit.), gives the same products and a trace of a substance, m.p. 240°, whereas KMnO<sub>4</sub> affords only a yellow substance,  $C_{42}H_{30}O_2$ , m.p. 277°. J. W. B.

Compounds of bivalent metallic selenates with aniline. C. H. KAO and T. L. CHANG (J. Chinese Chem. Soc., 1933, 1, 116—119).—Compounds,  $MSeO_4,2NH_2Ph$ , are prepared from the hydrated selenate and  $NH_2Ph$  at room temp. or that stated in parentheses, M being Cu, Zn, Ni (100°), Co<sup>II</sup> (80°), and Cd (in presence of a little  $H_2O$ ). The Mn compound could not be obtained. R. S. C.

Increase in the life-period of  $\beta$ -chloro- $\beta$ -phenylethylamine by carbon.—See this vol., 262.

Hydrolysis of substituted benzenesulphonanilides. R. S. SCHREIBER and R. L. SHRINER (J. Amer. Chem. Soc., 1934, 56, 114—117).—o- and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NPhR are decomposed by 80% NaOH at 195—220° to NHPhR, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH, and Na<sub>2</sub>SO<sub>3</sub>; the ease of fission is o > p. PhSO<sub>2</sub>·NHPh is similarly unaffected at 250°, m-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NHPh undergoes a small amount of fission at 240°, whilst 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·SO<sub>2</sub>·NPhR are readily cleaved at 125— 155°. 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·SO<sub>3</sub>H is prepared by oxidation (fuming HNO<sub>3</sub>) of 2:4:2':4'-tetranitrodiphenyl disulphide. NH<sub>2</sub>Ph and NHPhMe are separable from one another and from NPhMe<sub>2</sub> by o-nitrobenzenesulphonylation; the amines are recovered as above. o-Nitrobenzenesulphon-anilide, m.p. 114— 115°, and -methylanilide, m.p. 71—72°, p-nitrobenzenesulphon-anilide, m.p. 135—136°, and -methylanilide, m.p. 117—118°, and 2: 4-dinitrobenzenesulphon-anilide, m.p. 112—113°, and -methylanilide, m.p. 148—149°, are described. H. B.

Action of amines on esters of carboxy-carbamides, -thiocarbamides, and -guanidines. III. J. A. MURRAY and F. B. DAINS (J. Amer. Chem. Soc., 1934, 56, 144—146).—Prolonged treatment of Et allophanate (I) with NH<sub>2</sub>Me gives  $\alpha$ -methylbiuret (II); NH<sub>2</sub>Et similarly affords  $\alpha$ -ethylbiuret (III). (I) and CH<sub>2</sub>Ph·NH<sub>2</sub> at 135° give *Et*  $\gamma$ -benzylallophanate (IV), m.p. 103° (also prepared from CH<sub>2</sub>Ph·NH·CO·NH<sub>2</sub> and ClCO<sub>2</sub>Et);  $\alpha$ *z*-dibenzylbiuret (V), m.p. 169°, and *s*-dibenzylcarbamide (VI) are formed at 150° and 200°, respectively. (I) and PhNCO at 125° afford some  $\alpha$ -carbethoxy- $\varepsilon$ -phenylbiuret (A., 1919, i, 400), whilst Et  $\gamma$ -phenylallophanate and NHPh·NH<sub>2</sub> at 130° give NH<sub>2</sub>Ph and 1-phenylurazole (VII) (A., 1921, i, 61). (II) and (III) are obtained from carbonyldiurethane (VIII) and NH<sub>2</sub>Me and NH<sub>2</sub>Et, respectively. (VIII) and CH<sub>2</sub>Ph·NH<sub>2</sub> at 115° (or in H<sub>2</sub>O) afford (I) and CH<sub>2</sub>Ph·NH·CO<sub>2</sub>Et; (I) and (IV) are formed at 135°, (V) at 160°, and (VI) at 200°. N<sub>2</sub>H<sub>4</sub> and (VIII) give (I), whilst (VIII) and NHPh·NH<sub>2</sub> at 115° or 140° afford (VII) [at 160°, *iminodicarboxyphenylhydrazide*, NH(CO·NH·NHPh)<sub>2</sub>, m.p. 291°, results]. Et thioallophanate is hydrolysed by aq. NH<sub>2</sub>. NH<sub>2</sub>Alk, or

 $(H_1)^{(1)}$  (NH·NHPh)<sub>2</sub>, m.p. 291°, results]. Et thioallophanate is hydrolysed by aq. NH<sub>3</sub>, NH<sub>2</sub>Alk, or EtOH-KOH to CS(NH<sub>2</sub>)<sub>2</sub>; with NH<sub>2</sub>Ph and o-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> at 160°, CO(NHAr)<sub>2</sub> results.

CS(NH·CO<sub>2</sub>Et)<sub>2</sub> or SMe·C(:N·CO<sub>2</sub>Et)·NH·CO<sub>2</sub>Et (IX) (A., 1930, 1276) and the appropriate NH<sub>2</sub>R in EtOH give the  $\gamma$ -substituted  $\alpha\beta$ -dicarbethoxyguanidines, NHR·C(:N·CO<sub>2</sub>Et)·NH·CO<sub>2</sub>Et; the following are described: R=Me, m.p. 71°, Et,  $\beta$ -hydroxyethyl, m.p. 98°, benzyl, Ph, m.p. 71°, o-tolyl, m.p. 75°, anilino, m.p. 192°, o-hydroxyphenyl, m.p. 135°, p-carboxyphenyl, m.p. 198°, o-carboxyphenyl (X), m.p. 174°, o-carbomethoxyphenyl (XI), m.p. 67°, carboxymethyl, m.p. 210° [hydrolysed (5% EtOH-KOH) to carbethoxyguanidinoacetic acid, chars 250—275°], and carbethoxyguanidinoacetic acid, chars 250—275°], and carbethoxymethyl, m.p. 56°. (X) and (XI) are hydrolysed (EtOH-KOH) to 2-carbethoxyimino-4-hydroxy-1:2:3:4tetrahydroquinazoline, m.p. 163°, also formed when (XI) is heated. (IX) and NH<sub>2</sub>OH in EtOH give the

compound, O<

pounds, NH $<_{\rm CO-NH}^{\rm NH\cdot C:N\cdot CO_2Et}$ , m.p. > 335°, and

 $C_6H_4 < NH > C:N \cdot CO_2Et$ , m.p.  $320^{\circ}$  (decomp.), are formed from  $N_2H_4$  and  $o \cdot C_6H_4(NH_2)_2$ , respectively. s-Di-o-carbomethoxyphenylcarbamide, m.p. 144°, is obtained from  $o \cdot NH_2 \cdot C_6H_4 \cdot CO_2Me$  and  $COCL_2$  or (IX) (at 140°).  $\alpha\gamma$ -Dicarbethoxyguanidine (A., 1930, 1276) ( $\alpha$ -Me derivative, m.p. 85°, from the K salt and Me<sub>2</sub>SO<sub>4</sub>) and NH<sub>2</sub>Ph at 140° give the triazine,

NPh $\langle CO\cdot NH \rangle$ C:NH, m.p. > 335°; PhNCO affords the ester, CO<sub>2</sub>Et·N:C(NH·CO·NHPh)<sub>2</sub>, m.p. 151° (decomp.), whilst PhNCS gives the triazine,

NPh<CS-NH>C:NH, m.p. 180° (decomp.) (S-Me ether, m.p. 247°). H. B.

Structure of 8-nitro-1-naphthalenesulphonyl-N-phenylglycine. R. E. STEIGER (Bull. Soc. chim., 1933, 53, [iv], 1249—1254).—Interaction of 1-nitro-8naphthalenesulphonanilide (Na derivative) in EtOH with  $CH_2Br\cdot CO_2Et$  during 2 hr. affords *Et* 1-nitro-8naphthalenesulphonyl-N-phenylglycine (I), m.p. 150°, hydrolysed by boiling dil.  $H_2SO_4$  to the acid (II), m.p. 182.5—183°. The brucine salt of (II) cannot be resolved, which indicates that the NO<sub>2</sub>-group does not impede free rotation about the S·C linking (cf. A., 1928, 748). J. L. D.

Action of nitrous acid on the peri-naphthylaminesulphonanilides. R. E. STEIGER (Bull. Soc. chim., 1933, 53, [iv], 1254—1259).—Reduction of l-nitronaphthalene-8-sulphonanilide with FeSO<sub>4</sub> in NaOH affords the  $NH_2$ -compound, m.p. 143.5— 144.5°, the diazonium chloride from which is converted by N-NaOH at 100° into the sultam of 1-oaminophenylnaphthalene-8-sulphonic acid, m.p. 184— 185° (cf. A., 1907, i, 909), which cannot be resolved. Similarly, 1-nitro-5-methylnaphthalene-8-sulphonanilide is converted through the amine, m.p. 207.5— 208.5°, into the sultam, m.p. 215.5—216.5°, of 1-oaminophenyl-5-methylnaphthalene-8-sulphonic acid. J. L. D.

Application of electronic theory to organic compounds. II. Study of the nature of the nitrogen in amine oxides from the viewpoint of the electronic theory. A. M. BERKENHEIM and A. N. TCHIVIKOVA. III. Regrouping of the charges on the carbon ions of the phenyl group during the formation of aromatic amine oxides. A. M. BERKENHEIM, S. I. LURIE, and M. F. ELISEEVA (J. Gen. Chem. Russ., 1933, 3, 411-418, 419-431; cf. this vol., 176).—II. The action of H<sub>2</sub>O<sub>2</sub> on tert.amines with the formation of amine oxide was investigated from the viewpoint of the electronic theory, the mechanism being explained as oxidation-reduction. According to this theory, the ion N<sup>III</sup> should be changed to NV, and the same product, containing SIV and possessing marked reducing properties, should be obtained by the action of  $SO_2$  on the amine oxide as by SO<sub>3</sub> on the *tert*.-amine itself. NPhMe<sub>2</sub> oxide, m.p. 152—153° (decomp.), and SO<sub>2</sub> gave a *compound*, m.p. 240—241°, containing S and showing marked reducing properties, and the same compound was obtained from  $SO_3$  and the amine itself.

III. The theory that oxidation of tert.-amines with amine oxides is accompanied by regrouping of the C atom electrons right around the  $C_6$  ring is propounded, and investigated experimentally by introducing groups into the nucleus which might inhibit such a regrouping and so prevent the oxidation. Oxidation of the tert.-N in NPhMe<sub>2</sub> alters the charges of the C atom in the p-position from C''' to C<sup>\*\*\*</sup>. If, therefore, this atom already carries a group like SO<sub>3</sub>H<sup>\*\*\*\*</sup>, NO<sub>2</sub><sup>\*\*\*\*</sup>, or CO<sup>\*\*\*\*</sup>, such an electronic rearrangement should not occur, and experiments show that N-dimethylsulphanilic acid and Michler's ketone cannot be oxidised. Similarly, a group such as OMe in the m-position prevents oxidation : Ndimethyl-m-anisidine cannot be oxidised, whereas the o-compound gives the oxide (picrate, m.p. 151°) which is highly hygroscopic. M. Z.

*p*-Dimethyl- and *p*-diethyl-aminophenylhydrazines. R. STOLLÉ and K. T. GUNZERT (J. pr. Chem., 1934, [ii], 139, 141-161).---

p-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·NH·SO<sub>3</sub>H, m.p. 179° (decomp.) (cf. A., 1912, i, 920) (Na salt), is prepared by reduction of the corresponding diazosulphonate with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>; it is converted by H<sub>2</sub>O at the b.p. into p-aminodimethylaniline p-dimethylaminobenzenediazosulphonate, m.p. 149° (decomp.), but is hydrolysed by dry HCl in EtOH to p-dimethylaminophenylhydrazine dihydrochloride, m.p. 161° (decomp.) {benzylidene, m.p. 138° (decomp.); salicylidene, m.p. 185°; NN'-Bz<sub>2</sub>, m.p. 199° (loc. cit.) [hydrochloride, m.p. 196° (decomp.)]; and Bz, m.p. 145° (from the Bz<sub>2</sub> derivative and N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O in EtOH at the b.p.), derivatives of the free base; the last-named is oxidised by Ca(OCl)<sub>2</sub> to p-dimethylaminobenzeneazobenzoyl, m.p. 126° (de-

comp. >200°)}. p-Diethylaminophenylhydrazine dihydrochloride, decomp. 164° [p-tolylidene (hydrochloride, decomp. 165°) and NN'-Bz2, m.p. 159°, derivatives of the free base], is similarly prepared. p-Diethylamino-benzenediazonium borofluoride, m.p. 113° (decomp.), -benzenediazosulphonic acid [Na (anhyd. and  $+6H_2O$ ), K, and  $NH_4$  salts], and  $-phenyl-hydrazinesulphonic acid, m.p. 132° (decomp.); Bz, m.p. 209°, and benzylidene, m.p. 145°, derivatives of <math>4-NH_2\cdot C_6H_4\cdot NPh_2$ ; p-diphenylaminobenzene-diazon-ium chloride, m.p. 150° (decomp.), and borofluoride, diazondecomp. 162°, and -diazosulphonic acid (Na salt, decomp. 120°); p-aminodiethylaniline p-dimethylaminobenzenediazosulphonate, m.p. 158° (decomp.) (by double decomp.); and p-dimethylaminobenzenediazonium borofluoride, m.p. 150° (decomp.), are also described. p - Dimethylaminobenzenediazosulphonic acid exists in yellow and red (stable) modifications, m.p. 118° (decomp.), of which crystallographic data are given; its Na salt with aq. H2S gives the (?) diazohydrosulphide (+H<sub>2</sub>S), decomp. 78°. H. A. P.

4:4'-Dihydrazinodiphenylmethane. W. BOR-SCHE and R. MANTEUFFEL (Ber., 1934, 67, [B], 144; cf. A., 1910, i, 781).—4:4'-Dihydrazinodiphenylmethane has m.p. 141—143° (cf. Finger *et al.*, A., 1906, i, 892). Its (:CHPh)<sub>2</sub> derivative has m.p. 200° after softening at 196°, whilst ditetramethyleneindolylmethane has (air-dried) m.p. 265° (decomp.) and (vac.-dried) m.p. 281—282° when heated slowly. H. W.

Action of acetic acid on 3:4-dimethoxybenzenediazonium borofluoride. L. E. SMITH and H. L. HALLER (J. Amer. Chem. Soc., 1934, 56, 237— 239).—3:4-Dimethoxybenzenediazonium borofluoride, m.p. 123° (decomp.), heated with AcOH gives 2-hydroxy-4:5-dimethoxyacetophenone (I) [instead of the expected 3:4-dimethoxyphenyl acetate (II) (cf. this vol., 183)] and (probably) a little 1-fluoro-3:4-dimethoxybenzene, b.p. 98°/14 mm. (II) may be first formed and subsequently rearranged to (I) under the influence of BF<sub>3</sub>. 2:4:5-Trimethoxyacetophenone [semicarbazone, m.p. 206° (softens at 200°) (lit. 186— 188°)] is oxidised (aq. KMnO<sub>4</sub>) to 2:4:5-trimethoxyphenylglyoxylic acid, m.p. 186°, and thence (alkaline H<sub>2</sub>O<sub>9</sub>) to asaronic acid. H. B.

Aristol and the preparation of iodophenols. C. V. BORDEIANU (Arch. Pharm., 1934, 272, 8-22).-Thymol 2: 6-dimercuriacetate in dil. aq. NaOH with I-KI-AcOH affords 2:6-di-iodothymol (I), m.p. 45-47° (Ac derivative, m.p. 72-73°), 6-bromo-2-iodothymol (II), being similarly obtained from the 6-bromo-2-mercuriacetate (giving the internal oxide by CO<sub>2</sub> into its NaOH solution). p-Xylenol with Hg(OAc)<sub>2</sub> gives 2:6-dimercuriacetate, whence 2:6-di-iodo-pits xylenol (III), m.p. 63° (Ac derivative, m.p. 102-103°), is obtained. Iodination of thymol (IV) in alkaline solution gives, successively, the 6-I-compound [prepared in 93% yield by addition of I in MeOH to (IV) in 5% NH<sub>3</sub>-MeOH; oxidised by CrO<sub>3</sub>-AcOH to iodothymoquinone], (I), and, finally, aristol (V), but (V) is not formed in Na<sub>2</sub>CO<sub>3</sub> solutions. Since either (I) or (II) is converted by NaOH (or better with alkaline K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, since oxidation is involved) into (V) thus:  $2(I)+2NaOH=C_{20}H_{22}O_2I_2$  (V)+2NaI+2H<sub>2</sub>O, the 6-position must be involved, (V) being the dimeride of 3:3'-di-iodo-2:2'-dimethyl-5:5'-diisopropyldiphenyl-4:4'-quinone. Similarly (III) affords the dimeride of 3:3'-di-iodo-2:5:2':5'-tetramethyldiphenyl-4:4'-quinone (xylenolaristol), not melting  $< 220^{\circ}$ . J. W. B.

Preparation of *p*-nitrosophenol by nitrosation of phenol. C. L. TSENG and M. HU (J. Chinese Chem. Soc., 1933, 1, 183—187).—A 90% yield of *p*-NO·C<sub>6</sub>H<sub>4</sub>·OH is obtained from PhOH, KNO<sub>2</sub>, and AcOH at  $-10^{\circ}$ . R. S. C.

Acyl derivatives of phenetidines. D. M. BIROSEL and H. L. HUANG (Univ. Philippines Nat. Appl. Sci. Bull., 1933, 3, 1-5).—Lauryl chloride and o-phenetidine (I) at 120—130° in 6 hr. afford *lauryl*-o-phenetidide, m.p. 69·7—70°, in 30% yield. Acid chlorides with (I) in dry COMe<sub>2</sub> in presence of anhyd. Na<sub>2</sub>CO<sub>3</sub> gave in 30 min. the following o-phenetidides: myristyl-, m.p. 77° (6% yield); palmityl- (II), m.p. 82—83° (18%); stearyl- (III), m.p. 84·7° (30%); chaulmoogryl-, m.p. 280·3° (40%); benzoyl-, m.p. 104·2° (12%); cinnamyl-, m.p. 118° (32%). Mixtures of (II) and (III) melt sharply and behave as individuals. The following p-phenetidides were obtained similarly: *lauryl-*, m.p. 109—110° (17%); myristyl-, m.p. 110·8—111° (9%); palmityl-, m.p. 117·5° (3%); stearyl-, m.p. 112·5° (30%).

CH. ABS. Synthesis of chloromethyl derivatives of phenol ethers. R. QUELET (Compt. rend., 1934, 198, 102— 105).—Ph alkyl ethers are converted by saturating their mixture with 40% CH<sub>2</sub>O in ligroin with gaseous HCl at  $0-5^{\circ}$  into p-(or o-)CH<sub>2</sub>Cl·C<sub>6</sub>H<sub>4</sub>·OR (cf. A., 1933, 707) and thus are obtained : p-methoxy- (50% yield), p-ethoxy-, unstable, b.p. 123°/15 mm., 4-methoxy-3-methyl-, b.p. 119°/12 mm., 4-methoxy-2-methyl-, unstable, b.p. 123°/15 mm., 4-methoxy-5-methyl-, b.p. 148°/16 mm., -benzyl chloride, together with 4:4'-dimethoxy-3:3'-, m.p. 24°, b.p. 207—209°, and -2:2'-, m.p. 66°, b.p. 215—216°/12 mm., and 2:2'dimethoxy-5:5'-, m.p. 55°, b.p. 197—199°/10 mm., -dimethyldiphenylmethane, as by-products.

J. W. B. Influence of the phenyl group on the reactions of thionyl chloride with primary aliphatic alcohols. P. CARRÉ and D. LIBERMANN (Compt. rend., 1934, 198, 274—276).—Unlike CH<sub>2</sub>Ph·OH, CH<sub>2</sub>Ph·CH<sub>2</sub>·OH and CH<sub>2</sub>Ph·CH<sub>2</sub>·CH<sub>2</sub>·OH (I) behave as aliphatic alcohols with SOCl<sub>2</sub>. Thus, at room temp. first neutral sulphites (II) and then chlorosulphites (III) are formed, the existence of the latter being proved (a) by hydrolysis to the alcohol and (b) by reaction with an alcohol and C<sub>5</sub>H<sub>5</sub>N to, e.g., Bu<sup>a</sup>  $\gamma$ -phenylpropyl sulphite, b.p. 191—193°/24 mm. C<sub>5</sub>H<sub>5</sub>N renders formation of (II) almost instantaneous and lowers the temp. of decomp. of (III) by 20°. Thus, (I) in C<sub>5</sub>H<sub>5</sub>N with SOCl<sub>2</sub> (0·5 mol.) gives  $\gamma$ -phenylpropyl sulphite (IV), b.p. 248—254°/11 mm., which decomposes at about 310°/760 mm. to SO<sub>2</sub>, (I), and CH<sub>2</sub>:CHPh. The temp. of decomp. of (IV) is lowered by C<sub>5</sub>H<sub>5</sub>N by about 100°. R. S. C.

Synthesis of phenols with unsaturated sidechains. R. MAJIMA and K. TAMURA (Proc. Imp. Acad. Tokyo, 1933, 9, 606–608).— $\alpha\gamma$ -Dichloro- $\Delta^{\beta\beta}$ - hexadiene and PhONa in PhMe give Ph chlorohexadienyl ether [reduced (catalytically and then Na-EtOH) to the hexyl ether, b.p. 75—77°/1 mm.] and  $\gamma$ -chloro- $\Delta^{\beta\delta}$ -hexadienylphenol, b.p. 120—140°/1 mm., unstable except in Et<sub>2</sub>O, which is a mixture of o- and p-isomerides, since the Me ether, b.p. 108—117°/1 mm., obtained by Me<sub>2</sub>SO<sub>4</sub>, with KMnO<sub>4</sub> yields anisic and o-methoxybenzoic acids; by hydrogenation (Pdblack) is obtained a mixture of c- and p-hexylanisole, b.p. 85—100°/1 mm. Pyrocatechol gives similarly the mono-, b.p. 93—96°/0·8 mm., and possibly the di-chlorohexadienyl ether and  $\gamma$ -chloro- $\Delta^{\beta\delta}$ -hexadienylpyrocatechol, decomp. when distilled, the Me ether (obtained by Me<sub>2</sub>SO<sub>4</sub>) of which gives with KMnO<sub>4</sub> veratric acid, and by reduction hexylveratrole, b.p. 100—105°/0·5 mm. R. S. C.

Chloro-derivatives of 4-hydroxydiphenyl. J.C. COLBERT, W. MEIGS, and B. MACKIN (J. Amer. Chem. Soc., 1934, 56, 202-204).-Passage of Cl<sub>2</sub> into a suspension of 4-hydroxydiphenyl (I) in CHCl<sub>3</sub>, CCl<sub>4</sub>, or CS2 until dissolution occurs gives the 3-Cl-derivative (II), m.p. 76-77.5° (corr.) (benzoate, m.p. 95-97°; 2:4-dinitrophenyl ether, m.p. 109-111°); further chlorination affords the 3:5-Cl2-derivative, m.p. 80.5-82° (corr.) [benzoate, m.p. 144-146°; 2:4dinitrophenyl ether, m.p. 112-113.5° (corr.)]. (I) and  $Cl_2$  in AcOH give a mixture containing some control  $3:5:4'-Cl_3$ -derivative, m.p.  $133\cdot5-137^\circ$  (corr.) (benzoate, m.p. 161°; 2:4-dinitrophenyl ether, m.p. 174-176°). (II) and Br (1 mol.) in CCl<sub>4</sub> afford afford 1.4-5 human 4-hudroxudiphenyl, m.p.  $84-86^\circ$ 3-chloro-5-bromo-4-hydroxydiphenyl, m.p.  $84-86^{\circ}$  (corr.); with 2 mols. of Br in CS<sub>2</sub>, 3-chloro-5:4'-dibromo-4-hydroxydiphenyl, m.p. 143-146° (corr.), results. H. B.

Action of nascent thiocyanogen on di- and trihydric phenols. G. MACHEK (Monatsh., 1933, 63, 216-219).—Addition of Br in MeOH to pyrocatechol and NH<sub>4</sub>SCN (giving nascent SCN) in dry MeOH gives a 48% yield of *thiocyanopyrocatechol*, m.p. 142° (corr.) [ $Ac_2$  derivative, m.p. 58° (corr.)], but similar treatment of quinol, resorcinol, pyrogallol, and phloroglucinol gives gelatinous products containing polymerised SCN. J. W. B.

Pseudo-quinonoid character of tribromoresorcinol. T. L. DAVIS and V. F. HARRINGTON (J. Amer. Chem. Soc., 1934, 56, 129-132).-I is liberated when tribromoresorcinol (I) is heated with NaI or KI in EtOH; reaction is facilitated by AcOH and retarded by a large excess of HI. (1) is converted by aq. C<sub>5</sub>H<sub>5</sub>N into an amorphous polynuclear compound, composition C6HO2Br; a similar compound is formed using aq. NaOH (preferably  $\ge 2$  equivs.). (1) is reduced by aq. or alkaline  $Na_2SO_3$  to 2:4-dibromo-, m.p. 92.8-93.7°, and thence to 2-bromo- (II), m.p. 101.2-102°, -resorcinol; (I) is also reduced to (11) by  $SnCl_2$  [in solution containing some  $Sn(OH)_2$ ]. These reactions [and the results previously described (A., 1929, 439)] are readily explained by assuming the intermediate formation, by loss of HBr, of the radical CO<CBr:C(OH) CBr=CH>C<. Oxidation (CrO<sub>3</sub>, AcOH) of the Me ether of (I) gives 3:5:6-tribromo-2-methoxyp-benzoquinone (III), m.p. 168-168.5°; free Br is not produced and it is suggested that addition of HBr to the 3:5-Br<sub>2</sub>-quinone and subsequent oxidation of the resulting quinol occur. (III), which is also obtained from methoxyquinol and excess of Br in CHCl<sub>3</sub>, is reduced (H<sub>2</sub>SO<sub>3</sub>) to 3:5:6-tribromo-2-methoxyquinol, m.p. 175–176°, and with 2N-KOH gives the K salt of methylbromanilate, C<sub>7</sub>H<sub>4</sub>O<sub>4</sub>Br<sub>2</sub>, m.p. >350°. H. B.

Bromoquinol (adurol). G. A. KIRKHGOF and R. Y. ASTROVA (Bull. Nauch. Issledov. Khim. Farm. Inst., 1931, 304—305).—HBr is passed into 108 g. of benzoquinone in CHCl<sub>3</sub> containing 1.5 g. of C; bromoquinol, from CHCl<sub>3</sub>, has m.p. 106—107°. CH. ABS.

[Preparation of] quinol. G. A. KIRKHGOF and R. Y. ASTROVA (Bull. Nauch. Issledov. Khim. Farm. Inst., 1931, 303—304).—Benzoquinone is reduced in dil.  $H_2SO_4$  by CaSO<sub>3</sub> at 30—35°. CH. ABS.

Oxidation products of organic developers. A. SEYEWETZ and S. SZYMSON (Bull. Soc. chim., 1933, 53, [iv], 1260—1268).—Quinol (I) with PbO<sub>2</sub> or AgBr in Na<sub>2</sub>SO<sub>3</sub> (or K<sub>2</sub>SO<sub>3</sub>)-alkali in air affords Na quinoldisulphonate (II). (I) with AgBr and Na<sub>2</sub>SO<sub>3</sub> in H<sub>2</sub>O-COMe<sub>2</sub> in air affords the monosulphonate (III). (I) reduces AgBr twice as easily as (II), but (III) has no action. Similarly  $o - C_6 H_4(OH)_2$  in presence of HgCl<sub>2</sub> affords the monosulphonate, whereas with AgBr or PbO<sub>2</sub> the disulphonate is formed.

J. L. D.

Diaryls and their derivatives. I, II. Ringclosure of 2:7:2':7'-tetrahydroxy-1:1'-dinaphthyl. J. S. JOFFE and (II) J. V. GRATSCHEV (J. Gen. Chem. Russ., 1933, 3, 453-462, 463-469).β-Naphthol-7-sulphonic acid on oxidation by boiling with aq. FeCl<sub>3</sub> gives 2: 2'-dihydroxy-1: 1'-dinaphthyl-7:7'-disulphonic acid (I), which by alkali fusion yields 2:7:2':7'-tetrahydroxy-1:1'-dinaphthyl (II), m.p.  $(+2H_2O)$  114.5°, (anhyd.) 151—152°, also obtained by oxidising 2:7-C<sub>10</sub>H<sub>6</sub>(OH)<sub>2</sub> with FeCl<sub>3</sub>. Oxidation of this with FeCl<sub>3</sub> does not give the expected perylene derivative, but a brown substance which could not be further identified. It is considered that this is due to the existence of (II) in the transform giving rise on further oxidation to dihydroxydinaphthylene dioxide (III) and decomp. products. Bromination of (II) gives the  $Br_6$ -derivative, m.p.  $250-251^{\circ}$ , and ring-closure by removing NH<sub>2</sub> gives a blue dye, probably the tetrabromodinaphthylene dioxide quinone (IV), reducible to the (OH)<sub>2</sub>-compound. By heating the Pb salt of (II) with  $AlCl_3$ , 1:6:7:12. tetrahydroxyperylene is formed, but cannot be isolated, since ring-closure takes place with formation of 6:7-dihydroxy-1:12-furoperylene, m.p. (impure) 250-260° (V).





166).—Et  $\beta$ -bromo- $\alpha$ -phenylpropyl ether, b.p. 114°/9 mm. (from Et  $\alpha\beta$ -dibromopropyl ether and MgPhBr), and MeOH-NH<sub>2</sub>Me at 125—130° give Et  $\beta$ -methylamino- $\alpha$ -phenylpropyl ether [*dl*- $\psi$ -ephedrine Et ether), b.p. 116—122°/18 mm., de-ethylated (HBr) to *dl*- $\psi$ -ephedrine. H. B.

Constitution of triarylmethyl salts. P. RUMPF (Compt. rend., 1934, 198, 269—272).—The vals. of the dissociation consts. of the mono- and di-salts of p-amino-, pp'-diamino-, and pp'p''-triamino-triphenyl-carbinol, compared with those of the salts of the corresponding derivatives of CHPh<sub>3</sub>, support the view that the coloured mono-salts are carbonium salts, not quinonoid. R. S. C.

Synthesis of condensed polynuclear hydrocarbons by cyclodehydration of aromatic alcohols. I. Indanes. M. T. BOGERT and D. DAVID-SON (J. Amer. Chem. Soc., 1934, 56, 185-190).-Alcohols of the types  $CPhR_2 \cdot CR(OH) \cdot CHMe_2$  and  $CPhR_2 \cdot CHR \cdot CMe_2 \cdot OH$ , where R is H or Me, are dchydrated by 85% H<sub>2</sub>SO<sub>4</sub> to 1 : 1-dimethylindanes, which are also formed by similar treatment of the olefines,  $CPhR_2 \cdot CR: CMe_2$ , which are assumed to be formed first. Thus,  $\gamma$ -phenyl- $\alpha\alpha$ -dimethylpropyl alcohol, b.p. 123°/15 mm. (from  $CH_2Ph \cdot CH_2 \cdot MgBr$  and COMe<sub>2</sub>), and a benzylisobutyl alcohol, b.p. 118-122°/ 15 mm., both give 1:1-dimethylindane (I), b.p. 191°  $(SO_3H$ -derivative, m.p. 67°), which is oxidised (aq.  $KMnO_4$ ) to a a-dimethylhomophthalic acid, m.p. about 120° (with loss of H<sub>2</sub>O). Some (I) is also formed when y-phenyl-y-methylbutyl alcohol, b.p. 137-138°/16 mm. [prepared by reduction (Na, EtOH) of CPhMe<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et], is dehydrated with  $H_3PO_4$  at 230-240°; admixed olefine is removed with 85% H<sub>2</sub>SO<sub>4</sub>. Benzylmethylisopropylcarbinol, b.p. 122-124°/18 mm. (from CH2Ph·MgCl and COMePr<sup>B</sup>), similarly affords 1:1:2-trimethylindane, b.p. 208° (SO<sub>3</sub>H-derivative, m.p. 109°);  $\gamma$ -phenyl-a $\gamma$ -dimethylbutyl alcohol yields 1:1:3-trimethylindane, and  $\gamma$ phenyl-aay-trimethylbutyl alcohol, b.p. 133°/17 mm. (from MgMeI and CPhMe<sub>2</sub>·CH<sub>2</sub>·COMe), gives 1:1:3:3tetramethylindane, b.p. 206-209° (SO3H-derivative, m.p. 107-108°). Polymeric material only is obtained from  $\gamma$ -phenylpropyl (using H<sub>3</sub>PO<sub>4</sub> at 230— 240°),  $\gamma$ -phenyl- $\alpha$ -methylpropyl, and  $\gamma$ -phenyl- $\alpha\beta$ -di-methylpropyl alcohol, b.p. 135–136°/21 mm. [prepared by reduction (Na, EtOH) of CHPh.CMe.COMe], and benzylmethylethylcarbinol.  $\delta$ -Phenylbutyl alcohol is dehydrated by H\_3PO4 to 1:2:3:4-tetrahydronaphthalene;  $\delta$ -phenyl- $\Delta^{\alpha}$ -buteno is not an intermediate since this is polymerised under the same conditions, and in this case direct cyclodehydration must take place. H. B.

Supposed isomerism of  $\alpha\alpha\beta\beta$ -tetraphenylethanol. R. WEGLER (Ber., 1934, 67, [B], 35-39). The homogeneity of  $\alpha\alpha\beta\beta$ -tetraphenylethanol (I), m.p. 236° (Bergmann et al., A., 1930, 979; Orckhov, A., 1921, i, 566), is confirmed. The "isomeric product" prepared by Paterno et al. (A., 1909, i, 393) by irradiation of COPh. and CH<sub>2</sub>Ph<sub>2</sub> is a mixture (II) of (I), OH·CHPh<sub>2</sub>·CPh<sub>2</sub>·OH (III), and CHPh<sub>2</sub>·CHPh<sub>2</sub>, difficulty separable into its components by crystallisation. (I) is most readily isolated from (II) by C<sub>2</sub>H<sub>5</sub>N at 135°, whereby (III) is transformed into COPh<sub>2</sub> and CHPh<sub>2</sub>·OH. Analogous observations are made with  $\alpha\beta\beta$ -triphenyl- $\alpha$ -*p*-tolylethanol. (I) is transformed by Na into CH<sub>2</sub>Ph<sub>2</sub>, COPh<sub>2</sub>, CHPh<sub>2</sub>·OH, BzOH, and, mainly, (·CHPh<sub>2</sub>)<sub>2</sub>. H. W.

Pinacol-pinacolin rearrangement. V. Rearrangement of unsymmetrical aromatic pinacols. W. E. BACHMANN and H. R. STERNBERGER (J. Amer. Chem. Soc., 1934, 56, 170-173; cf. A., 1932, 737).—as-Pinacols, OH·CR2·CR2·OH, prepared from OH·CR<sub>2</sub>·CO<sub>2</sub>Me and MgR'Br, are rearranged by AcCl in  $AcOH-C_6H_6$  (subsequent treatment with I in AcOH is occasionally necessary) to mixtures of pinacolins, which are analysed by fission with MeOH-KOH to  $R\cdot CO_2H+R'\cdot CO_2H$ . The relative migration aptitudes of the groups studied are : p-diphenylyl 1.18, Ph 1, *m*-tolyl 1, *p*-tolyl 0.96, *p*- $\hat{C}_{6}H_{4}Cl$  0.75, phenetyl 0.49, anisyl 0.39, *p*- $C_{6}H_{4}F$  0.099; there is no simple relationship between these vals. and those found for the s-pinacols (A., 1932, 515). Improved methods of prep. of anisilic (Me ester, m.p. 110- $110.5^{\circ}$ ) and 4:4'-diphenylbenzilic acid (Me ester, m.p. 130.5-131.5°) are given. 4:4'-Dichloro-, m.p. 143-144.5°, 4:4'-difluoro-, m.p. 166.5-167.5°, 4:4'-diethoxy-, m.p. 162-163°, 4:4'-diphenyl-, m.p. 190.5-191°, 4": 4"'-dimethoxy-3: 3'-dimethyl-, m.p. 153.3-154.5°, 4": 4"'-dimethoxy-4: 4'-dimethyl-, m.p. 159.5-161°, and 4": 4"'-diphenyl-3: 3'-dimethyl-, m.p. 160-161°, -benzpinacols; Ph 4:4'-difluorotriphenylmethyl ketone, m.p. 121.5-122.5°, and 4:4'-difluorotriphenylmethane, m.p. 55-56°, are described. H. B.

Silver-halogen complexes of carboxylic acids. C. PREVOST (Compt. rend., 1933, 197, 1661-1663).-Formation of an I-Ag complex (A., 1933, 711) also occurs with AgOAc, and Br may replace I. Addition (trans) to ethylenic derivatives occurs thus : AgI(OAc)<sub>2</sub> +CHR:CHR  $\rightarrow$  AcO·CHR·CHRI+AgOAc  $\rightarrow$  AgI+(AcO·CHR·)<sub>2</sub>; the second stage is slow, causing contamination with halogeno-esters. Various Ac2 and Bz<sub>2</sub> derivatives are thus prepared, the following being new:  $Bz_2$  derivatives of *n*-pentane- $\alpha\beta$ -diol (I), b.p. 233°/10 mm., phenyl-, m.p. 96°, and as-diphenyl-, m.p. 108°, ethylene glycol; Ac, derivative of (1), b.p. 103°/12 mm.; Bz derivative, m.p. 170°, of CHPhBr CHPh OH; Bz, derivative, m.p. 152°, of *n*-hexane- $\alpha\beta\epsilon\zeta$ -tetraol (from diallyl); and (by GIMEL) the  $Bz_2$  derivative of stycerol, and the  $Bz_2$  derivative J. W. B. of Et  $\beta$ -hydroxy- $\beta$ -phenyl-lactate.

Ring-system of sterols and bile acids. IV. Nomenclature of cholane group. O. ROSENHEIM and H. KING (Chem. and Ind., 1934, 91-92; cf. A., 1933, 1048).—It is suggested that the following substances be re-named as quoted in parentheses : coprosterol (I) (coprostanol), allocholesterol (II) (coprostenol), cholestenone (III) (coprostenone), 4-cholestane (coprostane),  $\psi$ -cholestene (IV) (coprostene); the nomenclature expresses the relationship (which is discussed) between (I), (II), (III), and (IV). The prefix allo- is used to denote derivatives (e.g., allocholanic acid) in which rings I and II are in the transposition. When isomerism is due to steric inversion of the OH group, the prefix epi- should be used (e.g., H. B. epicholestanol).

Position of the nuclear double linking in stigmasterol. E. FERNHOLZ (Annalen, 1934, 508, 215—224).—Oxidation (BzO<sub>2</sub>H) of stigmasteryl acetate in CHCl<sub>3</sub> at 5° gives (mainly) an  $\alpha$ -oxide (I), m.p. 143°,  $[\alpha]_{10}^{\mu}$  —36·7° in CHCl<sub>3</sub>, and a little of a  $\beta$ -oxide, m.p. 170°,  $[\alpha]_{10}^{\mu}$  —32° in CHCl<sub>3</sub>; these are hydrolysed (5% EtOH-KOH) to  $\alpha$ -, m.p. 152°, and  $\beta$ -, m.p. 153°, -stigmasterol oxides, respectively. Ozonolysis of (I) affords  $\alpha$ -ethylisovaleraldehyde (showing that O adds to the nuclear double linking), whilst hydrolysis (aq. EtOH-HCl) gives about 20% of stigmastenetriol (II), m.p. 254°. (II) contains a tert.-OH since it is oxidised (CrO<sub>3</sub>, AcOH) to stigmastenoldione (III), m.p. about 260° (with loss of H<sub>2</sub>O), which is dehydrated by HCl in CHCl<sub>3</sub> to stigmastadienedione (IV), m.p. 155° [phenylhydrazone, m.p. 250° (decomp.)].



This is reduced (Zn dust, AcOH) to stigmastenedione (III, with OH=H), m.p. 197°, which with 50% N<sub>2</sub>H<sub>4</sub>,H<sub>2</sub>O in EtOH affords an azine, decomp. about 260°. Reduction (H<sub>2</sub>, Pt-black, EtOAc) of (I) gives stigmastanediol monoacetate, m.p. 206°, which could not be acetylated (Ac<sub>2</sub>O) further. The above results are explained by the existence of a double linking in stigmasterol (V) between C<sub>5</sub> and C<sub>6</sub> (cf. A., 1933, 1290). (V) differs from cholesterol only in the structure of the side-chain. Sitostanoldione, m.p. 256°, is dehydrated (HCl in CHCl<sub>3</sub>) to sitostenedione, m.p. 129° (lit. 166°), which is reduced (Zn dust, AcOH) to sitostanedione, m.p. 196° (azine, m.p. 197-200°).  $\gamma$ -Sitosterol may differ from (V) in the arrangement of the asymmetric centres in the side-chain. H. B.

Addition products of halogens and benzene derivatives. I. T. VAN DER LINDEN (Rec. trav. chim., 1934, 53, 45-62).-The work of Matthews (J.C.S., 1900, 77, 1273) is confirmed and extended. PhCN is chlorinated in sunlight at room temp., the a-hexachloride, m.p. 156-157° (I), separated by addition of glacial AcOH (cf. loc. cit.) after removal of unchanged PhCN, and the residue separated by distillation at 0.06-0.1 mm., crystallisation of individual fractions, and hydrolysis of residues to amides by hot conc. H<sub>2</sub>SO<sub>4</sub>, and of final amide residues to acids by fuming  $HNO_3$ . The following are thus obtained in addition to (I) and known derivatives:  $\beta$ -hexachloro-, m.p. 197° (decomp.) [amide, m.p. 246.5-247.5; free acid, m.p. 219.5-221.5 (liberates HCl with hot  $H_2O$ ], and 1:2:3:4:4:5:6-heptachloro-cyclohexyl cyanide [amide, m.p. 309°; acid (II), m.p. 291° (decomp.)],  $\gamma$ -hexachlorocyclohexanecarb-oxylic acid (A., 1912, i, 698), 1:2:4:5-C<sub>6</sub>H<sub>2</sub>Cl<sub>4</sub>, (III) (below), and a little chloranil. The acid, m.p. 195°, corresponding with (I) loses HCl and CO2 with warm  $H_2O$  to give a (?) eutectic mixture from which penta-chlorocyclohexene, m.p. 103—104° (III), is isolated. This is unaffected by AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub>, conc. H<sub>2</sub>SO<sub>4</sub> at 100°, and alkaline KMnO<sub>4</sub>, but Cl<sub>2</sub> in sunlight gives enneachlorocyclohexane, m.p. 94°. Reduction of (II) with Z<sub>2</sub> in FOUR gives a CH CliCO H thus proving with Zn in EtOH gives p-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H, thus proving the structure of the parent nitrile. H. A. P.

cis- and trans-Cinnamic acids. Steric hindrance. J. MANTA (Bull. Soc. chim., 1933, 53, [iv], 1277-1286).-The rates of esterification of cinnamic and allocinnamic acid (I) (prep. described) are of the same order (cf. J.C.S., 1909, 95, 315) due to the conversion of (I) into the *trans*-acid, which is also formed when the cis-acid is esterified in presence of 2% HCl or H<sub>2</sub>SO<sub>4</sub>. Interaction of CPh:C·CO<sub>2</sub>H with cyclohexanol and some PhSO<sub>3</sub>H affords cyclohexyl phenylpropiolate, b.p. 190°/9 mm., reduced by H2-Pd to a mixture from which selective hydrolysis (KOH-EtOH) yields cyclohexyl allocinnamate, b.p. 180°/15 mm. Similarly prepared, benzyl phenylpropiolate has m.p. 35°, and benzyl allocinnamate, m.p. 34-35°. The rate of hydrolysis (II) in abs. EtOH of several cis- and trans-esters shows that  $K_{\text{trans}}/K_{\text{cis}}=2$ , and that (II) for esters of (I) is very small; hence (I) has a cis-structure. (II) of the propiolic and hydrocinnamic esters is much greater. (II) in 96% EtOH is increased sixfold (cf. J.C.S., 1921, 119, 970). J. L. D.

Isomerisation of phenylglycide methyl and ethyl ethers. (MLLE.) DARMON (Compt. rend., 1933, 197, 1649—1650).—When heated with a trace of anhyd. ZnCl<sub>2</sub>, phenylglycide Me ether isomerises exclusively to CH<sub>2</sub>Ph·CO·CH<sub>2</sub>·OMe (synthesis, this vol., 191), and the corresponding *Et ether*, b.p. 134— 135°/13 mm., similarly affords mainly CH Ph:CO·CH :OFE (loc cit) together with

135°/13 mm., similarly affords mainly CH<sub>2</sub>Ph·CO·CH<sub>2</sub>·OEt (*loc. cit.*) together with OEt·CH<sub>2</sub>·CHPh·CHO (Beaufour, A., 1913, i, 466). It is concluded that the affinity of CH<sub>2</sub>·OR is < that of Ph, and the migratory tendency of CH<sub>2</sub>·OR is < that of H. J. W. B.

Arylamides of 2: 3-hydroxynaphthoic acid.— See B., 1934, 88.

Iodo-derivatives of diphenyl ether. I. Monoand di-iodo-derivatives of diphenyl ether and of 2- and 4-carboxydiphenyl ethers. R. Q. BREWSTER and F. STRAIN (J. Amer. Chem. Soc., 1934, 56, 117-120).—The following derivatives of Ph<sub>2</sub>O are prepared (usually by standard methods): 2-I-, m.p. 56°, 3-I-, b.p. 155°/3 mm., 194—196°/20 mm. (from the 3-NH<sub>2</sub>-derivative), 4-I-, m.p. 47° (from Ph<sub>2</sub>O and ICl in AcOH), 2-iodo-4'-nitro-, m.p. 104°, 4-iodo-4'-nitro-, m.p. 70°, 2-iodo-4'-amino-, m.p. 69° (Ac derivative, m.p. 150°),  $2:4'-I_2$ -, m.p. 48°, 4-iodo-2'-nitro-, m.p. 86°,  $3:4'-(NO_2)_2$ -, m.p. 123° (from  $p-C_6H_4F\cdotNO_2$  and  $m\cdotNO_2\cdotC_6H_4\cdotOK$ ),  $3:4'-(NH_2)_2$ -, m.p. 72° (Ac<sub>2</sub> derivative, m.p. 192°),  $3:4'-I_2$ -, b.p. 200°/3 mm.,  $4:4'-I_2$ -, m.p. 139°, 4-nitro-2-amino-, m.p. 107° [by reduction (SnCl<sub>2</sub>, HCl) of the 2:4-(NO<sub>2</sub>)<sub>2</sub>-derivative; the compound is described by Bogert and Evans (B., 1926, 354) as the 2-nitro-4amino-derivative], 2-iodo-4-nitro-, m.p. 61°, 2-iodo-4amino-, b.p. 203°/3 mm. (hydrochloride, m.p. 245°; Ac derivative, m.p. 120°),  $2:4\cdotI_2$ -, b.p. 198°/3 mm., 3-nitro-4-acetamido-, m.p. 104°, 3-amino-4-acetamido-, m.p. 126°, 3-nitro-4-amino-, m.p. 82°, 3:4- $(NH_2)_2$ -, m.p. 69° (Ac<sub>2</sub> derivative, m.p. 188°), 4-iodo-3-nitro-, b.p. 195°/3 mm., 4-iodo-3-amino-, b.p. 188°/ 3 mm. (Ac derivative, m.p. 144°), and  $3:4\cdot I_2$ -, b.p. 208°/3 mm. p-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OPh and CICO<sub>2</sub>Et give Et p-phenoxyphenylcarbamate, m.p. 63°, converted by ICl in AcOH into Et p-p'-iodophenoxyphenylcarbamate, m.p. 126°, also obtained from 4-iodo-4'-amino-

diphenyl ether (I) and ClCO<sub>2</sub>Et. p-p'-Iodophenoxyphenylcarbamide, m.p. 201°, is prepared from (I) and KNCO. o-OPh·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (II) (improved prep. given) and HNO3 (d 1.42) at 40-45° give 2-p-nitrophenoxybenzoic acid, m.p. 157°, also prepared by phenotypenzoic acia, m.p. 157, also prepared by oxidation  $(Na_2Cr_2O_7, H_2SO_4)$  of 2-p-nitrophenoxybenz-aldehyde, m.p. 112° (from p-C<sub>6</sub>H<sub>4</sub>Cl·NO<sub>2</sub> and o-OK·C<sub>6</sub>H<sub>4</sub>·CHO). 2-p-Aminophenoxybenzoic acid (Ac derivative, m.p. 185°) has m.p. 180°. 2-p-Iodophen-oxybenzoic acid, m.p. 143° [from (II) and ICl], is converted by conc. H<sub>2</sub>SO<sub>4</sub> at 100° into 2-iodoxanthone (III) m p. 156° 5 4 mino 2 subsecutive social (III), m.p. 156°. 5-Amino-2-phenoxybenzoic acid, m.p. 164° [Ac derivative (+H<sub>2</sub>O), m.p. 111°, m.p. (anhyd.) 165°], is converted into the 5-I-derivative, m.p. 148°, and thence into (III). 2-o-Nitrophenoxybenzaldehyde, m.p. 77°; 2-o-nitro-(IV), m.p. 153°, -amino-, m.p. 153° (Ac derivative, m.p. 179°; lactam, m.p. 211°), and -iodo-, m.p. 133°, -phenoxybenzoic acids; 4-p-iodophenoxybenzoic acid, m.p. 217°; 217°; 5-nitro-, m.p. 178°, -amino-, m.p. 185°, and -iodo-, m.p. 176°, -2-p-iodophenoxybenzoic acids, and 5-nitro-2-p-nitrophenoxybenzoic acid, two forms, m.p. 158° and 170-171°, are also described. 4-Nitroxanthone, m.p. 190° (lit. 127°), is obtained from (IV) and conc. H<sub>2</sub>SO<sub>4</sub>. H. B.

Organic solvents and plasticisers [esters of 2-benzoylbenzoic acid].—See B., 1934, 87.

Relation of thyroxine with tyrosine. A. CANZANELLI, C. R. HARINGTON, and S. S. RANDALL (Biochem. J., 1934, 28, 68—72).—An optically active thyronine,  $[\alpha]_{5461}$  +13·3°, has been synthesised from natural *l*-tyrosine, and is identical with a sample prepared by catalytic deiodination of *l*-thyroxine which had been shown to be identical with the natural compound (A., 1930, 820). H. G. R.

Action of sulphuryl chloride on unsubstituted amides and imides. Phthalimidosulphonyl chloride. Sulphondiamide. M. BATTEGAY and L. DENIVELLE (Bull. Soc. chim., 1933, 53, [iv], 1242— 1249).—Interaction of SO<sub>2</sub>Cl<sub>2</sub> (I) with ONa-CMe:NH (A., 1931, 608) at 0—5° during 1 hr. affords an unstable oil [probably the N-sulphonyl chloride II]] which decomposes into HCl, SO<sub>2</sub>, and MeNCO, whereas the product from (I) and NH<sub>2</sub>Bz [probably NH:CPh-O·SO<sub>2</sub>Cl] affords PhCN. Phthalimidosulphonyl chloride (III) and dry NH<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> afford the sulphonamide(?), easily decomposed to phthalimide and SO<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>. (III) with NHPhMe affords a stable product, m.p. 160°, which has no labile H atom and is either the O- or N-sulphonamide. J. L. D.

Preparation of 3-aminophthalhydrazide for use in demonstration of chemiluminescence. E. H. HUNTRESS, L. N. STANLEY, and A. S. PARKER (J. Amer. Chem. Soc., 1934, 56, 241–242).—Crude 3nitrophthalhydrazide is obtained when an aq. solution of 3-nitrophthalic acid (1 mol.),  $N_2H_4, H_2SO_4$  (1 mol.), and NaOAc (2 mols.) is evaporated to dryness and then heated at  $160\pm10^\circ$ ;  $Na_2SO_4$  is removed by extraction with  $H_2O$ . Reduction (6N-NH<sub>4</sub>HS) gives 3aminophthalhydrazide ("luminol"), isolated as the Na salt. H. B.

*p*-Benzoquinonediarylimine-2 : 5-dicarboxylic acids and esters. H. LIEBERMANN and B. SCHULZE (Annalen, 1934, 508, 144—153).—Et 2:5-diarylaminoterephthalates (I) (A., 1914, i, 658) are converted into the  $(NO)_{2}$ -derivatives, which when heated in PhMe or xylene eliminate NO and give Et *p*-benzoquinonediarylimine-2:5-dicarboxylates (II). Reduction (Zn dust, AcOH) of (II) affords (I), whilst

CO2Et

 hydrolysis (EtOH-KOH) gives 2:5-diarylaminoterephthalic acids
CO<sub>2</sub>Et (III). p-Benzoquinonediarylimine-2:5-dicarboxylic acids (IV) are similarly prepared from (III). Solutions of (II) in org. solvents are
(II) violat or blood red: solutions in

(II.) violet- or blood-red; solutions in conc.  $H_2SO_4$  are emerald-green. (IV) give darkcoloured alkali-metal salts; solutions in CHCl<sub>3</sub> are reddish-violet or blue. By-products (insol. in  $CHCl_3$ ) often accompany (IV). The following are described : Et dinitroso-2: 5-di-p-toluidino-, m.p. 146° (decomp.) (becomes red at 100°), -di-p-anisidino-, -di-p-diphenylylamino-, m.p. 160° (becomes red at 120°), -dianilino-, and -diethylamino-, m.p. 114°, decomp. (evolution of NO) 170°, -terephthalates; Et p-benzoquinone-di-p-tolylimine-, m.p. 124°, -dianisylimine-, m.p. 136°, -di-pdiphenylylimine-, m.p. 185°, -diphenylimine-, m.p. 93-95°, and -diethylimine-, m.p. 122-125°, -2:5-dicarboxylates; dinitroso-2:5-di-o-, and -p-toluidino-, -dianilino-, and -di-p-anisidino-terephthalic acids; benzoquinone-di-p-tolylimine-, m.p.  $> 300^{\circ}$  (K<sub>2</sub> and Ba salts), -di-o-tolylimine-, -diphenylimine-, m.p.  $274^{\circ}$ (decomp.) ( $K_2$  salt), and -dianisylimine- ( $K_2$  salt), -2 : 5-dicarboxylic acids. The NO-derivative (V), m.p. 283° (darkens from 150°), of 2-anilino-5-hydroxyterephthalic acid (VI) eliminates NO when heated in PhNO<sub>2</sub>; (VI) only could be isolated from the resultant red solution. The NO-derivative of 2-3-naphthylamino-4-hydroxyterephthalic acid (NO-derivative of Et ester) readily loses NO in xylene; the original acid is again isolable from the reddish-brown solution. p-Aminodiphenyl and succinylsuccinic acid in EtOH-AcOH give (cf. loc. cit.) Et 2:5-di-p-diphenylylamino- $\Delta^{1:4}$ -dihydroterephthalate, m.p. 235°, oxidised (I in amyl alcohol) to Et 2: 5-di-p-diphenylylaminoterephthalate, m.p. 234°. H. B.

a-Phenyl-aa'-dimethylsuccinic acid. H. M. CRAWFORD (J. Amer. Chem. Soc., 1934, 56, 139-141). -CNaMe(CO<sub>2</sub>Et)<sub>2</sub> and CHBrPh·CO<sub>2</sub>Et give Et  $\alpha$ -phenylpropane- $\alpha\beta\beta$ -tricarboxylate (I), b.p. 210-217°/ 17 mm., hydrolysed to a-phenyl-a'-methylsuccinic acid. Methylation of (I) could not be effected. a-Phenylpropionitrile [conveniently prepared from CH, Ph. CN (II), MeI, and NaNH, in Et, O; unchanged (II) is removed by condensation with PhCHO], CHBrMe CO2Et, and NaNH2 in Et2O afford Et β-cyano-β-phenyl-α-methylbutyrate, b.p. 172-173°/14 mm., hydrolysed [HBr (const. b.p.)] to a-phenyl-aadimethylsuccinic acid, two forms, m.p.  $159-160^{\circ}$  (Ag salt) and  $170-172^{\circ}$  (III) (Ag salt), separable by fractional crystallisation of the Ca salts. (III) is identical with the acid previously obtained (A., 1928, 523) by oxidation of 3-phenyl-2:3:5:6-tetramethyl- $\Delta^{5}$ -cyclohexene-1 : 4-dione. H. B.

Combination of certain dyes with deoxycholic acid. M. STOCKHOLM and C. L. A. SCHMIDT (Proc. Soc. Exp. Biol. Med., 1933, 30, 877-879).—Compounds of deoxycholic acid with halogenofluoresceins are described. CH. Abs.

Humic acids. I. Determination of carboxyl and phenolic groups. I. UBALDINI and C. SINI-RAMED (Annali Chim. Appl., 1933, 23, 585–597).—For humic acids separated from lignite and peat (B., 1932, 758), determinations have been made of: (1) total acidity, by boiling with 0·2N-KOH-EtOH and determining the residual excess of KOH, and (2) carboxylic acidity, by treating the K humate, suspended in EtOH, with CO<sub>2</sub> and determining the liberated  $K_2CO_3$  by titration:  $2OK\cdot R\cdot CO_2 K + CO_2 + H_2O =$  $2OH\cdot R\cdot CO_2 K + K_2CO_3$ . The total acidity val. found is 492—500, the carboxyl val. 263—267, and the phenol val. (by diff.) 229—232; these indicate a mol. wt. of about 1700. Comparison of these results with those obtained by methylation with CH<sub>2</sub>N<sub>2</sub> shows that such methylation is only partial. T. H. P.

Synthesis of pinastric acid. G. KOLLER and A. KLEIN (Monatsh., 1933, 63, 213—215).—Condensation of equimol. quantities of  $CH_2Ph\cdot CN$  and its *p*-OMederivative with  $Et_2C_2O_4$  and NaOEt affords p-methoxy-pulvinodinitrile,

p-OMe·C<sub>6</sub>H<sub>4</sub>·CH(CN)·CO·CO·CHPh·CN, decomp. 255° (in vac.), acid hydrolysis of which gives mixtures, but with KOH-MeOH affords pinastric acid (A., 1933, 508), identical with the natural product. J. W. B.

Saxatilic and capraric acid. G. KOLLER, A. KLEIN, and H. PÖPE (Monatsh., 1933, 63, 301–310). —Protocapraric acid (I) extracted from *Parmelia* caperata and freed from usnic acid has a mol. formula  $C_{18}H_{14}O_{9}$ , confirmed by condensation (-H<sub>2</sub>O) with  $m \cdot C_{6}H_{4}Br \cdot NH_{2}$  to a bromoanilide  $C_{20}H_{18}O_{8}NBr$ , and by boiling EtOH to an OEt-compound  $C_{20}H_{18}O_{9}$ , decomp. 260°. Since no trace of orcinol is obtained from atranole under the conditions of its fission from (I), both atranole and orcinol nuclei must be present, and



the partial structure (A) is suggested for (I). Fractional extraction of saxatilic acid (II) from *P. saxatilis* gives all fractions of composition  $C_{18}H_{14}O_{10}$ (2  $CO_2H$ ), giving a *di*-m-*bromoanilide*,  $C_{30}H_{24}O_9N_2Br_2$ , decomp. 280° (in vac.), and with boiling EtOH a  $(OEt)_2$ -

derivative  $C_{22}H_{20}O_{10}$ , decomp. 172° (in vac.) (m-bromoanilide). With Zn-NaOH in H<sub>2</sub> (II) gives traces of atranole (3:5-dihydroxy-*p*-tolualdehyde) and an unidentified phenol. The partial formula (B) is suggested for (II), the ether linking being assumed. J. W. B.

Compounds from salicylidene- and hydrocyanosalicylidene-aniline and related substances. G. ROHDE (J. pr. Chem., 1933, [ii], 139, 17–26, 27– 43; cf. A., 1910, i, 775).—The compound (I), m.p. 155—156°, obtained by Schwab (A., 1901, i, 380) by action of KCN on o-OH·C<sub>6</sub>H<sub>4</sub>·CH:NPh (II) is better prepared by interaction of OH·C<sub>6</sub>H<sub>4</sub>·CH(CN)·NHPh

X

(III) [from (II) and HCN] with o-OH·C<sub>6</sub>H<sub>4</sub>·CHO (IV) and Na<sub>2</sub>CO<sub>3</sub> in boiling MeOH (best in CO<sub>2</sub>), and is also obtained from (IV), NH<sub>2</sub>Ph, and KCN. The isomeride (V), m.p. 142—143°, of (III) simultaneously formed is produced by the action of KCN alone on (III) in a yield of 84% of theory. Condensation of this with (II) or (IV) in MeOH gives (I), and with PhCHO the corresponding *CHPh*. derivative, m.p. 146—146·5°, is formed; similarly, it gives the benzenesulphonyl derivative of (I) with o-PhSO<sub>2</sub>·O·C<sub>6</sub>H<sub>4</sub>·CHO. Oxidation of (V) with KMnO<sub>4</sub> gives the nitrile o-OH·C<sub>6</sub>H<sub>4</sub>·C(:NH)·CO·NH<sub>2</sub>, m.p. 175—176°, and resinous matter. The oxazine formula for (I) (loc. cit., 1910) is therefore abandoned, and the formulæ below are assigned to (I) and (V). A compound, m.p. 175-5—176°,

$$C_{6}H_{4}$$
  $O$   $C:N:CH:C_{6}H_{4}OH$   $C_{6}H_{4}$   $O$   $C:NH$   
 $C:NHPh$   $(V)$ 

corresponding with (V) is obtained from the *p*-tolil of (IV), and on acid hydrolysis gives (IV) and the *amide*, *o*-OH·C<sub>6</sub>H<sub>4</sub>·CH(NH·C<sub>6</sub>H<sub>4</sub>Me)·CO·NH<sub>2</sub> (hydrochloride, m.p. 193°). The N-Me derivative of (I), m.p. 166— 166·5° (O-Bz derivative, m.p. 144—144·5°), is similarly obtained from NHPhMe and *o*-OH·C<sub>6</sub>H<sub>4</sub>·CH(OH)·CN or NHPhMe, (IV), and KCN. H. A. P.

Formation of ketones from cycloparaffins in presence of aluminium chloride. N. D. ZELINSKI and E. M. TARASSOVA (Annalen, 1934, 508, 115—143). —Largely a more detailed account of work previously reviewed (A., 1932, 1120). cycloHexane (I) is considered to react with AcCl and AlCl<sub>3</sub> in its cis- and trans-forms. The initial change, especially at lower temp., is dehydrogenation. The cis-form is thus readily converted (at 18—35°) into cyclohexene (II), which then affords  $\Delta^1$ -tetrahydroacetophenone (III) (formed by loss of HCl from the intermediate 1chloro-2-acetylcyclohexane). Dehydrogenation of the trans-form (at 18—70°) gives the dicyclic system (A) which undergoes fission to (B) or (C) [some (C) is also transformed into (II)]; (B) and (C) with AcCl+2H give 2-acetyl-1-methylcyclopentane (IV) and cyclohexyl Me ketone (V), respectively. The production of



2-methylcyclohexanone from (I) and CO (Hopff, A., 1932, 514) is explained by the intermediate formation of (D) and subsequent addition of 2H. Reduction (H<sub>2</sub>, Pd-black, MeOH) of (III) gives [according to the method of prep. of (III)] stereoisomeric forms, b.p. 76—76.5°/27 mm. (semicarbazone, m.p. 171—172°; oxime, m.p. 48°), and b.p. 63°/13 mm. (semicarbazone, m.p. 150—151°; oxime, b.p. 126—128°/27 mm.), of (V); these differ from the (V) obtained by oxidation (CrO<sub>3</sub>) of cyclohexylmethylcarbinol. 2 - Acetyl - 1methyl- $\Delta^1$ -cyclopentene (VI), b.p.  $82^{\circ}/17$  mm. (semicarbazone, m.p.  $212-213^{\circ}$ ), is obtained from methylcyclopentane or -cyclopentene, AcCI, and AlCl<sub>3</sub>; it is reduced (H<sub>2</sub>, Pd-black, EtOH) to 2-acetyl-1-methylcyclopentane, b.p.  $59\cdot8-60^{\circ}/15$  mm. (semicarbazone, m.p. 162°), which, contrary to Unger (A., 1932, 514), could not be obtained in different forms. The (VI) described by Unger (loc. cit.) is (III). H. B.

Compounds containing the carbon ring of  $\beta$ -ionone and several ethylenic linkings. P. KARRER and R. MORF (Helv. Chim. Acta, 1934, 17, 3-7).— $\delta$ -(1:1:3-Trimethyl-2- $\Delta^2$ -cyclohexenyl)- $\beta$ -methylbutadiene- $\alpha$ -carboxylic acid (I) (from the ester, A., 1932, 852) with PCl<sub>3</sub> gives its chloride, converted by ZnMeI into  $\delta$ -(1:1:3-trimethyl-2- $\Delta^2$ -cyclohexenyl)- $\beta$ -methylbutadienyl Me ketone (II) ( $\beta$ -euionone), b.p. 105-106°/0·1 mm., reduced by Al(OPr $\beta$ )<sub>3</sub>-Pr $\beta$ OH to  $\zeta$ -(1:1:3-trimethyl-2- $\Delta^2$ -cyclohexenyl)- $\delta$ -methyl- $\Delta^{\gamma\epsilon}$ -hexadien- $\beta$ -ol (III), b.p. 105°/0·05 mm. With Zn and CH<sub>2</sub>Br·CO<sub>2</sub>Et in C<sub>6</sub>H<sub>6</sub>, (II) affords Et  $\zeta$ -(1:1:3-trimethyl-2- $\Delta^2$ -cyclohexenyl)- $\beta\delta$ -dimethyl- $\Delta^{\alpha\gamma\epsilon}$ -heptatrienoate (IV), b.p. 142-143°/0·15 mm. Repetition of the syntheses with (IV) was not successful: (II), (III), and (IV) all give colours with SbCl<sub>3</sub>-CHCl<sub>3</sub>, but are inactive in vivo. J. W. B.

ω-Nitrophenylglyoxalarylhydrazones. G. D. PARKES and E. H. WILLIAMS (J.C.S., 1934, 67–68). ω-Nitroacetophenone couples with diazonium salts in solution with NaOAc to give: ω-nitrophenylglyoxalphenyl-, m.p. 101°, -p-chloro-, m.p. 134°, -2:4-dichloro-, m.p. 135·5°, -2:5-dichloro-, m.p. 137°, -p-bromo-, m.p. 137°, -2:4-dibromo-, m.p. 139°, -2:4:6-tribromo-, m.p. 111°, -3:4:5-tribromo-, m.p. 169°, and -o-nitro-phenyl-hydrazone, m.p. 118°. The action of Br causes replacement of NO<sub>2</sub> by Br. ω-Bromophenylglyoxal -2:4-dibromophenylhydrazone with NH<sub>3</sub> gives ω-amino-, m.p. 134°, and with NH<sub>2</sub>Ph yields ω-anilino-phenylglyoxal-2:4-dibromophenylhydrazone, m.p. 137°. F. R. S.

Palladium catalyst. III. Reduction of ketones. W. H. HARTUNG and F. S. CROSSLEY (J. Amer. Chem. Soc., 1934, 56, 158—159).—COPhEt is reduced [H<sub>2</sub>, Pd-C (A., 1929, 184), EtOH] to PhPr; CHPhEt•OH could not be isolated even when reduction is interrupted. o-, m-, and p-C<sub>6</sub>H<sub>4</sub>Pr•OH, o-, m-, and p-C<sub>6</sub>H<sub>4</sub>Pr•OMe, and propyl-resorcinol and -pyrocatechol are similarly obtained from the corresponding propionyl derivatives. A Pt-C catalyst is inactive. H. B.

4-Cyano-1-hydrindone. H. HOYER (J. pr. Chem., 1934, [ii], 139, 94—96).— $\beta$ -o-Nitrophenylpropionic acid is converted into its chloride, which is cyclised by AlCl<sub>3</sub> in CS<sub>2</sub>. The resulting 4-*nitro*-1-*hydrindone*, m.p. 104—105° (oxime, m.p. 212—213°), is reduced by Fe(OH)<sub>2</sub> to 4-amino-, m.p. 122—123° (Bz derivative, m.p. 184—185°; oxime, m.p. 180—181°), which is converted (Sandmeyer) into 4-cyano-1hydrindone, m.p. 116—117°. This does not give an aldehyde by Stephen's method and on attempted hydrolysis with aq. AcOH-H<sub>2</sub>SO<sub>4</sub> gives (?) truxenetricarboxylic acid. H. A. P

Ester enolates and keten acetals. XVII. Reactions of ester enolates with acyl halides. H. SCHEIBLER and H. STEIN (J. pr. Chem., 1934, [ii], 139, 105—112; cf. A., 1930, 1037).—Interaction of CHPh:C(OK)·OEt with BzCl gives, in addition to CHPh:C(OBz)·OEt and CHPhBz·CO<sub>2</sub>Et, BzOH and CH<sub>2</sub>Ph·CO<sub>2</sub>H; similarly, ClCO<sub>2</sub>Et gives, in addition to CHPh.C(OEt)·CO<sub>2</sub>Et (I), the *C*-substitution product, CHPh(CO<sub>2</sub>Et)<sub>2</sub>. (I) is not affected by NaOEt, but an additive product is formed with KOEt, which regenerates (I) with dry CO<sub>2</sub>, and with EtOH gives CH<sub>2</sub>Ph·CO<sub>2</sub>Et. Et *iso*butyrate does not give a metal derivative with Na, K, NaOEt, KOEt, or NaNH<sub>2</sub> (II); with (II) the main products are CMe<sub>2</sub>·C(NH<sub>2</sub>)·ONa and di*iso*butyramide. A Na derivative is, however, formed with CPh<sub>3</sub>Na, but after treating this with BzCl only CMe<sub>2</sub>Bz·CO<sub>2</sub>Et was isolated. H. A. P.

Colour and structure of aromatic oximes. (MME.) RAMART-LUCAS (Compt. rend., 1934, 198, 97—99).—The positions of the bands and form of the ultra-violet absorption curves of oximes ArCR:NOH are closely similar to those of the corresponding olefines ArCR:CHR' (R=H, alkyl or aryl; R'=H or Me), although the absorption coeffs. of the latter are smaller, several examples being given. The structure of the absorbing form of oximes derived from such ketones can thus be determined. J. W. B.

Colour and structure of aromatic oximes. (MME.) RAMART-LUCAS (Compt. rend., 1934, 198, 267-269).—Absorption spectra show that oximes of substances of the types,  $CH_2Ph\cdot COAr$ ,  $CHPh_2\cdot COAr$ , and  $CH_2Ph\cdot CO\cdot CO_2Et$ , have the >C:NOH, and not the C:C·NH·OH, structure, resemblance being to the methylene, rather than to the stilbene, analogues.

R. S. C.

Nitration of chalkone. I. TANASESCU and A. GEORGESCU (J. pr. Chem., 1934, [ii], 139, 189—192; cf. Le Fèvre and collaborators, A., 1933, 611; Goldschmidt, A., 1895, i, 422).—Nitration of chalkone gives a mixture of 2- and 4-NO<sub>2</sub>-derivatives (*phenylhydrazones*, m.p. 162—164°, and 148—150°) only. The former is converted by hot NaOH-EtOH into indigotin. H. A. P.

7-Nitrodeoxybenzoin. J. MEISENHEIMER and E. MAHLER (Annalen, 1934, 508, 185-191).-Successive treatment of 7-nitrostilbene (I) with 15% MeOH-KOH, H<sub>2</sub>O, and Br-H<sub>2</sub>O gives an oily product (A) which gradually solidifies (m.p.  $58-68^{\circ}$ ) and is a mixture of stereoisomeric  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -methoxy- $\alpha\beta$ -diphenylethanes (the pure  $\alpha$ -form, m.p. 91°, is obtained by crystallisation from AcOH). Successive treatment of (A) with MeOH-KOH and aq. NH<sub>4</sub>HCO<sub>3</sub> gives 7-nitrodeoxybenzoin  $Me_2$  acetal ( $\alpha$ -nitro- $\beta\beta$ -dimethoxy- $\alpha\beta$ -diphenylethane) (II), m.p. 117—118° [the compound, m.p. 202—203°, described as this by Wieland and Blümlich (A., 1921, i, 554), is benziloxime Me2 acetal], and some 7-nitro-7'-aminostilbene, m.p. 157°. (II) is hydrolysed by 75%  $H_2SO_4$  at 100– 110° to 7-nitrodeoxybenzoin (III), m.p. 73° (Br-deriv-ative, m.p. 91–91.5°), which could not be oximated [fission to benzhydroxamic acid and CH2Ph·NO2 (IV) occurs], is converted by EtOH at 100° into (IV) and EtOBz, and is decomposed by aq.  $NH_3$  to  $NH_2Bz$ . Successive treatment of (A) with MeOH-KOH and conc. HCl gives (mainly) 7-nitro-7'-methoxystilbene,

m.p. 87°, and (I). Unsuccessful attempts to prepare (III) by other methods are summarised.  $NH_2OH,HCl$  in  $C_5H_5N$  is a good oximating reagent; anthraquinonedioxime, decomp. 245–250°, is thus prepared.

H. B.

Possible existence of three 2: 6-dibenzylcyclohexanones. R. CORNUBERT and M. DE DEMO (Compt. rend., 1933, 197, 1656-1658).-Three forms (I), m.p. 122°, (II), m.p. 55°, and (III), m.p. 103° (A., 1931, 161), of 2: 6-dibenzylcyclohexanone have been isolated in previous work and their interconversions directly or by way of various oximes, semicarbazones, tetrahydropyrones, and reduction products are summarised. Catalytic reduction (H2-Pt in Et<sub>2</sub>O) of (I) gives a hexahydro-ketone (IV), m.p. 79° [reduced by Na-EtOH to (V)], and the corresponding sec. alcohols, m.p. 72-73° (phenylurethane, m.p. 149°) and m.p.  $93-94^{\circ}$  (V) (phenylurethane, m.p. 137-138°), whereas (II) gives mainly an alcohol, m.p. 53-56° (phenylurethane, m.p. 102-103°), and 4% of (IV) resulting from slight conversion of (II) into (I) by Pt-black. These results suggest that (I) and (II) are true isomerides. (III) gives a different oxime, m.p. 123°, and no tetrahydropyrone.

J. W. B. Heteropolarity. XXIII. Tetraphenylcyclopentadienone and its reduction products. W. DILTHEY, W. BRAUN, and O. TROSKEN (J. pr. Chem., 1933, [ii], 139, 1–16; cf. A., 1931, 91).  $-\Delta^3 \overline{-2}: 3: 4: 5$ -Tetraphenylcuclopentenone (I) [(enolic) Ac derivative, m.p.  $183^{\circ}$ ] is converted by PCl<sub>5</sub> into its 2-*Cl*-deriv-ative, m.p.  $166^{\circ}$  (decomp.) (cf. J.C.S., 1901, **79**, 1256), which loses HCl at  $180-190^{\circ}$  to give tetraphenylcyclopentadienone (II), which is also formed directly from (I) by prolonged boiling with KOH in MeOH. (I) is formed by reduction of  $\Delta^4$ -3-hydroxy-2:3:4:5tetraphenylcyclopentenone (III) or of (II) with HI and P in boiling AcOH, and is converted by further reduction with Zn-Hg and AcOH into  $\Delta^4$ -2:3:4:5tetraphenylcyclopentenol (IV), m.p. 176°, which is similarly formed from (II) or the derived sec. alcohol (V). (IV) is isomerised to (I) by heating with AcOH in H<sub>2</sub>. Reduction of (III) with Pd-BaSO<sub>4</sub> and H<sub>2</sub> gives  $\Delta^2$ -tetraphenylcyclopentenone (VI), m.p. 163°; with Pt-black (I) and  $\Delta^3: 3\cdot 2: 3: 4: 5: 2': 3': 4': 5'$ octaphenyl-2: 2'-biscyclopentenone, m.p. 228°, are formed in addition. Distillation of the last-named with Zn dust gives (VI); (I), (II), (IV), and (V) give tetraphenylcuclopentadiene. H. A. P. tetraphenylcyclopentadiene.

Dicyclo-[3, 0, 3]-octane-2: 6-dione. L. RUZICKA, A. BORGES DE ALMEIDA, and A. BRACK (Helv. Chim. Acta, 1934, 17, 183-200).-Cyclisation (Na in C<sub>6</sub>H<sub>6</sub>) of Et *n*-butane- $\alpha\beta\beta\delta$ -tetracarboxylate affords a mixture, b.p. 145-150°/0.2 mm. of Et cyclopentanonc-2:3:3- and -2:4:4-tricarboxylate. Similarly, cyclisation of Et n-butane-aßd-tricarboxylate (Kay and Perkin, J.C.S., 1906, 89, 1643, improved) gives a mixture (separated by NaHCO<sub>3</sub>-2N-NaOH) of Et cyclopentanone-2: 3- (I), b.p. 115°/0.1 mm., and -2: 4-(11), b.p. 115°/0·1 mm., -dicarboxylate. (I) with CHCl<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et gives a mixture of Et cyclopentan-1-one-2: 3-dicarboxylate-2-propionate, and Et n-hexane-ayou-tetracarboxylate, separated by hydrolysis with 20% HCl, trans-n-hexane-xy&\_-tetracarboxylic

acid (V), m.p. 202-203°, crystallising. Re-esterification and fractionation of the residue gives the Et ester (III), b.p. 113-115°/0.05 mm., hydrolysed to cyclopentanone-3-carboxylic-2-β-propionic acid (IV), m.p. 119–120°, and the *Et* ester, b.p.  $162-166^{\circ}/0.2$ mm., hydrolysed to cis-n-hexane-ayog-tetracarboxylic acid (VI), m.p. 161.5-162°. Similarly, from (II) are obtained cyclopentanone-4-carboxylic-2-3-propionic acid and n-hexane- $\alpha\beta\delta\zeta$ -tetracarboxylic acid (VII), sinters 140°, m.p. 149—150° (probably a mixture of stereoisomerides). Et  $\alpha$ -cyanoglutarate (improved prep.) with Et *x*-bromoglutarate (VIII) gives  $Et \gamma$ -cyano-n-hexane- $\alpha\gamma\delta\zeta$ -tetracarboxylate, b.p. 152°/0.03 mm. [also obtained by condensation of CH2Cl·CH2·CO2Et with Et α-cyano-n-butane-αβδ-tricarboxylate, b.p. 142°/0.18 mm., from CN.CH2.CO2Et and (VIII)], hydrolysed by 20% HCl to a separable mixture of the trans- and cis-acids identical with (V) and (VI), respectively: (VI) is converted into (V) by 20% HCl at 185°. Condensation of Et propane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate with  $CH_2Cl\cdot CH_2\cdot CO_2Et$  affords Et n-pentane- $\alpha\beta\beta\delta\delta$ -pentacarboxylate, b.p. 158—160°/0·1 mm., which with CH<sub>2</sub>Br·CO<sub>2</sub>Et gives Et n-hexane-αββδδζ-hexacarboxylate, b.p. 173°/0.05 mm., hydrolysed to (VII). Cyclisation of the Et ester of (V) or (VI) with 2.4 atoms of Na gives mainly Etdicyclo-[3, 0, 3]-octane-2: 6-dione-3: 7-dicarboxylate,  $CHR < \underbrace{CO-CH \cdot CH_2}_{CH_2 \cdot CH-CO} > CHR'(IX) (A; R=R'=CO_2Et),$ m.p. 57.5°, and a little Et cyclopentanone-3 : 5-dicarboxylate-2-\beta-propionate, b.p. 169-171°/0.15 mm. [hydrolysed to (IV)], which is the main product when 1.2 atoms of Na is used. Hydrolysis of (IX) with 20% HCl in N<sub>2</sub> or in vac. gives dicyclo-[3, 0, 3]-octane-2:6-dione (X) (A; R=R'=H), b.p. 83°/0·15 mm., m.p. 45° [dioxime, m.p. 201°; dibenzylidene derivative, m.p. 239–240°; di(hydroxymethylene) derivative, m.p. 110° (decomp.) (giving *n*-butane- $\alpha\beta\gamma\delta$ -tetra-carboxylic acid on ozonolysis)]. Hydrolysis of (IX) with KOH-MeOH gives (IV), but with 2N-Na<sub>2</sub>CO<sub>3</sub> in N<sub>2</sub> Et dicyclo-[3, 0, 3]-octane-2 : 6-dione-3-carboxylate (A; R=H, R'=CO<sub>2</sub>Et), b.p. 119°/0·2 mm., and (X) are J. W. B. obtained.

Preparation of 3-phenyl-β-(β'-hydroxy-β'phenylpropionoxy)propionic acid, α-hydroxyγ-keto-α-phenylpentane, and α-hydroxy-γ-ketoα-phenylheptane. M. E. DITZ (Bull. Soc. chim., 1933, 53, [iv], 1286—1288; cf. A., 1931, 848).—Interaction of PhCHO and CH<sub>2</sub>Br·CO<sub>2</sub>Et in presence of Zn (cf. A., 1909, i, 158) affords Et β-hydroxy-β-phenylpropionate, hydrolysed by EtOH-NaOH followed by incomplete acidification to β-phenyl-β-(β'-hydroxy-β'phenylpropionoxy)propionic acid (I), m.p. (+2H<sub>2</sub>O) 188°. (I) is hydrolysed by cold acid to β-hydroxy-βphenylpropionic acid (II) (Ag salt). The amide of (II) (0·25 mol.) and MgEtBr (2 mols.) in Et<sub>2</sub>O during 24 hr. afford α-hydroxy-γ-keto-α-phenylpentane, b.p. 127— 130°/2 mm. (semicarbazone, m.p. 168°). Similarly prepared, α-hydroxy-γ-keto-α-phenylheptane has b.p. about 135°/2 mm. (semicarbazone, m.p. 133°).

J. L. D.

Tautomerism of  $\alpha$ -diketones. I. Phenyl benzyl diketone. E. P. KOHLER and R. P. BARNES (J. Amer. Chem. Soc., 1934, 56, 211–214).—Ph benzyl

diketone (I) is prepared by treatment of  $\alpha$ -benzoyl- $\beta$ phenylethylene oxide with HCl in AcOH and subsequent distillation at 30 mm. in  $N_2$ . The equilibrium mixture obtained when the enolic form, m.p. 89-90° (II), is heated for  $\leq 1$  hr. in soft glass or in presence of a trace of NaOMe at 100° contains 28.5% of (II) (cf. Moureu, A., 1931, 92) (as determined by indirect titration with Br); the vals. at 125°, 145°, and 165° are 25.5, 23.5, and 21%, respectively. Equilibration by a trace of NaOMe in McOH, EtOH, CHCl<sub>3</sub>, and  $C_6H_6$ gives (for 0.1N-solutions) 43, 38, 53, and 39%, respectively, of (II). (II) is oxidised by O<sub>2</sub> in Et<sub>2</sub>O to BzOH and BzCO<sub>2</sub>H. Alkaline solutions of (I) are oxidised rapidly by atm.  $O_2$ , and in such solutions (I) undergoes the benzilic acid rearrangement. (I) and NaOEt in EtOH-Et<sub>2</sub>O give a Na salt (+0.5EtOH), which dissolves in  $Et_2O$  or MeI and then separates in the "anhyd." form. Acetylation (various methods) of (I) gives the O-acetate, b.p. 195-200°/5 mm.; Cacylation does not occur. Methylation (Me<sub>2</sub>SO<sub>4</sub> or MeI and alkali under various conditions) of (II) gives a mixture of O-Me (III), b.p. 180-185°/0.05 mm., m.p. 32°, and C-Me (IV) derivatives; treatment of the mixture with 40% KOH affords a-hydroxy-ab-diphenylbutyric acid, m.p. 179-180° [from (IV) by the benzilic acid rearrangement], and unchanged (III) [obtained in max. yield (80.9%) from the Na salt (V) and Me<sub>2</sub>SO<sub>4</sub> in COMc<sub>2</sub>]. (V) and I in Et<sub>2</sub>O give the *tetraketone*, (COPh·CO·CHPh·)<sub>2</sub>, m.p. 198°, oxidised (alkaline  $H_2O_2$ ) to BzOH and (·CHPh·CO<sub>2</sub>H)<sub>2</sub>. MgPhBr and (I) afford phenylacetyldiphenylcarbinol, m.p. 60°, oxidised (CrO<sub>3</sub>, AcOH) to COPh<sub>2</sub>, CH<sub>2</sub>Ph·CO<sub>2</sub>H, and a little BzOH. The experiments are usually carried out in  $N_2$ . H. B.

Syntheses of 2-acylresorcinols by the "Nidhon" process. I. 2-Benzoylresorcinol. D. B. LIMAYE (Ber., 1934, 67, [B], 12-15).-4-Methylumbelliferone benzoate or a mixture of 4-methylumbelliferone and BzCl is converted by AlCl<sub>3</sub> at 160-170° into 8-benzoyl-4-methylumbelliferone (I), m.p. 210°, and a substance, m.p. 174°, probably the corresponding 6-Bz compound. (I) is transformed by CH2Br CO2Et and NaOEt in boiling EtOH into 7carbethoxymethoxy-8-benzoyl-4-methylcoumarin, m.p. 130°; the corresponding acid, m.p. 203°, is smoothly transformed by NaOAc and boiling Ac<sub>2</sub>O into 3-phenyl-4'-melhyl-7': 8'-furocoumarin, m.p. 170°, showing that Bz in (I) is ortho to OH, and hence occupies position 6 or 8. Treatment of (I) with boiling aq. NaOH leads to 2-benzoylresorcinol (II), m.p. 135°,  $COMe_2$ , and  $CO_2$ ; the position of Bz follows from the non-identity of (II) with 4-benzoylresorcinol, the possible theoretical alternative. (II) condenses with CH<sub>2</sub>Ac·CO<sub>2</sub>Et in presence of conc. H<sub>2</sub>SO<sub>4</sub> to (I); it yields a Me2 ether, m.p. 99°, b.p. 345°, and a dibenzoate, m.p. 115°. The above method of preparing 2-acylresorcinols is termed the Nidhon process. H. W.

[Preparation of] benzoquinone. G. A. KIRKH-GOF, D. F. ALEXEEV, R. Y. ASTROVA, and R. I. GRAYURSKAYA (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 303).—Benzoquinone forms a foam with the gases formed in the NH<sub>2</sub>Ph-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> reaction, whilst other reaction products separate at the bottom of the vessel. CH. ABS. Preparation of 2-iodophenanthraquinone. L. McMASTER and R. S. WOBUS (J. Amer. Chem. Soc., 1934, 56, 164—165).—2-Iodophenanthraquinone, m.p. 223—224° (corr.), is prepared by the Sandmeyer method from 2-aminophenanthraquinone [obtained in 91% yield by reduction (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, aq. NaOH) of the 2-NO<sub>2</sub>derivative] (cf. Brass and Ferber, A., 1922, i, 355). H. B.

Anthraflavone derivatives. H. DE DIESBACH and S. G. QUINZÁ (Helv. Chim. Acta, 1934, 17, 105–113).—With Cl<sub>2</sub> at 50° in conc.  $H_2SO_4$  anthra-flavone CHA:CHA (A=2-anthraquinonyl) (I) gives a Cl<sub>1</sub>-derivative, CHACl·CH<sub>2</sub>A, m.p. 284-286°, whilst with SO<sub>2</sub>Cl<sub>2</sub> in PhNO<sub>2</sub> the dichloride (•CHACl)<sub>2</sub>, not melting at 320°, is obtained contaminated with nuclear chlorinated products from which nuclear Cl is eliminated by heating with Cu in PhNO2. Reduction of (I) with either Al-HCl-AcOH or Al-conc. H<sub>2</sub>SO<sub>4</sub> gives (·CH<sub>2</sub>A)<sub>2</sub> (Eckert, A., 1925, i, 413). Nitration of 4:4'-dimethylbenzil (KNO3-H2SO4 at  $<40^{\circ}$ ) gives its  $3:3'-(NO_2)_2$ -derivative, m.p. 181-182°, reduced (SnCl<sub>2</sub>-HCl) to the  $(NH_2)_2$ -derivative, m.p. 159°, which by the Sandmeyer reaction gives the 3:3'-dinitrile, m.p. 207°, hydrolysed to the 3:3'dicarboxylic acid, m.p. 318-319°, the acid chloride of which condenses with  $C_6H_6$  (AlCl<sub>3</sub>) to give 3:3'dibenzoyl-4: 4'-dimethylbenzil, m.p. 143°. This with  $Cl_2$  at 180–190° in  $C_6H_3Cl_3$  affords di-10 : 10-dichloro-2-anthronylglyoxal, m.p. 185° (decomp.), converted by hot H<sub>2</sub>SO<sub>4</sub> into di-2-anthraquinonylglyoxal (A·CO·)<sub>2</sub>, m.p. 280° (quinoxaline, m.p. 326.5°; monohydrazone, decomp. 260°, m.p. 265°), which with NaOEt at 160° gives αβ-di-2-anthraquinonylethyl alcohol. J. W. B.

Chemical properties of puberulic acid  $C_8H_6O_6$ and a yellow acid  $C_8H_4O_6$ . G. BARGER and O. DORRER (Biochem. J., 1934, 28, 11—15; cf. A., 1932, 651).—Puberulic acid (I) is prepared from the Ac<sub>2</sub> compound (II) by hydrolysis with aq. NH<sub>3</sub>. Sublimation of (I) gives a decarboxylated compound. Treatment of tetramethylpuberulic acid (III) with cold NaOH gives trimethylpuberulic acid, m.p. 204°. No CHO group is present, and the Windaus test (A., 1924, i, 72) is negative. (I) is unsaturated. (II) takes up 12 H on catalytic reduction, whilst (III) takes up 10 H. The acid  $C_8H_4O_6$  could not be decarboxylated nor acetylated, and no CHO group is present. Colour changes on neutralisation resemble those of a  $\psi$ -acid. H. D.

Santonin series. XVIII. Constitution of santonic acid. E. WEDEKIND and O. ENGEL (J. pr. Chem., 1934, [ii], 139, 115—128; cf. A., 1932, 271).— Santonic acid, m.p. 170—172°, is not affected by vac. distillation (cf. A., 1877, i, 470) or by  $H_2$ -PtO<sub>2</sub> in AcOH. It is formed from metasantonin and 10% NaOH at 100°. Its  $H_2$ -derivative (modified prep.), m.p. 190—192°, is converted by Ac<sub>2</sub>O at the b.p. into the Ac<sub>2</sub> derivative, m.p. 232° (Me ester, m.p. 151°), and a (mono)acetyl-lactone (I), m.p. 204°, from both of which it is regenerated on alkaline hydrolysis. Tetrahydrosantonin (II) is converted by boiling 30% KOH into  $\alpha$ -tetrahydrosantonic acid, which is reconverted into the lactone (II) in warm Et<sub>2</sub>O. 30% KOH is without effect on  $\alpha$ -santonin oxide, monochlorosantonin, desmotroposantonin, and artemionic acid. No recognisable products were obtained by dehydrogenation of (I) with Se. H. A. P.

Amber. II. L. SCHMID and F. TADROS (Monatsh., 1933, 63, 210—212).—Direct comparison, after purification through its picrate, of the hydrocarbon  $C_{13}H_{14}$  (I) obtained by Se dehydrogenation of sukzinin (A., 1933, 831) proves it to be  $1:2:5-C_{10}H_5Mc_3$ . Oxidation of (I) with KMnO<sub>4</sub> and methylation of the acid product with  $CH_2N_2$  affords hemimellitic acid (II) as its Me<sub>3</sub> ester, whereas HNO<sub>3</sub> hydrolysis of the residue gives (II), also converted into its imide-acid. J. W. B.

Fenchene series. IV.  $\alpha$ -Fenchene hydrate (methyl- $\alpha$ -fenchocamphorol) and  $\alpha$ - and  $\beta$ -fenchane. G. KOMPFA and S. BECKMANN (Annalen, 1934, 508, 205—214).—dl- $\alpha$ -Fenchocamphorone and MgMeI give dl-methyl- $\alpha$ -fenchocamphorol ( $\alpha$ -fenchene hydrate) (I), b.p. 76—77°/7 mm., 86·5—87°/14 mm., m.p. 46—47° (phenylcarbamate, m.p. 117—118°), which when distilled under atm. pressure loses H<sub>2</sub>O and affords dl- $\alpha$ -fenchene (II), b.p. 154—156°. (I) is also obtained in small yield from dl- $\alpha$ -fenchene hydrochloride, m.p. 36—37° [from (II) and HCl in Et<sub>2</sub>O], and aq. KOH at 50—60°. Reduction (H<sub>2</sub>, colloidal Pd) of (II) gives  $\alpha$ -fenchane (III), b.p. 161—163°/755 mm. dl-isoFenchyl alcohol is dehydrated (KHSO<sub>4</sub>) to dl- $\beta$ -fenchene (IV), b.p. 151—153°, which is simi-

$$\begin{array}{c|c} CH_2 \cdot CH - CH_2 & CMe_2 \cdot CH \cdot CH_2 \\ (III.) & CMe_2 & | & CH_2 & | \\ CH_2 \cdot CH - CHMe & CH_3 - CH \cdot CHMe \end{array}$$
(V.)

larly reduced to dl- $\beta$ -fenchane (V), b.p. 158–160°/ 752 mm. (II) is oxidised (alkaline KMnO<sub>4</sub>) less readily than (IV); the mixture of fenchenes obtained by dehydration (KHSO<sub>4</sub>) of fenchyl alcohol is thus shown to contain 3–4% of (II). H. B.

5- and *π*-Hydroxycamphor and their derivatives. Y. ASAHINA and M. ISHIDATE [with H. SHIMIZU] (Ber., 1934, 67, [B], 71-77; cf. this vol., 79).-5-Ketocamphor (I) is converted by semicarbazide acetate in dil. EtOH at room temp. into the di-, azioe acetate in dil. EtOH at room temp. into the di-, m.p. 295°, and mono-, m.p. 238—240°, -semicarbazone; reduction (Wolff) of the latter affords *d*-borneol, m.p. 203°,  $[\alpha]_{10}^{39}$  +19.8° in abs. EtOH. Treatment of (I) in H<sub>2</sub>O with Na-Hg in presence of CO<sub>2</sub> leads to 5-hydroxycamphor, m.p. 210°,  $[\alpha]_{10}^{39}$  +47.4° in EtOH [semicarbazone (II), m.p. 222° (decomp.); Ac deriv-ative, b.p. 165—167°/22 mm., and its semicarbazone (III), m.p. 237—238° (decomp.)]. (II) or (III) is transformed by NaOEt in EtOH at 170—180° into transformed by NaOEt in EtOH at 170-180° into epiborneol, m.p. 188°,  $[\alpha]_{i}^{17}$  -3.4° in EtOH, oxidised by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in AcOH to d-epicamphor, m.p. 182°,  $[\alpha]_{15}^{17}$  +45.4° in EtOH (semicarbazone, m.p. 235°). trans-z-apoCamphor-7-carboxylic acid is converted by CH<sub>2</sub>N<sub>2</sub> into Me trans-π-apocamphor-7-carboxylate, m.p. 72-73°, the semicarbazone, m.p. 235-236° (decomp.), of which is transformed by the successive action of Na and EtOH and HCl into trans-*π*-hydroxycamphor (IV), 233°,  $[\alpha]_{15}^{15}$  +62.20° in abs. EtOH [semicarbazone (V), m.p. 224-225° (decomp.); Ac derivative, b.p. 176°/4 mm., and its semicarbazone, m.p.  $234-235^{\circ}$  (decomp.)]. Oxidation of (IV) with H<sub>2</sub>SO<sub>4</sub> and Na2Cr2O, yields trans-7-aldehydo---apocamphor, m.p.  $195-196^{\circ}$  (disemicarbazone, m.p.  $\Rightarrow 340^{\circ}$ ).

(V) is converted by NaOEt in EtOH at 170—180° into d- $\pi$ -borneol, m.p. 200.5°,  $[\alpha]_{16}^{16}$  +17.68° in EtOH, oxidised to  $\pi$ -camphor, m.p. 172—173° [semicarbazone, m.p. 214—215° (decomp.)]. The following compounds are obtained similarly from Me cis- $\pi$ apocamphor-7-carboxylate, m.p. 74—75° (semicarbazone, m.p. 259—260°); cis- $\pi$ -hydroxycamphor, m.p. 233—234°,  $[\alpha]_{15}^{16}$  +40.68° in abs. EtOH (semicarbazone, m.p. 216—217°; Ac derivative, b.p. 160°/22 mm., and its semicarbazone, m.p. 210—211°); cis-7-aldehydo- $\pi$ -apocamphor, m.p. 205° (disemicarbazone, m.p. 256°); 1- $\pi$ -borneol, m.p. 200.5°,  $[\alpha]_{15}^{16}$  —16.77° in EtOH (corresponding r-compounds, m.p. 200—200.5°);  $\pi$ -camphor, m.p. 172—173°,  $[\alpha] \pm 0°$  in EtOH. H. W.

**Preparation of camphorquinone.** W. C. EVANS, J. M. RIDGION, and J. L. SIMONSEN (J.C.S., 1934, 137).—Camphor is oxidised by SeO<sub>2</sub>-Ac<sub>2</sub>O to camphorquinone. F. R. S.

Constituents of the volatile oil from the wood of Chamæcyparis formosensis, Matsum. K. KAFUKU and N. ICHIKAWA (Bull. Chem. Soc. Japan, 1933, 8, 371-391; cf. B., 1931, 653).-This oil, 1955, 8, 3/1—391, cf. B., 1951, 053.—1118 off, obtained in 1·1% yield, contains α-pinene, d-cam-phene, α-terpineol, *l*-cadinol,  $C_{20}H_{26}O$ , b.p. 149—152°/ 10 mm.,  $[\alpha]_{16}^{16}$ —33°, allylpyrocatechol, a *phenol*, m.p. 127—128°, and a saturated *acid*,  $C_{10}H_{16}O_2$ , b.p. 146— 147°/7 mm., 263—265°/764 mm. (*NH*<sub>4</sub>, m.p. about 150°, and *Ag* salts; *chloride*, b.p. about 100°/10 mm.), a minute a character behaviored a character behaviored and the comparison of the main of the comparison of the co a primary, saturated alcohol, benihiol (1), C<sub>10</sub>H<sub>18</sub>O, b.p. 106-108°/10 mm.,  $[\alpha]_{D}^{\infty}$  +23.15° [H phthalate, cryst.,  $[\alpha] + 4.55^{\circ}$  in EtOH (Ag salt, decomp. about 165°); formate, b.p. 101–103°/10 mm.,  $[\alpha]_{D}^{\infty} + 20.5^{\circ}$ ; acetate, b.p.  $107 - 108^{\circ}/10 \text{ mm.}, [\alpha]_{D}^{32} + 22.5^{\circ}; benzoate,$ b.p. 161-162°/5 mm., [a]<sup>10</sup><sub>D</sub> +15°; propionate, b.p. 117—120°/10 mm.,  $[\alpha]_{D}^{32} + 14.24^{\circ}$ ; Me ether, b.p. 83— 84°/11 mm., [a], +24°; benihyl chloride (II), b.p. 94- $97^{\circ}/10 \text{ mm.}, [\alpha]_{ii}^{\alpha} + 11^{\circ}, \text{ and iodide (III), an oil]},$ benihinol (IV), an unsaturated primary alcohol,  $C_{10}H_{16}O$ , b.p. 96·3—97·7°/10 mm., 216°/766 mm.,  $[\alpha]_{10}^{10} + 46\cdot8^{\circ}$  [H phthalate, m.p. 107—108° (Ag salt, m.p. 88-90°)], benihinal, an unsaturated aldehyde, m.p. 88—90°)], beninnal, an unsaturated aldenyde,  $C_{10}H_{14}O$ , b.p. 87°/8 mm. [also obtained from (IV) by  $CrO_3$  in AcOH at 15—50°; semicarbazone, m.p. 214— 215°; oxime, m.p. 64—65°], d-sesquibenihene (V),  $C_{15}H_{24}$ , dicyclic, b.p. 127—131°/10 mm.,  $[\alpha]_{19}^{24} + 35.7^{\circ}$ (adds 2 mols. of Br in CCl<sub>4</sub>), and a primary, mono-ethylenic alcohol, probably  $C_{15}H_{24}O$ , b.p. 163°/10 mm., 294°/760 mm.,  $[\alpha]_{19}^{16} - 13.0^{\circ}$ . (I) with alkaline KMnO<sub>4</sub> gives benihic acid, b.p. 193—195°/7 mm., m.p. 175–175:5° (Ag salt) also obtained by CrO<sub>4</sub>-AcOH 175—175.5° (Ag salt), also obtained by  $\text{CrO}_3$ -AcOH together with the aldehyde, benihial, b.p. 76—77.8°/9.5 mm.,  $[\alpha]_{11}^{30} + 15^{\circ}$  (semicarbazone, m.p. 169°,  $[\alpha]_{11}^{30} + 151.6^{\circ}$ , in CHCl<sub>3</sub>; phenylhydrazone, m.p. 122°, [a] +167.5° in CHCl<sub>3</sub>; oxime, an oil), which is better prepared by Beckmann's reagent. (I) is dehydrated by 50%  $H_2SO_4$  at 80–90°, syrupy  $H_3PO_4$  at 100°, or  $ZnCl_2$  at 160-170°, to a hydrocarbon, b.p. about 172-173°,  $[\alpha] 0^{\circ}$ , which, when hydrogenated (Pd), gives a hydrocarbon,  $C_{10}H_{18}$ , b.p. 162°,  $[\alpha]_D^2 + 7.5^\circ$ , also obtained by hydrogenation (Pd) of (II) or (III) (the latter in 10% KOH-EtOH). (V) is stable to Na-amyl alcohol, is racemised by 50% H<sub>2</sub>SO<sub>4</sub>, and with Se gives cadinene; it gives a hydrochloride, m.p. 103-104°, hydrobromide, m.p. 112-114°, and unstable hydriodide, m.p. 117—118°, all inactive, whence NaOAc-AcOH yields the l-form of (V),  $[\alpha]_{U}^{U}$  -40·34°, which regenerates the same inactive halogen derivatives. R. S. C.

Volatile plant materials. I. Atlantone, the fragrant principle of cedarwood oil. A. S. PFAU and P. PLATTNER (Helv. Chim. Acta, 1934, 17, 129–157).—Fractionation of Atlas cedarwood oil gives a mixture of sequiterpenes (50%) containing cadinene, and 30% of a complex mixture of di- and tricyclic sesquiterpene alcohols (partial separation described), including an *alcohol*  $C_{15}H_{26}O$ , m.p.  $92-92\cdot5^{\circ}$ ,  $[\alpha]_{10}^{\infty} + 32\cdot6^{\circ}$  in EtOH, and ketones  $C_{15}H_{22}O$  (I), b.p.  $121-123^{\circ}/1$  mm.,  $\alpha_{p} + 2\cdot48^{\circ}$ , and  $C_{15}H_{22}O_{2}$  (II). The following results show that (I) is a mixture of siomeric  $\alpha$ . (III) and  $\gamma$ - (IV) -allantone. Reduction of (I) with Ni-H<sub>2</sub> at 70° gives hexahydro- $\alpha$ -atlantone, b.p.  $147\cdot5$ —148°/10 mm. (oxime, b.p. 139·5—140°/1 mm.), and tetrahydro- $\gamma$ -atlantone, whereas Na-EtOH gives a mixture (V), b.p. 158—160°/10 mm., of tetrahydro- $\alpha$ -atlantol, dihydro- $\gamma$ -atlantol, and [from (II)] a glycol  $C_{15}H_{26}O_2$ , b.p. 143—145°/1 mm.: (V) is oxidised (KMnO<sub>4</sub>-COMe<sub>2</sub>) to CH<sub>2</sub>Pr<sup>g</sup>·CO<sub>2</sub>H (VI) and a diketo-acid  $C_{15}H_{26}O_{42}$ .

 $[CH_2Pr^{\beta} \cdot C\ddot{O} \cdot CH_2 \cdot CHMe \cdot CH(\cdot CH_2 \cdot CO_2H) \cdot CH_2 \cdot CH_2Ac],$ isolated as the semicarbazone, m.p. 208-209°, of its Me ester. Reduction (Ni-H<sub>2</sub>) of (V) gives a mixture, b.p. 150.5-151°, of hexahydroatlantol and tetrahydro-y-atlantol, oxidised to (VI) and 4-methylcyclohexanone. With boiling aq. EtOH-NaOH (I) gives  $COMe_2$ , dl-4-methyl- $\Delta^3$ -cyclohexenyl Me ketone (VII) (hence the presence of this ketone in the steam-distillation products of the original oil), and a trace of mesityl oxide. Under milder hydrolytic conditions (I) affords  $\beta$ -(4-methyl- $\Delta^3$ -cyclohexenyl)- $\Delta^a$ -propenyl Me ketone, b.p. 125.5-126°/10 mm. (semicarbazone, m.p.  $152 \cdot 5 - 153^{\circ}$ ) [converted by KOH into COMe<sub>2</sub> and (VII)], from (II), and  $\beta$ -(4-methyl- $\Delta^3$ -cyclohexenylidene)-n-propyl Me ketone (as its semicarbazone, m.p. 195-195.5°) from (IV). Ozonolysis of (I) [giving CO(CHO)<sub>2</sub>, COMe<sub>2</sub>, CH<sub>2</sub>O, and HCO<sub>2</sub>H] and of various derived products, and the above results, show that (III) is (A) and (IV) is (B), the structures of

 $\begin{array}{c} \mathbf{CH}_2 \\ \mathbf{CMe} \\ \mathbf{CMe} \\ \mathbf{CH}_2 \end{array} \\ \begin{array}{c} \mathbf{CH} \cdot \mathbf{CO} \cdot \mathbf{CH} \cdot \mathbf{CO} \cdot \mathbf{CH} \cdot \mathbf{CMe}_2 \\ \end{array}$ 

CH (A.)

CH.

- Sister

C:CMe·CH<sub>2</sub>·CO·CH:CMe<sub>2</sub> CH<sub>2</sub> (B.)

the degradation products also being given. In confirmation of this, the (amorphous) semicarbazone from (I) when heated with KOH at 250°/vac. affords  $\alpha$ - and  $\gamma$ -bisabolene, identified as the trihydrochloride. (I) is also present in Himalayan, but not in Lebanon, cedarwood oil. J. W. B.

Orientation in furan nucleus. VII. 2:5-Disubstituted furans. H. GILMAN, N. O. CALLOWAY, and E. W. SMITH (J. Amer. Chem. Soc., 1934, 56, 220–221).—The 4-sulpho-derivative [and not the 3-, as stated by Hill and Palmer (A., 1889, 386)] is obtained by sulphonation of 5-bromo-2-furoic acid, since debromination (Zn) and fusion of the resulting sulphofuroic acid with  $HCO_2Na$  give furan-2: 4-dicarboxylic acid. Et 5-methyl-2-furoate, Ac<sub>2</sub>O, and SnCl<sub>4</sub> in  $C_6H_6$  afford *Et* 4-acetyl-5-methyl-2-furoate (I), m.p. 99°; the free acid, m.p. 235° (decomp.), is oxidised (alkaline KMnO<sub>4</sub>) to 5-methylfuran-2: 4-dicarboxylic acid (II), m.p. 270—272°, decarboxylated to 2-methyl-3-furoic acid. Et 4-bromoacetyl-5-methyl-2-furoate, m.p. 67—68° [from (I) and Br in AcOH-Ac<sub>2</sub>O], and  $C_5H_5N$  give the pyridinium bromide, converted by aq. 15% KOH into (II). If one of the substituents in a 2: 5-disubstituted furan is op-directing and the other is m-directing, an entering group is directed to the  $\beta$ -position adjacent to the former group. H. B.

Diazotisation of an aminofuran. H. GILMAN and G. F. WRIGHT (Rec. trav. chim., 1934, 53, 13— 17).—Et 4-nitro-5-acetamido-2-furoate is reduced by PtO<sub>2</sub>-H<sub>2</sub> in abs. EtOH to the 4-NH<sub>2</sub>-compound, m.p. 160·5°, which with HNO<sub>2</sub> and HCl gives the diazonium salt [ $\beta$ -naphthol derivative, m.p. 223·5—224·5° (decomp.)]. This with Cu gives Et 5-acetamido-2furoate, and with Cu and KCN (in dil. H<sub>2</sub>SO<sub>4</sub>) gives (?) Et 4-hydroxy-5-acetamido-2-furoate, m.p. 143—144°. Et 4-nitro-5-amino-2-furoate (prep. improved) is not extracted from Et<sub>2</sub>O by HCl. Neither this nor Et 5-amino-2-furoate could be diazotised, nor could their picrates, although NH<sub>2</sub>Ph picrate diazotised smoothly in dil. H<sub>2</sub>SO<sub>4</sub>. H. A. P.

Preparation and reactions of furylcarbimides. A. T. BLOMQUIST and H. B. STEVENSON (J. Amer. Chem. Soc., 1934, 56, 146-149).-5-Methyl-2-, m.p. 61-62°, 5-bromo-2-, m.p. 135.5-136°, 2:4-dimethyl-3-, m.p. 144-145°, 2-methyl-3-, m.p. 149.5-150°, and 2:5-dimethyl-3-, m.p. 136-136.3°, -furhydrazides, prepared from the appropriate Et esters and N2H4,H2O at 125-140°, are converted into the corresponding azides, m.p. 35-36°, 66-67°, an oil, 22-23°, and 24-25°, respectively, which when heated in light petroleum (b.p. 90—100°) afford 5-methyl-2-, b.p. 53—54°/35 mm., 5-bromo-2-, b.p. 75°/35 mm., 2:4-dimethyl-3-, b.p. 74—75°/31 mm., 2-methyl-3-, b.p. 42°/15 mm., and 2: 5-dimethyl-3-, b.p. 68°/20 mm., -furylcarbimides. The 3-derivatives are more stable to air and light. The following carbamides, carbamates, and benzfurylamides are obtained from the requisite carbimides and H<sub>2</sub>O, MeOH, and MgPhBr, respectively: s-di-5methyl-2-, m.p. 182°, -2: 4-dimethyl-3-, m.p. 285°, -2methyl-3-, m.p. 227°, and -2 : 5-dimethyl-3-, m.p. 247°, -furylcarbamides; Me 5-methyl-2-, m.p. 64-66°, 2:4-dimethyl-3-, m.p. 95—96°, 2-methyl-3-, b.p. 128°/ 14 mm., and 2:5-dimethyl-3-, b.p. 107°/2·5 mm., -furylcarbamates; benz-5-methyl-2-, m.p. 75—80°, -2:4dimethyl-3-, m.p. 169-170°, and -2-methyl-3-, m.p. 137.8-138°, -furylamides. H. B.

Bromine derivatives of tetrahydropyran. R. PAUL (Compt. rend., 1934, 198, 375–376).—With Br in CCl<sub>4</sub> at  $-15^{\circ}$  dihydropyran (I) affords 2:3-dibromotetrahydropyran, b.p. 96–98°/9 mm., converted by slow distillation into 3-bromo-5:6-dihydropyran, b.p. 63°/22 mm. (corr.), and by long contact with H<sub>2</sub>O into the acetal (CH<sub>2</sub><CH<sub>2</sub>-OCH<sub>4</sub>·CHBr>CH·)O, m.p. 110°. With dry HBr at 0° (I) affords 2-bromotetrahydropyran, b.p. 61°/6 mm. J. W. B.

Dihydro-1:4-pyrans. IV. Synthesis of  $\gamma$ -benzoyl- $\gamma$ -butyrolactone and  $\alpha$ -hydroxy- $\delta$ -benz-

oylvaleric acid. R. C. FUSON, M. E. DAVIS, B. H. WOJCIK, and J. A. V. TURCK (J. Amer. Chem. Soc., 1934, 56, 235–237).—The NaHSO<sub>3</sub> compound of  $\gamma$ -benzoylbutaldehyde (I) [prepared by oxidation (O<sub>3</sub>) of 1-phenyl- $\Delta^1$ -cyclopentene (II)] and aq. NaCN give  $\alpha$ -hydroxy- $\delta$ -benzoylvaleronitrile, m.p. 151–151.5°, hydrolysed (conc. HCl) to the free acid, m.p. 117.5– 118.5° (A., 1932, 279). Oxidation (KMnO<sub>4</sub>) of (I) or (II) affords  $\gamma$ -benzoylbutyric acid, m.p. 126°, which with Br in CCl<sub>4</sub> gives the  $\gamma$ -Br-derivative, m.p. 97–98°; this heated with H<sub>2</sub>O, aq. NaOH, or AgOBz in Et<sub>2</sub>O yields  $\gamma$ -benzoyl- $\gamma$ -butyrolactone, m.p. 78–79°. H. B.

Cyclic compounds containing a carbonyl group. Mechanism of the formation of pyrylium salts from 1:5-diketones. C. F. H. ALLEN and H. R. SALLANS (Canad. J. Res., 1933, 9, 574-582; cf. A., 1931, 845; 1903, i, 115).—Interaction of cyclohexanone with COPh CH:CHPh (I) in EtOH-NaOH affords Ph  $\beta$ -2-cyclohexanonyl- $\beta$ -phenylethyl ketone (II), m.p. 149° [dioxime (III), m.p. 186°; pyrylium ferrichloride, m.p. 161°, perchlorate, m.p. 214° and stannichloride, m.p. 143°], which adds 2 mols. of Grignard reagent (IV), indicating that it is a diketone. In the absence of EtOH-NaOH, a product, C<sub>36</sub>H<sub>34</sub>O<sub>3</sub>, m.p. 167-168° is formed which consumes 3 mols. of (IV). p-Chlorophenyl-\$2-cyclohexanonyl-, m.p. 125-126°, and - \beta-2-(3-methylcyclohexanonyl)- \beta-phenylethyl ketone, m.p. 155-156° (pyrylium ferrichloride, m.p. 133°, perchlorate, m.p. 231°, and stannichloride, m.p. 135°), are described. The additive product of (I) with cyclopentanone affords a pyrylium ferrichloride, m.p. 126°, perchlorate, m.p. 240° (decomp.), and stannichloride, m.p. 161°, whereas that with benzylidene-diacetophenone (cf. A., 1896, i, 556) gives a pyrylium stannichloride, m.p. 205°, and stibnichloride, m.p.  $320^{\circ}$  (decomp.). (II) in boiling EtOH with NH<sub>2</sub>OH,HCl during 3 hr., followed by cold NaOH, affords the *picrate*, m.p. 196° of 2:4-diphenyl-5:6:7:8-tetrahydroquinoline [also formed when (III) is heated with HCl in dry  $C_6H_6$ ]. (II) with conc.  $H_2SO_4$  in cold EtOH during 24 hr., affords mainly a H<sub>2</sub>O-sol. sulphonic acid, some 1: 3-diphenyl-4: 8endocarbonyl- $\Delta^{8}$ <sup>(1)</sup>-cyclooctene (?) (V), m.p. 143° (oxime, m.p. 156°), and an oil, b.p. 155–160°/25 mm., from which a solid (VI), m.p. 151°, isomeric with (V), separates; the stereoisomeride of (VI) is not obtained pure. (II) is unchanged by long boiling with AcCl or Ac<sub>2</sub>O. (V) reacts with 1 mol. of MeMgI; hydrolysis of the Grignard compound (VII) affords 1:3-diphenyl-4:8-endo- $(\alpha - hydroxyethyl) - \Delta^{8(1)}$ -cyclooctene, m.p. 147°, which re-forms (VII) and does not react with Br. (II) in CHCl<sub>3</sub>-MeOH with HBr at room temp. affords 2-methoxy-2:4-diphenylhexa-

hydrobenzopyran (VIII),  $CH_2 \cdot CH_2 \cdot C \cdot CHPh \cdot CH_2$ m.p. 171° [pyrylium ferrichloride identical with that from (II), which suggests that the pyrylium salts are formed via the OH-form of (VIII)] [also obtained from (II) and H<sub>2</sub>SO<sub>4</sub>], which does not react with (IV), NH<sub>2</sub>OH, or KMnO<sub>4</sub>, and is hydrolysed by a trace of H<sub>2</sub>SO<sub>4</sub> in EtOH to (II). (I) with anthrone (cf. A., 1919, i, 25) affords an additive product which yields a monoxime, m.p. 144—145°, but adds 2 mols. of (IV). The menthone analogue affords a monoxime, adds 2 mols. of (IV), and liberates 1 mol. of gas. It is not dehydrated without complete decomp.  $\alpha\varepsilon$ -Diketo- $\alpha\beta$ -diphenyl- $\varepsilon$ -p-diphenylylpentane (A., 1932, 385) affords a pyrylium perchlorate, m.p. 258°, stanni-chloride, m.p. 206°, and stibnichloride, m.p. 233° (decomp.). J. L. D.

Natural coumarins. VIII. Bergaptol, a new component of Calabrian oil of bergamot. E. SPATH and L. SOCIAS. IX. Heraclin. E. SPATH and S. RASCHKA (Ber., 1934, 67, [B], 59-61, 62-63; cf. A., 1933, 1056).-VIII. Treatment of oil of bergamot with KOH-MeOH at room temp. and of the solution with  $H_2O$ -light petroleum gives an aq. portion which on acidification affords bergaptol (I), m.p. 280-282°, transformed by  $CH_2N_2$  in MeOH into bergapten. The possibility that (I) does not exist as such in the oil is excluded by its isolation therefrom by distillation in high vac. and sublimation.

IX. The dried seeds of *Heracleum sphondylium*, L., are extracted with  $\text{Et}_2\text{O}$  and the conc. extract is treated with light petroleum, whereby, after further purification, heraclin (II), m.p. 189–190° (vac.), is isolated. The identity of (II) with bergapten is established by m.p. and mixed m.p. It is proposed to replace the name heraclin by bergapten. H. W.

Plant pigments. LVII. Caricaxanthine, cryptoxanthine, zeaxanthine monopalmitate. P. KARRER and W. SCHLIENTZ (Helv. Chim. Acta, 1934. 17, 55—57).—Caricaxanthine,  $C_{40}H_{56}O$ , m.p. 169° (cf. Yamamoto *et al.*, A., 1933, 1343), is identical (m.p., absorption spectra, feeding experiments) with cryptoxanthine (Kuhn *et al.*, this vol., 70) and is a monohydroxy- $\beta$ -carotene. Partial hydrolysis of physalien affords zeaxanthine monopalmitate, m.p. 148°.

J. W. B.

SKIES

Isomeric 6:6'-di-(2:4-bistrichloromethyl-1: 3-benzdioxinyl)sulphones. F. D. CHATTAWAY and A. E. BELL (J.C.S., 1934, 43-45).-6:6'-Di-(2:4-bistrichloromethyl - 1:3-benzdioxinyl)sulphone, prepared from 4:4'-dihvdroxydiphenylsulphone, chloral hydrate, and H<sub>2</sub>SO<sub>4</sub>, has been isolated in three out of possible six forms,  $\alpha$ -, m.p. 215°,  $\beta$ -, m.p. 240°, and  $\gamma$ -, m.p. 248°. The  $\alpha$ - and  $\gamma$ -compounds are converted by dil. EtOH-KOH into a-, m.p. 241°, y-6: 6'-di(trichloromethyldichloromethylene-1:3and benzdioxinyl)sulphone, m.p. 250°. Each of the isomerides with EtOH-KOH yields 4:4'-diethoxy-3:3'dicarboxydiphenylsulphone (I), m.p. 247°. o-Cresol is converted by heating with H2SO4 into 4: 4'-dihydroxy-3: 3'-dimethyldiphenylsulphone, m.p. 268°, which gives the OEt-compound, m.p. 134° (4'-OH-4-OEt-compound, m.p. 186°), oxidised to 4:4'-diethoxy-3-carboxy-3'-methyldiphenylsulphone, m.p. 211°, or the -3:3'-dicarboxy-compound, identical with (I). 4:4'-Diethoxy-3:3'-dicarbomethoxy-, m.p. 162°, and 4:4'-dihydroxy-3:3'-dicarboxy-diphenylsulphone, m.p. 299°, are described. F. R. S.

Rotenone. XVI. Physiological action of rotenone, deguelin, and rotenone resin. Chemical behaviour of deguelin. S. TAKEI and S. MIYAJIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, 12, 62).—Deguelin,  $[\alpha]_{12}^{ps}$ —23·22°, which has a physiological action on *Cobitis fossilis* weaker than that of

rotenone, yields on hydrolysis with alcoholic alkali βtubaic acid, C12H12O4, m.p. 161°, from which on hydrogenation, dihydro-\beta-tubaic acid, catalytic C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>, m.p. 170°, is obtained identical with the β-dihydrotubaic acid obtained from β-dihydrorotenone W. O. K. by hydrolysis.

Constitution of the colouring matter of Lawsonia alba, Lam., or Indian mehedi. J. B. LAL and S. DUTT (J. Indian Chem. Soc., 1933, 10, 577-582).—Details are given for the isolation of lawsone (I),  $C_{10}H_6O_3$ , m.p. 190° (decomp.) [Ag,  $NH_4$ , decomp. 150–170°, and Pb salts; salt,  $C_{10}H_5O_3Pb$ ·Ac; Ac, m.p. 128–129°, and Br-, m.p. 198°, derivatives; oxime, m.p. 180°; dioxime, m.p. 200° (decomp.); phenylhydrazone, m.p. 229° (decomp.); Et ether, m.p. 126-127°], from the fresh leaves. (I), moist Zn dust, and Ac<sub>2</sub>O afford triacetyldihydrolawsone, m.p. 134.5°; with NH<sub>2</sub>Ph in AcOH, anilinolawsone, C<sub>16</sub>H<sub>11</sub>O<sub>2</sub>N, m.p. 190°, results. Distillation of (I) with Zn dust gives  $C_{10}H_8$ , whilst oxidation (KMnO<sub>4</sub>, dil. NaOH) affords  $o-C_6H_4(CO_2H)_2$ . (I) is 2-hydroxy-1:4naphthaquinone. The lawsone, m.p. 192-195° (decomp.), described by Tommasi (A., 1920, i, 626) is H. B. probably identical with (I).

Structure of cubebin. A. S. GINZBERG and M. G. GERCHIKOV (Bull. Nauch. Issledov. Khim. Farm. Inst., 1931, 214-221).-Rast's method for determining mol. wt. does not give uniform results; b.p. determinations in CHCl<sub>3</sub> indicate the val.  $316\cdot6-323\cdot7$ , corresponding with  $C_{20}H_{20}O_6$ . Primary or sec. OH groups, or double linkings in the side chain, could not be detected. The formula OH.CMe[:(CMeR)2:]O, CH. ABS. where  $R=3: 4-C_6H_3$  CH<sub>2</sub>O<sub>2</sub>, is proposed.

Indigoid dyes. IV. 2:1-Naphthathiophenanthreneindigotin. V. P. C. DUTTA (Ber., 1934, 67, [B], 5-8, 9-12; cf. A., 1933, 1169).-IV. The condensation of 2:1-naphthoxythiophen (I) with phenanthraquinone by HCl in AcOH leads to dyes which are usually more intensely coloured than the



corresponding 1:2-derivat-ives (loc. cit.). The following substances are described : 2: 1 - naphthathiophen - 9' phenanthreneindigotin (A) and its  $4'-NO_2$ ,  $2'-NO_2$ ,  $4:5'-(NO_2)_2$ , 4'-Br,  $2'-NH_2$ ,  $NH_2$ , m.p. >290°,  $4'-NH_2$ ,

m.p. >290°, 2'-OH-, m.p. >290°, and 4-OH-derivatives.

V. The following substances are prepared by condensation of (I) with the requisite ketonic substance by anhyd. Na<sub>2</sub>CO<sub>3</sub> in EtOH; the method is applicable also in the 1: 2-series (loc. cit.): 2: 1-naphthathiophen-3'-indoleindigotin (II) and its 5'-Cl-, 5'-Br-, m.p. ≥295°,



5': 7'-Br2-, m.p. 285-287°, 5'-NO2-, sublimes at 280°, m.p. >295°, -derivatives; 2:1-naphthathiophen-2'-acenaphthyleneindigotin (III), m.p. >295°, and

its 5'-NO2-, m.p. 290-292° after evolving red fumes at 260°, and 5': 6'- $(NO_2)_2$ -, m.p. >295°, -derivatives;



2:1-naphthathiophen - 1 - aceanthryleneindigotin (IV), m.p. >295°; di-2: 1-naphthathiophenethyleneindigotin, R:CH·CH:R, m.p. >290°.

Syntheses of 2-substituted pyrroles and pyrryl sulphides. H. FISCHER and Z. CSUKAS (Annalen, 1934, 508, 167-184).-Opsopyrrolecarboxylic acid (I), HCN, and HCl give (cf. A., 1922, i, 758) β-2-aldehydo-3-methyl-4-pyrrylpropionic acid (II), m.p. 151° [Me ester (III), m.p.  $77^{\circ}$ ], which with  $CH_2(CO_2H)_2$  in EtOH-piperidine affords β-3-methyl-2-ββ-dicarboxy-vinyl-4-pyrrylpropionic acid, m.p. 173° ( $Me_3$  ester, m.p.  $80^{\circ}$ ;  $\beta$ -3-methyl-2- $\beta\beta$ -dicyanovinyl-, decomp.  $251^{\circ}$  [Br-derivative, m.p. 181° (decomp.)], and  $\beta$ -3methyl-2-B-cyano-B-carbethoxyvinyl-, m.p. 176°, -4pyrrylpropionic acids are similarly obtained from CH<sub>2</sub>(CN)<sub>2</sub> and CN·CH<sub>2</sub>·CO<sub>2</sub>Et, respectively. Me β-3methyl-2-33-dicarbethoxyvinyl-4-pyrrylpropionate, m.p. 89°, is prepared from (III) and CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>. β-5-Carbethoxy-2: 3-dimethyl-4-pyrrylpropionic acid and Br in  $Et_2O-AcOH-HCO_2\hat{H}$  give a compound,  $C_{12}H_{16}O_9NBr$ , decomp. 178°, which when crystallised from aq. C<sub>5</sub>H<sub>5</sub>N passes into di-(5-carbethoxy-3-methyl-4-β-carboxyethyl-2-pyrryl)methane, m.p. 277°. β-3-Bromo-2-carbethoxy-5-bromomethyl-4-pyrrylpropionic acid and CHNa(CO2Et)2 in dry C5H5N afford the ester (IV), m.p. 127°. Passage of HCl into a mixture of (I) and CN·CH2·CO2Et in Et2O-CHCl3 gives Et B-keto-B-3-methyl-4-B-

NH (IV.) carboxyethyl - 2 - pyrryl propionate, m.p. 164° (ketimine, m.p. 189°); hydrolysis and decarb-

oxylation of this gives  $\beta$ -2-acetyl-3-methyl-4-pyrrylpropionic acid, m.p. 178°, also prepared from (I), MeCN, and HCl. The oxime (V), m.p. 185°, of (II) is converted by Ac<sub>2</sub>O-KOAe into β-2-cyano-5-acetyl-3-methyl-4pyrrylpropionic acid, m.p. 144°, whilst (V) and SOCl<sub>2</sub> give β-2-chloro-5-cyano-4-methyl-3-pyrrylpropionic acid (VI), m.p. 170°, and di-(5-cyano-4-methyl-3-β-carboxyethyl-2-pyrryl) sulphide, m.p. 249° (decomp.) (Et<sub>2</sub> ester, m.p. 120°). The 5-Cl-derivative, m.p. 175° (decomp.), of (V) is prepared from (V) and  $SO_2Cl_2$  in Et<sub>2</sub>O; it is dehydrated (Ac<sub>2</sub>O-KOAc) to (VI). The 5-Br-derivative (hydrobromide, m.p. 188°) of (V) has m.p. 158°.

Et 2:4-dimethylpyrrole-4-carboxylate (VII) and SCl<sub>2</sub> in Et<sub>2</sub>O give di-(5-carbethoxy-2: 4-dimethyl-3pyrryl) sulphide (VIII), m.p. 252° (free acid, m.p. 193°), in almost quant. yield. (VIII) and Br in AcOH afford a compound, C<sub>8</sub>H<sub>11</sub>O<sub>2</sub>NBr<sub>2</sub>, m.p. 152°; attempted oxidation (H<sub>2</sub>O<sub>2</sub>, AcOH) gives (VII). Di-(5-carbethoxy-4-methyl-3- $\beta$ -carboxyethyl-2-pyrryl) sulphide, m.p. 217° [free acid, m.p. 240° (decomp.) (becomes blue at 210°)], and di-(4-acetyl-5-methyl-3-ethyl-2-pyrryl) sulphide, m.p. 219°, are similarly prepared from the appropriate pyrrole. B-5-Cyano-2: 4-dimethyl-3-
pyrrylpropionic acid, m.p. 153°, is obtained by dehydration (Ac<sub>2</sub>O) of the oxime, m.p. 187° [Cu salt, m.p. 256° (decomp.) (darkens at 180°)], of  $\beta$ -5-aldehydo-2:4-dimethyl-3-pyrrylpropionic acid. 5-Cyano-2:4dimethyl-3-ethylpyrrole (IX) (improved prep. described) and Br in AcOH give a compound,



Br in AcOH give a compound,  $C_9H_{11}N_2Br_3$ , m.p. 139° (decomp.), which when heated with AcOH passes into the 2-*CH*<sub>2</sub>*Br*-derivative. The product from (IX) and excess of SO<sub>2</sub>Cl<sub>2</sub> in Et<sub>2</sub>O is hydrolysed (H<sub>2</sub>O) to 2-cyano-3-methyl-4-ethylpyrrole-5-carboxylic acid, m.p. 228° (decomp.), which when heated at a the compound (X). Hydrolysis of

230-235° affords the compound (X). Hydrolysis of the product from (IX) and 2 mols. of SO<sub>2</sub>Cl<sub>2</sub> gives 5aldehydo-2-cyano-3-methyl-4-ethylpyrrole, m.p. 143°. H. B.

Acyl derivatives of 6-nitro-2-phenylindoxyl. P. RUGGLI, A. ZIMMERMANN, and O. SCHMID (Helv. Chim. Acta, 1934, 17, 9-22).—The pure 3-O-Ac derivative (I), m.p. 191° [a-compound (A., 1921, i, 812) is a slightly impure form : forms mixed crystals with (II)], of 6-nitro-2-phenylindoxyl (II) is obtained by heating (II) with  $Ac_2O$ . With  $Ac_2O$ -NaOAc (I) gives its 1-N: 3-O- $Ac_2$  derivative (III), m.p. 178° (probably identical with the  $\beta$ -derivative, loc. cit.). Hydrolysis (5% EtOH-piperidine) of (III) gives the 1-N-Ac derivative (IV), m.p. 178-180°, reconverted into (III) by boiling Ac<sub>2</sub>O. Similarly, with cold BzCl-C<sub>5</sub>H<sub>5</sub>N, (II) gives its 3-O-Bz derivative (V), m.p. 229°, which with  $BzCl-C_5H_5N$  at 45° gives the 1-N : 3-O- $Bz_2$  derivative (VI), m.p. 204°, giving (V) again on hydrolysis ( $C_5H_5N$ -piperidine). With  $Ac_2O$ -conc.  $H_2SO_4$  at 105° (V) gives the 3-O-Bz-1-N-Ac derivative, m.p. 184°, a very small amount of the isomeric 1-N-Bz-3-O-Ac derivative, m.p. 187—188°, being isolated by the action of  $BzCl-C_5H_5N$  on (I) at 45°. With excess of PhNCO (II) affords its 3-phenylurethane, m.p. 214°, and with ClCO<sub>2</sub>Et-C<sub>5</sub>H<sub>5</sub>N at <5°, its 3carbethoxy-derivative (VII), m.p. 170° [converted by BzCI-C5H5N into (VI)], is obtained. With Ac<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> (VII) gives the 1-acetyl-3-carbethoxyderivative, m.p. 133°, slightly contaminated by (III), but giving (IV) by partial hydrolysis. Reductive acetylation (Zn-Ac<sub>2</sub>O) of (I) gives 3-acetyl-6-acetamido-2-phenylindoxyl, m.p. 220° (picrate, m.p. 188°), the 1-N-Ac derivative, amorphous, m.p. indefinite  $< 100^{\circ}$ , of which is hydrolysed (piperidine-EtOH) to 1-acetyl-6-acetamido-2-phenylindoxyl, J. W. B. darkens 210°, m.p. 217-219°.

Action of ultra-violet light on pyridine. V. Reactions [of photopyridine] with further primary aromatic amines, behaviour of pyridine derivatives in ultra-violet light, and nature of photopyridine. H. FREYTAG (J. pr. Chem., 1933, [ii], 139, 44-62; cf. A., 1933, 1304).—The colour reactions of irradiated  $C_5H_5N$  with further primary amines are described; they are not sufficiently definite to identify the amine in every case but indicate its class. The colours produced are changed to yellow or orange by alkalis, but the original colour is restored by acids. The homologous methylpyridines are affected by irradiation similarly to  $C_5H_5N$ , but to a smaller degree, according to the no. of the groups and their position, and may be identified by the colour given with  $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> after irradiation. Other derivatives (NH<sub>2</sub>, NO<sub>2</sub>, SO<sub>3</sub>H, CO<sub>2</sub>H) also give "photo"-products, that from Et<sub>2</sub> collidinedicarboxylate apparently being the same as from its H<sub>2</sub>derivative. The photo-products are in most cases destroyed by diffused or direct sunlight. Photopyridine is not formed in absence of O<sub>2</sub>, but is not among the products of reaction of O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> with C<sub>5</sub>H<sub>5</sub>N. The colours it gives with arylamines are similar to those of the arylamine derivatives of glutacondialdehyde (I) and show the same behaviour with alkalis and acids. It has •CHO reactions (Schiff) and gives NH<sub>3</sub> with alkalis, and is consequently regarded as the NH<sub>4</sub> derivative of the enolic form of (I), viz., CHO•[CH:CH]<sub>2</sub>•ONH<sub>4</sub>. H. A. P.

Preparation of 2-halogenopyridines from 2-aminopyridine by the diazo-reaction. L. C. CRAIG (J. Amer. Chem. Soc., 1934, 56, 231–232).— Treatment of 2-aminopyridine (I) in 63% HBr (5 mols.) containing Br (3 mols) with aq. NaNO<sub>2</sub> (2·5 mols.) at 0° gives (after addition of aq. NaOH at < 25°) an 87% yield of 2-bromopyridine (II), b.p. 91–92°/25 mm. 2-Iodopyridine, b.p. 93°/13 mm., could not be similarly prepared; it is obtained in 65% yield from the Na *iso*diazotate of (I) and I (1 mol.) in HI (3 mols.) and subsequent basification. (II) warmed with anhyd. CuCN gives 74% of 2-cyanopyridine, b.p. 222·5–223·5° (lit. 212–215°), 118– 120°/25 mm. H. B.

Azopyridines. A. KIRPAL (Ber., 1934, 67, [B], 70-71).-2: 2'-Azopyridine (I), obtained by oxidation of 2-aminopyridine (II) with KOCl (A., 1932, 622), is contaminated by a small amount of 5-chloro-2: 2'-azopyridine (III), m.p. 135°, from which it separated by crystallisation from  $H_2O$ . It is then identical with that prepared by reduction of 2-nitropyridine, so that the supposed isomerism does not exist. (I) yields an octahydrate, m.p. 30°. Oxidation of a mixture of (II) and 5-chloro-2-aminopyridine (IV) by KOCl affords (I), (III), and 5:5'-dichloro-2:2'-azopyridine, m.p. 248°, which is the sole product of the oxidation of (IV).

Complex ferric salts.—See this vol., 241.

Homarine, an animal base. F. A. Hoppe-SEYLER (Z. physiol. Chem., 1933, 222, 105—115).— Homarine (I),  $C_7H_7O_2N$  [hydrochloride (II), decomp. 170—175°; aurichlorides, regular, m.p. 188—190°, irregular, m.p. 138—141°; platinichloride, m.p. 197— 198° (decomp.); picrate, m.p. 155—160° (decomp.); Et ester platinichloride, m.p. 199—206° (decomp.)], a base resembling trigonelline and obtained from lobster, Arca Now, and Arbatia pustulosa (cf. this vol., 96), is the methylbetaine of picolinic acid (III). With conc. HCl at 200°, (II) gives (III) (aurichloride, m.p. 218°). Methylation of (III) with Me<sub>2</sub>SO<sub>4</sub> and aq. Ba(OH)<sub>2</sub> yields (I). Similarly isonicotinic acid gives the methylbetaine [hydrochloride, m.p. 233—234° (decomp.); platinichloride, m.p. 222—223° (decomp.); picrate, m.p. 215—217°]. (I) may arise from lysine. J. H. B.

Quinoline derivatives. XLII. Derivatives of 4'-amino-2-phenylquinoline. H. JOHN [with E. PIETSCH] (J. pr. Chem., 1934, [ii], 139, 97–104). 4'-Amino-2-phenylquinoline, m.p. 136° [ $Ac_2$ , m.p. 153·5°; Bz, m.p. 234°; formyl, m.p. 160°, carbamido-, m.p. > 300°; thiocarbamido-, m.p. 206°, selenocarbamido-, m.p. 217°, CHPh', m.p. 153·5°,  $p \cdot C_6H_4Me \cdot CH'$ , m.p. 171°, p-anisylidene, m.p. 190°, and  $CH_2Ph$ , m.p. 144·5°, derivatives; s-bis-(2-phenyl-4'-quinolyl)-methylenediamine, m.p. 172° (CH<sub>2</sub>O), and -thiocarbamide, m.p. 218° (CS<sub>2</sub>)], is prepared by heating its -4-carboxylic acid (I), m.p. 273° (Me, m.p. 123°, and Et ester, m.p. 145°), at > its m.p. (I) is prepared from p-aminoacetophenone and isatin. H. A. P.

Comparison of the directive powers of elements having consecutive atomic numbers. VI. Examination of further possible comparative cases, and conclusions. (MRS.) C. G. LE FEVRE, R. J. W. LE FEVRE, and J. PEARSON (J.C.S., 1934, 37-43).-Salicylaldehyde (I), COPhPr, and HClO<sub>4</sub> afford 2-phenyl-3-methylbenzopyrylium perchlorate, m.p.  $174-177^{\circ}$ , which gives (HNO<sub>3</sub>) the 2-NO<sub>2</sub>-derivative, m.p.  $248-249^{\circ}$ , also obtained from mnitropropiophenone. Isatin, COPhPr, and NaOH, followed by MeI, yield 2-phenyl-3-methyl-N-methoguinolinium methiodide, converted into the picrate, m.p. 169—170°. 2-Hydroxy-α-phenylstyryl Me ketone, m.p. 180—181°, from CH<sub>2</sub>Ph·COMe (II), (I), and  $C_5H_{11}N$ , could not be caused to undergo ring closure. (I), (II), HClO<sub>4</sub>, and HCl form 3-phenyl-2-methylbenzopyrylium perchlorate, m.p. 189—191°, which does not give a pure nitration product.  $\beta$ -Naphthol-1-alde-hyde (III), COPhMe, HClO<sub>4</sub>, and HCl afford 2-phenyla-naphthapyrylium perchlorate, m.p. 216-220°. In a competition experiment of (III) and (I) for a deficiency of COPhMe, the former is more reactive. (II) and isatin give 3-phenyl-2-methylquinoline-4-carboxylic acid, m.p.  $> 250^{\circ}$ , which after distillation with Ca(OH)<sub>2</sub> yields a methopicrate, m.p. 170-175°.

(I), p-methylacetophenone (IV), and KOH form salicylidene - 4 - methylacetophenone, m.p. 158-159°, evelised by HCl-AcOH to 2-p-tolylbenzopyrylium perchlorate, m.p. 148-150°, which is nitrated to 3'-nitro-2-phenyl-4'-methylbenzopyrylium perchlorate, m.p. 199°, also obtained from the appropriate nitromethylacetophenone. Isatin, (IV), and NaOH afford 2-p-tolylquinoline-4-carboxylic acid, decarboxylated to 2-p-tolylquinoline, m.p. 82-83° (methosulphate, m.p. 158-159°), the methopicrate, m.p. 157-158°, of which is nitrated to the m-NO2-compound, m.p. 192-194°. o-Hydroxystyryl Me ketone and HClO<sub>4</sub>-HCl give 2-methylbenzopyrylium perchlorate, m.p. 153-158°, which cannot be nitrated. 2'-Hydroxy-2styrylbenzopyrylium perchlorate is dinitrated. Quinaldine methosulphate is nitrated and forms with pierie acid 75% of 5-nitro-2-methylquinoline methopicrate, m.p. 149-151°, also obtained from 5-nitroquinaldine. 2 - o - Hydroxy - 3 - methylbenzopyrylium perchlorate gives a  $(NO_2)_2$ -derivative, decomp. > 150°. Benzo-pyrylium ferrichloride with HNO<sub>3</sub> is nitrated and oxidised to dinitrosalicylic acid. 5-Nitrosalicylaldehyde, COPhMe, and HClO<sub>4</sub>-HCl give a salt, m.p. 180-185°, whilst the 3-NO2-compound yields ,3-nitro-2hydroxychalkone, m.p. 163-164. The conclusion is reached that experimental comparison of an oxonium salt with an NH4 salt is impracticable. F. R. S.

Phenanthridine series. III. Meso-substituted derivatives. L. P. WALLS (J.C.S., 1934, 104-109).-9-Bromophenanthridine (I), m.p. 123-124°, is prepared from phenanthridine, POBr<sub>3</sub>, and PBr<sub>a</sub>. The prep. of aliphatic diamines (Gabriel) is improved by isolating the phthalodialkylaminoethylimide :  $phthalo-\beta$ -diethyl-, m.p. 46-47°, and -diiso-butyl-aminoethylimide, m.p. 52°. (I) and  $\beta$ -aminotriethylamine in PhOH yield N-phenylphenanthridone, m.p. 118-119°; (I) and excess of the amine at 120° give on subsequent addition of HCl 9-β-diethylaminoethylaminophenanthridine dihydrochloride (+EtOH) or (+3H<sub>2</sub>O), m.p. 238—243° (dipicrate, m.p. 208—211°). 9-β-Piperidino- (+2H<sub>2</sub>O), m.p. 265—270° [dinitrate, m.p. 130—135° (decomp.)], and -diisobutylaminoethylaminophenanthridine dihydrochloride (+4H<sub>2</sub>O), m.p. 142-144°, are similarly obtained. The dihydrochlorides are inactive therapeutically. 9-88'-Dihydroxyisopropylphenanthridine, m.p. 129.5° (Ac, derivative, m.p. 93°), prepared from 9-methylphenanthridine, aq. CH<sub>2</sub>O, and EtOH, is oxidised (Kiliani's dichromate mixture) to Na phenanthridine-9-carboxylate (+3H<sub>2</sub>O) (acid; Et ester, m.p. 57-58°). o-Xenylamine and Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> give s-di-o-xenyloxamide, m.p. 233-235°, and Et o-xenyloxamate, m.p. 112-113°, whilst the amine and H2C2O4 afford o-xenyloxamic acid (II), m.p. 155–158° (decomp.). (II) and POCl<sub>3</sub> give s-di-o-xenyloxamide, a substance, m.p.  $> 310^\circ$ , sol. in AcOH, and a substance  $(C_{13}H_8ON)_2$ , m.p. > 310°, insol. in AcOH, which with Zn dust affords phenanthridine. o-Xenylamine and the appropriate acid chloride form di-, m.p. 104-106°, and tri-chloroaceto-xenylamide, m.p. 92-94°, which does not react with F. R. S. POCl<sub>3</sub>.

Spasmolytics of papaverine type. K. H. SLOTTA and G. HABERLAND (Angew. Chem., 1933, 46, 766-771).-Derivatives of C<sub>2</sub>H<sub>4</sub>Ph·NH<sub>2</sub>, prepared by electrolytic reduction of  $\omega$ -nitrostyrenes in EtOH-AcOH-HCl using Pb electrodes, are condensed with alkoxybenzoyl chlorides, and the resulting amides cyclised by POCl<sub>a</sub> to dihydroisoquinolines, which are finally dehydrogenated by Pd in boiling xylene. The following are described: 3:4-diethoxyphenylethylamine, b.p. 177°/20 mm. [hydrochloride, m.p. 200° (sinters 108°); picrate, m.p. 145°]; 3':4':5'-tri-methoxybenz- $\beta$ -3:4-diethoxy-, m.p. 132°, -3:4:5-trimethoxy-, m.p. 179°, and -3:4-dimethoxy-phenyl-ethylamide, m.p. 130°; 3':4'-methylenedioxybenz- $\beta$ -3: 4-methylenedioxyphenylethylamide, m.p. 127°; 3': 4'dimethoxybenz- $\beta$ -3: 4-dimethoxy-, m.p. 142°, 3': 4'-di-ethoxybenz- $\beta$ -3: 4-diethoxy-, m.p. 145°, and 3': 4': 5'triethoxybenz-\beta-3: 4-diethoxy-phenylethylamide, m.p. 88°; also the following derivatives of 1-phenyliso-



(I.)  $(1)^{(1)} (1)^{(1)}$ 

[hydrochloride,  $(+1H_2O)$ , m.p. 203°; 3:4-H<sub>2</sub>-compound (hydrochloride, m.p. 140—145°, 180°)], 6:7:8:3':4':5'-hexamethoxy- [hydrochloride, m.p. 188°; 3:4-H<sub>2</sub>-compound  $(+1H_2O)$ , m.p. 122° (hydrochloride, m.p. 108°)], 6:7:3':4':5'-pentamethoxy-, m.p. 160° [hydrochloride, m.p. 218°; 3:4-H<sub>2</sub>-compound  $(+1H_2O)$ , m.p. 160° (hydrochloride, m.p. 215°; picrate, m.p. 182°)], and 6:7:3':4':5'-pentaethoxy-1-phenylisoquinoline {hydrochloride (+0.5H<sub>2</sub>O), m.p. 160—167°, 196°; 3:4-H<sub>2</sub>-compound, m.p. 103° [hydrochloride (+1.5H<sub>2</sub>O), m.p. 218°]}. (II) has twice the pharmacological activity of papaverine. The dihydroquinoline bases form H<sub>2</sub>O-insol. nitrates.

H. A. P.

Effect of constitution on rearrangement of phenylhydrazones of unsymmetrically substituted distyryl ketones. L. C. RAIFORD and E. L. HILL (J. Amer. Chem. Soc., 1934, 56, 174-176; cf. A., 1933, 514).—The phenylhydrazone, m.p. 162—163°, of styryl p-dimethylaminostyryl ketone is rearranged by boiling AcOH to 1-phenyl-5-p-dimethylaminophenyl-3-styrylpyrazoline, m.p. 133—134°. 1-Phenyl-5-p-tolyl-, m.p. 167—168°, -5-anisyl-, m.p. 124°, -5-p-phenetyl-, m.p. 126—127°, -5-p-propoxyphenyl-, m.p. 118—119°, and -5-3': 4'-methylenedioxyphenyl-, m.p. 167—168°, -3-styrylpyrazolines are obtained directly from the requisite ketone and NHPh·NH2. p-Dimethylaminostyryl Me ketone similarly gives 1phenyl - 5 - p - dimethylaminophenyl - 3 - methylpyrazoline, m.p. 166-167°. 1-Phenyl-5-anisyl-, m.p. 196-197° -5-p-phenetyl-, m.p. 163-164°, and -5-p-dimethyl-aminophenyl-, m.p. 141-142°, -pyrazole-3-carboxylic acids are obtained by oxidation (KMnO<sub>4</sub>) of the appropriate pyrazolines. Styryl p-methyl-, m.p. 107-108°, p-ethoxy-, m.p. 77-78°, and p-propoxy-, m.p. 119-120°, -styryl ketones are prepared from CHPh:CH·COMe, C6H.R·CHO, and aq. EtOH-NaOH. H. B.

Structure and rearrangement of N-acylpyrazoles. K. von Auwers and K. DIETRICH [with R. NEUMANN] (J. pr. Chem., 1934, [ii], 139, 65-93).-The N-acylpyrazoles formed by cyclisation of the acylhydrazones of 3-diketones under mild conditions (POCl<sub>3</sub> at 0°) are converted by heat (at the b.p./vac.) into their more stable N'-isomerides, also obtained by direct acylation of the pyrazole. Thus cyclisation of the acetylhydrazone, m.p. 114-116°, of CH,BzAc gives 1-acetyl-5-phenyl-3-methylpyrazole, m.p. 45.5-46.5°, converted at its b.p./vac. into 1-acetyl-3-phenyl-5-methylpyrazole, m.p. 41°. The corresponding benzoylhydrazone, m.p. 130-132°. also obtained from CHBz.CMe OMe or CHBz.CMe OEt and NH2 NHBz, is, however, cyclised by POCl3 to 1-benzoyl-3-phenyl-5-methylpyrazole, m.p. 83-84°, but the unstable isomeric 1-benzoyl-5-phenyl-3-methylmyrazole, m.p. 88-89°, is obtained in moderate yield from OMe CPh:CH COMe and NH2 NHBz in abs. EtOH at 40-50° in absence of a condensing agent. The following are also described : benzoylacetone-propionyl-, m.p. 87-88°, -n-butyryl-, m.p. 61-63°, -phenylacetyl-, m.p. 94—96°, -carbethoxy-, m.p. 104— 105°, -o-, m.p. 113—114°, -m-, m.p. 111°, and -p-toluoyl-, m.p. 148—150°; hydroxymethyleneacetone-benzoyl-, m.p. 59-60°, and -o-nitrobenzoyl-, m.p. 137-139°: hydroxymethyleneacetophenone-benzoyl-, m.p. 148°,

-o-nitrobenzoyl-, m.p. 151-152°, and -carbethoxy-, m.p. 117-118.5°; and Et benzoylpyruvate acetyl-(amorphous), benzoyl-, m.p. 119°, and carbomethoxyhydrazone, m.p.  $88-89^{\circ}$ : 1-propionyl-5-phenyl-3-methyl-, m.p.  $33-34^{\circ}$ ; 1-propionyl-5-phenyl-5-methyl-, m.p.  $77-78\cdot5^{\circ}$ ; 1-n-butyryl-, m.p.  $34-35^{\circ}$ , 1-phenylacetyl-, m.p.  $104\cdot5-105\cdot5^{\circ}$ , 1-carbethoxy-, m.p.  $50\cdot5-51\cdot5^{\circ}$  (?),  $65-66^{\circ}$ , 1-o-, m.p.  $63-65^{\circ}$ , 1-m. m.p.  $79-80^{\circ}$ , and 1.p. tohenel 2-methyl-1-m-, m.p. 79-80°, and 1-p-toluoyl-5-phenyl-3-methylpyrazole, m.p. 78—79° (decomp. 83—85°); 1-prop-ionyl-, m.p. 77—78.5°; 1-n-butyryl-, m.p. 72—72.5°, b.p. 150-152°/10 mm., 1-phenylacetyl-, m.p. 58-59.5°, 1-carbethoxy-, m.p. 73.5-74.5°, b.p. 193°/10 mm., 1-o-, m.p. 36.5-37.5°, 1-p-, m.p. 68-70°, and 1-m-toluoyl-3-phenyl-5-methylpyrazole, m.p. 56-57°, b.p. 224-226°/11 mm.; 1-o-nitrobenzoyl-3-, m.p. 118.5-119.5°, and -5-methylpyrazole, m.p. 130°, b.p. 199—201°/13 mm.; 1-o-nitrobenzoyl-4:5-, m.p. 118— 120°, and -3: 4-dimethylpyrazole, m.p. 149–150°; 1-0-nitrobenzoyl-5-, m.p. 151–152°, and -3-phenylpyrazole, m.p.  $107 \cdot 5 - 108 \cdot 5^{\circ}$ , b.p.  $208 - 210^{\circ}/15$  mm.; Et 5., m.p.  $37 - 39^{\circ}$  (?),  $58 - 59^{\circ}$ , and 3-phenylpyrazole-1-carboxylate, b.p.  $192^{\circ}/13$  mm.; Et 5.-methylpyrazole-1: 3-dicarboxylate, b.p.  $178 - 179^{\circ}/13$  mm.; Et 1-0-1: 5-atcarboxylate, b.p. 178-179 [13 mm.; Et 1-0-nitrobenzoyl-, m.p. 107°, and 1-carbamyl-5-methyl-pyrazole-3-carboxylate, m.p. 131°; Et 1-acetyl-, m.p. 109-110°, and 1-carbomethoxy-3(or 5)-phenylpyrazole-5(or 3)-carboxylate, m.p. 80-81°. The structure assigned to many of these acylpyrazoles is confirmed by their optical exaltations. Interaction of 3-phenyl-5-methylpyrazole hydrochloride with KCNO in AcOH gives the known -1-carboxylamide, m.p. 154-156°. Attempts at cyclisation of the acetyl- and benzoylhydrazones of COPh·CH:CH·OH and of the acetylhydrazone of COMe·CH2·CO·CO2Et gave only the corresponding deacylated pyrazoles. H. A. P.

Action of alkali and ammonia on 2:4-dialkoxypyrimidines. G. E. HILBERT and E. F. JANSEN (J. Amer. Chem. Soc., 1934, 56, 134-139).-5-Bromouracil (I) (improved prep. given), PCl<sub>5</sub>, and POCl<sub>3</sub> at 125° give 2:4-dichloro-5-bromopyrimidine, b.p. 145-147°/78 mm., which with MeOH-NaOMe affords 5-bromo-2: 4-dimethoxypyrimidine (II), m.p. 63-64°, and Na a-bromo-3-methylisocarbamidoacrylate (III), NH<sub>2</sub>·C(OMe):N·CH:CBr·CO<sub>2</sub>Na, m.p. 248° (decomp.). (II) is separable by sublimation. (III) is converted by conc. HCl into (I) and by aq. AcOH into 5-bromo-4-keto-2-methoxy-3: 4-dihydropyrimidine, m.p. 190° (decomp.), hydrolysed (conc. HCl) to (I). (III) is also obtained from (II) and aq. EtOH-NaOH. (II) and MeOH-NH<sub>3</sub> at 80° give 5-bromo-4-amino-2-methoxypyrimidine, m.p. 134-136°, hydrolysed (conc. HCl) to 5-bromocytosine (IV), decomp. 245-255° (according to rate of heating). (IV) and 5:5-dibromo - 6 - hydroxy - 5 : 6 - dihydrocytosine hydrobromide, decomp. 175-180°, are obtained from cytosine and Br in H<sub>2</sub>O. 5-Bromo-2: 4-diethoxypyrimidine, m.p. 72-74°, and 5-bromo-4-keto-2-ethoxy-3: 4-dihydropyrimidine, m.p. 163° (sinters at 160°), are also prepared. All m.p. are corr. H. B.

Alkylation of pyrimidines. Attempt to prepare 1-glucosidocytosine. G. E. HILBERT (J. Amer. Chem. Soc., 1934, 56, 190-195).-4-Amino-2-methoxypyrimidine (I), m.p. 170° (sinters at 168°).

rearranges at 180° to 1-methylcytosine (II), m.p. 303° (decomp.) (lit. 278-279°), which with Br in H<sub>2</sub>O gives 5-bromo-1-methyluracil, m.p. 272-274° (decomp.) (lit. 255-260°). (I) and MeI in cold MeOH afford the 1-methiodide (III), m.p. 128° (decomp.), re-solidifying with m.p. 230-235° (sinters at 190°), which is converted by aq. Ag<sub>2</sub>SO<sub>4</sub>, warm cone. HCl, or boiling EtOH into (II). (III) heated at 130-135° gives (II), a little 1:3-dimethylcytosine (IV), m.p. 147.5°, and (probably) the impure methiodide (V) (below). Prolonged interaction of (II) and MeOH-McI affords the 3-methiodide (V), m.p. 265-266° (decomp.), which is converted by aq. NaOH into (IV). (IV) and Br in H<sub>2</sub>O give 5-bromo-1:3-dimethyluracil. The impure hydrobromides of (I) and (II) are the only cryst. products isolable from (I) and acetobromoglucose in MeNO<sub>2</sub>. Improved methods of prep. (cf. A., 1930, 789) of cytosine and isocytosine are given. All m.p. are corr. H. B.

Pyrimidines. CXL. Pyrimidines derived from carbethoxymalonaldehyde. E. DYER and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 222-225).—Et  $\beta\beta$ -diethoxypropionate, b.p.  $65^{\circ}/2$  mm. (from CHO·CHNa·CO2Ét and EtOH-HCl), HCO2Et, and Na in Et<sub>2</sub>O give carbethoxymalonaldehyde (as Na salt) (I)  $[Cu \text{ salt } (+2H_2O); K \text{ salt, m.p. } 264^{\circ} (\text{decomp.}), \text{ obtained by hydrolysis } (EtOH-KOH) of (II) (below)]. (I) and NHPh·NH<sub>2</sub> in AcOH give Et$ 1-phenylpyrazole-4-carboxylate, m.p. 99—100° (all m.p. are corr.) (lit. 96—97°), whilst (I) and SEt-C(:NH)·NH<sub>2</sub>,HBr in H<sub>2</sub>O afford an additive compound (II), SEt·C(:NH)·NH<sub>2</sub>,CHO·C(CO<sub>2</sub>Et):CH·OH, in.p. 143.5-144.5° (decomp.), and a little Et 2-ethylthiolpyrimidine-5-carboxylate (III), m.p. 47-48° (free acid, m.p. 182-183°). (II) is dehydrated (Ac.O at 100°) to (III). Hydrolysis (conc. HCl) of (III) gives 2-ketopyrimidine-5-carboxylic acid (+H2O), darkens >220°; esterification (EtOH-HCl) of this affords the Et ester (+H<sub>2</sub>O) (IV), m.p. 163-164°, and a substance, m.p. 186-187°. (I) and  $CO(NH_2)_2$  in AcOH give Et a-formyl-\beta-carbamidopropionate, m.p. 175° (decomp.), converted by EtOH-NaOEt into (IV) (poor yield). Et  $\alpha$ -formyl- $\beta$ -thiocarbamidopropionate heated at 150-160°/3 mm. affords Et 2-thiopyrimidine-5-carboxylate, m.p. 214-216° (decomp.) (2-CO<sub>2</sub>H·CH<sub>2</sub>· derivative, m.p. 175-176.5°).

H. B.

Derivatives of piperazine. I. C. B. POLLARD and D. E. ADELSON (J. Amer. Chem. Soc., 1934, 56, 150).—The following are described : 1:4-diphenylacetyl-, m.p. 150—151° (all m.p. are corr.), 1:4-di- $\beta$ -phenylpropionyl-, m.p. 122·5—123°, and 1:4-dianisoyl-, m.p. 192·5—193·5°, -piperazine; piperazine phenylacetate, m.p. 146·5—147·5°,  $\beta$ -phenylpropionate, m.p. 150·5—151·5°, anisate, m.p. 172—174°, ethylmalonate, m.p. 144°, H malonate, m.p. 180° (decomp.), and H diethylmalonate, m.p. 80—81°. H. B.

Synthesis of pyrazine by catalytic dehydrogenation of ethanolamine. J. G. ASTON, T. E. PETERSON, and J. HOLOWCHAK (J. Amer. Chem. Soc., 1934, 56, 153—154).—Pyrazine, b.p. 112—114°/730 mm., m.p. 48° (mercurichloride), is obtained in 5.6% yield when NH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH is passed over finelydivided Cu at 300°; smaller amounts are formed using Cu-ZnO and ZnO-Na<sub>2</sub>CO<sub>3</sub> catalysts. The catalyst rapidly becomes inactive owing to the formation of resin. H. B.

Benzoyl derivatives of indigo. II. H. DE DIESBACH, E. DE BIE, and F. RUBLI (Helv. Chim. Acta, 1934, 17, 113—128).—Correction and extension of results previously published (A., 1933, 285). The base given as  $C_{14}H_{10}N_2$ , obtained by NaOH-fusion of Ciba-yellow (I), is actually  $C_{15}H_{10}N_2$  (II), m.p. 332°, giving a compound  $C_{15}H_9O_2N_3$  (not  $C_{13}H_8O_5N_4$ ) with HNO<sub>3</sub> and oxidised (CrO<sub>3</sub>-AcOH) to an acid  $C_{13}H_8O_4N_2$ (not  $C_{12}H_8O_5N_2$ ), m.p. 325° (decomp.) (probably A;  $R=CO_2H$ ), decarboxylated at 325°/vac. to a base,  $C_{11}H_8O_2$ , m.p. 293—294° (A; R=H), from which oxalylanthranilic acid (III) is obtained by KMnO<sub>4</sub>



oxidation, and 4-hydroxyquinoline-3-carboxylic acid, with HNO<sub>3</sub> (d 1·4). (II) is therefore 3:4-indologuin-oline (A; RR=>C<sub>6</sub>H<sub>4</sub>). The main fusion product, C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub> (IV), sublimes about 430° (accompanied by a small amount of a tautomeride, m.p. about 400°), with HNO<sub>3</sub> gives  $C_{15}H_8O_6N_4$  (not  $C_{13}$ ) +2 mols. quinoline, and solvent-free, and is oxidised (KMnO<sub>4</sub>) to (III) and its constituents. With  $PCl_5$  (IV) gives the dichloride  $C_{15}H_8N_2Cl_2$  (V) (B; R=R'=Cl), accompanied by a  $Cl_1$ -derivative. Both Cl atoms in (V) are labile, one more readily so. Thus with aq. EtOH-NaOH (IV) is regenerated : with hot NH<sub>2</sub>Ph- $C_6H_6$  a monoanilino-derivative, m.p. 195° (B; R = Cl; R' = NHPh), is obtained, but with boiling  $NH_{2}Ph$  a dianilino-compound, m.p. 284° (B; R= R'=NHPh), results. Reduction of (V) (various reagents) gave inconclusive results, but with conc. aq. NH<sub>3</sub>-Cu<sub>2</sub>Cl<sub>2</sub> a small yield of an amino-hydroxyderivative, C<sub>15</sub>H<sub>11</sub>ON<sub>3</sub>, m.p. 285°, is obtained. On the basis of the structure of (II), (IV) is probably B (R=R'=OH), the least labile Cl being that in position 2 in the quinoline nucleus. The results of Hope et al. (A., 1933, 75) are explained by reduction occurring with the steel tube used. Fusion of Hochst-yellow R (VI) with NaOH at 245-255° gives BzOH, o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (VII), and a base C<sub>16</sub>H<sub>9</sub>O<sub>2</sub>N, m.p. 248° (VIII) [oxidised to (VII)], converted by Me<sub>2</sub>SO<sub>4</sub>-NaOH into the Me ester C<sub>17</sub>H<sub>13</sub>O<sub>3</sub>N+0.5H<sub>2</sub>O and anhyd., m.p. 189°, of the corresponding OH-compound, probably Me 3-hydroxy-2-phenylquinoline-2'carboxylate, (VIII) being the corresponding lactone.





fusion of (VI) at 140° gives a new form of (VI), m.p. 240—242°, in which the OH has migrated from position 4 to 3. Heating (VI) with 10% NaOH in a Cu autoclave at 220° gives BzOH, (VII), and a substance,  $C_{16}H_9O_2N$ , m.p. 228°. The structures C and D are proposed for (I) and (VI), respectively, related compounds also being formulated. J. W. B.

6:8-Dibromobenzoylenecarbamide [6:8-dibromo-2:4-diketo-1:2:3:4-tetrahydroquinazoline] and constitution of dinitrobenzoylenecarbamide. F. E. SHEIBLEY and D. P. TURNER (J. Amer. Chem. Soc., 1933, 55, 4918-4923).-The dinitro-2: 4-diketo -1:2:3:4-tetrahydroquinazoline (I) of Bogert and Scatchard (A., 1916, i, 672; 1920, i, 184) is converted through the (NH2)2-derivative into 6: 8-dibromo - 2: 4-diketo - 1: 2: 3: 4-tetrahydroquinazoline (II), m.p.  $305-306^{\circ}$  (corr.) [Na (+H<sub>2</sub>O) and Li salts], which is synthesised from  $CO(NH_2)_2$  and 3:5-dibromoanthranilic acid. (I) is, therefore, the 6: S-derivative. The 6-Br-derivative is prepared by fusion of  $CO(NH_2)_2$  and 5-bromoanthranilic acid; 2-chloro-3: 5-dinitrobenzoic acid similarly gives 3: 5dinitroanthranilic acid. (II) is ethylated [EtI in aq. EtOH-LiOH or (·CH<sub>2</sub>·OH)<sub>2</sub>-KOH] to the 3-*Et* derivative, m.p.  $251^{\circ}$  (corr.) (Na salt); the 3-Me, m.p.  $268^{\circ}$  (corr.), and 3-Pr<sup>a</sup>, m.p.  $225^{\circ}$  (corr.), derivatives are prepared similarly. H. B.

Synthesis of heterocyclic compounds by means of isothiocarbamide ethers. J. F. DECK and F. B. DAINS (J. Amer. Chem. Soc., 1933, 55, 4986— 4991).—Benzoxazines, quinazolines, benziminazoles, benzoxazoles, and glyoxalones are obtained from SMe·C(:NR)·NHR [prepared from CS(NHR)<sub>2</sub> and Me<sub>2</sub>SO<sub>4</sub> in COMe<sub>2</sub> followed by treatment with dil. Na<sub>2</sub>CO<sub>3</sub>] and o-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>R, o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH, and NHAr·CH<sub>2</sub>·CO<sub>2</sub>H, respectively. The following are described : S-methyldi-p-bromophenyl-, m.p. 129°, -m-nitrodiphenyl-, m.p. 87—89°, -di-m-tolyl-, m.p. 97·5°, -p-bromodiphenyl-, m.p. 79—80°, and -phenylmethyl-, m.p. 58—59° (perchlorate, m.p. 114°), -isothiocarbamides; the MeHSO<sub>4</sub> salt, m.p. 141—142°, of SMe·C(:NH)·NHPh; 2anilo-4.keto-3-phenyl-, m.p. 157—158°, 2-o-tolylimino-4-keto-3-o-tolyl-, m.p. 114° [hydrolysed (EtOH-conc. HCl) to 2:4-diketo-3-o-tolyl-, m.p. 163—164°, 2:4-diketo-3-p-tolyl-, m.p. 221°, 2-anilo-4-keto-3-p-bromophenyl-, m.p. 135—136°, 2:4-diketo-3-p-bromophenyl-, m.p. 214°, and 4-keto-2-phenyl-, m.p. 163°, 2:4-diketo-3-p-holyl-, m.p. 271°, 2-keto-3-phenyl-1-methyl-, m.p. 224·5°, 2-p-tolylimino-4-keto-3-p-tolyl-, m.p. 149°, 2:4diketo-3-p-tolyl-, m.p. 273°, 2:4-diketo-3-p-tolyl-1methyl-, m.p. 190°, 2-o-tolylimino-4-keto-3-p-tolyl-1methyl-, m.p. 190°, 4-o-tolyl-, m.p. 188°, 2-o-toluidino-, m.p. 182° (hydrochloride, m.p. 178°, 4-chloro-1-anilino-, m.p. 182° (hydrochloride, m.p. 178°, 4-chloro-1-anilino-, m.p. 199°, 4-chloro-1-p-toluidino-, m.p. 178°, 4-chloro-1-anilino-, m.p. 199°, 4-chloro-1-p-toluidino-, m.p. 204·5°, 4-nitro-1-anilino-, m.p. 235°, 4-nitro-1-0-, idino-, m.p. 173—174°, 207°, and 222—224°, respectively, 4-chloro-1-thio-, m.p. 262° (from 4-chloro-o-aminophenol and CS<sub>2</sub> in EtOH), and 4-nitro-1-thio-, m.p. 235—238°, -benzoxazoles; 2-anilo-1: 3-diphenyl-, m.p. 150—151° (4-m-nitrobenzylidene derivative, m.p. 170°), 2-keto-1: 3-diphenyl-, m.p. 138·5°, 2-p-tolyl-imino-1-phenyl-3-p-tolyl-, m.p. 158° (4-m-nitrobenzylidene derivative, m.p. 173°, 2-o-tolylimino-3-phenyl-1-o-tolyl-, m.p. 130°, 2-keto-3-phenyl-1-o-tolyl-, m.p. 126°, 2-anilo-1-phenyl-3-p-tolyl-, m.p. 126°, 2-anilo-1-phenyl-3-p-tolyl-, m.p. 176°), and 2-keto-1-phenyl-3-p-tolyl-, m.p. 155°, 5-glyoxalones. Heterocyclic compounds could not be prepared from o-C<sub>6</sub>H<sub>4</sub>(OH), and NHPh·CH<sub>2</sub>·CH<sub>2</sub>·OH. H. B.

Influence of attached rings on formation of heterocyclic compounds. I. T. N. GHOSH (J. Indian Chem. Soc., 1933, 10, 583-589).-o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO·CO<sub>2</sub>K and the appropriate ArNCS in EtOH give (after acidification) o-phenyl- (I), m.p. 173-174° (decomp.), 2-o-tolyl- (II), m.p. 208-210°, and 2-p-tolyl-, m.p. 165-166° (decomp.), -thiocarbamido-benzoylformic acid. (I) is converted by boiling with Ac,O into 6:7-diketo-2-thion-1-phenyl-4:5-benz-1:3heptadiazine,  $C_6H_4 < CO-CO$ NPh, m.p. 155-157°; the 1-o-tolyl derivative, m.p. 205-206°, is similarly formed from (II). o-Phenylcarbamidobenzoylformic acid has m.p. 179-180°. s-Ethylenedi-phenyl-, -otolyl-, m.p. 180°, -p-tolyl-, m.p. 194-195°, -allyl-, m.p. 103-104°, and -methyl-, m.p. 85-86°, -dithiocarbamides, prepared from  $(\cdot CH_2 \cdot NH_2)_2$  and RNCS (2 mols.), are unaffected by conc. HCl or 15% KOH. 1:2-Naphthylenedi-phenyl-, -p-tolyl-, m.p. > 300°, and -m-4-xylyl-, m.p.  $> 300^{\circ}$ , -dithiocarbamides are similarly converted into 1:2-naphthylenethiocarbamide,  $C_{10}H_6 < _{NH}^{NH} > CS$ , m.p. > 300°. 9 : 10-Phenanthrenethiocarbamide, m.p.  $> 300^{\circ}$ , is obtained directly from 9: 10-diaminophenanthrene and ArNCS in  $C_5H_5N$ ; the intermediate 9:10-phenanthrenediaryldithiocarbamides could not be isolated. Benzoylation of o-phenylenethiocarbamide (Lellmann, A., 1884, 49) under varying conditions gives only the Bz derivative,  $o - C_6 H_4 < NH > C \cdot SBz$ , m.p. 186—187°.

'H. B.

Condensations of toluenesulphonamides with trioxymethylene and formal dehyde. L. McMASTER (J. Amer. Chem. Soc., 1934, 56, 204-206).—p-C<sub>6</sub>H<sub>1</sub>Me·SO<sub>2</sub>·NH<sub>2</sub> (I), (CH<sub>2</sub>O)<sub>3</sub> (II), and AcOH-conc. H<sub>2</sub>SO<sub>4</sub> at 100° give tri-p-toluenesulphonyltrimethylene-tri-imide [1:3:5-tri - p-toluenesulphonyltrimethylene-tri-imide [1:3:5-tri - p-toluenesulphonyltrimethylene-tri-imide], and a little conc. HCl in EtOH. p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·NHMe and (II) or (III) similarly give methylenedi-(p-toluene-sulphonmethylamide) (+H<sub>2</sub>O, which could not be removed without some decomp.), m.p. 113-114°. o-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·NH<sub>2</sub> and (II) afford 1:3:5-tri-o-toluenesulphonyltexahydro-1:3:5-triazine (IV), m.p. 245·5-246·5° (slight decomp.), and di-o-toluenesulphonyltexahylenedi-imide,

 $C_6H_4Me \cdot SO_2 \cdot N < CH_2 > N \cdot SO_2 \cdot C_6H_4Me$ , m.p. 168.8-

169-9°; with (III), (IV) only is produced. The above triazines form additive compounds with  $NH_2Ph$ . H. B.

Heterocyclic compounds obtained by interaction of benzoins and hydrazine hydrochloride. V. J. VAN ALPHEN (Rec. trav. chim., 1934, 53, 74— 76; cf. A., 1933, 838, 964).—1:3:4:6-Tetraphenyl- $\Delta^2$ -trimidine [(+1.5EtOH); hydrochloride, m.p. 260° (decomp.)] is formed in small amount from benzoin and NH<sub>2</sub>·NHMe,2HCl in EtOH at 100°, hence is unlikely to contain a N·N linking. It is unaffected by ZnCl<sub>2</sub> at 300° and by HI (d 1.96) and P at the b.p. H. A. P.

[Reactions of the] 2:4:6-trinitrobenzylidene [derivatives of aromatic bases]. S. SECAREANU (Bull. Soc. chim., 1933, [iv], 53, 1016–1024, 1024– 1032).—2:4:6-Trinitrobenzylidene derivatives of aromatic bases or 2:4:6- $C_6H_2(NO_2)_3$ ·CHO when warmed with AcOH and excess of the base give good yields of 4:6-dinitro-2-hydroxy-1:3-diarylbenztriazol-

NO<sub>2</sub> NO<sub>2</sub> NR NR NR

-NR-NN-OH (I.) ines (I), by replacement of CH:NR and NO<sub>2</sub> by NHR and ring-closure by the HNO<sub>2</sub> liberated. Use of a foreign amine leads to complete or

partial exchange of R. Addition of KI to the reaction mixture lowers the yield of (I) by partial removal of the HNO2. The monocyclic NO-formula, alternative to (I), is excluded by the stability of the substances to HCl and the reduction of the NH<sub>2</sub>Phderivative by  $Na_2S_2O_4$  to 4: 6-dinitro-1: 3-diphenylbenztriazoline (Bz3 derivative, m.p. 236-240°). The following are described : derivatives of (I) in which R=Ph, m.p. 224° [previously (A., 1921, i, 337), described as an isomeride of trinitrobenzylideneaniline (II)], β-C<sub>10</sub>H<sub>7</sub>, m.p. 262°, p-C<sub>6</sub>H<sub>4</sub>Me, m.p. 272°, m-bromo-p-tolyl, m.p. 298°, and p-C6H4Br, m.p. 281°; 2:4:6-trinitrobenzylidene-m-bromo-p-toluidine, m.p. 209°, and -p-bromoaniline, m.p. 184°. Reduction of 2:4:6-trinitrodiphenylamine and subsequent benzoylation gives  $\hat{2}: 4: 6$ -tribenzamidodiphenyl-amine, m.p. 262°. (II) and hot AcOH give a substance, m.p. 257-258°, and a little C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>·CHO.

R. S. C. Action of ozone on porphyrins. I. H. FIS-CHER and M. DEZELIĆ (Z. physiol. Chem., 1933, 222, 270–278).—On treatment with 1% O<sub>3</sub> for 6 hr. actioporphyrin (I) gives a triozonide, sinters 150° (decomp.), (+2.5H<sub>2</sub>O) m.p. 100° (decomp.), (+H<sub>2</sub>O) sinters from 110° (decomp.); after 15 min. a diozonide, sinters from 112°, (+2H<sub>2</sub>O) sinters from 110°. Ætiohæmin affords an ozonide, no m.p. below 250°, changes from 150°. 6:7-Di-(β-carboxyethyl)-2:3:5:8tetramethyl-1: 4-dipropylporphin and its ester and isouroporphyrin ester II show changes in absorption spectra. Methylethylmaleimide affords a stable ozonide, m.p. 86—87°. J. H. B.

Chlorophyll. XL. Synthesis of deoxophylloerythrin; derivatives of phylloporphyrin. H. FISCHER, M. SPEITMANN, and H. METH (Annalen, 1934, 508, 154—167).—Phyllohæmin (I), CH<sub>2</sub>Cl·OMe, and SnCl<sub>4</sub> at 40° give hydroxymethylphyllohæmin (?) (II), converted by successive treatment with HBr-AcOH and 10% HCl into hydroxymethylphylloporphyrin (III),  $C_{33}H_{38}O_3N_4$ . Successive treatment of crude (II) with HBr-AcOH, MeOH, and 10% MeOH-KOH gives methoxymethylphylloporphyrin Me ester (IV),  $C_{35}H_{42}O_3N_4$ , m.p. 241° (corr.) (Cu salt,  $C_{34}H_{37}O_3N_4Cu$ ·Ac, m.p. 205—206°). Fusion of (III) or (IV) with methylsuccinic acid at 155° affords deoxophylloerythrin [Me ester, m.p. 261° (Cu salt, m.p. 254°)] (cf. A., 1931, 1431; 1933, 167). (IV) and HBr-AcOH at 35—40° give bromomethylphylloporphyrin hydrobromide,  $C_{33}H_{39}O_2N_4Br_3$ , which with CHK(CO<sub>2</sub>Et)<sub>2</sub> affords (after esterification of the intermediate acid with MeOH-HCl) the ester (V), m.p.



211—212°. (I), Ac<sub>2</sub>O, and SnCl<sub>4</sub> at 65—70° give a crude Ac derivative; removal of Fe by HBr-AcOH affords acetylphylloporphyrin [*Me* ester,  $C_{35}H_{40}O_3N_4$ , m.p. 286° (*Cu* salt, m.p. 318°; *hamin*, m.p. 314°)]. Phylloporphyrin [*Et* ester *Cu* salt, m.p. 256° (corr.); Me ester (*Fe* salt), converted by MgMeI into the corresponding tert.-*carbinol*,  $C_{33}H_{40}ON_4$ , m.p. 252° (corr.)] and cold conc. HNO<sub>3</sub> give (probably) 6-*nitrophylloporphyrin* [*Fe* and *Cu* salts; *Me* ester, m.p. 228° (corr.)]. Phylloporphyrin ester can be nitrated with fuming HNO<sub>3</sub> in CHCl<sub>3</sub>. H. B.

Chlorophyll. VI. Benzoyl derivatives and oximes of methylphæophorbide-a and phæophorbide-a. A. STOLL and E. WIEDEMANN (Helv. Chim. Acta, 1934, 17, 163-182).-The C<sub>5</sub>H<sub>5</sub>N compound of benzoylphæophorbide-a (I) (improved prep. in 80% yield described) retains its  $C_5H_5N$  in vac. and even on dissolution in acid and regeneration by dilution. Methylphæophorbide-a (II) with BzCl- $C_5H_5N$  also yields a  $C_5H_5N$ -compound, m.p. 182°, of its Bz derivative (III), hydrolysed to (II) with 20% HCl-Et<sub>2</sub>O, and to pheophorbide-*a* (IV) with  $30-35^{\circ}$ , HCl at room temp. By Willstatter's method (A., 1912, i, 285) (I), (III), (IV), and pheoporphyrin- $a_5$ (V) all retain NH<sub>3</sub>, indicating the presence of a free  $CO_2H$ , but (II) and the  $Me_2$  ester of (V) do not. Fischer's view that benzoylation of an enolic OH and not, as previously suggested, a sec. OH, is involved is accepted. With NH<sub>2</sub>OH, HCl and C<sub>5</sub>H<sub>5</sub>N at 100° (II) affords an oxime (VI), not melting  $< 260^{\circ}$  (corr.), hydrolysed by cold Et2O-saturated 18% HCl to pheophorbide-a oxime [which cannot be prepared directly from (IV)], and by Et<sub>2</sub>O-saturated 30% HCl to (IV), identical with the natural product. With HI-AcOH (VI) affords the Me ester of phæoporphyrin- $a_5$  oxime. Fischer's view that a CO group is present at  $C_9$  in phase-positive chlorophyll deriv-atives is thus confirmed. Spectroscopic data for all J. W. B. these derivatives are given.

Chlorophyll series. XII. Phæopurpurins. E. M. DIETZ and W. F. Ross (J. Amer. Chem. Soc., 1934, 56, 159-164).—The structure previously

assigned (A., 1931, 368; 1933, 403) to phæopurpurin 7 (I) is supported by its oxidation [K<sub>3</sub>Mo(CN)<sub>8</sub> in  $COMe_2-C_5H_5N$ ] to  $CO_2$  and chlorin a  $\beta$ -Me<sub>1</sub> ester, which is esterified  $(CH_2N_2)$  to the  $Me_3$  ester (II) (Cu,m.p. 235°, and Zn, m.p. 242°, salts), and converted by heating with Ph2 at 200° into phæopurpurin 18 (III). Mild hydrolysis  $(0.15N-KOH in C_5H_5N)$  of the Mc ester of (III) gives chlorin a  $\alpha$ -Me<sub>1</sub> ester. Hydrolysis (MeOH-KOH) of (II) affords chlorin a Me2 esters, m.p. 241-242° and 208° (according to conditions used). An unstable chlorin a and a small amount of chlorin a (IV) (A., 1930, 1299) [the chlorin  $p_6$  of Fischer *et al.* (A., 1932, 1263)] are formed by aeration of (III) in 20% HCl; the former gives a  $Me_3$  ester, the m.p. (227–228°) of which is not depressed by (II). The production of (III) from the unstable chloring (IV) obtained by phase text by unstable chlorins (V) obtained by phase-test hydrolysis of methylphæophorbide a, involves oxidation. A C atom is removed as CO<sub>2</sub> and not as HCO<sub>2</sub>H (during hydrolysis) (cf. Fischer et al., loc. cit.). (III) is most conveniently prepared by oxidation  $[K_3Fe(CN)_6 \text{ in dil. aq. }NH_3]$  of (V); (I) is similarly unaffected. (III) and  $NH_2OH$  in  $C_5H_5N$  give a compound (VI),  $C_{33}H_{35}O_5N_5$ , whilst methylphæopurpurin 18 similarly affords a compound (VII),  $C_{34}H_{37}O_5N_5$ . (VI) and (VII) are considered to be analogous to the compounds formed from  $o C_6H_4(CO)_2O$  and  $NH_2OH$ ; they are methylated (CH<sub>2</sub>N<sub>2</sub>) to the *Me ether* of (VII). Rhodoporphyrin- $\gamma$ -carboxylic acid anhydride furnishes a similar com-pound (Me ester Me ether, C<sub>35</sub>H<sub>37</sub>O<sub>5</sub>N<sub>5</sub>), which is also obtained [by dehydrogenation (?)] when (VI) is heated. (111) is regarded as the true anhydride of (IV). Rhodin g Me<sub>3</sub> ester oxime has m.p. 212°. H. B.

Derivatives of 5-aminotetrazole. R. STOLLE and O. ROSER (J. pr. Chem., 1933, [ii], 139, 63—64).— Interaction of 5-aminotetrazole with the corresponding chloronitrobenzenes in AcOH and xylene, respectively, at the b.p. gives  $5 \cdot 2' : 4' : 6' \cdot trinitro-$ , m.p. 224° (*Pb* and *Ag* salts), and  $5 \cdot 2' : 4' \cdot dinitro-anilinotetrazole,$ m.p. 174° (decomp.). H. A. P.

Condensation of the anhydride and esters of diacetyltartaric acid with aniline and phenyl-hydrazine. A. WRÓBEL (Rocz. Chem., 1933, 13, 588-600).—Me, m.p. 102°, Et (I), an oil, and Ph diacetyltartrate, an oil, yield on heating with NH<sub>2</sub>Ph at 135° N-phenyl-2: 3-dihydro-oxazine-2: 3-dicarboxylphenylimide (II), m.p. 264° (dibromide, m.p. 123°; nitrate, m.p. 230-250°), together with the corresponding alcohol, H<sub>2</sub>O, and AcOH. (II) decomposes in conc. H<sub>2</sub>SO<sub>4</sub> to yield PhNCO, CH<sub>2</sub>O, and CO. The above esters condense with NHPh·NH<sub>2</sub> at 100° to yield 1-anilino-3: 4-dihydroxy-2: 5-diketopyrrolidine, m.p. 239° (Ac<sub>2</sub> derivative, m.p. 110°), and NHPh·NHAc; (I) gives in addition its phenylhydrazone, m.p. 156°. R. T.

Preparation of quinoxazones. H. EICHLER (J. pr. Chem., 1934, [ii], 139, 113—114).—Resorufin is formed in 95—99% yield by addition of NaNO<sub>2</sub> (0.8—3 pts.) or KNO<sub>2</sub> (1—3.7 pts.) to m-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> (2 pts.) in conc. H<sub>2</sub>SO<sub>4</sub> (19 pts.) at room temp.

H. A. P.

Isomeric 2-tolylimino-3-tolyl-4-p-chloro- and -p-bromo-phenyl- $\Delta^4$ -thiazolines. R. M. HANN and E. E. REID (J. Amer. Chem. Soc., 1933, 55, 4998—5000).—p-Chloro- and -bromo-phenacyl bromides and CS(NHPh)<sub>2</sub> in EtOH give 2-anilo-3-phenyl-4-p-chlorophenyl-, m.p. 204° (all m.p. are corr.) (hydrochloride, m.p. 228—229°; picrate, m.p. 206°), and -4-p-bromophenyl-, m.p. 206° (picrate, m.p. 203°),  $-\Delta^4$ thiazoline, respectively. 2-o-Tolylimino-4-p-chlorophenyl-, m.p. 132° (picrate, m.p. 187°), and -p-bromophenyl-3-o-tolyl-, m.p. 123° (picrate, m.p. 196°), and 2-p-tolylimino-4-p-chlorophenyl-, m.p. 227° (picrate, m.p. 183°), and -p-bromophenyl-3-p-tolyl-, m.p. 239° (picrate, m.p. 193°),  $-\Delta^4$ -thiazolines are similarly prepared using di-o- and -p-tolylthiocarbamides.

H. B. Bromination of thiazole in gaseous phase at elevated temperatures. J. P. WIBAUT and H. E. JANSEN (Rec. trav. chim., 1934, 53, 77-80).—Bromination of thiazole (I) over pumice at 250° gives 2bromothiazole (II), b.p. 69°/15 mm. ( $HgCl_2$  compound, m.p. 165.5°), and a *dibromothiazole*, m.p. 46-47° ( $HgCl_2$  compound, m.p. 188.5°); at 400° (II) only is isolated. (I) forms a perbromide with Br in CHCl<sub>3</sub>. H. A. P.

Rearrangement of arylbenzthiazoles. M. MEYER, N. MOLOMUT. M. NOWAK, and M. OGUR (Rec. trav. chim., 1934, 53, 37–40).—1-Anilinobenzthiazole is unchanged by 63% H<sub>2</sub>SO<sub>4</sub> at 200° or by conc. HCl at its b.p., but at 180—190° the latter converts it into an isomeric primary *amine* (? 2-o-aminophenylbenzthiazole), m.p. 156·4°. The *phenyl*-, m.p. 206·5°, and p-tolyl-thiocarbamido-derivative, m.p. 198·5°, of dehydrothio-p-toluidine are described. Phenyl-p-tolyl thiocarbamide is converted by the Hugershoff reaction into a 1-anilinomethylbenzthiazole, m.p. 128·5° (cf. A., 1930, 1452). All m.p. are corr. H. A. P.

Interaction of s-phenylmethylthiocarbamide s - phenyl - n - butylthiocarbamidewith and bromine. M. R. CHOWDHURY and R. F. HUNTER (Rec. trav. chim., 1934, 53, 1-6).—Interaction of NHPh·CS·NHMe with Br (2 equivs.) in CHCl<sub>3</sub> gives 1-methylaminobenzthiazole (I), but excess of Br gives a mixture of hydroperbromides (the "tetrabromide" of A., 1926, 849; cf. A., 1927, 263) reduced by SO<sub>2</sub> to 5-bromo-1-methylaminobenzthiazole (II), m.p. 224-225° (synthesised for comparison from 1-chloro-5bromobenzthiazole and NH2Me). Prolonged action of excess of Br gives 3: 5-dibromo-1-methylaminobenzthiazole, m.p. 235°, also obtained by further bromination of (II), and synthesised by cyclisation of 5-2: 4-dibromophenylmethylthiocarbamide, m.p.  $164^{\circ}$  (from  $\mathrm{NH}_2\cdot\mathrm{CS}\cdot\mathrm{NH}\cdot\mathrm{C}_6\mathrm{H}_3\mathrm{Br}_2$  and  $\mathrm{NH}_2\mathrm{Me}$ ) with Br. The hydrotribromide, m.p.  $118-120^{\circ}$  (sinters  $108^{\circ}$ ), of (II) is obtained by acting with Br on (II) or s-pbromophenylmethylthiocarbamide. Bromination of NHPh·CS·NHBu<sup>a</sup> similarly gives the hydrodibromide, m.p. 65-75°, of 1-n-butylaminobenzthiazole, m.p. 86°, and (with excess of Br) the hydrohexabromide of 5bromo-1-n-butylaminobenzthiazole, m.p. 118° (hydrotribromide, m.p. 100-110°). H. A. P.

Nature of bromo-additive compounds of dehydrothio-*p*-toluidine and its acetyl derivative and synthesis of 4'-acetamido-1-phenyl-5-methylbenzthiazole and 3'-bromo-4'-acetamido-1-phenyl-5-methylbenzthiazole. M. AllAZAM, R. D. DESAI, and R. F. HUNTER (Rec. trav. chim., 1934, 53, 7-12).-Bromination of dehydrothio-p-toluidine (I) gives the hydrotribromide, m.p. 240° (decomp.), of a Br-derivative (II) of m.p. 184° [Ac derivative (III), m.p. 212°] (cf. A., 1889, 602). The Ac derivative of (I), synthesised from the Zn salt of 4-amino-*m*-thiocresol (IV) and *p*-NHAc·C<sub>6</sub>H<sub>4</sub>·COCl, gives a different [from (III)] Br-derivative, m.p. 206° [hydrotribromide, m.p. 185° (decomp.)]. 2-Bromoacet-p-toluidide is oxidised by KMnO<sub>4</sub> to 3-bromo-p-acetamidobenzoic acid (V), m.p. 230°, the chloride of which condenses with the Zn salt of (IV) to give 3'-bromo-4'-acetamido-1-phenyl-5methylbenzthiazole, m.p. 250°, which is different from either of the preceding. Bromination of p-NHAc·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H in AcOH gives (?) (V) (3-bromo-4aminobenzoic acid, m.p. 204°) and a Br2-derivative, m.p. >280° (free  $NH_2$ -acid, m.p. >280°). (IV) is conveniently prepared by bromination of p-tolylthiocarbamide and fission of the resulting thiazole with conc. aq.-alcoholic KOH. Two intermediate substances, m.p. 240° and 266°, possibly the N- and S-carbamido-derivatives of (IV), were isolated. H. A. P.

Naphthathiazole series. II. Methylation of 1-anilino- and 1-p-bromoanilino-a-naphthathiazole. Aromatic character of the heterocyclic nucleus in a-naphthathiazoles. M. R. CHOWD-HURY, R. D. DESAI, and R. F. HUNTER (J. Indian Chem. Soc., 1933, 10, 637-642).-1-Anilo-, m.p. 182° (picrate, m.p. 218°), and 1-p-bromoanilo-, m.p. 182°, -2-methyl-1: 2-dihydro-a-naphthathiazoles are obtained from 1-anilino-, and 1-p-bromoanilino-a-naphthathiazoles, respectively, and MeI at 100°. 1-N-Methylanilino- (picrate, m.p. 184°) and 1-N-methyl-p-bromoanilino-, m.p. 245°, -a-naphthathiazoles are prepared from the 1-Cl-derivative and NHArMe. 1-Amino-anaphthathiazoles (I) resemble aminothiazoles much more closely than 1-aminobenzthiazoles (II); the heterocyclic nucleus in (I) is much more aromatic than in (II). H. B.

Bisbenzthiazine, and rules for the formation of thiazoles and thiazines. G. WALTER, R. HÜBSCH, and H. POLLAK (Monatsh., 1933, **63**, 186–200).— Heating together equimol. quantities of dichloroquinoxaline and o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SH (I) affords bisbenzazine-thiazine, C<sub>6</sub>H<sub>4</sub> $<_{\text{NH-C'N}}^{\text{N=C}\cdot\text{S}}$ >C<sub>6</sub>H<sub>4</sub>, m.p. 270°. The Na salt of (I) (2 mols.) with CCl<sub>3</sub>·COCl gives o-aminophenyl benzthiazole-2-thiocarboxylate, C<sub>6</sub>H<sub>4</sub> $<_{\text{N}}^{\text{N}}$ ·C·CO·S·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> (II), decomp. 160–170°

(phenylhydrazone, m. p. 198°), which affords  $H_2S$ ,  $NH_2Ph$ , and o-CHMe:N·C<sub>6</sub>H<sub>4</sub>·SH with HI-P at 180°. (I) does not react with C<sub>2</sub>Cl<sub>6</sub>. Similarly CHBr<sub>2</sub>·CO<sub>2</sub>H and Zn 4-chloro-2-aninothiophenoxide at 150° give 6-chloro-2-(4'-chloro-2'-aninophenylthiol) - 3-keto - 2 : 3 - dihydro-1 : 4-benzthiazine, C<sub>6</sub>H<sub>4</sub>Cl $\sim$ NH-CO 1 : 4-benzthiazine, Condensation of (I) with 2 : 3-diketo-2 : 3-dihydro-1 : 4-benzthiazine (Zahn, A., 1923, i, 375) at 200° gives bisbenzthiazine, C<sub>6</sub>H<sub>4</sub><S·C:N>C<sub>6</sub>H<sub>4</sub> (IV), decomp. 301-305° (Brderivative, decomp. 157°, with Br-CHCl<sub>3</sub>), which closely resembles (n, absorption and fluorescence spectra) the isomeric bisbenzthiazole (V), m.p. 304° [not depressed by (IV)] [from (·COCl)<sub>2</sub> and (I)], but with Br-CHCl<sub>3</sub> (V) gives a  $Br_2$ -derivative, Br evolution at 168°, m.p. >300°, and not a Br<sub>4</sub>-derivative (Hunter, A., 1925, i, 987). With 2:2-dichloro-3-keto-2:3-dihydro-1:4-benzthiazine (Zahn, *loc. cit.*) at 180°, (I) gives a *substance*  $C_{29}H_{20}O_4N_4S_4$ , m.p. 204°. Rules for the formation of these heterocyclic types are given. J. W. B.

Constitution of peganine. E. SPATH and E. NIKAWITZ (Ber., 1934, 67, [B], 45-55).—Peganine (I), m.p. 208-210° (vac.), obtained from the technical residues of the prep. of the alkaloids of Peganum harmala, is  $C_{11}H_{12}ON_2$ . It does not contain OMe or NMe and does not react with CH2N2 or with the customary ketonic reagents. With Ac2O it yields an acetate, b.p. 230-240°/0.01 mm., very readily hydrolysed to (I). The presence of OH in (I) (Zerevitinov) is confirmed by its conversion by POCl<sub>3</sub> into chlorodeoxypeganine, m.p. 136-137°. Oxidation of (I) with  $KMnO_4$  (=50) in feebly alkaline suspension at room temp. and subsequent treatment of the product with CH<sub>2</sub>N<sub>2</sub> leads to Me 4-keto-3: 4-dihydroquinazolyl-3-acetate (II), hydrolysed by KOH to anthranilic acid (III) and glycine without production of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, NH<sub>3</sub>, (11) and give the without production of  $1_{2}c_{2}o_{4}$ ,  $141_{3}$ , or NH<sub>2</sub>Me. [Analogously, 4-keto-3:4-dihydroquin azoline-2-carboxylic acid is hydrolysed to (III),  $H_{2}C_{2}O_{4}$ , and NH<sub>3</sub>.] Conc. HCl converts (II) into 4-keto-3:4-dihydroquinazolyl-3-acetic acid (IV), m.p. 237° (slight decomp.) (methylamide, m.p. 233–235°), reconverted into (II) by CH<sub>2</sub>N<sub>2</sub> and decarboxylated by Cu powder in quipeline but not when heated above by Cu powder in quinoline, but not when heated above its m.p. or with fuming HCl under pressure, to 4-keto-3-methyl-3: 4-dihydroquinazoline, m.p. 103-105°. Hydrogenation of (I) by Pd-C at 50° gives only unchanged material, whereas reduction with Sn and HCl affords deoxyhexahydropeganine (V), C11H16N2, b.p. 70-90° (bath)/high vac. Treatment of (I) with Na and amyl alcohol leads to small amounts of a substance, m.p. 123°, and deoxytetrahydropeganine, m.p. 69.5° [Ac derivative, b.p. 190-200° (bath)/0.01 mm.], which



contains NH (Zerevitinov), is unstable towards  $KMnO_4$ , and is converted by Sn and HCl into (V). (I) is therefore A, the constitution being confirmed by its ready

oxidation by  $KMnO_4$  in  $COMe_2$  to (IV). The question of the identity of (I) and vasicine remains open. H. W.

Characterisation of nicotine by Roussin's reaction. J. A. LABAT (Bull. Soc. Chim. biol., 1933, 15, 1339–1343).—Optimum conditions for the detection of nicotine (I) by solutions of I in Et<sub>2</sub>O were investigated. With 0.1% of (I) in Et<sub>2</sub>O, 1 drop of 1% of I in Et<sub>2</sub>O suffices for a positive reaction (formation of iodonicotine,  $C_{10}H_{14}N_2I_2$ , HI). F. O. H.

Lupine. VI. Alkaloids of Lupinus corymbosus, Heller. I. J. F. COUCH (J. Amer. Chem. Soc., 1934, 56, 155–156).—Details are given for the isolation of hexalupine,  $C_{15}H_{20}ON_{2,3}H_2O$ , m.p. 197– 198°,  $[x]_D^{-}+126\cdot1^{\circ}$  in EtOH [dihydrochloride (+3H<sub>2</sub>O), passes when heated slowly into the hydrochloride, m.p. 304—305°, m.p. 136—138° (softens at 122°) when "drying" is effected at 125°; aurichloride,  $C_{15}H_{20}ON_2,1.5HAuCl_4,2.5H_2O$ , m.p. 204° (decomp.); picrate, m.p. 245—246°], from the air-dried plant. A new system for naming lupin alkaloids is proposed. H.B.

Rotatory dispersion of sparteine.—See this vol., 241.

Sophora alkaloids. IV. Alkaloids of the seeds of S. pachycarpa. A. OREKHOV and N. PROSKURNINA (Ber., 1934, 67, [B], 77-83; cf. A., 1933, 840).-The dried seeds are percolated with EtOH containing 2% of AcOH; the liquid is neutralised with NH3, evaporated, and the residue is treated with 10% H<sub>2</sub>SO<sub>4</sub>. After extraction with Et<sub>2</sub>O, the acid liquor is saturated with K2CO3 and extracted with  $Et_2O$ , thereby giving 2.23% of crude alkaloids which do not contain the volatile bases isolated from the foliage (loc. cit.). Crystallisation of the hydriodides leads to the isolation of the individual alkaloids. Sophocarpine,  $C_{15}H_{24}ON_2$ , m.p. 54-55° (monohydrate, m.p. 81-82°,  $[\alpha]_{19}^{19}$ -29.44° in EtOH), is a strong, monoacid base, stable towards KOH-EtOH, and contains O and the second N in an indifferent, non-reactive form. It yields a hydrochloride, m.p. > 300° after darkening at  $230-240^{\circ}$ , hydrobromide, m.p. >  $300^{\circ}$ after darkening at  $230-240^{\circ}$ , hydriodide, m.p. >  $300^{\circ}$ after darkening at  $230-240^{\circ}$ , hydriodide, m.p.  $166-170^{\circ}$ , after darkening at  $240^{\circ}$ , aurichloride, m.p.  $166-170^{\circ}$ , platinichloride, m.p. 209–212° (decomp.), picrate, m.p. 155–157°, and methiodide, m.p. 200–202°. Sophocarpidine (I),  $C_{15}H_{21}ON_2$ , m.p. 73–76°,  $[\alpha]_{11}^{22}$ +38.38° in EtOH, is possibly identical with matrine, but does not appear to exist in isomeric forms. It yields a hydrochloride, hydrobromide, hydriodide, platinichloride, m.p. 228-230° (also trihydrate), and hygroscopic methiodide (also +2EtOH). (I) is converted by boiling KOH-EtOH into sophocarpidic acid (II), C15H26O2N2, m.p. 202-204° [tetrahydrate, m.p. 170–175°,  $[\alpha]_{15}^{\mu}$  +19·16° in H<sub>2</sub>O; hygroscopic K salt (III), m.p. 222–226°, and its mono- and tetra-hydrate; aurichloride, m.p.  $194-195^{\circ}$ ; platinichloride, m.p.  $\geq 250^{\circ}$ ]. (II) is transformed by Ac<sub>2</sub>O at 100° into (I). MeI in boiling MeOH transforms (III) into  $Me_2$ sophocarpidate methiodide, m.p. 212-214° (also H. W.  $+1H_{2}O$ ).

Sempervirine, an oxygen-free alkaloid of Gelsemium sempervirens. V. HASENFRATZ (Bull. Soc. chim., 1933, [iv], 53, 1084–1087).—The rhizomes and roots of G. sempervirens contain sempervirine,  $C_{19}H_{16}N_2$ ,  $+H_2O$ , m.p. 258–260° (block), [ $\alpha$ ] 0° in CHCl<sub>3</sub>, orange-red (intense bluish-violet fluorescence in very dil. solution; hydrochloride,  $+2H_2O$ ; nitrate,  $+2H_2O$ , pptd. in conens. >1:20,000; platinichloride; picrate). R. S. C.

Yohimba alkaloids. H. HEINEMANN (Ber., 1934, 67, [B], 15—21).—The following subsidiary alkaloids have been isolated. (I) A base  $C_{21}H_{26}O_3N_{2,3}H_2O$ , m.p. (hydrated) 104—105°, m.p. (anhyd.) 133—140°,  $[\alpha]_{10}^{\infty}$ —73·6° in  $C_5H_5N$ , identical with alloyohimbine of Hahn et al. (A., 1927, 471) and the dihydroyohimbine of Warnat (A., 1926, 1263). (II)  $\alpha$ -Yohimbine,  $C_{21}H_{26}O_3N_2$ ,MeOH, m.p. 234—235°, from MeOH or  $C_{21}H_{26}O_3N_2$ ,EtOH,H<sub>2</sub>O from 95°, EtOH (anhyd.).  $[\alpha]_{10}^{\mu}$ —28·0° in abs. EtOH (hydrochloride,  $[\alpha]_{10}^{\mu}$ +53·6° 311

in EtOH), hydrolysed by KOH-EtOH to a-yohimboaic acid, decomp.  $276^{\circ}$  according to the rate of heating,  $[\alpha]_{\rm P}^{a}$  +47.5° in  $C_5H_5N$ , readily purified by treatment with EtOH. Et a-yohimboate, m.p. 236°,  $[\alpha]_{11}^{22}$  -6.7° in C<sub>5</sub>H<sub>5</sub>N, and its hydrochloride,  $[\alpha]_{1D}^{21}$  $+64.0^{\circ}$  in H<sub>2</sub>O, are described. The identity of the compound is established by comparison with Merck's  $\alpha$ -yohimbine, but unexplained discrepancies remain between the author's work and that of Warnat (loc. cit.), and Hahn et al. (A., 1930, 1194; 1927, 243). (III)  $\beta$ -Yohimbine, C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>,2MeOH, m.p. 235-236°,  $[\alpha]_0^{20}$  -46.8° in C<sub>5</sub>H<sub>5</sub>N, characterised by very sparing solubility in McOH, not identical with the  $\gamma$ -yohimbine of Hahn *et al.* (A., 1930, 1194). The  $\beta$ -yohimbine described previously is a mixture (cf. Hahn *et al.*, A., 1932, 760); a monohydrate and the hydrochloride, decomp. 292°,  $[\alpha]_{11}^{11} + 27.7°$  in H<sub>2</sub>O, are described. Hydrolysis of the base affords  $\beta$ -yohimbine  $\beta$ boaic acid, decomp. 257° after softening at 253° (other vals. according to method of purification),  $[\alpha]_{D}^{20} + 15 \cdot 8^{\circ}$ in C<sub>5</sub>H<sub>5</sub>N. The base gives a marked depression of the m.p. with allo- or  $\alpha$ -yohimbine, but not with yohimbine itself. Constancy of m.p. is therefore inadequate evidence of homogeneity. (IV) y-Yohimbine, C21H26O3N2, m.p. 254°, [a]; -50.0° in C5H5N, present only in minor amount and characterised by very sparing solubility in boiling EtOH. The hydrochloride (+ $H_2O$ ), decomp. 288° (anhyd.),  $[\alpha]_D^{20} - 18.6°$ in MeOH, and 8-yohimboaic acid, m.p. 253°, [a]? H. W.  $+1.5^{\circ}$  in C<sub>5</sub>H<sub>5</sub>N, are described.

Alkaloids of fumaraceous plants. VIII. Corydalis aurea, Willd., and the constitution of bicucine. R. H. F. MANSKE (Canad. J. Res., 1933, 9, 436—442).—The dried roots of *C. aurea* contain 1.6% of protopine, whereas only 0.025% is present in the leaves and stem. By the procedure used with Adlumia fungosa (A., 1933, 728) are isolated 1-tetrahydropalmatine, m.p. 142°,  $[\alpha]_{12}^{n}$ —278° in 95% EtOH, capauridine, C<sub>21</sub>H<sub>27</sub>O<sub>5</sub>N, darkens at 180—190°, m.p. 203—204° [O-Me ether, m.p. 142° (I)], and the isomeric capaurine, m.p. 164° [O-Me ether, m.p. 150— 151°, probably not identical with (I)] (both containing 1 phenolic OH and 4 OMe groups), bicuculline (II),  $[\alpha]_{12}^{n}$ +130.5° in CHCl<sub>3</sub>, and bicucine (III),  $+H_2O$ , m.p. 222° (decomp.),  $[\alpha]_{13}^{n}$ —145° to -100° in 24 hr. in N-HCl (both previously obtained from Dicentra

cucullaria, A., 1933, 617), and at least four others not yet characterised. Oxidation of (III) with  $KMnO_4$ dil. KOH at 0° and treatment of the product with NH<sub>2</sub>Et affords N-ethyl-3 : 4methylenedioxyphthalimide, identical with a specimen prepared from (II). (III) is a free  $\gamma$ -OH-acid of which (II) is the corresponding

lactone, since alkali converts (II) into (III), whereas an equilibrium mixture is produced by boiling (III) with dil. HCl. The structure (A) is suggested for (III). All m.p. are corr. J. W. B.

Cocaine silicotungstate. B. A. KLYACHKINOV, M. K. STRUGATZKI, and V. M. MERLIS (Bull. Nauch.



Issledov. Khim. Farm. Inst., 1931, 268–274).—In the determination of cocaine the amount of reagent required depends on the conen. of electrolyte. The ppt. is at first amorphous, and then becomes cryst.; the ratio is then 4 (alkaloid): 1. For the determination, either (1) cocaine in 0.5% HCl is treated with 5% aq. silicotungstic acid, diluted to 100 c.c. with 0.5% HCl, warmed 3–4 hr., kept 12–18 hr., and filtered, the ppt. being washed with 0.5% HCl and weighed (factor 0.426), or (2) a known amount of silicotungstic acid is used, an aliquot portion of the filtrate is evaporated, and the residue ignited. CH. ABS.

LXXVIII. Strychnos alkaloids. Isomeride of benzylidenedihydrostrychnine. H. LEUCHS and H. BEYER (Ber., 1934, 67, [B], 108-112).--Repetition of the work of Kotake et al. (A., 1933, 1061) shows that the product, m.p. 255°, obtained by the condensation of dihydrostrychnine with PhCHO by NaOEt in EtOH is accompanied by isobenzylidenedihydrostrychnine, m.p. 187-189°, [a]17 -325.1°/d in EtOH,  $[\alpha]_{1}^{19} - 665^{\circ}/d$  in CHCl<sub>3</sub>, which does not give Otto's reaction or a colour with FeCl<sub>3</sub>. It gives a methiodide,  $C_{28}H_{28}O_2N_2$ , MeI, m.p. 278—280° (de-comp.), and an Ac derivative,  $C_{30}H_{30}O_3N_2$ , m.p. 157— 159°,  $[\alpha]_{17}^{17}$ —295°/d in EtOH, but does not react with NH<sub>2</sub>OH or NH<sub>2</sub>·CO·NH·NH<sub>2</sub>. It is moderately stable towards KMnO<sub>4</sub> in COMe<sub>2</sub>, does not absorb H (PtO<sub>2</sub>) in cold AcOH, but adds 12—14 atoms of H in warm HCl giving a regiment Origination of warm HCl, giving a resinous product. Oxidation of benzylidenedihydrostrychnine by KMnO<sub>4</sub> in AcOH (loc. cit.) leads to a product,  $C_{28}H_{30}O_4N_2$  (or  $C_{28}H_{28}O_4N_2$ ) instead of  $C_{28}H_{28}O_5N_2$ , m.p. 268 (lit. 280°), giving a sulphate, hydrochloride, m.p. 233-236°, perchlorate, Ac derivative  $C_{32}H_{34}O_6N_2$ , m.p. 242–245°, and its perchlorate. Extraction of the pptd.  $MnO_2$ with 2N-NH<sub>3</sub> yields the acid, m.p. about 300° (decomp.),  $[\alpha]_{D}^{18} + 91 \cdot 3^{\circ}/d$  (as Na salt in H<sub>2</sub>O). In addition, a neutral compound, (?)  $C_{28}H_{30}O_4N_2$ , m.p. 263-264°,  $[\alpha]_{\nu}^{17} - 308^{\circ}/d$  in 95% HCO<sub>2</sub>H, is present in the COMe<sub>2</sub>. H. W.

Curare alkaloids. II. Constitution of curine (bebeerine). E. SPATH and F. KUFFNER (Ber., 1934, 67, [B], 55—59; cf. A., 1928, 1264).—Examination of curine Me ether (I) shows that it has no tendency to form basic salts and that it resembles curine (II) (loc. cit.) in that its mol. wt. is about 20% > expected. Treatment of (I) with relatively small

OMe NMe O OMe CH<sub>2</sub> CH<sub>2</sub> O NMe OMe OMe (4.)

amounts of MeI leads to a compound  $(C_{19}H_{21}O_3N)_2MeI$ , m.p. NMe 257—258° (vac., decomp.), thus indicating for (I) (now termed curine Me<sub>2</sub> ether) the composition  $C_{38}H_{42}O_6N_2$ , and for (II)  $C_{36}H_{38}O_6N_2$ . Confirmation is found by treatment of (II) with  $CH_2N_2$  in presence of Et<sub>2</sub>O, COMe<sub>2</sub>, and MeOH, whereby, in addition to (I), a curine Me ether, m.p. 206—208°, and a possible mixture of isomeric Me<sub>1</sub> ethers is obtained. The constitution of (I) is therefore modified to A, which explains the production of

protocatechuic acid in addition to p-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H

when (II) is fused with KOH and the formation of 5:6:4'-tricarboxy-2:3-dimethoxydiphenyl ether by oxidation of the final product of the Hofmann degradation of (I). H. W.

Molecular condition of the alkaloid silicotungstates. B. A. KLYACHKINA, M. K. STRUGATZKI, and F. D. ZILBERG (Bull. Nauch. Issledov. Khim. Farm. Inst., 1931, 203-208).-Nicotine in quantity too small for acidimetric titration can be titrated with silicotungstic acid (I). For cocaine, methylecgonine, ecgonine, morphine, codeine, thebaine, papaverine, narceine, hydrastine, atropine, piperine, harmine, harmaline, pilocarpine, and aq. strychnine the ratio (I) : alkaloid is 1 : 4. For eserine, quinine, nicotine, emetine, cephadine, anabasine, and strychnine (in 15% HCl) it is 1:2. Alkaloids with weakly basic N (dissociation const.  $< 10^{-11}$ ), which do not form salts with acids in aq. solution, react with (I) to form sparingly sol. salts. CH. ABS.

Naphthylarsinic acids. Application of Béchamp reaction to  $\alpha$ -naphthylamine. H. P. BROWN and C. S. HAMILTON (J. Amer. Chem. Soc., 1934, 56, 151—153).—The acid obtained (a) from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> H arsenate (I) at 195°, (b) by fusion of (I), and (c) from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> and H<sub>3</sub>AsO<sub>4</sub> at 165—175°, is 1-amino-2-naphthyl- (II) (A., 1932, 409) and not 4-amino-1-naphthyl- (III) -arsinic acid as stated by Adler and Adler (A., 1908, i, 492; cf. Benda and Kahn, *ibid.*, 591). (III) heated with  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> at > 175° gives (II). The Ac derivatives of (II) and (III) are converted by PCl<sub>5</sub> in CCl<sub>4</sub> into 2-chloro-1-acetamido- and 1-chloro-4-acetamidonaphthalene, respectively. H. B.

Diarsyls. 3:3':3":3"-Tetra-nitro-, VI. -amino-, and -acetamido-tetraphenyldiarsyl. F. F. BLICKE, U. O. OAKDALE, and J. F. ONETO (J. Amer. Chem. Soc., 1934, 56, 141-144).-3:3'-Dinitrodiphenylhydroxyarsine,  $H_3PO_2$ , and a little HI in AcOH give 3:3':3'':3'''-tetranitrotetraphenyldiarsyl, m.p. 203-204° (sealed tube; in N2) (cf. Michaelis, A., 1902, i, 515). Similar reduction of 3:3'-diaminodiphenylarsinic acid, m.p. 235° (de-comp.), affords 3:3':3'':3'''-tetra-aminotetraphenyldiarsyl, m.p. 168-169° (sealed tube; in N2) [tetrahydrochloride, m.p. about 283° (decomp.); Ac4 derivative (I), m.p.  $> 300^{\circ}$ ], also obtained (a) from 3 : 3'-di-aminodiphenylarsine (II) and 3 : 3' : 3'' : 3'''-tetra-aminotetraphenylarsyl oxide (III) ( $Ac_4$  derivative, m.p.  $236-237^{\circ}$ ), (b) from AsHPh<sub>2</sub> and (III), and (c) from (II) and  $(AsPh_2)_2O$ .  $(AsPh_2)_2$  is also formed in (b) and (c). (I) absorbs  $O_2$  very slowly when suspended in C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>. H. B.

Evidence for an asymmetrical arsenic atom. C. F. H. ALLEN, F. B. WELLS, and C. V. WILSON (J. Amer. Chem. Soc., 1934, 56, 233—234; cf. A., 1933, 1177).—7-Chloro-7:12-dihydrobenzophenarsazine and Ag d-bromocamphorsulphonate in  $Ac_2O$  give small amounts of two isomeric compounds,  $C_{26}H_{35}O_4NBrSAs$ , m.p. 182—183°,  $[\alpha]_{17}^{sp}$  +35·1° (all rotations are in 95% EtOH), and m.p. 188—189°,  $[\alpha]_{17}^{sp}$  +59·5°; solids, m.p. 200° and 211—212°, are also formed. 7-Chloro-9methyl - 7: 12 - dihydrobenzophenarsazine similarly affords a very small amount of a compound,  $C_{27}H_{37}O_4NBrSAs, m.p. 250^\circ, [\alpha]_D^3 + 32.6^\circ.$  12-Chloro-7:12-dihydrobenzophenarsine (?) gives isomeric compounds,  $C_{26}H_{35}O_4NBrSAs, m.p. 218-219^\circ$  and 224-225°, in addition to two other substances. H. B.

Organic compounds of mercury. VI. Synthesis of organic compounds of mercury with negative substituents by the diazo method. A. N. NESMEJANOV, N. T. GLUSCHNEV, N. T. EFI-FANSKI, and P. T. FLEGONTOV (Ber., 1934, 67, [B], 130—134; cf. A., 1933, 292).—Optimum conditions are described for the prop. of compounds,  $RN_2Cl,HgCl_2$ , in which R=0- $NO_2$ · $C_6H_4$ , 116—117°, p- $NO_2$ · $C_6H_4$ , m- $NO_2$ · $C_6H_4$ , decomp. 138°, 2:5- $C_6H_3Cl_2$  and  $SO_3H$ · $C_6H_4$ , m.p. 152—153°. Slow addition of these compounds to a well-stirred mixture of a suitable solvent (usually COMe<sub>2</sub>) and Cu powder generally at -20° to -10°, but occasionally at -70°, affords the corresponding HgCl-derivatives in 30% to 70% yield. H. W.

Aryl selenohalides. IV.  $\alpha$ -Anthraquinonyl selenohalides and  $\alpha$ -anthraquinoylselenenic acid. O. BEHAGEL and W. MÜLLER (Ber., 1934, 67, [B], 105— 108; cf. A., 1933, 842).—Di-1-anthraquinonyl diselenide (I) is converted by Br in boiling CHCl<sub>3</sub> into Se 1-anthraquinonyl bromide (II), m.p. (indef.) 217°. Treatment of (I) in AcOH with Cl<sub>2</sub> or SO<sub>2</sub>Cl<sub>2</sub> leads to Se 1-anthraquinonyl trichloride, m.p. 203° after darkening, transformed by COMe<sub>2</sub> in CHCl<sub>3</sub> into Se 1-anthra quinonyl chloride (III), m.p. 220°, also obtained from (I) and the calc. amount of Cl<sub>2</sub>. (II) and NPhMe<sub>2</sub> in boiling Et<sub>2</sub>O afford 4-dimethylaminophenyl 1-anthra quinonyl selenide, m.p. 270°, whilst Ph 1-anthra quinonyl selenide, m.p. 178°, results from (II) and MgPhBr. (II) or (III) is transformed by AgOAc in boiling McOH into 1-anthraquinonylselenenic acid, m.p. > 250°, which yields a dark blue Na salt.

H. W.

Triphenylsilicyl ethylammine, SiPh<sub>3</sub>,NH<sub>2</sub>Et. C. A. KRAUS and H. EATOUGH (J. Amer. Chem. Soc., 1933, 55, 5008—5014).—SiPh<sub>3</sub>Br and Li (1 equiv.) in NH<sub>2</sub>Et give triphenylsilicyl ethylammine (I), m.p. 45°, which dissociates in boiling Et<sub>2</sub>O and affords ( $\cdot$ SiPh<sub>3</sub>)<sub>2</sub>. (I) can be distilled in a high vac., does not react with Na in liquid NH<sub>3</sub>, but with Li in NH<sub>2</sub>Et gives LiSiPh<sub>3</sub> (II). (II) and NH<sub>4</sub>Br in liquid NH<sub>3</sub> afford SiHPh<sub>3</sub>; SiPh<sub>4</sub> is formed using PhBr. (II) and SnMe<sub>3</sub>Cl in liquid NH<sub>3</sub> give trimethylstannyltriphenylsilicon (III), SnMe<sub>3</sub>·SiPh<sub>3</sub>, which is decomposed by Na in liquid NH<sub>3</sub> to NaSiPh<sub>3</sub> and NaSnMe<sub>3</sub> (subsequent treatment with MeI gives SiPh<sub>3</sub>Me and SnMe<sub>4</sub>). SiPh<sub>3</sub>Br and SnMe<sub>3</sub>Br are obtained from (III) and Br in Et<sub>2</sub>O. H. B.

Reactions of sodium triphenylstannide with polyhalogenated methanes. C. A. KRAUS and H. EATOUGH (J. Amer. Chem. Soc., 1933, 55, 5014-5016).—NaSnPh<sub>3</sub> (I) and  $CH_2Cl_2$  in liquid  $NH_3$  give  $di(triphenylstannyl)methane, CH_2(SnPh_3)_2, m.p. 104.5^{\circ}$ (corr.); with  $CHCl_2$ , tri(triphenylstannyl)methane, m.p.128° (corr.), and a little  $SnPh_3$  (II) result. (I) and  $CCl_4$  afford (II). H. B.

Iodometric determination of protein degradation products. L. UTKIN (Biochem. Z., 1933, 267, 69-73; cf. A., 1930, 1217).—The method of Kober and Sugiura (A., 1917, ii, 398) is improved by pptg. the  $Cu(OH)_2$  in the protein solution which is then buffered with borate and using alkaline KI solution. OHacids must be absent. The procedure can be applied in following the degradation of proteins and polypeptides, but not in determining the composition of simple peptides or in measuring dipeptidase action. W. McC.

Nucleoproteins. S. J. PRZYŁECKI (Rocz. Chem., 1933, 13, 681-685).—A classification of nucleoproteins (I) and nucleins is proposed, based on considerations of the nature and no. of the constituent groups. Nucleic acid (II) is combined with protein by its free  $H_3PO_4$  groups; the no. of  $H_3PO_4$  valencies so combined varies with the relative concn. of protein and (II). R. T.

Effect of dilute alkali on cystine content of casein. D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1934, 104, 99—106).—Successive pptn. of very pure casein from NaOH solutions with AcOH produces a loss in the cystine (I) content; after five pptns. 90% of (I) is destroyed. The % arginine, histidine, lysine, tyrosine, and tryptophan are not materially changed. The importance of the losses of (I) in relation to dietary experiments is emphasised.

H. D. Determination of sulphur in organic substances. E. KAHANE and M. KAHANE (Compt. rend., 1934, 198, 372–375).—The substance (0·1— 0·2 g.) is heated with 2 c.c. of a 2:1 mixture of  $HClO_4$  (d 1·61) and  $HNO_3$  (d 1·39) with a little  $HIO_3$ and the escaping gases are washed with  $HIO_3$  (apparatus described). The  $HIO_3$  is then reduced (NaI,  $CH_2O$ , or  $N_2H_1$ ), the solution neutralised, and  $SO_4^{\prime\prime}$ pptd. as  $BaSO_4$ . J. W. B.

Detection of selenium in organic compounds. M. J. HORN (Ind. Eng. Chem. [Anal.], 1934, **6**, 34– 35).—The sample is completely oxidised with  $H_2SO_4$ containing a little  $HgSO_4$  and a few drops of 3% aq. codeine sulphate are added. A green coloration, rapidly changing to blue, is observed if Se is present. Presence of more than a trace of  $H_2O$  prevents the development of colour, and V gives a dark greenishblue coloration. H. A. P.

Determination of active hydrogen. O. SCHMITZ-DUMONT and K. HAMANN (J. pr. Chem., 1934, [ii], 139, 162—166).—The disturbing effects caused by reaction (I) of  $C_5H_5N$  with the Grignard reagent when used as solvent in the Zerevitinov determination are obviated by plotting the vol. of gas evolved against time. This increases rapidly at first, but soon falls to a const. rate due to (I) alone. Extrapolation of the corresponding straight line to zero time therefore gives the true vol. H. A. P.

Micro-method for determination of iodine values. J. O. RALLS (J. Amer. Chem. Soc., 1934, 56, 121-123; cf. A., 1933, 709).—The substance (0.75-25 mg.) is treated with IBr in  $CCl_4$  at 0°; after addition of KI and titration with  $Na_2S_2O_3$ , the mixture is treated with KIO<sub>3</sub> to determine HHal produced during the reaction. Results are given for 30 substances. H. B.

Determination of gaseous olefines. V. SORO-KIN, A. BELIKOVA, and O. BOGDANOVA (J. Rubber Ind., U.S.S.R., 1931, 5, No. 4—5, 26—27).—With HBr in glacial AcOH,  $C_2H_4$  is unchanged,  $C_3H_6$  gave Pr<sup> $\beta$ </sup>Br with some Pr<sup> $\alpha$ </sup>Br,  $\Delta^{\beta}$ -butylene gave the bromide, b.p. 90—91°,  $\beta$ -methyl- $\Delta^{\alpha}$ -propylene gave the bromide, b.p. 92—93°, butadiene gave the mono-, b.p. 103°, and di-, b.p. 170—172°, -bromides. CH. ABS.

Detection of disubstituted urethanes by colour reactions. F. BECKER and G. A. HUNOLD (Z. ges. Schiess- u. Sprengstoffw., 1933, 28, 372-376).-With HNO<sub>3</sub>, d 1.18 (I), urethanes of the type NPhR·CO<sub>2</sub>Et (R=Me or Et) give  $(NO_2)_1$ -derivatives, converted by NaOH-EtOH into p-NO2 ·C6H4·NHR, no red colour being produced, but with HNO<sub>3</sub>, d 1.42 (II), (NO<sub>2</sub>)<sub>2</sub>derivatives are formed (the R group suffering fission), hydrolysed to 2: 4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH<sub>2</sub> with production of a red colour. Similarly centralite CO(NPhEt)2 gives no red with (I)-NaOH-EtOH, but does so with (II)-NaOH-EtOH. NPh<sub>2</sub>·CO<sub>2</sub>Et with (I) gives a p-NO2-derivative hydrolysed to p-NO2.C6H4.NHPh, a red colour being formed, and with (II) the ultimate hydrolysis products are 4:4'- and 4:2'-dinitrodiphenylamine, also giving a red colour. Similarly akardite (NPh2·CO·NH2) gives a red colour with either (I) or (II), the initial products being 2:4:2':4'-tetra-2:4:6:2':4':6'-hexa-nitrodiphenylamine. and Thus the usual colour reaction for smokeless powders J. W. B. is not sp.

Reactions of some phenols with (a) antimony pentachloride, and (b) sulphuric-arsenic acid mixture. L. EKKERT (Pharm. Zentr., 1934, 75, 49-50, 50-51).—Colour reactions of (a) 21, (b) 18, phenol derivatives with SbCl<sub>5</sub>-CHCl<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>-Na<sub>3</sub>AsO<sub>4</sub>, respectively, are given. E. H. S.

Detection of *p*-chlorobenzoic acid in the presence of benzoic acid. F. WEISS (Z. Unters. Lebensm., 1934, 67, 84—86).—If, in carrying out Mohler's test by Grossfeld's method (A., 1915, ii, 158), the NH<sub>2</sub>OH is added so as to form a distinct upper layer, p-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H (I) gives a green, BzOH

(II) an orange-red, ring. If the solutions are mixed, (I) gives a red colour and cannot be distinguished from (II). E. C. S.

Determination of pyridine in dilute solution. M. V. IONESCU and H. SLUSANSCHI (Bull. Soc. chim., 1933, [iv], 53, 1087—1096).—This is effected by noting the time taken for formation of a ppt. with N-(CdCl<sub>2</sub>+2NaCl) or N-(HgCl<sub>2</sub>+2NaCl) in concess of 0.045—0.075 and 0.012—0.006%, respectively.

**B.** S. C. **Aminometry of alkaloids.** D. VORLANDER (Ber., 1934, 67, [B], 145; cf. this vol., 198).—Cinchonine and quinine behave quantitatively as diacidic amines, whereas strychnine and brucine are monoacidic. Anhyd. PhSO<sub>3</sub>H or other aromatic sulphonic acids can replace HCl. H. W.

**Reaction of methylene ether groups in aromatic** compounds. J. A. LABAT (Bull. Soc. Chim. biol., 1933, 15, 1344—1345).—With regard to the colour reaction with gallic acid in  $H_2SO_4$  (A., 1909, ii, 771), priority to Sanchez (A., 1932, 866) is claimed. In the event of nornarcotine proving to be related to vitamin-*C*, the application of the reaction to vitamin-*C* research is indicated. F. O. H.

Quantitative spectro-photo-electric analytical method applied to solutions of chlorophylls a and b. F. P. ZSCHEILE, jun. (J. Physical Chem., 1934, 38, 96-102).-Using the apparatus previously described (this vol., 272), quant. light absorption data have been obtained for chlorophylls a and b and their mixtures, and it is shown that the composition of such mixtures can be determined with an error of < 1%. Measurements at  $\lambda$  4400 Å. give total concn. and at  $\lambda$  4100 or 4279 Å. the ratio of a to b. Beer's law is valid for chlorophyll solutions in 90% COMe2. The method may be applied to all coloured solutions obeying Beer's law and should be especially useful in biochemistry. A supplementary method with an accuracy within 5% is given. M. S. B.

## Biochemistry.

Comparison of methods for collection of blood to be used in the determination of gases. J. M. LOONEY and H. M. CHILDS (J. Biol. Chem., 1934, **104**, 53—58).—A method of withdrawing and handling blood for gas analysis employing a capped syringe is described. Blood kept in 10-c.c. portions for  $\ge 2$  hr. under 5 cm. of oil loses < 7.98 vol.-% of CO<sub>2</sub> and gains < 6.44 vol.-% of O<sub>2</sub>. The effect of stasis on the gas content of blood can be avoided by drawing the blood 1 min. after the removal of the tourniquet. A. L.

Van Slyke method of blood-gas analysis. F. RAPPAPORT and K. KÖCK-MOLNAR (J. Biol. Chem., 1934, 104, 29—31).—The reagent is modified by the addition of urea (450 g. per litre) to prevent protein pptn. and so permit more exact readings. A. L.

Stimulating action of copper on erythropoiesis. H. B. STEIN and R. C. LEWIS (J. Nutrition, 1933, 6, 465-472).—Feeding of evaporated milk to rats reduces the haemoglobin (I) without the corresponding reduction in erythrocyte (II) count such as occurs when raw milk is the sole diet. The Cu in evaporated milk causes the temporary maintenance of a high (II) count. Addition of 0.25-0.5 mg. Cu daily to a milk dict has an erythropoietic action without effect on (I). A. G. P.

Spectrophotometric differentiation of the hæmoglobins of different species. H. M. WINE-GARDEN and H. BORSOOK (J. Cell. Comp. Physiol., 1933, 3, 437—448).—It is possible to observe, by spectrophotometric methods, intersp. and (in the case of the rabbit) intrasp. differences in the hæmoglobins. Of the erythrocyte-Fe, 4-6% is in a form simpler than hæmoglobin. A. G. P.

Crystalline forms of (a) hæmin and mesohæmin; (b) esters of hæmin, mesohæmin, and protoporphyrin. K. LINDENFELD (Rocz. Chem., 1933, 13, 645-659, 660-680).-(a) The prep. and properties of the polymorphs of X-hæmin (I) (A., 1931, 1079) (X=Cl, Br, I, CNS) are described. "Acetone-(I)," prep. by adding COMe<sub>2</sub> to a solution of Cl-(I) in aq. NH<sub>3</sub>, and acidifying with HCl at 50°, is rapidly converted into the ordinary Teichmann form of Cl-(I) on immersion in boiling 80% AcOH. Cl-, Br-, and CNS-mesohæmin (II) are obtained in hexagonal plates by adding a solution in CHCl<sub>3</sub>-C<sub>5</sub>H<sub>5</sub>N of the Teichmann crystals (from mesoporphyrin) to 80% AcOH containing NH<sub>4</sub>Cl, NH<sub>4</sub>Br, or NH<sub>4</sub>CNS at 50°; under analogous conditions I-(II) does not yield a polymorph. These polymorphs are contaminated with impurities adsorbed from solution.

(b) The  $Me_2$  and  $Et_2$  esters of protoporphyrin (III) are prepared by heating (III) in MeOH or EtOH containing 2% of HCl. The  $Et_2$  esters of X-(I), (II), and X-(II) are prepared analogously. The esters exist in two cryst. forms, viz., fusiform obtained by rapid, and octahedral or monoclinic by slow, crystallisation from CHCl<sub>3</sub>-C<sub>5</sub>H<sub>5</sub>N; the formation of the latter crystals, which are the more stable, is favoured by the presence of NH<sub>4</sub>X in the solvent. R. T.

Fluorescence spectrum of the tin complex of blood-protoporphyrin. H. BIERRY and B. GOUZON (Compt. rend., 1934, 198, 615-617).—The Sn complex produced by the action of SnCl<sub>2</sub> on blood in AcOH can be identified with that of protoporphyrin by means of its fluorescence spectrum, which is distinct from that of hæmatoporphyrin. P. G. M.

Determination of blood-bile acids. II. In serum. K. KUSUI (J. Biochem. Japan, 1933, 18, 345-368; cf. A., 1932, 1053).—Serum (1 c.c.) is treated with EtOH (25 c.c.) and the EtOH-sol. material is separated and extracted with Et<sub>2</sub>O. The Et<sub>2</sub>O-insol. fraction is extracted with EtOH and the extract treated with sucrose and  $H_2SO_4$ , the resulting colour being compared with suitable standards. The method is applicable to lymph. Human serum contains 6·3-11·6 and dog's serum 6·24-10·5 mg. of bile acid per 100 c.c. F. O. H.

Determination of indoxyl compounds in blood. H. SHARLIT (J. Biol. Chem., 1934, 104, 115—120; cf. A., 1933, 301).—The method for determining indican (I) in urine is applied to blood; all reactions must be carried out at room temp. In normal fasting individuals the concn. of (I) is negligible; in cases of N retention it may be > 6 mg. per 100 c.c. H. D.

Extraction of cholesterol from blood. O. MUHLBOCK (Z. physiol. Chem., 1933, 222, 233—234).— Bloor's method is applicable to whole blood (cf. Milbradt, A., 1933, 624). 1 c.c. of oxalated blood is dropped into EtOH-Et<sub>2</sub>O (3:1). After a few hr. the solution is filtered and dried. The COMe<sub>2</sub> extract of the residue is examined nephelometrically (cf. A., 1932, 666). J. H. B.

Determination of fructose in blood. R. STÖHR (Z. physiol. Chem., 1933, 222, 261–269).—2 c.c. of the protein-free blood filtrate (from 0.2 c.c. of blood) are treated with 2 c.c. of phosphomolybdic acid reagent. After 25 min. at 100°, the cooled solution is titrated with 0.01N-KMnO<sub>4</sub> to disappearance of the blue colour. AcCHO, OH·CH(COMe)<sub>2</sub>, CH<sub>2</sub>Ac·OH, glyceraldehyde, and CO(CH<sub>2</sub>·OH)<sub>2</sub> interfere, but glucose does not. J. H. B. Fluctuations of blood-sugar in vitro. I. NEU-WIRTH (J. Biol. Chem., 1934, 104, 129-130).—The results of Kleiner (A., 1933, 966) on the fluctuations in the blood-sugar curve of undialysed hyperglycæmic blood could not be repeated. H. D.

Iron content of the blood. O. H. HELMER and C. P. EMERSON (J. Biol. Chem., 1934, 104, 157-161). —The average Fc content of whole blood is  $52 \cdot 5$  and  $49 \cdot 8$  mg. per 100 c.c. for men and women, respectively, by Kennedy's method (A., 1927, 987), which gave higher vals. than Wong's method (A., 1928, 785). Hæmoglobin determined by Fe content and O<sub>2</sub> capacity was in good agreement. H. G. R.

Ultrafiltration of serum and plasma. Content of ultrafiltrates in chlorine, potassium, sodium, calcium, and magnesium. J. Lévy and M. M. PACU (Bull. Soc. Chim. biol., 1933, 15, 1317—1329).— Ultrafiltrations of serum (I) and plasma (II) under 2 atm. pressure indicate the following degrees of ultrafilterability: Cl of (I) and (II), 100%; K of (I) and (II), 95%; Na of (I) and (II), 90%; Ca of (I), 64%, of (II), 72%; Mg of (I) and (II), 60—70%. F. O. H.

Citration of blood and precipitation of calcium by oxalate. L. BRULL and R. POVERMAN (Bull. Soc. Chim. biol., 1933, 15, 1281—1289).—Addition of up to 1.0% of Na citrate (I) to aq. CaCl<sub>2</sub> (0.01% in Ca) does not influence the pptn. of Ca by  $(NH_4)_2C_2O_4$ , whilst concerns. of (I) of 3.0% or more partly inhibit the pptn. With serum, the concernst of (I) must not be >1.0%. Addition of 0.3—0.5% of (I) to whole blood influences neither the partition of Ca between serum and fibrin nor the pptn. of Ca from the plasma. That low concernst of (I) cause complex-formation by Ca is therefore refuted (cf. A., 1932, 293).

F. O. H.

Proteinates and cations of blood-serum. J. LÉVY and F. GALLAIS (Bull. Soc. Chim. biol., 1933, 15, 1330—1335).—The non-ultrafilterable fraction (I) of Na and K in serum equals that fraction of these cations bound to the proteins (II) isolated by pptn. with EtOH, whilst with Ca, (I) (32%) is < that bound to the pptd. (II) (61%). F. O. H.

Concentration and distribution of phosphorus in blood of merino sheep on pasture. R. H. WATSON (Austral. J. Exp. Biol., 1933, 11, 253— 260).—The total, inorg., org. acid-sol., and org. acidinsol. blood-P of sheep on natural pasture were  $16\cdot5-20\cdot8$ ,  $2\cdot8-5\cdot9$ ,  $3\cdot4-6\cdot0$ , and  $8\cdot0-11\cdot3$  mg. per 100 c.c., respectively. H. D.

Significance of the iodine content of human blood. G. M. CURTIS, C. B. DAVIS, and F. J. PHIL-LIPS (J. Amer. Med. Assoc., 1933, 101, 901-905).---Blood-I is normally 0.012 mg. and urinary I 0.025---0.075 mg. per 100 e.c. Vals. are increased in toxic goitre, menstruation, and I medication. Human blood-I is a measure of thyroid function.

CH. ABS.

Analysis of serum with the ultracentrifuge. Serum fractions. P. VON MUTZENBECHER (Biochem. Z., 1933, 267, 460).—A correction of the author's papers (this vol., 93). P. W. C. Surface tension of the blood-plasma and -serum in certain marine animals. E. ZUNZ (Bull. Acad. roy. Belg., 1933, [v], 19, 1107—1125).—The dynamic surface tension of the plasma is > that of  $H_2O$  in the Selachians examined and < that of  $H_2O$  for Teleosteans, Crustaceans, and Cephalopods. Both dynamic and static surface tensions of the sera are always < those of the plasma. J. W. S.

Chemistry of mitogenetic radiation of blood. A. GURVITSCH (Russ. J. Physiol., 1933, 16, 495— 500).—The mitogenetic radiation (I) of hæmolysed blood is due to glycolysis; (I) is in particular associated with dissociation of hexosediphosphoric acid, and with dismutation of phosphoglyceraldehyde. R. T.

Physical chemistry of avian erythrocytes. F. J. BERENSCHTEIN, D. I. LJACH, and N. P. BEDRI-KOVSKAJA (Russ. J. Physiol., 1933, 16, 530-540) .---Duck erythrocytes (I) suspended in aq. sucrose undergo agglutination (II) at  $p_{II}$  5.9, goose (I) at  $p_{\rm H}$  5.3-5.6, and hen (I) at  $p_{\rm H}$  3.54-5.3; alkali and alkaline-earth salts inhibit (II) in Hofmeister's series. The rate of sedimentation (III) of avian (I) in their homologous plasma (IV) is 1/25 to 1/30 that of horse (I); similar results are obtained for suspensions of horse (I) in avian (IV), and of avian (I) in horse (IV). In all cases (III) is greater for (IV) than for serum suspensions; it increases for avian and diminishes for horse (I) when isotonic solutions of NaCl, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, glucose, or sucrose are substituted for (IV). R. T.

Concentration of anti-venom serum. G. C. MATTRA, B. P. B. NAIDU, and M. L. AHUJA (Indian J. Med. Res., 1933, 21, 229—236).—Dil. serum is treated with Na<sub>2</sub>SO<sub>4</sub> and pseudoglobulin (I) removed from the pptd. globulin with saturated aq. NaCl. The filtered solution of (I) is treated with AcOH and the ppt. is dialysed in 2% Na<sub>2</sub>CO<sub>3</sub> against H<sub>2</sub>O until free from SO<sub>4</sub>". The  $p_{\rm H}$  is adjusted to 7.4; 1% NaCl and 0.35% of tricresol are added. CH. ABS.

Microelectrodialysis and its use for the isolation of serum precipitins. T. ASABA (Arb. Med. Fak. Okayama, 1933, 3, 561-568).—Immune bodies were isolated from antigen-antibody complexes in a modified Pauli apparatus. Precipitins with a trace of NaCl were obtained. CH. ABS.

Action of infra-red, visible, and ultra-violet rays on hæmolytic complement and the absorption spectrum of guinea-pig serum. M. PAIC and P. HABER (Compt. rend., 1934, 198, 613-615)... Complete destruction of complement by the light from a Hg-vapour lamp takes place in 10 hr. P. G. M.

Morphology and fine structure of collagen fibres. A. KUNTZEL and F. PRAKKE (Biochem. Z., 1933, 267, 243—295).—Tendon fibres (of Achilles of ox and calf, of rat's tail) are cellular and  $10 \mu$  in width, and skin-collagen fibres are not in general cellular and  $2 \mu$  in width. The fibres are composed of fibrils  $0.5 \mu$ wide. The fibres are examined under the polarisation microscope and by X-ray analysis, and the changes of form on swelling in H<sub>2</sub>O and dil. acid and on contraction are investigated. Swelling of a dry fibre in H<sub>2</sub>O leads to thickening and lengthening, the absorption of H<sub>2</sub>O being chiefly intramicellar and partly intermicellar. Swelling in acid leads to thickening and shortening with an increase of vol. This effect with rat's tail fibres is reversible. Fibres swollen in  $H_2O$  readily decrease in length on drying at 62–90° or on placing in conc. solutions of electrolytes. P. W. C.

Structure of collagen fibres and the point of attack by proteolytic enzymes. D. J. LLOYD and M. E. ROBERTSON (Nature, 1934, 133, 102—103).— Proteolytic enzymes appear to attack collagen fibres with case at a cut end, but only with difficulty at the undamaged side. L. S. T.

Isolation of a crystalline depressor substance from the brain. C. J. WEBER, J. B. NANNINGA, and R. H. MAJOR (Proc. Soc. Exp. Biol. Med., 1933, 30, 573-515).--0.1 mg. of the substance (prep. described) caused a fall in blood-pressure of 8 mm. in a 12-kg. dog. CH. Abs.

Chemistry of adrenal medulla. S. HUSZÁK (Z. physiol. Chem., 1933, 222, 229–232).—The reducing substance in adrenal medulla is ascorbic acid. It fails to produce the reduction of  $AgNO_3$  shown by the cortex, owing to the presence of inhibitors, which, however, are removed by Pb acetate. J. H. B.

Chemistry of marine animals. I. Sponge, Microciona prolifera. W. BERGMANN and T. B. JOHNSON (Z. physiol. Chem., 1933, 222, 220–226).— From M. prolifera there was isolated in yield of  $1\cdot25\%$ on dry wt. microcionasterol,  $C_{27}H_{46}O$ , m.p. 126—127°,  $[\alpha]_{15}^{*}$ —19.8° in CHCl<sub>3</sub> (acetate, m.p. 125—126°,  $[\alpha]_{14}^{*}$ -24.8° in CHCl<sub>3</sub>; propionate, m.p. 128°; benzoate, m.p. 143°, clears at 146°, changing through violet and green,  $[\alpha]_{19}^{*}$ —10.7° in CHCl<sub>3</sub>; chloride (I), m.p. 104— 105°; Cl-containing product, m.p. 60—65°). Reduction of (I) with Na in BuCH<sub>2</sub>OH gives microcionastene,  $C_{27}H_{46}$ , m.p. 61—62°. The pigment, m.p. 167°, is probably a carotene. J. H. B.

Protein of the chrysalis of the domesticated silkworm. R. INOUE, T. MIWA, and K. KITAZAWA (Bull. Sericult. Japan, 1933, 6, 1-3).--NH<sub>2</sub>-acid composition of the proteins of the pupa of the domesticated and tussah silkworms are similar.

H. G. R. [Silkworm] pupa-oil emulsion. II. Physical properties. Н. КАNЕКО and К. ҮАМАМОТО (Bull. Scricult. Japan, 1933, 6, 3—4).—The emulsion (0.93% oil) is very stable. H. G. R.

Hydrogen carbonate content of living muscle. N. BROOKENS (Biochem. Z., 1933, 267, 349–356).— Resting muscle in equilibrium with scrum contains 30% less NaHCO<sub>3</sub> than scrum, whereas in Ringer's solution at lower CO<sub>2</sub> pressure a smaller but similar difference exists which disappears at higher CO<sub>2</sub> pressure. P. W. C.

Distribution of inorganic salts in birds. A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1933, 267, 460).—A correction of the authors' paper (A., 1933, 968). P. W. C.

Gastric secretion. V. Composition of gastric juice as a function of its acidity. F. HOL-LANDER (J. Biol. Chem., 1934, 104, 33-42).—In the parietal secretion (I), neutral Cl', combined acid, inorg. and org. P, and org. solids are absent, and the sp. gr. is that of aq. HCl of 170 m.-mol. concn. (I) is therefore essentially an isotonic solution of HCl. A. L.

Gastric mucin. Effect on gastric acidity. D. H. ROSENBERG and L. BLOCH (J. Lab. Clin. Med., 1933, 18, 1041—1052).—Commercial gastric mucin in  $\frac{1}{2}$ -oz. doses inhibited secretion of HCl for 40 min. (aver.) after ingestion. The inhibition was due largely to the "peptone ash fraction." Milk and cream had similar inhibitory powers in 3-oz. doses.

NUTR. ABS.

Gastric secretion in a horse with gastric fistula. S. V. EGOROV and V. N. TSCHEREDKOV (Russ. J. Physiol., 1933, 16, 520-529).—A fasting horse secreted 10-30 litres daily of gastric juice (I), during 2.5 days; (I) had a total acidity of 0.22, free HCl 0.14, and a digestive capacity of 3.5 (Mett). Food residues were absent after 1.5 days. R. T.

Determination of pepsin and rennin activity in gastric juice. B. ANDERSEN (Compt. rend. Lab. Carlsberg, 1933, 19, No. 19, 1—24).—The titratable NH<sub>2</sub>-groups liberated by digesting infants' gastric , juice (I) with 3% caseinogen for 2 hr. at 30° and  $p_{\pi}$  2·3 were employed to define pepsin activity (II). Rennin activity (III) was measured by Holter's method (A., 1933, 94). Const. vals. for a given (I) could be obtained only by keeping the coagulation mixture at  $p_{\pi}$  6·25—6·40. The ratio of (II) to (III) in the (I) of four infants was approx. const. H. D.

Analysis of pyloric secretion. M. G. NIKOLAEVA (Russ. J. Physiol., 1933, 16, 199-204).—Section of the splanchnic nerves in dogs with isolated pylorus increased the secretion of gastric juice, but did not alter the % increase brought about by HCl. The effect of irrigation of the mucous membranes by solutions of various salts and drugs is recorded.

W. O. K.

Blood composition in relation to milk secretion. S. J. FOLLEY and G. L. PESKETT (Nature, 1934, 133, 142).—Attention is directed to sources of error involved in obtaining samples of blood.

L. S. T.

Dietary requirements for lactation. I. Failure of lactation on an apparently complete synthetic diet. W. NAKAHARA and F. INUKAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 301-307).—A diet of polished rice powder (75 g.), fish-protein (10 g.), butter (10 g.), salt mixture (5 g.), and brewer's yeast (5 g.) was adequate for growth, pregnancy, and parturition of rats but failed to support lactation. W. O. K.

Lactation in a barren heifer. I. JOHANSSON and M. H. KNUDSEN (J. Dairy Sci., 1933, 16, 523— 528).—Milk produced by a barren heifer showed normal chemical composition. A. G. P.

Fatty acids and glycerides of the milk-fat of Indian camels. D. R. DHINGRA (Biochem. J., 1934, 28, 73-78).—Camel milk-fat has lower Kirschner and Reichert-Meissl vals. than that of other animals. The fatty acids of the mixed saturated-unsaturated glycerides differ little from those of cow and buffalo butters, but more so from those of goat and sheep milk-fats. H. G. R. Determination of alcohol in milk. M. SATO and K. MURATA (J. Agric. Chem. Soc. Japan, 1932, 8, 1303—1309).—EtOH is oxidised with  $Cr_2O_7''$ , the excess being determined iodometrically. Cow's milk contained 1.61—4.95 mg. EtOH per 100 c.c.

CII. ABS.

Precipitation of nitrogenous substances by alkaline mercuric reagents, particularly in urine. M. E. EVERETT, F. SHEPPARD, and E. O. JOHNSON (J. Biol. Chem., 1934, 104, 1-10).-A study of Hg-nitrogenous compounds in alkaline solution indicates that the amount of pptn. is related to the structure, less pptn. occurring with alkylated or acylated N. Whilst glycine and the higher homologues are quantitatively pptd., alanine (I), sarcosine (II), and branched-chain NH<sub>2</sub>-acids, except leucine, are only partly pptd. Cryst. Hg compounds sol. in  $H_2O$  of (I), aminoisobutyric, aminomethylbutyric, aspartic, and hippuric acids, isoleucine. methionine, hydroxyproline, proline, and (II), and also Hg compounds of adip-, hexo-, diethylform-, dimethylacet-, hept-, myrist-, phenylacet-, stear-, and valer-amide (no descriptions given) have been prepared. Using the prescribed method of N determination in Hg filtrates from biological fluids, 1.6, 20, and 30% of N remain in the Hg filtrates of urine (III), muscle extract, and liver extract, respectively, hippuric acid being the chief N-constituent of (III). A. L.

Sugar of normal urine. II. Behaviour of carbohydrates in bromine water and the ketose of normal urine. M. R. EVERETT, B. G. EDWARDS, and F. SHEPPARD (J. Biol. Chem., 1934, 104, 11-28). -The progressive effect of Br oxidation (I) of sugars on the Sumner/Folin-Wu ratio of glucose equivs. assists in identification, particularly in the case of NH2-sugars, methylpentoses, and higher oligosaccharides, and indicates the existence of new reducing derivatives of l-fucose, inulin, dextrin oligosaccharides, and d-glucosamine. (I) also indicates that the chief reducing material, designated uroketose (II), of normal urine is a ketose, keturonic acid, or aminoaldose, although a small amount of rapidly hydrolysable sugar more casily oxidised is also present. Some reactions of (II) are described. The major portion of the free sugar of tungstic acid bloodfiltrates is oxidised like aldoses, but a second substance is also present. A. L.

Uroflavin, maltoflavin, and redox potentials of lyochromes. K. G. STERN (Nature, 1934, 133. 178-179).-Uroflavin (I) from normal human urine and maltoflavin (II) from malted barley both show a strong green fluorescence (III) of their yellowish-red solutions; visible blue-violet light and ultra-violet radiation are responsible for (III). Strong irradiation in alkaline solution gives CHCl<sub>3</sub>-sol. "lumiflavins." Colour and (III) are lost on reduction and regained on reoxidation. (I) and (II) have sharp absorption bands at 281 and 255 mµ, respectively, but there is no sp. absorption at longer wave-lengths. The potentiometric measurements recorded show that hepatoflavin, (I), and (II) represent stable oxidationreduction systems. L. S. T.

Isolation of phæophorbide *a* from silkworm fæces. H. FISCHER and A. HENDSCHEL (Z. physiol.

Chem., 1933, 222, 250–260).—In the COMe<sub>2</sub> extract of the fæces phæophorbide a (I) was identified. Cold HI reduction gave *iso*phæoporphyrin  $a_6$ , hot,  $a_5$  (II). The AcOH extract gave phæopurpurins 7 (III) and 18. HI reduction of the phæophorbide fraction afforded mainly (II). (III) arises by secondary oxidation in the prep. of the Na salt. Phyllobombycin is a mol. compound of (I) and (III). The silkworm thus eliminates phytol and Mg from chlorophyll with production of (I). J. H. B.

Anæmia. II. Goat's milk anæmia. C. BOM-SKOV and M. AUFFARTH (Z. ges. exp. Med., 1933, 89, 804-808; Chem. Zentr., 1933, ii, 1889).—Anæmia of young rats fed with goat's milk is not due to lack of vitamin-A or -C or to a toxic effect of the volatile unsaturated fatty acids. A. A. E.

Metallised and irradiated milk in the treatment of nutritional anæmia. J. L. McGHEE and B. FERGUSON (J. Elisha Mitchell Sci. Soc., 1933, 49, 18—19).—Finely divided Cu and Fe suspended in milk fed to anæmic rats causes a rapid rise in hæmoglobin and complete recovery without ill effects due to acid hydrolysis of Cu and Fe salts. CH. ABS.

"Lipoid" extract of spleen that prevents Bartonella muris anæmia in splenectomised albino rats. Protective action of copper and iron against B. muris anæmia. D. PERLA and J. MARMORSTON-GOTTESMAN (Proc. Soc. Exp. Biol. Med., 1932, 29, 987—989, 989—991).—An extract of ox spleen probably contains a sp. hormone. A small amount of Cu was insufficient in absence of splenic hormone (I) but an excess compensated for the deficiency of (I). CH. ABS.

Pigeon as a hæmatopoietic test animal. W. A. PEABODY and R. C. NEALE (J. Amer. Pharm. Assoc., 1933, 22, 1231—1237).—Although the pigeon responds to the active principle of liver-extract, the effects are not parallel with the clinical utility.

Acute extrarenal azotæmia. M. RACHMILEWITZ (Lancet, 1934, 125, 78—81).—Acute loss of fluids after vomiting and diarrhœa may result in a rise in nitrogenous constituents of the blood. Probably a disturbance in the mineral balance of the body occurs with a consequent disturbance of general metabolism. This is revealed as an abnormal protein breakdown. The administration of chlorides and of glucose lowers the azotæmia. L. S. T.

Vitamin-C and cancer. M. COPISAROW (Chem. and Ind., 1934, 135).—The suggested application of ascorbic acid to cancer (A., 1933, 1252) is criticised.

F. O. H.

W. S.

Growth of transplanted tumours in albino rats maintained on a diet with protein hydrolysates as substitute for protein. U. SUZUKI, W. NAKAHARA, N. HASHIMOTO, and R. IKEDA (Sci. Pap. Inst. Phys. Chem. Res., Tokyo, 1933, 23, 1— 8).—The growth of tumours transplanted into albino rats is the same when practically all the protein in the diet is replaced by acid or alkaline hydrolysates of protein. W. O. K.

Influence of alcohol on the growth of transplanted tumours in rats. U. SUZUKI, W. NAKA- HARA, N. HASHIMOTO, and R. IKEDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 9–15).—The growth rates (I) of sarcomata transplanted into albino rats as well as that of the animals themselves are low on a carbohydrate-free, fat-rich diet, are slightly improved when fat is partly replaced by MeOH (5%), and much improved when it is replaced by EtOH (10%). The partial replacement of carbohydrate in a balanced diet by EtOH has little effect, but replacement by MeOH decreases (I), both of animals and tumours. W. O. K.

Tumour arginase. IV. Significance of accompanying substances for the activity of arginase in normal and malignant tissue. G. KLEIN and W. ZIESE (Z. physiol. Chem., 1933, 222, 187— 202; cf. A., 1933, 315).—Purified arginase (I) is inhibited strongly at every  $p_{\rm H}$  by thiol compounds such as H<sub>2</sub>S, cysteine, and glutathione, even in absence of PO<sub>4</sub><sup>'''</sup>. Crude (I) is activated by the same thiol compounds, especially in alkaline media. The activation occurs also after treatment with O<sub>2</sub>, and is produced by Fe<sup>\*\*</sup> and N<sub>2</sub>H<sub>4</sub>. It consists in a non-sp. reduction of "carriers." A combination of heavy metal and  $\cdot$ SH is possible, but not essential. Purified (I) is not inactivated by O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> in alkaline solution. J. H. B.

Anthelmintic power of some chloro-derivatives of butane in cylicostomosis of horses. MARCENAC (Compt. rend., 1934, 198, 510—512).—  $\beta\beta$ -Dichlorobutane and  $\beta$ -chlorobutylene are very effective. R. S. C.

Intermediate metabolism in puncture diabetes. I. Puncture technique. II. Sugar and blood - amylase. III. Blood - lipins. G. D. OBRAZTSOV, E. T. MINKER-BOGDANOVA, and M. N. KALLINIKOVA (Russ. J. Physiol., 1931, 14, 158—162, 219—230, 231—240).—I. A method for the Claude Bernard puncture (I) is described.

II. The extent of the hyperglycamia produced by (I) varies in different experiments; liver-glycogen does not entirely disappear. The rise in blood-sugar is accompanied by a reduction in blood-amylase.

III. Neutral fat and cholesterol are but little affected, whilst there is a sudden initial increase in cholesteryl esters, fatty acids, and phosphatides, followed by a decrease. P. G. M.

Bryonia cretica. Action and value in diabetes. M. A. F. SHERIF (Quart. J. Pharm., 1933, 6, 634-642).—The EtOH-sol. material of the powdered root (I) depresses the activity of both cardiac and plain muscle. The min. lethal dose is 0.1 g. [equiv. to 2.5 g. of (I)] per kg. subcutaneously in rabbits and 0.075 g. per kg. intravenously in dogs. The drug reduces diuresis, but has no effect on blood-sugar or glycosuria in the diabetic. F. O. H.

Insulin-resistance in diabetes mellitus. C. M. MACBRYDE (Arch. Int. Med., 1933, 52, 932—944).— Insulin-resistance (I) and -sensitivity (II) are often associated with characteristic responses to alterations in the diet. Thus increase of fat produces a diminution in glucose tolerance with (I), but not with (II), whilst increase of carbohydrate produces immediate glycosuria with (II), but does not affect the sugar excretion with (I). Whilst (I) is generally due to hyperactivity of the adrenal-sympathetic system, other disorders (e.g., pancreatic, endocrine, hepatic, and infective diseases) are probable factors. F. O. H.

Modified glucose tolerance test. T. L. ALT-HAUSEN and H. T. RICKETTS (Arch. Int. Med., 1933, 52, 984—990).—A discussion regarding the merits of the test (see A., 1930, 1470; 1933, 971). F. O. H.

Physiological disturbances during experimental diphtheritic intoxication. I. Bloodsugar, -lactic acid, and -non-protein- and -amino-nitrogen. II. Hepatic glycogenesis and glycogen concentration of cardiac and skeletal muscle. H. YANNET and D. C. DARROW. III. Respiratory quotients and metabolic rate. H. YANNET and W. GOLDFARB (J. Clin. Invest., 1933, 12, 767-778, 779-786, 787-791).—I. Rabbits exhibited hypoglycæmia and rise in blood-NH<sub>2</sub>- and -non-protein-N.

II. During intoxication liver-glycogen (I) is diminished; muscle- and heart-(I) are unchanged. Hepatic glycogenesis following injection of glucose is diminished.

III. There is no significant change in carbohydrate metabolism or metabolic rate. CH. ABS.

Exophthalmos in thyroidectomised guineapigs by thyrotropic substance of the anterior pituitary, and the mechanism involved. D. MARINE and S. H. ROSEN (Proc. Soc. Exp. Biol. Med., 1933, 30, 901-903). CH. ABS.

Is anterior pituitary hormone demonstrable in urine of Graves' disease; in urine of guineapigs injected with anterior pituitary extract? M. G. SMITH and E. MOORE (Proc. Soc. Exp. Biol. Med., 1933, 30, 735—739).—Failure to demonstrate the presence of the thyroid-stimulating hormone in urine of Graves' disease is not inconsistent with a possible increase in pituitary function. CH. ABS.

Hypoproteinæmia probably due to deficient formation of plasma-proteins. W. K. MYERS and F. H. L. TAYLOR (J. Amer. Med. Assoc., 1933, 101, 198—200).—Hypoproteinæmia in a case of chronic œdema, low plasma-protein, and reduced colloid osmotic pressure was not influenced by protein feeding. CH. ABS.

Lathyrism in the rat. B. J. GEIGER, H. STEEN-BOCK, and H. T. PARSONS (J. Nutrition, 1933, 6, 427— 442).—Lathyrism (produced by eating lathyrus peas) causes red coloration, and abnormal growth and calcification of bones, and is not counteracted by feeding cod-liver oil or dried yeast. Boiling peas for  $2\frac{1}{2}$  hr. did not destroy their toxicity, but the toxic factor was extractable by  $H_2O$  at b.p. A. G. P.

Cystine content of finger-nails in pellagra. S. A. PAYNE and W. A. PERLZWEIG (J. Clin. Invest., 1933, 12, 899—908).—Low vals. are observed when dermatitis is present. CH. ABS.

Experimental rickets. V. In chicks. F. ROGOZIŃSKI and Z. GŁÓWCZYŃSKI (Bull. Acad. Polonaise, 1932, B, 369-384; cf. A., 1932, 1159).-Chicks fed on a diet of corn, butter, NaCl, and Fe<sup>III</sup> citrate develop leg weakness and die within 30-42 days. This does not occur when the chicks are irradiated by ultra-violet light or when cod-liver oil or  $CaCO_3$  (1%) is added to the diet. F. O. H.

Disappearance of trypan-blue from the blood in experimental scurvy and malnutrition. P. N. VESELKIN (Russ. J. Physiol., 1931, 14, 241–247).— Trypan-blue disappears more rapidly from the blood of scorbutic than of normal guinea-pigs; this is not characteristic of C-avitaminosis, although it always accompanies malnutrition. P. G. M.

Ultra-violet absorption spectra of syphilitic sera. M. PAIČ (Compt. rend., 1934, 198, 286–288). —Normal sera do not differ from those of syphilitic patients in ultra-violet absorption spectra.

R. S. C.

Influence of vitamin-A and -D on the humoral reactions in human tuberculosis. J. DONATO, R. JACQUOT, and H. PENAU (Compt. rend., 1934, 198, 397-399).—Intramuscular injection of an oil solution of a mixture of carotene and vitamin-D into tubercular subjects causes an increase in Ca (from 80-90 mg. to approx. 115 mg.), cholesterol (1.44-1.80 g. to 2.5 g. per litre), and P in the blood, a return to normal serum-flocculation (Vernes), and an increase in the proportion of hæmoglobin and in body-wt.

J. W. B. Reaction of the organism to intradermal administration of tuberculin. Changes in the blood-serum. C. LUCCHINI, M. BELLI, and C. GERBI (Arch. Ist. Biochim. Ital., 1933, 5, 485—536). —Intradermal administration of tuberculin to patients suffering from tuberculosis and other diseases produced an allergic reaction and a parallel disturbance in the sedimentation velocity of the erythrocytes, but not in the flocculation reaction of Vernes. In nearly all the cases the total protein content of the serum diminished, whilst the globulin level increased so that the albumin/globulin ratio decreased. A diminution in the serum oncotic pressure also occurred.

F. O. H.

Diazo-substance in typhoid urine. M. MIYA-ZAKI (J. Biochem. Japan, 1933, 18, 379–385).—When antioxyproteic acid (A., 1906, i, 122) from typhoid urine (29 g. of Ba salt were obtained from 80 litres) is injected into rabbits, the greater part does not appear in the excreta, whilst the blood gives a positive Ehrlich diazo-reaction (I) for only a short period. Human fæces give a positive (I) whether the (I) of the urine is positive (due to typhoid) or negative (with healthy persons). F. O. H.

Synthesis of protoplasm. A. L. HERRERA (Bull. Lab. Plasmogenie, 1933, 1, 41–42).—Cell-formation is discussed. H. G. R.

Ciliary movement. II. Intracellular oxidation-reduction potential limiting ciliary movement. S. NOMURA (Protoplasma, 1933, 20, 85–89). —Ciliary movement (I) probably derives its energy from glycolysis (II). When intracellular redox potential falls below a certain crit. point (e.g., as in anaerobiosis) (II) is suppressed and (I) ceases. A. G. P.

Kinetics of the oxidation processes in fertilised eggs. I. Velocity of oxidation during embryonic development of *Trutta iridea* (Rainbow trout). W. SCHLENK, jun. (Biochem. Z., 1933, 267, 424–437).—The  $O_2$  utilisation and  $CO_2$  production of unfertilised (I) and fertilised eggs (II) of the rainbow trout are followed continuously from fertilisation to the end of embryonic development (67 days). The respiration of (II) was always much > that of (I), but was different for eggs from different sources. The increase in velocity of oxidation appeared to be logarithmic from the 15th to the 43rd day. P. W. C.

Gaseous metabolism of "natural" and "artificial" nerve impulses. R. W. GERARD and H. K. HARTLINE (Naturwiss., 1933, 21, 882–883).—An increase of 40—50% in the O<sub>2</sub> uptake of the optic nerve of the horseshoe crab *Limulus polyphemus* is observed both when stimulation is electrical and when the eye is illuminated. R. K. C.

Oxygen consumption of stimulated nerve. S. HARASHIMA (J. Cell. Comp. Physiol., 1933, 3, 418– 424).—With a const. current applied, the excess  $O_2$ consumption of the nerve is practically the same whether the stimulus is applied to the nerve "inside" or "outside" of the microrespirometer in which the  $O_2$  is determined. A. G. P.

Anoxic recovery of asphyxiated nerve. R. A. COMEN and R. W. GERARD (J. Cell. Comp. Physiol., 1933, 3, 425–436).—Restoration of asphyxiated nerve can be induced by oxidising substances (other than  $O_2$ ) which yield sufficient energy on reduction. A. G. P.

Gaseous metabolism during muscular work. III. Changes of oxygen saturation of venous blood during the restitution period. J. L. KAHN and M. K. MILOVIDOVA (Russ. J. Physiol., 1933, 16, 155—158).—During the period of recovery from intense muscular work the  $O_2$  capacity of the venous blood gradually falls to the resting level, but the degree of  $O_2$  saturation at first rises, reaches a max. in 3 min., and finally falls, the max. corresponding with the min. val. of the  $O_2$  uptake coeff. W. O. K.

Effect of carbon dioxide and asphyxia on the elimination of phosphoric acid from muscle. V. S. ILJIN and V. V. TICHALSKAJA (Russ. J. Physiol., 1931, 14, 284-288).—CO<sub>2</sub> increases the rate of elimination of PO<sub>4</sub><sup>'''</sup> from resting frog's gastrocnemius after. exercise. Asphyxia by H<sub>2</sub> produces a much smaller increase. P. G. M.

Elimination of phosphoric acid from muscle at rest and after work. V. S. ILJIN and V. V. TICHALSKAJA (Russ. J. Physiol., 1931, 14, 289—295). —The rate of elimination of  $PO_4^{\prime\prime\prime}$  is increased both by direct electrical stimulation of the muscle and by stimulation by way of the nerve. Resting muscle is permeable to  $PO_4^{\prime\prime\prime}$ . P. G. M.

Lactic acid in sweat and protein in urine during muscular exercise. A. F. KORIAKINA and A. N. KRESTOVNIKOV (Russ. J. Physiol., 1931, 14, 257-262).—No definite quant. relationship exists between the lactic acid in sweat and the protein in urine, although large amounts of lactic acid are accompanied by small amounts of protein and vice versa. P. G. M.

Effect of controlled muscular exercise on the lactic acid and  $CO_2$  capacity of the blood. G. E.

VLADIMIROV, G. A. DMITRIEV, and A. P. URINSON (Russ. J. Physiol., 1934, 16, 139—154).—In man, the blood-lactic acid (I) during rest is not influenced by previous training (II), but after dynamical work (III) the (I) and  $CO_2$  capacity (IV) depend on (II). Increase of duration of (III) did not increase the change of (I) nor of (IV). Statical work did not change (II) or (IV). The  $O_2$  debt cannot be fully attributed to accumulation of (I). During the recovery after (III) hypolactacidæmia was often observed. W. O. K.

Influence of glutathione and iodoacetic acid on the production of lactic acid from hexose diphosphate by animal tissues. S. YAMAZOYE (J. Biochem. Japan, 1933, 18, 445–456).—In the decomp. of hexose diphosphate to lactic acid by the enzyme system phosphatase-glycolase-glyoxalase (I) in autolysed liver, glutathione (II) and  $CH_2I \cdot CO_2H$ (III) have an accelerating and an inhibitory effect, respectively, due to their action on (I); with (III) the action is probably not on (I) itself, but on the co-enzyme, reduced (II). F. O. H.

Influence of the preceding diet on the rate of glucose absorption and glycogen synthesis. E. M. MACKAY and H. C. BERGMAN (J. Nutrition, 1933, 6, 515-521).—In albino rats, the preceding diet did not appreciably affect, after 24-48 hr. starvation, the rate of absorption of glucose administered by the intestine, or the rate of deposition of glycogen in the liver and skeletal muscle.

A. G. P.

Absorption of glucose from chronic jejunal loops. I. S. RAVDIN, C. G. JOHNSTON, and P. J. MORRISON (Amer. J. Physiol., 1933, 105, Proc. 82– 83).—The rate of absorption of glucose from 1-65%solutions varied directly as the concn. with const. vol. or as the vol. with const. concn. NUTR. ABS.

Comparison of concentration of glucose in the stomach and intestine after intragastric administration. I. S. RAVDIN, C. G. JOHNSTON, and P. J. MORRISON (Proc. Soc. Exp. Biol. Med., 1933, 30, 955-958). CH. ABS.

Possibility of the conversion of fatty acids into glucose in the animal body. H. H. MITCHELL (J. Nutrition, 1933, 6, 473-491).---A review.

A. G. P.

Possibility of gluconeogenesis from fat. II. Effect of high-fat diets on the respiratory metabolism and ketosis in man. E. E. HAWLEY, C. W. JOHNSON, and J. R. MURLIN (J. Nutrition, 1933, 6, 523-557).-Following high-fat diets containing varying proportions of butter-fat the R.Q. in a no. of subjects was < the theoretical level for fat oxidation. The occurrence of low vals. depended more on the tolerance of the subjects than on the amount of fat taken or on the ratio fatty acid : glucose in the diet. The level of the R.Q. was not closely related to the demonstrable ketosis or ketonuria. Depression of the R.Q. is not attributable solely to the production of glycogen from protein or from the glycerol of fats. A. G. P.

Fat metabolism. G. QUAGLIARIELLO (Mem. R. Accad. d'Italia, 1933, 4, 17-32).-Adipose tissue

(I) contains a lipase comparable in activity to the stomach lipase, and also a dehydrogenase, which can act on the free fatty acids, but apparently not on their esters. Both enzymes are active in the isolated (I). Starvation in dogs is accompanied by a gradual rise in the degree of unsaturation of both the (I) and blood-fats; this falls again on feeding. The disappearance of deposited fat is evidently preceded by enzymic lipolysis and sufficient desaturation of the fatty acids to permit diffusion through the cell wall; deposition of fat in normal feeding probably occurs through the same mechanism. R. N. C.

Effect of fat on protein metabolism. G. SANT (Pharm. Weekblad, 1934, 71, 97–98).—Administration of fat produces changes in  $\alpha$  of blood-serum after hydrolysis. S. C.

Activation of proteolysis in regenerating tissue. V. N. ORECHOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1933, 27—33).—Following amputation of the axolotl's tail, the regenerating tissue (I) has a much higher content of reduced glutathione (II) than has the normal tissue (averaging 0.0196%), attaining a val. of 0.046% in 5 days, remaining const. for the next 5—6 days (average 0.0456%), and returning to normal vals. after a total period of 15—20 days. The normal tissue in close proximity to (I) also experiences a slight increase in the content of (II). These variations are related to disturbances in normal respiration and to increased proteolytic activity.

F. O. H.

Proliferative response of neurones to thiol and sulphoxide in the regenerating ganglion of *Nereis pelagica*. F. S. HAMMETT (Protoplasma, 1933, 19, 117—124).—The neurone increment of regeneration is accelerated by ·SH and retarded by .SO. A. G. P.

Proliferative growth-regulating property of the naturally occurring chemical equilibrium composed of thiol and its partly oxidised derivatives. D. W. HAMMETT and F. S. HAMMETT (Protoplasma, 1933, 19, 161—169).—The retarding effect of :SO and the accelerating action of ·SH on the proliferation of the regenerating right chela of the hermit crab are demonstrated in the same growth process of individual specimens by alternate exposure to appropriate substances. A. G. P.

Glutathione concentration and hereditary body size. II. Non-nursed young of rabbits differing in genetic constitution for adult size. P. W. GREGORY and H. Goss (J. Exp. Zool., 1933, 66, 155— 173).—Glutathione content is correlated with adult body-size. CH. ABS.

Distribution of the urinary representatives of nitrogen metabolism and its physiological significance. V. Exogenous protein metabolism. E. F. TERROINE and G. Boy (Bull. Soc. Chim. biol., 1933, 15, 1163—1220; cf. A., 1933, 529).—A study of N excretion of rats, pigs, and dogs fed on normal and protein-free diets indicates that the terms endogenous and exogenous N-metabolism are advantageously replaced by "sp. min. N excretion" (I) and "contingent N excretion" (II), respectively. The exeretory products (III) may be classified as "differential" [creatinine and creatine related to (I) and (II), respectively] and "common" [urea, NH3, peptides, NH2-acids, S compounds, etc.]. The distribution of (III) corresponding with (I) differs with different animals, whilst that of the (III) arising from ingested protein is approx. the same; hence (I) fails as an independent criterion of protein metabolism. The protein and purine oxidation coeffs. (calc. from the excess N excretion on changing from a carbohydrate to a protein diet) during (I) are > those during (II). Such a change in diet also produces an increase in the abs. NH3-N, but a fall in the urinary  $NH_3-N/(NH_3+urea+NH_2)-N$  ratio, which is not necessarily accompanied by a change in  $p_{\rm H}$  of the urine. No transformation of creatine to creatinine due to protein metabolism is evident. F. O. H.

Constitution of muscle-proteins. I. Total and protein starvation. A. ROCHE (Bull. Soc. Chim. biol., 1933, 15, 1290—1307).—Deprivation of protein (I) in rats produces death in 1—2.5 months, the loss in body-wt. being approx. 48%. With complete starvation the loss at death amounts to 30%. The losses in total N are respectively 23—55\% and approx. 15% of the body-N. With (I) starvation, the excreted N originates not only from complete disintegration of body-(I), but also from polypeptide side-chains, so that the (I)-nature of the protoplasm is preserved. F. O. H.

Influence of temperature on protein metabolism. II. Nitrogenous extractives from toad's liver during winter. H. MAKINO (J. Biochem. Japan, 1933, **18**, 387–393).—Aq. extraction of the toad's liver during winter yields *l*-leucine  $(5 \cdot 0\%)$ , *d*-alanine  $(0 \cdot 8\%)$ , *d*-valine, *l*-proline, *l*-scrine, *l*-phenylalanine, *d*-glutamic acid, guanine, adenine, xanthine, and hypoxanthine. The contents of these substances in the toad's liver during winter and summer are compared (cf. A., 1932, 299). F. O. H.

Influence of asparagine and betaine on the nitrogen metabolism of pasture cows. P. BRIGL and O. BENEDICT (Bied. Zentr. [Tierernahr.], 1933, B, 5, 532-553).—Replacement of the N of a clover-hay ration for sheep by betaine (I) or asparagine (supplemented with starch) in proportions equiv. to > 10% of the total N resulted in the breakdown of body-proteins. The amides were excreted as urea.

A. G. P.

Creatinephosphoric acid. Influence of denervation on the creatinephosphoric acid content of muscle. A. PALLADIN and R. SIGALOVA (Bull. Soc. Chim. biol., 1933, 15, 1263—1271).—Section of the sciatic nerve in rabbits or guinea-pigs produces within 24 hr. an increase in the creatinephosphoric acid content of the gastrocnemius muscle, whilst the  $H_2O$ , total N, and creatine remain unchanged.

F. O. H.

Creatinuria in adolescent males. A. B. LIGHT and C. R. WARREN (J. Biol. Chem., 1934, 104, 121— 128).—The average creatine excretion (I) of boys aged 14—19 decreases with increasing age. A close relationship exists between (I) and muscular activity; an increase in (I) occurs after exercise following a period of confinement. H. D. Metabolism of sulphur. XXI. Metabolism of *l*-cystine and *dl*-methionine in the rabbit. R. W. VIRTUE and H. B. LEWIS (J. Biol. Chem., 1934, 104, 59-67).—*dl*-Methionine (I) administered orally and subcutaneously is metabolised, the S occurring in the urine as  $SO_4''$ . The urine also contains a substance giving the S·S group and the cyanidenitroprusside reactions, but not the Sullivan test for cystine.  $\alpha$ -Benzoylmethionine is not attacked by the organism, and it is suggested that the course of the reaction with (I) is a demethylation followed by the formation of homocystine. A. L.

Oxidation of stereoisomerides of cystine in the animal body. V. DU VIGNEAUD, H. A. CRAFT, and H. S. LORING (J. Biol. Chem., 1934, 104, 81–89).— Rabbits were fed on l- (I), d- (II), meso- (III), and dl-cystine and the S fractions in their urine determined. After feeding (I), about 80% of the extra S excreted was SO<sub>4</sub>", after (II), 45%. (III) and (IV) produced intermediate results. H. D.

Deamination of amino-acids in the animal organism. Y. KOTAKE, sen., Y. KOTAKE, jun., and I. TANIGUCHI (J. Biochem. Japan, 1933, 18, 395— 415).—Hydroxyphenylpyruvic acid (I) in urine is determined by acidification, extraction with  $\text{Et}_2\text{O}$ , and iodometric titration of the residue on evaporation. Oral administration of dl- and, to a smaller extent, of *l*-tyrosine to rabbits and dogs produces an excretion of (I), whilst ingestion of (I) yields hydroxyphenyllactic acid in the urine. The mechanism is discussed. F. O. H.

Food value of germinating grain. V. V. FAMIANI (Atti R. Accad. Lincei, 1933, [vi], **18**, 68— 73; cf. A., 1933, 183, 309, 743).—Experiments with rats indicate that this is > that of grain in the resting state. T. H. P.

Digestion and assimilation of soya-bean preparations in the human body. E. S. LONDON, N. I. SHOKHOR, A. G. GAGINA, A. I. KOLOTILOVA, R. M. KUTOK, E. A. MARKARYAN, and L. V. POPEL (Schr. zentr. biochem. Forschungsinst. Nahr. Genussm., U.S.S.R., 1932, 1, 211–234).—The food val. of soyabean protein is 88% of that of meat and fish; the carbohydrate food val. is 100%. CH. ABS.

Acid-base coefficients and the food-value of meat. I. A. SMORODINCEV (Bull. Soc. Chim. biol., 1932, 15, 1256—1262).—Various parts of meat were extracted with 0.1N-AcOH and with N-NaOAc, and the extracts were titrated with alkali. The two titres gave the acid/base ratio (I), the NaOAc extraction being accompanied by the liberation of free AcOH due to the action of tissue-acids. The val. of (I) for muscle was five times that of connective tissue; hence (I) forms a criterion of the food-val. of meat. F. O. H.

Effect of cranberries on urinary acidity and blood alkali reserve. C. R. FELLERS, B. C. RED-MON, and E. M. PARROTT (J. Nutrition, 1933, 6, 455-463).—When fed to normal young men in amounts of 100-300 g. daily cranberries (I) caused an increase in the titratable acidity, total org. acids, hippuric acid, [H], and NH<sub>3</sub> of the urine, and a slight decline in uric acid and urea. The hippuric acid recovered was approx. proportional to the amount of (I) eaten, and was nearly all voided within the following 24 hr. It is probably derived from the quinic acid (or a glucoside yielding quinic acid) in (I). Large amounts of (I) reduce the  $\rm CO_2$ -combining capacity of the blood. A. G. P.

Acid-base balance of newborn infants. IV. Effect of ingestion of alkali. V. W. LIPPARD and E. MARPLES (Amer. J. Dis. Children, 1933, 46, 495— 511).—Ingestion of small quantities of NaHCO<sub>3</sub> or Na citrate decreases serum-Cl, -protein, -acid, and -fixed base. The CO<sub>2</sub> tension diminishes proportionally to the amount of alkali ingested. Older infants require larger amounts to affect the balance.

CH. ABS.

Sodium chloride metabolism. I. Influence of injection of bacteria and colloid substances. II. Effect of changing the function of the reticulo-endothelial system by blocking. III. Relationship between the function of the reticuloendothelial system and retention of sodium chloride in the tissues. H. SAITO (Japan. J. Gastroenterol., 1933, 5, No. 2, 57-66, 67-71, 72-77).—I. Intravenous injection of substances which stimulate the reticulo-endothelial system stimulates NaCl metabolism.

II. Transfer of NaCl from tissues by way of the blood into the urine is no longer observed.

III. Excretion of injected NaCl is diminished by blocking. CH. ABS.

Distribution of water in living tissues. C. I. Cox and C. S. HICKS (Austral. J. Exp. Biol., 1933, 11, 269–287).—Rabbits deprived of food and  $H_2O$ for 16 hr., and in some of which a diuresis had been induced, were injected with hypertonic saline for 90 min. under paraldehyde anæsthesia. The total urinary output, plasma-alkali reserve, blood dilution, blood-Cl', tissue-H<sub>2</sub>O, urinary Cl, and osmotic pressure of the serum-colloids were determined. A direct proportionality between the alkali reserve and the reserve H<sub>2</sub>O of the body exists; dehydration of the muscle tissue appears to account for the H<sub>2</sub>O loss. H. D.

Effect of body-weight and wool production by merino sheep of adding sulphur to the diet. A. W. PEIRCE (J. Counc. Sci. Ind. Res. Australia, 1933, 6, 294—298).—Addition of 2 g. of S daily to the ration increased neither body-wt. production nor wool yields. A. G. P.

Bromine metabolism. II. Relation between blood-bromine and internal secretions. T. KURANAMI (J. Biochem. Japan, 1933, 18, 417-443; cf. A., 1932, 876).—During pregnancy the blood-Br (I) rises, attains a max. at parturition, and returns to normal after 3 weeks. The (I) of the blood from the umbilical vessels of new-born infants is < that of their circulating blood, but > the normal adult level. (I) is increased during diabetes mellitus and thyroid diseases. The (I) of dogs (normally 0.00055-0.00069%) is increased by subcutaneous injection of thyroxine, adrenaline, or anterior pituitary extract and decreased by that of insulin, posterior pituitary extract, or æstrin; ovariectomy or orchidectomy, however, both produce a rise in (I). Vagus stimulants (pilocarpine) decrease, whilst vagus depressants and sympathetic stimulants (atropine and adrenaline) increase, (I). Injection of physiological saline produces a transient decrease in (I), the main controlling factor of which appears to be the anterior pituitary gland. F. O. H.

Influence of unbalanced mineral constituents in the diet on the growth and composition of rats. (a) Variations in potassium and calcium. (b) Influence of vitamin-A deprivation. L. EME-RIQUE (Bull. Soc. Chim. biol., 1933, 15, 1221-1234, 1235-1238).-(a) Variations in the proportions of Ca or K in the otherwise normal diets of rats do not produce very marked changes in the mineral composition of the body. With high doses of K, the Ca: P and Ca: K ratios decrease, whilst that of Ca: Mg is unchanged, the abs. content of K being increased. With high doses of Ca, the Ca: Mg and Ca: K ratios are increased, whilst that of Ca: P is unchanged, the abs. content of Ca being diminished. The anomaly in the abs. contents of K and Ca is probably due to the different effects on browth.

(b) The subnormal growth of rats on a vitamin-Afree diet (I) is emphasised by a high Ca : K ratio of (I). With either high Ca : K or K : Ca ratios of (I), the abs. contents of the body in P and Ca are increased, that of K is slightly diminished, whilst that of Mg is approx. const. Increases also occur in the P : K, Ca : K, and Ca : Mg ratios of the body.

F. O. H.

Inorganic salts in nutrition. VII. Change in composition of bone of rats on a diet poor in inorganic constituents. R. O. BROOKE, A. H. SMITH, and P. K. SMITH (J. Biol. Chem., 1934, 104, 141-148).—On a low-salt diet, there is a decrease in Ca, P, and CO<sub>3</sub>, and the ratio  $Ca_3(PO_4)_2$ : CaCO<sub>3</sub> is increased. The negative Ca balance is at expense of the CaCO<sub>3</sub>. H. G. R.

Significance of mineral metabolism [in animals] especially by alkaline earths and phosphoric acid. O. WELLMANN (Biol. generalis [Adametz Festsch.], 387—396; Bied. Zentr., 1933, A, 4, 82). —The Ca and P requirements of various animals and the effects and correction of deficiencies are discussed. A. G. P.

Calcium and phosphorus in the development of the turkey embryo. W. M. INSKO, jun., and M. LYONS (J. Nutrition, 1933, 6, 507-513).—The increase in wet and dry wts. and ash content of the developing embryo is small until the 12th day, and that of the Ca and P contents until the 17th day. The Ca : P ratio is < 1 until the 19th day and > 1thereafter. The Ca content of the embryo serves as an index of growth provided the yolk material drawn into the body cavity is removed prior to analysis.

A. G. P.

Metabolism of calcium and phosphorus. I. Influence of carotene and gallosterol. I. ISHIDA (J. Biochem. Japan, 1933, 18, 479–493).—Subcutaneous administration of  $\beta$ -carotene (I) or of gallosterol (II) (vitamin-A-choleic acid) increases the Ca or P balance (III) (*i.e.*, ingested minus excreted Ca or P). On discontinuing the administration of (I) or (II), the P (III) returns almost immediately to its normal level, whilst the Ca (III) persists for several days. The effect with (II) is > that with bile acids. F. O. H.

Influence of acid and phosphate on metastatic calcification. D. J. STEPHENS and D. P. BARR (Proc. Soc. Exp. Biol. Med., 1933, 30, 920-924).— Rats fed for 15 days on acid, or alternating acid and alkaline, diets with excess of Ca and P developed calcification (I) in the soft tissues. (I) did not occur in absence of any one of these three factors.

CH. ABS.

**Resorption of calcium sulphate in the digestive tract.** A. I. VIRTANEN and J. TIKKA (Suomen Kem., 1934, 7, 75B).—100—250 g. per day of CaSO<sub>4</sub> were fed to cows without any harmful effect. The Ca<sup>\*\*</sup> appeared almost quantitatively in the fæces, whilst the SO<sub>4</sub><sup>\*\*</sup> appeared mainly in the urine, indicating a resorption process. P. G. M.

Effect of iodine on the growth and metabolism of thyroid tissue in vitro. R. McCARRISON and G. SANKARAN (Indian J. Mcd. Res., 1933, 21, 183— 186).— $12.5 \times 10^{-6}$  g. I per 100 c.c. of medium had no effect; 25 stimulated tissue growth (I) and rate of metabolism (II), 50 increased (II) without affecting (I), whilst 100 increased (II) but halved the life of the tissue in vitro. CH. ABS.

Determination of the functional activity of the thyroid by means of urine and serum. III. Influence of autonomic nerve on thyroid function. M. Koh (J. Chosen Med. Assoc., 1933, 23, 853-862). Ch. Abs.

Relation between toxicity, resistance, and time of survival. L. REINER (Proc. Soc. Exp. Biol. Med., 1933, 30, 574—576).—An equation is derived showing that asymmetry is to be expected whenever the time which registers the event is a non-linear fuction of the parameter on which the occurrence of the event depends, even although the variation follows the probability rule. A. L.

Behaviour of hæmatoporphyrin in the animal body. R. HUTSCHENREUTER (Z. physiol. Chem., 1933, 222, 161-176).-Rats on meatless diet (I) receiving intramuscularly regular moderate doses of hæmatoporphyrin-Nencki (II) increased in wt.; large doses caused a decrease, but oral administration always produced an increase. The orally given (II) in contrast with intramuscular (11) produced no photodynamic action. Hæmateric acid (III) was detected in the fæces of rats on (I). (II) was always detected in the fæces after dosage, but its transformation into (III) was not established. Coproporphyrin was excreted in the urine by rats on (I). After intramuscular, but not oral, doses of (II), (II) J. H. B. was found in the urine and blood.

Toxicity of urine- and serum-proteic acids. Y. GAMO (J. Biochem. Japan, 1933, 18, 457–478).— Following bilateral nephrectomy in rabbits, the  $p_{\rm H}$ and CO<sub>2</sub> capacity of the blood decrease. The toxicity of urea, creatine, or creatinine to such animals is relatively small. The urine contains a toxic substance, the oxyproteic acid fraction (I), the Ba salt of which is insol. in H<sub>2</sub>O, but sol. in EtOH, and which is inactivated by acid hydrolysis and is dialysable through collodion membranes. A similar substance is also present in the serum. The rôle of (I) in uræmia is discussed. F. O. H.

Relation of interfacial tension to cytolysis of sea-urchin eggs by soaps. I. H. PAGE, H. A. SHONLE, and G. H. A. CLOWES (Protoplasma, 1933, 19, 213—227).—Soaps containing the ricinoleate (I) grouping kill the egg without the corrosive, disintegrating action shown by other soaps. The pigment of the egg is liberated rapidly. The oleate, linoleate, and linolenate class (II) of soaps release the pigment slowly, and the condition of the cytolysed egg is very different from the above. The action of Na laurate is intermediate. In the  $p_{\rm H}$  range 6.0—9.0 soaps of the (I) type show max. catalytic effects towards the acid extreme and those of the (II) type at the alkaline end of the scale. Points of max. cytolysis correspond with points of min. surface tension. A. G. P.

Neuro-muscular action of amides and ammonium salts. R. BONNET (Compt. rend., 1934, 198, 284–285).—Org.  $NH_4$  salts are toxic for both nerve and muscle, amides only for the latter. R. S. C.

Acetylcholine in tissue. III. Oxytocic action of acetylcholine for the induction of labour and in other obstetrical conditions. A. WONG and H. CHANG (Chinese Med. J., 1933, 47, 987–1009).— The acetylcholine (I) content of the placentæ varies largely, being > normal in cases of abortion, uterine tetany, premature separation of placenta, fœtal death *in utero*, and Cæsarean section, and < normal in uterine inertia, prolonged labour, pulmonary tuberculosis, and general debility. The oxytocic action of (I) is studied and its use instead of pituitrin for the induction of labour suggested. A. L.

Influence of acetylcholine on absorption of glucose. E. GELLHORN and D. NORTHUP (Amer. J. Physiol., 1933, 105, 684-686).—Addition of acetylcholine to Ringer's solution perfusing frog intestine influenced the permeability of the gut to glucose in a manner opposite to that of adrenaline; it increased permeability in small concn. and decreased it in greater. NUTR. Abs.

Action of certain ethers of  $\beta$ -alkylcholine derivatives. A. SIMONART (J. Pharm. Exp. Ther., 1934, 50, 1—14).—Of alkyl ethers of  $\beta$ -methyl-,  $\beta$ -ethyl-, and  $\beta$ -propyl-choline the Me and Et ethers have a muscarine-like action, as also has  $\beta$ -butylcholine Me ether (I), whilst the higher alkyl ethers show little or no action. With increase in mol. wt. the nicotine-like action tends to diminish except in the case of (I), in which it is marked. Most of the compounds show a paralysing action on the sympathetic synapses and on the neuro-muscular junctions of voluntary muscle. W. O. K.

Hypoglycæmic and glycogen-forming action of methylated guanidine. M. TENNENBAUM (Arch. Verdauungskrankh., 1933, 53, 397-401; Chem. Zentr., 1933, ii, 1054).—Administration of decamethylenediguanidine carbonate (I), synthalin (II), and synthalin-B (III) to rabbits diminished the bloodsugar, (I) having an effect > that of (II). The glycogen-forming effect of (I) was also > that of (II) or (III). The difference between the active and lethal doses of (I) is small. A. A. E.

Santonin and the hyperglycæmia due to glucose ingestion. S. BERTINO (Arch. Farm. sperim., 1933, 56, 601-606).—Intramuscular injection of large doses (0.08-0.15 g. per kg.) of santonin (in glycol) into rabbits increases the hyperglycæmia due to ingestion of glucose, whilst smaller doses .(0.01 g. per kg.) have no effect. F. O. H.

Picrotoxin-stramonium antagonism. L. SHUT-TER and B. MYERS (Proc. Soc. Exp. Biol. Med., 1933, 30, 935-939).—Picrotoxin convulsions in rats are prevented by subcutaneous administration of dealcoholised tincture of stramonium. CH. ABS.

(a) Action of cinchophen on nitrogen metabolism. (b) Studies on the denervated kidney. I. Action of cinchophen on the uric acid and allantoin excretion in dogs, and its effect on the nitrogen and sulphur excretion. G. P. GRAB-FIELD and M. G. GRAY (J. Pharm. Exp. Ther., 1934, 50, 28-31, 123-130).—(a) In dogs on a submaintenance diet, administration of cinchophen (I) increases the rate of excretion (II) of total N, total S, uric acid (III), and allantoin (IV).

(b) Denervation of the kidneys does not influence the action of (I) on the (II) of total N and total S, but its action on (II) of (IV) is slightly increased. (I) at first decreases (II) of (III), but after some time again acts normally probably after regeneration of the renal nerves. W. O. K.

Influence of caffeine on effects of acetanilide. J. A. HIGGINS and H. A. McGUIGAN (J. Pharm. Exp. Ther., 1933, 49, 466—478).—NHPhAc (I) has little or no effect on the heart. The toxic effects of (I) and EtOH are additive. Citric acid has a variable toxicity in mice. The toxicity of (I) is scarcely affected by caffeine. H. D.

[Pharmacological] action of hydroxyphenylmethylpyrazole. J. W. C. GUNN (Quart. J. Pharm., 1933, 6, 643—649).—The general symptoms and the action on the circulation and smooth muscle of 4-hydroxy-1-phenyl-5-methylpyrazole (I) (A., 1931, 742) are similar to those of antipyrine (II). (I), however, has a toxicity to mice (min. lethal dose 0.55 mg. per g.) and an antipyretic action in pyrexia due to *B. coli* infection in rabbits > those of (II).

F. O. H.

(a) Physiological action of principles isolated from secretion of S. African toad (Bufo regularis). (b) Jamaican toad (B. marinus). (c) Poisonous secretions of five N. American species of toads. (d) Parotid secretion of B. bufo gavgarizans as source of Ch'an Su. (e) Active groupings in molecules of cino- and marinobufagins and cino- and vulgaro-bufotoxins. (f) Similarity and dissimilarity of bufagins, bufotoxins, and digitaloid glucosides. K. K. CHEN and A. L. CHEN (J. Pharm. Exp. Ther., 1933, 49, 503 - 513, 514 - 525, 526 - 542, 543 - 547, 548 -560, 561-579).-(a) From the parotid secretions (1) of B. regularis cholesterol (II), two digitalis-like compounds, bufagin (III) and bufotoxin (IV), an indole derivative, bufotenine (V), which stimulates rabbit's

intestines (VI) and guinea-pigs' uteri and raises arterial blood-pressure, and adrenaline (VII) were isolated.

(b) (II), a (III), and a (IV) with digitaloid properties, and (VII) are found; the (V) found has no pressor action on pithed cats, and has no effect on (VI) or frog's heart tonus.

(c) The (I) of *B. valliceps, fowleri, alvarius, quercicus,* and *americanus* contain characteristic (II), (III), (IV), and (V).

(d) The (I) of the common Chinese toad (B. bufo gargarizans) is almost identical with the prep. Ch'an Su (A., 1933, 530) which is evidently prepared from it.

(e) Breaking the lactone ring or saturation with  $H_2$  destroys the activity of cino- and marino-bufagin; acetylation, chlorination, or oxidation of the OH groups modifies their activity; the acid radical attached to OH is almost as important as the lactone ring.

(f) The solubility, colour reactions, chemical composition, structural groupings, crystallisation phenomena, m.p., and physiological properties of 10 (III) and 12 (IV) are compared with those of scillarene A, (VII), ouabain, digitonin, and theretin. (III) and (IV) are generically similar and resemble (VII) most. H. D.

Rotenone. XVI. Physiological action of rotenone, deguelin, and rotenone resin. Chemical behaviour of deguelin. See this vol., 301.

(a) Comparative assay of standard preparations of *Digitalis* and *Adonis vernalis* originating from different years. (b) Activity and stability of gitalin and adonilin. A. I. MOCH-NATSCHEVA (Russ. J. Physiol., 1933, 16, 541-546, 547-551).-(a) The pharmacodynamic activity of standard preps. of the above plants varies from year to year by > 100%.

(b) The activity of various preps. of gitalin (I) and adonilin (II) varies by > 200%; that of (II) is > that of (I) in all cases. The rate of deterioration of (I) is > that of (II): R. T.

Potassium and calcium content of frog's blood-serum at different temperatures and resulting from stimulus of the central nervous system (strychnine and curare). O. F. TSCHISTO-VITSCH (Russ. J. Physiol., 1931, 14, 320—323).—The Ca content of the serum at 3° (0.0041%) is slightly < that at room temp. (0.0046%); the K content (0.0148%) is appreciably > that at room temp. (0.0125%). Strychnine (0.2 c.c. of 1:5000 solution) and curare (0.4 c.c. of 1:1000 solution) raise the Ca content by 50%, but the K content is unaffected. P. G. M.

Chronic morphine poisoning in dogs. V. Recovery of morphine from tissues of tolerant and non-tolerant animals. O. H. PLANT and I. H. PIERCE (J. Pharm. Exp. Ther., 1933, 49, 432—449).— Morphine (I) was determined in tissues by pptn. of proteins from the aq. suspension of the ground up tissue with CCl<sub>3</sub>·CO<sub>2</sub>H; the conc. filtrate was treated as for urine (A., 1932, 1284). Oxalated blood was diluted with 2% aq. AcOH and evaporated to dryness, and the residue extracted with AcOH. The average total recovery from the liver, muscle, central nervous system (II), heart, lungs, and blood in tolerant dogs (III) was  $46\cdot 2$  and in non-tolerant dogs (IV)  $42\cdot 8\%$ . In (II), (III) give less (I) than (IV); in the blood the reverse is true. Possibly (I) is stored in the tissues of (III) in a form that is not readily extracted. H. D.

Toxicity of  $\alpha$ - and  $\beta$ -nicotines and nornicotines. Chemopharmacodynamic relationships. D. I. MACHT and M. E. DAVIS (J. Pharm. Exp. Ther., 1934, 50, 93—99).—To a variety of animals and plants, dl- $\beta$ -nicotine (I) and dl- $\beta$ -nornicotine (II) are more toxic than dl- $\alpha$ -nicotine (III) and dl- $\alpha$ -nornicotine (IV), respectively, but no const. relationship held between the actions of (I) and (II) or between those of (III) and (IV). l- $\beta$ -Nicotine is usually more toxic than (I). W. O. K.

Pharmacological action of the alkaloids of fumaraceous plants. I. *iso*Corydine. R. A. WAUD (J. Pharm. Exp. Ther., 1934, 50, 100-107)... The action of *iso*corydine on frogs and various mammals closely resembles that of bulbocapnine.

W. O. K. Comparison of the pharmacological action of atropine and its optical isomerides, *l*- and *d*-hyoscyamine. W. F. VON OETTINGEN and I. H. MAR-SHALL (J. Pharm. Exp. Ther., 1934, **50**, 15-20).--Atropine, *d*- and *l*-hyoscyamine are destroyed at equal rates when incubated with egg-white, but rabbit's serum destroys the *l*- more rapidly than the *d*-compound, atropine being intermediate. Differential rates of destruction may determine the relative activity of the three isomerides in different animal species and on different organs. W. O. K.

Absorption of methyl salicylate by the human skin. E. W. BROWN and W. O. SCOTT (J. Pharm. Exp. Ther., 1934, 50, 32—50).—The rate of cutaneous absorption of Me salicylate (measured by the excretion of salicylic acid compound in the urine) was increased by rise of temp., massage, and the use of various solvents of which the most effective was EtOH (50% solution), but the highest rate was found with an 11.8 vol.-% suspension of the ester in H<sub>2</sub>O.

W. O. K.

Elimination of barbituric acid derivatives in urine with special reference to sodium amytal and pentobarbital. H. A. SHONLE, A. K. KELTCH, G. F. KEMPF, and E. E. SWANSON (J. Pharm. Exp. Ther., 1933, 49, 393-407).—Barbituric acids (I) are isolated by acidifying the urine with AcOH, extraction with Et<sub>2</sub>O, and sublimation. 90% recovery of Na amytal (II) was obtained by this method; owing to the inadequacy of the chemical tests (I) were assayed with mice. Administration of (II) and pentobarbital to men and dogs produces no urinary excretion of (I), whereas barbital and phenobarbital are excreted in amounts up to 53 and  $1\cdot5\%$ , respectively, of the dosage. H. D.

Relative depressant effects of certain barbiturates on heart of elasmobranchs. G. B. ROTH (Proc. Soc. Exp. Biol. Med., 1933, 30, 563—565).— Activities of nembutal, amytal, and luminal were > that of veronal. CH. ABS. Narcotic potency of the aliphatic acyclic acetals. P. K. KNOEFEL (J. Pharm. Exp. Ther., 1934, 50, 88–92).—Acetals of various aliphatic aldehydes have definite hypnotic activity, but are inferior to paraldehyde. W. O. K.

Narcosis and mental function. ANON. (Nature, 1934, 133, 110—111).—A summary of Quastel's address to the British Association. L. S. T.

Hyperglycæmic action of certain drugs. D. CAMPBELL and T. N. MORGAN (J. Pharm. Exp. Ther., 1933, 49, 456-465).-2 c.c. of  $Et_2O$  given orally to rabbits produce hyperglycæmia (I), whilst with intravenous injection or oral dosage after amytal anæsthesia (II), no (I) is produced. If (II) is induced 20 min. after oral ingestion of  $Et_2O$ , (I) continues. Variable effects on the blood-sugar were obtained with pituitrin and ephedrine. H. D.

Influence of liver degeneration and recuperation on the acid-base equilibrium of the blood. W. DE B. MACNIDER (J. Pharm. Exp. Ther., 1934, 50, 108—122).—Dogs intoxicated with EtOH for 12, 18, and 24 hr. develop liver damage demonstrable anatomically and by the phenoltetrachlorophthalein test, whilst kidney function is apparently normal, the elimination of phenolsulphonephthalein being increased. The liver damage is accompanied by a fall in the blood alkali-reserve which returns to normal with recovery of the liver. W. O. K.

Determination of alcohol in blood. J. PELTZER (Chem.-Ztg., 1934, 58, 48).—A reply to the criticisms of Heiduschka and Flotow (A., 1933, 744) of the author's method (*ibid.*, 310). Further details are given, and the correction factor of 5.3% is discussed. F. O. H.

Reliability of cerebrospinal fluid analysis in the diagnosis of drunkenness. H. W. NEWMAN and H. G. MEHRTENS (Proc. Soc. Exp. Biol. Med., 1933, 30, 725—727).—In man the intravenous injection of 1 c.c. EtOH per kg. gave max. blood-EtOH of 150 mg. per 100 c.c. in 20 min., max. cisternal fluid-EtOH of 120 mg. in 50 min., and max. cerebrospinal fluid-EtOH of 100 mg. in 3 hr. CH. ABS.

Photodynamic action. IV. Photo-stimulation of skeletal muscle. C. R. SPEALMAN and H. F. BLUM (J. Cell. Comp. Physiol., 1933, 3, 397–404).— The production of contraction in skeletal muscle of frogs is independent of the presence of  $O_2$ , whereas the photodynamic response occurs only in presence of  $O_2$ . A. G. P.

Effect of ultra-violet rays and of methylthionine chloride and heparin on snake venoms. D. I. MACHT and M. E. DAVIS (Proc. Soc. Exp. Biol. Med., 1933, 30, 990—993).—Ultra-violet rays produced rapid decrease in the potency of snake venoms. Methylene-blue or heparin does not affect the toxicity. CH. ABS.

Toxicity of aluminium and method of administration. G. BERTRAND and P. SERBESCU (Compt. rend., 1934, 198, 517—520).—The m.l.d. of Al [as  $Al_2(SO_4)_3$ ] in the rabbit is 10 mg. per kg. body-wt. when injected subcutaneously. The salt has only 1/4of this toxicity when introduced directly into the stomach, but is even more toxic by the peritoneal route. 20 mg. per kg. by way of the stomach is harmless. P. G. M.

Chronic arsenic poisoning. I. Arsenic content of "mosquito incense." P. L. LI and C. S. YANG (Chinese Med. J., 1933, 47, 979—986).—Mosquito incense made from orpiment and sawdust contains 0.5—1.5% As, 80\% of which is liberated on burning. A. L.

Arsenic in tobacco smoke. C. R. GROSS and O. A. NELSON (Amer. J. Publ. Health, 1934, 24, 36-42).—Cigars (I), cigarettes (II), and pipe tobacco (III) contain  $8\cdot3$ —50 p.p.m. of  $As_2O_3$  (cf. A., 1927, 798). The proportions of As volatilised (and partly inhaled) are  $15\cdot1$ — $34\cdot7\%$  for (I),  $32\cdot2$ — $41\cdot3\%$  for (II), and  $32\cdot8\%$  for (III). Data for the As contents of the ash and residues are also given. F. O. H.

Micro-determination of bismuth in animal tissues. G. F. HALL and A. D. POWELL (Quart. J. Pharm., 1933, 6, 628—633; cf. A., 1933, 1264).—The tissue is digested with  $HNO_3+H_2SO_4$ , excess  $H_2SO_4$  is removed, and the aq. solution of the residue is boiled to remove  $NO_2$  and diluted with  $2\cdot5\%$   $H_2SO_4$  containing 1% of  $H_3PO_2$  until 1 c.c. contains  $0\cdot4-4\cdot0\times10^{-6}$  g. of Bi. 5 c.c. are then treated with  $0\cdot1$  g. of KI and 2 c.c. of EtOAc, shaken, and the colour of the EtOAc layer compared with suitable standards. Modifications for tissues containing fat or bone are necessary. F. O. H.

Electromigration of bismuthoiodide in colloidal systems. P. J. HANZLIK, F. DE EDS, and J. B. SPAULDING (Proc. Soc. Exp. Biol. Med., 1933, 30, 721-724).—An electrolytic cell is described. Results are correlated with those of absorption and cerebrospinal penetration. CH. ABS.

Toxicology of chromium. K. AKATSUKA and L. T. FAIRHALL (J. Ind. Hygiene, 1934, 16, 1–24).– Cr<sup>III</sup> salts are harmless to cats either by inhalation or when given orally. H. G. R.

Microchemical detection of lead. R. U. HARwood and D. BROPHY (J. Ind. Hygiene, 1934, 16, 25—28).—The Fairhall method (A., 1924, ii, 61) is modified to determine  $0.5 \times 10^{-6}$  g. of Pb in 5 c.c. of cerebrospinal fluid. H. G. R.

Interaction of magnesium with sodium, potassium, and ammonium ions. S. V. TSIGANOV (Russ. J. Physiol., 1931, 14, 121–128).—Subcutaneous injection of Na<sup>•</sup> in the rat has no effect on the course of Mg narcosis, whilst K<sup>•</sup> increases the diastolic action of Mg. In limited doses Mg<sup>••</sup> is antagonistic to the stimulating effect of  $NH_4^{•}$ . P. G. M.

Interaction of magnesium with calcium, strontium, and barium ions. S. V. TSIGANOV (Russ. J. Physiol., 1931, 14, 129–136).—Subcutaneous injection of CaCl<sub>2</sub> in rats inhibits MgSO<sub>4</sub> narcosis, which is stimulated by Sr<sup>\*</sup> and Ba<sup>\*</sup>. Mg<sup>\*</sup> is antagonistic to the excitatory effect of Ca<sup>\*</sup>, Sr<sup>\*</sup>, and Ba<sup>\*</sup>. P. G. M.

Health aspects of radium dial painting. III. Measurements of radioactivity in workers. J. E. IVES, F. L. KNOWLES, and R. H. BRITTEN. IV. Medical and dental phases. L. SWARTZ, F. C. MAKEPEACE, and H. T. DEAN (J. Ind. Hygiene, 1933, 15, 433-446, 447-455).—Determinations of  $\gamma$ -radiation from the bodies and in the exhaled air of Ra dial painters indicated that accumulations of radioactive material were present. No bone changes were observed and red cell and hæmoglobin vals. were > normal. Determinations of the radioactivity of the dust in the workrooms suggested that inhalation plays an important part in the poisoning. A. L.

Effect of sulphur on nitrogen metabolism and relation of suphur and thyroid to the phenomena. S. SHINGU (Folia Endocrinol. Japon., 1932, 8, 7—8).— Intramuscular injection of colloidal S increased urinary N, urea, NH<sub>3</sub>, and creatine increasing in parallel. Creatinine was unchanged. Ingestion of colloidal S decreased total N, urea, and creatine, but increased NH<sub>3</sub>. Increased urinary N following thyroidectomy is reduced by ingestion of colloidal S. CH. ABS.

Effect of potassium cyanide poisoning on the blood-fat and -lipin, and the effect of various hormones on the action of potassium cyanide. I. Insulin, thyroid substance, and adrenaline. II. Sex organs. III. Injection of extract of adrenal cortex, and thyroidectomy. S. KUBO (Folia Endocrinol. Japon., 1931, 7, 169—170, 170— 171, 188—189).—I. After injection of aq. KCN into rabbits, blood-fat and -lipin increase. Adrenaline promotes, whilst insulin or thyroid (oral) retards, this increase.

II. The effect of extracts of testicle and ovary on the above increase has been studied.

III. Thyroidectomy promotes, whilst injection of adrenal cortex extract checks, the increase.

CH. ABS.

Effect of sodium thiosulphate on potassium cyanide poisoning. C. ACHARD and L. BINET (Compt. rend., 1934, 198, 222-224).—Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> reduces the toxicity of aq. KCN to carp and revives nearly dead fish. R. S. C.

Alcoholic fermentation of d-glucose in deuterium water. E. PACSU (J. Amer. Chem. Soc., 1934, 56, 245-246).—Fermentation occurs about nine times as fast in ordinary distilled H<sub>2</sub>O as in 100% H<sup>2</sup>O. H. B.

Pharmacological experiments with deuterium. D. I. MACHT and M. E. DAVIS (J. Amer. Chem. Soc., 1934, 56, 246).—Germination of *Lupinus* seeds is slightly slower in  $H_3^2O$  (concn. 1:2000) than in ordinary distilled  $H_2O$ . No differences were found in other experiments (e.g., fermentation; contraction of smooth muscle; assay of digitalis).

H. B.

Harmony [between ionic concentrations]. See this vol., 254.

Relation of life to electricity. VIII. Mechanism of oxidation-reduction potentials of living tissues. R. BEUTNER and J. LOZNER (Protoplasma, 1933, 19, 370—380).—Systems consisting of a nonoxidised and a corresponding oxidised substance, e.g., alcohol-fatty acid, produce a p.d. of kind and magnitude similar to those occurring in living tissues, and with increasing oxidation show a shift of potential towards the positive side. The e.m.f. of these systems

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consists of phase boundary potentials and depends on the distribution of ions within the system. A. G. P.

Electromotive force in biological systems. I. Effect of homologous carbamates on the electromotive force of frog skin. E. J. BOELL and A. B. TAYLOR. II. Surface activity of homologous carbamate solutions. A. B. TAYLOR and E. J. BOELL (J. Cell. Comp. Physiol., 1933, 3, 355— 383, 385—395).—I. The depression of the e.m.f. of urethanes (I) is a function of the concn. of (I) applied. Traube's rule is applicable to the effects of a homologous series. Absorption of (I) by skin with consequent inhibition of reactions giving rise to the e.m.f. explains the action of these substances.

II. A parallelism exists between the lowered surface tension of (I) solutions and the depressive effect of these solutions on the e.m.f. of frog skin. A. G. P.

Influence of electrolytes on the physicochemical properties of colloidal systems comparable with cytoplasm. I. Influence of electrolytes on the viscosity of diluted egg-yolk. B. ZAWADZKI (Protoplasma, 1933, 19, 484—509).—With increasing concn. of chlorides, HCl, or NaOH the viscosity of dil. yolk increases to a sub-max. (80—200 millimols. of chloride per litre), declining subsequently to a sub-min. (400—500 millimols. per litre) and finally rising steadily at higher concns. The effect of HCl and NaOH is far > that of salts, the activity of which was in the order CaCl<sub>2</sub>>MgCl<sub>2</sub>>NaCl>KCl. A. G. P.

Biological oxido-reduction and the respiration theories of Wieland and Warburg. J. KAUP and A. GROSSE (Z. ges. exp. Med., 1932, 84, 171-223; Chem. Zentr., 1933, ii, 1531-1532).

Direct spectroscopic identification of oxygencarrying enzyme in Azotobacter. E. NEGELEIN and W. GERISCHER (Naturwiss., 1933, 21, 884).—In the living cells the presence of the reduced enzyme is indicated by an absorption band at 632 m $\mu$ . The band shifts to 647 m $\mu$  on oxidation, or to 637 m $\mu$  on reaction with CO, and disappears on reaction of the oxidised enzyme with HCN. R. K. C.

Decolorisation of methylene-blue by milk and animal tissue. A. BOUTARIC and T. JACQUINOT (Bull. Acad. Méd., 1933, [iii], 109, 114—118; Chem. Zentr., 1933, ii, 1880—1881).—Camphor, S, Me salicylate, PhOH, resorcinol, quinol, guaiacol, HgCN, Na salicylate, and tannin arrest the decolorisation of methylene-blue (I) by milk (containing CH<sub>2</sub>O) or liver tissue; Me arsinate, Na<sub>3</sub>AsO<sub>4</sub>, and Na<sub>2</sub>HPO<sub>4</sub> accelerate the reduction of (I). A. A. E.

Glyceraldehydephosphoric acid as hydrogen donator. B. Gözsy (Z. physiol. Chem., 1933, 222, 279–280).—Glyceraldehydephosphoric ester is an active H donator in presence of co-enzyme and compares favourably with fructose diphosphate.

J. H. B.

Amylase of mulberry leaves. S. MATSUMURA and T. KASUGA (Bull. Scricult. Japan, 1933, 6, 6).— The physical properties of leaf-amylase are tabulated. H. G. R.

Amylase system of the liver. L. HOLLANDER (Science, 1934, 79, 17-18).—Comparison of rat-liver BRITISH CHEMICAL ABSTRACTS .--- A.

preps., using the Waldschmidt-Leitz and Samec method for observing starch digestion, shows that the amount of maltose (I) formed at the blue-violet I end-point (11) varies markedly in different preps. In a few cases (II) was reached without measurable formation of (I). An amylase prep. can thus be made which in the early stages of starch digestion yields no reducing groups. Incubation of an aq. liver suspension increases its capacity to form (I), whilst the I end-point activity increases only slightly. Two amylases with different characteristic (I) levels at the same (II) and an unstable inhibitor (III) sp. for the component showing more (I) formation appear to exist. (III) can be pptd. at  $p_{\rm II}$  5.2, and has a quant. inhibiting effect on the formation of (I) from starch by liver preps. The digestion of starch by liver-amylase is performed by two different com-L. S. T. ponents.

Ultrafiltration of malt-amylase solutions. C. T. SNELL (J. Biol. Chem., 1934, 104, 43—51).— Cellulose nitrate membranes made by the method of Pierce (A., 1928, 233) and graded by varying the amount of  $(\cdot CH_2 \cdot OH)_2$  in the collodion have corresponding permeabilities. Using these, malt extract is purified threefold. A. L.

Enzymic hydrolysis of irisin. R. WEIDEN-HAGEN (Z. Ver. deut. Zucker-Ind., 1933, 83, 1042— 1044).—Irisin is completely hydrolysed to *d*-fructose by fructosidase at  $p_{\rm H} 4.62$ . For equal enzyme concn., the velocities of hydrolysis of sucrose and irisin are in the ratio  $4 \times 10^5$ : 1, although for hydrolysis by acid the velocities are of the same order. H. F. G.

III. Enzymic fission of polysaccharides. Fission of chitin by emulsin. W. GRASSMANN, L. ZECHMEISTER, R. BENDER, and G. TOTH (Ber., 1934, 67, [B], 1-5; cf. A., 1933, 55).-Merck's emulsin (loc. cit.) hydrolyses oligosaccharides of low mol. wt. from chitin appreciably more slowly than higher members of the series; chito-biose (I) and -triose (II) are scarcely affected. Crude, de-fatted almond powder hydrolyses the two N-containing oligosaccharides only slightly more slowly than the more complex chitodextrins (III). Emulsin purified by pptn. with tannin is appreciably active, whereas samples further purified by fractional pptn. with AgOAc are almost without action. There is no parallelism between the case of hydrolysis of (III) and (I) or (II). The assumption that chitin is a  $\beta$ -glucoside (loc. cit.) is withdrawn. Comparison of the effect of different emulsin preps. on salicin, cellobiose, (III), (I), (II), and cellodextrin shows that the enzyme active towards chitin is not identical with  $\beta$ -glucosidase, from which it also appears to differ in its distribution in the almond kernel. H. W.

**Emulsin of hips** (*Rosa canina*). E. HOFMANN (Biochem. Z., 1933, **267**, 309–312).—An emulsin prep. obtained from the hips of the wild rose had scarcely any action on  $\beta$ -glucosides, but readily hydrolysed  $\beta$ -galactosides. The extent of hydrolysis of  $\beta$ -phenol-*d*-glucoside and -galactoside at  $p_{\rm H}$  5 was 3 and 70%, respectively. P. W. C.

Enzymic behaviour of glycuronides and glycyrrhizinic acid. F. BERGMANN (Biochem. Z., 1933, 267, 296–308).—A simplified method for the prep. of NH<sub>4</sub> glycyrrhizinate is described (cf. A., 1907, i, 545; 1921, i, 259) and the compound shown to be dextrorotatory and unattacked by emulsin, maltase, takadiastase, etc. On hydrolysis with N-H<sub>2</sub>SO<sub>4</sub> the acid gave glycyrrhetinic acid (I),  $C_{23}H_{36}O_{37}$ , m.p.  $303^{\circ} [\alpha]_{20}^{\infty} + 145 \cdot 5^{\circ}$  [Me ester, m.p.  $255^{\circ}$ ,  $[\alpha]_{20}^{\infty} + 166 \cdot 7^{\circ}$ ; Ac derivative (II), m.p.  $317^{\circ}$ ,  $[\alpha]_{10}^{\infty} + 144 \cdot 6^{\circ}$  (Me ester, m.p.  $299^{\circ}$ ,  $[\alpha]_{10}^{\infty} + 147 \cdot 6^{\circ}$ )]. (I) is not reduced by Pd and H<sub>2</sub> and is stable to KMnO<sub>4</sub> and C(NO<sub>2</sub>)<sub>4</sub>, whilst (II) is not attacked by CrO<sub>3</sub>. P. W. C.

Enzymic scission of lecithin. A. CONTARDI (Boll. Chim. farm., 1934, 73, 3–12).—A review. R. N. C.

Natural activation of plant tissue proteinase. K. MOTHES (Naturwiss., 1933, 21, 883).—Papain preps. can be inactivated by  $H_2O_2$ , by  $O_2$  in presence of Pd, or by  $O_2$  in presence of various plant extracts (plant dehydrases) and then re-activated by  $H_2$  in presence of Pd or plant extracts. Active material contains SH groups, and inactive material S·S groups, and reversible activation and inactivation is regarded as a non-sp. process affecting these groups, which form part either of the prosthetic group of the enzyme or of an adsorbed associated substance. R. K. C.

Inhibition of cathepsin and activation of papain by  $\alpha$ -thiolcarboxylic acids. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, 222, 207—214). —Papain is activated by  $\alpha$ - and  $\beta$ -thiolcarboxylic acids, the position of the SH being without effect. Many substances activate only slowly, and show at first slight inhibition. Cathepsin (I) is inhibited by  $\alpha$ -thiolcarboxylic acids, most strongly by  $\alpha$ -thiolbutyric acid. Cysteine, SH-glutathione,  $\beta$ -thiolpropionic acid [which activates (I)], and ascorbic acid do not, but Fe does, reverse the inhibition by  $\alpha$ -SH-acids. The first stage in the inhibition seems to involve removal of Fe

Catheptic proteinase. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, 222, 215—219).— In preps. of guinea-pig's, hen's, and pig's liver, treated with EtOH to remove sol. SH compounds, the cathepsin present is mostly fully activated. This confirms earlier results (A., 1933, 1081). J. H. B.

Effect of dehydration on pancreatic and intestinal enzymes. J. R. Ross and M. M. SHAW (J. Biol. Chem., 1934, 104, 131–139).—Rats maintained discontinuously at 37.5° for several days show diminished production of both intestinal and pancreatic enzymes; individual variations were large. H. D.

Thiol compounds and crystalline urease. J. B. SUMNER and L. O. POLAND (Proc. Soc. Exp. Biol. Med., 1933, 30, 553—555).—Jack-bean meal contains a substance which reacts similarly to glutathione. Cryst. urease does not contain glutathione, but may contain SH groups. This may account for the readiness with which urease is inactivated by Ag, Hg, and Cu ions and by benzoquinone and other oxidising agents, and why urease is protected by SH-compounds.

CH. ABS.

J. H. B.

Phosphorylated intermediate products and the later phases of alcoholic fermentation. O. MEYER-HOF and W. KIESSLING (Biochem. Z., 1933, 267, 313348).—Fermentation reactions using yeast maceration extract in presence of NaF and  $CH_2I \cdot CO_2H$ , with sugar and hexose phosphate in presence and absence of MeCHO, are investigated. In the absence of MeCHO and presence of NaF an equimol. mixture of  $\alpha$ -glycerophosphoric and phosphoglyceric (I) acids is obtained and in presence of MeCHO exclusively (I), MeCHO being reduced to EtOH. These intermediate compounds are isolated and identified with the corresponding compounds of lactic acid fermentation using muscle extracts. Glyceraldehyde phosphate is also here to be regarded as the intermediate product. A new scheme of intermediate fermentation reactions is given. P. W. C.

Biochemical formation of optically active phosphoglyceric acid from various sugars. T. BABA (Biochem. Z., 1933, 267, 452–455).—Tables show that, using yeast maceration extract or fresh yeast, sucrose, maltose, glucose, and fructose all give phosphoglyceric acid, the yield for maltose being very slightly > for the remaining sugars. P. W. C.

Method for determining sedimentation velocity of yeast. (Agglutination tendency.) N. NIEL-SEN (Compt. rend. Lab. Carlsberg, 1933, 19, No. 17, 1—11).—The agglutination of a uniform yeast suspension (I) is measured by the change in concn. at the lower end of a column of (I) in a burette. Yeast taken from the bottom of a column of (I) has a sedimentation velocity and N content > those at the top. H. D.

Relation between inorganic salt concentration, hydrogen-ion concentration, and physiological processes in Amæba proteus. I. Rate of locomotion, gel/sol ratio, and [H<sup>\*</sup>] in balanced salt solutions. R. F. PITTS and S. O. MAST (J. Cell. Comp. Physiol., 1933, 3, 449–462).—In balanced salt solution the rate of locomotion (I) of A. proteus shows a max. at  $p_{\rm H}$  6·2 and decreases (with an intermediate max.) to zero at  $p_{\rm H} > 8\cdot0$ . Over the whole range of  $p_{\rm H}$  examined locomotion rates vary inversely with salt conen. (II). The gel/sol. ratio varies directly with acidity and with (II), but is not directly correlated with (I). A. G. P.

Oxidation-reduction potential of protozoan cultures. I. Effect of  $\cdot$ SH on Chilomonas paramecium. T. L. JAHN (Protoplasma, 1933, 20, 90— 104).—Acceleration of cell division by  $\cdot$ SH is antagonised by H<sub>2</sub>O<sub>2</sub>. This phenomenon and also the effect of methylene-blue on *C. paramecium* are explained on the basis of changes in oxidation-reduction potential in the medium. A. G. P.

Course of growth of strains of actinomycetes and its quantitative examination on various potato substrates. L. E. KIESSLING (Zentr. Bakt. Par., 1933, II, 89, 177-196).—On nutrient media containing the expressed juice of potatoes, the wts. of mycelium produced by various actinomycetes showed well-defined differences according to the variety of potato used and the stage of development. A. G. P.

Composition of fungi. N. V. SABUROV and A. V. VASILIEV (Schr. zentr. biochem. Forschungsinst. Nahr.-Genussm., U.S.S.R., 1931, 1, 77-91).—Ash, protein, fat, mannitol, trehalose, and glucose have been determined in numerous fungi. CH. ABS.

Metabolism and energetics of growth of moulds. H. TAMIYA (Acta Phytochim., 1933, 7, 27-41).—The interpretation of energy data is discussed. F. O. H.

Respiration of moulds. III. Respiration of synthesis and of maintenance. H. TAMIYA and S. YAMAGUTCHI (Acta Phytochim., 1933, 7, 43-64; cf. A., 1932, 1167).—With spores of Aspergillus melleus grown in sugar-containing media, the rate of growth (I) increases parallel with the rate of respiration (II) until a max. is attained in 50-60 hr., following which both (I) and (II) decrease, the val. of (I) reaching zero before (II). The R.Q. also rises to a max. and then falls to approx. 1. With 50-hr. cultures, 40% of the total O<sub>2</sub> respiration is utilised for synthesis and the remainder for maintenance. With older cultures less is used for synthesis. The efficiency of energy utilisation decreases from 85% with young moulds to approx. 60% with old moulds. The relation of the rate of (II) to that of (I) can be expressed as an equation of the second degree. F. O. H.

Influence of poisons and of temperature on the utilisation of respiratory energy during growth of moulds. A. YAMAMOTO (Acta Phytochim., 1933, 7, 65—92).—True respiratory poisons, e.g., KCN, act firstly on the respiration (I) of Aspergillus niger and secondly on the growth (II), thus producing a preliminary increase in utilisation (III). Other poisons, e.g., phenylurethane, CO, and NaF, primarily decrease (II), resulting in a decrease in (III). Iodoacetate forms a third group which acts on both (I) and (II), so that (III) remains approx. const. The younger is the culture the greater is the val. of (III). (III) has a temp. optimum of 25°, whilst that of (I) or (II) is 35°. F. O. H.

Action of certain alkaloids on the utilisation of carbohydrates by Aspergillus niger. G. MEZ-ZADROLI and A. AMATI (Atti R. Accad. Lincei, 1933, [vi], 18, 161-165).—The utilisation of glucose or sucrose by A. niger in Wehmer's or Raulin's solution at 37° is enhanced by the presence in the solution of 0.05-0.2% of strychnine (nitrate) or 0.05-0.3% of quinine (sulphate), but 0.05-0.3% of caffeine (base) has the opposite effect. These effects are, in general, not dependent on the composition of the nutrient liquid, the nature of the carbohydrate, or the temp.

T. H. P. Electrophoresis of trypanosomes and spirochætes. F. P. FISCHER and V. FISCHL (Biochem. Z., 1933, 267, 403—404).—Both types of living organism, both in their natural medium and in physiological solutions, and also the dead organisms, always migrate to the cathode. P. W. C.

Dissociation constant of nitrogen-nitrogenase in Azotobacter. H. LINEWEAVER, D. BURK, and W. E. DEMING (J. Amer. Chem. Soc., 1934, 56, 225– 230).—The nature of the dissociation of the complex (N<sub>2</sub>E) formed between gascous N<sub>2</sub> and the enzyme nitrogenase (E) during the fixation of N<sub>2</sub> by Azotobacter (I) at ordinary temp. and pressure has been studied (method; A., 1930, 1068). The thermodynamic dissociation const.,  $K_{N_4} = [E][N_2]/[N_2E]$ , is  $21 \cdot 5 \pm 0.2 \text{ vol.-}\% (0.215 \pm 0.002 \text{ atm.})$  (as a function of N<sub>2</sub> pressure) and is independent of wide variations in the conens. of Ca, Sr, Fe, and C<sub>2</sub>O<sub>4</sub>",  $p_{\text{H}}$ , O<sub>2</sub> pressure, max. velocity of irreversible decomp. of NE<sub>2</sub> (to form protein) at saturating N<sub>2</sub> pressures, and species, age of culture, and conen. of (I). Statistical analysis of the collective data is carried out. The mol. heat and free energy of dissociation of N<sub>2</sub>E are 0 (within experimental errors of 1000 and 100 g.-cal., respectively). H. B.

Agar-digesting bacteria. H. E. GORESLINE (J. Bact., 1933, 26, 435–457).—Three new species are described. A. G. P.

Utilisation of certain sugars and their derivatives by bacteria. S. A. KOSER and F. SAUNDERS (J. Bact., 1933, 26, 475-488; cf. A., 1933, 639).--The action of a no. of organisms is examined. Organisms utilising glucose rarely acted on a-methyl-dglucoside, and -mannoside ;  $\beta$ -methyl-*l*-arabinoside and -d-xyloside were not fermented by any organisms which utilise the corresponding pentoses. In most instances d-arabinose was much less rapidly attacked than the *l*-form. Rhamnose and fucose were readily decomposed. None of the organisms examined utilised α-gluco-heptose or -heptulose. Glucose-fermenting bacteria in general utilised glucosamine, but more slowly. Many organisms fermented gluconic acid, but none attacked glucose Et mercaptal. A. G. P.

Transformation of optically active phosphoglyceric acid by B. coli. C. ANTONIANI (Biochem. Z., 1933, 267, 376—379).—Fresh cultures and dry preps. of B. coli convert phosphoglyceric acid into  $AcCO_2H$ . P. W. C.

Degradation of *dl*-glyceric acid by *B. coli* and *B. lactis aërogenes.* C. ANTONIANI (Biochem. Z., 1933, 267, 380–382).—Using loop cultures of *B. coli* and an inorg. medium, glyceric acid gave chiefly AcOH, some  $HCO_2H$ , and traces of EtOH. Lactic acid was not obtained. With *B. lactis aërogenes* similar results were obtained, but the amount of AcOH was greater and acetoin was also present.

P. W. C.

Fermentation of pyruvic acid by B. coli. J. TIKKA (Suomen Kem., 1934, 7, 75B).—The action of B. coli on AcCO<sub>2</sub>H takes the following course:  $AcCO_2H+H_2O \longrightarrow AcOH+HCO_2H \longrightarrow AcOH+H_2$  $+CO_2$ . It is possible to detect 57% of the theoretical quantity of HCO<sub>2</sub>H. 19% of the original AcCO<sub>2</sub>H is reduced to lactic acid by the nascent H. P. G. M.

Respiration and fermentation of lactic acid bacteria. II. J. G. DAVIS (Biochem. Z., 1933, 267, 357-359).—Two strains of *B. casei* (*Lactobacillus casei*, O. Jensen, and a strain from Reading) differ from other lactic acid bacteria in using practically no  $O_2$ . Methylene-blue does not increase the  $O_2$ -utilisation, but inhibits glycolysis. COMe<sub>2</sub>-preps. of *B*. Delbrücki oxidise lactic acid with the formation of  $H_2O_2$ . P. W. C.

Activator of the metabolism of propionic acid bacteria. C. FROMAGEOT and E. L. TATUM (Biochem. Z., 1933, 267, 360—375).—Potato extract contains an activator which is indispensable for the metabolism of dissolved glucose and assists in the utilisation of starch, but is unnecessary for the utilisation of lactic acid. The activator probably converts glucose into a labile form. P. W. C.

**Prodigiosine, the red pigment of** Bacillus prodigiosus. V. F. WREDE and A. ROTHHAAS (Z. physiol. Chem., 1933, 222, 203—206; cf. A., 1933, 1172).—Oxidation of prodigiosine (I) with  $CrO_3$  in AcOH gives maleimide and methoxymaleimide. Oxidation of hydrogenated (I) with  $KMnO_4$  affords proline. This affords further evidence of the nature of rings II and III. J. H. B.

Human tubercle bacilli. F. ULZER and H. GRUBER (Wiss. Mitt. œsterr. Heilmittelstelle, 1933, No. 11, 1—2; Chem. Zentr., 1933, ii, 1882).—The proportions of the dry bacilli dissolved by various solvents are recorded. A. A. E.

Presence of salicylic and phenylacetic acids in the acetone-soluble fat of the tubercle bacillus. N. STENDAL (Compt. rend., 1934, 198, 400-401).— Isolation and identification of o-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and CH<sub>2</sub>Ph·CO<sub>2</sub>H from the residual aq. liquor after slow steam-distillation of the fatty acids from the COMe<sub>2</sub>sol. fat of the tubercle bacillus (myristic acid in the distillate) are described. It is unlikely that these acids exist in the free state in the fat, since they are not present in the vapour from the unsaponified fat. J. W. B.

Precipitated diphtheria toxoid. L. C. HAVENS and D. M. WELLS (J. Infect. Dis., 1933, 53, 138– 139).—1—2.5% K alum completely ppts. the toxoid with little or no loss of sp. antigen. CH. ABS.

Antibodies in placental extracts. C. F. MC-KHANN and F. T. CHU (J. Infect. Dis., 1933, 52, 268—277).—The protein material contains substances, presumably antibodies, which neutralise diphtheria toxin, blanch scarlet-fever rashes, neutralise poliomyelitic virus, and prevent measles. CH. ABS.

Non-specific precipitins for pneumococcic fraction C in acute infections. R. Ash (J. Infect. Dis., 1933, 53, 89-97). Ch. Abs.

Effect of tyrosine on C. botulinum toxin. W. BURROWS (Proc. Soc. Exp. Biol. Med., 1933, 30, 823-825).—The toxin produced by C. botulinum in oxheart medium was not decreased by addition of tyrosine (I) and/or phenylalanine (40 mg. per 100 c.c.). Incubation with the NH<sub>2</sub>-acids does not affect the toxin, and injection of (I) does not protect the mouse. CH. ABS.

Characteristics of hypertoxic tetanus toxin (hypertoxin). R. LEGROUX and G. RAMON (Compt. rend., 1934, 198, 620—622).—Tetanus toxin becomes more toxic on acidification of the medium with  $PrCO_2H$  to  $p_{\rm H}$  3—4. To some extent mineral acid produces the same effect, but addition of HCl to  $p_{\rm H}$  2.0 destroys toxicity. Addition of alkali to a hypertoxic bouillon to  $p_{\rm H}$  7.0 causes the original toxicity to return. The acidification also produces loss of flocculating power which is not regained on addition of alkali. Tetanus anatoxin does not acquire any toxic characteristics on acidification. P. G. M.

Fixation of the lytic principle ("bacteriophage"). W. MUTSAARS (Ann. Inst. Pasteur, 1934, 52, 118—135).—Emulsions of staphylococci (I) in contact with media containing bacteriophage (II) absorb a definite amount of (II), the equilibrium attained indicating a physico-chemical process such as adsorption rather than a penetration of (II) into the cells. This is confirmed by the fixation by (I) of (II) inactivated by heating to 65°. The combination of (II) with antilytic serum, however, follows the normal antigen-antibody reaction; a state of equilibrium is attained, but the proportions of the constituents vary. Such a complex is readily dissociated, but becomes more stable with age. Heat-inactivated (II) forms similar, but less stable, complexes.

F. O. H.

Enzymes of the agalactia virus. A. PRIE and B. E. HOLMES (Brit. J. Exp. Path., 1933, 14, 290— 296).—The dehydrogenase and oxidative systems are very sensitive to mechanical agitation. Broth has a protective effect. Enzyme activity and viability are greatly reduced by exposure to light in presence of traces of methylene-blue. Growth of a culture is accompanied by a small decrease in lipin-P.

CH. ABS.

Antigenic properties of rabies virus. L. C. HAVENS and C. R. MAYFIELD (J. Infect. Dis., 1933, 52, 364—373).—All strains of rabies virus contain the same antigenic constituents, but in varying quantities. Heterologous strains can be neutralised if large amounts of serum are employed. After passage through the rabbit there is a rearrangement of antigenic structure. CH. ABS.

Effect of the formalin-vapour-contact method of rearing the silkworm on muscardine and flacherie. Y. NAKAZAWA (Bull. Sericult. Japan, 1933, 6, 5).—The method increases the bactericidal power of the digestive fluid and reduces bacterial growth in the litter. H. G. R.

Bactericidal power of rivanol. N. P. GOVOROV and V. K. MURSAEV (Russ. J. Physiol., 1931, 14, 175-182).—Storage of a rivanol solution for 15 days has no effect on its bactericidal properties towards *B. paratyphosus* B and *B. pyocyaneus*, whilst it is inactive towards *S. albus* after 5 days. P. G. M.

Carbohydrate-phosphate metabolism and the influence of certain hormones thereon. O. MA-NOILOVA, N. UTOCHNIKOVA, and A. GORDON (Russ. J. Physiol., 1931, 14, 309—319).—The intimate relation between carbohydrates and P compounds in the organism is emphasised by the fact that hormones such as insulin (I) and adrenaline (II), which influence carbohydrate metabolism, produce a change in the content of inorg. P in the blood parallel with the change in sugar content. (I) lowers the inorg. P by promoting its conversion into the org. P compound, lactacidogen. (II) at first raises the inorg. P content of the blood by furthering the decomp. of lactacidogen. The effects of pituitrin in this direction are negligible. Diverse results are due to the facts that the change in the blood-P often follows a rhythmic course and that the inorg. P has not always been determined at regular time-intervals after introduction of the hormone. T. H. P.

Effect of the glands of internal secretion on the sulphur content of the various organs. I. Sulphur, insulin, and thyroid substance. II. Adrenal capsule. III. Genital glands. S. KUBO (Folia Endocrinol. Japon., 1931, 7, 176—177, 178, 179).—I. Ingestion of S and injection of insulin increase total S (I) and neutral S (II) of most organs, especially of adrenal capsule (III), where SO<sub>4</sub> is also increased. Ingestion of thyroid decreases (I) and (II), and increases SO<sub>4</sub> of (III).

II. Ingestion of (III) and injection of interrenin increase (I) and (II) in (rabbits') organs. (III)-SO<sub>4</sub> is also increased. Injection of adrenaline decreases (I) and (II) in most organs, but increases SO<sub>4</sub> in thyroid, parotid glands, liver, and testicles.

III. Ingestion of testicle powder by male rabbits decreases (I), (II), and  $SO_4$  of most organs; only testicular  $SO_4$  is increased. Ingestion of ovarian tissue decreases, and of corpus luteum increases, the S content of most organs of female rabbits.

CH. ABS. Is the hormone which initiates movement of intestinal villi specific? E. DE KOKAS and G. DE LUDANY (Compt. rend. Soc. Biol., 1933, 113, 1447— 1449).—This hormone ("villikinin"), which is prepared from the duodenal mucosa by extraction with HCl, is not sp., preps. from different animals acting on the intestinal villi of the dog. Its activity is greater when prepared from the duodenal mucosa of the cat and fowl than from that of the sheep, pig, or cow. NUTR. ABS.

Presence in the fœtal intestine of a hormone causing movement of intestinal villi. G. DE LUDANY (Compt. rend. Soc. Biol., 1933, 113, 1449— 1450).—" Villikinin" (I) is not contained in the intestinal mucosa as such, but as a substance which is converted into (I) by acids. When a HCl extract of the intestinal mucosa of embryo dogs was injected intravenously into anæsthetised dogs, stimulation of the villi was observed. (I) was of the same nature when prepared from the duodenal mucosa of the embryo and the adult. NUTR. ABS.

Influence of the spleen on the excretion of bile and bile acids. T. TANAKA (J. Biochem. Japan, 1933, 18, 369—377).—In dogs with biliary fistulæ, splenectomy increases the excretion of bile acids and the secretion of bile. Administration of atropine or of spleen extracts (A., 1933, 308) inhibits this action. Hence the spleen appears to exert a hormonal action on the liver. F. O. H.

Absorption of insulin from the intestinal tract. D. CAMPBELL and T. N. MORGAN (J. Pharm. Exp. Ther., 1933, 49, 450–455).—Insulin (I) is equally effective in the rabbit when injected in the systemic or portal circulation. An  $Et_2O$  extract of a lecithin-(I) hydrochloride was active when intravenously, but not when orally, administered. H. D. Colorimetric iodometric determination of adrenaline. G. WELLER (Bull. Soc. Chim. biol., 1933, 15, 1308—1316).—The tissue (1 g.) is extracted with 10% aq. CCl<sub>3</sub>·CO<sub>2</sub>H [in which adrenaline (I) is stable for at least 48 hr.] and the extract (60 c.c.) is treated with KOAc (6 g.). After addition of 0·1 mg. of (I) to one half, both are treated with 10 c.c. of 0·01N-I, excess of I is titrated with 0·1N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and the resulting violet solutions are compared colorimetrically. Pyrocatechol, pyrogallol, and gallic and salicylic acids do not interfere. The adrenal glands of female dogs have a content (0·1540%) of (I) > that of males (0·1425%). F. O. H.

Decomposition of adrenaline by isolated organs. B. S. SENTJURIN (Russ. J. Physiol., 1931, 14, 189–194).—Liver tissue destroys adrenaline *in* vitro; all other tissues are inactive in this respect. P. G. M.

Adrenal capsules and metabolism of electrolytes. I. Effect of adrenaline, adrenal capsule extract, and choline on blood-serum-potassium and -calcium. II. Effect of loss of the medullary and cortical portions of adrenal capsules on blood-serum-potassium and -calcium. Liverand muscle-glycogen of rabbits having adrenal capsules removed. III. Skeletal muscle-potassium and -calcium of rabbits having adrenal capsules removed, and effect of fatigue. S. SUGIMOTO (Folia Endocrinol. Japon., 1932, 8, 2—3, 5—7, 11— 12).—I. Adrenaline (injected) decreases -Ca and -K; interrenin or 1% choline slightly increases -K. 2% Choline decreases -K.

II (a). -K increases; -Ca temporarily decreases.

III. After adrenalectomy -K changes; -Ca increases. Fatigue decreases -K and -Ca in normal or adrenalectomised animals. CH. ABS.

Influence of the adrenal-cortex hormone on the chemistry of active muscle. R. INDOVINA (Biochem. Z., 1933, 267, 383—388).—The time required for complete exhaustion of rats in a treadmill under standard conditions is lengthened by 4—6 hr. on injection of the hormone, and the decrease of glycogen and increase of residual N in the fatigued muscles are not so great in the injected as in the uninjected animals. P. W. C.

Dependence of metabolic action of thyroid secretions on the condition of the central nervous system. R. INDOVINA (Biochem Z., 1933, 267, 389-399).—The increase of basal metabolism in the rat by injection of thyroxine is greatly enhanced under the influence of strychnine, but is unaffected by cocaine. P. W. C.

Production of serum inhibitory to the thyreotropic hormone. J. B. COLLIP and E. M. ANDERSON (Lancet, 1934, 126, 76—78).—Rats (I) and guineapigs (II) treated for a long period with anterior pituitary extracts containing the thyreotropic hormone (III) develop an apparent resistance to (III). Blood-serum from animals containing such an inhibitor prevents the usual response of normal (I) and (II) to (III). L. S. T.

Effect of thyroid and pituitary extracts on the composition of the blood and on diuresis. L.

LANGERON, M. PAGET, and J. LEDIEU (Bull. Acad. Méd., 1933, [iii], **109**, 843—846; Chem. Zentr., 1933, ii, 1887).—Administration of thyroid increases the ratio plasma vol.: corpuscle vol. when this is low. Plasma-Cl concn. remains unchanged; corpuscle-Cl becomes normal. Plasma-albumin: -globulin is unchanged. Diuresis and Cl excretion are slightly decreased. Administration of theobromine with thyroid also increases the blood-plasma. The effect of pituitary extract is opposite to that of thyroid.

A. A. E. Effect of pituitrin on water balance of rabbits. C. I. Cox and C. S. HICKS (Austral. J. Exp. Biol., 1933, 11, 288—294).—Rabbits infused with 5% saline containing 0.4% of pituitrin show inhibited diuresis, blood dilution, and increased excretion of Cl'. The excretions of  $H_2O$  and of salt by the kidney occur independently. H. D.

Mass excretion of æstrogenic hormone in the urine of the stallion. B. ZONDEK (Nature, 1934, 133, 209-210).-The amount of œstrogenic hormone (II) excreted in the urine of the stallion (I) varies from  $10^4$  to  $4 \times 10^5$  mouse units per litre, average val.  $1.7 \times 10^5$  units per litre, corresponding with an excretion of  $1.7 \times 10^6$  units a day or 62 g. of (II) per year. This val. is much > that excreted by other mammals, and the higher val. is confined to the male. The castrated or sexually-immature horse excretes only small quantities (0.2-0.5%) of (II). Comparative vals. for other animals are given. The male sex hormone is not excreted in increased quantities in the urine of (I), whilst gonadotropic hormone, prolan, and corpus luteum hormone are not excreted. An alteration in solubility of (II) occurs in the animal outside the testes, which are the richest (II)-containing tissues known. L. S. T.

Dehydrogenation of the follicular hormone. A. BUTENANDT and H. THOMPSON (Ber., 1934, 67, [B], 140—144; cf. A., 1933, 540).—Distillation of the follicular hormone over electrolytic Zn dust and purification of the distillate by crystallisation from EtOH and light petroleum, and then through the additive compound with 2:7-dinitroanthraquinone, leads to the isolation of chrysene in very small amount.

H. W. Vitamin content of lichens. N. R. ELLIS, L. J. PALMER, and G. L. BARNUM (J. Nutrition, 1933, 6, 443-454).—Vitamin-A occurs in short but not tall lichens. The vitamin-D potency of tall was > that of short lichens. No appreciable amounts of vitamin-B occurred in any species examined. A. G. P.

Vitamin-A reaction with antimony chloride. II. Spectroscopic investigation of chromogens. III. Placenta and serum. H. GOLDHAMMER and F. M. KUEN (Biochem. Z., 1933, 267, 406—416, 417— 423).—II. The colours with SbCl<sub>3</sub> and carotene (I), xanthophyll (II), ergosterol (III), cholesterol (IV), oxycholesterol (V), and vitamin-A (VI) are investigated and the corresponding absorption spectra determined. The spectra of (I) and (II) are similar and of (III) and (IV) each have four bands, two of which are common to both substances; that of (V) has four bands completely different from those of (IV). Whereas the bands of (IV) gradually disappear on heating in air and on irradiation, those of (V) intensify. Liver oil gives the (VI) bands at 610 mµ, a band at 572 mµ, and the four bands of (IV). In alcoholic extracts, the bands are displaced towards the short wave-length. The bands of the unsaponifiable fraction are similarly displaced, but towards the red end of the spectrum. In the unsaponifiable fraction of butter after addition of SbCl<sub>3</sub>, the characteristic bands of (VI), (I), and (IV) are obtained.

III. In human and horse blood-serum a colourless chromogen is present which on treatment with SbCl<sub>3</sub> gives a blue colour and bands at 595 and 541 mµ. (I) and (II) are detected, but (VI) only in certain cases. By drying the human placenta in air at  $35-40^{\circ}$ , lipochrome was destroyed and a colourless chromogen formed which with SbCl<sub>3</sub> gave a blue colour and bands at 595 and 541 mµ. The formation of the chromogen depends on the presence of (II).

P. W. C.

Conversion of carotene into vitamin-A in the animal body. B. SKARZYNSKI (Bull. Acad. Polonaise, 1933, B, 31-41).—Ingestion of 0.1 mg. of carotene (I) daily by rats on a vitamin-A (II)-free diet is followed by the appearance of (II) in the liver; (I) and possibly other related substances also appear to be present (cf. A., 1932, 657). (II) is present in the blood in small amount, but not in the spleen. Unchanged (I), but not (II), occurs in the contents of the cæcum (cf. A., 1931, 1196; 1932, 309). F. O. H.

Effect of vitamin-A on the mineral economy [of rats]. C. BOMSKOV and G. SEEMANN (Z. ges. exp. Med., 1933, 89, 771—779; Chem. Zentr., 1933, ii, 1889).—Large doses of vitamin-A (I) lead to brittleness and low mineral content of bones. (I) hinders the curative action of vitamin-D on rickets. A. A. E.

Effect of vitamin- $\Lambda$  on the composition of the blood. C. BOMSKOV and G. SIEVERS (Z. ges. exp. Med., 1933, 89, 780—785; Chem. Zentr., 1933, ii, 1889).—In rabbits only high blood-PO<sub>4</sub> and slightly diminished -Ca, attributed to the vitamin-D content of the prep., were observed. A. A. E.

Keratoplastic reaction of hoof formation to some physiological factors. V. KLEMOLA (Bied. Zentr. [Tierernähr.], 1933, B, 5, 657-675).—Abnormalities in hoof formation in horses during prolonged feeding of dry rations are ascribed to vitamin-A deficiency. A. G. P.

Vitamin-A deficiency as related to reproduction in range cattle. G. H. HART and H. G. GUIL-BERT (Calif. Agric. Exp. Sta. Bull., 1933, No. 560, 30 pp.).—Physiological effects of vitamin-A deficiency are discussed. A. G. P.

Avitaminosis-A and use of lipins. L. RANDOIN and R. NETTER (Compt. rend., 1934, 198, 395—397).— Growth of rats fed on diets containing vitamin-B and -D, but not -A (I), with addition of either peanut oil or lard, ceases after 50—70 days, death occurring within 3 months. Hence lard contains no (I), and has no effect on the alterations in the tissue-lipins resulting from deficiency of (I). J. W. B.

Spectroscopic evaluation of solutions of vitamin-D in fatty oils. I. L. FUCHS and Z. BECK (Pharm. Presse, 1933, 38, Wiss.-prakt. Heft, 81–87; Chem. Zentr., 1933, ii, 1903).—The method employs the ultra-violet absorption spectra of the solutions and their unsaponifiable fractions. The curve relating extinction to  $\lambda$  shows at 265 mµ a characteristic max. for vitamin-D. Long preservation in the dark in presence of air causes appearance of a yellow colour. A. A. E.

Effect of feeding a cod-liver oil concentrate to cows on the vitamin-D content of milk. W. E. KRAUSS, R. M. BETHKE, and W. WILDER (J. Dairy Sci., 1933, 16, 549-555).—Addition of "Vitex" (codliver oil concentrate) to cows' rations increased the vitamin-D (I) content of the milk, in proportion to the amount supplied. The decline in the fat content of milk following heavy feeding of fish oils is probably not to be associated with the high intake of unsaturated fatty acids or of (I). A. G. P.

Comparative antirachitic efficiency of irradiated ergosterol, irradiated yeast, and cod-liver oil for the chicken. R. M. BETHKE, P. R. RECORD, and D. C. KENNARD (J. Nutrition, 1933, 6, 413–425). —Irradiated yeast, and irradiated ergosterol (I) dissolved in linseed, maize, or cod-liver oils were less effective for chicken than the rat-equiv. proportion of cod-liver oil (II). The antirachitic potency of (I) was not reduced by admixture with (II). A. G. P.

Copper and vitamin-B. J. KARP (Z. ges. exp. Med., 1933, 89, 765—770; Chem. Zentr., 1933, ii, 1890).—Products and organs rich in vitamin-B are relatively rich in Cu. In fruit (poor in -B) the Cu content is particularly low. Fe and vitamin-B content are not parallel. There is no regular relation between Cu and other vitamins. A. A. E.

Activity of crystalline preparations of vitamin-  $B_1$ . A. G. VAN VEEN (Nature, 1934, 133, 137).— A cryst. product, approx. twice as active as the author's former prep. (A., 1932, 782), has been isolated. L. S. T.

Activity of crystalline preparations of vitamin- $B_1$ . H. W. KINNERSLEY, J. R. O'BRIEN, and R. A. PETERS (Nature, 1934, 133, 177).—A discussion of van Veen's results (preceding abstract). L. S. T.

Necessary versus optimal intake of vitamin-B<sub>2</sub>. H. C. SHERMAN and L. N. ELLIS (J. Biol. Chem., 1934, 104, 91—97).—Increasing the intake of vitamin-B<sub>2</sub> (I) above the actual requirement level results in successive increases in the rate of growth and vitality in rats. The power of the weaned rat to resist the effects of (I) deficiency depends on the diet of its mother. H. D.

Other factors than vitamin- $B_1$  and  $-B_2$  in the vitamin-B complex. R. C. LEWIS (J. Nutrition, 1933, 6, 559-570).—A review. A. G. P.

Vitamin-C distribution in Baldwin and McIntosh apples. C. R. FELLERS, P. D. ISHAM, and G. G. SMITH (Proc. Amer. Soc. Hort. Sci., 1932, 29, 93—97). —The freshly expressed juices are, respectively, rich and poor in vitamin-C. In both cases the epidermis is richer than the flesh. CH. ABS.

Staining of vitamin-C in adrenal glands. G. BOURNE (Austral. J. Exp. Biol., 1933, 11, 261-267; cf. A., 1933, 872).—A reducing substance (I) in the fixed tissue from the adrenal glands of mice, rats, cats, and guinea-pigs was demonstrated by the reduction of  $AgNO_3$ ,  $OsO_4$ , Fehling's solution, and  $HAuCl_4$ . Differentiation from lipins was obtained by using alcoholic  $AgNO_3$ , fixing the tissue with  $CH_2O$  and soaking in  $Et_2O$ , and fixing in  $CHCl_3$ . Impregnation with  $HAuCl_4$  confirmed the  $AgNO_3$  findings. (I) may be vitamin-C.

Reaction of methylene ether groups in aromatic compounds. See this vol., 314.

Electrical charge of the colloid particles of protoplasm. B. SEN (Ann. Bot., 1934, 48, 143— 152).—In cataphoretic investigations the protoplasmic particles of the petiole hairs of *Urtica dioica* and of the root hairs of *Azolla pinnata* show a negative charge. If the current applied is not sufficient to injure the protoplasm, the movement of the particles is reversed immediately the current is broken. The rate of migration is independent of the size and shape of the particles. A. G. P.

Hydrogen-ion concentration and the isoelectric reaction of plant protoplasts, especially the cell nucleus and the plastids. G. YAMAHA and T. ISHII (Protoplasma, 1933, 19, 194—212).—Free surviving nuclei of a no. of plant cells show  $p_{\rm II}$  vals. ranging from 4.0 to 5.0. The  $p_{\rm H}$  of living cell nuclei in the embryonic condition approach the isoelectric point more nearly than those in the actively growing condition. Thixotropy is recorded in free surviving nuclei from *Vicia faba*. Intracellular variations in  $p_{\rm H}$  during karyokinesis in pollen cells are recorded. A. G. P.

Physiologically polarised photosynthetic exchange in submerged water plants. I. K. ARENS (Planta [Z. wiss. Biol.], 1933, 20, 622-658).-Leaves of *Elodea* immersed in Ca(HCO<sub>3</sub>)<sub>2</sub> and exposed to light liberate O<sub>2</sub> and an alkaline material from the upper surface, and take up Ca(HCO<sub>3</sub>)<sub>2</sub> or the corresponding pairs of ions at the under-surface without change of reaction in the surrounding medium. In distilled H<sub>2</sub>O the upper-surface changes continue for a time until the reserve Ca in the leaves is exhausted. Normal changes recommence if Ca(HCO<sub>3</sub>)<sub>2</sub> (but not aq.  $CO_2$ ) is applied to the under-side only. Starch formation occurs mainly near the upper surface of the leaf. The alkaline reaction produced in the vicinity of the upper surface probably results from the elimination of the hydroxide or normal carbonate of the base (Ca, Na, K, etc.) with which the underside of the leaf is in contact. A. G. P.

Catalase and photosynthesis. E. YAKUSHIJI (Acta Phytochim., 1933, 7, 93—115).—The action of various catalase (I) preps. (from taka-diastase, yeast, fish liver, *Hydrilla verticillata*, and *Chlorella ellipsoidea*) is inhibited by low concns. of NH<sub>2</sub>OH (A., 1905, i, 107) and, to a smaller extent, by HCN. The sensitivity of (I) towards heat varies with the different preps. The dissociation const. of (I)-H<sub>2</sub>O<sub>2</sub> is 0.083 for yeast-(I) and 0.094 for fish liver-(I) (cf. A., 1932, 1062). The gaseous metabolism of *C. ellipsoidea* and of *Ulva conglobata* indicates that the evolution of O<sub>2</sub> during photosynthesis is totally due to the (I) of the chloroplasts. The decrease in plant assimilation by  $NH_2OH$  or KCN also depends on the inhibition of (I). F. O. H.

Copper in relation to chlorophyll and hæmoglobin formation. O. S. ORTH, G. C. WICKWIRE, and W. E. BURGE (Science, 1934, **79**, 33—34).—The addition of  $CuSO_4$  to soil increased the chlorophyll (I) content of the leaves of orange trees suffering from (I) deficiency. No Cu was found in the leaves. L. S. T.

Chlorophyll content of grain sorghums. J. C. IRELAND and P. A. YEATS (Bot. Gaz., 1933, 95, 300— 315).—The chlorophyll content (I) of Kaffir corn increases up to seed maturity and declines as the grain hardens. It varies directly with the amount of evaporation and the temp. A positive relationship is established between yield and (I). A. G. P.

The SH radical and other sources of sulphur affecting growth of isolated root tips of wheat seedlings. P. R. WHITE (Protoplasma, 1933, 19, 132–135).—The elongation of root tips was influenced by S compounds in the following order: NaSH> control> $K_2$ S>CS(NH<sub>2</sub>)<sub>2</sub>>NH<sub>4</sub>CNS. A. G. P.

Influence of thiol and its sub-oxidised derivatives on the developmental cycle of hydranths of the genus Obelia. F. S. HAMMETT (Protoplasma, 1933, 19, 510—540).—The metaplasic formation of a hydranth on the distal end of a stolon outgrowth is favoured by 'SH and retarded by its suboxidised derivatives. A. G. P.

Significance of growth-substance in the growth and geotropic response of roots of Vicia faba. P. BOYSEN-JENSEN (Planta [Z. wiss. Biol.], 1933, 20, 688—698).—Geotropic deviation in roots is associated with the presence of larger proportions of growth substance (I) on the lower than on the upper side of the root tip. (I) retards the elongation of roots.

A. G. P.

Catalase activity as a measure of seed viability. C. W. LEGGATT (Canad. J. Res., 1933, 9, 571-573).— Statistical analysis of earlier work shows that the viability of wheat may be ascertained by determination of the total and thermostable catalase activity. A. G. P.

Biological action of metals at a distance. G. A. NADSON and C. A. STERN (Compt. rend., 1934, 198, 282—284).—The rate of germination of seeds of *Sinapis alba* is decreased by Pb, Au, Pt, and Al discs placed at a distance of 2—3 mm., the effect decreasing in the order given (that of decreasing atomic no.) and being greater for a disc 0.6 than for one 0.02 mm. thick. R. S. C.

Physico-chemical properties of seed extracts. C. A. SHULL and J. W. MITCHELL (Bot. Gaz., 1933, 95, 258—278).—Analyses and f.-p. determinations of the cold-H<sub>2</sub>O and hot-EtOH extracts of various seeds are recorded. The f.-p. depression is almost entirely accounted for by the proportion of sugars and salts present in the extract, and proteins are a negligible factor in this respect. Autolysis of seeds is indicated at temp. very little above 0°. A. G. P.

Effect of seed formation on the rate of respiration of fruit of the Japanese persimmon or kaki (*Diospyros kaki*, L.). K. MATSUMOTO (Japan. J. Bot., 1932, 6, 125—137; Bied. Zentr., 1933, A, 4, 37).—Seed-bearing fruits show higher respiratory activity than parthenocarps. No definite relationship is apparent between respiration rates. Treatment with McCHO increases respiration, especially in unripe fruits, but EtOH is without effect.

A. G. P.

Physiology of apples. XIV. Determination of chemical change and rate of respiration in stored apples. G. LALL (Ann. Bot., 1934, 48, 273-292).—Appropriate technique for the application of the "half-apple " method of examination is described. The cutting of apples results in a temporarily increased rate of respiration which disappears after approx. 7 days' storage at 12°. Considerable variations occur in the ratio of sugars and acid lost to CO2 produced by individual varieties. Differences in the course of respiratory activity in Bramley's Seedling and Cox's Orange Pippin are probably related to the waxy coating on the skin of the former. Wax accumulation may account for a part of the sugar loss which takes place during respiration. Substances synthesised from CO<sub>2</sub> during respiration include EtOH, MeCHO, and esters but no non-volatile compounds.

A. G. P.

Influence of physico-chemical phenomena in the ripening of corn. M. PIETTRE (Compt. rend., 1934, 198, 608—611).—The disappearance of sol. sugars (complete in about 8 days) even at low temp. coincides with the gradual diminution (glutinogenesis) of globulin (0.75—0.34%) and albumin (0.31—0.18%), and with an active evaporation process. At 26° the loss of wt. by evaporation is 35% in 2 days.

P. G. M.

Significance of mannitol in the metabolism of some higher plants. T. ASAI (Japan. J. Bot., 1932, 6, 63—101; Bied. Zentr., 1933, A, 4, 44).— Leaves and bark of stems contain more mannitol (I) than wood or roots. Seasonal variations in (I) content are recorded, but no relationship is apparent between assimilation rates and the distribution of (I) in the plants. A. G. P.

Transport in the cotton plant. II. Ontogenetic study of concentrations and vertical gradients. T. G. MASON and E. J. MASKELL (Ann. Bot., 1934, 48, 119-141).—During the development of the plants, polysaccharides are stored chiefly in the bark; total N in the bark with little, if any, in the wood; P in the bark and also in wood with depletion from lower zones in the later stages of growth; Ca in the bark and wood. No evidence of accumulation of K was obtained. Vertical concn. gradients of materials stored in the bark are negative and that of K is consistently positive. Stored N in bark occurs principally as asparagine-N and accounts for the negative gradient of crystalloid N. Residual N shows a consistent positive gradient and is probably the mobile component. Gradients of sugar concn. and of total osmotic pressure in the bark become less steep as growth proceeds. A. G. P.

Nitrogen metabolism of leaves of Atriplex nummularium. J. W. WOOD (Austral. J. Exp. Biol., 1933, 11, 237-252).—Below  $p_{\rm H}$  5.5 NH<sub>2</sub>-acids accumulate in the leaves, whilst above this  $p_{\rm H}$  NH<sub>3</sub> and amides accumulate. During wilting the  $p_{\rm H}$  of the leaves changes from 6.5 to 6.2 and thence to 7.8, corresponding with an increase in NH<sub>3</sub>- and amide-N and a decrease in NH<sub>2</sub>-acid- and protein-N and H<sub>2</sub>O content. A rise in temp. of leaves allowed to autolyse at  $p_{\rm H}$  8.1 appears to favour protein synthesis.

H. D.

Composition of different regions of mounds of *Eutermes exitiosus*, Hill. F. G. HOLDAWAY (J. Counc. Sci. Ind. Res. Australia, 1933, 6, 308).—A correction (cf. A., 1933, 1193). A. G. P.

Composition of Saksaul wood. I. M. ORLOVA (J. Appl. Chem. Russ., 1933, 6, 1120–1121).—The wood of *Haloxylon ammodendron* from Turkestan contains ash  $3\cdot4$ , pentosans 19.0, lignin 29.1, cellulose  $36\cdot2$ ,  $Et_2O$ -sol. substances 1.6,  $H_2O$ -sol. substances  $8\cdot0$ , galactan 9.0, and mannan  $0\cdot2\%$ . R. T.

Spectroscopic study of wood of Pinns sylvestris. L. LEMMEL (Compt. rend., 1934, 198, 496–497).— The presence of Ca, Mg, Na, K, Mn, Al, B, Pb, Ag, P, Fe, Si, and (?) Cr and Sn is shown. C. A. S.

Action of chlorine on lignified tissues. F. M. WOOD (Biochem. J., 1934, 28, 52—61).—The pink colour (I) in lignified tissues produced by the  $NH_2Cl$ reaction is associated with the presence of I and lignin. It is concluded that (I) is produced in the presence of I by a vanillylidene derivative formed from vanillin (II) which is in loose association with a form of lignocellulose. (II) predominates in older tissues. H. G. R.

Composition of common heather (Calluna vulgaris). B. THOMAS (J. Agric. Sci., 1934, 24, 151-155).—The crude fibre content of heather declines with age and the highest vals. found were < those of very poor grass. Nearly all of the total N occurs as protein, the small balance consisting of NH<sub>3</sub>- and amide-N. The pepsin digestibility of the crude protein is low. The fibre content is similar to that of grass, and shows no regular variation with age. The Et<sub>2</sub>O extract increases with age and is always > that of grass. A. G. P.

Analyses of certain winter pears. J. C. MOORE (Oregon Agric. Exp. Sta. Bull., 1933, No. 316, 10 pp.). —Analytical data show pears to have high total sugars and crude fibre, low fat and protein, and relatively high Cu contents. The fresh tissue has a low buffer val. and the ash a high proportion of bases. A. G. P.

Determination of pectins in fruits, berries, and vegetables. N. V. SABUROV and S. S. CHER-NUISHEVA (Schr. zentr. biochem. Forschungsinst. Nahr.-Genussm., U.S.S.R., 1931, 1, 53-60).—Mehlitz's method gives rather high vals. for fruits and berries. For vegetables Norman and Nanji's method is modified, the extraction being effected by boiling for 1 hr. with 0.5% aq.  $(NH_4)_2C_2O_4$ . CH. ABS.

Mucilage from slippery elm bark. E. ANDER-SON (J. Biol. Chem., 1934, 104, 163—170).—The mucilage of *Ulmus fulva* consists of two or more polyuronides, in which the uronic acid is combined with 2 mols. of simple sugars and a coloured non-saccharine substance. The presence of galacturonic acid, *l*- rhamnose, and *d*-galactose has been established and there are indications of a pentose, a methylated hexose, and a methylated uronic acid. H. G. R.

Sugar of Rivularia bullata. H. COLIN and J. PAYEN (Compt. rend., 1934, 198, 384–386).—The dextrorotation of the residue (sucrose and reducing sugars absent) from the EtOH extract of R. bullata is decreased by the action of dil. acids or glucosidase (which produce reducing sugars), and trehalose is isolated. The EtOH-extracted residue with boiling  $H_2O$  gives a dextrorotatory, pectin-containing gum, giving, with 2%  $H_2SO_4$  at  $120^\circ$ , a reducing hydrolysate which contains uronic acid and from which the osazones of arabinose and glucose are obtained. J. W. B.

Presence of myrosin in certain plant families and its histochemical detection. P. MARSILI (Boll. Soc. Eustach., 1933, 31, 9—16; Chem. Zentr., 1933, ii, 2032).—The violet coloration given by orcinol and HCl is not sp. for myrosin. A. A. E.

Infra-red absorption spectra of some plantpigments. See this vol., 238.

Pigment of red cabbage (Brassica oleracea). I. I. CHMIELEWSKA (Rocz. Chem., 1933, 13, 725– 735).—An anthocyanin (I),  $C_{28}H_{33}O_{16}Cl$ , containing 1 OMe and 1 mol. of an unidentified disaccharide, has been isolated from red cabbage. (I) eliminates MeOH and 2 mols. of glucose on acid hydrolysis, yielding cyanidin, and is isomeric but not identical with peonin or mecocyanin. On alkaline hydrolysis (I) yields protocatechuic acid and phloroglucinol; crude (I) yields in addition about 4% of sinapic acid. R. T.

Pigments of the sunflower. II. L. ZECH-MEISTER and P. TUZSON (Ber., 1934, 67, [B], 170– 173; cf. A., 1931, 402).—Re-examination has confirmed the presence of lutein,  $C_{40}H_{56}O_2$ , m.p. 193° (corr., Berl),  $[\alpha]_{c}^{a}$  +136° in EtOAc. Chromatographic adsorption leads to the detection of unimportant amounts of polyenes, possibly including violaxanthin, and to the ready isolation of taraxanthin,  $C_{40}H_{56}O_4$ , m.p. 184° (Berl). The small amount of carotene is remarkable. H. W.

Water-soluble organic acids of sunflower seeds. A. GOLDOVSKI and A. BOZHENKO (Masloboino-Zhir. Delo, 1933, No. 1, 13-20).—Citric, tartaric, and chlorogenic acids are present. CH. Abs.

Characteristics and composition of Wisconsingrown tobacco-seed oil. W. L. ROBERTS and H. A. SCHUETTE (J. Amer. Chem. Soc., 1934, 56, 207-209).—The oil expressed from "Havana 142" seed has the same consts. as that obtained by extraction of an unknown strain with light petroleum; the consts. are also similar to those of foreign oils. The oils contain 1.25% of unsaponifiable matter and give palmitic (3.1%), stearic (4.8%), oleic (16.2%), and linoleic acid (I) (70.4%); (I) appears to be present (as glyceride) in two isomeric forms. H. B.

Rye oil. II. Properties as affected by choice of menstruum. A. W. STOUT, H. A. SCHUETTE, and R. G. FISCHER (J. Amer. Chem. Soc., 1934, 56, 210-211; cf. B., 1932, 899).—Extraction of rye embryos with light petroleum, b.p. 40-60°, Et<sub>2</sub>O,  $CCl_4$ ,  $C_2H_4Cl_2$ ,  $CS_2$ ,  $C_6H_6$ ,  $CHCl_3$ , and  $COMe_2$  gives 11.46, 13.66, 13.84, 14.13, 14.14, 14.45, 15.57, and 17.23%, respectively, of oil. The variations in the vals. of  $d_{25}^{25}$ ,  $n_{10}^{20}$ , I val., P content, and unsaponifiable matter are recorded. H. B.

Plants containing oxalates with regard to oxaluræmia. A. GOUDSWAARD (Pharm. Weekblad, 1934, 71, 114—119).— $H_2C_2O_4$  occurs only in mushrooms, but the Ca (I) and K salts are very widely distributed. (I) is insol. in gastric juice and passes unchanged through the intestine. Of fifty vegetables and fruits examined, amaranth, beetroot, cocoa, spinach, pepper, purslane, rhubarb, tea, figs, sorrel, and species of Oxalis contained considerable quantities of  $C_2O_4''$ . S. C.

Hydrocyanic acid in grasses : Melica and Gynerium. P. GUÉRIN (Compt. rend., 1934, 198, 383-384).—The leaves of M. ciliata, L. (collected in June), contain 0.151-0.306 g. HCN per kg., and those of M. mutans, L., or M. uniflora, Retz, 0.10-0.15 g. per kg. HCN is also detected in the roots, but not in the fruit. The leaves of G. argenteum, Nees, contain 0.23 g. per kg. in June, but the quantity decreases as autumn approaches (0.054-0.068 g. in Sept.), whereas the open inflorescences contain 0.28 g. HCN per kg., but HCN is absent from the fruit.

J. W. B.

Proteins of grasses. III. Cystine content of certain grasses and other pasture plant proteins. A. POLLARD and A. C. CHIBNALL (Biochem. J., 1934, 28, 326—336).—The cystine (I) content of several typical grass and pasture plant proteins was determined by Prunty's modification of Sullivan's colorimetric method. Grass proteins contain 0.3-0.95% of (I); lucerne leaf protein contains 1.2% of (I). Vickery and White's gravimetric method always gives a much higher val. for (I).S than corresponds with the amount known to be present, due to S from an unknown  $NH_2$ acid. Calculation of the (I) content of grasses and pasture plants at various protein levels indicates that pasturage contains ample (I) for the wool-protein requirements of the sheep which it normally carries. C. G. A.

Systematic value of leaf ash. S. SEN (J. Dept. Sci. Calcutta Univ., 1933, 10, 8 pp.).—The mode of deposition of minerals on cell walls is discussed. CH. ABS.

Iodine compounds in seaweed. E. MASUDA (Proc. Imp. Acad. Tokyo, 1933, 9, 599–601).—An EtOH extract of *Ecklonia cava* powder, freed from reducing substances and iodides, with aq. H<sub>2</sub>O<sub>2</sub> and C at room temp. gives slowly CH<sub>2</sub>I·CO<sub>2</sub>H (0.02%), CHI<sub>2</sub>·CO<sub>2</sub>H (0.02%), m.p. 106° (anilide, m.p. 187°), CI<sub>2</sub>:CH·CO<sub>2</sub>H (0.009%), m.p. 133° (anilide, m.p. 134°), (CH<sub>2</sub>I)<sub>2</sub>CO (0.08%), m.p. 65° [gives (CH<sub>2</sub>·OBz)<sub>2</sub>CO with AgOBz in ligroin], and (probably) *tri-iodoacetaldehyde* (0.007%), m.p. 126—127° (decomp.), unstable to light and cold KMnO<sub>4</sub>. R. S. C.

Manganese in wheat-grains. P. BRUÈRE (Compt. rend., 1934, 198, 504—506).—Different parts of wheat-grains have the following Mn content (mg. per 100 g. of dry product): albumen, central 0.2, median 0.28, peripheral 0.21; envelope, external 2.47, internal 10.54; germ 0.285. R. S. C. Absorption of manganese by wheat seedlings. J. DAVIDSON (Proc. 2nd Internat. Cong. Soil Sci., 1933, 2, 84).—The intake of Mn from  $MnO_2$  by wheat in H<sub>2</sub>O cultures was decreased by addition of NaNO<sub>3</sub> and CaCO<sub>3</sub>, but not by NH<sub>4</sub>Cl, which increased the [H<sup>\*</sup>] of the media. When Mn was supplied as MnCl<sub>2</sub> the inhibitory action of NaNO<sub>3</sub> and CaCO<sub>3</sub> was negligible. Absorption of Mn was reduced by PO<sub>4</sub><sup>'''</sup>, especially in cultures containing MnCl<sub>2</sub> or MnSO<sub>4</sub>. The intake of Mn by plants is controlled not only by the soil  $p_{\rm H}$ , but also by the nature of anions present. A. G. P.

Physiological importance of mineral elements in plants. V. Distribution of diastase, invertase, and catalase in normal and potassiumstarved bean plants. M. CATTLE (New Phytol., 1933, 32, 364-381).-In K-starved plants (I) the diastatic activity of leaves of all ages was < that of normal plants, differences being more pronounced in young and old leaves than in those of intermediate age. The effect of K on the activity of the enzyme is not attributable to a control of the NH<sub>2</sub>-acid content. Both the rates of formation and disappearance of starch from leaves were smaller in (I). In normal plants, invertase activity in upper was > in lower leaves and uniformly low in mature leaves. During K starvation the activity of upper leaves was <, and of lower leaves >, that in normal plants. The distribution of catalase resembled that of diastase in all respects. A. G. P.

Distribution of potassium in normal and scorched foliage. L. G. G. WARNE (Ann. Bot., 1934, 48, 57-67).—The scorching of leaves resulting from K deficiency is associated with a lowered proportion of K in the dry matter and a steeper K gradient from main veins to margins in the leaves. A negative correlation exists between the dry matter in leaves and the K content of the dry matter. The withdrawal of K from older leaves and its translocation to young growing points is probable.

A. G. P.

**Reaction of sphagnum.** E. KIVINEN (Bull. Agrogeol. Inst. Finland, 1932 : Proc. Internat. Soc. Soil Sci., 1933, 8, 219).—Differences are recorded in the  $p_{\rm H}$  of expressed juices of sphagnum from moor soils of different types. A. G. P.

Turgidity pressure. W. W. LEPESCHKIN (Ber. Deut. bot. Ges., 1934, 51, 455–469).—A mathematical analysis of the pressure relationships between the cell-contents and cell-wall. P. G. M.

Inhibitive influence of radium on the growth of the rootlets of *Lens esculenta*, Moench: modification of the minimum preventive dose under the influence of favouring ions. A. SARTORY, R. SARTORY, I. MEYER, and ERNST (Compt. rend., 1934, 198, 386—388).—The inhibitory effect of Ra on the growth of the rootlets of *L. esculenta* is not affected by  $Sr(NO_3)_2$ , but is increased by  $ZnSO_4$  or  $CuSO_4$ , all in isotonic solution. When a mixture of a Rasensitising ion (I) (Cu) and one (II) (Mg) which tends to counteract the effect of the Ra is employed, the effect of (I) is much more pronounced than is that of (II). J. W. B. Nutrition of various saprophytic and parasitic fungi. M. VOLKONSKY (Ann. Inst. Pasteur, 1934, 52, 76—101).—Of 26 forms of Saprolegniaceæ of the genera Saprolegnia, Isoachlya, Achlya, Dicthyuchus, and Aphanomyces (I) investigated, none used  $NO_3'$ or  $SO_4''$  as sources of N and S, respectively; all, with the exception of (I), hydrolysed glucose, maltose, dextrin, and sol. starch, but not pentose, galactose, sucrose, etc. Of other fungi (mainly parasitic) studied, a few utilised  $NO_3'$  as a source of N, whilst all assimilated  $SO_4''$ . There appeared to be no relation between the mode of S or N utilisation and parasitism. F. O. H.

Cytosporina, Phomopsis, and Diaporthe. V. Analysis of chemical factors influencing fungal growth in the apple. L. N. SETH (Ann. Bot., 1934, 48, 69—107).—Close relationships are established between concess. of malic acid and sugars in the apple and the rate of penetration of the fungi. In general, increasing concess. of both constituents tend to retard fungal growth, but the various species respond very differently to any one set of conditions. The nature of the sugar and the relative proportions of sugars (if mixed) are also of importance in this respect. A. G. P.

Physiology of parasitism. XIV. Comparison of enzymic extracts obtained from various parasitic fungi. K. P. V. MENON (Ann. Bot., 1934, 48, 187—210).—Interrelationships between the activity of fungal enzymes and the composition of the medium are examined with special reference to the effect of  $p_{\rm H}$ , and the retarding action of certain plant extracts. The effect of the latter is largely associated with the presence of simple org. substances. The secretion of pectinase by fungi is favourably affected by the presence of pectin in the medium. A. G. P.

Possible chemical nature of tobacco mosaic virus. J. CALDWELL (Nature, 1934, 133, 177).— Barton-Wright and McBain's results (this vol., 230) have been partly confirmed. N-free viruscontaining crystals have not been obtained. The virus (I) present after successive recrystallisations has been determined, but there is no evidence that the crystals contain (I) except as an impurity. They have no sp. relation to (I). L. S. T.

Some dicarboxylic acids as components of fixing fluids. C. ZIRKLE (Protoplasma, 1933, 19, 565—577).—Examination of the fixative action of oxalic, malonic, succinic, glutaric, malic, and tartaric acids used directly and as Cu and Ni salts in conjunction with  $CH_2O$  or chromic acid is recorded. The ability of the acids to influence fixation by  $CH_2O$  is dependent on the rate of penetration of the specimen. This is directly correlated with the relative fat-solubility. A. G. P.

Verification of analytical technique for biological media, by the method of added quantities. H. GRIFFON (J. Pharm. Chim., 1934, [viii], 19, 30— 36; cf. A., 1933, 1218).—The effect of experimental errors on the calc. systematic error is discussed mathematically. D. R. D.

Determination of cystine. B. J. KRIJGSMAN and E. F. BONMAN (Arch. neerl. Physiol., 1933, 18, 458-471).-Whilst Folin and Looney's method (A., 1922, ii, 539) for the determination of cystine (I) is unsuitable when applied to blood, that of Sullivan (A., 1925, ii, 1211) (II) determines only total (I). Using (II) the (I) content of the blood of fasting rats (a trace) increases to about 14 mg. per 100 c.c. after feeding. A. L.

Micro-determination of urea in blood and urine. O. DA RIN and C. PASTORINO (Rass. Clin. Terap. Sci. aff., 1932, 31, 306-334; Chem. Zentr., 1933, ii, 2167).-Vals., obtained by Van Slyke and Cullen's modification of Marshall's method, of urea, NH<sub>3</sub>, NH<sub>3</sub>-, and urea-N are tabulated. A. A. E.

Determination of lactic acid. B. J. KRIJGSMAN (Arch. néerl. Physiol., 1933, 18, 503-513).-The methods of Mendel and Goldscheider (A., 1926, 212) and Dische and Laszlo (A., 1927, 985) are modified for the photometric determination of lactic acid in blood with an error of  $\pm 4$ , and  $\pm 5$  mg. per 100 c.c. respectively.

Analysis of tissues. J. B. GRAESER, J. E. GINS-BERG, and T. E. FRIEDEMANN (J. Biol. Chem., 1934, 104, 149-155).—The tissue is crushed in an apparatus cooled by solid CO<sub>2</sub>, after freezing in liquid air. A method for the determination of glucose and lactic acid is described. H. G. R.

Micro-determination of cholesterol. T. MEU-WISSEN and E. NOYONS (Biochem. Z., 1933, 267, 405). -Comments on Monasterio's paper (this vol., 122). P. W. C.

Quantitative spectro-photo-electric analytical method applied to solutions of chlorophyll a and **b**.—See this vol., 314.

Titration of betaine in acetone. K. LINDER-STROM-LANG (Biochem. Z., 1933, 267, 45-47).-Despite the statements of Fodor and Kuk (A., 1933, 621) betaine in  $COMe_2$  can be determined by titration with HCl. W. McC.

Enzymic histochemistry. VI. Micro-determination of ammonia. K. LINDERSTRØM-LANG and H. HOLTER (Compt. rend. Lab. Carlsberg, 1933, 19, No. 20, 1-8).-NH<sub>3</sub> is determined by allowing the solution to react with a drop of NaOH in a paraffined reaction vessel (A., 1933, 864), the NH3 formed being collected on a film of H<sub>2</sub>O containing HCl and bromocresol-purple. The excess HCl is titrated with NaBO<sub>2</sub>. Amounts of NH<sub>3</sub> between 2 and  $0.0135 \times 10^{-6}$  mol. may be determined with a max. error in the latter case of 10<sup>-9</sup> mol. H. D.

Method of "chlorine-ashing." J. ERDÖS and B. GROAK (Z. anal. Chem., 1933, 95, 327-329).-Org. matter is destroyed by refluxing with HCl, and adding slowly saturated aq. NaClO3. The method is applied to the determination of Pb in fæces.

J. S. A.

Micro-determination of potassium.-See this vol., 269.

"Elon" and sodium sulphite as reducing agents in the colorimetric determination of phosphorus. G. VAN DER LINGEN (Analyst, 1933, 58, 755—756).—EtOH-extracted plant materials are ignited with  $Ca(OAc)_2$ , and the colour developed by 10 c.c. of an extract of the residue in 5% HNO<sub>3</sub>, with 1.5 c.c. each of the H<sub>2</sub>SO<sub>4</sub>-NH<sub>4</sub> molybdate reagent, 3.1275% clon (p-methylaminophenol sulphate), and of 20% Na<sub>2</sub>SO<sub>3</sub> solutions, after dilution to 16.5 c.c. with dil. HNO<sub>3</sub>, is matched after 20 min. at 26°. The accuracy is > when quinol is used, and CCl<sub>3</sub>·CO<sub>2</sub>H from blood-filtrates does not interfere. J. G.

Determination of organic phosphorus. O. H. FULCHER (J. Lab. Clin. Med., 1933, 18, 1053-1057).-The sample (2-6 mg. P) is kept over-night at  $100^{\circ}$  with 1.4 c.c. of conc.  $H_2SO_4$ ; on continued heating over a small flame  $Al_2(SO_4)_3$  is used as catalyst, and  $HNO_3$  is added dropwise to clarify. Fiske and Subbarow's colorimetric method is then applied.

CH. ABS. Colorimetric determination of phosphoric acid in presence of arsenate ions. A. E. BRAUNSTEIN (Biochem. Z., 1934, 267, 400-402).-Reply to criticisms of Barrenscheen, Banga, and Braun (A., 1933, P. W. C. 1261).

Determination of iron. Adaptation of the mercaptoacetic acid colorimetric method to milk and blood. G. LEAVELL and N. R. ELLIS (Ind. Eng. Chem. [Anal.], 1934, 6, 46-47).-In the adaptation of this method to the determination of Fe in biochemical products wet-ashing with H<sub>2</sub>SO<sub>4</sub> M. S. B. and  $HClO_4$  is preferable to dry-ashing.

Destruction [of tissue] by nitro-sulpho-perchloric acid in the toxicology of gold. E. KAHANE and V. STEFANESCO (Bull. Soc. Chim. biol., 1933, 15, 1239-1246).-During the destruction of Au-containing tissue by  $H_2SO_4$ +HNO<sub>3</sub>+HClO<sub>4</sub> significant amounts of Au are volatilised. Condensation of the vapour followed by a separate re-distillation effects recovery of most of the Au thus lost. F. O. H.

Determination of antimony in viscera and excreta. F. BAMFORD (Analyst, 1934, 59, 101-102).—In the absence of other group II metals, Sb is determined by ashing with MgO and  $Mg(NO_3)_2$ . The ash is acidified with HCl, Fe is removed, and Sb is pptd. as colloidal Sb<sub>2</sub>S<sub>2</sub> and determined colorimetrically. E. C. S.

Microdetermination of silica in body-fluids and -tissues. W. PARRI and G. SCOTTI (J. Pharm. Chim., 1933, [viii], 18, 513-527; cf. A., 1924, ii, 499; 1928, 1205).—The material (0.2 c.c. of blood or 0.05 g. of dried tissue) is calcined with NaHCO<sub>3</sub>. The ash is treated with  $HNO_3$  and  $H_2SO_4$ , and the  $SiO_2$  pptd. with  $(NH_4)_2MoO_4$  and EtOH. NH<sub>4</sub> citrate is added to ppt. phosphomolybdate. The silicomolybdate is reduced with NH2OH,HCl and Na2S2O4 and is determined colorimetrically. E. C. S.

Determination of chlorine in biological material. E. KAHANE and M. R. DUMONT (Bull. Soc. Chim. biol., 1933, 15, 1247-1255).-The method of Laudat (A., 1917, ii, 539) for serum is applicable to tissue when sufficient KMnO<sub>4</sub> is used. A modified tissue when sumcient  $\operatorname{ICHO}_4$  in place of  $\operatorname{KMnO}_4$ . F. O. H.

Determination of bromine in blood. T. F. DIXON (Biochem. J., 1934, 28, 48-51).-A method is described for the determination of Br in 10 ml. of blood, containing 0.1—100 mg. Br per 100 ml.

H. G. R.