BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1934.

General, Physical, and Inorganic Chemistry.

New band system in nitrogen. J. KAPLAN (Physical Rev., 1934, [ii], 45, 675-677).-Bands previously reported in the luminoscence of solid N₂ and in the aurora have been photographed for the first time in the spectrum of gaseous N2. Measurements and data are revised and extended (cf. A., 1933, 205). The bands are attributed to vibrating N, mols. in the afterglow. N. M. B.

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Temperatures indicated by intensity distributions in band spectra. O. S. DUFFENDACK, R. W. REVANS, and A. S. Roy (Physical Rev., 1934, [ii], 45, 807-814).-Distributions of intensity, other than those expected from the temp. of the gas, among the rotational and vibrational mol. states are reported. and discussed for the negative bands of N_2^+ , alone and mixed with He, excited in low-voltage arcs.

N. M. B.

Wave-lengths and term systems of the fluorine spectrum. F VII and F VI. B. EDLEN (Z. Physik, 1934, 89, 179-182). A. B. D. C.

Width of neon lines. E. LAU and J. JOHANNESson (Physikal. Z., 1934, 35, 457-460; cf. A., 1933, 991; this vol., 123).-Redetermination of the width of neon lines gives results 2-5 times as high as those of Schutz and Schillbach, but in agreement with those of Lau, Reichenheim, and Johannesson.

A. J. M.

Measurement of intensity distribution and width of predissociation lines of the AlH molecule. L. FARKAS and S. LEVY (Z. Physik, 1934, 89, 256-258).-A reply to Burger and van Cittert (this vol., 344). A. B. D. C.

Infra-red spectrum of argon. R. M. Woods and B. J. SPENCE (Physical Rev., 1934, [ii], 45, 669-670).-A special hot-cathode discharge tube for use up to 10 amp. is described. Data for 46 lines in the range $0.69 - 1.80 \mu$ are tabulated.

N. M. B. Hyperfine structure of the resonance lines of Potassium. D. A. JACKSON and H. KUHN (Nature, 1934, 134, 25-26). L. S. T.

Intensities of some multiplets of Fe II and Ti II in stellar spectra. C. T. ELVEY (Astrophys. J., 1934, 79, 263-270). L. S. T.

Absorption spectrum of diatomic arsenic. G. E. GIBSON and A. MACFARLANE (Nature, 1934, 133, 951).-Eighty absorption bands between 2200 and 2750 Å. have been discovered in the spectrum of As, and can be assigned to the diat. mol.

L. S. T.

Structure of singly-ionised selenium. S. G. MURTY and K. R. RAO (Current Sci., 1934, 2, 384).--Some of the abs. vals. of the energy states characteristic of Se II are recorded. L. S. T.

Isotope effect and quenching in the fluorescence of bromine. H. J. PLUMLEY (Physical Rev., 1934, [ii], 45, 678-684).-The fine structure of the resonance spectrum of Br₂ excited by the Hg green arc line has been photographed and interpreted. The fluorescence intensities were studied at $\lambda\lambda$ 6450, 6100, and 5660 as a function of the pressure, and are approx. 300 times weaker than for I_2 ; this is accounted for on the basis of less initial absorption and greater quenching, due to longer mean life of N. M. B. the mol. in the upper state.

Influence of electric field on the absorption spectrum of rubidium. N. T. ZE (Compt. rend., 1934, 198, 2156-2159).-The absorption of Rb vapour in parallel and perpendicular fields of 303 volts per cm. was measured. The intensities of the principal series lines diminished more rapidly than without a field, and the forbidden S-D and S-S lines were strongly enhanced. B. W. B.

Strontium II and barium II spectra. F. A. SAUNDERS, E. G. SCHNEIDER, and (MISS) E. BUCKING-HAM (Proc. Nat. Acad. Sci., 1934, 20, 291-296) .--Full data for Sr II and Ba II, and new lines and terms for Ba II in the Lyman and Schumann region, are tabulated. Ba II shows anomalous reversal of relative intensity in the principal series pairs 6S-7Pand 6S-8P, as compared with 6S-6P, and also faintness and odd separation in the 5D-5F group.

N. M. B.

Nuclear spin of tin. S. TOLANSKY (Proc. Roy. Soc., 1934, A, 144, 574-587).—The fine structures of the visible lines of the Sn II spectrum have been analysed. The nuclear spin of the two main odd isotopes is -1/2, and g(I) for these isotopes is -1.78. L. L. B.

Absorption spectrum of the iodine atom. J. H. McLEOD (Physical Rev., 1934, [ii], 45, 802-804; cf. Turner, A., 1932, 1183).—Using a H or I discharge tube, the absorption of I dissociated by heating to 1000° was investigated in the range 2100-1400 Å. The first source showed $\lambda\lambda$ 1830 and 1783 as absorption lines; the second source showed weakening by absorption in the heated I of $\lambda\lambda$ 1830, 1783, 1642, 1618, 1583, 1515, 1507, and 1422. N. M. B.

Hyperfine structure in the arc spectrum of xenon. E. G. JONES (Proc. Roy. Soc., 1934, A, 144, 587-595).-16 lines in the region 4200-8800 Å. of the Xe I spectrum are complex, so that the lines of Xe I are not suitable as wave-length standards. The observed line structures are analysed, and the nuclear moments I=0 assigned to the even isotopes, I=1/2 to Xe¹²⁹, and $I \ge 3/2$ to Xe¹³¹.

L. L. B.

Nuclear mechanical moment of lanthanum from hyperfine structure. O. E. ANDERSON (Physical Rev., 1934, [ii], 45, 685–688).—The hyperfine structure of the lines $\lambda\lambda$ 5212, 5234, and 6250 of La I has been photographed. The no. of components, intensity ratios, and interval spacing are in good agreement with the val. (7/2) for the nuclear mechanical moment. N. M. B.

Spectrum of Ce III. P. N. KALIA (Current Sci., 1934, 2, 384).—A reply to criticism (this vol., 467). L. S. T.

First spectrum of tantalum. C. C. KIESS and E. Z. STOWELL (Bur. Stand. J. Res., 1934, 12, 459— 469).—Wave-length and intensity data are tabulated for > 2100 lines emitted by the arc in air between Ta electrodes in the range 10,300—2300 Å. Heads of an accompanying band spectrum, shaded towards the red and due to TaO₂, were measured. Ta is now identified in the sun by the 5997, 5944, and 5939 Å. lines. N. M. B.

Spectral distribution of radiation from highand low-pressure Hg arcs. B. T. BARNES (J. Opt. Soc. Amer., 1934, 24, 147—148).—Intensities of all the ultra-violet, visible, and infra-red lines easily measurable with a single spectro-radiometric apparatus are tabulated. N. M. B.

Experimental demonstration of the existence of dipolar magnetic radiation. H. NIEWOD-NICZANSKI (Compt. rend., 1934, 198, 2159-2161).-Triplet Zeeman separation of the forbidden Pb I line, 4618 Å., confirms the view (cf. Physical Rev., 1934, 45, 64) that it consists of pure dipolar magnetic radiation. B. W. B.

Comparison of continuous spectra of some stars of types A and B. Nocturnal proportions of O_3 . D. BARBIER, D. CHALONGE, and E. VASSY (Compt. rend., 1934, 198, 2139—2142).—A spectrograph for study of atm. ultra-violet absorption is described. Comparison of stellar spectra with a distant continuous source enabled intensity- λ curves and also terrestrial $[O_3]$ to be determined. B. W. B.

Ionised argon in the spectrum of Upsilon Sagitarii. W. W. MORGAN (Science, 1934, 79, 454). L. S. T.

B band of oxygen in the spectrum of Mars. W. S. ADAMS and T. DUNHAM, jun. (Astrophys. J., 1934, 79, 308—316).—The amount of O_2 in the atm. of Mars is probably < 0.1% of that in the earth's atm. L. S. T.

Radiation of the night sky between 5000 and 8000 Å. J. CABANNES (Compt. rend., 1934, 198, 2132—2135; cf. this vol., 232; Sommer, A., 1933, 332).—H₂O and O₂ ($^{1}\Sigma \rightarrow ^{3}\Sigma$) bands are prominent.

B. W. B.

Intensities of magnetic dipole lines. J. BLATON (Z. Physik, 1934, 89, 155-165).—Selection rules and intensity formulæ are derived for ${}^{1}S - {}^{3}P$ and ${}^{1}D - {}^{3}P$ transitions. A. B. D. C.

Scattering of X-rays by cold-worked and by annealed beryllium. J. E. BOYD (Physical Rev., 1934, [ii], 45, 832—834).—Intensities of reflexion of Mo $K\alpha$ radiation by crystallographic planes in powdered Be were measured under various conditions of cold-working and annealing. At. structure factors showed no appreciable change. The mass absorption coeff. was 0.26. N. M. B.

X-Ray emission spectra and chemical binding. III. $K\alpha_1\alpha_2$ doublet of sulphur in various sulphides. O. LUNDQUIST (Z. Physik, 1934, 89, 273— 276; cf. A., 1932, 1072).—Other sulphides investigated are MgS, Al₂S₃, CaS, FeS, NiS, Cu₂S, CdS, SnS₂, Sb₂S₃, and BaS. The doublet width is unchanged, but appreciable displacements are recorded. A. B. D. C.

True absorption coefficients for the elements Au to Bi in the neighbourhood of the L-absorption edges. C. G. PATTEN (Physical Rev., 1934, [ii], 45, 662—666).—Using thin films of Tl, Pb, and Bi evaporated on very thin mica the L X-ray absorption spectra gave vals. $\propto \lambda^{2.56}$ for the true absorption coeffs. corresponding with the photo-electric absorption by the three types of L electrons. N. M. B.

Mass-absorption coefficients for 16 elements and paraffin with monochromatic X-rays between 0.128 and 2.5 Å. K. GROSSKURTH (Ann. Physik, 1934, [v], 20, 197—232).—The mass-absorption coeffs. (μ/ρ) of paraffin and 16 elements were found with monochromatic X-rays (cf. A., 1931, 993). The coeff. follows the law $\tau = C\lambda^n$, C and n varying with the element. The classical mass-scattering coeffs. (σ_0/ρ) are for paraffin 0.18, C 0.16, Al and S 0.14. The val. is greater for the heavier elements. A. J. M.

Fock-Dirac atom model and the existence of ionisation potentials. L. BRILLOUIN (J. Phys. Radium, 1934, [vii], 5, 185—192).—Mathematical. The Fock-Dirac atom is discussed in analogy with the Fermi-Thomas atom relative to the exchange term and its bearing on the evaluation of ionisation potentials. N. M. B.

Thermionic work function and the slope and intercept of Richardson plots. J. A. BECKER and W. H. BRATTAIN (Physical Rev., 1934, [ii], 45, 694– 705).—A crit. theoretical survey. N. M. B.

Supposed relation between the work function and the electron potential in a metal. K. F. NIESSEN (Physica, 1934, 1, 623-626).—Frenkel's relation (A., 1928, 823) is criticised. H. J. E.

Atomic work function of tungsten for potassium. R. C. EVANS (Proc. Roy. Soc., 1934, A, 145, 135-144).—The method developed for the measurement of the rate of evaporation of ions of the alkali metals from a hot W surface (A., 1933, 442) has been extended to investigate the rate of evaporation of K atoms under the same conditions of very small surface concn. The val. 2.80 e.v. is derived for the at. work function, which in conjunction with the val. 2.43 volts for the positive-ion work function is in good agreement with the val. 2.73 volts required to close the Born cycle. L. L. B.

Scattering of a beam of potassium atoms in various gases. W. H. MAIS (Physical Rev., 1934, [ii], 45, 773—780).—The distribution of a narrow beam of neutral K atoms scattered by H_2 , He, Ne, N_2 , A, and CO₂ at low pressures was measured. The calc. effective collision radii were in good agreement with vals. based on the quantum theory of elastic sphere collisions in the case of H_2 and He, but for the other gases the experimental vals. were much larger, indicating the existence of considerable interat. forces. N. M. B.

Recording of electrons. O. GOCHE, P. MOLLET, and (MILE.) J. CUDELL (Bull. Acad. roy. Belg., 1934, [v], 20, 447—456).—A survey of methods previously described (cf. A., 1932, 799; Henriot, A., 1932, 211) and their extension with improved apparatus to slow electrons. Carr's observations (cf. A., 1931, 278) are interpreted as due, not to a gaseous surface film, but to the deposition of atoms formed by ionisation due to the electron beam. N. M. B.

Behaviour of electrons in nitric oxide. V. A. BAILEY and J. M. SOMERVILLE (Phil. Mag., 1934, [vii], 17, 1169—1176; cf. A., 1930, 1081; 1932, 559; 1933, 109).—The relationships between the mean free path, probability of attachment, and the fractional energy loss of an electron on collision with NO (λ) indicate that an electron is more likely to remain attached the further it penetrates into the mol. The attachment of electrons is also influenced by the magnetic properties of the mol. The peak of the λ -u (electron velocity) curve corresponds with the first harmonic vibration absorption band, not, as with other gases, with the fundamental band. J. W. S.

Excitation of neon by electron impact. J. E. TAYLOR, R. WHIDDINGTON, and E. G. WOODROOFE (Proc. Leeds Phil. Soc., 1934, 2, 534—535).—Electrons of 120 e.v. are passed through Ne at a pressure of 0.01 mm. and the resulting beam is analysed with a magnetic field and spectroscopically. Three energy losses correspond with 16.76 ± 0.02 , 19.98 ± 0.04 , and 18.63 ± 0.04 volts with relative probabilities 16, 5, and 4, respectively, as indicated by the intensity of the spectrum. The normal state is $1s^22s^22p^6$, and the various excited states are shown. W. R. A.

Excitation of the nitrogen molecule by electron impact. J. E. ROBERTS (Proc. Leeds Phil. Soc., 1934, 2, 536—543).—Consideration of the excitation of diat. mols. by electrons from normal to higher electronic states raises two questions : (a) the most probable energy loss of the exciting electron and (b) the probability of excitation of vibrational levels near the most probable level. The $X \rightarrow a$ transition in N_2 is fully discussed. Potential energy curves are obtained from spectroscopic data and the Morse formula, W. R. A.

Least excitation potential of the nitrogen molecule. H. MAIER-LEIBNITZ and H. SPONER (Z. Physik, 1934, 89, 431-436).—Electron collision measurements give crit. potentials at 6.7, 7.2, and 8.0 volts. A. B. D. C. Positive electrons : focussing of beams, measurement of charge-mass ratio, absorption, and conversion into light. J. THIBAUD (Physical Rev., 1934, [ii], 45, 781—787).—The "trochoid" method of concentrating and focussing weak electron beams to form sharp lines on a photographic plate, and the determination of e/m from the displacement of the beam by an imposed field, are described. The method is applied to the absorption of positive and negative electrons produced by γ -rays incident on Pb. Above a crit. thickness of absorber an imprint attributed to secondary X-rays or to the merging of positive and negative electrons and their conversion into photons is observed. Evidence of positive electrons proceeding directly from radioactive substances was found.

N. M. B.

Photo-electric creation of positive and negative electrons. Y. NISHINA, S. TOMONAGA, and S. SAKATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 1—5, and Japan. J. Physics, 1934, 9, 21).— Mathematical. Calc. probability of the photo-electric creation of pair electrons agrees with that of Heitler (cf. this vol., 1927), but differs from the result of Oppenheimer (cf. Physical Rev., 1933, [ii], 44, 53).

N. M. B. Scattering of electrons in ionising collisions with gas atoms. C. B. O. MOHR and F. H. NICOLL (Proc. Roy. Soc., 1934, A, 144, 596–608).—Measurements have been made of the angular distribution of electrons which have lost different amounts of energy over and above that required for ionisation, in H₂, He, N₂, CH₄, Ne, A, and Hg vapour. Curves are given for several incident energies < 300 volts. L. B.

Zero-angle energy losses in helium. R. L. WOMER (Physical Rev., 1934, [ii], 45, 689–693).— Using an electrostatic analyser for inelastic electron scattering at angle 0° and below 100 volts, four energy losses corresponding with transitions $1^{1}S$ — $2^{1}P$, $1^{1}S$ — $3^{1}P$, $1^{1}S$ — $2^{1}S$, and $1^{1}S$ — $2^{3}S$ have been identified and investigated. N. M. B.

Energy spectrum of positive electrons from aluminium. L. MEITNER (Naturwiss., 1934, 22, 388—390).—The energy distribution of positive electrons emitted in the transmutation ${}_{13}\text{Al}{}^{27}+{}_{2}a^{4}\longrightarrow$ ${}_{15}\text{P}{}^{30}+n, {}_{15}\text{P}{}^{30}\longrightarrow {}_{14}\text{Si}{}^{30}+e^{+}$, has been investigated. There is a continuous spectrum with max. frequency of occurrence at 800—1000 kv. and 1400—1500 kv. A. J. M.

Calcium isotopes and the problem of potassium. F. W. ASTON (Nature, 1934, 133, 869).— Using the purest materials the effect of K in the mass spectrum of Ca has been reduced to a negligible quantity; the line 41 disappears, and it is concluded that Ca^{41} does not exist, at least to 1 in 1000, in Ca. Mass nos. and abundances for Ca are 40, 42, 43, and 44, and 97, 0.8, 0.2, and 2.3, respectively. The mass spectra of Ca compounds from biotite used by Hevesy and from pegmatites used by Kendall are the same as that of ordinary Ca, hence the abnormal at. wts. reported (A., 1933, 658) are not due to Ca^{41} . The failure to detect Ca^{41} favours a more complex theory of the radioactive disintegration of K. L. S. T.

The new hydrogen. (LORD) RUTHERFORD (Proc. Roy. Inst., 1934, 28, 277–289).—A lecture. Determination of isotopic masses from band spectra. R. DE L. KRONIG (Physica, 1934, 1, 617– 622).—The discrepancy between Bainbridge's and Holst and Hulthen's vals. for the mass of H² (cf. A., 1932, 1185; this vol., 472) is due to the assumed identity of the potential energy curves of the two isotopes of H. H. J. E.

Radioactive recoils by the Wilson apparatus. F. JOLIOT (J. Phys. Radium, 1934, [vii], 5, 219-224). --Using a new variable-pressure expansion apparatus the individual disintegration of radioactive atoms was observed and trajections of recoils were measured. Anomalous collisions of recoil particles undergoing deviation exceeding that due to an elastic collision were found; the recoil particle appears to be activated at the moment of disintegration and gives up its activation energy as kinetic energy following an at. collision. N. M. B.

Distribution of Th-C" in thallium salt solutions. I. J. ZIEKLER (Z. Physik, 1934, 89, 439–442).— The distribution coeff. is given for active TlNO₃ and the non-active sulphate, and for active Tl₂SO₄ and the non-active perchlorate. The free interchange of the metal atom and the corresponding acid radicals was determined for Tl² compounds in aq. solutions.

A. B. D. C.

Transmutation of hydrogen into neutron. D. D. IVANENKO (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 155-157).—Theoretical. W. R. A.

Ionisation by z-particles in gaseous mixtures. G. GLOCKLEE and R. LIVINGSTON (J. Physical Chem., 1934, 38, 655-661; cf. A., 1932, 671).-Range, stopping power, total ionisation relative to air, and the mol. ionisation are calc. for z-particles from Rn in spherical vessels. F. L. U.

Theory of 5-radiation. G. BECK and K. SFITE (Z. Physik, 1934, 89, 259-260).—Polemical, against Fermi (this vol., 579). A. B. D. C.

Transmutation effects observed with heavy hydrogen. M. L. E. OLIPHANT, P. HARTECK, and (LOED) RUTHERFORD (Proc. Roy. Soc., 1934, A, 134, 692-703) .- Compounds containing H² when bombarded by diplons yield two groups of particles in large nos., one of protons of 14-3 cm. range and one of singlycharged particles of 1-6 cm. range. The two groups contain an equal no. of particles. Reasons are given for supposing that the short-range group consists of nuclei of an isotope of H of mass 3-0151, the reaction being $H_1^{i} - H_3^{i} \longrightarrow He \longrightarrow H^{1} + H^{3}$. The no. of particles emitted has been investigated as a function of the energy of the bombarding diplon, and the abs. yield for a pure diplon beam hitting a pure H² target is calc. to be about 1 in 10⁶ at 10⁵ volts. In the same bombardment neutrons are observed in large nos. Their energy is about 2×10^6 e.v., and they may arise from another method of disintegration of the unstable form of the He nucleus formed initially by the union of two diplons. This consists in the expulsion of a neutron and a He isotope of mass 3 in opposite directions $(H_{i}^{z} - H_{i}^{z} \longrightarrow He \longrightarrow He^{3} + {}_{0}n^{1}).$ L. L. B.

Experiments with high-velocity positive ions. III. Disintegration of lithium, boron, and carbon by heavy hydrogen ions. J. D. COCKCEPOFT

and E. T. S. WALTON (Proc. Roy. Soc., 1934, A, 144, 704-720).-The disintegration of Li, B, and C, when bombarded by fast ions of H2, has been examined. Li gives a group of protons of 30.5 cm. range, interpreted as due to the transmutation of Li⁶ to Li⁷. B gives proton groups of ranges 92, 58, and 31 cm., together with a continuous distribution of a-particles with ranges up to 15 cm. C gives a proton group of range 14 cm., probably due to the transformation of C12 into C¹³. The emission of long-range protons always appears to be connected with the change of one isotope of an element into its next heavier isotope, the neutron being captured and the proton ejected. The emission of a 14-cm. group of protons from the heavier elements studied (Cu, Fe, Ag, W) is probably due to C atoms present on the surface as a thin film of grease. A smaller no. of 15-cm. protons are emitted from the heavy elements due to the disintegration of H² adsorbed on the surface. L. L. B.

New type of artificial β -radioactivity. A. J. ALICHANOW, A. J. ALICHANIAN, and B. S. DZELEPOW (Nature, 1934, 133, 871–872).—The bombardment of Mg by α -rays of 6.3 cm. range from Ra-C' produces about four times as many negative (I) as positive electrons. The half-period of (I) is approx. 3 min. and the limit of their continuous spectrum is $> 2 \times 10^6$ e.v. The probable reactions for (I) are (i) ${}_{12}Mg^{25}+{}_{2}He^4 \longrightarrow$ ${}_{13}Al^{23}+{}_{1}H^1$; ${}_{13}Al^{23} \longrightarrow {}_{14}Si^{28}+e^-$ or (ii) ${}_{12}Mg^{26}+{}_{2}He^4 \longrightarrow {}_{13}Al^{29}+{}_{1}H^1$; ${}_{13}Al^{29} \longrightarrow {}_{14}Si^{29}+e^-$. L. S. T.

Radioelements created by bombardment by neutrons. New types of radioactivity. (MME.) I. CURIE, F. JOLIOT, and P. PREISWERK (Compt. rend., 1934, 198, 2089-2091; cf. this vol., 234, 470).-Radioelements were obtained by irradiation of Ag, Si, Zn, I, and Fe with neutrons (n) of high energy, the results confirming Fermi's observations (this vol., 714). The approx. identical decay periods (2-3 min.) and identical max. 3-ray energies $(2.3 \times 10^6 \text{ e.v.})$ given by the products of Mg- α -rays, Si-n, and P-n suggest that 13Al23 is formed in all three cases. Secondary electrons with energies $> 5 \times 10^6$ e.v. were produced, probably from y-rays, during decay of irradiated Si and P, indicating the transmutations : ${}_{13}Al^{28} = {}_{14}Sl^{28} + {}_{5} + h_{2}$ and ${}_{14}Sl^{31} = {}_{15}P^{31} + {}_{5} + h_{2}$. Hence ${}_{13}Al^{28} = {}_{13}Al^{27} - {}_{0}n^{1}$ and ${}_{14}Sl^{31} = {}_{14}Sl^{30} + {}_{0}n^{1}$ should be possible; the emission of *n* from irradiated P was confirmed. S and P also produced positrons possibly by material-isation of photons. The transition ${}_{15}P^{31}+{}_{0}n^{1}=$ $_{16}S^{31}$ \div $_{1}H^1$ is also suggested, $_{16}S^{31}$ then emitting positrons. The production of negative protons may explain Fermi's reported element of at. no. 93.

B. W. B.

Artificial disintegration. D. VAN DEB VEEN (Chem. Weekblad, 1934, 31, 383-388).—A review, with a full bibliography. H. F. G.

Spontaneous emission of neutrons by artificially-produced radioactive bodies. M. Gold-HABER (Nature, 1934, 134, 25).—Theoretical. L. S. T.

Possible production of elements of atomic number higher than 92. E. FERMI (Nature, 1934, 133, 898-899).—Th and U are strongly activated by neutron bombardment. Th activity shows at least two periods, whilst for U the periods are approx. 10 sec., 40 sec., 13 min., and at least two more periods from 40 min. to 1 day. It is difficult to establish whether the periods represent successive or alternative processes of disintegration. The 13-min. activity is copptd. with MnO_2 after addition of a Mn salt to the irradiated U solution. It is apparently not due to isotopes of U, Pd, Th, Ac, Ra, Bi, or Pb; it may be an element of at. no. > 92. L.S.T.

Relations involved in the disintegration of atoms by "non-capture" collisions. W. D. HARKINS and D. M. GANS (J. Amer. Chem. Soc., 1934, 56, 1420—1421).—The equations developed show that the disintegration of N nuclei by neutrons (I) involves the capture of (I). It appears that up to the present there is no authentic case of disintegration by collision without capture of the projectile. J. G. A. G.

Disintegration of α -particle. K. C. KAR and A. GANGULI (Current Sci., 1934, 2, 387; cf. this vol., 5).—A note. L. S. T.

Theory of β -disintegration. G. GAMOW (Physikal. Z., 1934, 35, 533—542).—A review of work up to May 20, 1934.

Nuclear changes in the atoms of radioactive substances. H. J. WALKE (Phil. Mag., 1934, [vii], 17, 1176—1189; cf. A., 1933, 550).—The theory of Landé is extended to radioactive nuclei, which according to this view may contain neutrons, a proton, and α -particles, but no free electrons. Instability in the nucleus appears to be favoured by the presence of a proton, or of an odd no. of neutrons. J. W. S.

Production of showers by cosmic radiation. C. W. GILBERT (Proc. Roy. Soc., 1934, A, 144, 559— 573).—The frequency of showers produced in Pb by the passage of cosmic radiation is proportional to the general cosmic radiation. Three types of radiation are needed to explain the experimental results: a primary radiation, a shower-producing radiation, and the shower particles. L. L. B.

Active nitrogen and the auroral spectrum. J. KAPLAN (Physical Rev., 1934, [ii], 46, 671-674).— A detailed account of work already noted (cf. this vol., 339, 823). N. M. B.

Excitation energy of metastable nitrogen. W. WEIZEL and H. FISCHER (Z. Physik, 1934, 89, 283– 285).—Dispersion measurements give this energy for the ${}^{3}\Sigma$ term as $6 \cdot 1 \pm 0 \cdot 5$ volts. A. B. D. C.

Negative nuclear spins and a proposed negative proton. S. TOLANSKY (Nature, 1934, 134, 26).—The negative and positive nuclear spins of odd at. wt. atoms with even at. charges can be accounted for by postulating the existence of two types of nuclear neutrons: (i) proton+electron and (ii) negative proton+positron (cf. this vol., 826). L. S. T.

Exchange forces between neutrons and protons and Fermi's theory. I. TAMM (Nature, 1934, 133, 981).—Theoretical. Either Fermi's theory requires modification, or the origin of the forces between neutrons and protons does not lie in their transmutation considered in detail by Fermi. L. S. T. Interaction of neutrons and protons. D. IWANENKO (Nature, 1934, 133, 981-982).—A discussion (cf. preceding abstract). L. S. T.

Neutrino hypothesis. E. FERMI (Z. Physik, 1934, 89, 522).—Polemical, against Beck and Sitte (this vol., 826). A. B. D. C.

Asymmetry of positive and negative β -spectra and the intrinsic mass of the neutrino or ergon. F. PERRIN (Compt. rend., 1934, 198, 2086–2088; cf. this vol., 127).—The ascription of zero mass to the neutrino is not invalidated by a consideration of nuclear field action during electron expulsion.

B. W. B. Quantum theory of the neutron. G. TEMPLE (Proc. Roy. Soc., 1934, A, 145, 344-358).—A theory of the neutron is developed from Dirac's wave equation without the use of any special assumptions. The second-order wave equation for the H atom is shown to possess two sets of solutions H and N, distinguished by their behaviour as $r \longrightarrow 0$ (r being the distance of the electron from the proton). The H-solutions are the accepted wave functions of the H atom, the N-solutions those of the neutron.

L. L. B. Electron theory of metals. S. SCHUBIN and S. WONSOWSKY (Proc. Roy. Soc., 1934, A, 145, 159– 180).—A modification of the Heisenberg scheme is worked out, which allows the electric and magnetic properties of metals to be treated simultaneously. L. L. B.

Numerical solution of Schrödinger's equation. G. E. KIMBALL and G. H. SHORTLEY (Physical Rev., 1934, [ii], 45, 815—820).—Mathematical. Solutions may be approximated to any desired accuracy by a difference equation over a lattice covering the region of integration. N. M. B.

Nuclear structure, γ -ray fission, and the expanding universe. A. C. BANERJI (Nature, 1934, 133, 984).—A discussion. L. S. T.

Atomic theory. J. TUTIN (Nature, 1934, 134, 23-24).—A reply to criticism. L. S. T.

Atomic theory. R. H. FOWLER (Nature, 1934, 134, 24-25).—Further criticism (cf. preceding abstract). L. S. T.

Equation of the photon. K. NIKOLSKY (Compt. rend., 1934, 198, 1901—1902). B. W. B.

Molecules in the sun and stars. H. N. RUSSELL (Astrophys. J., 1934, 79, 317-342).—Mol. consts. derived mainly from band spectra have been collected for about thirty diat. mols. likely to occur in the sun and stars, and the dissociation consts. calc.

L. S. T. Addition theorem for spherical harmonics and its application to space quantisation of atoms. H. HONL (Z. Physik, 1934, 89, 244-253).

A. B. D. C. Grating images. K. STEEHL (Z. Physik, 1934, 89, 254—255).—Theoretical. A. B. D. C.

Factor 137 136 in quantum theory. (SIR) A. S. EDDINGTON (Nature, 1934, 133, 907). L. S. T.

Theory of the elementary particle. I. TAMM (Compt. rend. Acad. Sci., U.R.S.S., 1934, 2, 151155).—The val. of the magnetic spin moment of a proton in nuclear magnetons is discussed. W. R. A.

Magnetic moment of the deuton. I. ESTER-MANN and O. STERN (Nature, 1934, 133, 911).—The val. obtained is 0.7 nuclear magneton (cf. A., 1933, 1226). L. S. T.

Electronic energy bands in metals. J. C. SLATER (Physical Rev., 1934, [ii], 45, 794-801).--Mathematical. The method of Wigner and Seitz (cf. A., 1933, 660) is extended to the computation of the excited bands of electrons in a metal. N. M. B.

General and simple relation of molecular spectra to the electrons and electronic shells of the constituent atoms. H. DESLANDRES (Compt. rend., 1934, 198, 2037—2041; cf. A., 1932, 791).— Conditions of electronic excitation of NaCl, NO, and CH_4 are deduced from their spectra (I). A general relationship exists between frequencies (II) of band heads of visible and ultra-violet electronic (I) and (II) of infra-red bands. B. W. B.

Absorption of oxygen between 7000 and 3000 Å. L. HERMAN (Compt. rend., 1934, 198, 2154-2156).—Absorption spectra of O_2 in a tube 100 m. long, at pressures up to 13 kg. per sq. em., and of the setting sun, confirmed Janssen's observations (A., 1886, 749) and revealed new bands. B. W. B.

Atmospheric ozone absorption in the visible spectrum. O. R. WULF, A. F. MOORE, and E. H. MELVIN (Astrophys. J., 1934, **79**, 270–272).

L. S. T.

Angström bands of CO. D. COSTER and F. BRONS (Physica, 1934, 1, 634—648; cf. this vol., 237). —Perturbations in the vibrational levels v=0, 1, 2, 3, and 4 of the final $A^{1}\Pi$ state have been classified. The most probable dissociation energy of CO is 8.41 e.v. H. J. E.

Afterglow of carbon dioxide. A. G. GAYDON (Nature, 1934, 133, 984—985; cf. this vol., 8).— Further details of the spectrum of the afterglow produced by a modified method at higher pressures are given. L. S. T.

Band spectrum of aluminium chloride. B. N. BHADURI and A. FOWLER (Proc. Roy. Soc., 1934, A, 145, 321-336).—A band system extending from 2555 to 2810 Å., with its greatest intensity at 2610 Å., has been observed with high dispersion in vac. tubes containing AlCl vapour. Most of the bands are degraded towards the red, but there are two strong short sequences of bands of the same system which are shaded in the opposite direction. The main bands due to the mols. AlCl³⁵ are associated with bands due to AlCl³⁷. L. B.

Absorption spectrum of SCl₂. R. K. ASUNDI and R. SAMUEL (Current Sci., 1934, 2, 433—434).— The spectrum of SCl₂ vapour shows continuous absorption at approx. 4100 Å., a band system between 3400 and 2750 Å., and continuous absorption again between 2600 and 2400 Å., and from 2280 Å. onwards. L. S. T.

Band systems of CdF. R. K. ASUNDI, R. SAMUEL, and M. Z. UDDIN (Current Sci., 1934, 2, 429-430).— The arc spectrum of CdF shows a yellowish-green band system between 5300 and 5550 Å. and an orange system between 6025 and 6300 Å. L. S. T.

New band system of tin oxide. F. W. LOOMIS and T. F. WATSON (Physical Rev., 1934, [ii], 45, 805— 806).—Frequency and intensity data for a new band system of SnO in the region 2400—3100 Å. are tabulated. N. M. B.

Absorption spectrum of mercuric sulphide. T. IREDALE and K. E. GIBSON (Nature, 1934, 133, 985).—Evidence only of Hg vapour and of S_2 and, at higher pressures, S_8 has been obtained (cf. this vol., 237). L. S. T.

Ultra-violet absorption of heavy water vapour. J. FRANCK and R. W. WOOD (Physical Rev., 1934, [ii], 45, 667—668).—A comparison of the absorption spectrum of normal and heavy H_2O down to 1450 Å. shows that the long wave-length limit of the continuous absorption band is shifted towards shorter wave-lengths in the case of H_2^3O . N. M. B.

Absorption spectra of some polyatomic molecules containing methyl and ethyl radicals. H. W. THOMPSON (J.C.S., 1934, 790-797).—The absorption spectrum of ZnMe₂ is continuous (threshold at about 2600 Å.). That of ZnEt₂ is continuous below about 2800 Å. with four pairs of superposed diffuse bands between 2396.5 and 2216 Å. PbEt₄ gave a system of seven groups of sharp bands, degraded to the red, between 2700 and 2200 Å. without an overlapping continuum. H. J. E.

Auxochrome action. V. Action of the NH_2 group. VI. Of the OH and OMe groups. VII. Di-derivatives. M. HORIO (J. Soc. Chem. Ind. Japan, 1934, 37, 284—285B, 285B, 285—288B).—V. 313 bands and lines have been observed in the ultraviolet vapour spectrum of NH_2Ph . The NH_2 group has a powerful effect, vals. for the electron displacement and energy of activation being much < for C_6H_6 .

VI. The spectra of PhOH and PhOMe are similar to the above; the OH and OMe groups exert practically the same effect as NH_2 on the nuclear electrons.

VII. In the series for o-, m-, and p-C₆H₄Me·NH₂, the o- and m- are similar to NH₂Ph, but marked differences occur with p-C₆H₄Me·NH₂. Analogous results are obtained with the anisidines. S. C.

Absorption spectra of aldehydes. C. P. SNOW and E. EASTWOOD (Nature, 1934, 133, 908—909).— The ultra-violet absorption bands of a homologous series of aldehydes show vibrational structure probably due to a nuclear vibration $\underset{H}{\mathbb{R}}C \rightarrow \leftarrow O$. Max. absorption is approx. const. at about 2900 Å. or 34,500 cm.⁻¹ The absorption spectrum of acraldehyde shows several bands having a fine structure equal to those of the diat. gases in simplicity and sharpness. L. S. T.

Optical absorption and fluorescence of benzene vapour in the ultra-violet. F. ALMASY and C. V. SHAPIRO (Z. physikal. Chem., 1934, **B**, 25, 391–398). —The fluorescence spectrum and the long-wave part of the absorption spectrum coincide almost completely over the range 37,486–35,349 cm.⁻¹ R. C. Spectrographic study of phloridzin and its derivatives. Ultra-violet spectra of phloretin, phlorin, and phloroglucinol. A. LAMBRECHTS (Compt. rend., 1934, 198, 1852–1854; cf. A., 1933, 336).—Absorption band max. were determined in EtOH (I) and in aq. solutions (II) of varied $p_{\rm II}$. All the above compounds assumed keto-structures in (I) and showed reversible keto-enol tautomerism in (II). Tautomerism was most marked in phloroglucinol.

B. W. B.

Infra-red absorption of water from 2.5μ to 6.5μ . E. K. PLYLER and C. J. CRAVEN (J. Chem. Physics, 1934, 2, 303-305).—New bands for liquid H₂O were observed at 3.30, 5.56, and 5.83 μ . The band at 4.7μ contains several components. The position of max. absorption at about 3μ changes with the cell thickness, due to differences in sharpness of the band components. The 6.15μ band shows no such shift. H. J. E.

Infra-red absorption of acid solutions. E. K. PLYLER and E. S. BARR (J. Chem. Physics, 1934, 2, 306—310).—Measurements were made on aq. HCl, HF, HBr, H_2SO_4 , HNO₃, NaCl, and NaBr between 1·7 and 6·5 μ , and for aq. HCO₂H and BzOH between 5 and 6·5 μ . No bands were found for HCl and HBr at 3·5 μ and 3·8 μ , respectively, where there is strong absorption by gaseous HCl and HBr. For all the acid solutions a band was observed at about 5·5 μ , attributed to vibration of the acid mol. as a whole against the H₂O mol. through the acid H. A new band observed at 2·40 μ may be due to the same cause, or to H^{*} attached to H₂O. H. J. E.

Photography of the second overtone of HCl at 1.19 μ under high dispersion. G. HERZBERG and J. W. T. SPINKS (Z. Physik, 1934, 89, 474–479).— Mol. consts. are deduced, and the isotope displacement agrees very well with the mass defect val.

A. B. D. C.

Nuclear vibrations of solid and liquid hydrogen chloride between 20° and 160° abs. G. HETTNER (Z. Physik, 1934, 89, 234—243).—The 3.7μ band is single in the liquid and β -solid form, but shows two max. 50 cm.⁻¹ apart in the α -form; the transition occurs near 38° abs. The α -form has a dielectric const. of 4.7, the β -form one of 14.6. At lower temp. the double band becomes very unsymmetrical.

A. B. D. C.

Broadening by collision damping of rotationvibration lines of hydrogen chloride by foreign gases. W. GRASSE (Z. Physik, 1934, 89, 261–272). —Observations on the increase of absorption max. of the HCl 3.46μ band are used to deduce effective radii of foreign gases; they are for He, H₂, A, N₂, and CO₂ 2.25, 2.97, 5.37, 6.68, and 10.15 Å., respectively. A. B. D. C.

Structure of the molecule of nitrogen dioxide from a study of its infra-red absorption spectrum. G. B. B. M. SUTHERLAND (Proc. Roy. Soc., 1934, A, 145, 278—287; cf. A., 1933, 1102).—The infra-red absorption spectrum of NO₂ has been studied under high dispersion. Analysis of the data shows that the form of the mol. is triangular. The most probable vals. for the fundamental frequencies are 641, 1373, and 1615 cm.⁻¹ The ONO angle lies between 55° and 58°. L. L. B.

Investigations in the infra-red region of the spectrum. X. Asymmetrical molecule nitrosyl chloride. C. R. BAILEY and A. B. D. CASSIE (Proc. Roy. Soc., 1934, A, 145, 336—344).—Five bands have been isolated in the infra-red absorption spectrum of NOCl between 4 and 16 μ . Owing to the asymmetry of the mol., no resolution was obtained. The mol. has a vertical angle of 140°, and falls into the SO₂ class. L. L. B.

Bands of "heavy" acetylene in the near infrared. G. HERZBERG, F. PATAT, and J. W. T. SPINKS (Nature, 1934, 133, 951).—The infra-red spectrum of C_2H_2 prepared from CaC₂ and 93% H²₂O shows four bands belonging to C_2HH^2 , but none due to $C_2H_2^2$. The moment of inertia of C_2HH^2 in its lowest state is 27.90×10^{-40} g.-cm.² The C-C and C-H distances are 1.205 and 1.062 Å., respectively.

Vibration spectra and structure of polyatomic molecules. R. TITÉICA (Ann. Physique, 1934, [xi], 1, 533—621; cf. A., 1933, 337).—Data for infra-red and Raman spectra of the following substances in the gaseous form are tabulated : CH_2O , $COMe_2$, $COEt_2$, COMeEt, HCO_2Me , HCO_2Et , HCO_2Bu^3 , HCO_2Bu^β , isoamyl formate, MeOAc, EtOAc, PrOAc, BuOAc, $EtCO_2Me$, $EtCO_2Et$, Et_2O , and EtOH. From the results obtained mol. structures, interat. distances, angles between valency directions, and moments of inertia are deduced. N. M. B.

Infra-red reflexion spectrum of silicates. C. SCHAEFER, F. MATOSSI, and K. WIRTZ (Z. Physik, 1934, 89, 210–233).—Infra-red reflexion spectra between 8 and 22 μ are given for Be₂SiO₄, troostite, topaz, cyanite, albite, andalusite, titanite, almandine, vesuvian, beryl, aquamarine, heulandite, bronzite, diopside, hornblende, muscovite, klinochlore, apophyllite, and adularia. Two bands, one between 8 and 12 μ and the other between 17 and 20 μ , are ascribed to the SiO₄ group. A. B. D. C.

Normal modes and frequencies of vibration of the regular plane hexagon model of the benzene molecule. E. B. WILSON, jun. (Physical Rev., 1934, [ii], 45, 706—714).—Mathematical. The 30 modes of vibration of the C_6H_6 hexagon are derived by Wigner's group theory method. From these the 20 vibration frequencies are calc. Selection rules for the Raman and infra-red spectra are listed.

N. M. B.

Raman effect for water in different states. I. R. RAO (Phil. Mag., 1934, [vii], 17, 1113—1134).—The infra-red absorption frequencies of the H₂O mol. are discussed with reference to the shape and dimensions of the mol. In the Raman spectra of H₂O in different states there is only one band at 3μ , whilst there are two, at 2.66 and 6.26 μ , in the infra-red absorption spectra. Variations of Raman frequencies in different states are ascribed to mol. association. J. W. S.

Modified scattering by crystalline HCl and HBr. D. CALLIHAN and E. O. SALANT (J. Chem. Physics, 1934, 2, 317—319).—HCl and HBr at just below the f.p. gave Raman lines 2784, 2480 cm.⁻¹,

L. S. T.

respectively. The difference between these vals. and those for the gases is too large to be due entirely to Lorentz-Lorenz forces. The cryst. structure is non-ionic. H. J. E.

Raman spectra and molecular constants of the hexafluorides of sulphur, selenium, and tellurium. D. M. Yost, C. C. STEFFENS, and S. T. GROSS (J. Chem. Physics, 1934, 2, 311–316; cf. A., 1933, 466).—For liquid SF₆, SeF₆, and TeF₆ three Raman lines were observed in each case. For gaseous TeF₆ there were three, and for gaseous SF₆ and SeF₆ one. The no. of lines indicates regular octahedral mols. The frequencies were assigned to their modes of vibration. The free energy of formation of SF₆ (gas) at 25° is -238,000 g.-cal. H. J. E.

Valency angle of oxygen in methyl ether and ethylene oxide. N. G. PAI (Current Sci., 1934, 2, 386—387).—The valency angles in Me_2O and $(CH_2)_2O$ calc. from Raman frequencies are 102° and 64° , respectively. The smaller val. is due to the C·C linking. The permanent dipole moments of these two compounds support these vals. L. S. T.

Raman spectrum of ethyl alcohol. G. BOLLA (Z. Physik, 1934, 89, 513-521).—Raman displacements are bands of half width from 15 to 45 cm.⁻¹ which show no fine structure with resolution of 1.4 cm.⁻¹ A band at 3360 cm.⁻¹ of half width 240 cm.⁻¹ is ascribed to the OH group. A. B. D. C.

Raman effect in di-iodoacetylene. G. GLOCKLER and C. MORRELL (J. Chem. Physics, 1934, 2, 349; cf. A., 1933, 1229).—Frequency shifts of 191, 310, 627, 688, and 2109 cm.⁻¹ were observed. That due to the C–I vibration (627 cm.⁻¹) is about 100 cm.⁻¹ > in the I-compounds of saturated hydrocarbons. The 2109 cm.⁻¹ frequency shift indicates an acetylenic structure. H. J. E.

Raman spectra of benzene and hydrogen iodide in the liquid and solid state. H. EFSTEIN and W. STEINER (Nature, 1934, 133, 910–911).— With C_6H_6 , there is a small decrease in wave nos. in passing from the liquid to the solid state. The decreases in wave no. for HI in passing from the gaseous to the liquid and to the solid states are recorded. Liquid HI has a diffuse Raman line of complex structure. L. S. T.

Raman spectrum of thiophen, furan, and derivatives. G. B. BONINO and R. MANZONI-ANSIDER (Z. physikal. Chem., 1934, B, 25, 327-347).—Raman spectra show that in thiophen, pyrrole, and furan there is only a plane of symmetry, or a binary axis of symmetry, olefinic C:C linkings are absent, and there are oscillations of the C·H linkings similar to those of C_6H_6 . Electronic formulæ which agree with all the physical and chemical properties of these substances are proposed (cf. A., 1933, 886). There is resonance between an aromatic configuration and a configuration with ordinary double linkings.

R. C. Raman spectrum of some pyrrole derivatives. II. G. B. BONINO, R. MANZONI-ANSIDEI, and P. PRATESI (Z. physikal. Chem., 1934, B, 25, 348— 362; cf. A., 1933, 886).—The spectra of various derivatives are discussed in relation to structural problems. R. C.

Raman spectra of double linkings conjugated in a nucleus. R. TRUCHET and J. CHAPRON (Compt. rend., 1934, **198**, 1934—1936).—*cyclo*Pentadiene and dicyclopentadiene were examined. Both include a strong line in the region 1400—1500 Å. attributed to C:C in the conjugated system. Similar lines are given by pyrrole and thiophen (Venkateswaran, A., 1930, 1345) and furan (Bonino, see above). Bonino's objection to the Kekulé formula for C_6H_6 (*loc. cit.*) is therefore overruled. B. W. B.

Scattering of light by binary mixtures in the neighbourhood of the critical point of complete miscibility : measurement of depolarisation factor. A. ROUSSET (Compt. rend., 1934, **198**, 2152–2154).—Depolarisation factors of $H_2O-Bu^{\beta}CO_2H$ and C_6H_{14} -PhNO₂ mixtures were measured and did not support Rocard's theory (A., 1928, 1310). It is suggested that superposed primary and secondary scattering is involved, completely and partly depolarised, respectively. B. W. B.

Rayleigh's law of scattering in the infra-red. A. H. PFUND (J. Opt. Soc. Amer., 1934, 24, 143— 146).—Transmission measurements on transparent particles of ZnO and MgO dispersed in rubber show that Rayleigh's law is obeyed for the smallest particles of 0.088μ diameter, but not for larger particles. The effect of varying *n* of the surrounding medium agrees qualitatively with Rayleigh's formula. N. M. B.

Colour and crystal structure of precipitated cadmium sulphide. W. O. MILLIGAN (J. Physical Chem., 1934, 38, 797—800).—It is inferred from Xray measurements that cubic β -CdS or hexagonal α -CdS may each be yellow or red, depending on the conditions of pptn. The differences in colour are attributed to differences in particle size and nature of surface. All dry samples become orange on grinding. CdSO₄ and hot, acid Cd(NO₃)₂ give β -CdS; CdCl₂, CdBr₂, and CdI₂ give mainly α -CdS. The lattice consts. agree with those of Ulrich and Zachariasen (A., 1926, 664). R. S. B.

Fluorescence of some pure substances. E. CANALS and P. PEYROT (Compt. rend., 1934, 198, 1992—1994).—The ratios of fluorescence intensity to mol. scattering were determined for H_2O and several org. liquids. Fluorescence was shown by H_2O (feeble), by all O-compounds (cf. A., 1925, ii, 1030), by cyclanes, cyclenes, and their derivatives, but not by all hydrocarbons. Intensities of fluorescence relative to H_2O are given in some cases (cf. this vol., 346).

B. W. B.

Relationships between absorption and luminescence spectra in concentrated solutions of dyes. V. L. LEVSCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 405-410; cf. A., 1931, 1351, 1353).—The mirror image correspondence between the absorption and luminescence spectra of rhodamine 6G solutions disappears at higher concn. when the increase in concn. is accompanied by a diminution in intensity of the luminescence. The symmetry tends to reappear, however, with rise of temp. The results are explained by the association of the dye mols., and can be used to calculate the degree of association. J. W. S.

Electrical breakdown in liquids from negative to high positive pressures. W. FERRANT (Z. Physik, 1934, 89, 317—356).—Measurements up to 70 atm. show three regions : that of low pressure where breakdown potential is independent of pressure, that of 2—4 atm. where the pressure coeff. is high, and that above 15 atm. Breakdown potential under the v.p. alone is independent of temp. Examples discussed are oil and hexanc. A. B. D. C.

Role of the unidirectional layer in rectification and in photo-electric phenomena. W. C. VAN GEEL (Physica, 1934, 1, 531-542).—Theoretical.

H. J. E. Anomalous electrical conductivity of thin metals. H. MURMANN (Z. Physik, 1934, 89, 426— 430).—Optical transmission of the 404.7 mµ Hg line shows that anomalous electrical conductivity of very thin metal foils is not due to poor contact between neighbouring mol. groups. A. B. D. C.

Anomalous behaviour of dielectric liquids. W. JACKSON (J. Inst. Electr. Eng., 1934, 75, 93—110).— A résumé of recent work.

Dipole moments and physico-chemical propreties. II. A. E. VAN ARKEL (Chem. Weekblad, 1934, 31, 264—267, 342—344).—A review, dealing especially with hydrate formation, the interaction of dipoles and ions, association of mols. in solution, and the formation of compounds such as polyiodides.

H. F. G.

Dielectric constant of nitrogen up to 1000 atm. between 25° and 150°. A. MICHELS, A. JASPERS, and P. SANDERS (Physica, 1934, 1, 627-633; cf. A., 1932, 793).—Data are tabulated. No deviation from the Clausius-Mosotti relation was found. H. J. E.

Polarity of nitrogen tetroxide and nitrogen dioxide molecules. J. W. WILLIAMS, C. H. SCHWINGEL, and C. H. WINNING (J. Amer. Chem. Soc., 1934, 56, 1427—1428).—The dielectric const. and d of equilibrium mixtures of N₂O₄ and NO₂ have been determined between 25° and 125°. In agreement with Zahn (A., 1933, 663) the dipole moment, μ , of NO₂ decreases with rise of temp., but contrary to Zahn, μ of N₂O₄ is approx. zero, since the mol. polarisation is independent of temp. and has a val. close to that required by the optical data of Cuthbertson (A., 1913, ii, 993). J. G. A. G.

Reactions relating to carbohydrates and polysaccharides. XLVII. Oxygen valency angle and structure of glucose and related compounds. J. S. ALLEN and H. HIBBERT (J. Amer. Chem. Soc., 1934, 56, 1398—1403).—A more detailed account of work previously reviewed (A., 1932, 1190; cf. *ibid.*, 1115). The electric moment ($\times 10^{18}$) and O valency angle are : (CH₂)₂O 1·88, 70° (cf. Smyth and Walls, A., 1932, 984); propylene oxide, 1·88, 70°; (CH₂)₃O 2·01, 94°: tetrahydrofuran —, 108° (cf. *loc. cit.*); tetrahydropyran 1·87, 93°; 2-hydroxy-2-dichloromethyl-1:3-dioxolan (glycol dichloroacetate), b.p. 106°/0·08 mm. [from (CH₂)₂O and CHCl₂·CO₂H in Et₂O at 0°], 3·35, about 90°; glycol chloroacetate 3·94, —. H. B. Dipole moments of some aromatic compounds. G. M. BENNETT and S. GLASSTONE (Proc. Roy. Soc., 1934, A, 45, 71-80).—An analysis of the data for the dipole moments of *p*-substituted anisoles, phenols, Ph₂ ethers, and anilines leads to the conclusion that in all these compounds a deviation Δ from strict additivity of the linking moment occurs. The vals. of Δ , which is an additional moment operating along the axis of the C₆H₆ nucleus, are consistent with those to be expected on the basis of the electronic theory of aromatic reactivity. It is unsound to base computations of valency angles of O and S on dipole moment data. L. B.

Dipole moments of mono-substitution products of mesitylene. F. BROWN, J. M. A. DE BRUYNE, and P. GROSS (J. Amer. Chem. Soc., 1934, 56, 1291— 1293).— d^{30} and n^{30} are recorded for the F, Cl, Br, and I monosubstitution products of mesitylene. d, n, and dielectric data are recorded for C₆H₆ and CCl₄ solutions, and the dipole moments, μ , of the mesitylene derivatives are : F- 1·36, Cl- 1·55, Br- 1·52, I- 1·42, NO₂-3·64, and OH- 1·36 × 10⁻¹⁸ e.s.u. PhF has μ 1·46. In general, these data are in good agreement with calc. vals. J. G. A. G.

Dielectric properties of acetylenic compounds. III. Substituted phenylacetylenes. M. M. OTTO and H. H. WENZKE (J. Amer. Chem. Soc., 1934, 56, 1314—1315).—The dipole moments of the following substituted phenylacetylenes are : p-Cl- 0.96, p-Br-0.95, m-Cl- 1.38, m-Br- 1.35, o-Cl- 1.69, o-Br- 1.79, p-Et- 1.05, p-Me- 1.01, p-Pr^β- 1.12, and p-NO₂- 3.42× 10⁻¹⁸ e.s.u., from which, with other data, it is inferred that the moment of CPh;CH is 0.56 and is opposite in direction to that of PhMe. J. G. A. G.

Thermal and photochemical equilibria of the cis-trans-isomerides of dichloro- and dibromoethylene. [Dielectric constants.] A. R. OLSON and W. MARONEY (J. Amer. Chem. Soc., 1934, 56, 1320—1322).—The dielectric consts. of cis- and trans- $C_2H_2Cl_2$ (I) and cis- and trans- $C_2H_2Br_2$ (II) at 25° are 9:30, 2:35, 7:08, and 2:88, respectively. The heat of transition of (I) is 500 g.-cal. per mol. at 350° and that of (II) 340 at 150°. The extinction coeffs. of the vapours of (I) between 100° and 250° are recorded for the range 2302—2753 Å., and the ratio of the probability that an excited mol. will return to the transform to the probability that it will return to the cis on deactivation increases from 0:95 at 100° to 1:46 at 300°. The change of this ratio with change of temp. and wave-length is in accord with theory.

J. G. A. G.

Variations in refractive index of benzene during intensive drying. J. J. MANLEY (Rec. trav. chim., 1934, 53, 785–791; cf. A., 1932, 323).—With progressive drying of C_6H_6 by P_2O_5 over a period of 2 years *n* increases, then passes through a stage during which it decreases, and finally increases again. An explanation in terms of polymerisation is attempted. The effect of P_2O_5 on boiling C_6H_6 in a few days is equiv. to that at room temp. for several years.

E. S. H.

Rotatory dispersion measurements with phenylmethylcarbinol. W. BODENHEIMER and C. BRUHN (Z. physikal. Chem., 1934, B, 25, 319-326).— Measurements have been made at 22° with the pure and dissolved substance from 3175 to 6560 Å. The dispersion curves of the pure substance and solutions in aliphatic alcohols are similar in position, but different from those of solutions in CCl₄ and C₆H₁₄. With increasing dilution the mol. rotation increases. These results are explained by Kuhn's theory of optical activity and the assumption of solvation in dil. solutions in alcohols. R. C.

[Rotatory polarisation of] certain compounds of tartramide and of tartramic acid. Y. K. HENG (Compt. rend., 1934, 198, 1985—1987).—Aq. tartramide (I) solutions gave [α] practically independent of conen. Vals. of [α] for various substances dissolved in aq. solutions of (I) or of tartramic acid (II) indicated the formation of the *compounds* [MoO₃,2*A*](NH₄)₂ (cf. Darmois, A., 1932, i, 299); *B*,NH₄BO₂; *B*,NaBO₂; [CuO,*A*]Na₂; [CuO,2*B*]Na₂ (III) (*A*= C₄H₇O₅N, *B*=C₄H₈O₄N₂). (III) was strongly dichroic; ellipticity measurements are tabulated. Al(OH)₃ was insol. in aq. (I) and gave a lævorotatory solution in aq. (II). B. W. B.

Optical rotatory power. A. R. CHAMBERS and H. G. RULE (Nature, 1934, 133, 910).—The optical activity of *d*-pinane (I), methylmenthane, and other non-polar solutes in numerous solvents is governed chiefly by the *n* of the solvent, supporting Boys' prediction (see below). $[\alpha]_{p}$ for (I) is practically unaltered when (I) is dissolved in CCl₄, which has approx. the same *n*. L. S. T.

Optical rotatory power. I. Theoretical calculation for a molecule containing only isotropic refractive centres. II. Calculation of the rotatory power of a molecule containing four refractive radicals at the corner of an irregular tetrahedron. S. F. Boys (Proc. Roy. Soc., 1934, A, 144, 655-675, 675-692).—I. Mathematical. A formula is derived by means of which the rotatory power of a mol. can be calc. Each atom is taken as a refractive centre, and the total rotatory power is the sum of the contributions from every possible combination of four atoms.

II. The formula is applied to the simplest type of optically active mol. Vals. of $[\alpha]_D$ are calc. for C_5H_{11} ·NH₂, C_5H_{11} ·OH, sec.-NH₂Bu, and sec.-BuOH, which agree in magnitude with those experimentally determined. A formula connecting the rotatory dispersion of a compound with that of the radicals contained in it is obtained. L. L. B.

Magneto-optical properties of hydrocarbons and their mixtures. Application to their identification. M. SCHERER (Chim. et Ind., 1934, 31, Spec. No., 383—400).—The magnetic rotatory power, dispersion, magnetic bircfringence, and d of hydrocarbons from C_7H_{16} to $C_{16}H_{34}$, of the corresponding e^thylenic hydrocarbons, and of a no. of C_6H_6 , cyclohexane, and cyclohexene hydrocarbons have been measured. Similar measurements have been made on numerous natural oils and products derived from them. In certain cases the composition of a mixture may be deduced from its magneto-optical properties.

H. J. E.

Magnetic birefringence of gaseous oxygen and nitrogen and of aqueous chlorate solutions. A. COTTON and T. BELLING (Compt. rend., 1934, 198, 1889—1893; cf. this vol., 132).—The magnetic birefringences of O_2 , N_2 (both at 100 atm.), H_2O , and NaClO₄ in aq. solution were respectively -4.05×10^{-4} , -0.33×10^{-14} , -0.14×10^{-14} , and -1.6×10^{-14} (cf. Chinchalkar, A., 1932, 1190). B. W. B.

Magneto-chemistry of rhenium : metallic and septavalent rhenium. N. PERAKIS and L. CAPATOS (Compt. rend., 1934, 198, 1905—1907).—The coeff. of magnetisation, χ , of Re, Re₂O₇ (I), and the perrhenates (II) of K and NH₄ were determined. The val. for Re confirmed the previous determination (A., 1933, 340) and not that of Albrecht and Wedekind (A., 1931, 153). χ of (I) and of Re^{VII} were, respectively, -15.7×10^{-6} (per mol.) and 8.2×10^{-6} (per g.atom). In every case χ was independent of temp. (-79° to 20°). The results for (II) indicated that XReO₄ cannot represent the mol. formulæ of both perrhenates. B. W. B.

Paramagnetism. II. Origin of the term " Δ " in paramagnetic salts. S. DATTA (Phil. Mag., 1934, [vii], 17, 1160—1168; cf. this vol., 350).— The temp. variation of χ has been determined for Co" and Ni" salts as powdered crystals of anhyd., hydrated, and other complex salts, and for solutions of CoCl₂ and NiCl₂ in different solvents. The vals. of the const. Δ in the Weiss formula are less for hydrated and complex salts than for the anhyd. salts; the sign of Δ also remains const. for the same anion, but varies with the state of aggregation. For solutions of NiCl₂ and CoCl₂ in acid and in EtOH, Δ varies with temp. The high vals. found for Δ in certain states of aggregation are attributed to interchange-interaction effect between the electrons attached to the paramagnetic atom and its halogen neighbours.

J. W. S.

Paramagnetic rotatory power of dysprosium ethyl sulphate at very low temperatures. Paramagnetic saturation. J. BECQUEREL, W. J. DE HAAS, and J. VAN DEN HANDEL (Compt. rend., 1934, 198, 1849—1851).—The paramagnetic rotation of Ds(EtSO₄)₃,9H₂O was measured at 1.62° , 4.13° , 14.12° , and 20.35° abs.; it comprised two components, (a) independent of temp., and (b) a function of field strength/abs. temp. At 1.62° abs., saturation was attained in a field of 27,000 gauss. B. W. B.

Temperature and diamagnetism. I. Susceptibility of some aromatic liquids. S. S. BHAT-NAGAR, M. B. NEVGI, and M. L. KHANNA (Z. Physik, 1934, 89, 506—512),—Susceptibilities at 20° and 70° are given for C_6H_6 , PhNO₂, PhCl, PhBr, 1- $C_{10}H_7Br, C_5H_5N, NH_2Ph, PhOMe, p$ -cymene, m-cresol, m- C_6H_4 MeBr, and CH₂PhCl. A. B. D. C.

Electrostatic theory of ionic equilibria. II. Highest oxygen acids of metalloids. J. V. CHODAKOV (Z. physikal. Chem., 1934, B, 25, 372– 390).—The theory previously developed (this vol., 254) is applied. The co-ordination no. for the addition of O to the metalloids of the third and fifth groups of the periodic system is shown to be four, and for the metalloids of the seventh group six or five. Unpolymerised antimonic acid must be H_7SbO_6 , agreeing with various experimental data. Sn^{IV} hydroxide is H_8SnO_6 , the ease with which two only of the H atoms are substituted being energetic and not constitutional. From dissociation consts. the chemical radius of the radicals PO_4 , AsO_4 , and SO_4 is calc. to be ~ 3 Å., and that of IO_6 , TeO_6 , and $SbO_6 \sim 3.2$ Å. It is found empirically that the radius of an ion of the inert gas type differs from that of the atom of the same element by approx. 0.75 Å., the atom being the larger or the smaller according as the ion is positive or negative, respectively. R. C.

Relations between isosterism and chemical character of acetylene, hydrogen cyanide, and derivatives. G. BAHR (Z. physikal. Chem., 1934, 168, 363–368).—There is striking chemical similarity between C_2H_2 , HCN, and their derivatives, which is closely connected with the fact that C_2H_2 and HCN are isosteric. The CCH radical has the properties of a pseudohalogen. R. C.

Structures of the metallic carbonyl and nitrosyl compounds. N. V. SIDGWICK and R. W. BALLEY (Proc. Roy. Soc., 1934, A, 144, 521—537).—For all carbonyls $M_x(CO)_y$, if *m* is the at. no. of M, *b* that of the neutral inert gas, then b - [(xm+2y)/x] = x-1. When x=1, M has effective at. no. of inert gas. Assuming that this is true when x > 1, M atoms must

be held together thus: M·C:O·M. Every M atom in the mol. is joined to every other through a linking of this kind. If the mol. contains 2M this is secured by joining them through a single CO; for 3, by placing them at the angular points of a triangle with a CO on each side; for 4, by placing them at those of a tetrahedron with a CO group on each edge. The crystal structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are compatible with this. Nearly all carbonyl derivatives follow these rules with the necessary modifications for other groups present. The structure of nitrosyl compounds is M.N.O., corresponding with M.C.O., and the NO contributes 3 electrons to the effective at. no. of M, as CO contributes 2. On this hypothesis, the structures of most nitrosyl compounds are found to follow the same rules as the carbonyls. The similarity of the volatile compounds Ni(CO)4, Co(CO)₃(NO), and Fe(CO)₂(NO)₂ is explained, also the characteristic colour reaction of the nitroprussides with the sulphides. For a mol. $M_x(CO)_y(NO)_y$, the equation b = [(xm+2y+3z)/x] = x-1 holds.

L. L. B.

Distances of the closest approach of atoms of rubidium, cæsium, and barium. B. N. SEN (Current Sci., 1934, 2, 434).—Calc. vals. are Rb 4.56, Cs 5.7, and Ba 6.57 Å. L. S. T.

Simple modification of Morse's rule. C. H. D. CLARK (Nature, 1934, 133, 873).—For non-hydride diat. mols. of the period containing two completed Krings associated with each nucleus, the empirical modification is $\omega_e r_e^3 \sqrt{n=9\cdot55 \times 10^{-21}}$ cm.², where ω_e and r_e are the equilibrium nuclear vibration frequency and separation, respectively, and n is the group no. equal to the no. of shared electrons, or total no. of valency electrons of the two separate atoms.

L. S. T.

Calculation of the lattice constant of potassium chloride. T. NEUGEBAUER and P. GOMBAS (Z. Physik, 1934, 89, 480–496).—The lattice const. and energy are calc. from the polarisation energy of an ionic crystal and the van der Waals energy.

A. B. D. C.

Surface tension. A. FERGUSON (Proc. Roy. Inst., 1934, 28, 195-206).—A lecture.

Physical relationships amongst the hydrides of elements of the fifth group with special reference to association in these compounds. A. A. DURRANT, T. G. PEARSON, and P. L. ROBINSON (J.C.S., 1934, 730—735; cf. A., 1932, 454).—d and surface tensions of NH₃, PH₃, AsH₃, and SbH₃ have been measured and their parachors deduced. The v.p. of AsH₃ and SbH₃ from 180.5° to 214.5° abs. and 212.7° to 255.9° abs., respectively, has been measured. These physical properties are discussed. AsH₃ and SbH₃ are normal liquids, PH₃ is somewhat associated, and NH₃ at its b.p. is largely bimol. H. J. E.

Volatile hydrides. I. Periodicity as a means of correcting and supplementing determined physical properties. II. The parachor, molar volume at absolute zero, and electronic structure and properties of compounds. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1934, 736-743).—I. In any group the m.p., b.p., mol. heats of vaporisation, and surface tensions vary directly with the period no. of the parent element, departures from linearity (e.g., with H_2O or NH_3) being due to association. Certain undetermined physical consts. are predicted.

II. The parachor of H in volatile hydrides varies from 10.28 in HF to 19.20 in BiH₃, the variation being correlated with electronic structures of the atoms, and shown to accord with a hydrolytic mechanism of ionisation. In each periodic group the ratio $MV_{b.p.}/MV_0$ for the hydrides is const. $(MV_{b.p.}, MV_0$ are mol. vols. at the b.p. and 0° abs., respectively). H. J. E.

Parachor of hydrogen bromide. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1934, 880–881).—The surface tension and d of liquid HBr have been measured. The liquid is slightly associated. Mc-Intosh and Steele's measurements (A., 1904, ii, 533) are not correct. H. J. E.

X-Ray wave-length from crystals and ruled gratings. A. E. RUARK (Physical Rev., 1934, [ii], 45, 827-831).—Crystal scale wave-lengths are supported by calculations of energies of photo-electrons ejected by X-rays from thin foils, and comparison with those calc. from wave-lengths of the incident rays and X-ray terms of the atoms in the foils, using wave-lengths measured with crystals and ruled gratings. N. M. B.

Calculation of intensity factors for the powder method of X-ray crystal analysis. F. C. BLAKE (J. Chem. Physics, 1934, 2, 320–330).—Theoretical. Calc. and observed vals. for wurtzite and sphalerite are compared. H. J. E.

State of ammonium salts at low temperatures. A. HETTICH (Z. physikal. Chem., 1934, 168, 353– 362).—NH₄Cl exhibits below the discontinuity point at about -30° the Giebe-Scheibe effect, which supports the theory that the rotating NH₄ groups become frozen in at this point. There is a hysteresis gap of 0.3° between the appearance and disappearance of the effect, corresponding with the gap observed in dilatometric investigation (cf. A., 1933, 1119). NH_4Br exhibits no Giebe-Scheibe effect down to liquid air temp., and becomes doubly-refracting at about -30° . With $(NH_4)_2SO_4$ the effect appears below -51° , and with RbNO₃ disappears at the temp. of transition to the cubic form. R. C.

Structural relations which must exist between two substances in order that one shall modify the crystal form of the other. L. ROYER (Compt. rend., 1934, 198, 1868—1870; cf. this vol., 249, 376). —Further examples are given. B. W. B.

Effect of a magnetic field on the linear rate of crystallisation. E. W. R. STEACIE and C. F. B. STEVENS (Canad. J. Res., 1934, **10**, 483–485).—A magnetic field of about 5000 gauss had no effect on the linear rate of crystallisation of $Na_2S_2O_3$ from supersaturated solution. NiSO₄ showed a slightly increased rate. O. J. W.

Change in the elementary cell by directed forces. F. LIHL (Physikal. Z., 1934, 35, 460—468). —X-Ray examination of steel crystals indicates that the lattice undergoes change on the addition of foreign atoms, or when subjected to mechanical strain. The measurement of interference lines can give no information concerning a mean lattice parameter for alloyed or cold-worked substances. For such substances, this quantity has no physical meaning.

A. J. M.

Transition of the cubic body-centred modification into the hexagonal close-packed modification of zirconium. W. G. BURGERS (Physica, 1934, 1, 561-586).—The transition from cubic to hexagonal Zr is shown, by X-ray measurements, to be due to a combination of shearing and dilatation processes parallel to definite crystallographic directions. H. J. E.

Perfection of quartz and other crystals and its relation to surface treatment. R. M. BOZORTH and F. E. HAWORTH (Physical Rev., 1934, [ii], 45, 821—826).—Rocking curve widths at half max. show that quartz is a perfect crystal, and that perfect specimens of Na K tartrate, fluorite, tourmaline, and pyrites might be found. Barite, rock-salt, gypsum, and crystals of Al, Fe, Ni, W, and permalloy are imperfect. The effect on perfection of etching permalloy and etching and grinding quartz surfaces was investigated. N. M. B.

Crystal structure of [high-temperature] α -silver iodide. L. W. STROCK (Z. physikal. Chem., 1934, B, 25, 441-459).- α -AgI crystallises in the cubic system with a_0 5.034 Å. and 2 mols. in the unit cell. The structure is of a new type and is outside the scope of the exact structure theory. It consists of a cubic body-centred I packing, with a distance I-I of 2.18 Å., in the 30 largest interstices of which 2 Ag' are inserted at random. The Ag is thus contained like a liquid in the I lattice. The Ag-I co-ordination no. is 4, 3, and 2. This structure explains the electrolytic conduction and the self-diffusion of Ag' in the lattice. R. C.

Diffraction of X-rays in glass. B. E. WARREN (Physical Rev., 1934, [ii], 45, 657-661).-Scattering curves for vitreous SiO_2 and GeO_2 , obtained from X-ray diffraction patterns, are in good agreement with calculation. In vitreous SiO_2 each Si atom is tetrahedrally surrounded by four O atoms at a distance Si-O=1.60 Å., and each O is shared between two such tetrahedral groups. The resulting network repeats irregularly, but the presence of permanent neighbouring atoms justifies the term "amorphous solid" rather than "supercooled liquid" for glass. N. M. B.

Structure of 1:3:5-triphenylbenzene. I. B. ORELKIN and K. LONSDALE (Proc. Roy. Soc., 1934, A, 144, 630—642).—s-C₆H₃Ph₃ crystallises in the orthorhombic hemihedral class; space-group *Pna* (C_{2r}^{*}). The unit cell contains 4 mols. and has a 7.55, b 19.76, c 11.22 Å. The optical and magnetic properties of the crystal and the X-ray measurements show that the mol. approximates to the "layer-lattice" type. There are, in effect, twice as many C atoms in the crystal surface at one end of the polar axis as at the other end. L. L. B.

Influence of magnetic fields on scattering of X-rays by liquids. H. SIRK (Z. Physik, 1934, 89, 129–142).—A magnetic field of 4×10^4 gauss gave no indication of fibre structure in $1 \cdot C_{10}H_7Cl$, but showed particles containing 10^4 mols. A. B. D. C.

Structure of the fatty acid esters of cellulose. J. J. TRILLAT (J. Phys. Radium, 1934, [vii], 5, 207– 215).—The propionate, butyrate, valerate, hexoate, heptoate, octoate, nonoate, decoate, palmitate, and stearate of cellulose have been investigated by X-ray examination of powder or of evaporated or deposited films. Lattice spacing increases regularly with the no. of C atoms; with increasing C chain length the esters pass from a cryst. to a mesomorphic form. The aliphatic chains attach perpendicularly to the principal valency-chain direction, and parallel to one another; the fatty acid character predominates increasingly with length of chain, tending to mask the cellulose character. N. M. B.

Mathematical treatment of a theory of rubber structure. T. R. GRIFFITH (Canad. J. Res., 1934, 10, 486-520).-The theory that the elasticity of rubber is due to the heat vibrations of very long chain mols., bound to one another at occasional points along their length, but able to move freely relatively to one another at all other points, has been considered. Assuming that the rubber mol. has a restricted rotation about the axis formed by joining two adjacent junction points, a stress-strain curve is derived which agrees approx. with the experimental curve. The following quantities have also been calc.: (1) the average distance between junction points, (2) length of the rubber mol., (3) the quantity of kinetic energy per c.c. causing the elastic effect, and (4) the min. quantity of S needed for vulcanisation, both for hard and for soft O. J. W. rubber.

Corniform crystals. E. ROSSMANN (J.S.C.I., 1934, 53, 135—137).—Corniform (horn-shaped) cryst. structures are occasionally observed at the surface of tung oil films which have been allowed to dry under abnormal conditions of intense illumination and retarded drying. They are truly cryst. and anisotropic when first formed, although they may become isotropic on further oxidation. The peculiar curved shape is regarded as the resultant of crystal-lattice and surfaceorienting forces acting simultaneously on large polar (asymmetric) mols. situated at the air-oil interface. Chemically, such crystals may consist of a peroxide of β -clæostearin. E. L.

Investigation of various forms of carbon by cathode-ray diffraction. M. MIWA (Sci. Rep. Tôhoku, 1934, 23, 242—257).—Amorphous C (I) is a fine form of graphite, the crystal lattice expanding in the direction of the principal axis as the grain size diminishes, in agreement with X-ray results. The magnetic susceptibility of (I) nearly \propto the grain size. H. S. P.

Electron diffraction by the oxides of nitrogen. L. R. MAXWELL, V. M. MOSLEY, and L. S. DEMING (J. Chem. Physics, 1934, 2, 331-336).—N₂O is a linear mol. with the end atoms separated by $2\cdot38\pm$ $0\cdot05$ Å., agreeing with Wierl's val. (A., 1931, 665). NO₂ (at about 150°) gave no diffraction rings, indicating a triangular mol. with the N-O distance $1\cdot15 1\cdot3$ Å. The N-N distance in N₂O₄ is $1\cdot6-1\cdot7$ Å. N₂O₅ gave one diffraction ring, best explained by a symmetrical model O₂N·O·NO₂ with the N-O distance $1\cdot3-1\cdot4$ Å. H. J. E.

Crystalline state of thin calcium fluoride films. W. G. BURGERS and C. J. DIPPEL (Physica, 1934, 1, 549—560; cf. A., 1931, 1226).—Thin transparent films of CaF₂ evaporated on to Cu or celluloid from a W filament coated with CaF₂ have been shown by electron diffraction to be cryst., with a random orientation of the crystallites in the first layers deposited. At thicknesses $> 0.1 \mu$ the outer layers are oriented with (111) planes parallel to the substratum for perpendicular incidence of the salt beam, or slightly inclined for oblique incidence. Heating to 400° in vac. does not change the diffraction pattern of the film. H. J. E.

Determination of crystal lattice constants by electron diffraction. N. A. SCHISCHAKOV and L. I. TATARINOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 164—168).—A cathode beam on passing between two convex specimens gives rise to double diffraction. A specimen of known lattice consts. is used, together with another specimen of unknown lattice consts. From the wave-length of the diffraction patterns vals. of the lattice consts. are obtained with an accuracy equal to that of the X-ray method. W. R. A.

Lattice dimensions of zinc oxide. G. I. FINCH and H. WILMAN (J.C.S., 1934, 751-754).—For the close-packed hexagonal lattice of ZnO electron diffraction measurements gave $a \ 3.258 \pm 0.005$, $c \ 5.239 \pm 0.005$ Å. H. J. E.

Diffraction of electrons by rubber. J. J. TRULAT and H. MOTZ (Compt. rend., 1934, 198, 2147— 2149).—Rubber films (order of thickness 1 mµ) extended by approx. 100% gave transmission patterns with 30—40-kv. electrons consisting of diffuse rings when thick or insufficiently stretched, or fine spots indicating lattice dimensions $c 8 \cdot 1$, $a 12 \cdot 4$ Å., the isoprene chains lying flat in the film surface. The change from diffuse rings to fine spots is attributed to orientation of the isoprene chains by stretching (cf. this vol., 480). The spots disappeared in 24 hr. B. W. B.

Behaviour of quartz crystals towards electric sparks. KREFT and STEINMETZ (Naturwiss., 1934, 22, 314—315).—In crystals with appreciable conductivity (e.g., NaCl), the electric spark passes through certain canals in the crystal. In non-conducting crystals, the discharge passes over the surface in definite lines. With *l*-quartz, the lines are the mirror images of those with *d*-quartz. A. J. M.

Change of resistance in a magnetic field. H. JONES and C. ZENER (Proc. Roy. Soc., 1934, A, 145, 268—277).—The theory of the change of resistance of a metal in a magnetic field is developed for an arbitrary lattice, assuming a const. time between electron collisions at all points on the surface of the Fermi distribution. The theory is applied to Li, with good agreement with the observations of Kapitza.

State of the cerium atom inside the metallic lattice. R. I. JANUS and V. I. DROSHSHINA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 411-414).—The magnetic susceptibility of Ce has been measured over the temp. range -180.5° to 103.5° . The magnetic momentum is $11.4 M_w$ and remains const. over this temp. interval. Comparison with theoretical vals. corresponding with different states of the atom indicates that the metallic lattice consists either of Ce[•] or Ce^{•••} ions, with the corresponding no. of free electrons. At temp. < 6° abs. Ce may be ferromagnetic. J. W. S.

New magnetic phenomenon : increasing paramagnetism superposed on diamagnetism in alloys with false Curie points. R. FORRER and (MLLE.) A. SERRES (Compt. rend., 1934, **198**, 1903— 1905; cf. A., 1932, 452; 1933, 1236).—The following series of alloys with false (*i.e.*, discontinuous) Curie points, Θ , all showed const. diamagnetism at temp. $< \Theta$, and paramagnetism increasing with rise of temp. above Θ : β -brass, γ -brass, AgZn, and Ag₅Zn₈. The magnitude of the paramagnetism was less as Θ was higher. B. W. B.

Ferromagnetic Curie point of thin films of electrolytically deposited nickel. S. PROCOPIU and T. FARCAS (Compt. rend., 1934, 198, 1983-1985). B. W. B.

(Magnetic) transformations of pyrrhotine and of ferrous sulphide. A. MICHEL and G. CHAUDRON (Compt. rend., 1934, 198, 1913—1915).—Temp.magnetisation curves of pyrrhotine and pptd. FeS showed that transition occurred at 200° between a ferro-magnetic form stable at low temp., and a feebly magnetic high-temp. variety. B. W. B.

Paramagnetic rotatory power of siderite. J. BECQUEREL, W. J. DE HAAS, and J. VAN DEN HANDEL (Compt. rend., 1934, 198, 1987–1989). B. W. B.

Relation between magnetic susceptibility and elastic stress. Y. WATASE (Sci. Rep. Tôhoku, 1934, 23, 208—212).—The variation of the susceptibility has been measured under a homogeneous stress. H. S. P.

L. L. B.

Abnormal permeability produced in a steel wire by loading. T. F. WALL (Nature, 1934, 133, 949). L. S. T.

Variation of saturated magnetisation at low temperatures, $T^{3/2}$ law. P. WEISS (Compt. rend., 1934, 198, 1893—1895).—Experiments on magnetic saturation of Fe and Ni were undertaken to discriminate between the proposed laws involving functions of T^2 (Weiss and Forrer, A., 1929, 1369) and $T^{3/2}$ (Bloch, A., 1930, 673), respectively. A slight correction is necessary in the previously accepted vals. of the Fe magneton. B. W. B.

Optical and crystallographical properties of the alkali zinc uranyl acetates. H. INSLEY and F. W. GLAZE (Bur. Stand. J. Res., 1934, **12**, 471— 474)—The Li and Na salts are monoclinic and isomorphous, forming a scries of solid solutions; the K salt is tetragonal. Refractive indices ± 0.002 are: Na salt, α_{Na} 1.475, γ_{Na} 1.480; Li salt, α_{Na} 1.495, γ_{Na} 1.503; K salt, ε_{Na} 1.487, ω_{Na} 1.477. N. M. B.

Elastic moduli and the variation with temperature of the principal Young's modulus of rocksalt between 78° and 273° abs. L. BALAMUTH (Physical Rev., 1934, [ii], 45, 715—720).—A new high-precision method is described, and data are given for rock-salt. N. M. B.

Mechanism of plastic deformation of single crystals of iron. N. AKULOV and S. RAEVSKI (Ann. Physik, 1934, [v], 20, 113—117).—A single Fe crystal was submitted to pressure beyond the elastic limit in the (100) direction, and the characteristic patterns formed by Fe_2O_3 on the surface of the crystal (A., 1933, 213) were examined for the (010) face. There are periodic slips in the cleavage planes (100), (010), and (001). A. J. M.

Mesomerism and tautomerism. C. K. INGOLD (Nature, 1934, 133, 946—947).—Theoretical.

L. S. T.

Theory of m.p., recrystallisation and polymorphic transition temperatures. L. TARSCHISCH (Physikal. Z., 1934, 35, 469-471).—The theory indicates that for monat. regular cryst. substances the m.p. is a function of the at. distance. It is applied to solid solutions, and to the phenomenon of recrystallisation. A. J. M.

 Theory of super-conductivity.
 R. SCHACHEN

 MEIER (Z. Physik, 1934, 89, 183—209; cf. A., 1932,
 453).
 A. B. D. C.

Theory of thermo-magnetic and thermoelastic phenomena. P. CHRAMOV and L. LVOVA (Z. Physik, 1934, 89, 443–446). A. B. D. C.

Electrical resistance of platinum at low temperatures. W. J. DE HAAS and J. DE BOER (Physica, 1934, 1, 609-616).—Data are recorded for the range 4-20° abs., disagreeing with vals. calc. from published formulæ. H. J. E.

Production of very low temperatures by the magnetic method : superconductivity of cadmium. N. KURTI and F. SIMON (Nature, 1934, 133, 907-908).—Cd becomes a superconductor at approx. 0.6° abs. A temp. of 0.1° abs. has been reached by this method using Mn NH₄ sulphate as the paramagnetic salt. L. S. T.

Melting ice. V. ALTBERG (Compt. rend. Acad. Sei. U.R.S.S., 1934, 2, 168—170).—Ice formation in relation to geo-physical problems is considered. C. W. G.

The form of m.p.[-pressure] curves. G. TAMMANN and G. MORITZ (Z. anorg. Chem., 1934, 218, 60-64).—An interpolation formula connecting the vol. change on fusion with pressure is used in conjunction with the Clausius-Clapeyron equation. F. L. U.

F.p. of rhodium. W. F. ROESER and H. T. WENSEL (Bur. Stand. J. Res., 1934, 12, 519-526).— The f.p. of Rh is $1966^{\circ}\pm 3^{\circ}$. Modifications in the method of preparing pure Rh are described.

H. J. E.

Direct determination of heat of condensation. I. Experiments with liquids not intensively dried. A. SMITS and D. CANNEGIETER (Z. physikal. Chem., 1934, 168, 391—410).—With a new type of apparatus, in which a const. temp. difference is maintained automatically between the calorimeter and a petroleum jacket surrounding it, heats of condensation of C_6H_6 , Br, and EtBr have been measured. R. C.

Thermochemical measurements on complexforming amines and alcohols. W. HIEBER and A. WOERNER (Z. Elektrochem., 1934, 40, 252—256).— The following data (in g.-cal. per mol.) are recorded : heat of vaporisation, $C_2H_4(NH_2)_2$ 16,040 (0°), 11,200 (20°), C_5H_5N 10,180 (0°), 9710 (20°); heat of melting, $C_2H_4(NH_2)_2$ 4620, N_2H_4 1020. E. S. H.

Latent heat of fusion and ideal solubility of naphthalene. H. L. WARD (J. Physical Chem., 1934, 38, 761-769).—The latent heat of fusion, ΔH , of very pure $C_{10}H_8$ (m.p. $80\cdot25-80\cdot30^\circ$) is given by $\Delta H=4090+9\cdot23t-0\cdot0522t^2$ g.-cal. ($t=^\circ$ C.). The ideal solubility has been calc. from ΔH , and agrees with data on the solubility in PhCl. R. S. C.

Calorimetric experiments on thallium. W. H. KEESOM and J. A. KOK (Physica, 1934, 1, 595–608; cf. this vol., 589).—The at. heat of Tl has been measured from 1.969° to 2.404° abs. with and without an external magnetic field, but with persistent currents flowing. The cooling by adiabatic magnetic disturbance of the superconductive state (I) between 1.32° and 2.32° abs., and the at. heat of non-superconductive Tl at 1.310—1.425° abs. in a magnetic field > the threshold val. have been measured. The transition between (I) and the non-superconductive state is reversible.

H. J. E.

Exact measurement of specific heats of solid substances at high temperatures. VI. Specific heats of vanadium, niobium, tantalum, and molybdenum. F. M. JAEGER and W. A. VEENSTRA (Rec. trav. chim., 1934, 53, 677-687; cf. this vol., 481).—The following revised true sp. heats are given: $V = 0.119795 \pm 0.18375 \times 10^{-4}t \pm 0.20457 \times 10^{-7}t^2 \pm 0.108004 \times 10^{-11}t^3$; Mo 0.061046 $\pm 0.1232086 \times 10^{-4}t \pm 0.103636 \times 10^{-8}t^2$. E. S. H.

Purification and physical properties of organic compounds. V. The specific heats of solid and liquid phases at the f.p. as criteria of **purity.** E. L. SKAU (Bull. Soc. chim. Belg., 1934, 43, 287—298).—Whilst traces of impurities increase the sp. heat of a solid $(C_p)_s$ in the neighbourhood of the f.p., the sp. heat of the liquid $(C_p)_l$ is little affected; hence, if existing data near the f.p. afford negative vals. for Tammann's relation, $x=(C_p)_l-(C_p)_s$, it is inferred that the substance is impure. This is confirmed by numerous cases. On the other hand, a substance affording a positive val. of x is not necessarily pure. J. G. A. G.

Specific heat of furan and ethyl ether vapours. W. H. JENNINGS and M. E. BIXLER (J. Physical Chem., 1934, 38, 747—751).—For furan vapour the sp. heat is given by C_p (molal at 1 atm.)=14·2341+7·188× $10^{-2}t-1.071\times10^{-4}t^2$ ($t=^{\circ}$ C.), and varies from approx. 44° to 99°. For Et₂O at 1 atm. C_p (molal)=23·3833+ $14.71\times10^{-2}t-5.929\times10^{-4}t^2$. R. S. B.

Heat capacities of crystalline, glassy, and under-cooled liquid glucose. G. S. PARKS and S. B. THOMAS (J. Amer. Chem. Soc., 1934, **56**, 1423).—The sp. heat of cryst. α -glucose (I) from -20° to the m.p. is given by $C_p(g.\text{-cal.}/g.)=0.270+0.00092t$. L_f is 41.7 g.-cal. per g. at 141° (approx.). With rise of temp., the C_p of non-cryst. (I) has a sharp max. at 28—38°, and during cooling there is a rapid fall of C_p between 40° and 10° (cf. A., 1928, 1189). J. G. A. G.

Isotherms of nitrogen between 0° and 150° and at pressures from 20 to 80 atm. A. MICHELS, H. WOUTERS, and J. DE BOER (Physica, 1934, 1, 587— 594; cf. A., 1929, 128).—Data are tabulated.

H. J. E.

Beattie-Bridgman and Huang form of the equation of state. W. JACYNA, S. DEREWJANKIN, A. OBNORSKY, and T. PARFENTJEW (Z. Physik, 1934, 89, 370—372).—This formula (A., 1929, 252) is shown to be identical with that of Jakob and Plank (Physikal. Z., 1910, 11, 633). A. B. D. C.

Principle of Le Chatelier and Braun. M. PLANCK (Ann. Physik, 1934, [v], 20, 196).—Attention is directed to work overlooked by the author (cf. this vol., 589). A. J. M.

Thermal conductivity of air. T. H. LABY (Proc. Roy. Soc., 1934, A, 144, 494–495).—The parallelplate and certain hot-wire methods for the determination of the conductivity of gases give concordant results. L. B.

Thermal conductivity of some gases at 0° C. W.G. KANNULINK and L. H. MARTIN (Proc. Roy. Soc., 1934, A, 144, 496—513).—Possible sources of error in hot-wire methods are discussed and the thermal conductivities of air, H₂, CO₂, O₂, CO, N₂O, He, Ne, and A have been measured by one of these methods. The const. ε in Maxwell's relation $k_0 = \varepsilon \eta_0 c_v$ is calc. for the above gases. Vals. obtained for He, Ne, and A are in good agreement with Chapman's theoretical val. 2.5 for monat. gases. L. L. B.

Thermal expansion of aragonite and its atomic displacements by transformation into calcite between 450° and 490° in air. I. S. Kôzu and K. KANI (Proc. Imp. Acad. Tokyo, 1934, 10, 222-225).-Thermal expansion is very rapid between these temp. C. W. G. Apparatus for measuring thermal conductivity of metals up to 600°. M. S. VAN DUSEN and S. M. SHELTON (Bur. Stand. J. Res., 1934, 12, 429-440).— The conductivity of the metal is compared directly or indirectly with that of Pb. Data are given for Ni, Zn, and Ni-Cr and other alloys. N. M. B.

Thermal conductivity of some irons and steels over the temperature range 100-500°. S. M. SHELTON (Bur. Stand. J. Res., 1934, 12, 441-450)...-Data, by comparison with Pb, are given for 20 specimens of Fe, steel, Cr-Fe, and Cr-Ni-Fe alloys.

N. M. B. Viscosity and mol. wt. H. MARK (Chim. et Ind., 1934, 31, Spec. No., 788—791).—Vals. $(3\cdot7-8\cdot1)$ of f(length/width of mol.) for hydrocarbons ($C_{22}-C_{53}$) calc. from the sp. viscosities of dil. solutions by the equation $\eta_{sp} = (2\cdot5+f^2/30)(v/V)$, where v and V are the vols. of the solute and solution, respectively, are < those found by examination of the crystals ($10\cdot2-22\cdot8$). In solution the mols. are probably not straight, but curved or spiral with an effective length proportional to \sqrt{l} , and the above vals. agree approx. with this relation. A. G.

Kinetic theory of the viscosity of liquids. R. O. HERZOG and H. KUDAR (Physikal. Z., 1934, 35, 437— 445).—The effect of the shape and dipole moment of mols. on viscosity is derived, and the equation is tested for various substances. A. J. M.

Electrostatic viscosity effect for liquids. R. O. HERZOG, H. KUDAR, and E. PAERSCH (Physikal. Z., 1934, 35, 446; cf. A., 1933, 1110).—The liquids were passed through a capillary tube having two Pt and two glass sides, an electric field being applied between the Pt sides. The viscosity of 13 liquids in a field of 110 volts was measured. There is no electrostatic effect with C_6H_{14} , CCl_4 , and cyclohexane, but dipole liquids, with the exception of Bu^eI and decyl iodide, show an increase in viscosity. A. J. M.

Viscosity, heat conductivity, and diffusion of gas mixtures. XXV. Viscosity of xenon, and its mixtures with hydrogen and helium. M. TRAUTZ and R. HEBERLING. XXVI. Viscosity of propylene and β -butylene, and their mixtures with helium or hydrogen. M. TRAUTZ and I. HUSSEINI. XXVII. Viscosity of chlorine and hydrogen iodide. Test of the determination of η for corrosive gases. M. TRAUTZ and F. RUF. XXVIII. Viscosity of chlorine, nitric oxide, and nitrosyl chloride. Viscosity during the reaction 2NO + Cl₂ = 2NOC1. M. TRAUTZ and A. FREYTAG (Ann. Physik, 1934, [v], 20, 118-120, 121-126, 127-134, 135-144).—XXV. The transpiration method was used with the pure gas from 289.7° to 550° abs., and on the mixtures at 293°, 400°, 500°, and 550° abs.

XXVI. Data are given for temp. between 20° and 250° .

XXVII. The viscosities of gases which attack Hg, e.g., Cl_2 and HI, were determined by a method previously described (A., 1931, 1117), the results agreeing well with those obtained by others. A no. of mol. consts. were derived.

XXVIII. The method used for Cl_2 was also employed to find η for NO, the results agreeing with those

obtained by the transpiration method. The Maxwell and Enskog-Chapman diameters of the pure gas were determined. η for NOCl increases more rapidly than is indicated by theory. This is due to decomp. into NO and Cl₂. A. J. M.

Diffusion coefficients in gaseous systems. E. R. GILLIAND (Ind. Eng. Chem., 1934, 26, 681– 685).—Diffusion coeffs. for mixtures of air with H_2O vapour, Bu°OH, PhMe, sec.-BuOH, EtOAc, sec.-amyl alcohol, PhCl, NH₂Ph, Ph₂, Hg, and Pr^βOH have been determined, and these together with published data for other substances are expressed graphically and also by a modification of Maxwell's equation.

D. K. M. Dilute liquid amalgams of the alkaline earths with special reference to their electrical conductivity, viscosity, and density. G. R. PARANJPE and V. S. PATANKAR (J. Univ. Bombay, 1933, 2, 40-61).-Amalgams containing < 0.364 g. Ba (I), 0.4545 g. Sr (II), and 0.023 g. Ca (III), respectively, have been examined. The electrical conductivities and viscosities of (I) and (II) do not change with time. The conductivities of (II) and (III) increase uniformly with conen., but that of (I) decreases and shows discontinuities at 0.130, 0.225, and 0.325 g.-% Ba. The same vals. correspond with max. in the viscosityconcn. curve of (I), but the density decreases uniformly. The results are discussed in connexion with the theories of Skaupy and Lewis. R. S.

Gold-calcium alloys. F. WEIBKE and W. BAR-TELS (Z. anorg. Chem., 1934, 218, 241–248).—The thermal diagram shows the compounds Au₄Ca and Au₂Ca. A homogeneous mixed crystal phase is formed between 49 and 56 at.-% Ca. Au₂Ca and the solid solution occur in two modifications. Au₃Ca, AuCa_{1:33}, and AuCa₂ are formed by peritectic decomp. Microscopical observations on alloys up to 35 at.-% Ca confirm the results of thermal analysis.

M. S. B.

System germanium-tellurium. W. KLEMM and G. FRISCHMUTH (Z. anorg. Chem., 1934, 218, 249— 251).—The only compound formed is GeTe, incongruent m.p. $725\pm3^{\circ}$, d^{25} $6\cdot20\pm0\cdot02$. Its existence is also confirmed by the X-ray diagram. GeTe is attacked to a small extent only by conc. HCl or H₂SO₄, NH₃, and H₂O₂, slowly by conc. HNO₃, and readily by aqua regia or a mixture of H₂O₂ and HCl. Comparisons are made with the corresponding Te compounds of Sn and Pb. M. S. B.

Kinetics and equilibrium diagram of the irreversible transformation in the iron-nickel system. U. DEHLINGER [with H. BUMM] (Z. Metallk., 1934, 26, 112—116).—On quenching the 29:71 Ni-Fe alloy in liquid air a purely martensitic structure is obtained, but X-ray examination shows the alloy to have a body-centred cubic lattice and not a tetragonal lattice like martensite. The quenched γ -phase has a hardness (H_B) of 145 and the α -phase produced from it by slip has $H_B=270$. Even on prolonged annealing at 1000° the α -phase is not completely converted into γ -, but X-ray examination shows that the movement of the atoms in the lattice takes place along the same lines as in the $\alpha \rightarrow \gamma$ transformation. The bearing of these factors on the equilibria in the Fe-Ni system is discussed.

A. R. P. Liquid-vapour equilibria of mixtures of aromatic and non-aromatic hydrocarbons. IV. Mixtures of xylenes with non-aromatic hydrocarbons. M. MIZUTA (J. Soc. Chem. Ind. Japan, 1934, 37, 282B).—For mixtures of xylene and petrol (b.p. 120—150°) the v.p. are < those represented by the simple mixture rule. Xylene can be conc. in the liquid phase to any desired degree, but not so efficiently as C_6H_6 or PhMe. A. G.

Degree of dehydration of binary azeotropes. W. SWIENTOSLAWSKI (Compt. rend., 1934, 198, 2246-2247).—The b.p. of C_6H_6 -EtOH, PhEt-EtOH, and CS_2 -COMe₂ azeotropes are more sensitive to traces of H₂O than those of their constituent liquids. A differential ebullioscope will detect 10^{-5} to 3×10^{-6} g. H₂O, and suitable liquids can be dried to this extent by distillation. B. W. B.

Displacement of the azeotropic point of the ternary azeotrope C_6H_6 -EtOH- H_2O as a function of pressure. W. SWIENTOSLAWSKI and B. KAR-PINSKI (Compt. rend., 1934, 198, 2166—2167).— Azeotropic data are tabulated for 1—19 atm.; vals. of dt/dp for the three corresponding binary azeotropes have also been determined. With increasing p, the % of C_6H_6 increases, that of H_2O decreases, and that of EtOH rises to a max. at 9.5 atm., and thereafter falls. B. W. B.

Liquid ammonia as solvent. II. Vapour pressures of solutions at 25°. H. HUNT and W. E. LARSEN (J. Physical Chem., 1934, 38, 801–807).— The v.p. of solutions of NH_4NO_3 , NH_4Cl , NH_4Br , and NH_4I in liquid NH_3 at 25° has been determined over a wide range of concn. R. S. B.

Behaviour of the magnesium ion towards ammonia in aqueous solution. III. Solubility of certain salts in ammoniacal solution. IV. Equilibrium in ammoniacal magnesium salt solutions through the incomplete precipitation of magnesium hydroxide by ammonia. H. FRED-HOLM (Z. anorg. Chem., 1934, 218, 225-234, 235-240).—III. The solubilities of 2-(C₁₀H₇·SO₃)₂Mg (1), Mg cinnamate (II), and MgC₂O₄ have been determined in aq. NH₃ of different concns. and the stability coeff. of the NH₃ complex has been calc. The changes in solubility due to changes in activity have been determined approx. by measuring the solubility of 2-(C10H7·SO3)2Ba and Ba(OBz), in aq. NH3 and of (I) and (II) in aq. MeOH which is physically similar to NH3. The changes observed are negligible.

IV. The equilibrium $Mg(OH)_2 + 2NH_4 \implies Mg' + 2NH_3 + 2H_2O$ has been investigated from both sides. The bearing of the results on the formation of complex NH₃ compounds is discussed. M. S. B.

"Induced " solubility of ferric hydroxide and other hydroxides in alkali hydroxides in presence of chromic hydroxide. II. H. KNOCHE (Kolloid-Z., 1934, 67, 307–317; cf. this vol., 726).—When excess of alkali is added to a mixture of $CrCl_3$ and $FeCl_3$, both $Fe(OH)_3$ and $Cr(OH)_3$ are redissolved, giving a solution with colloid properties. The amount of $Fe(OH)_3$ peptised increases with the amount of alkali; KOH is more effective than NaOH. Dissolution does not occur when the Fe^{\cdots} content exceeds about 40%. Dry Fe(OH)₃ is also peptised under the same conditions. When the amount of Fe(OH)₃ is varied and the peptising liquid kept const., the observed behaviour is consistent with the phase rule. Alkali-free Cr(OH)₃ sols have scarcely any peptising influence on Fe(OH)₃. The active agent is probably the alkali chromite.

E. S. H.

Solubilities of organic oxygen compounds in sulphuric acid-water mixtures. L. P. HAMMETT and R. P. CHAPMAN (J. Amer. Chem. Soc., 1934, 56, 1282—1285).—The data refer to 0-90% H₂SO₄ at 25°. With increase of $[H_2SO_4]$, the solubilities at first decrease and then increase. The latter is not entirely due to ionisation or salt formation in the case of BzOH, CH₂Ph·CO₂H, o- and p-NO₂·C₆H₄·CO₂H, and C₆H₄PhBz (I), since PhNO₂, which is a weak electrolyte, exhibits similar phenomena. With BzOH a new phase appears with > 79% aq. H₂SO₄ and (I) affords an intensely yellow liquid with > 80% aq. H₂SO₄. The other solutes do not exhibit changes of phase in the range investigated. J. G. A. G.

Theory of absorption of gases by liquids flowing in thin layers. S. HATTA (J. Soc. Chem. Ind. Japan, 1934, 37, 275—277B).—The double-film theory of absorption applies only when both gas and liquid are in turbulent flow. The absorption when the liquid flow is stream-line is calc. with the aid of simplifying assumptions. A. G.

Absorption of carbon dioxide by water flowing in a thin layer. S. HATTA and M. KATORI (J. Soc. Chem. Ind. Japan, 1934, 37, 280–282B).—The absorption of CO₂ by a flowing layer of H₂O agrees with the double-film theory when the flow is rapid. When the flow is slow and stream-line, the absorption is correctly expressed by the theoretical equations $C/C_s \propto \sqrt{x}$ and $C/C_s \propto (\sin 0)^{1.6}$, in which C is the concn. of the outflowing H₂O, C_s the saturation concn., x the length of the surface, and θ its angle of slope.

A. G. Vapour-binding power of active charcoal. IV. Dependence of the amount of bound vapour on the form of the charcoal layer. F. KRCZIL and H. WEJROCH (Kolloid-Z., 1934, 67, 277-279; cf. this vol., 358).—The amount of bound vapour retained by Cafter the passage of an indifferent gas is independent of the form of the C layer. E. S. H.

Absorption of hydrogen by nickel. J. SMITTEN-BERG (Nature, 1934, 133, 872).—Between 200° and 650° and pressures (p) up to 0.2 mm. there is no measurable adsorption of H_2 by thin Ni wire. Absorption is appreciable, however, at higher p, and at const. temp. $\propto \sqrt{p}$. At const. p it increases with rise of temp. according to $\log a = A - B/T$. The calc. heat of absorption is somewhat < 3 kg.-cal. per g.-mol. of H_2 . Agreement with measurements (A., 1911, ii, 895) for thicker wire at higher temp. and p is good. L. S. T.

Absorptive power of palladium-boron alloys for hydrogen. A. SIEVERTS and K. BRÜNING (Z. physikal. Chem., 1934, 168, 411-418).—Alloys with 2.5-16.6 at.-% B have been studied. Up to a B 3 K content of 6.9 at.-% the alloys are homogeneous, whilst alloys with 13.8 and 16.6 at.-% are two-phase systems. The hardness is > that of Pd and increases with the proportion of B, rapidly at first and then more slowly. For all the alloys the absorptive power for H decreases with rising temp. At a given temp. the amount absorbed is approx. proportional to the square root of the pressure, except for alloys with 2.5 and 6.9 at.-% B below 500°. For an alloy with 2.5 at.-% B below 500° the isotherms resemble those for the system Pd-H₂. At 160—900° the absorption at 1 atm. passes through a max. at about 7 at.-% B. At 100° and 20° it falls continually with increasing % B.

R. C. **Coloured bromine adsorbates.** E. BEUTEL and A. KUTZELNIGG (Monatsh., 1934, 64, 114—122).—The following substances adsorb Br vapour to give more or less highly coloured products : Ca(OH)₂, Sr(OH)₂,8H₂O (I), marble (3 varieties), fibrous Al₂O₃, basic Al acetate, SiO₂ gel, Zr(OH)₄, Sb₂O₃ (II), As₂O₃ (III), cotton, kapok, ramie, flax, and jute. A reaction occurs with (I), (II), (III), KI, CuI, S, keratin, and (probably) CsCl and RbCl. The remission curves of several of the products are given. MgO, ZnO, BeO, and basic Zn carbonate do not adsorb Br. The plant fibres behave more similarly towards Br than I (cf. this vol., 22, 358) in dry and moist atm. H. B.

Adsorption of hydroxy- and amino-anthraquinones by cotton cellulose. K. BRASS and K. LAUER (Kolloid-Z., 1934, 67, 322—327).—Adsorption measurements in EtOH solution show the influence of the nature and position of the substituent groups. The following distribution coeffs. are recorded: 1-hydroxy- 1.88, 2-hydroxy- 1.29, homonuclear dihydroxy- 5.6—58.1, heteronuclear dihydroxy- 3.42— 17.7, 1-amino- 70.0, 2-amino-anthraquinone 6.2.

E. S. H. Surface tension and molecular volume of nitroglycerol. T. C. SUTTON and H. L. HARDEN (J. Physical Chem., 1934, 38, 779—781).—The surface tension of pure glyceryl trinitrate (I), determined by the bubble-pressure method, is 50.4 dynes per cm. at 20.5° ; the same result is obtained by methods involving a stationary surface. From $d^{20.5} = 1.595$ the parachor has been calc. to be 379.3 (mean), which agrees with the val. 378.9 derived from Sugden's consts. The parachors of (I) solutions in PhNO₂ have been determined and shown to be additive.

R. S. B. Superficial properties of certain dyes. E. VELLINGER and R. DELION (Compt. rend., 1934, 198, 2084—2086).—The variation of the interfacial tension between 0.01% aq. bromothymol-blue (I) solutions and paraffin oil with the $p_{\rm H}$ of the solution suggests that the dissociation consts. of H₂O or of (I) are altered by differential adsorption of the ion and undissociated mol. of (I) at the interface. B. W. B.

Study of adsorption at the benzene-sodium oleate solution interface. K. M. SEYMOUR, H. V. TARTAR, and K. A. WRIGHT (J. Physical Chem., 1934, 38, 839-851).—The adsorption of Na oleate at the aq. solution– C_6H_6 interface at 25° has been studied by dropping C_6H_6 through the aq. solution; the adsorption layer corresponds with 20-30 mols. calc. from

the gain of oleic acid and with 1—10 mols. calc. from gain of Na. Equilibrium and non-equilibrium solutions give similar results. R. S. B.

Laws of spreading of liquid drops on filterpaper. K. PROSAD and B. N. GHOSH (Current Sci., 1934, 2, 430).—The relations involved in the spreading of a single drop of liquid on filter-paper have been studied by experiments in a closed chamber containing saturated vapour. The velocity diminishes exponentially with the distance covered. L. S. T.

Mechanism of ascent of colloidal solutions in porous bodies. A. BOUTARIC (Compt. rend., 1934, 198, 2247—2250).—The height of ascent of the colloidal particles depends on their polarity relative to the wetted surface of the porous body, and is least when the signs are opposite. The surface tension of the intermicellary liquid is without effect. B. W. B.

Porosity determinations of dispersoids from the velocity of penetration of liquids. Z. V. VOLKOVA (Kolloid-Z., 1934, 67, 280–284).—An apparatus for measuring the penetration velocity of liquids in powders is described. The "mean penetration radius" r is defined as $\pi^2 l^2 \eta/2t\sigma$, where l is the distance penetrated in time t. For a given powder ris const. for non-polar liquids, but is less for polar liquids, especially for H₂O. The decrease of r for polar liquids is ascribed to peptisation of the powder, orientation, or swelling. In the displacement of a non-polar liquid by H₂O the simple formula l^2/t is valid, as r for H₂O is very small. E. S. H.

Formation and properties of precipitates. Theory of coprecipitation. III. I. M. KOLTHOFF (Chem. Weekblad, 1934, 31, 395-400; cf. this vol., 727).—Imre's views on adsorption on crystal lattices are adversely criticised. Both Imre's and the author's experimental data lead to the conclusion that in the first stage the adsorbed ions displace ions of the same sign in the hydrated surface layer of the adsorbent; if of appropriate type these adsorbed ions may then exchange places with ions in the underlying lattice, but this is a relatively slow process. Paneth and Thimann's simple expression for calculating the sp. surface of ppts. from the adsorption of non-isotopic radioactive ions does not yield accurate results.

H. F. G.

Structural changes taking place during the ageing of freshly formed precipitates. I. Ageing of lead sulphate precipitated at room temperature. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1934, 56, 1264-1269; cf. this vol., 594) .- The sum of the external and internal surfaces of PbSO₄ freshly pptd. at room temp. from 0.1M-Pb(NO₃)₂ and 0.1M-K₂SO₄ is determined in terms of the adsorption of Th-B, and the magnitude of the external surface only is given by the adsorption of wool-violet. The crystals of the freshly formed ppt. are highly porous and all the Pb ions then behave as though present at the surface. An exceedingly rapid ageing occurs, resulting in the perfection of the internal structure of the pptd. crystals, and at the same time any adsorbed Th-B is incorporated. Growth of the crystals is evident only after long periods of ageing. The entire process is markedly accelerated by digestion, especially in the presence of HNO_3 . J. G. A. G.

Liesegang rings. E. B. HUGHES (Biochem. J., 1934, 28, 1086—1106).—Occurrence of a ppt. in band formation during diffusion of one electrolyte into a solution of another of lower equiv. cenen. is shown by experimental evidence to depend on: (1) the gradient of the concn. of the entering ion (I) and the resulting gradient on the ppt. front of the ion (II) contained in the medium; (2) removal of (II) by more (I) until diffusion of (I) again proceeds normally; (3) the rapid collection of the ppt. into a more closely defined zone; (4) the metastable solubility of the ppt.; (5) growth of the ppt. particles at the expense of the smallest. A theory of the formation of Liesegang rings is discussed. H. G. R.

Rhythmic precipitates. III. Effects of the presence of acids, alcohols, or amino-acids in gelatin jellies. T. ISEMURA (Bull. Chem. Soc. Japan, 1934, 9, 236—239).—EtCO₂H and PrCO₂H destroy the rhythmic bands of Ag_2CrO_4 in gelatin; hexoic and octoic acids give bands containing Ag soap. Alcohols increase, NH₂-acids decrease, the no. of Ag_2CrO_4 bands. The formation of bands consisting entirely of Ag soap is also described. R. S. B.

Iridescence of old glasses. Formation of Liesegang strata by rhythmic precipitation of calcium carbonate in glass in contact with hydrogen carbonate solution. M.GUILLOT (Compt. rend., 1934, **198**, 2093—2095).—The artificial production of iridescence (I) in glass is discussed. Contact with a no. of aq. solutions, particularly saturated NaHCO₃, at 15°, slowly produces (I) due to stratified CaCO₃ pptn. B. W. B.

Equilibria at colloidal bounding phases in aqueous silicate systems. W. ETTEL and H. E. SCHWIETE (Naturwiss., 1934, 22, 403-406).—The Donnan theory has been applied to the equilibria in aq. silicate systems in connexion with cements.

A. J. M.

Statistical foundation of membrane equilibrium. A. GANGULI (Kolloid-Z., 1934, 67, 304– 306).—Theoretical. E. S. H.

Exact thermodynamics of membrane equilibria. II. F. G. DONNAN (Z. physikal. Chem., 1934, 168, 369—380; cf. A., 1933, 127).—Equations are derived for the exchange equilibria of ions having charges of the same sign, the effect of non-diffusible non-electrolytes on the distribution of diffusible solutes, membrane potentials, and osmotic pressure. A new coeff., g, is introduced which can be regarded as a mean osmotic coeff. or mean activity index.

R. C.

Colour and acid properties of α -naphtholphthalein. K. BUCH (Finska Kem. Medd., 1934, 43, 6—17).—Measurements have been made of the extinction curves of this indicator prepared by the method of Sorensen and Palitzsch, in 0·1N-HCl, 0·1N-NaOH, and some buffer solutions. By using light of two λ the curves for both the primary and secondary ions have been obtained. H. S. P.

Spectrophotometric investigation of a-naphtholphthalein. C. GUSTAFSSON (Finska Kem. Medd., 1934, 43, 18-24).—The measurements made were similar to those in the preceding abstract, but the indicator was made by the method of Schulenburg. H. S. P.

Osmometric investigations of dilute solutions of polymeric carbohydrates. V. State of solution of cellobiose and maltose octa-acetates in glacial acetic acid. M. ULMANN and K. HESS (Ber., 1934, 67, [B], 818—823; cf. A., 1933, 492).—Osmometric measurements show that maltose octa-acetate (I) in AcOH follows van 't Hoff's law down to the smallest conens. The osmotic pressure of solutions of cellobiose octa-acetate (II) in AcOH (c > 0.5%) diminishes less rapidly than expected, and the decrease becomes \propto the conen. when c=>0.13%. The hypothesis that (II) forms a complex with AcOH which is appreciably dissociated at c=>0.5% and completely dissociated at about c=0.1% is supported by measurements of the conductivity of the solutions. The electrical behaviour of solutions of (I) and glucose penta-acetate in AcOH is normal. H. W.

Dimensional relations in the theory of electrolytes. A correction. P. VAN RYSSELBERGHE (J. Chem. Physics, 1934, 2, 350; cf. this vol., 25).

H. J. E.

Magnetic investigation of the mutual influence of potassium iodide and water in solution. H. CABRERA and H. FAHLENBRACH (Z. Physik, 1934, 89, 166—178).—Hydration of KI and depolymerisation of H_2O with increasing concn. of HI have been followed by measurements of magnetic susceptibility. The influence of temp. has also been studied; hydration at room temp. is small for all concns. A. B. D. C.

Strong electrolytes as dispersion media. A. VOET (Rec. trav. chim., 1934, 53, 818–819).—Sols of metal sulphides, halides, etc. have been prepared by electro-dispersion in conc. H_2SO_4 , H_3PO_4 , saturated aq. KOAc, and other media. The particles appear to have no electrokinetic potential and exhibit spontaneous reversible coagulation. E. S. H.

Preparation of colloid solutions by the silent electric discharge. S. MIYAMOTO (Kolloid-Z., 1934, 67, 284—288).—Compounds of Au, Ag, Pt, etc. are reduced by H₂ under the influence of the silent electrical discharge. The properties of hydrosols of Au, Ag, Pt, and of sols of Ag and Au in EtOH, Bu^gOH, and amyl alcohol, prepared in this way, are described. E. S. H.

Mechanism of the formation of aurosol Au_F (Zsigmondy), and the part played by traces of sodium sulphide. R. WERNICKE and R. B. LOSSON (Anal. Asoc. Quím. Argentina, 1934, 22, 5–10).— Alkaline solutions of HAuCl₄, when boiled or kept in the cold for some hr., form colloidal particles which accelerate the reducing action of CH₂O. Traces of Na₂S in solutions of HAuCl₄ form colloidal particles of Au₂S₃, which form aurosols by reduction with CH₂O. Na₂S inhibits reduction by CH₂O of solutions in which HAuCl₄ has been completely converted into AuO₂', or when present in excess. R. N. C.

Structure of colloidal particles. III. Electrochemical properties of atakamite. I. N. PUTI-LOVA. IV. Electrochemical study of atakamite sols. A. A. MOROZOV (J. Gen. Chem. Russ., 1934, 4, 80-85, 86-103).—III. The concn. of $Cu(OAc)_2$ (I) in the intermicellar fluid (II) of saturated atakamite (III) sols is 0.00288%. The fall in conductivity, κ , of (III) sols on dilution with H₂O is < that found on similar dilution of (II), pointing to passage of (I) from (III) to (II) on dilution. The micellar wt. of (III) in its saturated sols in presence of excess of (I) is approx. 150,000, and the constitution of the micelle is [{[Cu(OH)₂Cu[•]]OH·Cl}₂₉₂{Cu(OAc)₂}₂₂Cu^{••}]₅. The fall in κ of (III) sols when diluted with 0.001N-(I) is explained by peptisation of (III), with adsorption of (I) on the fresh surfaces formed.

IV. The κ of (I)-NaCl solutions falls at first rapidly, and then more slowly, corresponding with the formation of particles of (III), and their subsequent aggregation. (III) sols are reversibly coagulated by >0.08N-NaCl, and irreversibly by 0.00025N-Na₂SO₄. In presence of excess of NaCl the structure of the micelles of (III) is

 $n\{[Cu([OH]_2Cu)_3]Cl_2\}, xCuCl_2, mCu''2mCl'. R. T.$

Concept of "eucolloids." Wo. OSTWALD (Kolloid-Z., 1934, 67, 330-333).—A discussion of nomenclature. E. S. H.

Rates of coagulation. I. Autocatalysis and sol purity. F. C. HILDEBRAND and C. H. SORUM (J. Physical Chem., 1934, 38, 809–816).—The coagulation-time curves of highly purified Fe_2O_3 sols in the presence of NaCl, Na_2SO_4 , and Na_3PO_4 have been determined, and show no induction period and no autocatalytic character. The rate corresponds with the second order. R. S. B.

Ionic interchange in sulphur sols. III. Mechanism of coagulation. T. R. BOLAM and J. J. MUIR (J.C.S., 1934, 754-766; cf. A., 1933, 1011).—The influence of temp., presence of EtOH, nature of cation and anion, acidity, and sol concn. on the ionic interchange and the coagulation vals. of salts has been examined. The coagulative action of a salt is closely related to the replacing capacity of the cation. It is supposed that coagulation is due to diminution of the actual charge on the S surface by the formation of non-ionised mols. or complexes between the coagulating cations and the micellar polythionic anions. H_2SO_4 is adsorbed on colloidal S, but the stability is not increased. R. S.

Nature and amount of non-diffusible calcium in protein sols. D. M. GREENBERG (J. Biol. Chem., 1934, 105, 511—513).—The results of Eversole *et al.* (this vol., 253) are criticised on the ground that the Ca electrode used is untrustworthy. H. D.

Nature and amount of non-diffusible calcium in protein sols. W. G. EVERSOLE (J. Biol. Chem., 1934, 105, 515—518).—A reply to Greenberg (preceding abstract). H. D.

Osmotic pressure of serum-albumin. W. PAULI and P. FENT (Kolloid-Z., 1934, 67, 288-304).— A modification of the apparatus of Krogh and Nakazawa (A., 1927, 1104) is described; the procedure enables accurate vals. of osmotic pressure Pto be obtained with 0.4 c.c. of liquid. For highlypurified, electrolyte-free, non-crystallised serumalbumin P is a linear function of concn.; the mol. wt. derived is 59,000. In presence of 0.125N-KCl the *P*-concn. curve shows a pronounced upward bend. E. S. H.

Denaturation of proteins. XIV. Titration curves of natural and heat-denatured ovalbumin. C. Y. CHOU and H. WU (Chinese J. Physiol., 1934, 8, 145-152).-Aq. re-cryst. (I) and denatured (II) (by heating at 90–95° for 30 min. at $p_{\rm H}$ 7) ovalbumin were treated with varying amounts of standard HCl and NaOH and the amounts of bound acid and base determined. The data indicate an isoelectric point (III) of p_{π} 4.75 for (I) and of approx. p_{π} 4.80 for (II). The titration curve for (II) has an inflexion at (III) and deviates from the curve of (I) on the acid side between (III) and $p_{\rm H}$ 3 and on the alkaline side between (III) and $p_{\rm H}$ 8; thus denaturation of aq. (I) at $p_{\rm H}$ 7 gives aq. (II) of $p_{\rm H}$ 7.25. The curves are compared with those previously obtained (cf. A., 1929, 459, 508; 1932, 181). F. O. H.

Colloidal behaviour of sericin. I. H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 207-221).—The solubility in H_2O at t° of sericin prepared from silk is given by $S=At^K$, where A and K are consts.; K changes at 60° and 90°. According to viscosity (η) data the mol. wt. of sericin in various batches varies from 4026 to 2382. Owing to gelatinisation η changes with time. The effect on η of the addition of acids and salts, and of variation in temp. is recorded. Results for different batches are correlated with the wt. of raw silk reeled per hr. R. S. B.

Lyophilic colloids. III. Solvatation of cellulose acetate. S. M. LIEPATOV and Z. A. PREOBRASHEN-SKAJA. IV. Hydration of the various fractions of gelatin. S. M. LIEPATOV and I. N. PUTILOVA (J. Gen. Chem. Russ., 1934, 4, 59—72, 73—79).—III. Measurements of the osmotic pressure and viscosity, and of their temp. coeff., of cellulose acetate (I) sols in MeOAc suggest that of the total quantity of solvent bound with (I), $\geq 20\%$ is chemically combined. The large increase in the vol. of the disperse phase points to considerable solvatation, chiefly due to osmotic imbibition by the micelles. The identical heat of dissolution of samples of (I) of high and low mol. wt. supports the view that intramicellar chemical combination with the solvent takes place.

IV. Osmometric measurements of gelatin (II) sols indicate that the mol. wt. of the fraction (III) of (II) which is insol. in cold H_2O falls from 141,000 to 32,000, whilst that of the sol. fraction (IV) decreases from 44,700 to 26,500 as the temp. rises from 20° to 40°. Hydration appears to be absent at 40°. The heat of imbibition of (III) is equal to that of dissolution of (IV), pointing to chemical combination of approx. 0.18 g. of H_2O per g. of (II). R. T.

Lyophilic colloids. XXI. Coacervation. I. Simple coacervation of gelatin sols. L. W. J. HOLLEMAN, H. G. B. DE JONG, and R. S. T. MODDER-MAN (Kolloid-Beih., 1934, 39, 334—420; cf. this vol., 27).—A comprehensive survey of published and new work on coacervation is made, with particular reference to the systems (a) gelatin-H₂O-Na₂SO₄ at 50°, (b) gelatin-H₂O-EtOH at 50°, and (c) gelatin-H₂O-resorcinol at 45°. The composition of the co-existing liquid layers has been determined, adsorption measurements have been made with gels and coacervates, and the mechanism of the processes preceding coacervation is examined. Viscosity determinations show that coacervation occurs when the viscosity val. of the dispersed material is reduced to about one half. The upper liquid layer is never free from colloid, although its concn. may be very low. The kinetics and theory of coacervation are discussed. E.S.H.

Diffusion of electrolytes in silica gel. W. A. PATRICK and B. W. ALLAN (J. Physical Chem., 1934, 38, 771—778).—(a) Methods of prep. of gels of silicic acid impregnated with salts are described. On dialysis salts are retained more tenaciously by gels containing a large excess of HCl. (b) Discs of SiO₂ gel, which can be dried without shattering, have been prepared, and the rates of diffusion through them of salt solutions have been determined. The diffusion of salt is diminished by the presence of HCl, and the diffusion of HCl is increased by the presence of salts, which is in accord with the experiments (a). R. S. B.

Effect of non-electrolytes on diffusion in gelatin gels. L. FRIEDMAN and W. N. SHEARER (J. Amer. Chem. Soc., 1934, 56, 1323—1324; cf. A., 1930, 693). —The rate of diffusion (I) of $CO(NH_2)_2$ (II) into 3% gelatin gel at 5° rises to sp. max. with increasing conen. of glycerol, sucrose, (II), MeOH, and glucose and then falls below the initial val. with 0.08—0.18*M*-nonelectrolyte. It appears that the non-electrolytes accelerate (I) by enlarging the pore size owing to decreased hydration of the solid phase and retard (I) by increasing the viscosity of the medium.

J. G. A. G. Action of electric current on fields of diffusion in colloidal gels. J. SWYNGEDAUW (Compt. rend., 1934, 198, 2098—2100).—Gelatin or gelose films 2—3 mm. thick spread on glass were cut into three segments by two parallel channels, and an e.m.f. was applied to the two outer segments. The channels were filled with various electrolytes and the swelling or contraction of the films was studied at various $p_{\rm H}$ vals. (cf. Veil, A., 1932, 226). B. W. B.

Influence of lipins on the elasticity of gelatin gels. P. BAMBERGER (Biochem. Z., 1934, 270, 366– 377).—The effect on the elasticity of pure ash-free gelatin of [H^{*}], neutral salts, and lipins is investigated. The vals. in the neighbourhood of the isoelectric point show a flat max., displacement of $p_{\rm H}$ to 3.8 or 6.9 resulting in a sharp fall. Cl' and I', lecithin, and Na taurocholate also decrease, whilst SO₄" increases, the elastic properties, and cholesterol antagonises the effect of lecithin. The results are discussed in relation to changes in muscle contraction (cf. A., 1933, 1318). P. W. C.

Inhibitive power of gelatin. B. N. DESAI and B. M. NAIK (J. Univ. Bombay, 1933, 2, No. 2, 90– 110; cf. this vol., 598).—The inhibitive power (1) of gelatin is a min. at $p_{\rm H}$ 5.75 with respect to Ag₂CrO₄. Changes in (I) and in the gold nos. of hydrolysed or electrodialysed gelatin are due to changes in $p_{\rm H}$. (I) decreases with $p_{\rm H}$ for AgI, but is a max. at $p_{\rm H}$ 5.0 for PbI₂. In all cases, the plot of log. gelatin concn. against log. time of inhibition is a straight line. R. S. Rhythmic cracking of silica gels in contact with hypertonic solutions. W. G. EVERSOLE and E. W. DOUGHTY (J. Amer. Chem. Soc., 1934, 56, 1263).—Two types of cracks develop in rectangular cells. Type (i) consists of a main cleavage plane parallel to the two faces of the cell and small lateral cracks perpendicular to this plane. In type (ii), the main cleavage has a wave form and lateral cracks are absent. In cylindrical cells, type (ii) only occurs. J. G. A. G.

VI. Similar coagulation phenomena are observed in the action of neutral salts on linseed sols in aq. and $aq.-COMe_2$ solutions. In certain circumstances the separation of fibrils can be observed; it is probable, therefore, that the "amorphous" coagula are also fibrillar. E. S. H.

Plant colloids. XXXVI. Preparation and degree of dispersion of erythro-substances from potato starch. XXXVII. Particle size of amyloses and their degradation products [formed] by acetylation, heating, and ageing. M. SAMEC and L. KNOP. XXXVIII. Roast dextrins. M. SAMEC and M. FÖRSTER (Kolloid-Beih., 1934, 39, 421-437, 438-463, 464-468)—XXXVI. The degree of dispersion of several erythro-products obtained in different ways from starch has been determined by measurements of diffusion and osmotic pressure. The products are polydisperse and the mean mol. wt. varies between 1700 and 534,000. Since all these substances are coloured red by I, there is no relation between this reaction towards I and the mol. wt.

XXXVII. Acetylation and subsequent deacetylation has little effect on some amyloses, whilst in certain amyloses the mol. wt. is reduced, although not to the limit of crystalloid dimensions. When amylose is heated in $C_{10}H_8$ at < 285° the products resemble the original substance in general properties, but the mol. wt. decreases as the duration of heating is prolonged. The products formed at 305° have greater reducing power and behave differently towards I.

XXXVIII. The degradation products of amylose form larger particles on ageing, but do not revert to the original substance. The viscosity and degree of hydration are lower. E. S. H.

Plant colloids. XXXIX. Thread-drawing power of starch solutions. M. SAMEC and B. BUDANKO (Kolloid-Z., 1934, 67, 258-264; cf. this vol., 637)—Thread-drawing power (I) is observed in fairly conc. starch solutions and in amylopectin fractions, but not in amylose solutions. The length of the thread decreases with rising temp. and increases with increasing conen. up to a certain val. The (I) of amylopectin varies with the kind of starch used and is highest in the most strongly hydrated forms; (I) is increased simultaneously with the degree of hydration by adding alkali. Amyloses exhibit (I) when combined with EtOH and NaOH. The factors involved are association and solvation. E. S. H.

Physical chemistry of starch and breadmaking. XV. Sharp lower temperature limit of peptisation and its variability for the individual granules of a sample of starch. J. R. KATZ and E. A. HANSON. XVI. Repeptisation of retrogressed starch paste (in relation to the organised structure of the starch granule). J. R. KATZ and J. C. DERKSEN. XVII. Attempts to render the organised structure of the starch grain microscopically visible, particularly in lintnerised starch. E. A. HANSON and J. R. KATZ (Z. physikal. Chem., 1934, 168, 321-333, 334-338, 339-352; cf. this vol., 145).-XV. In the peptisation of starch with H₂O there is a well-defined lower temp. limit, T, below which peptisation does not occur even with much H_2O . In a sample of starch, T varies from one granule to another, and is the lower the smaller is the size of the granule. The frequency curve of T is characteristic of the sample, and the mean val. of T depends on the variety of starch. Apparently each granule has an organised structure which opposes swelling in peptisation and must be broken down for dispersion to occur. At 20° there are considerable differences between the amounts of Congo-red adsorbed from very dil. aq. solution by various starches. If the starch is previously heated the adsorption increases, apparently running parallel with the no. of granules which have become isotropic; even below T the granules have been changed by heating.

XVI. Starch which has been peptised and then retrogressed undergoes repeptisation at a much lower temp. than the native starch. Peptisation probably consists in conversion into a more voluminous and highly hydrated phase and the breakdown of the organised structure of the granule, which resists swelling.

XVII. Maceration experiments with aq. HCl at room temp. have shown that the starch granule consists of doubly-refracting, approx. isodiametric, cryst. blocks of about 1 μ in size disposed in tangential layers and also exhibiting a radial arrangement. The spaces between these units are occupied by another substance, perhaps amylopectin. The granules, of potato starch at least, also have an external membrane. R. C.

Equilibria between hydrocarbons. VI. A. A. VEDENSKI and S. G. VINNIKOVA. VII. A. V. FROST (J. Gen. Chem. Russ., 1934, 4, 120–123, 124–131).– VI. The equilibrium consts. for C_2H_4 - H_2 = C_2H_6 have been determined at 510° (Pd catalyst) and at 500° (Cr_2O_3 catalyst).

VII. The sp. heat, entropy, and ϕ' -potential of C_2H_4 and C_2H_6 calc. from spectroscopic data are in good agreement with the experimental vals. R. T.

Equilibrium between carbon monoxide, hydrogen, formaldehyde, and methyl alcohol. II. Reaction $CO + 2H_2 \Longrightarrow CH_3OH$. R. H. NEWTON and B. F. DODGE (J. Amer. Chem. Soc., 1934, 56, 1287—1291; cf. this vol., 146).—The equilibrium has been studied by a dynamic method with Cu–Zn catalysts at 225°, 250°, and 275° and 3 atm. The products are essentially H_2O and MeOH. The data accord with $\log_{10}K_{p_0} = 3724/T - 9\cdot1293 \log_{10}T + 0\cdot00308T + 13\cdot412$, which is based on thermal data. J. G. A. G.

Colour and nature of iodine solutions in dif-ferent solvents. E. CHIRNOAGA and (MLLE.) E. CHIRNOAGA (Z. anorg. Chem., 1934, 218, 273-300). Observations on the dialysis of solutions of I in KI show that these are kryptocolloidal, containing I in the form of amicrons invisible in the ultramicroscope. The adsorption of I' by I has been determined and the rate of cataphoresis measured. The violet solutions only are true solutions of I and the change from violet to brown is accompanied by a change of structure resulting in a colloidal solution containing numerous micelles. By the action of alkaloids, especially quinine and cinchonine, on the violet solution, a brown colloidal solution containing numerous ultramicrons is obtained. Irradiation by ultra-violet light produces a similar effect which is reversed when the radiation M. S. B. ceases.

Hydrolysis of iodine monochloride. F. A. PHILBRICK (J. Amer. Chem. Soc., 1934, 56, 1257— 1259).—The hydrolytic equilibrium represented by $5ICl_2'+3H_2O \Longrightarrow 2I_2+IO_3'+6H^*+10Cl'$ has been examined in < 0.07N solution at 25°. In chloride solution, I monochloride is present chiefly as ICl_2' which dissociates into I' and Cl' with increasing dilution. This dissociation is negligible in conc. HCl. J. G. A. G.

Displacement of selenium by sulphur. M. LEMARCHANDS and M. BRUTEL (Bull. Soc. chim., 1934, [v], 1, 388-390).—S displaces Se from SeO₂ dissolved in H₂SO₄: 2S+3SeO₂ \implies 3Se+2SO₃. The reaction is too slow to be observed below 87°. At 100° the reaction reaches equilibrium in < 50 min., giving a green solution of Se in H₂SO₄. With rising temp. the equilibrium moves to the left, the reaction from left to right being exothermic. The heat of reaction of S on SeO₂, as calc. from thermochemical data, is approx. 18,800 g.-cal., and from van 't Hoff's relation it is 16,000 g.-cal. between 100° and 130°. No replacement of Se by S in Na₂SeO₃ has been observed.

M. S. B.

Electron-sharing ability of organic radicals. VII. Dissociation constants of organic acids and amines in water, methanol, and ethanol. L. D. GOODHUE and R. M. HIXON (J. Amer. Chem. Soc., 1934, 56, 1329—1333).—Measurements have been made in MeOH at 25° by methods analogous to those used for aq. solutions (a vac. tube potentiometer arrangement is used to eliminate the high internal resistance). pK_a and pK_b vals. are: AcOH 9.34, $p-C_6H_4Me\cdotCO_2H$ 9.33, BzOH 9.12, $p-C_6H_4Br\cdotCO_2H$ 8.74, $m-C_6H_4Cl\cdotCO_2H$ 8.57, NH_2Bu^a 4.92, $o-C_6H_4Cl\cdotCH_2\cdotNH_2$ 6.61, $p-C_6H_4Me\cdotNH_2$ 10.0, NH_2Ph 10.53, $m-C_6H_4Cl\cdotNH_2$ 12.14, and 2-cyclohexyl- 4.89, 2-benzyl- 5.42, 2-p-tolyl- 5.68, and 2-phenyl- 5.83, -pyrrolidines. Calc. vals. for RCO₂H and NH_2R in H_2O , MeOH, and EtOH agree generally with the determined vals. (above; Goldschmidt et al., A., 1922, ii, 135; 1924, ii, 825; 1926, 577). H. B.

Influence of sugars on the dissociation of boric acid. F. J. BERENSCHTEIN and L. N. AJZENBERG (Ukrain. Chem. J., 1933, 8, 307–315).—Fructose (I) has practically the same effect as mannitol in augmenting the dissociation of H_3BO_3 (II); the magnitude of the effect is greatest with 2 mols. of (I) per mol. of (II), and increases with the concn. Sucrose has no action, whilst that of maltose, lactose, glucose, erythritol, and galactose increases in the order given, being, however, considerably < that of (I). R. T.

Molecular size and phase distribution. III. J. N. BRÖNSTED and P. COLMANT (Z. physikal. Chem., 1934, 168, 381–390; cf. A., 1931, 1119, 1221).— Equations are derived for the activity coeffs. of the components of binary mixtures of non-electrolytes. These have been tested by v.-p. mcasurements for binary mixtures of Bu^a n-valerate and Bu^a sebacate with C_6H_6 and PrBr. R. C.

Activity. The cell Pb amalgam $|PbSO_4|$ CuSO₄ |Cu amalgam. A. LEBETTRE (J. Chim. phys., 1934, 31, 348-360).—The amalgam in each case consists of two phases and the e.m.f. remains const. so long as [Pb] lies between 2 and 6% and [Cu] between 3 and 5%. For concns. of CuSO₄ < 0.011*M*, Debye's theory, as modified by La Mer and others, is applicable. Experimental verification is not possible below 0.001*M* because the solubility of PbSO₄ then becomes important. The ionic radius is approx. 2.4 Å., but increases slightly with rise of temp. The results verify Quintin's conclusions (A., 1933, 468, 781). M. S. B.

Free energy of formation of lead amalgams. C. S. HOYT and G. STEGEMAN (J. Physical Chem., 1934, 38, 753—759).—From measurements of the e.m.f. of cells Pb|PbSO₄|ZnSO₄|PbSO₄|PbHg (satd.) and PbHg (unsatd.)|PbSO₄|ZnSO₄|PbSO₄|PbHg (satd.), the free energy of formation of Pb amalgams, and the activities of Pb and Hg, up to a mol. fraction of approx. 0.5, have been computed. The amalgam is saturated at 0.0142 mole fraction Pb, and all amalgams between this concn. and 0.66 have the same potential (same solid phase present). The heat of dissolution of Pb in unsaturated amalgams has been calc. from the temp. coeff. of the e.m.f. R. S. B.

Thermodynamic properties of fused salt solutions. VIII. Lead chloride in silver chloride. E. J. SALSTROM (J. Amer. Chem. Soc., 1934, 56, 1272– 1275).—The e.m.f. of the cell Ag(s)|0.0-0.9 mol. fraction PbCl₂ in $AgCl(l)|Cl_2(g)$ has been determined in the range $460-620^\circ$, and vals. of the activity, activity coeff., free energy and heat of formation, and partial mol. free energy are calc. for 500° and 600°. The activity of AgCl is in accord with Raoult's law in the range studied. The density of equimol. mixtures in the range $428-576^\circ$ is given by d=5.547-0.00128tand the contraction on mixing is < 0.2% at 500°. J. G. A. G.

Free energy change in the reaction between nitrogen peroxide and solid potassium chloride. C. W. WHITTAKER and F. O. LUNDSTROM (J. Amer. Chem. Soc., 1934, 56, 1323).—The most recent data lead to -6042 and -5502 g.-cal. for the free energy change in the reaction $\text{KCl}(s)+2\text{NO}_2(g)=\text{KNO}_3(s)+$ NOCl(g). J. G. A. G.

Lattice energies of ferrous halides and the nature of the radical $Fe^{II}(CO)_4$. W. HIEBER and E. LEVY (Z. Elektrochem., 1934, 40, 291-295; cf. this vol., 734).—Theoretical. In the $Fe(CO)_4$ halides the entry of CO does not appreciably affect the state of polarisation of the halogen atoms. The observed gradation of stability from Cl to I is adequately accounted for by lattice expansion.

F. L. U. Heats of dilution of salts. (MILE.) M. QUINTIN (Compt. rend., 1934, 198, 1856—1858).—An expression is derived for the mol. heats of dilution (I) of an electrolyte in terms of the temp. coeff. of e.m.f. and applied to the case of $CuSO_4$ (cf. A., 1933, 468, 781; this vol., 367). Vals. of partial and integral (I) are tabulated and compared with theoretical and calorimetrically determined vals. B. W. B.

Thermal dissociation of certain oxides and peroxides. VI. Rubidium and cæsium peroxides. M. BLUMENTHAL (Rocz. Chem., 1934, 14, 233-238).—Data for the oxides Rb_2O_2 , m.p. 570°, Rb_2O_3 , m.p. 489°, Rb_2O_4 , m.p. 412°, Cs_2O_2 , m.p. 594°, Cs_2O_3 , m.p. 502°, and Cs_2O_4 , m.p. 432°, indicate that the reactions $2M_2O_4 \implies O_2 + 2M_2O_3 \implies O_2 +$ $2M_2O_2$ are reversible only within certain temp. limits, above which association does not take place. R. T.

Thermal analysis of picrates. III. T. TUCHOL-SKI (Rocz. Chem., 1934, 14, 259—267).—Dehydration, fusion, and explosion temp. of the picrates of Cr, Mn, Fe^{II}, Fe^{III}, Co, and Ni are recorded. The following hydrates are indicated : Cr,2H₂O, Co,8H₂O, Ni,4H₂O, Fe^{III},4 and 5H₂O, Fe^{III},H₂O. The hydrates Co,5 and 9.5H₂O, Ni,2, 8, and 9.5H₂O, and Fe^{II},H₂O, recorded by other authors, are not confirmed. R. T.

System methyl thiocyanate-cobalt thiocyanate. J. GILLIS and A. DE SWEEMER (Natuurwetensch. Tijds., 1934, 16, 44–46).—The system shows a eutectic at -61.2° and 21.9% Co(CNS)₂, and a compound 2MeCNS,Co(CNS)₂ which is stable in contact with saturated solution up to about 38°, and forms greenish-blue crystals which evolve MeCNS when exposed to the air. H. F. G.

Thermal analysis of mixtures containing trinitrotrimethylenetriamine. T. URBAŃSKI and I. RABEK-GAWROŃSKA (Rocz. Chem., 1934, 14, 239— 245).—Neither solutions nor compounds are formed in the systems trinitrotrimethylenetriamine $p \cdot C_6 H_4 Me \cdot NO_2$, $-p \cdot NO_2 \cdot C_6 H_4 \cdot OMe$, $-1 \cdot C_{10} H_7 \cdot NO_2$, $-m \cdot C_6 H_4 (NO_2)_2$, $-s \cdot C_6 H_3 (NO_2)_3$, $-C_6 H_2 Me(NO_2)_3$, $-C_6 H_2 (NO_2)_3 \cdot OH$, tetryl, NPh₂·CO·NEt₂, NPh₂·CO·NMe₂, camphor, and NHPh₂. R. T.

System water-ether-alcohol. I. Freezing points. II. Densities at 0°. A. LALANDE (Bull. Soc. chim., 1934, [v], 1, 236—242).—Data are tabulated. No compound is formed between 0° and -125° . D. R. D.

X-Ray study of the system nickel-oxygenwater. E. OTT and R. W. CAIRNS (Z. Elektrochem., 1934, 40, 286; cf. A., 1933, 352).—A reply to criticisms by Le Blanc and Möbius (*ibid.*, 1013). The new lines observed relate to $Ni_2O_3, 2H_2O$. F. L. U.

Heterogeneous equilibrium in ternary systems composed of organic compounds. T. ASAHINA (Bull. Chem. Soc. Japan, 1934, 9, 222–235).—Phase diagrams are given for the system β -C₁₀H₇·OHmethylenedioxybenzylideneacetophenone-picric acid. R. S. B.

Reciprocal salt pair $NH_4NO_3+KCl \implies KNO_3$ + NH_4Cl at -10° and -15°. I. KRITSCHEVSKI and E. GOLDMANN (Z. anorg. Chem., 1934, 218, 253-254).—Equilibrium diagrams indicate that the prep. of KNO_3 from NH_4NO_3 and KCl at temp. below -10° is not technically practicable. M. S. B.

Field of saturation with regard to potassium and sodium chloride in quinary sea-salt systems. III. D. LANGAUER and W. OLPIŃSKI (Rocz. Chem., 1934, 14, 246—249).—Data at 83° and 95° are given for solutions saturated with respect to NaCl and KCl, and containing various proportions of MgCl₂ and MgSO₄. R. T.

Conductivities of dilute sulphuric acid solutions in anhydrous acetic acid $[at 25^{\circ}]$. B. V. WEIDNER, A. W. HUTCHISON, and G. C. CHANDLEE (J. Amer. Chem. Soc., 1934, 56, 1285—1287).—Anhyd. AcOH with sp. conductivity as low as 0.40×10^{-8} mho has been prepared. The mol. conductance of $0.35-0.0_529M$ - H_2SO_4 in anhyd. AcOH is independent of the conductivity of the AcOH except at high dilutions (cf. A., 1933, 230). J. G. A. G.

Iron complexes. II. Electrical conductivity of the system $nFeCl_3-mH_3AsO_4[-xH_2O]$. B. RICCA and R. LAMONICA (Gazzetta, 1934, 64, 294— 296).—Conductivity data indicate the formation of the strong *acid* H₃[FeCl₃(AsO₄)]'', the Ag *salt* of which has been isolated by pptn. D. R. D.

Anhydrous hydrazine as an ionising medium for electrolytes and non-electrolytes. II. Behaviour of aromatic nitro-compounds and typical half-electrolytes. P. WALDEN [with H. HILGERT] (Z. physikal. Chem., 1934, 198, 419-467; cf. A., 1933, 907).-Conductivity measurements have been made at dilutions up to ~ 5000 litres for aromatic NO₂-compounds, carboxylic acids, and phenols. The NO₂-compounds form strongly coloured, highly conducting solutions, which obey Kohlrausch's squareroot law and have conductivity-dilution curves similar to those of typical salts. The colour of the dil. solution is usually the same as that of the solid mol. compounds formed by the NO2-compound with aromatic amines. The vals. of λ_{∞} for NO_2 -, $(NO_2)_2$ -, and $(NO_2)_3$ -compounds are approx. in the ratio 1:2:3, and approximate to those for the mono-, di-, and tri-carboxylic acids, respectively. Transport experi-ments show that the coloured ion is an anion and contains the NO2-compound. The process of ionisation apparently consists in the transfer of an electron from solvent to solute: $ArNO_2 + N_2H_4 \rightleftharpoons$ $ArNO_2, N_2H_4 \Longrightarrow ArNO_2' + N_2H_4'$, the solvate being formed by a semipolar linking effected by juxtaposition of NO_2 and the amino-residue. In solutions of carboxylic acids and phenols the ionisation is $\begin{array}{ll} \mathrm{HA} \rightleftharpoons \mathrm{H}^{*} + \mathrm{A}^{\prime}, \mathrm{H}^{*} + \mathrm{N}_{2}\mathrm{H}_{4} \Longrightarrow \mathrm{N}_{2}\mathrm{H}_{5}^{*}. & \mathrm{The \ electro-}\\ \mathrm{lytic \ character \ of \ NO_{2}\ compounds \ dissolved \ in \ \mathrm{N}_{2}\mathrm{H}_{4}}\\ \mathrm{may \ be \ increased \ by \ substitution, \ e.g., \ of \ aromatic \ H}\\ \mathrm{by \ OMc \ or \ CO_{2}Me, \ to \ an \ extent \ which \ depends \ on \ the}\\ \mathrm{position \ of \ the \ substituent.} & \mathrm{R. \ C.} \end{array}$

Platinum electrode. A. FRUMKIN and A. SCHLIGIN (Compt. rend. Acad. Sci., U.R.S.S., 1934, 2, 173—179).—Polarisation and adsorption data for Pt electrodes in H_2SO_4 are recorded and discussed. W. R. A.

Electrode capacity in the presence of foreign ions and the electrocapillary capacity of mercury. N. THON (Compt. rend., 1934, 198, 2149—2151; cf. this vol., 718).—A discussion of the effects of ions other than those of the electrode metal. The difference between the a.-c. electrode capacity of Hg and that deduced from (static) electrocapillary curves is attributed to hindrance of dipole orientation in the double layer. B. W. B.

Diffusion potentials between solutions of hydrogen and potassium chlorides. V. CUPR (J. Chim. phys., 1934, 31, 326—347).—An apparatus for the determination of diffusion potentials is described. Quinhydrone electrodes are used and corr. for salt effect. The activity of H' in dil. HCl increases with the concn. of KCl, independently of the concn. of HCl when this is < 1.0N. HCl thus appears to be completely dissociated at these concns. and the diffusion potentials (I) between aq. HCl of different concns. below 1.0N can be calc. from Nernst's formula. Taking this into consideration, and neglecting (I) between aq. KCl of different concns., (I) between aq. HCl containing KCl may be calc. M. S. B.

Electrometric behaviour of thallium elements. L. W. ÖHOLM (Finska Kem. Medd., 1934, 43, 25– 44).—Investigations have been made of Tl elements of the type Tl|Tl^I salt, Hg^I salt|Hg, the negative pole being a rod of Tl for the SO_4'' and Cl' cells and 55% Tl for the Br' and I' cells. Measurements over long intervals and at different temp. show that the e.m.f. tends to diminish with time and that the temp. coeffs. are positive. The differences in the heats of formation of the corresponding Tl^I and Hg^I salts are deduced and agree with thermal measurements.

H. S. P.

Potentiometric study of photo-flavin. K. G. STERN (Biochem. J., 1934, 28, 949—964).—Photohepatoflavin (I) is a perfectly reversible redox system with a normal potential of -0.227 volt at $p_{\rm H}$ 7.0. At low $p_{\rm H}$ vals, there is a break in the titration curves, indicating that the oxidation takes place in two steps, the intermediate probably being a semiquinone. (I) appears to be identical with Warburg's photo-yeastflavin. It is suggested that photoflavin is related to the alloxazine structure. C. G. A.

Polarographic studies with the dropping mercury cathode. XXXIX. Electro-reduction of some alkaloids. J. PECH. XL. Lowering of the hydrogen over-potential by some organic substances. P. HERASYMENKO and I. ŠLENDYK (Coll. Czech. Chem. Comm., 1934, 6, 190-202, 204-210).—XXXIX. The H overvoltage (I) in acid solutions is catalytically lowered 0.2-0.3 volt in presence of the quinoline alkaloids (II), whilst isoquinoline alkaloids (codeine, morphine) increase (I). In presence of NH_4^{\bullet} , H[•] is discharged catalytically in solutions of (II) about 0.4 volt more positive than NH_4^{\bullet} .

 NH_4 . XI. The catalytic lowering of the H overvoltage by (II) is perceptible in high dilutions. With increasing voltage the "catalytic" current reaches a steady val., and normal deposition of H occurs. The effect is attributed to a reduction product of (II). J. S. A.

Electrolytic properties of hydrogen. I. Hydrogen as an anodic depolariser. II. Effect of anodic polarisation of the platinum electrodes. J. A. V. BUTLER and G. ARMSTRONG (J.C.S., 1934, 743-750).-H₂ liberated in the cathodic polarisation of bright Pt electrodes in H2-saturated solutions with small currents passes into the Pt. The H₂ in solution behaves similarly without cathodic treatment, but the process is slow. During subsequent anodic polar-isation, there is a change at $\varepsilon_{\rm H} = +0.5$ volt, which is attributed to ionic dissolution of the H₂ contained in the Pt. No depolarisation effects could be traced to the H₂ of the solution. Successive anodic polarisations of a bright Pt electrode to +1.26 volts, when adsorption of O_2 begins, produces depolarisation at the reversible H, potential. The effect is increased by stirring. Such an activated electrode is reversible and the cathodic current-voltage curve is linear. It is suggested that the thermionic work function of the Pt is reduced, and the adsorption and subsequent ionisation of H₂ facilitated by the anodic treatment, probably during the formation or reduction of the 0_2 film. R. S.

Historical development of passivity research and critical discussion of different passivity theories. W. MACHU (Oesterr. Chem.-Ztg., 1934, 37, 109-112).

Activation energy of unimolecular reactions. H. GERSHINOWITZ and O. K. RICE (J. Chem. Physics, 1934, 2, 273—282).—Using the principle of microscopic reversibility, unimol. decomps. are considered from the point of view of the reverse reaction, which is a bimol. association. An explicit expression for the activation energy in terms of the energy of reaction and the thermal properties of the mols. is obtained. The calculation of the rate const. as a function of the pressure is discussed. N. M. B.

I. Determination of speed of flames and the temperature distribution in a spherical bomb from time-pressure explosion records. II. Determination of heat capacity of explosive gases. III. Heat capacity of gaseous ozone. B. LEWIS and G. VON ELBE (J. Chem. Physics, 1934, 2, 283–290, 291–293, 294–295).—I. By the method described, flame speed can be evaluated at any moment during its progress from the centre of the bomb outwards, as well as the temp. in the unburned phase, the temp. immediately behind the flame front, the temp. gradient from the latter point to the centre, and the pressure in the bomb. The vol. occupied by the products for a given burned fraction can be found before and after expansion, and when combustion is complete. Data are tabulated for O_2 - O_3 mixtures. The temp. gradient does not affect the sp. heat results as calc. from the final temp. found from the max. pressure by means of the gas laws (cf. A., 1933, 343, 350, 368).

II. An application of the method given above to the determination of heat capacity up to several hundred degrees is given. The method is applicable to easily decomposed gases and to CO_2 at high and low temp.

III. Using the above method the heat capacity of O_3 in the range $300-476^\circ$ abs. is 10.94 g.-cal. per mol., against the val. 10.39 obtained from band spectra. Causes of the discrepancy are discussed. N. M. B.

Kinetics of reactions of heavy hydrogen. H. W. MELVILLE (Nature, 1934, 133, 947).—With excess H_2 at room temp. H^1 and H^2 atoms produced photochemically react with O_2 at the same speed. With excess of O_2 there is a difference due solely to collision frequency factors between the Hg atoms and the H_1^1 , H^1H^2 , H_2^2 , and O_2 mols. In the hydrogenation of O_1^1 and O_2^2 mols. In the hydrogenation of C₂H₂ and of N₂O and in the reduction of CuO by atoms there is no difference in the rate of reaction of the two isotopes. CuO is reduced at different speeds with H_2^1 and H_2^2 , the separation decreasing with a rise in temp. In the H_2-O_2 reaction where chains are propagated separation occurs at higher temp.; at 339° with a 2:1 mixture at 5 mm. pressure, the rate of reaction for a 66% H_2^2 mixture is 1.26:1, falling to 1.10:1 at 421°. In the H_2-N_2O and $H_2-C_2H_2$ reactions no separation occurs. The results show that H^1 and H^2 atoms react at the same speeds in the gas phase, but where the determination of rate involves a mol. or interaction of an adsorbed atom on a surface, the greater reactivity of H₂ is due mainly to the difference in zero point energies of H_2^1 and H_2^2 .

L. S. T.,

Synthesis of tetradeuteromethane. H. C. UREY and D. PRICE (J. Chem. Physics, 1934, 2, 300).—The ratio of the velocities of the reactions of H₂O and H₂O with Al_4C_3 is approx. 23 : 1. N. M. B.

Para-ortho-hydrogen conversion by the hydrogen iodide reaction and by iodine atoms. E. J. ROSENBAUM and T. R. HOGNESS (J. Chem. Physics, 1934, 2, 267—272).—From the rate of conversion, determined in presence of equilibrium concess. of HI and I₂, velocity coeffs. and collision efficiencies for the conversion by I atoms are calc., in agreement with Wigner's theoretical equation (cf. A., 1933, 1257). N. M. B.

Explosion of CS₂-NO mixtures. III. J. A. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1934, 53, 760—768; cf. A., 1933, 355, 910).—A method for measuring the intensity of light as a factor of time during the explosion is described. The max. intensity is attained after about $1-2\times10^{-2}$ sec., depending on the conditions. In the mixture $S_2:NO=1: 2\cdot25$ at 14 cm. total pressure the velocity of propagation is about 3 m. per sec. E. S. H.

Thermal decomposition of gaseous methyl iodide. E. W. R. STEACIE and R. D. MCDONALD (Canad. J. Res., 1934, 10, 591).—The reaction proceeds at a measurable rate above 450°, but is too complicated to give any trustworthy data on the kinetics. O. J. W. Homogeneous unimolecular decomposition of gaseous alkyl nitrites. II. Decomposition of ethyl nitrite. E. W. R. STEACIE and G. T. SHAW (J. Chem. Physics, 1934, 2, 345—348).—The thermal decomp. is homogeneous and of the first order between 190° and 240° and at pressures down to 5 cm. The main reaction is $EtNO_2 = NO + 0.5MeCHO + 0.5EtOH$. The reaction rate is given by $k=1.39 \times 10^{14}e^{-37,700/RT}$ sec.⁻¹ H. J. E.

Induction periods in chemical reactions. Action of phosphorous acid on alkali bromate and iodate. P. NEOGI, B. N. SEN, and A. MUKHERJEE (J.C.S., 1934, 767-769).—The influence of concn. and temp., and the effect of the addition of alcohols, HCl, Na₂S₂O₃, S sol, and salts, on the induction period of the reduction of alkali bromates and iodates by H_3PO_3 have been determined. The reaction is homogeneous. R. S. B.

Kinetic study of hydrolysis of esters by water. I, II. A. KIRRMANN (Bull. Soc. chim., 1934, [v], 1, 247—254, 254—259).—Hydrolysis of allyl pyruvate (I), Et pyruvate (II), allylidene acetate (III), and propylidene acetate (IV) proceeds in two concurrent ways, one unimol. and spontaneous (velocity coeff. k), the other with a velocity \propto [H^{*}] (proportionality const. b). At 25°, for (I), k=0.062, b=8; for (II), k=0.025, b=10; for (III), k=0.010, b=8; and for (IV), k= 0.004, b=7, the units being g.-mols., litres, and hr. These results support the view that an alkoxyl rather than an alkyl group is eliminated. D. R. D.

Mechanism of substitution reactions. A. R. OLSON and F. A. LONG (J. Amer. Chem. Soc., 1934, 56, 1294—1299; cf. this vol., 35).—Assuming that *l*-chloro- (I) and *l*-bromo-succinic (II) acids have the same configuration and that configurative inversion occurs at every substitution, the following velocity coeffs. at 50° have been determined in aq. 2N-H^{*} solution using 0·178*M*-*l*-(I) and -*l*-(II); (1) *l*-(II)= fumaric acid +H^{*}+Br' 0·0000305 (g.-mol. per litre, min.), (2) *l*-(II)+Br'=*d*-(II)+Br' 0·00164, (3) *l*-(I)+Cl'=*d*-(I)+Cl' 0·0000106, (4) *l*-(I)+Br'=*d*-(II)+ Cl' 0·000047 and (5) *l*-(II)+Cl'=*d*-(I)+Br' 0·000233. Within experimental error (approx. 1%) replacement without inversion does not occur. J. G. A. G.

Chlorinated fatty acid soap. I. Neutralisation and substitution of chlorostearic acid by alkali. II. Surface tension of aqueous chlorostearic acid soap solutions. Y. TANAKA, R. KOBAYASHI, and T. TAKAYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 197B, 197—198B).—I. The rate of reaction between a chlorostearic acid (I) and alkali depends on the rate of substitution, as neutralisation of CO_2H is very rapid, and is given by $dz/dt=k(a-z)^4$, where a is the initial concn. of (I) and z that of chlorohydroxystearic acid (II) at time t; k=1.84-2.2 for (I) containing 33% of Cl, reacting at the b.p.

II. The surface tension of 0.25% aq. solutions of the Na salts of (I) and (II), containing varying amounts of Cl and OH, ranges from about 48.5 to 53 dynes per cm. at 22° (cf. 62.3 for 0.25% aq. Na stearate).

Velocity of the reaction between sodium chloroacetate and sodium hydroxide. H. M. Dawson and W. Lowson (Proc. Leeds Phil. Soc.,

E. L.

1934, 2, 544—548; cf. A., 1933, 1276).—Using equiv. quantities of reactants the reaction is bimol. In experiments at 25° in which the CH₂Cl·CO₂' was present in excess, k remained practically const. until 70% NaOH had been used, and then increased appreciably. On addition of NaCl the initial vals. of k were increased from 1·10 to 1.48×10^{-4} , but again an increase was observed when 70% NaOH had disappeared. The latter stages of the reaction cannot be represented by CH₂Cl·CO₂'+OH' \longrightarrow OH·CH₂·CO₂'+Cl'. Available data for the hydrolysis of CH₂Br·CO₂Na (Dawson and Dyson, A., 1933, 234) suggest that reactions between CH₂Cl·CO₂' and H₂O, pairs of CH₂Cl·CO₂', and CH₂Cl·CO₂' and OH·CH₂·CO₂' play an important role when [OH'] is small. W. R. A.

Kinetics of the alkaline hydrolysis of the halogen-substituted acetates. H. M. DAWSON and E. R. PYCOCK (J.C.S., 1934, 778—783).—The velocity, v, of hydrolysis of CH₂X·CO₂Na (X=Cl or Br) by NaOH at 45° is given by $v=v_A+v_B+v_C+v_D=k_A[CH_2X\cdotCO_2'][OH']+k_B[CH_2X\cdotCO_2'][H_2O]+k_C[CH_2X\cdotCO_2']^2+k_D[CH_2X\cdotCO_2'][CH_2(OH)\cdotCO_2']$, where k_A — k_D are consts. Departures from the binol.

where k_{A} — k_{D} are consts. Departures from the bimol. formula $v=v_{A}$ were observed and successfully interpreted for the late stages of hydrolysis in the absence of excess of alkali and for the initial stages with equiv. reactants. R. S. B.

Dilatometric studies in the hydrolysis of the 2:5-diketopiperazines and polypeptides. I. Alkaline hydrolysis of glycine and alanine anhydrides. M. SRINIVASAN and M. SREENIVASAYA (J. Biol. Chem., 1934, 105, 563-570).—Alkaline hydrolysis of glycine (I) and alanine (II) anhydrides is accompanied by an increase in vol. which is not in accordance with the NH₂ liberated; the divergence increases with the concn. of the alkali. Hydrolysis of (I) by > 0.01N-alkali is accompanied by a disruption of the resulting dipeptide which does not occur in the case of (II). H. G. R.

Velocity of detonation of solid explosives. R. SCHWOB (Compt. rend., 1934, 198, 1990–1992).— The expression $V=1/(m-n\Delta^{1/3})$ (V=velocity of detonation, $\Delta =$ charge density, *m* and *n* are consts.) is derived. Application to Friederich's results (B., 1933, 493) for four nitrated explosives gives agreement to approx. $\pm 2\%$ for $\Delta 0.25$ —1.5. B. W. B.

Initiation of the detonation wave in solid explosives. W. E. GARNER (J.C.S., 1934, 720-722).—A study of the rate of decomp. of solid PbN_6 shows that the simultaneous decomp. of two adjacent mols. is an event possessing a probability of the same order as that of detonation, whereas simultaneous decomp. of > 2 adjacent mols. has a smaller probability. The no. of mols. forming a detonation centre cannot, therefore, exceed two. The character of the reaction interface in the detonating solid determines the rapidity with which the detonation wave is set up; e.g., Hg fulminate gives a diffuse interface, whereas that of PbN₆ is quite sharp, in agreement with their sp. explosive properties. A chain theory of the thermal decomp. of solid explosives is supported, and it is suggested that detonation occurs when two reaction chains intersect. O. J. W.

Calculation of heterogeneous reaction rates. [Decomposition of ammonia.] R. E. BURK (J. Amer. Chem. Soc., 1934, 56, 1279—1282).—The observed energy of activation of the decomp. of NH_3 (47,000—48,000 g.-cal. per mol.) at 1260—1480° abs. on W filaments "aged" at 2400° abs. for 1 hr. in vac. is consistent with the decomp. occurring uniformly on the dodecahedral faces of the W (A., 1933, 1098), and at such a rate that almost every vibration of the underlying W atoms with the requisite energy of activation leads to reaction. The effects of various factors not included in the calculation are considered. J. G. A. G.

Diatomaceous earth; equilibrium and rate of reaction in the system hydrated lime-diatomaceous silica-water. A. B. CUMMINS and L. B. MILLER (Ind. Eng. Chem., 1934, 26, 688-693). —Diatomite (I) reacts with $Ca(OH)_2$ more rapidly than other forms of SiO_2 , the liquid phase containing at equilibrium $CaO:SiO_2=2:3$, whilst the limit composition of the solid is $5CaO,6SiO_2,xH_2O$. The initial rate of reaction (II) depends on the fineness, heat treatment, etc., and approx. ∞ the vol. of the flocculated SiO_2 . Concrete made with (I) shows improved workability, roughly proportional to (II). J. S. A.

Action of nitric acid on tin. G. S. KASBEKAR and A. R. NORMAND (J. Univ. Bombay, 1933, 2, No. 2, 111—122).—Analytical data are given showing the influence of $[HNO_3]$, temp., and [Sn] on the reaction velocity and products. The amounts of Sn^{****} and N₂ formed are in linear relationship and increase with $[HNO_3]$ and rise of temp. R. S.

Influence of gelatin on the rate of dissolution of zinc. N. JERMOLENKO (Z. anorg. Chem., 1934, 218, 255—256).—Addition of a small quantity of gelatin, up to approx. 0.3%, greatly reduces the rate of dissolution of Zn in H₂SO₄, but further additions have very little effect. Gum arabie has a similar action. The action is not due to a diminution in the rate of diffusion, but probably to the formation of an adsorption layer of gelatin on the surface of the Zn. M. S. B.

Catalytic decomposition of hydrogen peroxide in an acid chlorine-chloride solution. II. Steady state function at 0-25°. B. MAKOWER (J. Amer. Chem. Soc., 1934, 56, 1315-1319; cf. this vol., 152).—The $[Cl_2]$ when the net reaction is $2H_2O_2 =$ $O_2 + 2H_2O$ in 2.84—5.25*M*-HCl at 25° has been determined by a distribution method. The vals. of the steady state function $R = [Cl_2]/[H^{\cdot}]^2[Cl']^2$ are in close accord at corresponding [HCl] with vals. calc. from the relation $R = k_1/k_2$ (I), where k_1 and k_2 are, respectively, the independently determined sp. rates of the reactions $H_2O_2+2H+2Cl'=Cl_2+2H_2O$ (II) and $H_2O_2+Cl_2=O_2+2H+2Cl'$ (III). Vals. of k_2 and Rbetween 0° and 25° using 3.84 M-HCl and other data (loc. cit.) show that the directly determined temp. coeff. of R is equal to that calc. by (I) from independently determined vals. of k_1 and k_2 , thus supporting the mechanism proposed. The heats of activation of (II) and (III) are 21,000 and 13,700±300 g.-cal., J. G. A. G. respectively.

Polymerisation products in concentrated hydrogen peroxide. E. H. RIESENFELD (Z. anorg. Chem., 1934, 218, 257–266).—The velocity of the H_2O_2 -KMnO₄ reaction at first increases with increasing $[H_2O_2]$, then falls, and finally rises again. The position of the max. and min. on the reaction velocity curve depends only on $[H_2O_2]$, so that the anomaly is due to the H_2O_2 mol. and not to the other reactants. H_2SO_4 accelerates the reaction at the max. and delays it at the min., whilst Mn^{••} catalyses the reaction strongly at the max. and less strongly at the min. It is concluded that H_4O_4 only is present in solutions of concn. > 500 milli-equiv. per litre, and H_2O_2 only at concn. < 5 milli-equiv., the two mol. species being in equilibrium at intermediate concns. M. S. B.

Catalysis of peroxide oxidations by ferrous ions. J. D. STIRLING (Biochem. J., 1934, 28, 1048-1062).-Experiments on the oxidation of tartaric acid, glucose, and inositol (I) indicate that production of Fe^{***} is a necessary preliminary to catalysis, the catalyst being actually a derivative of Fe^{III}. Regeneration of Fe^{II} is a side-reaction due to reduction of Fe^{III} by oxidation products, and with HCO₂H, the oxidation products of which are not further oxidisable, does not take place. It is probable that the Fe^{III} compound initially formed can donate O2 without change of valency. Oxidation is most favourably carried out by adding the requisite amount of H₂O₂ to a solution of the substrate (II) containing a trace of Fe". Formation of an ionisable complex of O₂ donator+(II) probably takes place. The first oxidation product of (I) gives a blue colour with Fe"

A. E. O.

Deactivation of chemically activated oxalic acid. K. WEBER (Z. physikal. Chem., 1934, B, 25, 363-371; cf. A., 1933, 792).—The reducing action of $H_2C_2O_4$ activated with KMnO₄ on HgCl₂ is decreased considerably by the presence of phenols or vat dyes, the reactivity of the $H_2C_2O_4$ decreasing exponentially with increasing concern. of foreign substance (I). The inhibiting action of (I) is the more pronounced the more positive is its normal reduction-oxidation potential. (I) undergoes no detectable chemical change. Baur's sensitisation-desensitisation theory (A., 1932, 578) affords a satisfactory explanation of these observations. R. C.

Catalytic influences in three-carbon tautomerism. III. Review of possible mechanisms, and further examination of catalysis by alkoxides. IV. Tautomeric changes of unsaturated acids at high temperatures. R. P. LINSTEAD and E. G. NOBLE. V. Acid catalysis in ketones and esters. G. A. R. KON and K. S. NARGUND (J.C.S., 1934, 610-614, 614-623, 623-629; cf. A., 1931, 438).—III. Three C tautomeric changes can proceed by at least three different mechanisms: (1) intramol., (2) removal of the mobile H by negative ions, (3) reversible addition of catalyst mols. The rôle of alkoxide ions in changes of type (2) is discussed in the light of new experimental evidence.

IV. The reversible interconversion of Δ^{a} - and Δ^{β} -unsaturated acids at their b.p. (cf. A., 1930, 1162) has been studied in the case of *n*-hexenoic, -pentenoic, and -butenoic acids in the pure state and in solution. In inert org. solvents the tautomeric change is inde-

pendent of the environment provided there is no secondary decomp. In aq. solution the change is greatly accelerated by inorg. substances. The effect of alkalis has been studied in detail.

V. The action of alcoholic mineral acids has been examined on the two equilibria involving the four isomeric homomesitones : CMeEt:CH-COEt (I) == CHMe:CMe·CH·COEt (II) and CMeEt:CMe·COMe (III) CHMe:CMe·CMe·COMe (IV). The order of catalytic activity is $HCl>H_2SO_4>H_3PO_4$. The mobility of (III) and (IV) is much < that of (I) and (II). In the latter pair the point of equilibrium is considerably nearer the Δ^{β} -side than the val. (67% Δ^{a} -) found with alkaline catalysts. Displacement of equilibrium towards the Δ^{g} -form was also observed in esters, viz., cyclopentylidene-, a-methylcyclopentylidene-, and cyclohexylidenc-acetic, and 3-methylpentenoic esters. The hexenoic esters are not isomerised at all in acid solution. The interconversion of esters with EtOH-HCl is complete only with very conc. acid. The simple ionic explanation of isomeric change is not supported. O. J. W.

Catalytic hydrogenation of organic halogen derivatives. M. MLADENOVIĆ (Bull. Soc. Chim. Yougoslav., 1933, 4, 187—196).—Monobromo- α -elemolic and -elemonic acid yield dihydro- α -elemolic and -elemonic acid on hydrogenation (Pd-black). The velocity of hydrogenation of aryl halides is greater in alkaline than in neutral media. R. T.

Organic catalysts. IX. Structure specificity of esterase models. W. LANGENBECK and J. BALTES (Ber., 1934, 67, [B], 1204-1209).—The rate of hydrolysis of Et H succinate (I), Et H malonate, and acetylmandelic acid is not influenced by the presence of benzoylcarbinol (II), which accelerates the hydro-lysis of Et H adipate. The specificity of the org. catalyst is quite different from that of OH' and is identical with that of esterase. w-Hydroxyacetophenone-4-carboxylic acid (III), m.p. 248-250° (decomp.), accelerates the hydrolysis of EtHSO4, but is less sp. than (II), since it causes slow but distinct hydrolysis of (I). Since restriction of the hydrolysis of Pr^aCO₂Me by glycollanilide is not caused by the presence of (I), it appears that, as in the case of esterase, there is no union of substrate and catalyst. The active group of esterases is alcoholic OH and the enzymes are therefore main valency catalysts. Similarly, carboxylase is a main valency catalyst with active NH2.

4-Aminoacetophenone is converted into the corresponding nitrile, hydrolysed by boiling H_2SO_4 (1:1) to acetophenone-4-carboxylic acid, m.p. 205°, whence (Br in AcOH) ω -bromoacetophenone-4-carboxylic acid, m.p. 220—221°, and (III) are obtained. H. W.

Optical activity in relation to tautomeric change. IV. Comparison of the rates of racemisation and of bromination of a ketone. C. K. INGOLD and C. L. WILSON (J.C.S., 1934, 773-777).-In accordance with theoretical predictions, the unimol. velocity coeffs. of racemisation and bromination of 2-o-carboxybenzylindan-1-one in 16N-AcOH in presence of 0-0.4N-HBr at 25° are identical.

R. S. B.

Active oxides. LXXIV. System zinc oxidecupric oxide as a catalyst of the decomposition of methyl alcohol. O. KOSTELITZ and G. F. HUTTIG (Kolloid-Z., 1934, 67, 265—277; cf. this vol., 606).— The yields of H₂, CO, CO₂, CH₄, C₂H₄, HCO₂H, CH₂O, and HCO₂Me obtained in the decomp. of MeOH over pastilles of different ZnO-CuO catalysts at 270°, 300°, and 320° have been determined. The results are not in accordance with the simple mixture rule. With rising temp. the yields of CO₂, CH₄, and CH₂O increase, whilst those of HCO₂H and HCO₂Me decrease. The kinetics of the process have been investigated. E. S. H.

Active oxides. LXXV. Active intermediate stages between an oxide mixture and the [resulting] chemical compound. G. F. HUTTIG, D. ZINKER, and H. KITTEL (Z. Elektrochem., 1934, 40, 306-313; cf. this vol., 371, 490).—The systems $ZnO-Fe_2O_3$, $BeO-Fe_2O_3$, $CaO-Fe_2O_3$, $MgO-Cr_2O_3$, and $MgO-Al_2O_3$ have been studied with respect to their catalytic activity in promoting the reaction $2CO+O_2=2CO_2$ as a function of the temp. of heating of the oxide mixture. Well-defined max. of activity are found corresponding with the formation of active intermediate forms. F. L. U.

Active oxides. LXVI. Methods and results of structure determination of active zinc oxides. G. F. HUTTIG [with, in part, H. SCHWARZER, O. HNEVKOWSKY, W. NESTLER, H. KITTEL, and O. KOSTELITZ] (Kolloid-Beih., 1934, 39, 277-333; cf. A., 1933, 774).—A summary of published work and new experiments on the prep. of active ZnO from ZnC_2O_4 , $ZnCO_3$, and $Zn(NO_3)_2$, the kinetics of the reactions, X-ray examination of structure, d, sorptive power for MeOH and for dye solutions, microscopical examination, sedimentation analysis, solubility, magnetic susceptibility, sp. heats, energy content, fluorescence, and catalytic properties. The characteristic properties of the different forms of active ZnO are not due to modifications in crystal structure, to space-lattice distortions, or to the presence of an amorphous component; the chief factors are (a) peculiarities in the pore systems, (b)faults in the crystals, and (c) the distribution of the different crystal planes in the total surface.

E. S.-H.

Kinetics of reaction between nitrous oxide and hydrogen at a silver surface. [Decomposition of nitrous oxide.] A. F. BENTON and C. M. THACKER (J. Amer. Chem. Soc., 1934, 56, 1300–1304).—In flow experiments at 60—180°, the rate of formation of H₂O, using 9—109 mm. N₂O and 17—111 mm. H₂, at a Ag catalyst reduced at 100°, is independent of [N₂O], increased by rise of [H₂], and retarded by H₂O which is strongly adsorbed. The temp. coeff. indicates an energy of activation of 13 kg.-cal. The reaction involves a primary decomp. of N₂O followed by interaction of H₂ with the adsorbed O. N₂O alone is decomposed by the catalyst at 60°, and in static experiments at 160° the N₂O is not appreciably adsorbed as such, but slowly decomposes into N₂ and an adsorbed O atom, which may react with another N₂O mol. to give gaseous O₂ and N₂. The O atoms (or possibly oxides of N) inhibit the ordinary activated adsorption of O_2 . J. G. A. G.

Mode of action of catalyst mixtures in decomposition of nitrous oxide. III. G. M. SCHWAB and H. SCHULTES. IV. G. M. SCHWAB and R. STAEGER (Z. physikal. Chem., 1934, B, 25, 411– 417, 418–440; cf. A., 1932, 689).—III. The catalysis of the decomp. by oxides and binary mixtures of oxides has been studied. The activity of a CuO-TiO₂ mixture is additively constituted of those of the constituents, whilst BeO reduces the activity of CdO slightly and that of CuO considerably. For CuO-CdO and CuO-Al₂O₃ mixtures the heat of activation is > that for either component, yet the catalytic activity is > corresponds with additivity.

IV. The decomp. on CuO is retarded by O_2 , and, at lower temp., by N_2O also. The heat of activation on a CuO-Al₂O₃ catalyst is > on CuO by about 3 kg.-cal., and N_2O and O_2 are adsorbed in comparable amounts at all the temp. studied. Cr₂O₃ reduces the activity of CuO considerably. The high activity of the CuO-Al₂O₃ catalyst is ascribed to the formation of a spinel on which the adsorption d is especially high. R. C.

Catalytic action of Japanese acid earth. XI. Relation between catalytic activity and adsorption. K. ISHIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 180—181B).—The conversion of $C_{10}H_8$ into $\beta\beta'$ -dinaphthyl by heating with Japanese acid earth at 300° is promoted by O-containing substances such as H₂O and alcohols, and poisoned by nitrogenous substances. The adsorption of H₂O and MeCN by the earth was studied, and it is probable that H₂O is able to displace MeCN. A. G.

Catalytic decomposition of sodium amalgam. I. A. S. FOKIN and M. A. RABINOVITSCH. II. P. B. SHIVOTINSKI and A. P. MASCHOVETZ. III. A. P. MASCHOVETZ and P. B. SHIVOTINSKI (Ukrain. Chem. J., 1933, 8, 355—365, 366—371, 372—380).— I. Decomp. of Hg-Na (I) by aq. NaOH is catalysed by reduced Fe, V, W, Ni, Mn, and by alloys of Fe with V, W, Si, Mo, Ti, Zr, and B, as well as by salts of V and W. Cast Fe has only a feeble action. Anhyd. EtOH reacts with (I) in presence of the above catalysts.

II. Inactivation of Fe-Si catalyst (II) is due to the covering of its surface with a suspension of Fe in Hg; (II) can be reactivated by shaking in an atm. of H₂. The activity of (II) falls with increasing Si content from 12 to 52%.

III. A continuous process for the electrolytic prep. of NaOH from NaCl, involving the catalytic decomp. of (I) in a side chamber, is described. R. T.

Change of chemical reactivity and catalytic activity of silica on loosening its lattice with ferric oxide. J. A. HEDVALL, R. HEDIN, and S. LJUNGKVIST (Z. Elektrochem., 1934, 40, 300—302; cf. A., 1931, 582).—Cristobalite containing 0.24%Fe₂O₃ in solid solution reacts with CaCO₃ at about 50° lower than when pure. When used as a catalyst in the thermal decomp. of EtOH to C₂H₄, the solid solution produces the same effect at 380° as does the pure substance at 460°. It has 0.1 of the catalytic activity of Pt-asbestos in promoting the reaction $2SO_2+O_2=2SO_3$, pure SiO_2 being inactive. F. L. U.

Catalysts for ammonia synthesis.—See B., 1934, 623.

Catalysts for conversion of carbon monoxide.— See B., 1934, 611.

Interaction of carbon monoxide and steam over iron catalysts. B. G. SIMEK and R. KASSLER (Chim. et Ind., 1934, 31, Spec. No., 330-337).-The part played by secondary reactions in the conversion of CO and H_2O into CO_2 and H_2 has been studied. As catalysts a reduced alumino-ferric contact and cast-Fe filings were used, both being activated by K₂CO₃. At 500° reduction of the oxide catalyst by CO stopped before the liberation of Fe. Fe formed by the re-duction of the catalyst by H_2 was re-oxidised by H_2O at 500° to a definite equilibrium ratio of $H_2: H_2^{\circ}O$ in the gaseous phase. Some C deposition occurred when CO was passed over the catalyst at 500°, and it is concluded that the main reaction $\rm CO+H_2O\longrightarrow$ CO_2+H_2 probably proceeds in stages, $2CO \longrightarrow C+CO_2$ and $C+H_2O \longrightarrow CO_2+H_2$. The amount of conversion passed through a max. as the rate of passage of the gases over the catalyst was increased, the rate giving max. conversion varying with the temp. The presence of H₂S adversely affected the conversion. A. B. M.

Catalytic hydrogenation of simple molecules by light and heavy hydrogen. H. W. MELVILLE (J.C.S., 1934, 797-805).—The kinetics of reaction of H_2 , and of H_2 - H_2 mixtures, with O_2 , N_2O , and C_2H_4 , and of H_2 with CO, have been studied on Ni wire at 100-300° at pressures 1-760 mm. H_2 reacts with N_2O and O_2 from 160° to 250° about twice as fast as H_2 , a difference attributable to the different zero point energies of Ni- H^1 and Ni- H^2 ; a similar variation with C_2H_4 cannot be given a quant. interpretation. It is inferred that the rate is controlled by the rate of migration of adsorbed H^1 or H^2 to adsorbed O atoms. Measurements on the Hg-photosensitised reaction between H_2^1 or H_2^2 and N_2O give almost equal rates for H_2^1 and H_{22}^2 , since the atoms are free and considerations of zero point energy do not enter.

R. S. B.

Catalytic properties of electrolytically deposited smooth layers of platinum metals. I. I. SHUKOV, A. A. GLAGOLEVA, and V. I. STRUKOVA (J. Gen. Chem. Russ., 1934, 4, 9—12).—The velocity of decomp. of H_2O_2 in presence of Au foil covered with Pt- or Ir-black is the same as for smooth layers of the metals, whilst Rh-black is approx. twice, and Pd-black 10 times, as active as in smooth layers. R. T.

Reactions of pyrogenous condensation. I. Kinetics of condensation of benzene. G. I. KRASNOKUTSKI and M. S. NEMTZOV (J. Gen. Chem. Russ., 1934, 4, 132—144).—Ph₂ in 0.5% yield is obtained by heating C₆H₆ in presence of Fe at 470°, and in 0.46% yield with Ni catalyst. The catalytic action of brass, Al, Cu, and Cr is considerably < that of Fe or Ni. The reaction is one of zero order in presence of Fe, and of the first order with Ni. The temp. coeff. of the reaction for the interval 450— 460° is 2.63 for active C, and about 2 for metallic catalysts. Dihydrodiphenyl is not a reaction product. The velocity of formation of $C_6H_4Ph_2$ is < that of Ph₂. Condensation is practically inhibited by high pressures of H₂. R. T.

Catalytic reduction of organic halogen compounds; 5-bromo-5-alkylbarbituric acids. G. K. HUGHES, A. K. MACBETH, and S. W. PENNYCUICK (J.C.S., 1934, 769—773).—The unimol. velocity coeffs., k, for the reduction of 5-bromo-5-alkylbarbituric acids by EtOH in excess in presence of colloidal Pt have been determined at 30°. The variation of k with change in alkyl group is small, except in the case of the Pr^{β} acid, for which k is abnormally large. k is not ∞ the concn. of EtOH, and is abnormal for variation in the concn. of Pt. Colloidal W gives a slower rate than Pt. R. S. B.

Catalysis in the pyrolysis of hydrocarbons. T. S. WHEELER (J. Univ. Bombay, 1933, 2, No. 2, 123—124).—Theoretical. It is suggested that catalytic activity is due to the presence of looselybound electrons at the surface. R. S.

Catalytic hydrogenation of aromatic hydrocarbons in solution in presence of nickelblack.—See this vol., 877.

Catalytic conversion of acetylene and acetaldehyde into acetone.—See B., 1934, 567.

Catalytic preparation of butaldehyde and butyl alcohol from acetaldehyde.—See B., 1934, 567.

Surface reaction between acetylene and iodine. C. P. ELLIS (J.C.S., 1934, 726—727).—Crystals of I kept in C_2H_2 for 2—3 days at 25° are converted into acetylene di-iodide. The rate of the reaction depends to some extent on the nature of the surface of the vessel used, but not to so marked a degree as in the reaction between C_2H_4 and I. O. J. W.

Energetics of catalysis. III. Poisoning coefficients of hydrogenation processes. E. B. MAXTED and V. STONE (J.C.S., 1934, 672-674; cf. this vol., 262).—The poisoning coeff., α , is a const. for the hydrogenation on a Pt catalyst of COPhMe, PhNO₂, C₆H₆, and oleic acid, using Hg^{**} ions as poison, and of COPhMe and C₆H₆ using CS₂ as poison. The vals. of α are approx. 2 and 8 for Hg^{**} and CS₂, respectively. O. J. W.

Depolymerisation of trisobutene.—See this vol., 864.

Separation of the hydrogen isotopes by electrolysis. I. B. TOPLEY and H. EYRING (J. Chem. Physics, 1934, 2, 217-230).—From the calc. equilibrium consts. of the reactions $H_2O+2H^2=H_2O+$ 2H and $H_2O+H_2^*O=2HH^2O$ an expression is obtained for the electrolytic separation coeff., valid when zeropoint energy and tunnelling are negligible in the activated state. The change of this coeff. with increase in concn. of H² is calc. Experimental vals., in the range 7.6-2.8, were determined for the separation coeff. at cathodes of Pb, Pt, Pt (black), Pt (activated), W, Fe, Ni, Cu, Ag, Hg, and Ga.

N. M. B. Continuous-flow methods of concentrating deuterium. L. C. ANDERSON, J. O. HALFORD, and J. R. BATES (J. Chem. Physics, 1934, 2, 342-344).-- H_2O is passed from an 8-litre Mariotte bottle through a no. of cells with Ni cathode and Fe anode arranged in series, and operated on the 110- or 220-volt supply. A method of recovering the gases evolved in electrolysis of partly heavy H_2O by combustion on Ptasbestos is described. H. J. E.

Preparation of deuterium oxide by electrolysis of water. K. SCHWARZ, L. KÜCHLER, and H. STEINER (Z. Electrochem., 1934, 40, 298-299).— Apparatus and procedure for preparing H.O by the electrolysis of 0.8N-NaOH are described.

F. L. U. Electrodeposition of tin from sodium stannate solutions with the use of insoluble anodes.—See B., 1934, 583.

Electrolytic separation of tantalum from aqueous solutions. N. ISGARISCHEV and A. F. PREDE (Z. Elektrochem., 1934, 40, 295–297; cf. A., 1933, 681).—Cathodic deposition of Ta is possible from acid solutions containing glucose, K salicylate, or resorcinol, provided no diaphragm is used. The current yield is $\ge 0.16\%$. F. L. U.

Electrolysis of sodium nitrate in liquid ammonia solution. N. KAMEYAMA and H. MORI (J. Soc. Chem. Ind. Japan, 1934, 34, 167–168B).— NaNO₃ when electrolysed in liquid NH₃ at -40° to -47° with Pt electrodes at c.d. 0·1 amp. per sq. cm. gives N₂ at the anode and NaNO₂ with a little NaOH and H₂ at the cathode. The reaction is $3NaNO_2+$ $2NH_3=3NaNO_2+N_2+3H_2O$. R. S. B.

Reduction of oxygen to hydrogen peroxide by the irradiation of its aqueous solution with X-rays. H. FRICKE (J. Chem. Physics, 1934, 2, 340).—O₂ dissolved in H₂O yields H₂O₂ on irradiation with X-rays, the amount of H₂O₂ being independent of the O₂ pressure and falling to approx. 50% of its val. in acid solution at $p_{\rm H} > 8$. H. J. E.

Colour changes in light and darkness of ammonium thiocyanate solutions. B. S. V. R. RAO (J.C.S., 1934, 880—881).—The colour changes undergone by conc. aq. NH_4CNS in light and darkness are due to reversible oxidation and reduction processes associated with the presence of Fe as impurity. R. S. B.

Errors in the photographic method of comparing light intensities. J. T. LAY and I. C. CORNOG (J. Opt. Soc. Amer., 1934, 24, 149—154).— The causes and magnitudes of errors due to variations in density over the plate caused by its irregular structure and uneven development were investigated. N. M. B.

Photographic sensitivity after the Herschel effect. J. M. BLAIR (J. Opt. Soc. Amer., 1934, 24, 155-156).—An emulsion when exposed to white and then to red light fully regains its original sensitivity. N. M. B.

Photographic inversion due to simultaneous action of two different radiations. V. DOLEJŠEK and A. NEMEJCOVÁ (Compt. rend., 1934, 198, 2081— 2082; cf. A., 1932, 29).—Inversion was produced when photographic plates were exposed successively to two different radiations in the following orders: X-W, C-W, X-H, C-H, C-X (X=X-rays, W=white light, C=cathode-rays, H=heat rays). In all except the last case, it was essential to expose to the shorter λ first. The effects were not due to solarisation. B. W. B.

Influence of anti-oxygens on the sensitivity of photographic emulsions. A. CHARRIOU and (MILE.) S. VALETTE (Compt. rend., 1934, 198, 2078-2080; cf. B., 1933, 333).—The following fluorescencesuppressing anti-oxygens decreased sensitivity (I) and contrast when incorporated in an emulsion : resorcinol, guaiacol, PhOH, NH₂Ph, Na salicylate, and PhNO₂. NHPh₂ reduced (I) only. In all cases the effects were < those produced by KI. B. W. B.

Reaction produced by light of very short wavelength. F. PALMER, jun. (J. Chem. Physics, 1934, 2, 296—297).—Light from a capillary discharge tube containing H_2 at 1—2 mm. pressure, when passed through a fluorite window into air at atm. pressure, causes the formation of a film of unknown nature on the outside of the window. N. M. B.

Catalysis of acetylene polymerisation in ultraviolet light by mercury vapour. F. TOUL (Coll. Czech. Chem. Comm., 1934, 6, 162-189).-Pure C2H2 (prep. described) does not polymerise in sunlight either alone, when mixed with N2, or in presence of Hg. Slow polymerisation takes place in ultraviolet light even in the purest C2H2, the reaction being catalysed by Hg vapour, with which an equilibrium is reached when approx. 10% of the C_2H_2 has polymerised. This reaction is not due to photosensitisation, and is still observed with a source not containing the Hg lines. Pure dry C2H2 after irradiation with cathode rays causes condensation of H₂O when mixed with undried C₂H₂ up to 60 min. after exposure. No effects were observed on exposure to X-rays. Some properties of the polymeride are described. A. A. L.

Primary photochemical reactions. IV. Decomposition of methyl ethyl ketone and methyl butyl ketone. R. G. W. NORRISH and M. E. S. APPLEYARD (J.C.S., 1934, 874—880).—Light of $\lambda 2200$ —3000 Å. decomposes (1) COMeEt giving (a) (70—80%) $\frac{1}{3}(C_2H_6+C_3H_8+C_4H_{10})+CO$ and (b) (20—25%) C_2H_4 +MeCHO, (2) COMeBu giving COMe₂+CHMe:CH₂. It is inferred that (a) occurs by the formation of free radicals. The mechanism by which the energy of the chromophoric group (CO) is transferred to the other groups is discussed. R. S. B.

Photochemical studies. XVII. Chlorination of chlorobenzene; a comparison with benzene. E. J. HART and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1934, 56, 1305—1310; cf. this vol., 40).—The gas-phase photochemical chlorination of PhCl proceeds by short reaction chains, and initially the rate of reaction of Cl₂ is proportional to a power of the light intensity between 0.5 and 1.0. The ratio of substitution to addition increases from $\ll 1$ to > 1 as the ratio of Cl₂ used to initial pressure of PhCl is increased (cf. C₆H₆, *loc. cit.*), and the relation is independent of temp. between 25° and 35°, but in the purely thermal reaction substitution dominates and the rate \propto [Cl₂][PhCl] and is increased by surface. The rate of addition of Cl_2 to $p \cdot \text{C}_6 \text{H}_4 \text{Cl}_2$ is slightly < to PhCl. Some intermediate substances have been isolated and the final product is $\text{C}_6 \text{Cl}_{12}$. The mechanism of the reaction is discussed. J. G. A. G.

Electrometric measurement of Röntgenenergy. N. WATERMAN and H. LIMBURG (Phil. Mag., 1934, [vii], 17, 1144—1150; cf. A., 1933, 1020).—The electrochemical effects of X-rays consist of an electrode effect and a secondary process. The former depends quantitatively on the energy received by the system and can be utilised for its measurement. An apparatus for this purpose, utilising the reducing action of Xrays on methylene-blue, is described. J. W. S.

Periodic system of the elements and its gaps. I. NODDACK (Angew. Chem., 1934, 47, 301-305).—A crit. review of the lit. indicates that the elements with at. nos. 61 (a rare-earth metal), 85 (eka-I), and 87 (eka-Cs) have not yet been discovered. Attempts by the author to concentrate eka-Cs by crystallisation of Cs alum and $3CsCl_2SbCl_3$ from numerous sources, and detect it by means of X-ray or infra-red spectra have been unsuccessful. The possible reasons for the non-existence or rarity of these elements and of elements heavier than U are discussed. Possible developments in the conception of the periodic system, due to the discovery of the neutron, the positron, and isotopes (particularly H²), are considered. D. R. D.

Natural separation of the isotopes of hydrogen. I. Concentration of deuterium in benzene, kerosene, and honey. M. DOLE (J. Chem. Physics, 1934, 2, 337–341; cf. this vol., 613).—Methods of combustion, purification of H_2O , and measurement of d are described. H. J. E.

Increase of the percentage of diplogen in water during very slow evaporation. T. TUCHOLSKI (Nature, 1934, 134, 29).—Evaporation of 25 litres of H_2O to approx. 600 c.c. over a period of three years gave H_2O of d^4 1.0016 corresponding with 1.65% H_2^2O . Slow evaporation is more effective than boiling. L. S. T.

Isotopic exchange between H_2O and C_2H_2 . L. H. REYERSON and S. YUSTER (J. Amer. Chem. Soc., 1934, 56, 1426—1427).—Isotopic exchange was not detected between C_2H_2 and 18.5% H_2^3O alone or in presence of H_3PO_4 , but exchange occurs in presence of NaOH, thus confirming the acidic nature of C_2H_2 . J. G. A. G.

Reaction of atomic hydrogen with metallic copper. F. A. McMAHON and P. L. ROBINSON (J.C.S., 1934, 854-855).—At. H passed at the rate of 0.5 litre per hr. over Cu which has been oxidised and reduced, or roughened, gives a black Cu^I hydride sol. in 70% HCl in absence of air. R. S. B.

Action of aqueous solutions of cupric sulphate on copper oxide. O. BINDER (Compt. rend., 1934, 198, 2167—2169).—The basic salt produced by the action of aq. CuSO, on CuO, 3CuO,Cu(OH)₂, Cu(OH)₂, NiO, Ni(OH)₂, or NiCO₃ was shown by analysis, X-ray spectrum, and paramagnetic susceptibility $(\chi=11.5\times10^{-6}$ at 17°) to be 4CuO,SO₃,4H₂O in all cases, and not to contain admixed Cu(OH)₂ (cf. this rol, 376). B. W. B. Silver silicate. B. BOGITCH (Compt. rend., 1934, 198, 1928—1929).—Various oxidising, neutral, and reducing gases were bubbled through a melt of sodaglass and AgNO₃. The effects on the resultant glass are described. Ag silicate appears to be formed, and is readily reduced to colloidal Ag. B. W. B.

Mechanism of oxidation of alloys of magnesium at high temperatures. R. DELAVAULT (Compt. rend., 1934, 198, 1929—1932; cf. following abstract). —Microscopical study during heating in air of etched surfaces of Mg alloyed with 0.2—10% of Na, Te, Ca, Zn, Cd, Al, Pb, Sn, Bi, Si, Cu, or Ag showed that oxidation commences at grain boundaries, at which rapidly attacked protuberances of liquid metal are formed. Similar results were obtained with Ca. B. W. B.

Superficial oxidation of molten metals. R. DELAVAULT (Bull. Soc. chim., 1934, [v], 1, 419–424).—The behaviour of Mg, Al, and alloys of Mg and Al on oxidation in air is in agreement with Pilling and Bedworth's theory according to which the oxide of a metal forms a protective coating preventing further oxidation only when Wd/wD is > 1, W and w being mol. wts. and D and d densities of oxide and metal, respectively. The presence of BF₃ in the air results in the formation of a temporarily protective layer of MgF₂ on Mg for which the ratio is > 1. The same probably applies to the presence of SiF₄. The possible practical application in the prep. of alloys of Mg is discussed. M. S. B.

Hydrated calcium sulphatoaluminate and calcium chloroaluminate. J. LEFOL (Compt. rend., 1934, 198, 1858—1860; cf. this vol., 31).—Thermal analysis showed: (i) $Al_2O_3,3CaO,3CaSO_4,30H_2O$ rapidly loses H_2O on heating, forming a heptahydrate stable at 145° and decomposed at higher temp.; free $CaSO_4$ is not liberated; (ii) $Al_2O_3,3CaO,CaCl_2,10H_2O$ (I) is stable to 120° and forms a hexahydrate at 175° which is stable to 280°. At temp. > 100° (I) decomposes to $CaCl_2+Al_2O_3,3CaO$. B. W. B.

Celite $(4\text{CaO},\text{Al}_3\text{O}_3,\text{Fe}_2\text{O}_3)$ of Portland cement. S. NAGAI and G. SAWAYAMA (J. Soc. Chem. Ind. Japan, 1934, **37**, 264—267B).—A mixture $4\text{CaO}:\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ readily forms $4\text{CaO},\text{Al}_2\text{O}_3,\text{Fe}_2\text{O}_3$ at 1250°. A mixture $5\text{CaO}:\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ (or $3\text{CaO},\text{Al}_2\text{O}_3:2\text{CaO},\text{Fe}_2\text{O}_3$) forms $2\text{CaO},\text{Fe}_2\text{O}_3+6\text{CaO},\text{Al}_2\text{O}_3;2\text{Fe}_2\text{O}_3$ (I) at $1400-1420^\circ$ and $3\text{CaO},\text{Al}_2\text{O}_3+(I)$ at $1250-1370^\circ$. (I) is probably a mixture of $2\text{CaO},\text{Fe}_2\text{O}_3$ and the eutectic (CaO 47, Al_2O_3 53%) between $3\text{CaO},\text{Al}_2\text{O}_3$ and $5\text{CaO},3\text{Al}_2\text{O}_3$.

Reactions between nitrogen dioxide and sulphur dioxide in the condensed phase. E. TERRES and M. CONSTANTINESCU (Angew. Chem., 1934, 47, 470–471).—NO₂ is absorbed by SO₂ at -70° . The m.p.-composition curve indicates a cutectic containing 6% NO₂. Probably SO₂NO₂ is formed, which is converted by a slight temp. rise into SO₃NO, from which (SO₃)₂N₂O₃ is also formed. A. G.

Reactions of oxides of nitrogen and of sulphur. Nitrosisulphonic acid anhydride and its reversible conversion into nitrosylsulphuric acid anhydride. E. TERRES and M. CONSTANTINESCU (Angew. Chem., 1934, 47, 468–470).—The reaction $SO_2+2NO=SO_3+N_2O$ is reversible. The formation of NO begins at 550° and increases with rising temp.; it never exceeds 1% of the mixture because the decomp. of N₂O is much more rapid than its oxidation. N₂O is formed from NO and SO₂ only in presence of Pt and at 250–470°, with a max. at 350–400°. Crystals of the composition SO₃NO are formed at the inlet end of the reaction tube, and may also be produced from SO₃ and NO at 90° and from SO₂ and NO₂. SO₃NO melts at 93° with formation of (SO₃)₂N₂O₃. A. G.

Nitrosoamine. R. SCHWARZ and H. GIESE (Ber., 1934, 67, [B], 1108-1115).-N₂O₃ and NH₃ at its m.p. form a red compound (I) regarded as nitrosoamine; $N_2O_3+2NH_3=2NH_2\cdot NO+NH_4NO_2$. With $H(NO)SO_4$ the total reaction is: $5H(NO)SO_4+15NH_3=2NH_4NO_2+3N_2+5(NH_4)_2SO_4+H_2O$, and the intermediate changes are: $H(NO)SO_4+3NH_3=4NH_4 + 2NH_4 + 2$ $(I) + (NH_4)_2 SO_4$; $4(I) = 2NH_4 NO_2 + 2N_2$; $(I) = N_2 + 2$ H_2O . (I) is also formed from (NO)ClO₄ and NOCl. The formulation of (I) is strengthened by the observations that NHPhMe and N_2O_3 at -5° yield NPhMe NO and that (I) and KNO result from the action of NO under pressure on KNH2 in solid NH2: KNH₂+2NO=KNO+(I). (I) cannot be obtained in any solvent other than liquid NH₃, from which it cannot be separated owing to decomp. into NH4NO2 and N₂, also obtained in MH_3-H_2O . (I) unites with H_2O to give NH_4NO_2 . Na NH_2 at -40° reacts with dil. NoCl vapour: $3NaNH_2+2NOCl=2NaCl+NaNO_2+2NH_3+N_2$. Nitrous esters do not react with an MH_2 is not set with the set of the set o anhyd. liquid or gaseous NH3; with KNH2 in NH3 change occurs : $2\ddot{R}NO_2 + KN\dot{H}_2 = R_2O + KN\ddot{O}_2 + N_2 + N$ H2O. NH2Cl does not react with liquid NH3 or with KNO suspended therein. $NH_2 \cdot SO_3 H$ does not react with KNO_2 in liquid NH_3 ; $H(NO)SO_4$ and KNH_2 afford $NH_2 \cdot SO_3 K$ and KNO_2 . The possible structures of (1) are discussed. H. W.

Hydration of phosphoric anhydride. A. TRAVERS and Y. K. CHU (Compt. rend., 1934, 198, 2169—2171).—Addition of P_2O_5 to ice- H_2O did not give dimetaphosphoric acid, $H_2P_2O_6$ (I) (cf. Réchid, A., 1933, 475), as chief product, local overheating causing hydration or polymerisation. With special precautions, P_2O_5 + an ethereal solution of either H_2O or of anhyd. H_3PO_4 gave a mixture of (I) and its polymeride (II), readily hydrated to pyro- (III) and ortho- (IV) -phosphoric acids, respectively. (I) may be separated from admixture with (II), (III), and (IV) by pptn. of Pb salts of the last three in dil. NaOH solution. B. W. B.

The two forms of phosphorous acid. R. DOLIQUE and A. GRANGIENS (Bull. Soc. chim., 1934, [v], 1, 380-387).—A detailed account of work already noted (A., 1933, 1129).

Dimetaphosphoric acid. A. TRAVERS and Y. K. CHU (Compt. rend., 1934, 198, 2100-2102).—Na dimetaphosphate, $Na_2P_2O_6$, prepared by Pascal and Réchid's method (A. 1933, 475), always contains $Na_2H_2P_2O_7$. The following modification of Knorre's method (A. 1900, ii, 651) is satisfactory. A mixture of 5 parts Na_2HPO_4 , $12H_2O + 1$ part $NH_4NO_3 + 1$ part

 $\rm NH_4Cl$ is heated in vac. at 250° for 8 hr.; crystallisation of the product from H₂O gives pure, birefringent Na₂P₂O₆, 3H₂O (I), mol. wt. 65 (extrapolated from cryoscopic data; cf. Na₂P₂O₆, 68). Dimetaphosphoric acid (II), prepared by the action of H₂S on PbP₂O₆, did not coagulate albumin (III) and was slowly hydrolysed by cold H₂O to H₄P₂O₇. (I) after heating for 2 hr. at 900° and treatment with AcOH gave a polymeride of (II) (mol. wt. 338) which coagulated (III). The latter is a property of highly polymerised metaphosphoric acids. B. W. B.

Structure of hypophosphoric acid. P. NYLÉN and O. STELLING (Z. anorg. Chem., 1934, 218, 301– 303).—Blaser and Halpern's experiments (this vol., 43) do not bring any important evidence against the authors' formula for hypophosphoric acid (A., 1933, 664) and their formula does not account for the properties of the acid. M. S. B.

Oxidation of phosphoformic acid by bromine and permanganate. P. NYLEN (Z. anorg. Chem., 1934, 218, 304—306).—Oxidation by Br takes place quantitatively and rapidly between $p_{\rm H}$ 4 and 11·2. In neutral solution it is practically instantaneous. A no. of other acids, *e.g.*, phosphoacetic, β -phosphopropionic, methanediphosphonic, arsinoacetic, and dithionic acids are resistant to Br. Et phosphite is slightly attacked. Oxidation by KMnO₄ takes place rapidly at room temp. with the employment of approx. 93% of the KMnO₄ theoretically required. As with H₂C₂O₄, there is an induction period. The results support the structural formula CO₂H·PO(OH)₂.

M. S. B. Wet-way preparation of antimony iodosulphide. F. FRANÇOIS (Compt. rend., 1934, 198, 1994—1996).— SbSI, prepared by long shaking of mixed aq. solutions of SbI₃, HI, and H₂S, or of Sb₂S₃+aq. HI, was a red cryst. powder, m.p. 392°, unattacked by H₂O or H₂S. Sb cannot be determined by pptn. with H₂S from solutions containing HI. B. W. B.

Preparation of sodium bismuthate. I. VACHRO-MEEV (Zavod. Lab., 1934, 3, 269).—100 g. of Bi(OH)₂·NO₃ are dissolved in 200 g. of NaOH at red heat, after which 20 g. of Na₂O₂ are added. The melt is leached with 1500 c.c. of H₂O, and the insol. residue of NaBiO₃ is collected, washed, and dried at 100—105° during 16 hr. R. T.

Complex bismuth oxalates. S. ŠKRAMOVSKÝ (Coll. Czech. Chem. Comm., 1934, 6, 145—162; cf. A., 1930, 1008).—The course of dehydration of the double oxalates of Bi, and of $Bi_2(C_2O_4)_3, 5, 6, 7, and 8H_2O$, shows them to be derived by substitution from aquooxalato-complexes of 4- or 6-co-ordinate Bi, some polynuclear, containing $-C_2O_4$ - bridges. The following compounds were prepared : $LiBi(C_2O_4)_3, 2H_2O$;

 $\begin{array}{c} \text{Compounds} & \text{were prepared}: \quad \text{InBi}(C_2O_4)_2, 2H_2O; \\ & \text{NH}_4\text{Bi}_2(C_2O_4)_3\text{NO}_3, 3 \text{ and } 1H_2O; \\ & (\text{NH}_4)_2\text{Bi}_2(C_2O_4)_3(\text{NO}_3)_2, 3H_2O \text{ and anhyd.}; \\ & (\text{NH}_4)_2\text{Bi}(C_2O_4)_2F, 2H_2O; \quad (\text{NH}_4)_2\text{Bi}_3(C_2O_4)_5\text{Cl}, 8 \quad \text{and} \\ & 2H_2O; \quad \text{Bi}_2(C_2O_4)_3, 5 \text{ and } 8H_2O; \\ & (\text{NH}_4)_2\text{Bi}_4(C_2O_4)_7, 11H_2O. & J. S. A. \end{array}$

Purification of half a gram of protoactimum. (element 91). G. GRAUE and H. KADING (Naturwiss., 1934, 22, 386-388).—The working up of 5.5 tons of pitchblende residues after extraction of Ra is described. A. J. M.

Isotopic composition of oxygen made by the fractionation of liquid air and oxygen of ordinary air. E. R. SMITH (J. Chem. Physics, 1934, 2, 298).— Increase in d of H₂O prepared from the fractionation specimen of O₂ was $2 \cdot 2 \pm 0 \cdot 5$ p.p.m., indicating the presence of 2 in 10⁵ more atoms of O¹⁸ than O¹⁶.

N. M. B.

Reactions of inorganic compounds with liquid hydrogen sulphide. H. F. GUEST (Iowa State Coll. J. Sci., 1933, 8, 197–198).—CaO forms CaS and Ca(OH)SH; CaC₂ forms CaS and Ca(SH)₂; C₂H₂ forms a little CHMeS; dry SO₂ at > -68° reacts with explosive violence; VOCl₃ forms VSCl₃ and VCl₃(OH)SH; Na₂S and CS₂ in H₂S form Na₂CS₃; POCl₃ oxidises H₂S slowly; in EtOH-H₂S+CS₂, NH₃ forms NH₄S(NH₂)CS. CH. ABS.

Formation of pyrosulphate by treatment of sulphur trioxide with aqueous sulphate solutions. P. BAUMGARTEN (Ber., 1934, 67, [B], 1100—1104).— Introduction of SO₃ vapour under precise conditions into aq. alkali sulphate at 5—10° and immediate treatment of the solution with C_5H_5N yields 1-pyridinium-sulphonic acid identified as glutacondialdehydedianil hydrochloride. With H₂O the reaction is scarcely observed and the formation of pyrosulphate is postulated. Similar results are observed in presence of CO_3'' , ClO_4' , and particularly of PO_4''' , but not of Cl'.

Reaction of sulphur trioxide with ammonia in aqueous solution and the chemical composition of the so-called "sulphur trioxide fog." Ρ. BAUMGARTEN and A. H. KRUMMACHER (Ber., 1934, 67, [B], 1257-1260).-The main product of the action of SO₃ as vapour mixed with air on 25% NH₃ at about -15° is $(NH_4)N(SO_3NH_4)_2$ accompanied by $(NH_4)_2SO_4$ and minor amounts of $NH_2 \cdot SO_3NH_4$. With $C_5H_5N-10^{\circ}$ H₂O, SO₃ vapour yields pyridiniumsulphonic acid, converted by alkali into *enol*-glutaconaldehyde, recognised by its yellowish-brown colour, or, more readily, by the production of the intensely red dianil hydrochloride after subsequent addition of NH₂Ph and HCl. Application of this test to "sulphur trioxide fog" shows the latter to contain only H2SO4 particles unless the fog has been in contact with H₂O or aq. solutions H. W. for only a very short time.

Uranyl salts. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 410-411).-UO₂(NO₃)₂ reacts with the following substances in aq. solution : NHPh-NH₂, forming hydrated U_3O_8 ; (CH₂)₆N₄, giving

 $(\mathrm{NH}_4)_2\mathrm{UO}_4,\mathrm{H}_2\mathrm{O}$; antipyrine, forming uranyl antipyrine nitrate, $C_{11}\mathrm{H}_{12}\mathrm{ON}_2,\mathrm{UO}_3(\mathrm{NO}_3)_2,10\mathrm{H}_2\mathrm{O}$, as a yellow ppt. sol. in warm $\mathrm{H}_2\mathrm{O}$; $(\mathrm{CH}_2)_4(\mathrm{NH})_2$, forming uranylpiperazine ($\mathrm{CH}_2)_4\mathrm{N}_2\mathrm{UO}_2,2\mathrm{H}_2\mathrm{O}$, as a yellow ppt. insol. in boiling $\mathrm{H}_2\mathrm{O}$ and sol. in cold acids; K xanthate, giving a brown coloration; K guaiacolsulphonate (I), giving a blood-red coloration in the cold and, after evaporation, a reddish-brown, cryst., deliquescent mass containing a mixture of (I) and UO₂ guaiacolsulphonate; thiosinamine, with formation of NH_3 and $C_3\mathrm{H}_5$ SCN. M. S. B.

Reduction of polonium in solution. M. GUILLOT and M. HAISSINSKY (Compt. rend., 1934, 198, 1911-3 L 1913).—The existence of Po^{III} and Po^{IV} (cf. A., 1931, 591, 697, and Joliot, A., 1930, 713) is confirmed by the effects of reducing agents (N_2H_4 , NH_2OH , $H_2C_2O_4$, and H_2O_2 in acid solution) on the crit. deposition potential. Metallic Po was pptd. by CH_2O in alkaline solution and by H_3PO_2 or $Na_2S_2O_4$. Electrolytic deposition was suppressed by $NaNO_2$ in HNO₃ solution. B. W. B.

Recovering radium-D and polonium. T. BJERGE (Z. Physik, 1934, 89, 277–282).—The radioactive layer of used emanation tubes may be recovered by etching. A. B. D. C.

New fluorides. O. RUFF [with A. BRAIDA, W. KWASNIK, and M. GIESE] (Angew. Chem., 1934, 47, 480).—A review of Ruff's work on I, Re, Ag, Cu, and Au fluorides. D. R. D.

 ψ -Halogens. XXIV. Reaction of metallic sulphates with iodine in concentrated sulphuric acid. L. BIRCKENBACH and J. GOUBEAU [with H. G. KRALL] (Ber., 1934, 67, [B], 917–927; cf. A., 1933, 1281).—I is slightly sol. in conc. H_2SO_4 with a pale pink colour unaffected by anhyd. $CuSO_4$ what a pate pink colour unaffected by anhyd. $CuSO_4$, $PbSO_4$, FeSO₄, NiSO₄, ZnSO₄, K₂SO₄, and Na₂SO₄. I, Ag₂SO₄, and H₂SO₄ give a reddish-violet solution in which I: Ag=I: 4—5 for solutions very dil. in Ag and =1: 1.8 in saturated solution. The relationship oxidation val. : total I=1:1 and the absence of AgI exclude the possibility of the presence of I_2SO_4 or analogous mixed ψ -halogen, and the existence of adducts $I_2[Ag_2SO_4]_3$ or $I_2[AgHSO_4]_6$ is assumed. Addition of C_6H_6 to the solution causes almost immediate disappearance of the colour and formation of AgI, but the production of PhI is gradual, indicating that the reactive I_2SO_4 is not immediately present. I, H_2SO_4 , and $HgSO_4$ or Hg_2SO_4 yield brown solutions, Hg_2SO_4 being first oxidised by I. The relationship oxidising power: total I exceeds 1:1, indicating $HgSO_4 + 2I_2 \implies HgI_2 + I_2SO_4$. At the commencement of the change the ratio (max.) is 3:1, rapidly declining to 2:1 and ultimately becoming const. at 1.25:1. Similar brown solutions are obtained from I, conc. H₂SO₄, and KIO₂, MnO₂, KIO₄, and KMnO₄. Treatment of I-HgSO₄-H₂SO₄ mixtures with C₆H₆ causes immediate separation of I and production of $\begin{array}{l} p\text{-}C_6H_4I_2 \text{ with a little PhI (possibly } C_6H_6+I_2SO_4,3I_2\\ \xrightarrow{} C_6H_4I_2+H_2SO_4+3I_2). \text{ An analogous change}\\ \text{occurs with } I-H_2SO_4 \text{ and } AgI, PbI_2, \text{ or } HgI_2, \text{ leading to} \end{array}$ complete separation of I with production of only a pale pink solution; possibly 2HgI2+ISO4,3I2 =HgI₂,HgSO₄+5I₂.

Sublimed iron. W. KROLL (Z. Elektrochem., 1934, 40, 303-306).—An Fe crucible was sublimed in a high vac. at 1100-1200° at the rate of 0.054 g. per sq. cm. per hr. The sublimate was examined microscopically, spectrographically, and chemically. There was more Mn and less C in the sublimate than in the crucible, and approx. the same proportion of other impurities. F. L. U.

Complex salts of tervalent rhodium with 2:2'-dipyridyl. F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 284–290).—6.5 g. of finely-powdered RhCl₃,4H₂O, added to 15 g. of boiling dipyridyl (dipy), heated for 10 min., and then heated on the H₂O-bath, with addition of some H₂O and

EtOH, for several hr. yields a solution which on cooling deposits the pale yellow *compound*,

 $[Rh(dipy)_2Cl_2]Cl_2H_2O$ (I). If the mother-liquor is extracted with Et₂O and conc. on the H₂O-bath addition of EtOH ppts. the almost colourless compound $[Rh(dipy)_3]Cl_3,3H_2O$ (II), which crystallises in rhombic-pyramidal form isomorphous with

 $[Co(dipy]_3Cl_3,2H_2O.$ Traces of a compound, probably $[Rh_2(dipy)_3Cl_6]$, are also obtained. If 9 g. of $Na_3RhCl_6,12H_2O$ be dissolved in 40 c.c. of H_2O and heated on the H_2O -bath with 6 g. of dipyridyl in EtOH, (I) and (II) are formed, but the yield of (I) is 37 times that of (II). In presence of H_2O partial hydrolysis of (I) occurs, yielding the compounds $[Rh(dipy)(H_2O)_4]Cl_3$, $[Rh(dipy)(H_2O)_2Cl_2]Cl_3$.

hydrolysis of (I) occurs, yielding the compounds $[Rh(dipy)(H_2O)_4]Cl_3$, $[Rh(dipy)(H_2O)_2Cl_2]Cl$, $[Rh(dipy)(H_2O)_3Cl]Cl_2$, and $[Rh(dipy)(H_2O)Cl_3]$, according to the conditions of hydrolysis. When Na₃RhCl₆ is treated with an equiv. amount of AgNO₃, and the Ag₃RhCl₆ obtained treated with the calc. amount of BaCl₂, rcd crystals of Ba₃(RhCl₆)₂,7H₂O are obtained on evaporation. These when treated with the calc. quantity of dipyridyl sulphate give a brownish-red solution which on evaporation in vac. yields reddish-brown needles of the compound $[Rh_2(dipy)_2Cl_6],3H_2O$. J. W. S.

Direct oxidation of platinum under pressure. P. LAFFITTE and P. GRANDADAM (Compt. rend., 1934, 198, 1925—1927).—The oxidation of heated Pt was studied at high pressures of O_2 . Wire was superficially oxidised at 300—500° and 50—200 kg. per sq. cm. In 6 hr. at the optimum temp., 455°, sponge increased in wt. by 2·1% at 40 atm. and 7·37% at 150 atm. At 450° and 150 atm. Pt-black increased by 13.94% (cf. 8.19% O in PtO and 16.4% in PtO₂), d decreasing to 11·1; PtO₂, isolated from the product (I) by washing with aqua regia, was a blue powder, d 10·2, stable to 350°, and reduced by H₂ at room temp. (I) also contained PtO. B. W. B.

Stromholm's [platinum] triamminosulphite. I. I. TSCHERNIAEV and A. M. RUBINSCHTEIN (Compt. rend. Acad. Soc., U.R.S.S., 1934, 2, 179—184).— On oxidising $Pt(NH_3)_3SO_3$ the SO₃ undergoes oxidation first, whilst simultaneously NH₃ is eliminated. The transition from triammino-sulphite to -chloride cannot be accomplished. The solubilities at 25° of $Pt(NH_3)_3SO_3$ in H₂O and 0·1N-acids and NaOH have been determined. W. R. A.

Quantitative spectral analysis of gas mixtures. F. KLAUER (Ann. Physik, 1934, [v], 20, 145-160).— The spectroscopic detection of H_2 in He and A, and of He and A in H_2 , was investigated by examination of the high-frequency glow discharge of the gas mixtures. Such a method is suitable for the determination of these gases in admixture. A high degree of sensitivity cannot be claimed for the detection of H_2 in these mixtures, a result in contrast with that of earlier workers, whose gas probably contained hydrocarbons. A. J. M.

Cadmium sulphate as a basis for acidimetry. S. E. Q. ASHLEY and G. A. HULETT (J. Amer. Chem. Soc., 1934, 56, 1275—1278).—Clear crystals of $CdSO_{4,3}H_2O$ (I) have a highly uniform composition; by removing at a Hg cathode the Cd from an aq. solution containing a known wt. of (I), standard aq. H_2SO_4 is obtained. This solution is as trustworthy a standard as aq. HCl of const. b.p., BzOH, and K phthalate. J. G. A. G.

Micro-determination of heavy water. P. GOLD-FINGER and L. SCHEEPERS (Compt. rend., 1934, 198, 1916—1918).—A micro-flotation method (cf. Lewis and Macdonald, A., 1933, 894) requiring 0.1—0.2 c.c. of H₂O is described. Flotation temp. were reproducible to $\pm 0.05^{\circ}$. B. W. B.

New mode of expression of analytical data for mineral waters. L. NENADOVIĆ (Bull. Soc. Chim. Yougoslav., 1933, 4, 221—226).—Graphical and other methods of presenting analytical results are proposed. R. T.

Determination of water in liquid sulphur dioxide.—See B., 1934, 624.

Photometric micro-analysis of drinking and service water. X. Determination of sulphate. XI. Determination of lead.—See B., 1934, 654.

Chronometric catalytic method for determining micro-quantities of iodine. E. B. SANDELL and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1934, 56, 1426).—The reaction between H_3AsO_3 and $Ce(SO_4)_2$ in aq. H_2SO_4 is greatly accelerated by traces of I', the rate being approx. $\infty[I']$ when other factors are const. Thus, the time required for the yellow colour of Ce^{***} to disappear, or with *o*-phenanthroline–FeSO₄ as indicator, the pink colour to appear, is inversely ∞ the wt. of I. Alkali chlorides and bromides and other salts have only small effects and by a special procedure 0.01-1 micro-g. of I at a dilution of $1:10^7$ is determined to within 20%. Micro-quantities of Os may be determined similarly. The test appears to be sp. for I, Os, and presumably Ru. J. G. A. G.

Determination of iodide by photometric titration. S. HIRANO (J. Soc. Chem. Ind. Japan, 1934, **37**, 177-178B).—I' may be determined by photometric titration with IO_3' ; at the end-point the [I] is a max. and there is a sharp max. in the optical density. A. G.

Determination of iodine in hard drinking waters. J. STRAUB (Z. anal. Chem., 1934, 97, 259– 262).—In the determination of I by von Fellenberg's method, no formation of $Ca(IO_3)_2$ could be detected with hard H₂O, but repeated extraction with EtOH is necessary for quant. removal of I'. J. S. A.

Determination of fluorine in silicate rocks, waters, etc. O. HACKL (Z. anal. Chem., 1934, 97, 254-258).—To the neutralised solution of the rock, after fusion and treatment with $(NH_4)_2CO_3$, are added H_2O_2 and 1—10 c.c. of aq. Ti(SO₄)₂ (1 mg. TiO₂ per c.c.), then H_2SO_4 . The comparison solution is treated identically, and standard aq. NaF added until a colour match is obtained. J. S. A.

Mindalev's volumetric method of determination of sulphate. C. B. MEDINSKI, V. L. NIKOPOL-SKAJA, and M. D. TRUSOV (Zavod. Lab., 1934, 3, 230– 231).—Mindalev's method (A., 1929, 162) gives untrustworthy results in presence of Ca^{**} and Cl', or at >25°, and is unsuitable for factory practice. R. T.

Kjeldahl method. III. Further comparisons of selenium with mercury and with copper catalysts. R. A. OSBORN and A. KRASNITZ (J. Assoc. Öff. Agric. Chem., 1934, 17, 339-342; cf. A., 1933, 520).-HgO alone and HgO+Se are equally effective catalysts, giving 25% saving of time when compared with Se alone or Se+CuSO4. When the digestion period is extended the danger of loss of N increases in the order: HgO, Se, HgO+Se. The danger can be by using larger amounts of H_2SO_4 . E. C. S.

Detection of phosphoric acid in hydrogen peroxide solutions.—See B., 1934, 572.

Determination of carbon dioxide using the Geissler-Vorišek apparatus. J. VORIŠEK (Chem. Listy, 1934, 28, 116-118).-Modifications of the Geissler apparatus are described, and the use of a citric acid-HCl mixture is recommended for expulsion of CO₂ from carbonates. R. T.

Continuous determination of carbonate-caustic ratio in a carbon dioxide absorption system.—See B., 1934, 623.

Determination of carbon monoxide. R. Gou-BAU and J. EEOKHOUT (Natuurwetensch. Tijds., 1934, 16, 117-130).-The CO content of a gas mixture containing 0.001% CO may be determined by a spectrophotometric method in which the λ at which the absorption curve of a solution of hæmoglobin (I) intersects that of a solution of Congo-red (II) is compared with the corresponding point of intersection for solutions of carboxyhæmoglobin (III) and (II). The solution of (II) must be buffered to prevent change of colour with time. Under specified conditions, the observed point of intersection ranges from 5243 Å. for solutions of 100% (III) to 5415 Å. for solutions of 100% (I). The error depends on the degree of refine-100% (1). The error depends on the part of the λ reading, but should be $\geq 2\%$. H. F. G.

Lawrence Smith method for the determination of alkalis in rocks. W. VAN TONGEREN (Z. anorg. Chem., 1934, 218, 252).—The powdered rock is ground still more finely under EtOH, NH4Cl moistened with EtOH is added, and the mixing with CaCO₃ is M. S. B. carried out under EtOH.

Determination of sodium by means of uranyl magnesium acetate. I. I. NAZAROV and L. P. BANINA (Zavod. Lab., 1934, 3, 226-229).-Kahane's method (A., 1930, 726), with minor modifications, R. T. gives trustworthy results.

Rapid determination of silver in argentiferous galena.—See B., 1934, 582.

Rapid identification of silver cyanide in presence of silver halides. E. V. ZAPPI and A. MANINI (Anal. Asoc. Quím. Argentina, 1934, 22, 21-23).-A sample of the ppt. is treated with $Hg_2(NO_3)_2$; AgCN (I) is blackened, but Ag halides (II) are unaffected. (I), if present, is destroyed by boiling the remainder of the R. N. C. ppt. with HNO_3 before testing for (II).

electrodes. I. Potentiometric Indifferent titration of calcium. C. A. NIERSTRASZ and H. J. C. TENDELOO (Rec. trav. chim., 1934, 53, 792-797).-Electrodes of the type M_1 , CuC_2O_4 , CaC_2O_4 (where $M_1 =$ Ag. Au. or Pt) are satisfactory for titrating Ca with $(NH_4)_2C_2O_4$. Electrodes of Au and Pt, or Ag and Pt,

using CuC_2O_4 in both cases, are still more satisfactory for $Ca(NO_3)_2$. Cl' does not interfere. E. S. H.

Separation of beryllium from iron by means of "cupferron." A. TETTAMANZI (L'Ind. Chimica, 1934, 9, 752-755).—The solution is acidified with conc. HCl and treated with excess of clear, fresh 6% cupferron solution. After 15-20 min., the Fe ppt. is collected, with the help of gentle suction, on a tared filter supported on a Pt cone and washed 4-5 times with dil. HCl (5 c.c. conc. HCl+100 c.c. H₂O), 2-3 times with dil. NH₃ (1 vol. conc. NH₃+1 vol. H₂O), and 4-5 times with H_2O . The ppt. and paper are dried in a Pt crucible for 30 min. at 100-105°, heated gently, and later strongly, and weighed. Any Cu is pptd. with the Fe. Ť. H. P.

Volumetric determination of zinc. A. CHIAROT-TINO (L'Ind. Chimica, 1934, 9, 468-470).-Disadvantages of the method based on the reaction between ZnS and AgCl are discussed. In the method recommended, the Zn (0.1 g.) is pptd. as ZnS in the usual manner; the washed ppt. is heated on the H₂Obath for a few min. with 50 c.c. of H₂O and an excess of HgCl₂, and the HgS is allowed to settle after a few drops of dil. H₂SO₄ have been added. The filtered solution is treated with HNO3 and 0.1N-AgNO3, and titrated with NH₄CNS. H. F. G.

Quantitative spectral analysis. II. R. BRECK-POT and A. MEVIS (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 99-119).-Data for the determination of Cd, Sn, Zn, Al, Ba, Ca, Mg, Ge, and Au are given.

C. W. G. Indirect potentiometric determination of cadmium. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 97, 263—266).— $[Cd(CNS)_2(C_5H_5N)_2]$ is pptd. quantitatively by addition of excess of 0.1N-KCNS+ C₅H₅N. An aliquot portion of the liquid is neutralised with HNO₃ (Me-orange), and excess of CNS' titrated back potentiometrically with AgNO₃. J. S. A.

Gravimetric determination of thallium as cobaltinitrite and its separation from other metals. S. NISIHUKU (J. Soc. Chem. Ind. Japan, 1934, 37, 180B).—The reagent is prepared by mixing equal vols. of solutions containing 28.6 g. of Co(NO3)2 and 50 c.c. of 50% HCO₂H in 500 c.c. and 180 g. of NaNO₂ in 500 c.c., respectively, and after heating at $30-40^{\circ}$ is added to the Tl solution containing 5% HCO₂H and heated at $30-50^{\circ}$. The scarlet ppt. is collected in a glass filter, dried at 120°, and weighed; it contains 64.67% Tl. A. G.

Separation of thallium as bromide by means of ether. I. WADA and R. ISHII (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 135-148).-Tl may be separated from the alkali, alkaline-earth, rare-earth, and Pt-group metals, also Cu, Zn, Cd, Hg, Al, Ga, In, Ti, Zr, Pb, Th, V, Sb, Bi, Cr, Mo, Te, U, Mn, Fe, Co, and Ni, by extracting with Et₂O in presence of N-HBr. Au, which also passes into the Et₂O, may be separated by heating the extract with H₂O, and adding successively 2 c.c. of 10% NH₂OH,HCl, 2 c.c. of 10% KCN, 2 c.c. of 2N-KOH, and 1 c.c. of 5% KI for 100 mg. of Au and 100 mg. of Tl; the Au remains in solution. R. S. B.

Titrimetric determination of copper. E. BOYE (Ber., 1934, 67, [B], 1119—1121).—The sol. Cu salt (0·1—0·2 g.) is dissolved in about 75 c.c. of H₂O slightly acid with H₂SO₄ or HCl and 25 c.c. of MeOH are added. The solution is heated to boiling in a stream of N₂ or CO₂, which is continued until the end of the titration. (NH₂OH)₂, H₂SO₄ (0·5—1 g.) is added in small portions until reduction is complete, as shown by the decolorisation of the solution. The liquid is cooled to about 15—20° and titrated with 0·5N-KCNS in presence of Fe^{III} alum. H. W.

Quantitative spectral analysis of "pure" metals. R. BRECKPOT (Natuurwetensch. Tijds., 1934, 16, 139-143).-In electro-refined Cu (99.94-99.975%) very few of the impurities can be determined directly. By recourse to co-pptn. on suitable substances $[MnO_2, Fe(OH)_3]$, 0.01 mg. of As and Sb and 0.001 mg. of Bi can be determined in 10 mg. of Cu. Since CuS adsorbs Sb₂S₃, separation by the sulphide method is not satisfactory; the MnO₂ ppt. should be washed as free as possible from Cu, the residual Cu determined colorimetrically, and sufficient Cu added to yield a total of 100 mg., which can then be examined spectrographically. Alkaline-earth metals in Al should be co-pptd. with Fe carbonate from a solution in NaOH; traces (10-4%) of Ba may be so determined. The method may be applied to the determination of traces of Ba etc. dissolved from glassware, and of Pb in H₂O. H. F. G.

Use of sodium diethyldithiocarbamate in the determination of minute amounts of copper. H. W. MOSELEY, A. G. ROHWER, and M. C. MOORE (Science, 1934, 79, 507—508).—The addition of gum tragacanth or gelatin prevents the turbidity which often occurs. Details of a modified method (cf. A., 1930, 53) for the microcolorimetric determination of Cu using Na diethyldithiocarbamate are given.

L. S. T.

Colorimetric determination of small quantities of copper in presence of iron. A. CASTIGLIONI (Z. anal. Chem., 1934, 97, 270–273).—By boiling an aq. HCl solution with $Na_2S_2O_4$, Cu+CuS is pptd. The ppt. is dissolved in HNO₃, excess of aq. NH₃ added, and then $(NH_4)_2S$. Colloidal CuS is pptd., and may be determined colorimetrically. J. S. A.

Microchemical reaction of mercurous mercury. S. AUGUSTI (Gazzetta, 1934, 64, 322—324).—1 drop of the solution is evaporated cautiously to dryness on a microscope slide. After cooling, 1 drop of dil. aq. KCNS or NH_4CNS and one of aq. $Co(NO_3)_2$ or $CoSO_4$, or 1 drop of aq. $K_4[Co(CNS)_6]$, is added. Blue crystals of $Hg_4[Co(CNS)_6]$ indicate the presence of Hg^I . 0.6×10^{-6} g. may be detected, using a magnification of 300 diameters. Cu^{II} , Pb^{II} , Bi^{III} , OH', NH_3 , and large quantities of NO_3' and Cl' interfere. D. R. D.

Analysis of mercurian monium compounds. S. AUGUSTI (Gazzetta, 1934, 64, 324–334).—Published methods are reviewed, the author's results with various Hg_2N^I salts being quoted. D. R. D.

Volumetric determination of mercuric chloride. M. RAGNO (Annali Chim. Appl., 1934, 24, 270-272).—HgCl₂ in sublimate tablets may be determined volumetrically in accordance with the reactions: (1) $2KMnO_4+5K_2SnCl_4,2H_2O+16HCl=5SnCl_4+12KCl+2MnCl_2+18H_2O$, and (2) $HgCl_2+$

 $K_2SnCl_4, 2H_2O = Hg + 2KCl + SnCl_4 + 2H_2O;$ NaHCO₃ is added to give an atm. of CO₂ to prevent oxidation of the K₂SnCl₄. Results to within about $\pm 0.1\%$ are recorded. T. H. P.

Determination of aluminium in spring waters. V. GAZZI (Annali Chim. Appl., 1934, 24, 226–229).— Chemical analysis of natural H_2O often indicates amounts of Al greatly in excess of the true amounts. The val. of spectrographic analysis is emphasised.

T. H. P. Separation of aluminium from nickel and cobalt by hydrazine carbonate. A. JILEK and J. VREŠT'AL (Chem. Listy, 1934, 28, 113—115).—4 c.c. of 50% aq. N₂H₄,H₂CO₃ are added to 200 c.c. of solution, containing > 0.1 g. each of Al, Ni, and Co, the solution is filtered after heating for 1 hr.at 100°, and the ppt. is washed with 1% aq. NH₄NO₃, and dissolved in HNO₃, excess of which is removed by evaporation. The pptn. is repeated, and the ppt. is ignited, and weighed as Al₂O₃. Ni and Co are determined in the united filtrates by the ordinary procedures. R. T.

Acidimetric titration in presence of manganous salts. P. MARANGONI (Boll. Chim. Farm., 1934, 73, 361—363).—Free acid in a solution containing Mn^{II} salt cannot be determined by titration with NaOH in presence of Me-orange, Me-red, etc., owing to decolorisation of the indicator, unless NH₄Cl is added. Titration with Na₂CO₃ needs no such addition (cf. Perret and Krawczynski, A., 1932, 1220). T. H. P.

Modified thiocyanate procedure for the determination of small quantities of iron. H. A. DANIEL and H. J. HARPER (J. Assoc. Off. Agric. Chem., 1934, 17, 286-290).—The *iso*amyl alcohol modification of the CNS' method (B., 1932, 78) is untrustworthy owing to fading of the coloration at all temp., and to the undesirable colours introduced by Ca salts. The colour does not fade in dil. aq. HNO₃, but fades in presence of HCl or H_2SO_4 . Ca does not interfere when present as $Ca(NO_3)_2$. A procedure for the determination of Fe in forage and grain is outlined. E. C. S.

p-n-Butylphenylarsinic acid as a reagent for determining iron. K. A. CRAIG and G. C. CHAND-LEE (J. Amer. Chem. Soc., 1934, 56, 1278—1279; cf. A., 1933, 1263).—0.75 g. of reagent in 100 c.c. of H_2O at 80—90° is added slowly to > 70 mg. of Fe in 200 c.c. of > 0.4N-HCl, HNO₃, or H_2SO_4 at $< 100^\circ$. After digestion (30 min.), the cold ppt. is washed with 0.02N-HCl and ignited to Fe_2O_3 . In this way, Fe is separated quantitatively from Ni, Zn, Co, Mn, Cu, Cd, K, Al, Mg, Ca, Be, La, Er, Nd, V, Cr (repptn. necessary), and Tl (special procedure). F', PO₄", tartrate, citrate, Zr, Sn, Ti, Th, U, and Ce interfere. J. G. A. G.

Quantitative optical spectral analysis. W. SEITH and E. HOFER (Z. Elektrochem., 1934, 40, 313– 322; cf. A., 1932, 1195).—Tables are given for the determination of Ni in Pb, Pb in Sn, Mg in Pb, and Ca in Pb by the method of homologous pairs. A photometric method, devised for Cu in Pb, Pb in Cd, and Cd in Pb, yields reproducible results. F. L. U.
Colorimetric determination of tungsten. F. A. FERJANTSCHITSCH (Zavod. Lab., 1934, 3, 301–303).-0.1 g. of mineral (containing 0.02-1% WO₃) is ignited, treated with HF to eliminate SiO₂, the residue is fused with 0.5 g. of Na₂CO₃, MnO₄" in the solution of the melt is reduced with EtOH, the solution is filtered, and the filtrate is evaporated to dryness. The residue is dissolved in 3 c.c. of H₂O, 10 drops of 25% KCNS, H₂O to 5 c.c., 4 c.c. of conc. HCl, and a few drops of 0.75% TiCl₃ in 50% HCl are added, and H₂O to 10 c.c. The coloration obtained is compared with that given by standard aq. Na₂WO₄. R. T.

Separation of tin by nitric acid and contamination of stannic oxide by accompanying metals. W. TILK and R. HÖLTJE (Z. anorg. Chem., 1934, 218, 314—320).—A systematic study has been made of the amounts of Cu, Pb, Zn, Ni, and Fe retained by SnO₂ in the quant. analysis of Sn alloys when Sn is separated by repeated evaporation with HNO₃. M. S. B.

Solutions of bivalent vanadium salts as reducing agents in potentiometric analysis. K. MAASS (Z. anal. Chem., 1934, 97, 241–253).—Acid VCl₂ or VSO₄ solutions maintain a stable titre in the absence of air. Titration is best effected at 90–100°, using a Pt indicator electrode. Fe^{...}, Cu^{...} in HCl and AcOH, and Ag[.] oxidise V^{II} to V^{IV}, which is reduced by further V^{II} to V^{III}, giving two potential increments (equal if the reagent contains no V^{III}). Cu^{...} in H₂SO₄ solution oxidises to V^{III} only, as do VO^{...} salts. CrO₄^{...}, MnO₄['], etc. oxidise to V^v, which is reduced by further reagent giving three increments. Simultaneous determination of Fe^{...} and Cu or VO^{...} (in HCl), or of Ag and Fe^{...} or Cu (in H₂SO₄) is possible. Addition of inert salts (e.g., NaCl, Na₂SO₄, NaOAc) frequently sharpens the end-point. J. S. A.

Determination of small amounts of bismuth, antimony, tin, and molybdenum in copper.— See B., 1934, 630.

Rapid separation of gold and silver from cyanide and chloride solutions. M. MLADENOVIĆ and V. STAJIĆ (Bull. Soc. Chim. Yougoslav., 1933, 4, 207-209).—10—50 c.c. of solution are diluted to 500 c.c., 20 c.c. of 10% Pb(OAc)₂ or CuSO₄ are added, the temp. is raised to 50°, and aq. Na₂S is added to complete pptn. R. T.

Determination of gold by photometric titration. S. HIRANO (J. Soc. Chem. Ind. Japan, 1934, 37, 178—179B).—Au may be determined photometrically by reduction with SnCl₂, a break in the curve corresponding with complete formation of purple of Cassius. Cu, Pb, and small amounts of Fe do not interfere. A. G.

Registering apparatus for studying reactions at regularly varied temperatures. P. VALLET (Compt. rend., 1934, 198, 1860—1863).—Guichard's method (A., 1925, ii, 559) has been modified to give simultaneous automatic records of wt. and temp. during thermal analysis. The results obtained with several hydrated salts are described. B. W. B.

Electric furnace for micro-Kjeldahl digestions and similar purposes. S. J. FOLLEY (Biochem. J., 1934, 28, 890-891). F. O. H. Preventing overheating of oil-baths. H. LEVIN and R. LANARI (Ind. Eng. Chem., 1934, 26, 696).— Melting of a fusible alloy strip immersed in the bath breaks the heating current if overheating occurs.

J. S. A.

Automatic registration of rapidly proceeding thermal processes. J. I. LEVANDO (Zavod. Lab., 1934, 3, 316-325).—Apparatus and methods for the thermal analysis of steels are described. R. T.

Cathode-ray furnace. F. TROMBE (Bull. Soc. chim., 1934, [v], 1, 262—266).—A simple and efficient furnace is described. D. R. D.

Gas blowpipe with electric preheating. A. A. GUNTZ (Bull. Soc. chim., 1934, [v], 1, 259–262).—By preheating the gas and air, hard glasses may be easily worked without O_2 . An apparatus is figured.

D. R. D.

Measurement of slow variations in the refractive index of solids. A. BIOT (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 93—99).—The substance studied is placed between the collimator and the telescope of a spectrometer, and the movement of the fringes produced is measured photographically. C. W. G.

Conversion of photographic sensitivity scales. J. A. M. VAN LIEMPT (Rec. trav. chim., 1934, 53, 816-817).—Conversion formulæ for the Scheiner, Hurter and Driffield, and DIN systems are given. E. S. H.

Combined light and electron microscope, its properties and use. W. KNECHT (Ann. Physik, 1934, [v], 20, 161—182).—An arrangement of apparatus for combining in the same tube a light- (I), magnetic- (II), and electron-microscope (III) for the study of cathode images is described. (II) and (III) appear to be equally suitable. Combinations of electrical and magnetic lenses were investigated. Images formed by (III) show many details not observed in (I), particularly phenomena occurring in the interface between metal and oxide paste of an oxide cathode. A.J.M.

Permeability of glasses to ultra-violet light, measured by fluorescence. P. W. DANCKWORTT and E. JURGENS (Arch. Pharm., 1934, 272, 713–715). —Apparatus for determination of the absorption of ultra-violet light of different $\lambda\lambda$ by glass, using a fluorescent screen or a camera, is described.

R. S. C.

Broad-range vacuum spectrograph for the extreme ultra-violet. K. T. COMPTON and J. C. BOYCE (Rev. Sci. Instr., 1934, [ii], 5, 218-224).—A 2-m. focus normal-incidence instrument, covering on one plate the range zero order—first order of λ 2500, is described. Dispersion is 4.27 Å. per mm., and the body is exhausted to 2×10^{-5} mm. pressure.

N. M. B.

Apparatus for the examination of fluorescent materials, particularly for television receivers. M. VON ARDENNE (Angew. Chem., 1934, 47, 483— 484).—The properties which a substance should possess in order to be suitable for use on the fluorescent screens of television receivers are listed. It is important that it should fluoresce intensely and with a pleasing colour and that the luminescence should not persist for > 0.04 sec. after irradiation has ceased. An apparatus for testing these points under standardised conditions is described. D. R. D.

Objective colorimeter. A. H. W. ATEN, N. GALEMA, and C. A. GOETHALS (Chem. Weekblad, 1934, 31, 258—264).—A simple form of apparatus in which the light intensity is determined by means of a Se cell and a millivoltmeter is described. Concns. may be determined to within 0.25% if special precautions are taken, or rapidly to within 2.5% if certain refinements are omitted. H. F. G.

Precipitation of silver chloride. I. Photronic nephelometer. C. H. GREENE (J. Amer. Chem. Soc., 1934, 56, 1269—1272).—The apparatus consists of a Weston photronic cell for determining the light from a standard source scattered by suspensions prepared under carefully controlled conditions. The reproducibility of the opalescence of AgCl suspensions made from dil. AgNO₃ and excess of HCl increases with increase of [HCl] and added HNO₃. J. G. A. G.

Methods of focussing in analysis of crystalline powders and in spectrography of X- and γ -rays. H. HULUBEI (Compt. rend., 1934, 198, 2164—2166; cf. this vol., 163).—A discussion and suggested modifications of the author's method. B. W. B.

Influence of polarisation on the effects of selenium electrolytic photo-cells. R. AUDUBERT and J. ROULLEAU (Compt. rend., 1934, 198, 1907—1909; cf. this vol., 584).—Photo-potential (I)-polarisation potential (II) curves for polarised Se/Pt electrolytic photo-cells were determined for a range of λ and light intensities. The results support the proposed electronic mechanism (*loc. cit.*). The sign of (II) was reversed at high vals. of (I), due to photo-electronic penetration of the Se-Pt boundary. Se functions as an inert polarisable electrode.

B. W. B. Constancy of the selenium unidirectional-layer photo-cell. L. BERGMANN (Physikal. Z., 1934, 35, 450-452).—The conclusion of Grundmann and Kassner (this vol., 276) that these cells are unsuitable for

meteorological work is too general. The newer and more sensitive cells give const. results, not varying with age or duration of illumination. For very strong illumination the use of a shutter is recommended.

A. J. M.

Boundary-layer photo-electric cells. (MME.) ROX-POCHON (Compt. rend., 1934, 198, 2083—2084).— Practically non-rectifying Se cells, giving linear photocurrent-light intensity curves, have been constructed. The differences between the properties of such cells and of highly rectifying Se cells indicate that the photoelectric effect is independent of rectification.

B. W. B.

Fluorine generation cell. K. G. DENBIGH and R. WHYTLAW-GRAY (J.S.C.I., 1934, 53, 139–1407).— The cell is made of Cu and has a specially wide exit tube and a high diaphragm vessel to eliminate blocking up. The efficiency is 80% at 15 amp. The C fluorides (formed by attack of the graphite anode) are removed by passage through liquid air. A cement compounded of CaF₂ and water-glass is described. Conductivity recorder. S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1934, 34, 158– 159B).—A conductivity recorder operating on a.c. suitable for industry is described. R. S. B.

Simple heavy-current resistance. F. A. CUNNOLD and M. MILFORD (J. Sci. Instr., 1934, 11, 199).—A C rod is supported axially in an insulated Fe tube through which H_2O is flowing. C. W. G.

High-intensity mass-spectrometer. W. R. SMYTHE, L. H. RUMBAUGH, and S. S. WEST (Physical Rev., 1934, [ii], 45, 724—727).—An instrument, in which a new type of magnetic lens focusses on a slit all the positive ions of a given mass from an extended source, is described. Almost complete separation of the K isotopes, and the collection of samples of Li⁶ and Li⁷, have been carried out. N. M. B.

Significant vapour-pressure considerations of the Van Slyke manometric method of gas analysis. M. SHEPHERD (Bur. Stand. J. Res., 1934, 12, 551—566).—Van Slyke's C correction changes with temp. Modifications of the apparatus and method are suggested. H. J. E.

Apparatus for the study of chemical reactions under mechanical pressure. K. C. BEESON and J. B. KERSHAW (J. Assoc. Off. Agric. Chem., 1934, 17, 320-323). E. C. S.

Source of error in chemical measurements of high precision which depend on the use of compressed oxygen. I. L. J. P. KEFFLER (J. Amer. Chem. Soc., 1934, 56, 1259—1262).—The apparent val. of the H_2O equiv. of the calorimetric bomb decreases as the pressure of O_2 in a cylinder of commercial gas, from which the bomb is filled, gradually falls. The effect is attributed to the more rapid effusion through the valve of the O_2 as compared with the traces of combustible impurities. J. G. A. G.

Direct-reading manometer for low pressures. F. TROMBE (Bull. Soc. chim., 1934, [v], 1, 408—410).— The apparatus is not subject to the errors of the Mc-Leod gauge in the presence of vapours liquefiable at the temp. of measurement. It can be used for the measurement of small v.p. and low pressures between 0.001 and 1 mm. M. S. B.

Spring tubing in high-vacuum technique. F. DURAU (Z. Physik, 1934, 89, 152–154).

A. B. D. C.

High-vacuum lubricant-free metal valve. High-vacuum lubricant-free metal seals and joints. F. DURAU (Z. Physik, 1934, 89, 143-147, 148-151). A. B. D. C.

Wilson apparatus for variable pressures. F. JOLIOT (J. Phys. Radium, 1934, [vii], 5, 216—218).— An apparatus in which the pressure in the expansion chamber can be varied from 1 cm. to several atm. is described. N. M. B.

Determination of the volume of dielectric bodies suspended or deposited in an electrolyte by the method of two tubes. A. SLAWINSKI (Bull. Soc. Chim. biol., 1934, 16, 448—460).—A description of the technique of the author's method (A., 1919, 1142) of determining suspension conces. A. L. Water-tight "lead-in" to an enclosed chamber, suitable for ordinary temperatures. W. F. COPE (J. Sci. Instr., 1934, 11, 198—199).—Rubber rings on the tubes are squeezed between the countersunk faces of two brass plates. C. W. G.

Pressure measurements by photographic determination of the levels attained by liquids in tubes. A. FORTIER (Compt. rend., 1934, 198, 2142—2144).—Oblique upward illumination of the meniscus of a transparent liquid produces two real, curvilinear images, < 0.01 mm. wide, which may be photographed directly for continuous record.

B. W. B.

Continuous extractor for liquids heavier or lighter than the solvent. E. A. GAUTHIER and B. ROSSI (Annali Chim. Appl., 1934, 24, 257—259).— In this apparatus solvents heavier and lighter than the liquid to be extracted may be used successively.

Improvements in the Dufton-Crismer fractionating column. O. MILLER (Bull. Soc. chim. Belg., 1934, 43, 279—286).—The efficiency of the column is increased (1) by progressively increasing the distance between the turns of the spiral from 2.5 mm. as the column is descended, and (2) by winding the column with an electrically heated wire and varying the current so that the column is always on the point of flooding. J. G. A. G.

Dependence of velocity of filtration on the chemical and colloidal properties of the impurities. R. KÖPPEN (Arch. Pharm., 1934, 272, 698— 700).—Lactose does not prevent oxidation of metals during the prep. of colloidal solutions by friction. Membranes which give similar speeds of filtration for H₂O may behave differently towards all except very stable colloids, owing to large variations in the size of the particles. R. S. C.

Solvents for micro-mol. wt. determinations according to the method of mol. depression of m.p. for the practice of organic chemistry. J. PRSCH (Ber., 1934, 67, [B], 1115—1119).—Suitable alcoholic and ketonic solvents of m.p. about 100° are tetrahydro- α -dicyclopentadien-3-ol, b.p. 118°/12 mm., m.p. 85°, E=49 [obtained by hydrogenation (Pd-BaSO₄-anhyd. EtOH) of dihydro- α -dicyclopentadien-3-ol], tetrahydro- α -dicyclopentadien-3-one, m.p. 101°, E=56.8, and dihydro- α -dicyclopentadien-3-one, m.p. 53°, E=92. H. W.

Limiting gas-density method for mol. wts. R. T. BIRGE and F. A. JENKINS (J. Chem. Physics, 1934, 2, 167–183).—Methods of reducing available data are examined critically; the most satisfactory methods are applied to data for MeCl and NH₃ and discrepancies of previous results are discussed.

N. M. B. Easy method of removing adhering rubber tubing and stoppers from laboratory glassware. L. SKAZIN (Canad. J. Res., 1934, 10, 592).—The rubber is softened by allowing steam to circulate inside the glassware. O. J. W.

Periodicities of precipitation [studied] by the two-drop method. (MLLE.) S. VEIL (Compt. rend., 1934, 198, 1854—1856).—The advantages of studying periodic pptn. by interaction between two drops of solutions placed in proximity on gelatin are discussed (cf. A., 1933, 224). B. W. B.

Collecting spilled mercury. C. V. Boys (Nature, 1934, 134, 29).—Hg spilled on a smooth surface can be collected into one mass by sprinkling with H₂O. L. S. T.

Chart for [determining] logarithmic mean. S. HATTA (J. Soc. Chem. Ind. Japan, 1934, 37, 165— 166B).—A nomograph is given for reading the logarithmic mean of two nos. from one no. and their ratio. A. G.

Muhammad Ibn Umail: an early Muslim alchemist. E. J. HOLMYARD (Nature, 1934, 133, 937-938). L. S. T.

Early history of Mendeleeff's periodic law. B. N. MENSCHUTKIN (Nature, 1934, 133, 946).

L. S. T.

Geochemistry.

Density of Dead Sea water. R. J. CLARK and F. L. WARREN (Nature, 1934, 134, 29).—No difference in d could be detected between H₂O from the Dead Sea and redistilled H₂O, by two methods in which the uncertainty is approx. 1 in 10⁵. L. S. T.

Mineral water of the Chief Spring in Krynica. S. JURKOWSKI (Arch. Chem. Farm., 1934, 1, 81–92).— The analytical data obtained are practically identical with those found by Schultes in 1807. R. T.

Water of some lakes of the Kurgan forest steppe. A. V. GOLOVIN (Trav. inst. recherch. biol. Perm, 1932, No. 3-4, 61-75).—Chemical differences are recorded. Most of the lakes fall into groups I and III of Palmer's classification. As the lake passes from "youth" to "maturity" it shows an increase in dry residue, and in alkali and Cl concn., and a decrease in [Ca"] and [CO₃"]. CH. ABS. Physical tests and properties of oil and gas sands. G. H. FANCHER, J. A. LEWIS, and K. B. BARNES (Penn. State Coll. Min. Ind. Exp. Sta. Tech. Paper, 1933, No. 4).—Petrographic examination, screen analysis, and porosity and permeability tests are described and discussed. CH. ABS.

Physical characteristics of oil sands. G. H. FANCHER, J. A. LEWIS, and K. B. BARNES (Penn. State Coll. Min. Ind. Exp. Sta. Bull., 1933, 12, 65—171).— Porosity and permeability determinations are described and data for 130 sands are recorded. No consistent relationship was found between porosity, permeability, and screen analysis. CH. ABS.

Berthierite from Kisbanya, Carpathians. V. ZSIVNY and L. ZOMBORY (Min. Mag., 1934, 23, 566— 568).—This rare mineral, previously known from two localities in old Hungary, also occurs at Kisbanya in

T. H. P.

comitat Szatmár (now Chiuzbaia in Satu Mare, Romania), as bundles of needles with stibnite and rhombohedral carbonates. Analysis agrees closely with $FeSb_2S_4$, but d 4.65 is higher than previously recorded for the mineral. L. J. S.

Zeolites. VII. "Clinoptilolite," a silica-rich variety of heulandite. M. H. HEY and F. A. BANNISTER (Min. Mag., 1934, 23, 556-559).—The "mordenite" from Wyoming described by Pirsson (1890) has been named "clinoptilolite" by Schaller (A., 1932, 1228). X-Ray examination of the original material shows that it bears no relation to either mordenite or ptilolite, the structure being that of heulandite with a replacement of CaAl by NaSi in the unit cell formula $Na_x Ca_y Al_{x+2y} Si_{36-(x+2y)}O_{72}, 24H_2O$.

L. J. S.

Zoning in plagioclase felspar. J. PHEMISTER (Min. Mag., 1934, 23, 541—555).—Felspar phenocrysts in Scottish basalts show several types of zoning: (a) normal, proceeding outwards from more basic to more acid plagioclase; (b) simple reverse; and (c) oscillatory, which may be oscillatory-normal or oscillatory-reverse. The alternating composition of the thin zones is possibly the result of lack of balance between rate of growth of the crystal and rate of diffusion from the surrounding magma. Recurrence of calcic plagioclase in the inner part of main zones is explained as the result of irruption of hot magma into the crystallising liquid, probably consequent on eruption of lava at higher levels. L. J. S.

Zoned associations of antigorite, talc, actinolite, chlorite, and biotite in Unst, Shetland Islands. H. H. READ (Min. Mag., 1934, 23, 519-540).—Large spheroidal bodies up to 20 ft. across occurring in garnet-staurolite-kyanite-gneisses consist in the interior of antigorite followed outwards by successive zones of talc, actinolite, chlorite, and biotite. An intrusion of peridotite into pelitic sediments was followed by intense metamorphism separating the former into smaller masses and converting the latter into gneisses. Fluids from later granitic intrusions were then supposed to give rise to differences in composition in the successive zones of the balls, this further metamorphism being accompanied by a transfer of material on a considerable scale. L. J. S.

Diminution in the density of quartz on grinding. G. TAMMANN and G. MORITZ (Z. anorg. Chem., 1934, 218, 267—272).—The d of quartz (I) may be reduced by grinding by as much as 10%. The X-ray diagram shows no marked change in crystal structure and the phenomenon is attributed to the formation in (I) of hollow channels which do not reach the surface. By the same process the d of cristobalite (II), and also of (I) glass, is, on the contrary, increased by approx. 2%. The transition of both (I) and (II) is prevented by grinding. M. S. B.

Structure of kaolin. II. Refractiveness of the aluminosilicate nucleus of kaolin and its derivatives. M. DOMINIKIEWICZ (Arch. Chem. Farm., 1934, 1, 115—119; cf. A., 1933, 37).—The view that kaolin (I) is the Na₆ salt of the hexabasic acid, $H_{12}Al_6Si_6O_{27}$ (II) is supported by the following: (I), on fusion with Na₂CO₃, yields the Na₁₂ salt (III) of (II), which on heating with H_2O at 180° regenerates (I), crystallising as 4(I),3H₂O (IV). (IV) and (III) yield the corresponding Ag₆ (V) and Ag₁₂ (VI) salts on prolonged heating with aq. AgNO₃. Dehydrated (I), Na₆Al₆Si₆O₂₄, does not react with AgNO₃, whence it follows that $H_6Al_6Si_6O_{24}$ is a stronger acid than (II), in which 6 H atoms are combined with Si, and 6 with Al. (V) yields the corresponding K₆ salt on heating with aq. KCl, and $H_{10}(NH_4)_2Al_6Si_6O_{27}$ with aq. NH₄Cl, whilst (VI) affords on heating with aq. NaCl successively Ag₃Na₉Al₆Si₆O₂₇ and $H_3Ag_3Na_6Al_6Si_6O_{27}$. R. T.

Superficial alteration of copper deposits and prospecting. F. BLONDEL (Chim. et Ind., 1934, 31, Spec. No., 295-305).—In general Cu deposits exhibit three zones, (a) an oxidation zone, where most of the minerals are oxidised and where the seam is usually impoverished, (b) a cementation zone, lying below a and generally enriched in sulphides, and (c) lower still, a zone of primary minerals. The character and extent of the first two zones are discussed. A. B. M.

Geochemistry of manganese in West Siberia. P. I. LEBEDEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 422-427).—The Mn contents of different types of rocks from Oirotia have been determined and are discussed with reference to the development of Mn ore deposits. J. W. S.

Physico-chemical properties of Japanese acid clay. X. Formula of crystalline aluminium silicate. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 272—275B; cf. this vol., 628).—Natural clays of the type Al₂O₃,8SiO₂,H₂O yielded, after treatment with dil. alkali, an insol. residue,

 $Al_2O_3, 4SiO_2, H_2O$. The SiO₂ obtained from the alkaline solution was highly active (oil decolorising). The less acid clays ($Al_2O_3: 4-5SiO_2$) have a similar constitution and after treatment with H_2SO_4 are more active than the natural more acid clays. J. A. S.

Change of inner structure of siliceous materials by heat treatments. I. X-Ray study of natural minerals. T. NAKAI and Y. FUKAMI (J. Soc. Chem. Ind. Japan, 1934, 37, 283—284B).—Analyses and structures of chalcedony, flint, jasper, opal, and diatomaceous earth are given. The effect of impurities on the rate of inversion of quartz at high temp. was studied. J. A. S.

Limestones of Canada. Their occurrence and characteristics. II. Maritime Province. M.F. GOUDGE (Canada Dept. Mines, Mines Branch, No 742, 186 pp.).

Chemical composition of rocks at Dinantien, Belgium. (MLLE.) Y. CALLEBAUT (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 128–146).—Analyses are given. C. W. G.

Gold-bearing rock on Olkhon Island and the genesis of the brown iron ore and manganese ore deposits in the Olkhon region. L. KOTELNIKOV (Bull. Acad. Sci. U.R.S.S., 1934, 2, 209-214).-Analyses are given. C. W. G.

Occurrence of mercury. A. STOCK and F. CUCUEL (Naturwiss., 1934, 22, 390-393).—The development of analytical methods capable of detecting quantities of Hg of the order of 0.001 mg. has made it possible to indicate the presence of traces of Hg in many minerals, waters, and animal and vegetable matter. The view is expressed that traces of Hg are to be found in everything. A. J. M.

Relation between P_2O_5 and insoluble residue of Chibin apatite-nepheline deposits dissolved in aqua regia. S. N. ROZANOV and E. N. ISAKOV (Zavod. Lab., 1934, 3, 310—314).—A linear relationship exists between P_2O_5 content and that of substances insol. in aqua regia; the vals. for P_2O_5 calc. on this basis are in good agreement with those given by direct determination of P. R. T.

Composition of Moravian igneous rocks. K. PRECLIK (Tsch. Min. Petr. Mitt., 1934, 45, 269—332). —Many analyses are given of rocks of various types from Moravia and Czech Silesia, and these are compared on diagrams with analyses of rocks from Bohemia and Austria. L. J. S.

Rocks from the Lieser gorge on the Drave. H. HERITSCH (Tsch. Min. Petr. Mitt., 1934, 45, 333— 348).—Descriptions with chemical analyses of amphibolite, eclogite, and garnet-gneiss are given.

L. J. S.

"Chess-board" albite in pegmatite from the Lieser gorge, Carinthia. K. SCHOKLITSCH (Tsch. Min. Petr. Mitt., 1934, 45, 349–354).—Analysis shows albite 63.9% and quartz 34.1%, which form an oriented intergrowth. The albite is a secondary replacement of microcline. L. J. S.

Cause of the red coloration of acid lavas. F. ANGEL and H. GAMERITH (Tsch. Min. Petr. Mitt., 1934, 45, 355-358).—Analysis is given of a soda-liparite from Bulgaria. The red colour of the rock is due to hydrothermal alteration. L. J. S.

New meteoric stone from Silverton, New South Wales. L. J. SPENCER (Min. Mag., 1934, 23, 569—572).—A stone of 350.7 g., showing on the surface a well-marked oriented flow of fused material, probably dates from the time (1883) of the discovery of the mineral deposits in the Broken Hill district. It is a white hypersthene-olivine-chondrite with a small amount of metallic Ni-Fe. L. J. S.

Soil survey of north Shropshire. I. Geography, geology, parent materials, soils. W. M. DAVIES and G. OWEN (Empire J. Exp. Agric., 1934, 2, 178–188).—Descriptive. A. G. P.

Characteristics of brown earths. T. SEKI (J. Sci. Soil and Manure, Japan, 1934, 8, No. 1; Proc. Internat. Soc. Soil Sci., 1934, 9, 111).—Brown earth soils of grassland and forest types are described and their classification is discussed. A. G. P.

Nature of the vegetal substances constituting coal, as shown by microscopic examination in reflected light. A. DUPARQUE (Chim. et Ind., 1934, 31, Spec. No., 279—285; cf. A., 1931, 818, 931).—Petrographic examination of the coals of Northern France permits them to be classified as follows: (a) "cutin" coals rich in spores and cuticle; these are bituminous coals of > 26% volatile matter content, (b) lignitous coals containing woody tissue and sclerenchyma; these belong in general to the class of coking coals of > 18% and < 26% volatile matter content, (c) cellulosic coals consisting principally of amorphous colloidal substances derived from the disintegration of cellulosic material; these are anthracites. A. B. M.

Organic Chemistry.

Robinson's electronic theories of organic chemistry. (1) W. A. NOYES. (2) R. ROBINSON (Chem. and Ind., 1934, 559-562, 562-563).—A discussion.

Stability of organic compounds in the gaseous or vapour state towards impact of potassium ions. O. SCHMIDT (Ber., 1934, 67, [B], 1145— 1152).—Comparison of the behaviour of gases and vapours of inorg. and org. substances towards K ions with a velocity corresponding with 25 and 200 volts shows that the energy losses on impact of K with the scarcely deformable atom of Hg and the rare gases increase with decreasing wt. of the disrupted gas particle. With the paraffin hydrocarbons the loss of energy increases with chain length and hence with mol. wt., showing that more energy is absorbed by the mol. as its size increases, with consequent diminution of stability. As in cracking, the hydrocarbons with longer are less stable than those with shorter chain. Similar but less marked phenomena are observed with C_2H_4 and CH_2CMe_2 , since the double linking in $CH_2:CMe_2$ strengthens the neighbouring C-C unions. C_2H_2 , CO, CO₂, and MeCl are stable, NH₃ is very unstable. H. W.

Thermal decomposition of organic compounds from the viewpoint of free radicals. VIII. Comparison of thermal and electrical decomposition of organic compounds into free radicals. F. O. RICE and F. R. WHALEY (J. Amer. Chem. Soc., 1934, 56, 1311—1313).—The following compounds decompose at 800—1000° at low pressures (method: A., 1932, 1108; cf. A., 1933, 1270; this vol., 276) into fragments which remove Sb (and usually Pb) mirrors at varying rates: C_2H_6 , C_3H_8 , C_4H_{10} , CHMe₃, C_7H_{16} ; gasoline, Et₂O, EtCHO, C_3H_6 , AcOH, EtOAc, EtCO₂Et, Et maleate, Bu°OH, and NMe₂; C_2H_4 does not give active fragments. X-Ray powder photographs of the HgRBr obtained by combination of the fragments from C_4H_{10} with Hg and subsequent treatment with EtOH-HgBr₂ indicate the formation of Me and Et at about 850° and Me only at about 950°. When $n \cdot C_4H_{10}$, $n - C_7H_{16}$, C_2H_4 , MeOH, EtOH, MeCHO, AcOH, and COMe₂ are passed through a discharge tube, fragments are formed which remove Sb or Pb (but not Zn or Cd) mirrors and have a half-life of $0 \cdot 7 - 2 \cdot 1 \times 10^{-3}$ sec. It is shown by the above method that COMe₂ gives Me; the product from $n \cdot C_4H_{10}$ could not be identified. Pr could not be detected in any of the decomp. products examined.

[Chlorination of paraffins.] H. B. HASS and P. WEBER (Ber., 1934, 67, [B], 974-975).-Reasons are advanced for considering that the "isoamyl chlorides" of Wertyporoch (A., 1933, 590) are derivatives of *n*-pentane. The b.p. of γ - and β -chloropentane are $97\cdot1-97\cdot4^{\circ}/760$ mm. and $96\cdot6-96\cdot8^{\circ}/760$ mm., respectively. H. W.

Decomposition of aliphatic and alicyclic hydrocarbons by aluminium chloride. K. H. BAUER and U. TOMA (Ber., 1934, 67, [B], 1135—1138).— When heated with 25% of its wt. of AlCl₃, octadecane, b.p. 181—187°/15 mm., m.p. 28°, gives 23% of C, 3·3% of condensation products, 13% of noncondensable gases (CO₂ 1·3%; H₂ 13·6%; gaseous hydrocarbons 85%), and 60% of volatile liquids, b.p. 20—175°, I val. 0. Under similar conditions, hexatriacontane, m.p. 76°, affords 24% of C, 30·0% of heavy oils, b.p. >450°, and 33% of volatile liquids, b.p. 20—175°; the gases consist of CO₂ 0·5%, H₂ 14·3%, and hydrocarbons 85%. Octahydroanthracene at 175—320° yields 36% of C, 10·0% of heavy oils, and 53·3% of volatile liquids, b.p. 90—350°; the gases contain 2·3% of CO₂, 54·0% of H₂, and 43·6% of hydrocarbons. H. W.

Peroxide effect in addition of reagents to unsaturated compounds. M. S. KHARASCH and M. C. MCNAB (J. Amer. Chem. Soc., 1934, 56, 1425).— A reply to Sherrill *et al.* (this vol., 630). Previous work (A., 1933, 805) on the addition of HBr to C_3H_6 is confirmed. H. B.

Thermal preparation of ethylene hydrocarbons from alcohols. W. TREIBS (Ber., 1934, 67, [B], 942—943; cf. A., 1928, 68; Ssakmin, this vol., 508).— The catalytic activity of unglazed porcelain is considerably < that of amorphous Al₂O₃, but is sufficient to lead to the production of ethylenic hydrocarbons in good yield from the alcohols at the temp. indicated for work in tubes and autoclaves, respectively: Et (450°); Pr^a (450°); Pr^β (400°); Bu (450°), $n \cdot C_8 H_{17}$ (475°; 300°); linalyl (400°; 250°); cyclohexyl (400°; 300°). Borneol, isoborneol, and fenchyl alcohol (450°, 250°; 400°, 200°; 400°, 200°) yield camphene (I) and liquid isomerides also produced from (I). Menthol (400°, 250°) yields menthene. At 500° alcohols and phenols with the Pr^β group commence to lose $C_3 H_6$. H. W.

[Laboratory preparation of pure ethylene and propylene.] V. N. IPATIEV (Ber., 1934, 67, [B], 1061).—A question of priority (cf. Ssakmin, this vol., 508). H. W.

Polymerisation of isobutene. H. I. WATER-MAN, J. OVER, and A. J. TULLENERS (Rec. trav. chim., 1934, 53, 699—702).—isoButene and AlCl₃ in C_5H_{12} at -78° to 16° give mixtures of olefinic (I) and cyclic products of mol. wt. 132—4800, (I) having the lower mol. wts. Physical consts. are given for products obtained at -35° and 16° , before and after hydrogenation. Lower temp. produce products of higher mol. wt. Reaction is often explosive at -78° , the products at this temp. being highly viscous. R. S. C.

Reaction of *n*- and *iso*-pentenes with hydrogen chloride and aluminium chloride at low temperatures. J. J. LEENDERTSE, A. J. TULLENERS, and H. I. WATERMAN (Rec. trav. chim., 1934, 53, 715—724).—Pentan- γ -ol with active Al₂O₃ at 380—400° gives an 81% yield of n- Δ^{β} -pentene (I). n- Δ^{α} -Pentene (II) could not be satisfactorily obtained from n-amyl alcohol under similar conditions, owing to cracking and isomerisation to (I); its prep. (impure) from allyl bromide and MgEtBr is modified. At -80° (II) and CH₂:CHPr^{β} (III) do not react with HCl alone, (I) reacts slowly, and CHMe:CHEt (IV) and CHMe:CMe₂ (V) give rapidly CMe₂EtCl. (I), (III), (IV), and (V) with HCl and AlCl₃ at -80° give rapidly C₅H₁₁Cl and a mixture of chlorides derived from polymerise only slowly, (IV) and (V) rapidly in presence of AlCl₃ alone at -80° . R. S. C.

Action of chlorine on isoprene. W. J. JONES and H. G. WILLIAMS (J.C.S., 1923, 829-835).-Pure isoprene (I), b.p. 33.9-34.3°/760 mm. (improved prep. through the sulphone described), with 1 mol. of Cl_2 in CCl_4 in a freezing mixture, affords α -chloro- β methylbutadiene, b.p. 50.4°/100 mm. (38%) [purified through α -chloro- β -methyl- Δ^{β} -butene-1 : 4-sulphone, m.p. 73° (corr.), obtained by treatment with liquid SO₂; affords 1-chloro-2-methyl-1:4:4a:9a-tetrahydroanthraquinone, m.p. 146° (corr.), with α -naphthaquinone in N_2 at 80°] {polymerises to approx. $[(C_5H_7Cl)_3O)]_x$ on keeping}, $\alpha\delta$ -dichloro- β -methyl- $\Delta\beta$ -butene (II) (45%), b.p. 56°/10 mm. (CH₂ClAc and CH₂Cl·CHO, oxidised to CH₂Cl·CO₂H, by ozonolysis), a small amount (6%) of a Cl₂-compound of lower b.p., and residue (11%). Oxidation of (II) with $KMnO_4-H_2O-COMe_2$ at -5° gives $\alpha\delta$ -dichloro- β -methylbutane- $\beta\gamma$ -diol, m.p. 106.5° (corr.); with Zn J. W. B. and boiling EtOH it regenerates (I).

Isomeric transformation of hydrocarbons of the diallyl series in presence of silicates. S. V. LEBEDEV and J. M. SLOBODIN (J. Gen. Chem. Russ., 1934, 4, 23-30).—CH₂:CMe₂ and Br yield a mixture of $\alpha\beta\gamma$ - and $\alpha\alpha\beta$ -tribromoisobutane; the former affords diisobutenyl (I) on treatment with Mg, and the latter diisocrotyl (II). (I), on passing over floridin at 205°, is converted partly into (II), the equilibrium mixture containing 20-25% of (I) and 75-80% of (II). The equilibrium mixture obtained similarly from diallyl (III) contains 42% of dipropenyl (IV) and 58% of (III). Part of (II) and (IV) undergoes conversion into polymerides under the above conditions. R. T.

Polymerisation. XIV. Depolymerisation of triisobutene. S. V. LEBEDEV and I. A. LIVSCHITZ (J. Gen. Chem. Russ., 1934, 4, 13–22).–99% of $(C_4H_8)_3$ is dissociated at > 50° in presence of active silicate (floridin) to afford $(C_4H_8)_2$ (I) and C_4H_8 (II), whilst 0.5–1% is converted into isobutane. Part of (I) is polymerised under these conditions to $(C_4H_8)_4$ and higher polymerides. The (I) obtained is identical with that formed by polymerisation of (II). R. T.

Organo-alkali compounds. XI. Mechanism of polymerisation of unsaturated hydrocarbons by alkali metals and alkali metal alkyls. K. ZIEGLER, F. DERSCH, and H. WOLLTHAN. XII. "Catalysis" of polymerisation of unsaturated hydrocarbons by organo-alkali compounds. K. ZIEGLER and L. JAKOB. XIII. Primary reaction products of alkali metals on butadienes. K. ZIEGLER, L. JAKOB, H. WOLLTHAN, and A. WENZ (Annalen, 1934, 511, 13-44, 45-63, 64-88).-XI. (cf. A., 1928, 404; 1929, 1091.) Exclusive 1:4addition of 1 mol. of an alkali metal alkyl to 1 mol. of butadiene (I) occurs; with >1 mol. of (I), some 1:2-addition also occurs. The possibility of allyl tautomerism between the 1:2- and 1:4-adducts [and its relation to the further addition of (I)] is discussed. (I) (approx 1.5 mols.) and CKPhMe₂ (II) (1 mol.) in Et₂O give (after decomp. with H₂O) (mainly) ε -phenyl- ε -methyl- Δ^{β} -hexene (III), b.p. 224-226°, 102°/13 mm.; hydrocarbons, CPhMe2·[C4H6]nH (IV), with n=2, b.p. $90^{\circ}/0.2$ mm., $146-148^{\circ}/10$ mm., n=3, b.p. 189-192°/10 mm., and n=4, b.p. 130-170°/0.2 mm., are also formed. (III) is oxidised (0_3) to MeCHO, β -phenylisovaleraldehyde (V), b.p. 115-116°/11 mm. (semicarbazone, m.p. 123.5-124.5°; p-nitrophenylhydrazone, m.p. 125°), and β -phenylisovaleric acid (VI), m.p. 59–60°. (IV, n=2) similarly gives (mainly) resin and small amounts of MeCHO and (V); oxidation (CrO₃, AcOH, conc. H₂SO₄) affords (\cdot CH₂·CO₂H)₂ (VII) and unidentified oily acid. Oxidation (O₃ followed by CrO₃) of (IV, n=3) gives (VI) and (VII); (VII) is also obtained by similar oxidation of a polymeride from (I) (100 mols.) and (II) (1 mol.). Isoprene (VIII) and (II) (1:1) afford (by 1:4-addition in both possible ways) a mixture, b.p. 117°/13 mm., of ε-phenyl-βε- and $-\gamma \epsilon$ -dimethyl- Δ^{β} -hexenes, since ozonolysis gives MeCHO, $COMe_2$, (V), and β -phenylisobutyl Me ketone (IX) (semicarbazone, m.p. 164°). Oxidation (O3 followed by Ag₂O) of a polymeride from 6 mols. of (VIII) affords HCO₂H, AcOH, lævulic acid, (V), (VII), (IX), and acetonylacetone. Ozonolysis is considered to be unsatisfactory; CH₂O (which could not be detected) is probably formed and then condenses with other fission products to give resins.

LiCH₂Ph and (I) (4 mols.) afford (after decomp. with aq. NH₄Cl) a product which is a mixture containing phenylparaffins, Ph·[CH2]4n+1H; fractionation gives (with some difficulty) a-phenylpentane, b.p. 81°/10 mm. [p-Ac derivative, b.p. 146-148°/10 mm. (semicarbazone, m.p. 185°), obtained using AcCl and AlCl₃ in CS₂], α -phenylnonane, b.p. 146°/14 mm. [p-Ac derivative, b.p. 190°/10 mm. (semicarbazone, m.p. 172°)], *a-phenyltridecane*, b.p. 188—189·5°/10 mm. [p-Ac derivative, b.p. 177°/0·4 mm., m.p. 35° (semicarbazone, m.p. 168°)], and a-phenylheptadecane, m.p. 38° [p-Ac derivative, m.p. 53° (semicarbazone, m.p. 158-161°)]. 1:4-Addition is not proved to be exclusive, since substances other than the above are also formed. The above hydrocarbons are also $\operatorname{COCl} \cdot [\operatorname{CH}_2]_{4n} \operatorname{H} + \operatorname{C}_6 \operatorname{H}_6 + \operatorname{AlCl}_3 \longrightarrow$ synthesised : COPh [CH2]4nH, and thence by reduction (Wolff-Kishner) of the semicarbazones to $Ph \cdot [CH_2]_{4n+1}H$. Tridecoic acid is prepared by dehydration and subsequent oxidation (cf. Skraup, A., 1928, 882) of di-phenyltridecylcarbinol, m.p. 43° (from MgPhBr and Me myristate). The semicarbazones of Ph dodecyl and hexadecyl ketones have m.p. 101° and 87.5° , respectively. Reduction (H₂, Pd-BaSO₄, EtOAc) of the product from LiBu (1 mol.) and (I) (3 mols.) does not give fully saturated material; reduction with Raney Ni at 130-140° and 180 atm. affords a mixture

of paraffins, $C_{4n}H_{8^{n+2}}$ (from which *n*-octane is isolable), which appears to contain branched-chain compounds (formed by 1:2-addition). Thus, the dodecane fraction has a b.p. < that of *n*-dodecane. An artificial mixture of *n*-paraffins (above; n=2-9) could not be separated sharply by fractional distillation.

XII. Polymerisation of butadiene (I) and styrene (II) is "catalysed" by CMAr₃, CHMAr₂, and CMAr₂Alph (M=alkali metal). (I) is unaffected by the Na or Li derivatives of fluorene, indene, phenylindene, and 1:3-diphenylindene, whilst $\Delta^{\alpha\nu}$ -pentadiene and $\beta\gamma$ -dimethylbutadiene are, in general, unaffected by any of the above alkali compounds. Prolonged interaction of (I) (0·1 mol.) and CHPh₃ (0·1 mol.) in presence of Et₂O-CNaPh₃ gives resinous material; practically all the CHPh₃ is recovered. Very slow passage of (I) (4 mols.) during 38 days into CHPh₃+CNaPh₃ in Et₂O results in the addition of about 70% of the CHPh₃: CNaPh₃+CH₂:CH·CH:CH₂

 \rightarrow CPh₃·CH₂CH:CH·CH₂Na $\xrightarrow{\text{CHPh}}$ CNaPh₃+ CPh₃·CH₂·CH:CHMe. Passage of (I) into CHPh₃+ CNaPh₃ in N₂ at 130—140° results in the addition of >90% of the CHPh₃; distillation of the reaction mixture gives a *triphenylpentene* (III), b.p. 162°/0·2 mm., m.p. 115°, and a little $\alpha\alpha\alpha$ -triphenyl- Δ^{γ} -pentene (IV), m.p. 83° [oxidised (CrO₃, AcOH) to CPh₃·CH₂·CO₂H]. The former reaction mixture

CPh₃·CH₂·CO₂H]. The former reaction mixture similarly affords a *triphenylpentene* (V), m.p. 124°. (IV) and a little (V) are also obtained from (I), dicyclohexylamine, and CNaPh₃. (III), (IV), and (V) are all reduced to $\alpha\alpha\alpha$ -triphenylpentane, m.p. 61·5°. Addition of CHPh₃ to (II) can be effected in presence of CNaPh₃ at 130—140°. (I) does not react with fluorene and its Na derivative at 140°. The amount of CHPh₃ in mixtures containing neutral resin is determined (accuracy 3—5%) by successive treatment with CKPhMe₂ (VI), dicyclohexylamine [which removes excess of (VI), but has practically no action on the CKPh₃ now present], CO₂, and dil. H₂SO₄; the resultant CPh₃·CO₂H is dried and titrated with (VI) in Et₂O.

XIII. When a 0.5M-Et₂O solution of butadiene (I) is shaken with "mol." Na (2 atoms) the resulting solution contains only a small amount of combined Na. $\Delta^{\alpha\gamma}$ -Pentadiene (II) and $\beta\gamma$ -dimethylbutadiene (III) similarly give solutions which are 0.01 and 0.006 N, respectively, in alkali. Hydrolysis of the resultant products affords undistillable resinous oils. (II) and Na in presence of CHPh₃ give CNaPh₃ (0.17N; theory 0.8N); decomp. of the reaction mixture with EtOH and repeated further treatment with (II) afford pentene and products, $H[C_5H_8]_nH$ (n=2 to 6-7). (III) similarly gives CNaPh₃ (0.5N; theory 0.8N); CMe₂:CMe₂ (IV) and hydrocarbons, $C_{12}H_{22}$, b.p. 81-83°/14 mm., and $C_{18}H_{32}$, b.p. 156.5°/14 mm., are isolable (as above). In presence of fluorene, the adduct from Na and a butadiene reacts rapidly to give Na fluorenyl. Analogous results are obtained with amines (NHEt2, dicyclohexylamine, NHPhEt, NH₂Ph); ready addition of 2 H to the diolefine occurs [thus, (III) gives (IV); C₁₀H₈ affords 1:4dihydronaphthalene]. Octadiene, b.p. 120°, is obtained from (I), Li, CPh₂:CH₂CH₂Ph, and NHPhEt

in Et₂O, whilst (I), Li, and 2-dimethylaminofluorene in Et₂O give octadiene and some dodecatriene, b.p. $90-95^{\circ}/15$ mm. When 0.5M-Et_oO solutions of (I), (II), (III), and isoprene are shaken with finelydivided Li, the resulting solutions are 0.03, 0.27, 0.5, and 0.24N, respectively, in alkali. The product from (I) is hydrolysed (H₂O) to a high-mol. resin. Decolorisation of the solution from (II) with MeOH and further addition of (II) give pentene and condensation products $H[C_5H_8]_nH$ (n=2-5). (III) similarly affords a little (IV), (mainly) a bimol. product, b.p. 78°/8 mm., and some higher polymerides; the intermediate CH2Li CMe CH2Li reacts rapidly with a second mol. of (III), but subsequent addition of (III) to the new complex is slow. Thus, the orangered solution from Li and (III) treated with (III) gives (after 45 min.) a yellow solution [hydrolysis (H_2O) of which affords no (IV)]; the major part of the (III) has not reacted [complete disappearance of the (III) is found after 18-24 hr.]. No evidence has been obtained indicating the formation of radical-like intermediates. **H.** B.

Preparation of pure $n-\Delta^{\alpha}$ -octene. H. I. WATER-MAN and W. J. C. DE KOK (Rec. trav. chim., 1934, 53, 725—729).—The consts. of $n-\Delta^{\alpha}$ -octene, prepared from $n-C_5H_{11}$ ·MgBr and allyl bromide, reported by Whitmore *et al.* (A., 1933, 1033), are confirmed.

R. S. C.

Isomerisation of olefines. I. Conversion of tert.-butyl-, as-methylisopropyl-, and tetramethyl-ethylene into equilibrium mixtures of the three olefines. K. C. LAUCHLIN, C. W. NASH, and F. C. WHITMORE (J. Amer. Chem. Soc., 1934, 56, 1395—1396).—Essentially the same mixture of CMe₂:CMe₂, CH₂:CMePr^β, and CH₂:CHBu^γ is obtained when each olefine is passed over P_2O_5 on SiO₂ gel at 300°, as is formed by similar dehydration of CHMeBu^γ·OH (A., 1933, 1140). The possible changes involved are discussed. H. B.

Catalysis of acetylene polymerisation in ultraviolet light.—See this vol., 852.

Surface reaction between acetylene and iodine. --See this vol., 851.

Chlorination of solid paraffins. II. Molecular volumes of chloroparaffins and chlorostearic acids. III. Lowering of m.p. by chlorination. Y. TANAKA, R. KOBAYASHI, and I. NISHI (J. Soc. Chem. Ind. Japan, 1934, 37, 208-209B, 209B).—II. The mol. vol. of chlorinated *n*-paraffins (m.p. 46—51°) and of chlorinated stearic acids are directly ∞ the Cl content.

III. In the above cases chlorination produces a marked lowering of m.p. (to -37° for 44% chlorinated stearic acid) and increase in η . H. A. P.

Action of inorganic bases on sec.- and tert.butyl bromides. H. E. FRENCH, W. H. MCSHAN, and W. W. JOHLER (J. Amer. Chem. Soc., 1934, 56, 1346—1348).—C₄H₈ is obtained in 13—47% yield from sec.-BuBr and AgOH (I), KOH, NaOH, Ca(OH)₂, and Ba(OH)₂ in aq. solution or suspension at 30—60°; the amount produced is approx. ∞ to the concn. of dissolved hydroxide [except for (I)]. The yield of C₄H₈ from Bu'Br varies from 0 [(I) at 30°] to 2·2%. H. B. Hydrolysis of tertiary aliphatic halides. I, H. M. WOODBURN and F. C. WHITMORE (J. Amer. Chem. Soc., 1934, 56, 1394—1395).—The ease of hydrolysis of Bu^vCl (I), tert.-amyl chloride (II) and bromide, CMeBu₂Cl, and CBu^a₃Cl with hot H₂O or aq. Na₂CO₃ decreases with increase in mol. wt. (probably owing to decreased solubility); olefines are formed exclusively. The rate of hydrolysis of (I) and (II) decreases in the order H₂O > 5%, Na₂CO₂ > 40% Na₂CO₃, and is thus dependent on the solubility in the hydrolysis medium. Hydrolysis with cold H₂O or cold aq. NaOH gives olefine and some tert.-alcohol. CR₃Hal are more resistant to hydrolysis than is usually supposed. H. B.

Optical rotation and atomic dimension. D. H. BRAUNS (J. Amer. Chem. Soc., 1934, 56, 1421—1422). — α -Chloro-, $[M]_{10}^{\infty} + 179^{\circ}$, α -bromo- (I), $[M]_{10}^{\infty} + 610^{19}$, and α -iodo-, $[M]_{10}^{\infty} + 1124^{.7}^{\circ}$, - β -methylbutanes are prepared from (-)- β -methylbutyl alcohol and HHal; α -fluoro- β -methylbutane, $[M]_{10}^{\infty} - 799^{.1}^{\circ}$, is obtained from (I) and AgF. The differences in the above vals. are ∞ to the differences in at. diameter (cf. A., 1925, ii, 633), but not to the differences in at. wt. (Guye's hypothesis). H. B.

Mechanism of the condensation of nitromethane with formaldehyde and preparation of nitroethanol. I. M. GORSKI and S. P. MAKAROV (Ber., 1934, 67, [B], 996-1000).—Interaction of CH_2O (I) with MeNO₂ (II) in presence of K_2CO_3 with or without EtOH involves the equilibria, (I) +(II) $NO_2 \cdot CH_2 \cdot CH_2 \cdot OH$ (III) $RO_2 \cdot CH(CH_2 \cdot OH)_2$ (IV) $RO_2 \cdot C(CH_2 \cdot OH)_3$ (V). Conditions are described for the prep. of (III), b.p. 89-90°/4 mm., (IV) b. p. 157-158°/7 mm., m.p. 58-59°, and (V), m.p. 159°. H. W.

Electrochemical oxidation of α -glycols. E. TOMMILA (Ann. Acad. Sci. Fennicæ, 1934, 39, 3-65). —Electrochemical oxidation of ethylene, propylene, and phenylethylene glycols and of pinacol in alkaline and acid solution under varying conditions has been examined. Two reactions may take place with a smooth Pt anode, either oxidation of the OH group to an OH-aldehyde or -ketone, or the breaking down of the mol. into two aldehyde or ketone mols., the latter reaction being more pronounced at higher potentials. With a platinised anode, two interconvertible products are obtained, the oxidation being facilitated by the catalytic effect of the anode metal. F. R. S.

Determination of butane- $\beta\gamma$ -diol. C. MATG-NON, H. MOUREU, and M. DODE (Bull. Soc. chim., 1934, [v], 1, 411—419; cf. A., 1933, i, 1041).—Butane- $\beta\gamma$ -diol (1 mol.) with Br-H₂O (8—10 mols.) at 100 during 3 min. affords OH·CHMe·Ac (I) (76.5% yield), oxidised to Ac₂, which is determined as Ni dimethylglyoxime. The yield of (I) is not much influenced by temp. or the quantity of Br-H₂O. J. L. D.

Plant pigments. LXI. Products of the action of magnesium alkyl salts on esters of dihydrobixin. I. P. KARRER and F. RUBEL (Helv. Chem. Acta, 1934, 17, 773—774).—Dihydrobixin Me ester (I) is converted by MgMeI into $\alpha\alpha\phi\phi$ -tetramethyldihydrobixinol, m.p. 166—167°, the visible absorption spectrum of which scarcely differs from that of (I). (I) does not readily lose H_2O . The term "bixinol" is used to denote the primary alcohol obtained by replacing the $2CO_2H$ of bixin by $2CH_2 \cdot OH$. H. W.

Olefinic ethyl ethers of α -glycols. D. BARDAN (Bull. Soc. chim., 1934, [v], 1, 368—370; cf. A., 1932, 143).—Interaction of γ -ethoxy- β -methylheptan- β -ol (cf. this vol., 754) with P_2O_5 in boiling C_5H_5N during 2 hr. affords γ -ethoxy- β -methyl- Δ^β -heptene, b. p. 107— 109°/42 mm. The following are prepared similarly: δ -ethoxy- γ -ethyl- Δ^{γ} -octene, b.p. 119—121°/34 mm.; ϵ -ethoxy- δ -n-propyl- Δ^{δ} -nonene, b.p. 132—136°/21 mm; ζ -ethoxy- ϵ -n-butyl- Δ^{δ} -decene, b.p. 149—153°/17·5 mm.; δ -ethoxy- γ -ethyl- Δ^{γ} -decene, b.p. 120—126°/21 mm; ϵ -ethoxy- δ -n-propyl- Δ^{δ} -nonene, b.p. 155—159°/22 mm.; and ζ -ethoxy- ϵ -n-butyl- Δ^{ϵ} -dodecene, b.p. 174—179°/20— 19·5 mm. 20% H₂SO₄ de-ethylates these compounds to ketones. J. L. D.

Ether-like compounds. XIII. Hydrolysis of acylalkyl formals. M. H. PALOMAA and V. JAAK-KOLA (Ber., 1934, 67, [B], 949–954; cf. this vol., 625).—The rates of hydrolysis of acylalkyl formals measured at 15°, 25°, and 35°, are tabulated. In general, the temp. coeff. increases as the rate of ester hydrolysis decreases, and with increasing complexity approximates to but does not reach that of acetal hydrolysis. The following observations appear new: $CH_2 \cdot OMe$ n-butyrate, b.p. 151–152°; $CH_2 \cdot OMe$ βmethoxypropionate, b.p. 88·0–88·4°/18 mm.; $CH_2 \cdot OEt$ n-butyrate, b.p. 166°; $CH_2 \cdot OEt$ β-methoxypropionate, b.p. 95°/15 mm.; $CH_2 \cdot OPr^{\beta}$ acetate, b.p. 134– 135°; $CH_2 \cdot OPr$ propionate, b.p. 154–155°; $CH_2 OPr$ n-butyrate, b.p. 171–172°; $CH_2 OPr^{\beta}$ β-methoxypropionate, b.p. 105°/20 mm.; Pr^{β} methoxyacetate, b.p. 148°; Pr^{β} β-methoxypropionate, b.p. 67–68°/21 mm. H. W.

Preparation of ketals of alkylacetylenes with methyl alcohol. D. B. KILLIAN, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 1384—1385).—CHMc(OMe)₂, b.p. 64—65°, and $\beta\beta$ -dimethoxy-propane, b.p. 78—80°/747 mm., -butane, b.p. 48—50°/100 mm., -pentane, b.p. 30—31°/15 mm., -hexane, b.p. 58—60°/30 mm., and -heptane (I), b.p. 74—75°/27 mm., are prepared from CR:CH (R= H—C₅H₁₁) and MeOH by the method previously described (this vol., 759). (I) is hydrolysed (dil. acid) to Me n-amyl ketone. Ketals are not obtained from ROH other than MeOH. H. B.

α-Hydroxy-acetals of high mol. wt. and aldehydes derived from them. M. ROTBART (Ann. Chim., 1934, [xi], 1, 439-514).—The Na derivatives of aliphatic and cycloparaffin alcohols are best prepared by "mol." Na in PhMe, but CH₂Ph·OH (I) is partly hydrogenated by this method. CH₂Ph·OK is obtained by distillation of (I) in vac. with KOH-EtOH. The Na (or K) derivatives with CH₂Br·CH(OEt)₂, best in an autoclave at 170-180°, give alkyloxyacetals, OR·CH₂·CH(OEt)₂, in which R=n-octyl (II), b.p. 121-5-122°/5 mm., α-methyl-n-heptyl (III), b.p. 131-132°/14 mm., n-decyl (IV), b.p. 159-160°/14 mm., n-lauryl (V), b.p. 150-151°/3 mm., myristyl (VI), m.p. 25°, b.p. 161-162°/2 mm., cetyl (VII), m.p. 37°, b.p. 192-194/1 mm., cyclohexyl (VIII), b.p. 115°/12 mm., 2- (IX), b.p. 124-126°/18 mm., 3- (X), b.p. 120-121°/12 mm., and 4-methylcyclohexyl (XI), b.p.

125-126°/12 mm., Ph, b.p. 136-138°/16 mm., CPhMe₂ (XVII), b.p. 150-152°/16 mm., and CH₂Ph-CMe₂ (XVIII), b.p. 115-118°/2 mm. Similarly are prepared ax-dimethoxy- (XIX), b.p. 138-140°/15 mm., and ax-di-n-propoxy-ethyl n-octyl ether (XX), b.p. $163-165^{\circ}/15$ mm., from $CH_2Br \cdot CH(OMe)_2$, b.p. $49 \cdot 5-50 \cdot 5^{\circ}/15$ mm., and $CH_2Br \cdot CH(OPr^{\circ})_2$, b.p. $89 \cdot 5-90 \cdot 5^{\circ}/13$ mm. By hydrolysis with about 30% aq. H₂SO₄-AcOH (unless otherwise stated) were obtained the corresponding α -alkyloxyacetaldehydes [m.p. (block) of the semicarbazones being stated in parentheses], in which R = (II), b.p. 111-113°/18 mm. $(98\cdot5-99^{\circ})$, (III), b.p. $98-99\cdot5^{\circ}/15$ mm. $(78\cdot5-79\cdot5^{\circ})$, (IV), b.p. $133-135^{\circ}/15$ mm., m.p. $19\cdot5-20^{\circ}$ ($103-104^{\circ}$), (V), m.p. 18° , b.p. $118-119^{\circ}/3$ mm. (108°), (VI), m.p. 36° , b.p. $138-140^{\circ}/4$ mm. (97°) , (VII), m.p. 47° (102°), (VIII) (by 1°_{0} H₂SO₄), b.p. $71^{\circ}/14$ mm. (175°), (IX) (by 1°_{0} H₂SO₄), b.p. $85-88^{\circ}/12$ mm. ($152-152\cdot5^{\circ}$), (X) (by 1°_{0} H₂SO₄), b.p. $98-100^{\circ}/19$ mm. ($187-188^{\circ}$), Ph (by $1-5^{\circ}_{0}$ H₂SO₄), b.p. $101-103^{\circ}/15$ mm. (145°), (XII) (by 1°_{0} H₂SO₄), b.p. $109-111^{\circ}/11$ mm. (119°), (XIII) (only by $4-5^{\circ}_{0}$ H₂SO₄; poor yield), b.p. $157-160^{\circ}/15$ mm. ($160-160\cdot5^{\circ}$), (XIV) (by 7°_{0} H₂SO₄), b.p. $120-122^{\circ}/15$ mm. ($88-88\cdot5^{\circ}$), and (XV) (by 5°_{0} H₂SO₄), b.p. $134-136^{\circ}/16$ mm. ($89-89\cdot5^{\circ}$). (XIX) and (XX) are smoothly hydrolysed by 15 and mm. (98·5—99°), (III), b.p. 98—99·5°/15 mm. (78·5— (XIX) and (XX) are smoothly hydrolysed by 15 and 25% H_2SO_4 , respectively. The aldehydes in which R=(XVI), (XVII), and (XVIII) could not be obtained, since even very dil. H_2SO_4 hydrolysed the alkoxy-group. The analogous substances, p-anisylmethyl Et ether [prepared in 78% yield from p-OMe·C₆H₄·CH₂Cl and NaOEt at 160—200° (autoclave)], b.p. 111–113°/11 mm., and CHPhMe OEt, are hydrolysed by hot 5 and 1% aq. H_2SO_4 -AcOH, respectively. The semicarbazones are analysed by Veibel's method (A., 1927, 1172), which must be modified by addition of MeOH for aliphatic compounds. The aldehydes are best obtained from the semicarbazones by distillation in steam from 2-5% aq. R. S. C. H₂SO₄.

Reaction of dialkyl sulphates with OR·MgBr compounds. A. C. COPE (J. Amer. Chem. Soc., 1934, 56, 1342—1346).—The reaction 2OR·MgBr+ $2R'_2SO_4 = Mg(OR)_2 + 2R'Br + Mg(R'SO_4)_2$, occurs with R' = Me or Et and R = Ph, Bu^a, CHPh₂, CPh₃, and $CO_2Et \cdot C(CHPh_2)$:C(OEt). Evidence is given showing that the equilibrium 2OR·MgBr $= Mg(OR)_2 + MgBr_2$ exists in solution; treatment with R'_2SO_4 causes the change, MgBr₂+2R'_2SO₄ $\longrightarrow 2R'Br + Mg(R'SO_4)_2$, to occur. Thus, Me₂SO₄ and

CO₂Et·C(CHPh₂):C(OEt)·OMgBr [from

CHPh₂·CH(CO₂Ét)₂ and MgPhBr] in C₆H₆ give MeBr, Mg(MeSO₄)₂, and [CO₂Ét·C(CHPh₂):C(OEt)·O]₂Mg [which reacts further with Me₂SO₄ in C₆H₆ or PhMe at higher temp. to give CHPh₂·CMe(CO₂Et)₂ and Mg(MeSO₄)₂]. The production of Bu⁴I from p·C₆H₄Me⁴SO₃Bu⁴ and OEt⁴MgI or OPh·MgI (Gilman and Heck, A., 1928, 1124) is explained : 2OR·MgI+

 $2C_6H_4Me \cdot SO_3Bu \longrightarrow Mg(OR)_2 + 2BuI + Mg(SO_3 \cdot C_6H_4Me)_2$. The following appear to be new: $Mg(MeSO_4)_2$; $Mg(EtSO_4)_2$; Et benzhydrylmethyl-malonate, b.p. 180-182°/2 mm., m.p. 41-42°. H.B.

Electron-sharing ability of organic radicals. VIII. Condensation of mercaptans with chloral. I. B. JOHNS and R. M. HIXON (J. Amer. Chem. Soc., 1934, 56, 1333-1336).-The equilibrium consts. for the reaction $CCl_3 \cdot CHO + RSH \Longrightarrow CCl_3 \cdot CH(OH) \cdot SR$ (R=Et, Bu, CH₂Ph, Ph, p-C₆H₄Me, p-C₆H₄Cl) are calc. from f.-p. data; reaction is carried out in presence of C6H6 and a trace of HCl (catalyst). The consts. [and those for the reaction 2HgRI = HgR₂+HgI₂ (A., 1930, 1526)] are expressed as mathematical functions of the electron-sharing abilities of R. A new type of f.-p. apparatus is described. H. B.

Unusual reaction of 88'-dichlorodiethyl sulphide with halogen compounds. C. D. NENITZ-ESCU and N. SCARLATESCU (Ber., 1934, 67, [B], 1142-1144).—MeI and $(CH_2Cl \cdot CH_2)_2$ S (I) in boiling EtOH afford $(CH_2I \cdot CH_2)_2$ S, m.p. 62°, and dithian methiodide, S<CH2 CH2 S<Me , m.p. 174°, also obtained from (CH₂Br·CH₂)₂S. Similarly, (I) and CH₂PhBr yield dithian benzylbromide, m.p. 146° [also obtained from (CH₂Br·CH₂)₂S], and CH₂Cl·CH₂Br. (OEt·CH₂·CH₂)₂S and MeI do not react at low temp., but at 100-110° give dithian dimethiodide. The following scheme is suggested : $CH_2PhBr + S(CH_2 \cdot CH_2Br)_2 \rightarrow OH$

$$\begin{array}{c} \operatorname{CH}_{2}\operatorname{Ph} \cdot \operatorname{SBr}(\operatorname{CH}_{2} \cdot \operatorname{CH}_{2}\operatorname{Br})_{2} + \operatorname{S}(\operatorname{CH}_{2} \cdot \operatorname{CH}_{2}\operatorname{CI})_{2} \longrightarrow \\ \operatorname{CH}_{2}\operatorname{Ph} \cdot \operatorname{SBr}(\operatorname{CH}_{2} \cdot \operatorname{CH}_{2}\operatorname{Br}) \cdot \operatorname{CH}_{2} \cdot \operatorname{CH}_{2} \cdot \operatorname{SBr}(\operatorname{CH}_{2} \cdot \operatorname{CH}_{2}\operatorname{CI})_{2} \longrightarrow \\ \longrightarrow \operatorname{CH}_{2}\operatorname{Br} \cdot \operatorname{CH}_{2}\operatorname{CI} + \\ \operatorname{CH}_{2}\operatorname{S}\operatorname{CH}_{2}\operatorname{CI} + \\ \operatorname{CH}_{2}\operatorname{S}\operatorname{CH}_{2}\operatorname{CI} + \\ \operatorname{CH}_{2}\operatorname{CI} + \\$$

$$\begin{array}{c} \operatorname{H_2Ph}\operatorname{SBr}(\operatorname{CH_2}\operatorname{CH_2Br})\operatorname{CH_2}\operatorname{CH_$$

β-isoButyl sulphide. O. HINSBERG (J. pr. Chem., 1934, [ii], 140, 65–68; cf. A., 1929, 1269).—Bu^β₂S with 70% HClO₄ at 100° gives the perchlorate (I) (Bu^β₂S)₂HClO₄ of the β-form (II) (picrate, m.p. 79°), converted by warm aq. KOH into a mixture, b.p. 167–168°/735 mm of (II) (93%) and the g form (III) 167-168°/735 mm., of (II) (93%) and the α-form (III) distinguished and separated by the fact that only (II) gives (I) with HClO₄ in cold CHCl₃. By this method the relative amounts of conversion of (I) into (III) under various conditions are determined. Both forms on oxidation give the same sulphone. J. W. B.

Preparation and salts of cetylsulphonic acid. B. FLASCHENTRAGER and G. WANNSCHAFF (Ber., 1934, 67, [B], 1121-1124).-Interaction of cetyl alcohol and PBr_5 in boiling C_6H_6 and treatment of the product with H₂O gives a semi-solid mass, the liquid portion of which at 22° gives pure cetyl bromide, m.p. 15° after softening at 13.5°. Cetyl mercaptan (I), b.p. 123-128°/0.5 mm., m.p. 18°, is obtained in 85% yield from cetyl iodide and NaHS in abs. EtOH at 40-45°. Addition of (I) in COMe, to KMnO₄ in boiling COMe, leads to di-BB-cetylthiolpropane, m.p. 53° (yield 29%), and K cetylsulphonate (II) (29.4%). Oxidation of (I) with KMnO4 at 100° affords (II) (60%) and dicetyl disulphide, m.p. 50° (27.6%). Ba, Pb, Li, Na, and NH_4 cetylsulphonates are described. H. W.

Mechanism of ester condensations. G. V. TSCHELINCEV (Ber., 1934, 67, [B], 955-963).-The schemes of Claisen and Scheibler are criticised in detail and the following is suggested : EtOAc+ CH. C(ONa)·OEt → OEt·CMe(OH)·CH:C(ONa)·OEt \rightarrow COMe·CH·C(ONa)·OEt+EtOH. The new scheme enables condensations of (CH₂)₂O, epichlorohydrin, etc. with the Na derivatives of $CH_2(CO_2Et)_{2}$, CH₂Ac·CO₂Et, and CH₂Bz·CO₂Et to be included. The necessity for the presence of a trace of EtOH is exby the scheme, $EtOAc+EtONa \rightarrow$ plained OEt ·C(:CH2)·ONa+EtOH. Scheibler's observation of the production of keten acetals (I) and salts is due to a side reaction, $EtOBz + CH_{\circ}: C(OK) \cdot OEt \longrightarrow KOBz +$ CH2:C(OEt)2 whilst the formation of (I) by the decomp. of the intermediate products of the EtOAc condensation by H₂O is explained by the scheme: $CHAc:C(ONa) \cdot OEt + EtOAc \longrightarrow CHAc:C(OEt)_2$ (II) $(II) + NaOEt \longrightarrow ONa \cdot CMe: C:C(OEt)_2$ +NaOAc; (III)+EtOH; $(III) + H_2 O \longrightarrow NaOAc +$ The scheme is applied to the explan-CH2:C(OEt)2. ation of many condensations previously unexplained or explained with difficulty. H. W.

Production of acetyl chloride by action of phosphoryl chloride on acetic acid. Y. KATO, S. FUJINO, and S. KIKUCHI (J. Soc. Chem. Ind. Japan, 1934, 37, 170-171B).-AcCl is formed according to 2AcOH+POCl₃=2AcCl+HPO₃+HCl if the HCl and AcCl formed are continuously removed by distillation. H. A. P.

Nitroso-compounds. II. Reduction of derivatives of a-nitrosoisobutyric acid to the corresponding azoxy-compounds. J. G. ASTON and G. T. PARKER (J. Amer. Chem. Soc., 1934, 56, 1387-1388; cf. A., 1932, 602).-Bimol. α-nitrosoisobutyronitrile is reduced (SnCl2, conc. HCl) to a-azoxyisobutyronitrile (I), m.p. 37° (18% yield), whilst bimol. Et a-nitrosoisobutyrate similarly gives 42% of Et a-azoxy-isobutyrate, b.p. 142-144°/12 mm., 155-157°/20 mm. (free acid, m.p. 128-129°), also prepared from (1) and EtOH-HCl and by oxidation (method : Jolles, A., H. B. 1931, 1152) of Et a-azoisobutyrate.

Structure of acids obtained by oxidation of triisobutene. II. a-Acid of Conant and Wheland. F. C. WHITMORE and C. D. WILSON (J. Amer. Chem. Soc., 1934, 56, 1397; cf. this vol., 755).-The a-acid, C₁₂H₂₄O₂, m.p. 89°, of Conant and Wheland (A., 1933, 804) is dineopentylacetic acid (I); the chloride, b.p. 78-79°/4 mm., and NaN₃ in PhMe give [after hydrolysis (HCl)] dineopentylcarbinylamine (hydrochloride, m.p. 239–240°; Ac derivative, m.p. 134.5°), which with HNO₂ affords dineopentyl-carbinol. The mechanism of formation of (I) from H. B. as-dineopentylethylene is discussed.

General interpretation of fatty acid analyses by the ester fractionation method. T. P. HIL-DITCH (Biochem. J., 1934, 28, 779-785).-Discussion W. O. K. of methods and of results.

Catalytic influences in three-carbon tautomerism, III-V.-See this vol., 849.

Esterification of binary mixtures of fatty acids. Y. TOYAMA, T. ISHIKAWA, and G. AKIYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 193—195B).—Analysis of

the products obtained by esterification of binary mixtures of stearic, oleic, lauric, and behenic acids by EtOH, isoamyl alcohol, or glycerol in the presence of HCl shows that the acids have entered evenly into reaction, each in proportion to its concn. E. L.

Constituents of the triglycerides formed by esterification of the equimolecular mixture of stearic and oleic acids. T. TSUCHIYA and G. AKIYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 1958). -Oxidation by the Hilditch method showed that the neutral product of the esterification of a mixture of 3 mols. each of stearic and oleic acids with 1 mol. of glycerol in the presence of HCl at 225-230° contained 20% of tristearin; oxidation products corresponding with distearo-, stearodi-, and tri-olein were almost certainly formed, but could not be isolated. E. L.

Polymerisation of fatty oils. IV. Constitution of "dried" linseed and perilla oils. A. STEGER and J. VAN LOON (Rec. trav. chim., 1934, 53, 769-778; cf. B., 1934, 107).-Linseed and perilla oils, heated at 285° and 300°, respectively, contain all the glycerol as glycerides. By distillation of the Et esters prepared from the products it is shown that polymerisation " is a gradual process accompanied by formation of products of lower sap. val., that the linolenic esters polymerise less readily than the linoleic esters, and that the portion non-volatile in a high vac. is completely polymerised. R. S. C.

Raman effect and problems of constitution. V. Keto-enolic tautomerism in β -ketonic esters. K. W. F. KOHLRAUSCH and A. PONGRATZ (Ber., 1934, 67, [B], 976-989).-Raman spectra are recorded for the following compounds: HCO_2Et , $(CO_2Et)_2$, $CH_2(CO_2Et)_2$, $CHMe(CO_2Et)_2$, $CMe_2(CO_2Et)_2$,

 $CH(CO_2Et)_3$, $C(CO_2Et)_4$, $CAcMe_2 \cdot CO_2Et$, CHAcMe · CO₂Et, $CH_2Ac \cdot CO_2Et$,

AcCO₂Et, CMe,:CH·CO,Et, OEt CMe. CH. CO., Et, PhMe, NH₂Ph, CHMe₃, NH₂Pr³, MeOAc, NH₂·CO₂Me, EtOAc, NH₂·CO₂Et, COMe₂, NH₂Ac, COMeEt, NH₂·COEt. The data are discussed in their relation-H. W. ships to keto-enolic desmotropy.

Complex bismuth oxalates.—See this vol., 854.

Oxidation of fatty dibasic acids and of lævulic acid by hydrogen peroxide in presence of a cupric salt. A. P. PONSFORD and I. SMEDLEY-MACLEAN (Biochem. J., 1934, 28, 892-897).-Glutaric (I), adipic (II), suberic (III), and lævulic acid (IV) are readily oxidised by H2O2 at 60° in presence of Cu yielding succinic acid, CO2, etc. (I) produces small amounts of COMe, indicating β -keto-oxidation; similarly (II) affords (IV). With both (I) and (IV), CO₂ 18 liberated during the steam distillation of the oxidation product, indicating the presence of unstable intermediates. With (III), α -, β -, and γ -hydroxysuberic acids appear to be produced, hydroxypimelic acids being possible intermediates. Traces of ['CH2Ac], indicate a partial \$\$-keto-oxidation, whilst small amounts of monoketosuberic acid and other keto-derivatives are detectable. F. O. H.

Preparation and synthetic application of magnesiomalonyl ester. H. LUND (Ber., 1934, 67, [B], 935-938).-Inception of the action between Mg and EtOH is effected by CCl4 or less advantageously by

CHCl₃ or C₂H₂Cl₄, which appear to be partly hydrogenated. $(CCl_4 \text{ can also be used in the prep. of anhyd.}$ EtOH by Mg, since the products distil with the first few c.c. of EtOH.) The prep. from Mg, EtOH, $CH_2(CO_2Et)_2$, and $CH_2Cl \cdot CO_2Et$ of Et₄ propane- $\alpha\beta\beta\gamma$ -tetracarboxylate and from Mg, EtOH-Et₂O, $CH_2(CO_2Et)_2$, and BzCl or AcCl of Et₂ benzoylmalonate (Mg derivative) and Et_2 acetylmalonate is described. CH(CO₂Et)₃ is obtained by use of ClCO₂Et. H. W.

Polarimetric study of beryllium tartrates. J. L. DELSAL (Compt. rend., 1934, 198, 2076-2078).--Electrometric and polarimetric examination of the solutions obtained by dissolution of varying molecular proportions of $Be(OH)_2$ (I) in solutions of tartaric acid and its Na H salt (II), indicates the formation of only one complex, $Be < \stackrel{O\cdot CH \cdot CO_2 \cdot Be \cdot OH}{O \cdot CH \cdot CO_2 \cdot Be \cdot OH}$, $[\alpha]_D - 173 \cdot 5^{\circ}$ (isolated), and the Na derivative,

 $Be < O \cdot CH \cdot CO_2 Na \\ O \cdot CH \cdot CO_2 \cdot Be \cdot OH$, $[\alpha]_{b} - 214^{\circ}$, obtained only by the action of (\overline{I}) on (II). J. W. B.

Isomerism in chloralides. N. M. SHAH and R. L. ALIMCHANDANI (Current Sci., 1934, 2, 383-384; cf. this vol., 301).-d- and r-Tartaric and lactic acid each give two chloralides on condensation with $CCl_3 \cdot CH(OH)_2$ in presence of H_2SO_4 . The m.p. are 162° and 175°, 160° and 215°, 62° and b.p. 212°, L. S. T. respectively.

Selenium dioxide. New oxidising agent. IV. Preparation and properties of ethyl ketohydroxysuccinate. S. ASTIN and H. L. RILEY (J.C.S., 1934, S44-848).-Et d-tartrate (3 mol.) heated with SeO₂ (1 mol.) at 120-130° gives CO₂, complex organo-Se compounds, and a 16% yield of Et d-ketohydroxy-succinate, m.p. 98-99° (105-106° after drying over P_2O_5 , $[\alpha]_{10}^{21} + 14^{\circ}$ in $H_2O_5 - 15.6^{\circ}$ in EtOH (no reaction in $[\cdot CH_2 \cdot OH]_2$ or dioxan), hydrolysed by KOH to $H_2C_2O_4$, EtOH, CO_2 , and a little $[\cdot CH(OH) \cdot CO_2H]_2$, and by HCl to a mixture of d- and meso-tartaric acid; it gives osazones of [·CO·CO₂Et]₂ with NHPh·NH₂-AcOH. Its relationships to the two forms of Et dihydroxymaleate (probably cis and trans; Fenton, J.C.S., 1896, 69, 546) are discussed. Similar oxidation of Bu and amyl tartrates gives unidentified decomp. products, and Me fumarate is the only solid product isolated when the Mo ester is employed. Similar oxidation of OH·CHMe·CO₂Et gives only a trace of AcCO₂Et and, possibly, CHO·CO·CO₂Et (I) or CHO·CH(OH)·CO₂Et, since with NHPh·NH₂ the J. W. B. bisphenylhydrazone of (I) is obtained.

Synthesis of vitamin-C. F. MICHEEL, K. KRAFT, and W. LOHMANN (Z. physiol. Chem., 1934, 225, 13-27).-With 40% aq. NaOH in absence of O₂, α-keto-dgluconic acid undergoes conversion (44%) into a substance (I) reducing I on acidification. With dil. alkali the yield is less and also decreases on dilution of the conc. alkaline mixture. On keeping in acid solution, the yield of (I) falls to a const. val. of 6%. With Me_2SO_4 -aq. NaOH, (I) yields a syrup which, after treatment with CH_2N_2 and MeI and Ag_2O , contains 52% of OMe. Ozonisation then yields $H_2C_2O_4$. The product is evidently a methylated dienol ($\Delta^{2:3}$). *l*-Sorbose prepared from sorbitol by Bact. xylinum was

converted into the osazone, which afforded the osone (II) with PhCHO and AcOH. With Br (II) gave *l*sorburonic acid (III) [Na (+H₂O), m.p. 145° (decomp.), $[\alpha]_{1}^{\infty}$ -23.6 in H₂O, and brucine (+H₂O), m.p. 146° (decomp.) salts]. Treatment of (III) with conc. aq. NaOH afforded ascorbic acid (IV), identical with the natural (IV). (IV) is recovered unchanged from conc. aq. NaOH. J. H. B.

Behaviour of ascorbic acid towards nitrate and nitrite. P. KARRER and H. BENDAS (Helv. Chim. Acta, 1934, 17, 743—745).—At $p_{\rm II}$ 6·0, 7·0, or 9·3, ascorbic acid (I) does not appear to reduce KNO₃ to KNO₂ in boiling H₂O. In acidic or neutral, but not in alkaline, solution KNO₂ is reduced by (I) to NO. In presence of NH₄Cl, NO is liberated from alkaline solution. Most marked evolution of NO occurs in the vicinity of the neutral point. H. W.

Preparation of isovitamin-C (d-araboascorbic acid). II. K. MAURER and B. SCHIEDT (Ber., 1934, 67, [B], 1239-1241).-Me α-ketogluconate (prep. from diisopropylidenefructose described) is converted by NaOMe-MeOH ĊO COH O into Na isoascorbate. isoAscorbic acid (I), m.p. 168°, $[\alpha]_p - 21.95^\circ$ in H₂O, in chemical C.OH properties closely resembles ascorbic acid H·Ċ-(II). It is oxidised by 21 to the neutral H.C.OH diketone, $[\alpha]_{\rm p}$ +92.5° in H₂O, reduced by H₂S to (I). Its antiscorbutic action is approx. 0.05 of that of (III). It is an CH., OH (\mathbf{L}) excellent photographic developer. H. W.

Synthesis of a lactosecarboxylic acid $(5-\beta-d-galactosido-\alpha-d-glucoheptonic acid)$. R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 1390—1391).—Application of the modified Kiliani reaction (this vol., 757) to lactose gives $5-\beta-d-galactos-ido-\alpha-d-glucoheptonic acid$, m.p. 185—186° (all m.p. are corr.), $[\alpha]_{10}^{n}$ +11·2° in H₂O (quinine, m.p. 169—170° (decomp.), $[\alpha]_{10}^{m}$ -71·9° in H₂O, and brucine, m.p. 172—173° (decomp.), $[\alpha]_{10}^{m}$ -7·6° in H₂O, salts}, hydrolysed (2% H₂SO₄) to d-galactose and α -d-glucoheptonic acid (brucine salt, m.p. 155° (decomp.), $[\alpha]_{10}^{m}$ -18·4° in H₂O}. H. B.

Alkylthiol- and alkylsulphonyl-carboxylic acids. A. MELLANDER (Svensk Kem. Tidskr., 1934, 46, 99-108).-The SMe-acids are obtained from the SH-acids by Me₂SO₄ and NaOH. SEt-acids are derived from the halogeno-acids and EtSH in alkaline solution. Oxidation of SAlk- to SO2Alk-acids is effected by KMnO4 in neutral or slightly alkaline solution. The following compounds are described : methylthiolacetic acid, b.p. 107° (corr.)/9.5 mm.; methylsulphonylacetic acid, m.p. 114.5-115.5° (corr.). converted by Br into aa-dibromodimethylsulphone, converted by bi into a anti-philippionic acid, m.p. $65\cdot5-66\cdot5^{\circ}$ (corr.); α -methylthiolpropionic acid, b.p. $104-104\cdot5^{\circ}$ (corr.)/8 mm.; α -methylsulphonyl-propionic acid, m.p. $96-97\cdot2^{\circ}$, whence α -bromo- α -methylsulphonylpropionic acid, m.p. $172\cdot5-173\cdot5^{\circ}$ (corr.); α-ethylthiolpropionic acid, b.p. 113.7-113.8°/8 mm.; α-ethylsulphonylpropionic acid, m.p. 62.0-63.2° (corr.), whence a bromo-a ethyl sulphonyl propionic acid, m.p. 96.0-96.5° (corr.). Optical and affinity consts. of the compounds are recorded. H. W.

Reaction between ethyl a-bromoisobutyrate and sodium sulphide in alcoholic solution. E. LARSSON and K. JONSSON (Ber., 1934, 67, [B], 1263-1270).-The action of NaSH on Et a-bromoisobutyrate (I) in EtOH leads to thio- $\alpha\beta'$ -diisobutyric acid (II) $(+H_2O)$, m.p. 153°, thio- $\alpha\alpha'$ -diisobutyric acid (III), m.p. 142°, and thio- $\beta\beta'$ -diisobutyric acid (IV), m.p. 115°. (I) appears to behave as if containing the β -Brcompound, which is not appreciably present in the initial material. The constitution of the acids is decided mainly by consideration of their dissociation consts. and the behaviour of the corresponding SOacids towards HCl, whereby it is considered that fission occurs thus: $CH_2R \cdot SO \cdot R' \longrightarrow OH \cdot CHR \cdot SR' \longrightarrow R \cdot CHO + R' \cdot SH$, and hence is contingent on the presence of H attached to C. (II) is also obtained from (I) and SNa•CMe2•CO2Na in abs. EtOH. It is oxidised by Br-H_oO to sulphonyl-αβ'-diisobutyricacid, m.p. 193°, and by 30% H_2O_2 in COMe₂ at 0° to thionyl- $\alpha\beta'$ -diisobutyric acid, m.p. 103° (+H₂O, m.p. 100-101°), which is converted by HCl into a-dithiodiisobutyric acid (V) and passes when distilled into (V), Pr^BCO₂H, and methacrylic acid. (III) is isolated

from the reaction mixture after removal of (II) as the K salt. It is oxidised by Br to sulphonyl-aa'-diisobutyric acid, m.p. 190°, and by H_2O_2 to thionyl-aa'diisobutyric acid, which is stable towards HCl. (IV) is oxidised to sulphonyl- $\beta\beta'$ -diisobutyric acid, m.p. 141°, and thionyl- $\beta\beta'$ -diisobutyric acid, m.p. 128° (decomp.), unstable towards HCl. H. W.

[Polyoxymethylenes.] H. STAUDINGER (Ber., 1934, 67, [B], 948).—A reply to Hess (this vol., 493). H. W.

Comparison of the viscosity properties of synthetic and natural highly-polymerised compounds. I. SAKURADA (Ber., 1934, 67, [B], 1045-1051).—The viscosity data of a no. of synthetic and natural polymerides are separated into two components (a=form and charge factor, ϕ =sp. vol.) according to the author's formula $c/\eta_{sp} = 100/a\phi - c/a$ (cf. A., 1933, 901). With synthetic polymerides (polystyrene and polymeric w-hydroxydecoic acids) a increases regularly and almost linearly with log $[100(\eta_{sp}/c)_{lim. c=0}]$, whereas with cellulose nitrates and caoutchouc (I) it is independent of the viscosity. There exists, therefore, a fundamental difference between the viscosity properties of natural and synthetic polymerides, and Staudinger's viscosity rule is not applicable to substances such as cellulose, H. W. starch, and (I).

Action of Grignard reagent on $\alpha\beta$ -unsaturated aldehydes. P. G. STEVENS (J. Amer. Chem. Soc., 1934, 56, 1425).—MgBu[×]Cl and crotonaldehyde give approx. equal amounts (about 25%) of CHMe:CH·CHBu[×]·OH and $\beta\gamma\gamma$ -trimethylvaleraldehyde (semicarbazone, m.p. 166°). $\beta\gamma\gamma$ -Trimethylvaleramide has m.p. 163—164°. Me $\beta\gamma\gamma$ -trimethylvaleramide has m.p. 163—164°. Me $\beta\gamma\gamma$ -trimethylvaleramide from Me α -bromo- $\beta\gamma\gamma$ -trimethylvalerate and NPhEt₂. Some 1:4-addition also occurs with MgEtBr, MgPr^aBr, and MgPr^{\beta}Br. H. B.

Oxidation of citronellal. H. I. WATERMAN and E. B. ELSBACH (Rec. trav. chim., 1934, 53, 730-736).—Analysis of the gaseous and liquid products formed when citronellal autoxidises in a closed system shows that 1 mol. of CO_2 is formed for each mol. of peroxide formed and that little citronellic acid is produced. The main product is a viscous, unstable C_9 peroxide, isolated by distillation in a cathode vac.

R. S. C.

Dialkyl ketones derived from ethoxy-compounds of high mol. wt. D. BARDAN (Bull. Soc. chim., 1934, [v], 1, 370–373; cf. A., 1932, 368).— γ -Ethoxy- β -methyl- Δ^{β} -hoptene with 20% H₂SO₄ at 140–145° during 3—5 hr. affords COPr^{β}Bu^{α}, b.p. 158— 160° (cf. A., 1915, i, 497). The following are prepared similarly : γ -ethyloctan- δ -one, b.p. 122–125°/38 mm.; δ -n-propylnonan- ε -one, b.p. 142–144°/29 mm.; ε -nbutyldecan- ζ -one, b.p. 155–158°/23 mm.; γ -ethyldecan- δ -one, b.p. 155–158°/23 mm.; δ -n-propylundecan- ε -one, b.p. 157–162°/25–26 mm., and ε -n-butyldodecan- ζ -one, b.p. 180–183°/24 mm. These ketones do not afford oximes, semicarbazones, or H sulphite compounds. J. L. D.

Keto-ethers. I. [Alkyl] methoxymethyl ketones. H. R. HENZE and N. E. RIGLER (J. Amer. Chem. Soc., 1934, 56, 1350—1351).—OMe·CH₂·COR, where R is Me, b.p. 114·6°/746 mm. (all b.p. are corr.), Et, b.p. 133—133·6°/757 mm. (lit. about 130°), Pr^a, b.p. 152—153°/745 mm. (lit. 142—150°), Pr^β, b.p. 143·5—145°/748 mm., Bu^a, b.p. 167—169°/744 mm., Bu^β, b.p. 163—164°/751 mm., sec.-Bu, b.p. 164°/757 mm., Bu^γ, b.p. 158—159°/743 mm., n-amyl, b.p. 191— 191·5°/753 mm., and isoamyl, b.p. 185—186°/752 mm., are prepared from OMe·CH₂·CN and the requisite Grignard reagent. They give unstable liquid phenylhydrazones and reduce Fehling's and Tollens' reagents in the hot. H. B.

Reactions of carbohydrates [with diazobenzenesulphonic acid and alkali]. L. EKKERT (Pharm. Zentr., 1934, 75, 407-409).—Colour reactions of 13 carbohydrates are given. E. H. S.

Derivatives of xylose. G. J. ROBERTSON and xyloside (prep. with β -compound described) with HCl-COMe, at room temp. gives its 3: 5-isopropylidene derivative (I), b.p. 102-107°/0.1 mm., [a]D +17.3° in CHCl₃, converted by MeI-Ag₂O into its 2-Me derivative, b.p. $77^{\circ}/0.07 \text{ mm.}$, $[\alpha]_{D} + 24.6^{\circ} \text{ in CHCl}_{3}$, hydrolysed by boiling $N-H_2C_2O_4$ to 2-methylxylose, m.p. 132–133°, $[\alpha]_p -23.9°$ to +35.9° in 20 hr. in H₂O, the Ac_3 derivative, m.p. 95°, $[\alpha]_D - 2 \cdot 2^\circ$ in CHCl₃ (probably a mixture of α - and β -forms), of which is converted by HBr-AcOH and Ag₂CO₃-MeOH into 2methyl-β-methylxyloside 3:4-diacetate, m.p. 78-79°, [α]_D -38.1° in CHCl, hydrolysed to 2-methyl-β-methylxyloside, m.p. 111—112°, $[\alpha]_{\rm p} - 67.7^{\circ}$ in CHCl₃ (3 : 4-*di*-p-toluenesulphonyl derivative, m.p. 123°, $[\alpha]_{\rm p} - 16^{\circ}$ in CHCl₃). With BzCl-C₅H₅N at 0° (I) affords its 2-Bz derivative, hydrolysed by boiling 1% HCl-MeOH to methylzyloside 2-benzoate, methylated (Purdie) to its 3:4-Me2 derivative, debenzoylated (NaOMe-MeOH) to 3:4-dimethylmethylxyloside, b.p. 110-115°/0.2 mm., hydrolysed to 3:4-dimethylxylose (II), [a]D $+24.9^{\circ}$ to $+20.5^{\circ}$ in 5 hr. in H₂O (syrupy osazone). (II) does not condense with 1% MeOH-HCl, but its Bz₂ derivative with HBr-AcOH followed by Ag₂CO₃-MeOH and debenzoylation affords 3:4-dimethyl-β-

methylxyloside, m.p. 89-90°, [a]p -82.2° in CHCl_a (2-p-toluenesulphonyl derivative, m.p. 105°, [a] -34.8° in CHCl₃). β -Methylxyloside with CPh₃Cl gives a syrupy 3-CPh₃ derivative, from which by acetylation and hydrolysis is obtained β -methylxyloside 2:4-diacetate, the 3-nitrate, m.p. 120-121° (by CHCl₃-fuming HNO₃), of which with 33% NHMe₂-EtOH and methylation gives the 3-nitrate (a syrup) of 2:4-dimethyl- β -methylxyloside, b.p. 100–105°/0.06 mm., m.p. 60–61°, $[\alpha]_{\rm p}$ -82.4° in CHCl₃ (3-p-toluenesulphonyl derivative, m.p. 88°, [a] -58.9° in CHCl_a), which is obtained by treatment with 5% Na-Hg in H₂O-EtOH-AcOH. 2:3-Dimethylxylose (from xylan) gives its β -methylxyloside, b.p. 90-95°/0 03 mm., $[\alpha]_{\rm D} - 5.8^{\circ}$ in CHCl₃ (4-p-toluenesulphonyl derivative, m.p. 56–59°, $[\alpha]_D = 8.8°$ in CHCl₃). All b.p. are bath temp. J. W. B.

Munson-Walker method for reducing sugars. R. F. JACKSON (J. Assoc. Off. Agric. Chem., 1934, 17, 293—301; cf. A., 1906, ii, 634).—Direct weighing of Cu_2O is untrustworthy and tedious. Na₂S₂O₃ titration is slightly more exact than the electrometric K₂Cr₂O₇ method, but is less convenient, but both are more trustworthy than KMnO₄ titration. Standardisation of the time required for filtration of the Cu₂O ppt. is as important as standardisation of the conditions of boiling. E. C. S.

Natural interconversion of isomeric sugars. G. J. ROBERTSON and J. W. H. OLDHAM (Nature, 1934, 133, 871).—The hydrolysis of *p*-toluenesulphonyl derivatives of methylglucosides falls into two main groups according as the original substance contains one or two p-C₆H₄Me·SO₂ residues in neighbouring positions. When Walden inversion (I) occurs it is accompanied by anhydro-formation, which may be a necessary precursor to it. This supports Robinson's view that (I) within the sugar mol. is the agency for natural interconversion of simple sugars. L. S. T.

Relationships of isomeric d-glucoses and d-glucosephenylhydrazones. G. H. STEMPEL, jun. (J. Amer. Chem. Soc., 1934, 56, 1351–1355).—The mutarotation of α -d-glucosephenylhydrazone (I), m.p. 160°, $[\alpha]_{12}^{25} = 87^{\circ}$ (initial) $\rightarrow -52 \cdot 5^{\circ}$ (const.) in H_2O (convenient prep. given), is not unimol.; at least 3 substances are involved in the equilibrium. Hydrolysis (aq. $H_2C_2O_4$ at 30°) of (I) is pseudo-unimol.; an increase in the velocity coeff. towards the end of the reaction is ascribed to the adsorption of d-glucose on NHPh·NH₂ oxalate (pptd. towards the end of the reaction). Information concerning the structures of d-glucosephenylhydrazones and their relationships to the isomeric d-glucoses cannot be obtained from studies of hydrolysis (cf. Frérejacque, A., 1925, i, 635). The reactions of α - (I) and β - (II) -d-glucose with NHPh·NH, in aq. EtOH are followed polarimetrically; (I) reacts more rapidly than (II) [probably owing to the presence of a trace of catalyst in the (I) used, since in presence of 0.0073M-HCl the rates are identical]. Strong acids catalyse hydrazone but not osazone formation. H. B.

Oxidation of glucose and derivatives of glucose with periodic acid. P. KARRER and K. PFAEHLER (Helv. Chim. Acta, 1934, 17, 766-771).—Oxidation of glucose (I) by HIO_4 gives only approx. 1 mol. of CH_2O when 6 mols. of HIO_4 are used. With 1 mol. only about 0.03 mol. of CH₂O results, showing that main fission of (I) is not between C_5 and C_6 , but at some other position of the mol., and that the production of large amounts of CH_oO is a secondary process. If the oxidation of (I) by HIO₄ (mol. ratio 1:5) is interrupted after 10, 30, and 60 min., the corresponding amounts of formaldehyde are a trace, -CH-OMe 0.33 mol., and 0.46 mol. respectively. CH·OH Methylglucoside does not yield CH₂O O ĊHO even when an excess of HIO₄ is used, ĊHO -CH possibly owing to formation of (II). Mannosephenylhydrazone and HIO₄ CH, OH yield only 0.35 mol. of CH,O. Glucose-

(II.) phenylosazone and HIO_4 ($\hat{1}$: 3) in 50% EtOH readily yield 4-benzeneazo-1-phenylpyrazol-5one, m.p. 150°, fission occurring between C3 and C4. H. W.

Carbohydrates. IV. Peculiar behaviour of the 2-hydroxyl group in the glucose molecule. T. LIESER and E. LECKZYCK (Annalen, 1934, 511, 137-140).—Glucosediethylmercaptal (I) does not appear to yield a xanthate. Treatment of (I) with Ag₂O and much MeI yields 2-methylglucosediethylmercaptal in 51.4% yield. Attempts to substitute a solvent for the large excess of MeI proved unsatisfactory, whereas 2-methylglucosedibenzylmercaptal (II), m.p. 193–194° (corr.), is obtained in 13.2% yield in CHCl₃ and in 55.1% yield in abs. MeOH. Attempts to methylate the Et2 and (CH2Ph)2 mercaptals of galactose, arabinose, or rhamnose or xylosedibenzylmercaptal, m.p. 77.5-78° [Bz4 derivative, m.p. 170° (corr.)], were unsuccessful. (II) could not be caused to react with acetobromoglucose. H. W.

Acyl migration in the sugar group. L. VON VARGHA (Ber., 1934, 67, [B], 1223-1229).-The 6-triphenylmethylisopropylideneglucose 3-acetate (I) of Josephson is converted by Ag₂O and MeI into 6-triphenylmethyl - 3 - methyl - 1 : 2 - isopropylideneglucofur-anose 5-acetate (II), m.p. 155°, $[\alpha]_{10}^{20} - 37.0^{\circ}$ in CHCl₃ (in poor yield due to loss of CPh₃ with production of CPh₃·OMe), also obtained by the successive action of CPh₃Cl and Ac₂O in C₅H₅N on 3-methylisopropylideneglucose. (II) is converted by NaOH-MeOH 6-triphenylmethyl-3-methyl-1: 2-isopropylideneinto. glucofuranose, m.p. (indef.) 60° , $[\alpha]_{10}^{\infty}$ — $38 \cdot 6^{\circ}$ in CHCl₃, hydrolysed by AcOH to 3-methyl- α -glucose, m.p. $167-168^{\circ}$, $[\alpha]_{11}^{\infty}$ (equil.) $+55 \cdot 5^{\circ}$ in H₂O {phenyl-osazone, m.p. $176-177^{\circ}$, $[\alpha]_{11}^{\infty}$ (equil.) $-41 \cdot 6^{\circ}$ in EtOH}. The point at which acyl wanders is discussed, and it is suggested that (I) is a mixture of the 3- and 5-acetate. Diisopropylideneglucose in C6H6-5- and 5-actetate. Dissopropyintenegatics in C_6H_6 or PhMe into di(disopropylideneglucose) 3:3'-carbonate (III), m.p. 149°, $[\alpha]_1^m$ -50.8° in CHCl₃, which affords a tetra-acetate, m.p. 104° after softening, $[\alpha]_1^m$ +7.62° in CHCl₃, and is re-converted by COMe₂ and anhyd. CuSO₄ into (III). In H₂O, MeOH, EtOH, C₅H₅N, or dioxan (III) readily undergoes intramol. transformation into 1: 2-isopropylideneglucofuranose 5: 6carbonate and 1: 2-isopropylidencelucofuranose. The probability that acyl migration is accompanied by intermediate production of orthocarbonic esters is

strengthened by the observation that the transformation of (III) is independent of the solvent and hindered by acids which retard the production of orthocarbonates. H. W.

Preparation of methylglucosides of methylated glucoses. J. W. H. OLDHAM (J. Amer. Chem. Soc., 1934, 56, 1360–1362).—The methylglucoses are benzoylated (BzCl, C_5H_5N) and the resulting benzoates converted by HBr-AcOH in Et₂O-C₆H₆ into bromomethylglucose benzoates; these and MeOH+ Ag₂CO₃ give the corresponding methylglucosides, which are then debenzoylated. β -Methyl-2-methylglucoside, m.p. 97–98°, $[\alpha]_{\rm D}$ -37.5° in H₂O (tribenzoate, m.p. 119–120°, $[\alpha]_{\rm D}$ -40.4° in CHCl₃), β -methyl-3-methylglucoside, $[\alpha]_{\rm D}$ -26.6° in H₂O (tribenzoate, m.p. 125–126°, $[\alpha]_{\rm D}$ +14.7° in CHCl₃), β -methyl-2: 3-dimethylglucoside, m.p. 62–64°, $[\alpha]_{\rm D}$ -47.8° in CHCl₃, and β -methyl-2: 3:6-, m.p. 59– 60°, $[\alpha]_{\rm D}$ -47.5° in CHCl₃, and -2:4:6-, m.p. 70– 71°, $[\alpha]_{\rm D}$ -27.4° in CHCl₃, -trimethylglucosides are thus prepared. β -2- and β -3-Methylglucosides are thus prepared. β -2- and β -3-Methylglucosides are thus prepared. β -2- and β -3-Methylglucosides tetrabenzoates have m.p. 169–170°, $[\alpha]_{\rm D}$ -6.2° in CHCl₃, and m.p. 198–199°, $[\alpha]_{\rm D}$ +3.6° in CHCl₃, respectively. H. B.

d-Tagatose, diacetone-d-tagatose [d-tagatose disopropylidene ether], and d-tagaturonic acid. T. REICHSTEIN and W. BOSSHARD (Helv. Chim. Acta, 1934, 17, 753—761).—Anhyd. d-galactose (I) is heated in C_5H_5N at 145°, the solvent is removed, and the bulk of unchanged (I) is pptd. by addition of EtOH to a solution of the residue in H₂O. Remaining (I) is removed by fermentation, thus leading to the isolation of tagatose (II), m.p. 131—132° (corr.), $[\alpha]_p -2\cdot3^\circ$ in H₂O. d-Sorbose does not appear to be produced, but the formation of talose is probable. (II) is converted by COMe₂ and conc. H₂SO₄ at room



temp. into diisopropylidenetagatose (III), m.p. 65– 66°, $[\alpha]_{10}^{30}$ +81.5° in COMe₂, +71.8° in H₂O, oxidised by alkaline KMnO₄ to d-diisopropylidenetagaturonic acid (IV), m.p. about 118—121° (corr.) in capillary, m.p. 102—103° under the microscope (also +0.5H₂O, m.p. 117—121° in capillary, m.p. 98—99° under the microscope, $[\alpha]_{10}^{30}$ +33.5° in COMe₂). (IV) is hydrolysed by boiling H₂O to d-tagaturonic acid (V), m.p. 106—108°, $[\alpha]_{10}^{30}$ —12.55° (equilibrium val.) in H₂O {Me ester (VI), $[\alpha]_{10}$ about +13° in MeOH}. The constitution of (V) follows from its reduction to *l*-galactonic and d-altronic acid. Short treatment of (VI) with NaOMe gives very small amounts of substances which reduce I in acid solution. H. W. Carbohydrates. II. Xanthate reaction of mono- and di-saccharides. III. Xanthate reactions of polymeric carbohydrates with exception of cellulose. T. LIESER and A. HACKL (Annalen, 1934, 511, 121—127, 128—136; cf. A., 1932, 718).—II. Cu^I methylglucosidyl xanthate (improved prep.) is readily decomposed by dil. NaOH with formation of β -methylglucoside. With dil. AgNO₃ the Ba salt affords Ag methylglucosidyl xanthate, transformed by excess of McI at room temp. into Me methylglucosidyl xanthate, m.p. 67—68° (corr.), and by MeOH-I into the dixanthate, C₁₆H₂₆O₁₂S₂; Me₂ xanthate is described. Glucosephenylhydrazone and methylgalactoside afford the compounds

 $C_{13}H_{17}O_5N_2SCu$ and $C_8H_{13}O_6S_2Cu$, respectively, whereas fructose gives the substance, $C_7H_{10}O_6S_2Cu_2$. The compounds, $C_{14}H_{20}O_{11}S_4Cu_2$, from maltose, lactose, and cellobiose, respectively, are sol. in H_2O , from which they are pptd. by MeOH. Since sucrose and raffinose give the substances $C_{13}H_{21}O_{11}S_2Cu$ and $C_{20}H_{30}O_{16}S_4Cu_2$, respectively, it appears that the fructosidic portions of the higher sugars are incapable of xanthate formation.

III. Starch, glycogen (I), lichenin, mannan, inulin, and xylan yield xanthates with conens. of alkali <are required by cellulose. With the possible exception of (I), xanthate formation increases with conen. of alkali to an optimum, after which it declines. The optimal composition of the xanthates, with the exception of (I), indicates the relationship $2C_6H_{10}O_5$: CS_2 as with cellulose (II). Since this apparent ratio for (II) depends on a micellar surface reaction, it follows that the investigated polymerides with the exception of (I) have a micellar structure, and that on the average nearly as many sugar anhydride chains are situated on the surface of the micelles as in the interior.

H. W. Fructose anhydrides. XIV. Constitution of irisin. II. H. H. SCHLUBACH, H. KNOOP, and M. Y. LIU (Annalen, 1934, 511, 140—151; cf. A., 1933, 938).—Interruption of the hydrolysis of irisin (I) by N-H₂SO₄ at 20° at the point at which the greatest difference exists between reducing power and $[\alpha]_{\rm D}$ of the products discloses the complete disappearance of (I). The bulk of the fructose is readily removed from the product by treatment of the H₂O solution with EtOH, the remainder by acetylation and subsequent hydrolysis, whereby *di-irisan* (II),

$$\begin{array}{c} 0\mathrm{H}\cdot\mathrm{CH}_{2}\cdot\mathrm{CH}\cdot\mathrm{CH}(\mathrm{OH})\cdot\mathrm{CH}(\mathrm{OH})\cdot\mathrm{C}\cdot\mathrm{CH}_{2}\cdot\mathrm{OH}\\ 0\mathrm{H}\cdot\mathrm{CH}_{2}\cdot\mathrm{CH}\cdot\mathrm{CH}\cdot\mathrm{CH}\cdot\mathrm{CH}(\mathrm{OH})\cdot\mathrm{C}\cdot\mathrm{CH}_{2}\\ 0\\ \mathrm{OH}\cdot\mathrm{CH}_{2}\cdot\mathrm{C}\cdot\mathrm{CH}(\mathrm{OH})-\mathrm{CH}\cdot\mathrm{CH}\cdot\mathrm{CH}_{2}\cdot\mathrm{OH}\\ 0\\ \mathrm{OH}\cdot\mathrm{CH}_{2}\cdot\mathrm{C}\cdot\mathrm{CH}(\mathrm{OH})\cdot\mathrm{CH}(\mathrm{OH})\cdot\mathrm{CH}\cdot\mathrm{CH}_{2}\cdot\mathrm{OH} \\ 0\\ \mathrm{OH}\cdot\mathrm{CH}_{2}\cdot\mathrm{C}\cdot\mathrm{CH}(\mathrm{OH})\cdot\mathrm{CH}(\mathrm{OH})\cdot\mathrm{CH}\cdot\mathrm{CH}_{2}\cdot\mathrm{OH} \\ \end{array} \tag{II.)$$

 $[\alpha]_{\rm D} - 36 \cdot 6^{\circ}$, mol. wt. 642 (Ac derivative, $[\alpha]_{\rm D}^{\infty} - 1 \cdot 1^{\circ}$ in AcOH), is obtained. Marked difference exists in the period of semi-hydrolysis of (II) as judged reductometrically and polarimetrically, so that an intermediate product (III) is formed on the way to fructose. Treatment of (II) containing a small amount of (III) with MeSO₄-NaOH and Ag₂O-MeI leads to a non-distillable methyldi-irisan, $[\alpha]_D^m - 48.3^\circ$ in CHCl₃, -50.1° in COMe₂, hydrolysed to equiv. amounts of tetra- and di-methylfructose and a trimethylfructose, b.p. $93.5^\circ/0.06$ mm., $[\alpha]_D^m - 12.7^\circ$ to -45.6° in H₂O, $+13.1^\circ$ to $+10.1^\circ$ in CHCl₃, which is not the 3:4:6-derivative and contains OMe in position 1, since (with loss of OMe) it affords a phenylosazone, C₂₀H₂₆O₄N₄. The dimethylfructose yields an osazone without loss of OMe, and hence contains a free OH at 1. Irisan, the fundamental substance of (I), is therefore (IV).

$$\begin{array}{c} OH \cdot CH_2 \cdot CH \cdot CH(OH) \cdot CH(OH) \cdot C \cdot CH_2 \cdot OH \\ OH \cdot CH_2 \cdot CH \cdot CH \cdot CH(OH) \cdot C \cdot CH_2 \\ OH \cdot CH_2 \cdot CH \cdot CH \cdot CH(OH) \cdot C \cdot CH_2 \\ H. W. \end{array}$$

State of solution of cellobiose and maltose octa-acetates in acetic acid.—See this vol., 841.

Synthesis of p-aminophenyl- β -glucosides of maltose, lactose, cellobiose, and gentiobiose. F. H. BABERS and W. F. GOEBEL (J. Biol. Chem., 1934, 105, 473-479).—The method adopted in every case was to treat the acctobromo-compound of the sugar with p-OH·C₆H₄·NO₂ and NaOH in aq. COMe₂, deacetylate, and reduce the resulting p-NO₂-compound with H₂-PtO₂ in MeOH. The following are described : β -p-nitrophenyl-lactoside, m.p. 258-260° (darkens 250°), $[\alpha]_{11}^{24}$ -74·2° in H₂O [Ac₇ derivative, m.p. 132-133° (corr.), $[\alpha]_{12}^{25}$ -6° in MeOH [Ac₇ derivative, m.p. 132-176° (corr.), $[\alpha]_{12}^{25}$ +33·8° in CHCl₃], -maltoside, m.p. 221°, $[\alpha]_{22}^{25}$ +6° in MeOH [Ac₇ derivative, ative, m.p. 175-176° (corr.), $[\alpha]_{12}^{26}$ -85·1° in 40% MeOH (Ac₇ derivative, m.p. 215-216° (corr.), $[\alpha]_{12}^{26}$ -85·1° in 40% MeOH (Ac₇ derivative, m.p. 234-235°); β -p-aminophenyl-lactoside, m.p. 233° (decomp.), $[\alpha]_{12}^{26}$ -36·4° in H₂O, -maltoside, m.p. 91-92° (corr.), $[\alpha]_{12}^{26}$ +35·3° in 50% MeOH, -gentobioside, m.p. 237-238° (decomp.), $[\alpha]_{12}^{26}$ -52·9° in 50% MeOH.

Glucosides of Digitalis lanata. C. MANNICH (Helv. Chim. Acta, 1934, 17, 789-790).—The strongest evidence that the author's glucoside II is composed of genuine glucosides and is practically identical with the total digilanid prep. of Stoll and Kreis rests in the observation that it cannot be separated into differing components by careful crystallisation from EtOH. Decomp. products poor in sugar or free from Ac do not form isomorphous series with the genuine glucosides (cf. this vol., 636). H. W.

Glucosides of Digitalis lanata. A. STOLL and W. KREIS (Helv. Chim. Acta, 1934, 17, 790–794).— A reply to Mannich (preceding abstract). H. W.

Colouring matter of the seed-coat of Abrus precatorius, Linn. (scarlet variety). N. GHATAK (Current Sci., 1934, 2, 380, and Bull. Acad. Sci. Agra and Oudh, 1933, 3, 69-74).—Gallic acid and an anthocyanin, now named abranin (I), have been isolated from the seed-coat of A. precatorius. Abranin chloride, m.p. 178-179° (sintering), isomerises readily in H₂O, EtOH, etc., and yields glucose on hydrolysis. The *picrate* melts at 149–150°. (I) is a monoglucoside. L. S. T.

Sterol glucosides. O. GISVOLD (J. Amer. Pharm. Assoc., 1934, 23, 402-404).—A no. of sterol glucosides were synthesised by the method of Power and Salway (J.C.S., 1913, 103, 399). The following appear to be new: stigmasterolglucoside, m.p. 299°; phytosterolglucoside, m.p. 293°. A. E. O.

Highly-polymerised compounds. XCIX. Structure of highly-polymerised compounds and the law of viscosity. H. STAUDINGER (Ber., 1934, 67, [B], 1242—1256).—A statement of the author's views on the macro-mol. structure of highlypolymerised compounds, the determination of the mol. wt. of such substances from measurements of viscosity, the form of the mols., and the origin of the term "eucolloid." H. W.

Morphology and chemistry of organic highmolecular natural products. K. HESS (Naturwiss., 1934, 22, 469-476).—A lecture.

Degradation of starch by phosphoric acid, glycerol, and acetic anhydride and sulphuric acid (acetolysis). R. SUTRA (Compt. rend., 1934, 198, 1863—1865).—H₂O-sol. potato or maize starch (I) dissolves slowly in 85% H₃PO₄ at room temp. α of these solutions (II) is about the same as that of aq. solutions, does not change at room temp., but decreases rapidly at 100° owing to degradation and hydrolysis. Addition of EtOH ppts. a non-reducing product (III), which is obtained free from acid by washing with EtOH and Et₂O. (II) gives with I a blue colour, changed by heat successively to violet, red, and colourless. (III) is thus a dextrin, similar to that obtained by glycerol at 200° (results recorded in the lit. are confirmed) or by Ac₂O-H₂SO₄. The results are in agreement with Haworth's formula for (I).

R. S. C.

Sozoiodolic acid as precipitant for bases. D. ACKERMANN (Z. physiol. Chem., 1934, 225, 46-48).-Sozoiodolic acid (2:6-di-iodophenol-4-sulphonic acid) (I) affords cryst. salts with many bases and NH₂-acids. The base is regenerated (as hydrochloride) by BaCl₂, which ppts. the Ba salt of (I) (solubility 0.158 g. in 100 c.c. at 16°). Salts of the following were prepared : spermine A,B, decomp. 244-246°; putrescine, A2B (+2H₂O), decomp. 250°; histamine, A₂B, decomp. 241°; cadaverine, A2B, decomp. 242°; creatinine, AB, decomp. 229-231°; d-arginine, AB, decomp. 213-214°; guanidine, AB, decomp. 247-249°; l-histidine, AB, decomp. 207-208°; glycinebetaine, AB, decomp. 223-224°; lysine, A₂B, decomp. 234-235°; glucosamine, AB, decomp. 181-182°, carbamide, AB, decomp. 208°; choline, AB, decomp. 180°. Solubilities are given. J. H. B.

Decomposition of the nitrites of some primary amines. D. W. ADAMSON and J. KENNER (J.C.S., 1934, 838—844).—The relative proportions of the products of decomp. of *n*-amyl- (I) (*picrate*, m.p. 138—138.5°), -hexyl- (*picrate*, m.p. 126.5°), -heptyl-, -octyl, (II), -nonyl-, and -decyl- (*picrate*, m.p. 118— 118.5°), -amine with HNO₂ (NH₂R,HCl+AgNO₂, filtered and thermal decomp. of solution) are, respectively, alcohol: 50.0, 50.5, 48.3, 46.3, 48.5, and 50.0; olefine: 30.1, 28.0, 25.4, 24.4, 24.4, and 27.4; nitrososec.-amine: 1.9, 2.5, 5.3, 5.5, 9.0, and 15.3; unchanged NH₂R: 1.7, 1.5, 0.8, 4.5, 1.0, and 1.1; and NH₂R,HCl, 0.7, 1.0, 0.5, 0.8, 0.5, and <math>1.4%. The proportion of sec.-alcohol formed decreases rapidly as the series is ascended [58% for NH₂Pr^a, approx. 33% for (I), 5% in (II), and none in the higher members]. The following reaction mechanism is suggested: $OH \cdot N:O \rightarrow OH \cdot N:OH \longrightarrow (OH)_2N \cdot NH_2R \rightarrow O:N \cdot NH_2R$ $\xrightarrow{NO_4} HNO_2 + O:N \cdot NHR \longrightarrow R \cdot N:N \cdot OH \xrightarrow{H'}_{OH'} R \cdot N_2,$

whence olefines are formed by Ingold's mechanism and primary and sec.-alcohols by decomp. of the onium cation and attack of OH' at the α - or β -carbon atom. The correlation of such reactions with the pinacol and Wagner-Meerwein changes is fully discussed. The following new derivatives were prepared as reference compounds : a-naphthylurethanes of n-, m.p. 65.5°, and sec.-amyl, m.p. 74.5°, n-, m.p. 59°, and sec.-hexyl, m.p. 60.5°, sec.-heptyl, m.p. 54°, sec.-octyl, m.p. 62.5°, n-, m.p. 65.5°, and sec.-nonyl, m.p. 55.5° n. m. p. 73°, and sec.-decyl, m. p. 69°, a-, m. p. 106°, and β-phenylethyl, m.p. 117°, alcohols : the αβ-dibromides of C_7H_{14} , b.p. 99.5°/10 mm., C_8H_{16} , b.p. 123°/14 mm., and C_9H_{18} , b.p. 133.5°/12 mm.; slightly impure picrates of diheptyl-, m.p. 117-120°, di-octyl-, m.p. 110-110.5°, dinonyl-, m.p. 106-108°, didecyl-, m.p. 115°, and di-β-phenylethyl-, m.p. 153°, -amines. Similar decomp. of CH2Ph·CH2·NH2 (III) affords CH_Ph·CH_·OH, 49.1, CH_:CHPh, 4.8, (CH₂Ph·CH₂)₂N·NO, 14·1, unchanged (III) 5·2, and J. W. B. its hydrochloride, 9.4%.

Reaction of chloroamines with zinc alkyls. G. H. COLEMAN, H. P. ANDERSON, and J. L. HERMAN-SON (J. Amer. Chem. Soc., 1934, 56, 1381–1382).— The nos. quoted after the following pairs of reactants are the yields of primary and sec.-amines, respectively, when reaction is carried out in Et₂O (the nos. in parentheses are the respective yields in light petroleum): NMeCl₂+ZnEt₂, 78, 17 (44, 46); NEtCl₂+ ZnEt₂, 71, 17 (49, 42); NBu^aCl₂, 76, 18 (57, 43); dichloroisoamylamine+ZnEt₂, 78, 16 (52, 42); NBu^aCl₂+ZnPr^a₂, 61, 24. NBu^a₂Cl and ZnEt₂ in Et₂O give 71% of sec.- and 1.5% of tert.-amine. NEt₂Cl and ZnEt₂ in light petroleum afford 70% of sec.- and 1.8% of tert.-amine. H. B.

Factors governing the instability of carbon to nitrogen linking. I. Instability of the carbon to nitrogen linking in substituted methylamines. M. S. KHARASCH and L. B. HOWARD (J. Amer. Chem. Soc., 1934, 56, 1370—1373).—NH₂Bu^{γ}, CPhMe₂·NH₂ (?), and CPh₂Me·NH₂ (?) are unaffected by 0·05*N*-HCl at 100° for 50—100 hr.; CPh₃·NH₂ (I) is hydrolysed to the extent of 18% after 15 min. and 85% after 90 min. (I) is unaffected by heating in xylene at 150° (sealed tube) for 24 hr. or at 250° for 12 hr. Similar hydrolysis of 2 : 1·OH·C₁₀H₆·CHR·NH₂ (to β -C₁₀H₇·OH, R·CHO, and NH₄Cl) occurs with increasing ease when R is CH₂Ph·CH₂; Ph. p-tolyl, and anisyl (free amine not isolable). β -C₁₀H₇·OH, CH₂Ph·CH₂·CHO, and EtOH–NH₃ give the γ -phenylpropylidene derivative (II), m.p. 103—122° (liquid crystals), of 2-hydroxy- α -naphthyl- β -phenylethylmethyl-

m.p. 256°].

amine (111), m.p. 108° (hydrochloride, m.p. $205-210^{\circ}$); (111) is obtained from (11) by hydrolysis with 20% HCl. The p-methylbenzylidene derivative, m.p. 149° , of p-tolyl-2-hydroxy- α -naphthylmethylamine, m.p. $109\cdot5^{\circ}$ [hydrochloride, m.p. $195-220^{\circ}$ (decomp.)], is similarly prepared using p-C₆H₄Me·CHO. Anisyl-2-hydroxy- α -naphthylmethylamine is not obtained by hydrolysis (20% HCl) of its anisylidene derivative, m.p. 181° ; p-OMe·C₆H₄·CHO, β -C₁₀H₇·OH, NH₄Cl, and anisylidenedinaphthyl ether, m.p. 206° , are formed. The stability of the above amine hydrochlorides towards 20% HCl is attributed to (i) their insolubility and (ii) decrease in electronegativity of the NH₂ on conversion into NH₃Cl. H. B.

Laboratory method for the preparation of unsymmetrical β -diethylaminoethylamine. W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 401–402).—A modification of the method of Ristenpart (A., 1897, i, 46). Condensation of β -bromoethylphthalimide and NHEt₂ in boiling PhMe for 12 hr. followed by hydrolysis of the product with 20% HCl and extraction of the amine with Pr^{\beta}OHleads to β -diethylaminoethylamine in 61% yield. A. E. O.

Preparation of diaminobutanes. III. $\beta\gamma$ -Diaminobutane. E. STRACK and H. SCHWANEBERG (Ber., 1934, 67, [B], 1006-1011; cf. this vol., 283).-- β_{y} -Diaminobutane [r(I) : meso(II) = 4:1] is obtained in 92% yield by catalytic reduction of dimethylglyoxime (Pd) at room temp. in very dil. solution in MeOH. (I) is resolved into its optical isomerides as the H tartrate from EtOH, the resolution being completed by pptn. of the hydrochlorides from EtOH by Et.O. The following derivatives are described: hydrochlorides, (II), decomp. 325° , (I), m.p. $253-254^{\circ}$ after softening at 250° ; (+), m.p. $238-239^{\circ}$ after softening at 236° , $[\alpha]_{15}^{18} - 12 \cdot 1^{\circ}$ in H₂O, (--), m.p. $238-239^{\circ}$ after softening at 236° , $[\alpha]_D + 12 \cdot 1^{\circ}$ in H₂O; sulphates, (II), $+1.5H_2O$, m.p. $> 320^{\circ}$, (I), m.p. 239° relation blocking (II), $(+1) \cdot (-1)$, (II), m.p. $> 320^{\circ}$; platinichlorides, (I), (II), (+), (-), decomp. about 300°; aurichlorides, (II), decomp. 239-240° after softening at 234°, (I) +2H₂O, decomp. 239-240° after softening at about 230° , (+) and (-) +2H₂O, decomp. 245-246° after softening at 235°; compounds, $C_4H_{12}N_2(HgCl_2)_2$, (II), m.p. 152°, (I), m.p. 179° after softening at 172° and darkening at 176°, (+) and (-), m.p. 179°; $C_4H_{12}N_2,HgCl_2$ (II), m.p. 166°, (I), m.p. 188°, (+) and (-), m.p. 195°, all dependent greatly on mode of heating; $C_{4H_{12}N_{2}}(HgCl_{2})_{6}$, (II), (I), (+), and (-), m.p. about 190° (decomp.) after softening at 170-180°; picrates, (II), decomp. 275° after darkening at 265° , (I) $+2H_2O$, decomp. 250° after softening at 247°, (+) and (-), $+2H_2O$, decomp. 248°; picrolonates, (II), (I), (+), and (-) +H₂O, all decomp. $265-270^{\circ}$; Bz_2 derivatives, (II), m.p. 298° , (I), m.p. 251° , (+) and (-), m.p. 214°; di-m-nitrobenzoyl compounds, (II), m.p. 325°, (I), m.p. 245°, (+) and (-), m.p. 272°

m.p. 76° (yield 45%), and a non-cryst., non-distillable material transformed by boiling MeOH into ε benzamido-n-amyl alcohol in small yield. (I) is readily reduced by $SnCl_2$ to α -amino- ε -benzamidopentane, b.p. 180—185°/01 mm. (hydrochloride, m.p. 145°; picrate, m.p. 163°), which is not thus readily isolated and is best obtained by treatment of (I) with H₂ (Pd in MeOH). ac-Dibenzamido-npentane, m.p. 132°, is transformed by warm Ac₂O into α-acetamido-ε-benzamido-n-pentane, m.p. 119°. δ-Iodobutylbenzamide from δ-chlorobutylbenzamide (improved prep.) is converted by successive treatment with AgNO₂, boiling MeOH, and H₂(Pd-MeOH) into δ -benzamidobutyl alcohol, b.p. $180-200^{\circ}/0.3$ mm. (slight decomp.), m.p. $71-73^{\circ}$, and α -amino- δ -benzamidobutane, b.p. $176-178^{\circ}/0.1$ mm. (hydro-chloride, m.p. 167° ; platinichloride, decomp. 213° ; picrate, m.p. 168—170°). a-Acetamido-8-benzamido-butane has m.p. 143°. γ-Nitropropylphthalimide (III), b.p. 184-185°/0.1 mm., is converted by NaOH into o-carboxybenz-y-nitropropylamide, m.p. 119°, converted by Br and alkali into o-carboxybenz-yydibromo-y-nitropropylamide, m.p. 147°. (III) is not satisfactorily reduced by Sn and HCl, but is converted by H₂ into crude phthalyltrimethylenediamine [hydrochloride, m.p. 171°; platinichloride, m.p. 239° (de-

Methylcholines and analogous substances. I. R. HUNT. II. R. R. RENSHAW and F. I. LAWRENCE (J. Pharm. Exp. Ther., 1934, 51, 237-255, 255-262).—I. Earlier work on choline esters is discussed (cf. A., 1929, 349, 468). Some claims of Simonart (A., 1932, 1284) are refuted.

comp.); aurichloride, m.p. 294-296°; Ac derivative,

II. That Menge's alleged "acetyl- α -methylcholine" [actually synthesised by Karrer (A., 1922, i, 813)] is acetyl- β -methylcholine is confirmed (A., 1912, i, 949; 1925, i, 1502; 1932, 257). The β derivative, m.p. 148—149° (corr.), is prepared by a modification of Menge's method or by treating [CH₂]₃O (1 mol.) with AcBr (1 mol.) at low temp. to give α -bromo- β -acetoxypropane, which is condensed with NMe₃ at 45—50° under pressure, the cryst. product being acetylated and fractionally recrystallised from COMe₂. F. O. H.

Reactions of tri(hydroxyethyl)amine. E. JAFFE (L'Ind. Chimica, 1934, 9, 750-752).—Reactions with H_3PO_4 , phosphates, molybdates, vanadates, Hg^++I , H_3BO_3 , and Fe^{***} are described (cf. A., 1933, 246). T. H. P.

Reactions of ethylurethane. L. EKKERT (Pharm. Zentr., 1934, 75, 406-407).—Colour reactions with PhN_2SO_3H , m-C₆H₄(OH)₂-H₂SO₄, m-C₆H₄(NO₂)₂-NaOH, and MeCHO-H₂SO₄ and Jacquemin's and Schuster's reactions are described. E. H. S.

Alkaline hydrolysis of glycine and alanine anhydrides.—See this vol., 848.

Marasmin. E. SPATH and J. ZELLNER (Monatsh., 1934, 64, 123—124).—Marasmin (A., 1929, 108) is shown to be an impure specimen of (mainly) *l*- and some *dl*-leucine. H. B.

Synthesis of monoacyl derivatives of aliphatic diamines. J. VON BRAUN and W. PINKERNELLE [with, in part, H. HARTMANN] (Ber., 1934, 67, [B], 1056-1060).— ε -Iodoamylbenzamide is converted by AgNO₂ in Et₂O into α -nitro- ε -benzamidopentane (I),

H. W.

875

H. W.

Long dipole. R. KUHN and F. GIRAL (Ber., 1934, 67, [B], 1130—1132).—cycloPentadecanoneisooxime is converted by fuming HCl at 150° into ξ -aminopentadecoic acid semihydrochloride,

2NH₂·[CH₂]₁₄·CO₂H,HCl, m.p. 165–165.5°, transformed by repeated crystallisation from EtOH-conc. HCl into the monohydrochloride (I), m.p. 131–132°. (I), KOH, and Me₂SO₄ vield the corresponding betaine (II), C₁₈H₃₇O₂N,3H₂O, m.p. 259.5–260° [platinichloride, m.p. 214° (corr.); aurichloride, m.p. 120°]. The dipole moment of (II) is unusually high. H. W.

Synthesis of phosphoric esters of hydroxyamino-acids. II. dl-Serinephosphoric acid. P. A. LEVENE and A. SCHORMULLER (J. Biol. Chem., 1934, 105, 547-562).-dl-Serine-B-phosphoric acid (I) is synthesised by action of POCl₃ on benzylideneserine Ba salt in presence of MgO and hydrolysis of the product, $C_{20}H_9O_6N_2P_2Mg_3$, with 10% HCl. It is also obtained by action of H_3PO_4 and P_2O_5 on serine (II), and its anhydride is similarly obtained from serine anhydride. With EtPO3 in CHCl3 at the b.p. (II) gives a diphosphoric acid (isolated as $Ba \operatorname{salt}$; cf. A., 1911, i, 705). With CH_2O and $\operatorname{Ba}(OH)_2$ cf. A., 1911, i, 705). (II) gives a salt (C4H6O3N)2Ba, apparently of the N-CH₂·OH derivative, but the corresponding free acid in aq. solution does not give (I) with POCl₃ and MgO. The Me ester of (I) with CH₂O gives substances, $C_{11}H_{18}O_6N_2$, m.p. 137°, possibly $CH_2[O\cdot CH_2\cdot CH(N:CH_2)\cdot CO_2Me]_2$, and

CH₂[\dot{O} ·CH₂·CH(N:CH₂)· \dot{CO}_2 Me]₂, and b.p. 164– 168/0.9 mm.; the latter may be an oxazole. α -Bromo- β -hydroxypropionic acid (III) is converted by P₂O₅ and H₃PO₄ into a *phosphate* (isolated as *Ba* salt, C₆H₆O₁₂Br₂P₂Ba₃,2H₂O), which, however, gives a complex mixture with NH₃ under various conditions. OH·CH₂·CH(OEt)₂ similarly gives a *phosphate* (*Ba* salt) with POCl₃, but this could not be hydrolysed without loss of H₃PO₄. The *Me* ester, b.p. 94–98°/9 mm. (MeOH; CH₂N₂ failed), of (III) is converted by NaN₃ in MeOH into *Me* β -azido- α hydroxypropionate, b.p. 102–104°/9 mm., which is reduced by H₂-PtO₂ to *iso*serine; apparently an ethylene oxide ring is formed intermediately and is opened by HN₃ in the same way as by NH₃. The (*CO*₂·*CH*₂*Ph*)₂ derivative of (II), m.p. 94°, is described. H. A. P.

Guanido-acids and guanidopeptides. J. KAPF-HAMMER and H. MULLER (Z. Physiol. Chem., 1934, 225, 1-12).-Guanido-compounds of NH2-acids and peptides were prepared by an improved method using O-methylisocarbamide base (I) prepared from the hydrochloride in MeOH solution. The following derivatives were obtained. *l*-Cystine (with S-ethylisothiocarbamide) $\longrightarrow \alpha$ - diguanido - β - dithiodiprop ionic acid, decomp. $< 200^{\circ}$; dl-serine $\longrightarrow \beta$ -hydroxya-guanidopropionic acid, decomp. about 200°; dlphenylalanine $\longrightarrow \beta$ -phenyl- α -guanidopropionic acid, decomp. $< 200^{\circ}$; l-hydroxyproline \longrightarrow iminoamino-N-methylhydroxypyrrolidinecarboxylic acid (+H2O) (II), m.p. 240° [with 2 mols. of Reinecke acid (III) $\xrightarrow{}$ salt, m.p. 160°]; *l*-proline \longrightarrow iminoamino-N-methylpyrrolidinecarboxylic acid (+H2O) (IV), decomp. 236-242° [with 2 mols. of (III) \longrightarrow salt, decomp. 198°]; l-tryptophan $\longrightarrow \alpha$ -guanido- β -indolylpropionic acid, decomp. 225—230°; d-glutamic acid $\longrightarrow \alpha$ -guanidoglutaric acid, decomp. 155—160° [salt of (I), decomp. 150—160°]; glycyl-d-alanine \longrightarrow guanidoacetylalanine, decomp. 220—225°; dl-alanylglycine \longrightarrow guanido-dl-propionylglycine, decomp. > 235; glycyl-dlphenylalanine \longrightarrow guanidoacetyl - dl - phenylalanine, decomp. 225—230°; glycyl-l-leucine \longrightarrow guanidoacetyl-l-leucine, decomp. 215°. All the derivatives give the Ac₂ reaction, and all except (II) and (IV) the reaction with α -C₁₀H₇·OH and NaOCI.

J. H. B. Formamide. P. L. MAGILL (Ind. Eng. Chem., 1934, 26, 611-614).—Small-scale methods of prep. and properties of $HCO\cdot NH_2$ (I) are reviewed. A mechanism for the reaction between (I), NH_2Ph , and S is suggested. Glass and Al are the most satisfactory materials for the storage of (I). D. K. M.

Spontaneous resolution of *dl*-dilactyldiamide in aqueous solution. P. VIÈLES (Compt. rend., 1934, 198, 2102—2104).—Spontaneous evaporation of a saturated solution of *dl*-dilactyldiamide (A., 1932, 253) above 34— $35\cdot5^{\circ}$ (transition temp.) affords crystals of the *d*- and *l*-forms, m.p. 208°, but below this temp. the racemate $+2H_2O$ separates. Separation is best effected by seeding a supersaturated solution, at 40°, with the *d*-form, which causes rapid crystallisation of this form, and subsequent seeding of the mother-liquor, which contains a large excess of the enantiomorph, with the *l*-form. J. W. B.

Reaction between hydroferrocyanic acid and ethyl alcohol. F. Hölzl and J. KRAKORA (Monatsh., 1934, 64, 97–105).—H₄Fe(CN)₆ (I) {the etherate (cf. von Baeyer and Villiger, A., 1902, i, 355) is formulated as the oxonium compound $[Fe(CN)_6]H[Et_2OH]_3$ and abs. EtOH at 100° (sealed tube) for 15 hr. in absence of light give the complex $[(CN)_2:Fe(OH_2)_2:(CN)_2:Fe(OH_2)_2:$ $(CN)_2:Fe(OH_2)(CNEt):(CN)_2]$, which is a very weak acid (titration curve given). The reaction between (I) and EtOH at about 98° is followed titrimetrically and potentiometrically; after 8—10 hr. a stable dibasic acid (or equiv. amounts of two monobasic acids) is produced. H. B.

Cyanogen bromide and anhydrous hydrocyanic acid. K. H. SLOTTA (Ber., 1934, 67, [B], 1028– 1030).—Precise directions are given for the laboratory prep. of CNBr (I) from Br, H_2O , and NaCN in 90% yield and of HCN (II) from H_2SO_4 , H_2O , FeSO₄, and NaCN in almost quant. yield. (I) can easily be preserved unchanged if colourless, but rapidly polymerises if discoloured. (II) is stabilised by addition of a little conc. HCl. H. W.

Organic compounds of mercury. IX. Reaction of mercuric chloride with ethyl diazoacetate. A. N. NESMEJANOV and G. S. POWCH (Ber., 1934, 67, [B], 971—974; cf. this vol., 313).— NH₂Me,HCl, HgCl₂, and *iso*amyl nitrite in MeOH do not react; addition of Cu powder induces diazotisation and decomp. of the diazonium compound with production of CH₂Cl·HgCl, m.p. 130°, in small yield. CHN₂·CO₂Et and HgCl₂ react vigorously with production of CH₂Cl·CO₂Et and complex Hg compounds, from which the substance Hg[CCl(HgCl)·CO₂Et]₂ is isolated by repeated dissolution in C_5H_5N and pptn. with EtOH. H. W.

Organic compounds of gold. III. Monoethyldibromogold (monoethylgold dibromide). A. BURAWOY and C. S. GIBSON (J.C.S., 1934, 860—864). —Diethylmonobromogold (I), $Et_2Au \swarrow_{Br}^{Br} AuEt_2$ (A., 1931, 1316), is best prepared by the action of MgEtBr on pyridino-trichloro- or -tribromo-gold in C_5H_5N -Et₂O in a freezing mixture. With Br in CCl_4 (I) affords monoethyldibromogold (II) (monoethylauric dibromide of J.C.S., 1907, 91, 2064), probably $Br_2Au \swarrow_{Br}^{Br}AuEt_2$. Quant. decomp. of (II) \longrightarrow 2AuBr + 2EtBr occurs at room temp. and at 80—85°. Contrary to Kharasch *et al.* (A., 1931, 1043) (II) does not dissolve in C_6H_6 , but affords (I)

and brominated C_6H_6 , and, in general, (II) is decomposed by readily brominated or oxidised solvents (Et₂O, EtOH, COMe₂, also ligroin and H₂O) to give (I) with pptn. of AuBr and/or Au, bromination or oxidation of the solvent being due to the action of AuBr₃. Co-ordination compounds of the type [Et₂BrAuQ]Br (Q=a diamine) could not be obtained, and with [\cdot CH₂·NH₂]₂ (II) gives only [Au en₂]Br₃ and [AuEt₂en]Br, the latter giving (I) on acidification.

J. W. B.

Thermal decomposition of cyclopentane and methylcyclopentane. B. A. KASANSKI and A. F. PLATE (Ber., 1934, 67, [B], 1023-1028).--The liquid products of the thermal decomp. of cyclopentane at 650° in SiO₂ tubes are mainly unchanged (I) containing a little cyclopentadiene. The gaseous products consist of C_2H_4 and CHMe:CH₂ (II) (together 73%), H₂, saturated hydrocarbons (III), and traces of diolefines. Methylcyclopentane gives mainly (II) with some CH₂:CMe₂ (IV), and a higher % of (III) (? CH₄). The gases from cyclohexane contain much more H₂ and saturated hydrocarbons; the unsaturated portion is almost exclusively C₂H₄ containing very little (III) and about 6% of (IV).

H. W.

Biological and chemical nomenclature for the carotenoids. L. S. PALMER (Science, 1934, 79, 488–490).—A discussion, and a scheme of new generic and chemical names. L. S. T.

Mechanism of formation of aromatic hydrocarbons by pyrolysis. (a) E. N. HAGUE and R. V. WHEELER. (b) H. P. A. GROLL (Ind. Eng. Chem., 1934, 26, 697, 697-698).--(a) A reply to Groll (B., 1933, 691). The yield of aromatic compounds (I) in gals. per cu. ft. of olefines increases as the series is ascended. C_2H_4 , not C_3H_6 , is the essential intermediate in the formation of (I); a wt. conversion of 65% of C_2H_4 has been obtained at 750° against 42% of C_3H_6 and butylene (II). A mechanism for the formation of C_6H_6 is suggested. Hydroaromatic compounds, e.g., cyclohexene (III), are thought to be the forerunners of (I). The primary reaction of C_2H_4 is polymerisation to (II), which yields butadiene (IV) and C_2H_6 . (IV) may react with (1) C_2H_4 to give (III) and thence C_6H_6 , (2) C_3H_6 to give methylcyclohexenes and thence PhMe, (3) Δ^{α} -(II) to give PhEt and thence CHPh:CH₂, (4) Δ^{β} -(II) to give dimethylcyclohexenes and o-xylene. It is not confirmed that above 500° C₃H₆ prevails increasingly over (II) in the products obtained in the heat treatment of C₂H₄.

(b) A reply to the above. C_2H_2 is always formed when C_3H_6 etc. is cracked in the vapour phase. The yields of (I) from the pyrolysis of C_nH_{2n} are better represented by Groll's than by Hague and Wheeler's equation. It is doubtful if (III) is an essential intermediate to (I), since it does not form (I) more readily than any other olefine. D. K. M.

Hydrogenation of aromatic hydrocarbons in solution at room temperature in presence of nickel-black. R. TRUFFAULT (Bull. Soc. chim., 1934, [v], 1, 206-223; cf. Brochet, A., 1914, i, 645).— C_6H_6 (I) is reduced to C_6H_{12} by H_2 and a Ni (II) or, better, a Ni-3% Cr (III) catalyst, at room temp. and pressure without solvent. Reduction is also effected in C_6H_{12} and C_6H_{14} solution, but not in AcOH, Ac₂O, or EtOH. Thiophen present in commercial C6H6 greatly retards reduction, but cryoscopic (I) is sufficiently pure. Except with very small amounts of (III) H_2 absorption is approx. ∞ amount of (III), and almost independent of the amount of (I). The kinetics are complicated, the reaction order being < 1. Similar but slower reduction of PhMe (IV) and of *m*- and *p*-xylene occurs. The velocity of reduction of (I) is trebled by a temp. rise from 20° to 50° (optimum), and that of (IV) is doubled by rise from 20° to 70-80° (optimum), above which temp. the high v.p. of the hydrocarbon rapidly decreases the velocity. The optimum reduction temp. for the prep. of (II) is 220-225°, for Ni-Mg (3-9%), 350° [less efficient than (II)], and for (III), 300° $[1\cdot5-2$ times as efficient as (II)]. In C₆H₁₂ or C₆H₁₄ complete reduction of C10H8, fluorene, CH2Ph2, and Ph_2 (8 hr. at 50°) with (III) is effected, but is slower than that of (I). J. W. B.

Catalytic hydrogenation of aromatic hydrocarbons in solution in presence of nickel-black and phosphoric oxide. R. TRUFFAULT (Bull. Soc. chim., 1934, [v], 1, 391-406).-Interaction of C₆H₆ with H₂ in presence of Ni-black (I) and P₂O₅ at room temp. affords cyclohexane (II), together with phenylcyclohexane, which is further reduced to cyclohexylcyclohexane (III). PhMe gives analogous results. P_2O_5 diminishes the initial activity of (I); the activity of the catalyst diminishes rapidly after the second day. 1:2-Dibromocyclohexane with Na isoamyloxide in isoamyl alcohol affords the diisoamyloxycyclohexane (IV), b.p. 206°/750 mm., and cyclohexadiene [also formed from (IV) with KHSO4], which with P_2O_5 gives a resin (polymeride) which absorbs H₂ in presence of (I). cycloHexene (V) in (II) containing (I) and P_2O_5 with H_2 affords 2-cyclohexyl- Δ^1 -cyclohexene, b.p. 237° (cf. A., 1911, i, 473). (V) in boiling C_6H_6 containing P_2O_5 affords an oil, b.p. 106—107°/13 mm., hydrogenated to (III).

J. L. D.

Photochemical chlorination of chlorobenzene. —See this vol., 852.

Bromination of benzene. J. B. MENKE (Chem. Weekblad, 1934, 31, 344–345).—When Br, C_6H_6 , and FeCl₃,6H₂O are heated together, PhBr is formed with evolution of HBr and HCl. FeSO₄,7H₂O is also active, but with $Fe(NO_3)_3$ ($H_2O=30-40\%$) the reaction does not occur. Anhyd. $Fe_2(SO_4)_3$ is active, but cryst. K Fe^{III} sulphate is inert, although addition of K_2SO_4 to hydrated $Fe_2(SO_4)_3$ does not diminish the activity of the latter. Nitrates and nitrites inhibit the reaction. H. F. G.

Fluorination of organic substances with free fluorine. K. FREDENHAGEN and G. CADENBACH (Ber., 1934, 67, [B], 928-935).-The apparatus consists of a glass cylinder which can be rotated around a horizontal axis and externally cooled. F2, obtained by electrolysis of molten KHF₂ (modified method), is introduced through a Cu tube closed at the end and provided with numerous fine openings. The choice of experimental conditions is dictated by the v.d. of the material. If this is sufficiently high, fluorination is effected in the gas phase; dilution with 15 vols. of N₂ is essential to avoid risk of inflammation, and F does not enter the org. mol. If the Cu tube is greatly roughened and has many fine orifices the proportion of N₂ can be greatly reduced and addition or substitution occurs. A similar effect is not produced if glass is substituted for Cu. The action is enhanced by wrapping the tube in wire gauze, Cu, Ag, and Fe appearing equally effective. If the v.p. is not sufficiently high, the gas is allowed to play on the surface of the liquid. Rotation of the vessel, delivery of F₂ through a long tube, and initial dilution with N_2 prevent inflammation; subsequently the indifferent gas in the tube serves as diluent. Substances the m.p. of which is too high to permit safe manipulation may be dissolved in CCl₄ or AcOH. The fluorination of C_6H_6 , PhMe, $C_{10}H_8$, $n-C_6H_{14}$, amylene, dipentene, palmitic acid, C_5H_5N , PhOH, cresol, thymol, menthol, coumarin, geraniol, paraffin oil, petroleum, ligroin, tar oil, linseed oil, and various ethereal oils is described as far as concerns the % of H. W. F in the products.

Migration of bromine during side-chain chlorination of bromotoluenes. F. ASINGER (Monatsh., 1934, 64, 153—160).—Chlorination of o-, m-, and p-C₆H₄MeBr gives crude products which analyse (Cl+Br) correctly for C₆H₄Br·CH₂Cl (I), but are mixtures of (I) and C₆H₄Cl·CH₂Br, since hydrolysis (aq. EtOH-KOH) affords Cl' and Br'. The following reactions probably occur : C₆H₄MeBr+Cl₂ \rightarrow C₆H₄MeCl+ClBr \rightarrow C₆H₄Cl·CH₂Br+HCl. 3:5-C₆H₃MeBr₂ gives a similar mixture; the product obtained by crystallisation from EtOH in about 30%

obtained by crystallisation from EtOH in about 30% yield has m.p. 80° and contains 63% Br (indicating the presence of some $3:5\text{-}C_6\text{H}_3\text{Br}_2\text{-}C\text{H}_2\text{Br}$). Similar results are obtained on dichlorination. Cl and Br in CHArCl₂ are determined by hydrolysis with conc. H₂SO₄ at 100-140°; HCl and HBr (+Br) are removed in N₂ or CO₂ and absorbed in dil. NaHSO₃. H. B.

Nitration of chloro-*p*-xylene. H. WAHL (Compt. rend., 1934, 198, 2105-2107).—From the fraction, b.p. 170-175°/15 mm., obtained from the products of nitration of chloro-*p*-xylene after isolation of 2-chloro-*p*-tolualdehyde (I) (this vol., 772), is obtained 2-chloro-5-nitro-p-tolualdehyde (II), m.p. 100° [oxime, m.p. 145° (corr.); phenylhydrazone, m.p. 228° (corr., decomp.); semicarbazone, m.p. 310° (corr., decomp.)], the constitution of which is proved by its identity with the nitration product of (I), its oxidation (KMnO₄) to the corresponding benzoic acid, and its conversion by NaOH-COMe₂ into 5:5'-dichloro-6:6'-dimethylindigotin. The mother-liquor from (II) affords a phenylhydrazone, m.p. 145°, of an isomeric aldehyde. The nitration products of *p*-xylene contain *p*-tolualdehyde and its 3-NO₂-derivative.

J. W. B.

Volume effects of alkyl groups in aromatic compounds. III. Dinitration of 3-chloro- and 3-bromo-p-cymene. IV. Dinitration of 2-chlorocymene. S. N. GANGULY and R. J. W. LE FEVRE (J.C.S., 1934, 848-852, 852-854).-III. Mononitration of 3-chloro- or 3-bromo-p-cymene gives the 6-NO., derivative (Fileti et al., A., 1889, 493), the constitution being confirmed by replacement of the halogen by piperidine (I). Dinitration (HNO_3 , $d \colon 5$, at -5° , or HNO_3 , $d \colon 43$, $+\text{H}_2\text{SO}_4 < 10^\circ$) gives the $2: 6-(NO_2)_2$ -derivative (II), converted by (I) into 2:6-dinitro-3-piperidino-p-cymene (III), m.p. 123-124° [identical with a specimen prepared by successive action of PCl₅ and (I) on 2:6-dinitrothymol]. The supposed isomeric (NO2)2-derivative, m.p. 80° (Cl) and 94° (Br) (loc. cit.), is (II) contaminated with the ketone (IV) resulting from oxidation of Pr^{β} to Ac. $m-C_6H_4ClMe$ with AcCl-AlCl₃ gives 2-chloro-4-methylacetophenone [oxidised by KMnO₄-NaOH to 3-chloro-4-acetylbenzoic acid, m.p. 228°, further oxidised to chloroterephthalic acid (III)], converted by HNO_3 (d 1.5) at -10° into its 3 : $5 \cdot (NO_2)_2$ -derivative (IV), m.p. $91-92^\circ$, which with (I) affords 3 : $5 \cdot di$ nitro-2-piperidino-4-methylacetophenone, m.p. 108-109°, which can also be isolated by the action of (I) on the crude dinitration product (II).

IV. Nitration of pure 2-chlorocymene (by the Sandmeyer reaction from 2-cymidine) with HNO₃ (d 1.5), or HNO₃-oleum, < 0°, gives 2-chloro-3:5dinitrocymene [converted by (I) into 3:5-dinitro-2piperidinocymene (A., 1933, 1153)], and no trace of the compound (V), m.p. 88–89°, obtained by Lubs et al. (A., 1920, i, 153). (V) may be (IV) resulting from the presence of some 3-chlorocymene in the sample previously used, or 3-chloro-2:6-dinitro-4methylacetophenone, m.p. 97–98° (3-piperidino-derivative, m.p. 113–114°), synthesised by nitration (HNO₃, d 1.5, < 0°) of 3-chloro-4-methylacetophenone (VI) (by the Sandmeyer reaction on the 3-NH₂-compound). (VI) is oxidised by KMnO₄-NaOH successively to 2-chloro-4-acetylbenzoic acid, m.p. 228°, and (III). J. W. B.

Comparison of the activating effect of the sulphone and nitro-group. H. R. TODD and R. L. SHRINER (J. Amer. Chem. Soc., 1934, 56, 1382–1384).—C₆H₄Cl·SO₂Na (the acids are prepared from the diazonium sulphates, SO₂, and Cu-bronze) and EtOH-MeI give o-, m.p. 90°, m-, m.p. 106°, and p-, m.p. 96°, -chlorophenyl Me sulphones. The reactivity of Cl towards EtOH-NaOEt is o > p > m; the C₆H₄Cl·NO₂ show much greater activity (p > o > m). The NO₂-group has a much greater activating effect than \cdot SO₂Me. The dipole moment (SO₂ > NO₂) is not an index of activating power. H. B.

Stereochemical studies. I. Racemisation of optically active sulphinic esters. K. ZIEGLER and

A. WENZ (Annalen, 1934, 511, 109-120).-When freshly distilled (-)- β -octyl (I) and menthyl p-toluencsulphinates are kept in a high vac., the rotations do not alter during several months. In presence of air or O_2 the rotation alters after a short time, acid formation occurs, and O2 is absorbed; with absolutely dry O_2 , there is an induction period of about 100 hr. The rotations of mixtures of (-)- β -octanol (II) and (I) do not change over a long period in absence of air; addition of p-C₆H₄Me·SO₃H (III) causes a rapid alteration [the velocity depends on the concns. of (II) and (III)] at room temp. Addition of (III) to (I) causes a relatively slow change of rotation. The strong catalytic action of (II)+(III) is ascribed to ester interchange. The velocity of mutarotation of (I) (in CHCl₃) catalysed by (II)+(III) is similar to, but differs slightly (in the expected manner) from, that of Et p-toluenesulphinate (IV) catalysed by (III) + EtOH. Comparison of the rate of "autoracemisation" of (IV) with the catalytic racemisation [(II)+(III)] indicates that the former is explained (cf. Phillips, A., 1926, 159) by the formation of decomp. products (assuming that ester interchange occurs simultaneously). Indications of a true autoracemisation of toluenesulphinic esters at room temp. are not observed. H. B.

Convenient synthesis of durene and pentamethylbenzene from crude xylene. J. VON BRAUN and J. NELLES (Ber., 1934, 67, [B], 1094-1099; cf. A., 1933, 1283).—When heated with conc. HCl and CH₂O at 60-70° in a current of HCl, p-xylene affords 2-chloromethyl-, b.p. 100-103°/12 mm. (oxidised by HNO₃ to trimellitic acid), di-2:5-chloromethyl- (I), m.p. 133° (whence pyromellitic acid), and di-2:3-chloromethyl-, m.p. 68—70° (whence mellophanic acid), -xylene. (I) is transformed by KOAc in AcOH into di-2:5-acetoxymethyl-, m.p. 65°, which affords di-2: 5-hydroxymethyl-, m.p. 160°, and thence di-2: 5-bromomethyl-, m.p. 160°, -p-xylene. Similarly, m-xylene gives 4-chloromethyl-, b.p. 100-105°/14 mm. (oxidised to trimellitic acid), di-4:6chloromethyl- (II), m.p. 99° (whence pyromellitic acid), and di-2: 4-chloromethyl-, m.p. 58-60° (whence mellophanic acid), -m-xylene. (II) gives non-cryst. di-4: 6-acetoxymethyl-, hydrolysed to di-4: 6-hydroxymethyl-, m.p. 151°, whence di-4: 6-bromomethyl-, m.p. 111°, -m-xylene. o-Xylene is converted into a mixture of 3- and 4-chloromethyl-, and di-4: 5-chloromethyl- (III), m.p. 105-106°, -o-xylene. (III) gives non-cryst. di-4: 5-acetoxymethyl-, di-4: 5-hydroxymethyl-, m.p. 99°, and di-5:5-bromomethyl-, m.p. 120°, -o-xylene. Treatment of crude xylene (IV) with CH₂O and conc. HCl (2:5 by wt.) at 70° for 7 hr. and then with 2 parts of CH₂O and HCl for 12 hr., followed by reduction and distillation, gives a fraction from which, after crystallisation from EtOH, durcne, m.p. 80°, is obtained in 45% yield. Similar treatment of (IV) followed by reduction and re-treatment gives a trimethyldi(chloromethyl)benzene, m.p. 121°, converted by 2N-NaOH into C6HMe5, m.p. 47-49°. H. W.

Mechanism of chemical reactions. V. Importance of molecular compounds in catalytic hydrogenations. K. KINDLER, E. BRANDT, and E. GEHLHAAR (Annalen, 1934, 511, 209–212). Catalytic hydrogenation (Pd sponge) of CHPh:CH·NO₂ occurs rapidly in AcOH-H₂SO₄ yielding,

 $CH_2Ph \cdot C\hat{H}_2 \cdot \hat{N}H_2$ (I) in 84% yield. In absence of $H_2SO_4 H_2$ is absorbed much more slowly and (I) is produced only in traces. The formation of an intermediate product CHPh:CH·N(:O):O···H_2SO_4 is postulated. The reduction of Me phenylacetoxyacetate to $CH_2Ph \cdot CO_2Me$ is similarly facilitated greatly by H_2SO_4 . H. W.

Highly polymerised compounds. XCIII. Rupture of the thread molecules of polystyrene. XCIV. An insoluble polystyrene. H. STAU-DINGER and W. HEUER (Ber., 1934, 67, [B], 1159-1164, 1164-1172).-XCIII. Prolonged trituration of polystyrenes, mol. wt. 470,000 and 163,000, respectively, and periodic determination of $\eta_{sp.}$ of the products in tetrahydronaphthalene (I) shows that the process is accompanied by progressive degradation of the mol. to a mean mol. wt. of about 103,000, after which change ceases. It therefore appears probable that mechanical accompanies oxidative degradation during the grinding of caoutchouc. Similar degradation is observed when polystyrenes of mol. wt. 610,000 and 440,000 dissolved in (1) are forced repeatedly through fine Pb orifices; the change proceeds to mean mol. wt. about 350,000. A polymeride, mol. wt. 300,000, is stable under these conditions. Similar changes of viscosity have been observed in solutions of serum.

XCIV. A technical, monomeric styrene passed at 60-100° into a polystyrene glass, insol. in all media and swelling to a limited extent according to the nature of the medium with which it was brought into contact (this was usually accompanied by dissolution of small amounts of material of mean mol. wt. 60,000). The unusual behaviour is traced to the presence of very small amounts of p-divinylbenzene (I). Polymerised products containing 1% of (I) are insol. and swell little; with > 0.01% of (I) the swelling properties are very marked, but the material contains considerable amounts of sol. polymerides. Polymerides with unlimited ability to swell have therefore thread mols., whereas the completely insol. materials which scarcely swell have 3-dimensional mols. Materials with limited ability to swell are composed of thread mols. united at a few places to 3-dimensional mols. The effect of solvent on the swelling power of insol. polystyrenesis examined. Solvents with comparatively little action (EtOAc, BuOAc, cyclohexane) are considered to cause solvation only of the Ph group, whereas "good solvents" (C_6H_6 , CS2, CHCl3) also cause solvation of the paraffin chain. This conception is strengthened by the observed parallelism between swelling of the insol. polystyrenes in different media, viscosity of soluble polystyrenes in the same media, and precipitability of such polystyrenes from solution by MeOH. Good solvents which cause marked solvation also cause marked swelling and high viscosity. The conversion of sol. into insol. caoutchouc by traces of O_2 or light is attributed to the union of thread mols. by O-bridges or direct C·C unions. Similar processes occur during vulcanisation by S or S_2Cl_2 . The irregularities observed in the polymerisation of butadiene to butadiene-caoutchouc are ascribed to the possibility of union in the $\alpha\beta$ - as well as in the $\alpha\delta$ -positions. H. W.

Preparation and properties of substituted phenylacetylenes and mercury di(phenylacetylenyls). M. M. OTTO (J. Amer. Chem. Soc., 1934, 56, 1393—1394).—p-Methyl-, b.p. 65—67°/18 mm., pethyl-, b.p. 72—74°/16 mm. (Hg derivative, m.p. 142—143°), p-isopropyl-, b.p. 79—81°/12 mm. (Hg derivative, m.p. 109—110°), p-chloro-, m.p. 43·5— 44° (Hg derivative, m.p. 221—222°), p-bromo-, m.p. 63·5—63·7° (Hg derivative, m.p. 256—257°), and o-, b.p. 92—93°/20 mm. (Hg derivative, m.p. 184— 185°), and m-bromo-, b.p. 85—86°/16 mm. (Hg derivative, m.p. 143—144°), -phenylacetylenes are prepared thus: COMeAr+PCl₅ \rightarrow CArCl:CH₂ \rightarrow CAr:CH. o-, b.p. 71°/18 mm. (Hg derivative, m.p. 213—214°), and m-Chlorophenylacetylene, b.p. 64— 65°/12 mm. (Hg derivative, m.p. 138—139°), are prepared from o-, m.p. 131—132°, and m-, m.p. 140—141°, -chlorophenylpropiolic acid, respectively. o- and m-Bromophenylpropiolic acids have m.p. 118—119° and 135—136°, respectively. H. B.

Organo-alkali compounds. XIV. Lithium phenyl and fulvenes. K. ZIEGLER and W. SCHAFER (Annalen, 1934, 511, 101-109).—Dimethylfulvene and LiPh in Et₂O give 1-lithio-1-phenylisopropyl-cyclopentadiene (the hydrolysis product resinifies easily), addition occurring across the extracyclic double linking. 1-isoPropylideneindene and LiPh afford 1-lithio-1-phenylisopropylindene, which with MeI gives a hydrocarbon, $C_{19}H_{20}$, b.p. 116—117°/0·3 mm., and with OMe·CH₂Cl affords an ether, $C_{26}H_{22}O$ [1(or 3)-phenylisopropyl-1-methoxymethylindene], b.p. 155-158°/0.66 mm. 1-Lithio-1-benzhydrylindene (?), from benzylideneindene and LiPh, is hydrolysed (H₂O) to 3-benzhydrylindene (Courtot, A., 1915, i, 392), whilst 9-lithio-9-benzhydrylfluorene (from benzylidenefluorene) is hydrolysed (H_2O) to 9-henzhydrylfluorene. Di(diphenylene)ethylene and Et₂O-LiPh give α -lithio- β -phenyl- $\alpha\beta$ -di(diphenylene)ethane (I), hydrolysed (H_0O) to α -phenyl- $\alpha\beta$ -di-(diphenylene)ethane, m.p. 275° (scaled tube in N_2) (previous softening), which decomposes when distilled in a vac. to 9-phenylfluorene. a-Phenyl-aßdi(diphenylene) propane, m.p. 161°, is prepared from (I) and MeI. (I) and I in N₂ give the free radical β -phenyl- $\alpha\beta$ -di(diphenylene)ethyl, bluish-black, which dissolves in C₆H₆ to a KMnO₄-coloured solution (becoming reddish-brown in air). H. B.

Tautomerism of methylated fulvenes. K. ZIEGLER and F. CRÖSSMANN (Annalen, 1934, 511, 89—101).—9-Ethylidenefluorene, PhCHO, and KOEt in Et₂O-EtOH give 9-cinnamylidenefluorene; 9-pmethoxycinnamylidenefluorene, m.p. 142—143° (cf. Kliegl et al., A., 1930, 1031), is similarly obtained using p-OMe·C₆H₄·CHO (I). 3-Methyl-1-isopropylideneindene, b.p. 144—148°/11 mm., m.p. 48—49° (from 3-methylindene, COMe₂, and 27—28% MeOH-KOH), and (I) similarly afford 1- α -methyl-p-methoxycinnamylidene-3-methylindene, m.p. 152·5°; 3-phenyl-1-isopropylideneindene, m.p. 99·5—100°, gives 3phenyl-1- α -methyl-p-methoxycinnamylideneindene, m.p. 150—152°. Cryst. condensation products could not be obtained from 1-isopropylideneindene (II), be dimethylfulvene (III), (I), and $Et_2O-EtOH-KO$ afford 2(or 3)-anisylidene-1-isopropenylcyclopentadien m.p. 122°, reduced (H₂, Pd-BaSO₄, EtOH) to 2(3)-p-methoxybenzyl-1-isopropylcyclopentane, b.p. 175 176°/13 mm., which is demethylated (HI-AcOH) 2(or 3)-p-hydroxybenzyl-1-isopropylcyclopentane, b. 135-137°/0·15 mm., m.p. 59-60°. (III) thus read with (I) as an isopropenylcyclopentadiene; this established by the synthesis of β -anisylethylmethy fulvene (from cyclopentadiene,

p-OMe· C_6H_4 ·CH₂·CH₂·COMe, and EtOH-NaOE which is reduced to the *Me ether*, b.p. 178—179°/ mm., of γ -cyclopentyl- α -anisylbutane, b.p. 137 CMe.CH₂ 138°/0.075 mm. Et₂C₂O₄, (I.

CMe:CH₂

(IV.)

and Et_2O -EtOH-KÕEt affo, the unstable *iso*propenyl est (IV), reduced (as above) to

C(OH) CO₂Et 3-isopropyl-a-hydrindylglycolla b p 145-147°/0·3-0·4 mm

m.p. 66—67°, also obtained by reduction of the setter, m.p. 110—111°, of 1-oxalo-3-isopropylinder [prepared from isopropylindene (Thiele and Merc A., 1918, i, 484) and $\text{Et}_2\text{C}_2\text{O}_4$ by Thiele's method (A., 1901, i, 76)]. Alternative structures are suggest for the compound obtained by Thiele and Balhod (A., 1906, i, 639) from (III) and COMe_2 . H. B.

Isomerisation of decahydronaphthalen V. N. CHADSHINOV (Ukrain. Chem. J., 1933, 333-346).—Tetrahydronaphthalene (I) is converte into trans-decahydronaphthalene (II) at 430-440120 atm. H₂, in presence of MoS₃ catalyst, which alcatalyses further transformation of (II) into methy hydrindene and dimethyldicyclooctane, to an exten increasing with rise in temp. Hydrogenation of (does not take place with initial H₂ pressures of 70 atm. R. T.

Action of magnesium on dibromonaphtha enes. J. SALKIND [with V. SERGEEV, L. LEVI and A. EGOROV] (Ber., 1934, 67, [B], 1031-1036). Decomp. of the product from Mg and 2-C10H7Br presence of air with H_2O yields β - $C_{10}H_7$ ·OH and son C₁₀H₈; β-C₁₀H₇·CO₂H cannot be obtained from by CO₂. In H₂, a considerably increased yield $C_{10}H_8$ and moderately good yield of β - $C_{10}H_7$ - CO_2 result. Air has no appreciable influence in t prep. of 1-C10H7 MgBr. 1:4-C10H8Br2 (I) and M (1:2) react readily initially, then slowly until 86 of the Mg has entered into change. The product converted by H₂O into C₁₀H₈ (35-50%), 1-C₁₀H₇ (31-25%), and resinous products with unchanged (I). The product derived from (I) and Mg (1: is converted by CO_2 into 4-bromo- α -naphthoic ac (II), m.p. 220° (77%), and $C_{10}H_8$ (9%); I: $C_{10}H_6(CO_2H)_2$ (III) could not be isolated. The product from (I) and Mg (1:2) and CO_2 contains (I (50%), but not (III). 1:5- $C_{10}H_6Br_2$ (IV) react with 93.5% of Mg (ratio 1:2), forms very small amounts of condensation products and after treat amounts of condensation products, and after treament with CO_2 gives $1:5-C_{10}H_6(CO_2H)_2$ (V) in almost theoretical yield. The product from (IV) and I (1:1) when treated with CO₂ affords unchange (IV), much (V), and little 5-bromo-α-naphthoic aci $1:2-C_{10}H_6Br_2$ (VI) reacts with difficulty, but ultin ately 75.5% of the Mg enters into change. Mainly resinous condensation products result, which with H_2O yield $C_{10}H_8$ and a little $1-C_{10}H_7Br$ and with CO_2 give traces of $1:2-C_{10}H_6(CO_2H)_2$, a little $C_{10}H_8$ and $1-C_{10}H_7Br$. As in (VI), the β -Br in 1:6- and $1:7-C_{10}H_6Br_2$ appears the more reactive. H. W.

Sensitiveness of aromatic nitro-compounds to light. III and IV. peri-Derivatives of 1-nitronaphthalene. R. E. STEIGER (Helv. Chim. Acta, 1934, 17, 701-703, 794-803).--III. Mainly a historical résumé.

IV. The following 1-nitronaphthalene-8-derivatives have been prepared : -sulphonyl chloride, decomp. $167\cdot5^{\circ}$ (corr.); -sulphonamide, m.p. $190\cdot5-191\cdot5^{\circ}$ (corr.); -sulphonmethylamide, m.p. $195\cdot5-196^{\circ}$ (corr.); -sulphondimethylamide, m.p. $151\cdot5-152\cdot5^{\circ}$ (corr.); -sulphondiethylamide, m.p. $127\cdot5-128\cdot5^{\circ}$ (corr.); -sulphondiethylamide, m.p. $115-116^{\circ}$ (corr.); -sulphonanilide, m.p. $178\cdot0-178\cdot5^{\circ}$ (corr.); -sulphonmethylanilide, m.p. $177\cdot5-178\cdot0^{\circ}$ (corr.); sulphonethylanilide, m.p. $170-171^{\circ}$ (corr.) Me, m.p. $124-125^{\circ}$ (corr.), Et, m.p. $132\cdot5-124^{\circ}$ (corr.) after softening at 123° , Ph, m.p. $132\cdot5-133\cdot5^{\circ}$ (corr.), and NH_3Ph , decomp. $226-229^{\circ}$ (corr.) after darkening at 221° (corr.), 1-nitronaphthalene-8-sulphonate are described. H. W.

Fluoranthene and its derivatives. V. Substitution relationships of 1-phenylnaphthalene. J. VON BRAUN and E. ANTON [with G. MANZ] (Ber., 1934, 67, [B], 1051–1056; cf. A., 1932, 847).–1- $C_{10}H_7Ph$ (I), b.p. 187–189°/12 mm., is smoothly obtained by heating 1-phenyldihydronaphthalene with S. The products derived from treatment with Br obstinately retain halogen, whilst purely thermal dehydrogenation is accompanied by isomerisation to the 2-derivative. The position of NO₂ in 4-nitrophenylnaphthalene is confirmed by reduction of the NH2-compound (II) obtained therefrom (Na+ C_5H_{11} ·OH) to 4-amino-1-phenyl-5:6:7:8-tetrahydronaphthalene, b.p. 180-185°/0.5 mm. (hydrochloride, decomp. about 235°; Ac derivative, m.p. 198°), which can be diazotised. (II) is diazotised with difficulty and is more readily converted into 4hydroxy-1-phenylnaphthalene (III), m.p. 140°, by treatment with 0.1N-HCl at 210°. (I) is scarcely affected by conc. H₂SO₄ at 100°, but is transformed by acid containing 20% of SO₃ at 50°, but is transformed maphthalene-4-sulphonic acid (IV), m.p. 167° (Na salt; corresponding anilide, m.p. 167°), which is almost the sole product of the action. Fusion of (IV) with KOIL at 80° 200° lock to (III) (IV) (IV) with KOH at 260-300° leads to (III). (I) is converted by BzCl and AlCl₃ in CS₂ at 15-20° almost exclusively into 4-benzoyl-1-phenylnaphthalene, b.p. 225-228°/0.3 mm. (oxime, m.p. 177°), which passes when heated with NaOH-CaO at 270° into a little C₆H₆, much BzOH, and a small amount of 1phenylnaphthalene-4-carboxylic acid (V), m.p. 172°. (V) is obtained synthetically by converting 4:1-C10H6BrPh by CuCN at 270° into 4-cyano-1-phenylnaphthalene, m.p. 114-115°, which is hydrolysed by conc. HCl at 140°. 1-Keto-1:2:3:4-tetranydronaphthalene (VI) and p-C6H4Me.MgBr yield 1-p-tolyldihydronaphthalene, b.p. 185—188°/14 mm., m.p. 48°, dehydrogenated by S at 250°, but not

smoothly by Br, to 1-p-tolylnaphthalene, b.p. 192-195°/14 mm., m.p. 53°, which affords o-4'-toluoyl-benzoic acid, m.p. 118°, when oxidised by Na₂Cr₂O-(=30) in AcOH. (VI) and p-C₆H₄Br·MgBr lead to. 1-p-bromophenyldihydronaphthalene, b.p. 215°/14 mm., m.p. 98°, incompletely dehydrogenated by S. and converted by Br in CS2 into the dibromide C16H12Br2. b.p. 220°/14 mm., m.p. 104°, which does not lose HBr completely when heated with KOH-EtOH-H₂O. The product is transformed by CuCN at 270° in N2 into 1-phenylnaphthalene-4'-nitrile, b.p.. 230-240°/14 mm., m.p. 73-77°, whence 1-phenyl-naphthalene-4'-carboxylic acid, m.p. 229°. The doubleattachment of the C_6H_6 in fluoranthene appears to impart to it an enhanced reactivity in comparison-H. W. with (I).

New hydrocarbons from the anthracene oil of coal tar. O. KRUBER (Ber., 1934, 67, [B], 1000—1005).—Technical anthracene residues, b.p. 345—375°, after removal of 6% of acid and 10% of basic components are distilled under diminished pressure. The distillates deposit 20—25% of carbazole and its homologues. The fraction (I), b.p. 361—370°, thus prepared when treated with Na at 135° and subsequently with CO₂ affords 1:2:3:4tetrahydrofluoranthene-1-carboxylic acid (II), m.p. 188—189° (*Et* ester, m.p. 104°, b.p. 224—226°/15mm.), which passes when superheated into 1:2:3:4tetrahydrofluoranthene (III). (II) could not beobtained from fluoranthene (IV), Na, and CO₂ in presence of C₁₀H₇Me, or Ph₂. Passage of (I) over heated PbO₂ leads to (IV). The prep. of (II) from (III) by means of MgEtBr followed by CO₂ in boiling NPhMe₂ is described. Similar treatment of a fraction, b.p. 350—360°, leads to *phenanthrylene*.4:5-acetic acid (V), m.p. 253° (decomp.), which passes above its



m.p. into phenanthrylene-4: 5-methane (VI), m.p. 116° [picrate, m.p. 166°; condensation product with (COEt)₂, m.p. 91—92°; :CHPh derivative, m.p. 108°]. (VI) is oxidised by Na₂Cr₂O₇ in AcOH to phenanthrylene-4: 5-ketone (VII), m.p. 170°, or, under somewhat modified conditions, to 9: 10-diketophenanthrylene-4: 5-methane (VIII), m.p. 240—241° [converted by $o \cdot C_{c}H_{4}(NH_{2})_{2}$ into the compound $C_{21}H_{12}N_{2}$, m.p. 261°]. Further oxidation of (VII) leads to 9: 10-diketophenanthrylene-4: 5-ketone, m.p. 286— 287° (azine, $C_{21}H_{10}ON_{2}$, m.p. 328°), and fluorenone-4: 5-dicarboxylic acid (IX), m.p. 285° (decomp.) [anhydride, m.p. 253°]. (IX) is transformed when heated with CaO into fluorenone. When fused with KOH (VII) affords phenanthrene-4-carboxylic acid, m.p. 170—171°, transformed by CaO into phenanthrene. H. W.

Pentacyclic aromatic hydrocarbon from cholesterol. J. W. COOK, C. L. HEWETT, W. V. MAYNEORD, and (MISS) E. ROE (Chem. and Ind., 1934, 569—570).—The Grignard compound from β -5-tetrahydronaphthylethyl chloride condenses with 2:7-dimethyl-4-isopropylhydrindone to give 4-methyl-3- β -5'-tetrahydronaphthylethyl-7-isopropylindene, cyclised in almost theoretical yield to the hydrocarbon (I), which is dehydrogenated with loss of Me to 5-methyl-8-isopropyl-2': 1'-naphtha-1:2-fluorene (II), m.p. 198° (complex with 2:7-dinitroanthraquinone, m.p. 261°).



(II) is not identical with Diels' hydrocarbon (III) from cholesterol. It is readily oxidised to a golden-orange *ketone*, which, like that derived from (III), gives an

intense purple solution in conc. H₂SO₄. A similar colour is Pr^β given by 2': 1'-naphtha-1: 2fluorenone, m.p. 208°, the first product of the oxidation of 2':1'-naphtha-1:2-fluorene(IV), m.p. 327-328° (complex with 2:7-dinitroanthraquinone, m.p.

250°), but not by fluorenone or 1:2-benzofluorenone. The absorption curve of (IV) is intermediate in character between those of phenanthrene and picene and very closely analogous to that of (III). The spectra of (II) and (III) are still more closely similar. It is suggested that group migration during sterol dehydrogenation offers the most probable explanation of the facts. The synthesis of 4-3'-methyl-6'-isopropyl-benzylphenanthrene (V), m.p. 115—116°, is recorded. H. W.

(V.)

Perylene and its derivatives. XL. A. ZINKE and O. BENNDORF (Monatsh., 1934, **64**, 87—96).— The view previously expressed (A., 1932, 507) that perylene (I) reacts in two forms is supported by further work on the reduction of (I).

[With V. GRIMM and G. MANHART.] Reduction (Na, EtOH, C_6H_6) of (I) gives hexa-, m.p. 182–185°, and octa-, m.p. 119–120°, -hydroperylenes (cf. loc. cit.; A., 1920, i, 541). 3:9-Dibenzoylperylene (II) [dioxime (III), m.p. 336° (darkens at 300°)] is similarly reduced to an octahydro-derivative, m.p.

PhCH CHPh (IV.)

276°, which with NH₂·OH gives (probably) a little (III). Reduction (Na, amyl alcohol) of (II) affords 3 : 9-dibenzyloctahydroperylene, m.p. 154°, which when distilled over Cu in N₂ gives (I) and PhMe ; 3 : 9-dianisoylperylene is similarly reduced to 3 : 9-di - p - methoxybenzyloctahydroperylene, m.p. 195°. 3 : 4-Dibenzoylperylene

is reduced (H₂, Pt–C, AcOH) to (probably) the compound (IV), m.p. $289-291^{\circ}$. H. B.

[Diradical formula of rubene and the constitution of its dissociable peroxide.] C. DUFRAISSE (Ber., 1934, 67, [B], 1021—1023).—Mainly a reply to Schönberg (this vol., 643). The constitutions assigned to rubene (I) and its oxide are not new, and the reaction mechanisms, although plausible, are devoid of experimental foundation. The structure assigned to the isomerisation product of oxyrubene is probably incorrect, since the substance cannot be reduced to (I). H. W.

Aromatic parent hydrocarbons of anthanthrone, anthdianthrone (2:3:4:5-dibenzocoronen-1:6-quinone), pyranthrone or *amphi-iso*pyranthrone, violanthrone, *iso*violanthrone, 1:2:3:7:8:9-dinaphthacoronen-4:10-quinone, and dibenzrubicene. R. SCHOLL and K. MEYER (Ber., 1934, 67, [B], 1229—1235).—Anthanthrone (I) or a halogenated derivative is converted by HI (d 1.7) and red P at 190—200° and subsequent



dehydrogenation by sublimation through Cu at $500^{\circ}/20$ mm. into anthanthrene (II), m.p. 257° , reconverted into (I) by CrO_3 in boiling AcOH.

(II.) Similar treatment transforms mesoanthrodianthrone (III) into anthrodianthrene (IV) (2:3:4:5-vic.-diperi-dibenzocoronene), oxidised by dil. HNO₃ to (III). Di-



hydropyranthrene and Cu powder at $400^{\circ}/25$ mm. in CO₂ afford pyranthrene (V). Violanthrone, HI (d 1.7), and red P at 220° afford tetrahydroviolanthrene, converted by Cu powder at $450^{\circ}/25$ mm. in CO₂ into violanthrene (VI). Tetrahydroisoviolanthrene and isoviolanthrene (VII) are obtained similarly. The dilactone of 9: 10-dihydroxy-9: 10-di- α -naphthyl-9: 10dihydroanthracene-1: 5-dicarboxylic acid is converted by sublimation with Zn dust at $500^{\circ}/20$ mm. in H₂ into dibenzorubicene (VIII). Reduction of 1:2:3-7:8:9-dinaphthocoronene - 4:10-quinone with HI (d 1.7) and red P at 180—190° and treatment of the H-compound with Cu powder at $500^{\circ}/1$ mm. in H₂ leads to 1:2:3-7:8:9-dinaphthocoronene (IX). H. W.

Blue aromatic parent hydrocarbon of mesonaphthodianthrone and its conversion by maleic anhydride into anthrodianthrene. R. SCHOLL and K. MEYER (Ber., 1934, 67, [B], 1236-1238).-mesoNaphthodianthrone is transformed by HI (d 1.7)



0 .C0 .C0>0 (III.) and red P at 200° into hexahydromesonaphthodianthrene, which passes when heated with Cu at $500^{\circ}/20$ mm. in H₂ into mesonaphthodianthrene (I). Treatment with maleic anhydride in boiling PhNO₂ transforms (I) into 2:3-4:5-dibenzocoronene -9:10-dicarboxylic anhydride

(II). Oxidation of (II) with H_2SO_4 -CrO₃ yields 2:3-4:5-dibenzocoronene-1:6-quinone-9:10-dicarboxylic anhydride (mesoanthrodicarboxylic anhydride) (III), whereas distillation with soda-lime at 500°/1 mm. in H_2 gives 2:3-4:5-dibenzocoronene (mesoanthrodianthrene). H. W.

Preparation of aniline and aromatic amines by the contact method. SCHIPOV (Ukrain. Chem. J., 1933, 8, 347-354).—NH₂Ph is obtained in 6% yields by passing C_6H_6 vapour and NH₃ over Fe₂O₃ at 620°. The reaction is not catalytic, as the Fe₂O₃ undergoes reduction successively to FeO and Fe. R. T.

Introduction of the thiocyano-group into organic compounds. H. P. KAUFMANN and K. KUCHLER (Ber., 1934, 67, [B], 944–948).—Treatment of suitable materials in org. solvents with $Cu(CNS)_2$ leads to the introduction of $CNS : 2Cu(CNS)_2 + RH = 2CuCNS + RSCN + HSCN$ and $2Cu(CNS)_2 + \cdot CH \cdot CH \cdot = 2CuCNS + \cdot CH(SCN) \cdot CH(SCN) \cdot CH(SCN)$. Reaction can be effected in

CH(SCN)·CH(ŠCN)·. Reaction can be effected in H_2O and in presence of acids if hydrolysis of SCN is repressed by org. solvents. Reduction of the crude products leads to mercaptans, and treatment of them with alkali affords disulphides. Aromatic amines with substituted *p*-positions give 2-aminobenzo-thiazoles. Intimate mixtures of NaCNS and hydrated Cu salts afford pastes of Cu(CNS)₂ to which the reacting substance may be added in the presence of little, if any, solvent. Alternatively, substance and Cu^{II} salt (I) may be mixed and added to the thiocyanate (II) or substance and (II) may be added to (I). The following examples are cited : *p*-thiocyanoniline from NH₂Ph; 1:2-CNS·C₁₀H₆·NH₂ from β -C₁₀H₇·NH₂; 4:2-CNS·C₁₀H₆·OH from β -C₁₀H₇·OH;

Simplified preparation of anilides. R. C. SHAH and R. K. DESHPANDE (J. Univ. Bombay, 1933, 2, Pt. 2, 125—127).—To the crude mixture of acid chloride and POCl₃ obtained by the action of PCl_5 (1 mol.) on the acid (1 mol.), C_5H_5N , NPhMe₂, or NPhEt₂ (2 mols.) is added. The amine (1·25— 1·5 mols.) is added and the product treated with dil. HCl, dil. NaOH, and H₂O. The yields of recryst. product obtained by applying the method to the prep. of many acyl derivatives of aromatic amines are given. H. N. R.

So-called hexa-alkyltriaminodibenzoylbenzenes of Michler. A. WAHL (Bull. Soc. chim., 1934, [v], 1, 244—246).—The product obtained when COCl₂ is passed into NPhMe₂ at 190° is CO(NPhMe)₂ (MeCl being evolved), and not

 $\operatorname{NMc}_2 \cdot \operatorname{C}_6 \operatorname{H}_3(\operatorname{CO} \cdot \operatorname{C}_6 \operatorname{H}_4 \cdot \operatorname{NMe}_2)_2$ as stated by Michler et al. (A., 1877, ii, 233). Similarly NPhEt₂ and NPhBu^a₂ afford CO(NPhEt)₂ and CO(NPhBu^a)₂. A little CO:NPh is formed as a by-product.

J. W. B.

Constitution and reactions of thiocarbonyl tetrachloride. I. Reaction with arylamines. J. M. CONOLLY and G. M. DYSON (J.C.S., 1934, 822-824).—CSCl₄ (I) and p-C₆H₄Me·NH₂ in Et₂O with aq. Na₂CO₃ at 30° give p-toluidinodichloromethyl-chlorothiol (II), m.p. 73°, which with cold KOH– EtOH–Et₂O gives 2:2:5:5-tetrachloro-1:4-di-ptolyl-1:2:4:5-tetrahydro-3:6-dithiapyrazine (III), m.p. 142.5° (violent decomp.). The Ph, p-C6H4.OMe, and $p - C_6 H_4 Cl$ analogues of (II) are oils, but give compounds of type (III), m.p. 145.5° (decomp.), 113° (decomp.), and 160° (decomp.). The m-2-xylyl analogue of (II) is an oil. s-C6H2Br3·NH2 and 3:5dibromo-p-toluidine do not react with (I), whereas m-2-xylidine and 2:4-C₆H₃Cl₂·NH₂ give the compounds [as (II)], which with KOH-EtOH give thiocarbimides. (II) is hydrolysed by hot H₂O to p-C₆H₄Me·NCS (IV), HCl, (I), and p-C₆H₄Me·NH₂ (V), with HCl gives (I) and (V), and with dil. alkali forms (IV) and p-C₆H₄Me SCN, whence it follows that (II) contains the grouping R.N.C. (III) with HCl in Et₂O gives 3-chloro-p-toluidine (by way of p-C6H4Me·NHCl) and trichloromethylthiol, b.p. 125°/ 15 mm. (Hg salt; oxidised by air to a substance, m.p. 96°, probably the disulphide; gives chloropicrin with fuming HNO_3 ; gives SCl_2 and a cryst. solid when heated at atm. pressure; gives H_2 with Na), and with $HBr-Et_2O$ affords (V) and an oil, probably CCl2Br·SBr. The parachor of (I) agrees better with the formula $\text{CCl}_2 \leftarrow \text{SCl}_2(A)$ than with $\text{CCl}_3 \cdot \text{SCl}$, and (A) is confirmed by the above reactions, published data, and by the discovery of CSCl₂ as an inter-mediate product in the reaction of (I) with K_2SO_3 , which is best formulated: (I) + K_2SO_3 + $H_2O \rightarrow$ $CSCl_2 + K_2SO_4 + 2HCl; 2HCl + K_2SO_3 \longrightarrow KHSO_3 +$

alkylresorcinol \longrightarrow (III), were used. The PhOHcoeffs. (towards S. aureus at 20° using 5-8% EtOH solutions) of the above are 6, 45, 240, 625, and 665, respectively (n-hexylresorcinol=60). Chlororesorcinol Bu^a, b.p. 128-134°/1 mm., n-amyl, b.p. 140-150°/ 3 mm., n-hexyl, b.p. 152-162°/2 mm., n-heptyl, b.p. 173-183°/5 mm., and n-octyl, b.p. 184-187°/4-5 mm., ethers, prepared from (I) and alkyl bromide in EtOH-NaOEt, have PhOH-coeffs. of 50, 100, 250, 200, and 65, respectively; against B. typhosus, they have practically the same (much smaller) activity as (III). H. B.

Substitution products of 2'-nitro- and 2':4'dinitro-2-methoxydiphenyl ethers. H. A. SCAR-BOROUGH and J. L. ŚWEETEN (J.C.S., 1934, 867-869).—The presence of two NO₂-groups prevents bromination of 2-methoxydiphenyl ethers and further nitration is controlled by the OMe-group. Trinitroderivatives cannot be prepared by direct nitration of the mononitro-ethers. Guaiacol, KOH, and $o-C_6H_4Cl\cdot NO_2$ (I) at 150° give 2'-nitro-2-methoxydi-phenyl ether (II), m.p. 69°, which with SO₂Cl₂ gives the 5-Cl-derivative (III), m.p. 91°. Cl₂ in AcOH with (II), (III), or 4-chloro-2'-nitro-2-methoxydiphenyl ether (IV), m.p. 79° [obtained from (I), 4-chloroguaiacol, and KOH at 200°], gives the 4: 5-Cl₂-derivative (V), m.p. 98°, of (II), also obtained from (I) and 4:5-dichloroguaiacol. (V) with Cl_2 (excess) in AcOH in light yields the $x: 4:5-Cl_3$ -derivative, m.p. 107°. The 4-, m.p. 77°, and 5-Br-, m.p. 90°, and 4: 5-Br. derivatives, m.p. 112°, of (II) were prepared by all the methods used for the Cl-analogues, excepting that the dibrominations were effected at 90°. (I) and 4-nitroguaiacol give the 4-NO₂-derivative, m.p. 105°, of (II), and $2: 4 \cdot C_6 H_3 Cl(NO_2)_2$ and guaiacol give the 4'-NO2-derivative (VI), m.p. 92°. Similar condensations give the 4-Cl- (VII), m.p. 116°, 4: 5-Cl2- (VIII), m.p. 144°, 4-Br-, m.p. 132°, 5-Br-, m.p. 140° (prepared at 90° in EtOH) [also obtained from (VI) and Br-AcOH], and 4: 5-Br₂-derivatives, m.p. 165°, of (II), and the 5- NO_2 - (IX), m.p. 115°, 4: 4'-(NO_2)₂-, m.p. 138° (prepared in EtOH at 90°), 4': 5- $(NO_2)_2$ - (X), m.p. 161° (prepared in hot EtOH), and 3:4':5-(NO₂)₃-derivatives (XI), m.p. 174° (prepared in hot EtOH), of (II). (VI) and SO₂Cl₂ give 5-chloro-2': 4'dinitro-2-methoxydiphenyl ether, m.p. 117°, which with Cl₂ in warm AcOH gives (VIII), also obtained by chlorination of (VII). (II) with HNO_3 (d 1·4) at $<30^{\circ}$ gives (IX), whilst (VI) gives similarly (X). However, HNO_3 (d 1·5), first at $<30^{\circ}$ and then at 100° , yields (XI) from (II), (IX), (VI), (X), or 4'nitro- or 4': 5-dinitro-2-methoxydiphenyl ether. R. S. C.

Organic sulphides. C. LEFEVRE and C. DESGREZ (Compt. rend., 1934, 198, 1791–1793; cf. this vol., 766).—By fusion of the appropriate C_6H_6 derivative with S, glycerol, and PbCO₃ are obtained: *di*-p*amino*-, m.p. 106° (with the sulphide), *di*-p-*hydroxy*-, m.p. 116° (with the *sulphide*, m.p. 95°), and *di*-2: 4*dihydroxy*- (and sulphide) -*phenyl disulphide*. Similar sulphides are obtained from pyrogallol, guaiacol, $C_{10}H_7$ ·OH, borneol, salicylic and gallic acids. No action occurs with only COR, CO₂H, CO·NH₂, SO₂, or SO₂·NH₂ group in the C_6H_6 ring. J. W. B. [Synthesis of mescaline.] K. H. SLOTTA and G. SZYSZKA (Ber., 1934, 67, [B], 1106—1108).—A comment on the publication of Hahn and Wassmuth (this vol., 647). H. W.

[Synthesis of mescaline.] G. HAHN (Ber., 1934, 67, [B], 1210—1211).—A reply to Slotta *et al.* (preceding abstract). H. W.

Reversible transformation of benzoylmethylcarbinol and acetylphenylcarbinol. Keto-anol tautomerism. A. E. FAVORSKI and (MME.) T. I. TEMNIKOVA (Compt. rend., 1934, 198, 1998-2000).-CHMeBz·OH (I) or CHPhAc·OH (II) with MgMeBr give the same mixture, m.p. 35-44°, b.p. 154-5-155°, of glycols, OH·CMePh·CHMe·OH and OH-CHPh-CMe, OH. With MgPhBr, however, (II) gives only OH-CHPh-CPhMe-OH (III), whereas (I) gives (III) and OH·CPh₂·CHMe·OH (fractions melting between 45° and $97 \cdot 5^{\circ}$). With BzCl both (I) and (II) give mixtures of Bz derivatives of (I), m.p. 108-109°, and of (II), m.p. 51.5-52.5°. (I) and (II) thus have separate existence, but often react (e.g., as above and with semicarbazide and PhCNO) as isomerides. The change, which involves two H, is called keto-anol or keto-carbinol tautomerism. R. S. C.

1:3-Diphenylindan-1-ol and its derivatives. C. DUFRAISSE and L. ENDERLIN (Bull. Soc. chim., 1934, [v], 1, 267-280).-With MgPhBr 3-phenyl-ahydrindone affords 1: 3-diphenylhydrinden-1-ol, dimorphous, m.p. 85° and (stable form) m.p. 93-94° (Me ether, m.p. 127°, by cold 1% MeOH-H₂SO₁), readily dehydrated by most dehydrating agents to 1:3-diphenylindene (I), dimorphous, m.p. 68-69° (Ziegler et al., A., 1925, i, 131) and 85° (nitrosochloride, decomp. 84-85°, instantaneous fusion on block, 160°). In agreement with Weiss et al. (A., 1927, 970) (I) gives its Br₂ additive compound (II), m.p. 140° (block) (loc. cit., m.p. $92-96^{\circ}$) (oxidised to C₆H₄Bz₂ and reduced to the indane), but with excess of Br m Et₂O is obtained a stable compound (III), m.p. 118-119°, which gives only resins on oxidation with CrO₃-AcOH, or reduction with Fe-AcOH, and is probably 10-bromo-9-phenyl-9: 10-endobromomethyl-ÇPh-

ene-9: 10-dihydroanthracene, C_6H_4 CHBr C_6H_4 .

With Br in CS₂ (II) or (III) affords a Br_3 -derivative, probably C₂₁H₁₃Br₃,H₂O, decomp. 156–157° (bath), m.p. 216° (block). J. W. B.

(a) Action of selenious anhydride on cholesterol. (b) Various methods for nitration of cholesterol. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 290—291, 291—292).—(a) By heating cholesterol (I) and SeO₂ at 180—200°, or in EtOH at 80°, only metacholesterol (II) and unchanged (I) are obtained, no oxidation to cholestenone being detected. No transformation of (I) occurs in sunlight in presence of light-sensitive substances such as $UO_2(NO_3)_2$, AgNO₃, HgO, HgI₂, or CHI₃.

(b) With conc. HNO_3 -AcOH (I) affords a $(NO_2)_2$ derivative, m.p. 120—121°, but in AcOH with HNO_3 - H_2SO_4 is obtained a *compound*, m.p. 112° (positive Liebermann reaction; Br₂ additive *compound*), converted by KOH-EtOH into (II) and KOAc. When shaken with an emulsion of HNO₃ in EtOH, Et_2O , C_6H_6 , PhNO₂, or COMe₂, (I) gives its ψ -nitrosite. J. W. B.

Irradiation products of ergosterol. H. LETTRÉ (Annalen, 1934, 511, 280-291).-Under conditions in which cholesterol and ergosterol (I) give cryst. products, dehydrogenation of vitamin-D with Se at 320° gives only liquids from which no cryst. picrates could be obtained. Tachysterol acetate-citraconic anhydride compound is reduced by H2-Pd in EtOAc to its H_2 -derivative, m.p. 155-156°, $[\alpha]_D^{13}$ +79.7° in CHCl_a (since no CHMePra CHO is obtained on ozonolysis, the side-chain double linking has been reduced), further reduced in AcOH-EtOAc to the H_{4} -derivative; m.p. 134—135°, $[\alpha]_{D}^{19}$ +18.4° in CHCl₃, converted by heating with EtOH-NaOH and repptn. with H₂O into an amorphous substance, $C_{35}H_{56}O_4$, not yet character-ised. Analytical data and determination of the no. of double linkings in these derivatives and comparison with dehydroergosterol C28H42O (which it most resembles) show that tachysterol (II) is $C_{28}H_{44}O$. In the isomeric (I) there are four rings and three double linkings, but in (II) there are three rings and four double linkings, and structures obtained by opening the $C_{10}-C_9$ linking in (I) with H-migration are suggested. J. W. B. H-migration are suggested.

Dehydrogenation of neoergosterol with platinum. H. HONIGMANN (Annalen, 1934, 511, 292-301).—Dehydrogenation of neoergosterol (I) with Pt-black in CO₂ at 250—300° gives a phenol (II), $C_{27}H_{36}O, H_2O$, m.p. indef. 140° [Ac derivative, m.p. 150°, $[\alpha]_{15}^{15}$ +46.8° in CHCl₃, absorption max. 280 mµ; 3:5-dinitrobenzoate, m.p. 207—208°; Me ether, m.p. 114°, $[\alpha]_{15}^{15}$ +26.7° in CHCl₃ (by NaOH-Me₂SO₄), absorption spectrum resembles that of (II)]. Since such dehydrogenation is sp. for 6-hydroaromatic rings containing no quaternary C, the three double linkings in (I), and hence the two in ergosterol, must be in ring B (cf. Windaus et al., this vol., 768). α -Ergostanol, which has Me at C₁₀, is unchanged under these dehydrogenation conditions. J. W. B.

Phenyltrimethylglycerol and chlorohydrins of tetrasubstituted glycerols. H. RAVIER (Compt. rend., 1934, 198, 1787-1788).-MgPhBr (I) reacts with CMe₂:CHAc, or MgMeBr with CMe₂:CHBz, to give β -phenyl- δ -methyl- Δ^{γ} -n-penten- β -ol, b.p. 95—96°/-9 mm., converted by H₂C₂O₄ into β -phenyl- δ -methyl- $\Delta^{\alpha\gamma}$ -n-pentadiene, b.p. 77—80°/10 mm., and by HOCI into γ-chloro-β-phenyl-δ-methyl-Δa-n-pentene, b.p. 115-117°/9 mm. (I) and OH CMe2 CHClAc (II) afford γ-chloro.β-phenyl-δ-methyl-n-pentane-βδ-diol, m.p. 91°, hydrolysed with difficulty to β -phenyl- δ -methyl-n-pentane- $\beta\gamma\delta$ -triol, m.p. 74°, which is best obtained from (I) and OH · CMe, · CHAc · OH. With the appropriate MgRBr (II) affords γ-chloro-βδ-dimethyl-n-heptaneβδ-diol, b.p. 119-120°/10 mm., and -n-octane-βδ-diol, b.p. 129-130°/9 mm. (also by HOCl addition to the corresponding Δ^{β} -unsaturated alcohols). MgEtBr and OH·CMe2·CHCl·CO2Et afford γ-chloro-β-methyl-δ-ethyln-hexane-βδ-diol, b.p. 119-123°/10 mm., m.p. 78° hydrolysed by K2CO3 to the corresponding By8-triol, m.p. 91°, and giving the glycide with K in dry Et₂O. J. W. B.

Electrolyses with p-toluic and hexahydro-ptoluic (p-methylcyclohexanecarboxylic) acid. F. FICHTER and C. SIMON (Helv. Chim. Acta, 1934, 17, 717-725).-Electrolysis of p-C6H4Me·CO2K in MeOH-H₂O at a Pt wire anode leads to evolution of CO₂ in small amount and production of C₆H₄Me·CO₂Me, m.p. 33°, by a side reaction. Electrolysis of p-C6H4Me CO2H (I) in 0.2N-H2SO4-COMe, at 75° with PbO₂ anode and rotating Pb cathode yields mainly p-C₆H₄(CO₂H)₂ in 12.05% yield. Dark resinous compounds and oily products (derived from COMe₂) are formed in less amount and small quantities of toluquinol, m.p. 125° , (?) 2:5-dihydroxy-p-toluic acid, m.p. $210-212^{\circ}$, α -methylsuccinic acid, m.p. 108-110°, and trioxymethylene are isolated. (I) appears incapable of undergoing the Kolbe synthesis. p-Methylcyclohexyl bromide, Mg, and CO2 yield 4:4'-dimethyldicyclohexyl (III), b.p. 127- $132^{\circ}/15$ mm., 4-methyl- Δ^1 -cyclohexene (III), and a mixture of acids hydrolysed by conc. HCl to trans-hexahydro-*p*-toluic acid (IV), m.p. $107.5-108.5^{\circ}$ (*Ca* salt $+5H_2O$), in 3-4% yield. Electrolysis of a mixture of (IV) and its K salt in H₂O between Pt electrodes affords (III), 4-methylcyclohexanone, 4-methylcyclohexanol, possibly (II), di-p-methylcyclohexyl ether, b.p. 83-86°/0.7 mm., and 4-methylcyclohexyl 4-methylcyclohexylcarboxylate, b.p. 86-90°/ 0.7 mm. H. W.

Catalytic hydrogenation of hydroxybenzoic acids in aqueous solution. N. L. EDSON (J.S.C.I., 1934, 53, 138—139T).—Catalytic hydrogenation (PtO₂) in aq. solution results as follows : *p*-hydroxybenzoic acid gives hexahydrobenzoic acid (I) (75— 80%) together with *trans*-4-hydroxy*cyclo*hexane-1carboxylic acid, but no *cis*-acid or lactone; *m*-hydroxybenzoic acid yields (I) (60%) together with a residue (m.p. 107—110°) believed to be a mixture of *cis*- and *trans*-H₆-derivatives; salicylic acid forms hexahydrosalicylic acid, and a small quantity of (I) (10—15%). It is suggested that (I) arises during the intermediate formation and subsequent cleavage of a lactone ring.

Replacement of phosphorus pentachloride by thionyl chloride in the preparation of imidochlorides. J. VON BRAUN and W. PINKERNELLE (Ber., 1934, 67, [B], 1218—1220).—The use of COCl₂ in place of PCl₅ causes very smooth conversion of NBZMe₂ into CPhCl₂·NMe₂, but its general use in the laboratory is not advised. For amides of aromatic acids, SOCl₂ is a nearly ideal chlorinating agent, reaction being cleaner than with PCl₅, since analogues of the complex by-products containing P are not produced. With amides of aliphatic acids, SOCl₂ is less suitable. Amides derived from $\alpha\beta$ -unsaturated acids yield non-volatile materials containing S, probably formed by addition of SOCl₂ to the double linking. Simple amides, such as NHAcPh, give poorly cryst. materials containing S, possibly arising from addition of SOCl₂ to the chlorovinyl base arising by displacement of H in the imidochloride primarily formed. The following examples are cited : NHBzPh to CPhCl:NPh in 100% yield; NHBzMe to CPhCl:NMe; NBzMe₂ to CPhCl:NEt; NBzPhMe to CPhCl:NPh. SOCl₂ is particularly valuable for the conversion of $[CH_2]_4(NHBz)_2$ into $CH_2Cl\cdot[CH_2]_3$ ·NHBz and analogous reactions.

H. W.

Addition of halogens to benzene derivatives. II. Addition of chlorine to benzoyl chloride. III. Addition of chlorine to benzoic acid. T. VAN DER LINDEN (Rec. trav. chim., 1934, 53, 703-714, 779-784; cf. this vol., 293).-II. BzCl and Cl₂ (6 atoms) in sunlight slowly give a mixture (mixed crystals) (I), m.p. 153° , of equal parts of δ -1:2:3:4:5:6-hexachlorocyclohexanecarboxyl chloride (II), m.p. 158-159°, and

 β -1:2:3:4:5:6:4' - heptachlorocyclohexanecarboxyl chloride (III), m.p. 143.5-144.5°, a y-isomeride, m.p. 112-113°, of (II), an α-isomeride, m.p. 162°, of (III), and an oil, which after treatment with dil. KOH and distillation in steam yields a little 1:2:4:5- $C_6H_2Cl_4$ (IV), an oil, b.p. 93–98°/0·1 mm., three isomeric *hexachlorocyclohexenes* (V), m.p. 144°, b.p. 107—127°/0·15 mm., m.p. 71°, and 103—104°, respectively, a mixture, m.p. 223·5—225°, of C_6H_{11} ·CO₂H and OH·C₆H₄Cl₆·CO₂H or of OH·C₆H₅Cl₅·CO₂H and C₆H₅Cl₆·CO₂H, the acid (VI) of (III), m.p. 277°, and e-benzoic acid hexachloride (VII), m.p. 247°. (I) is inseparable by sublimation (150°/18 mm.) or distillation in steam, and is hydrolysed by hot aq. org. solvents to a mixture of (VI) and a δ -isomeride (VIII), m.p. 247°, of (VII). (VI), (VII), and the γ -isomeride (I \hat{X}) of (VII) with PCl₅ give the corresponding acid chlorides, but (IX) gives with PCl₅ a little and with $SOCl_2$ mainly the anhydride, $+C_6H_6$ and anhyd., m.p. 253°. The polychlorinated acid chlorides distil unchanged in steam. (V) is stable under the conditions used for isolation of (IV), whence it follows that (V) and (IV) are formed by loss of HCl and CO₂ from different acids.

III. BzOH and Cl₂ (6 atoms) in sunlight give the γ - (I), m.p. 237°, and β - (II) -hexachloride, m.p. 245° (rapid) or 220° (slow heating), a pentachlorocyclohexenecarboxylic acid (III), m.p. 217.5—218.5° [also obtained from (I) by heat or boiling H₂O], and a mixture which, when distilled in steam, yields (I), (II), the α -isomeride, 1:2:4:5-tetra-, penta-, and hexa-chlorobenzene, and (III). The formation of chlorobenzenes indicates that some Cl- and Cl₃-acids are formed. Benzoic acid hexachlorides decompose slightly below the m.p. exactly as in boiling H₂O. R. S. C.

Action of cold or warm sulphuric acid on aromatic esters. J. B. SENDERENS (Compt. rend., 1934, 198, 1827—1830).—The times for complete hydrolysis by cold H_2SO_4 are: EtOBz 12, $o \cdot C_6H_4(CO_2Et)_2$ 12, $Pr^\circ OBz > 15$, $OBz \cdot CH_2 \cdot CH_2 Pr^\beta >$ 15 days, and $C_6H_4Me \cdot CO_2Et$ and $Pr^\circ OBz$ immediate. Hydrolysis is immediate at 80° . $CH_2Ph \cdot CO_2Et$, $o \cdot OH \cdot C_6H_4 \cdot CO_2Et$, and $o \cdot OH \cdot C_6H_4 \cdot CO_2Pr^\beta$ are rapidly hydrolysed and slowly sulphonated in the cold, but rapidly sulphonated at 80° . $CH_2Ph \cdot CH_2 \cdot CO_2Et$ and $2: 4 \cdot C_6H_3Me_2 \cdot CH_2 \cdot CO_2Et$ are rapidly sulphonated in the cold. R. S. C.

5-Amino- and 5-nitro-diphenyl-2-carboxylic acid and 5-nitro-2-cyanodiphenyl.—See B., 1934, 535. Synthesis of $l-\alpha$ -naphthylmercapturic acid. H. R. ING, M. C. BOURNE, and L. YOUNG (Biochem. J., 1934, 28, 809—810).—The product from α -C₁₀H₇·NH₂ and d-acetylcysteine was heated in H₂O containing EtOH in presence of Cu-bronze powder to yield C₁₀H₇·S·CH₂·CH(NHAc)·CO₂H, m.p. 170·5—171°, identical with the compound found in rabbit's urine after C₁₀H₈ feeding (see this vol., 922). W. O. K.

Decomposition of α-keto-acids. C. D. HURD and H. R. RATERINK (J. Amer. Chem. Soc., 1934, 56, 1348—1350).—BzCO₂H decomposes at about 270° (method: A., 1933, 607) to CO (19%), CO₂ (49%), PhCHO (15—25%), and BzOH (35—45%); at 500° (flow method), a 62% yield of PhCHO is obtained. CH₂Ph·CO·CO₂H gives (at 250—280°) CO (57—66%), CO₂ (44%), H₂O, and CH₂Ph·CO₂H (30—43%); CH₂Ph·CHO could not be isolated. H. B.

XIII. Trihalogeno-Haloform reaction. methylketonic acids of mesitylene series. R. JOHNSON and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1417-1419).-3-Acetyl-2:4:6-trimethylphenyl styryl ketone, m.p. 95-96° [from diacetomesitylene (I), PhCHO, and aq. EtOH-NaOH], is oxidised (O_3 in CCl₄, followed by alkaline H_2O_2) to 3-acetyl-2: 4: 6-trimethylbenzoic acid, m.p. 144–145°, which with cold aq. NaOHal gives 3-trichloroacetyl-(II), m.p. 148-149°, and 3-tribromoacetyl- (III), m.p. 189° (decomp.), -2:4:6-trimethylbenzoic acid. (II) and (III) can be titrated with alkali (end-point not permanent); they are cleaved rapidly by warm aq. NaOH to 2:4:6-trimethylisophthalic acid (IV), m.p. 289° (corr.; decomp.) (lit. 283°), also prepared by oxidation of dicinnamoylmesitylene, m.p. 134-135° [from (I), PhCHO, and aq. EtOH-NaOH]. (III) shaken with 10% NaOH for about 15 hr. gives CBr₄ and 3-dibromoacetyl-2:4:6-trimethylbenzoic acid (V), m.p. 173.5—174.5°; the following reactions occur: $C_6HMe_3(CO_2H)_2 + CHBr_3 \leftarrow CBr_3 \cdot CO \cdot C_6HMe_3 \cdot CO_2H$ \rightarrow (V)+NaOBr; CHBr₃+NaOBr \rightarrow CBr₄. (V) and alkaline NaOBr give (IV) and CBr_4 . H. B.

Synthesis of acetoarylcarboxylic acids. F. FEIST (Ber., 1934, 67, [B], 938-943; cf. A., 1932, 851).-p-C₆H₄MeAc is converted by Cl₂ at 100-110° in presence of ultra-violet light into p-trichloroacetyl-trichloromethylbenzene, m.p. 38°, converted in Et_2O by insufficiency of 2N-NaOH into $p-C_6H_4(CO_2H)_2$ and trichloroacetylbenzoic acid (I), m.p. 193°, by protracted ebullition with MeOH into p-C₆H₄(CO₂Me)₂, and by restricted action of boiling MeOH into Me trichloroacetylbenzoate (II), m.p. $60-62^{\circ}$, and its methylate (III), $CO_2Me \cdot C_6H_4 \cdot C(OH)(OMe) \cdot CCl_3$, m.p. 138.5-140.5°. (II) and (III) are transformed by H₂ in presence of Pd-CaCO3 or Pd-BaSO4, respectively, into p-C₆H₄Ac·CO₂Me, m.p. 94° (acid, m.p. 205) 13 4-trichloroacetyl-3-trichloromethylbenzoate Me most readily hydrolysed by H2SO4-AcOH giving trichloroacetylisophthalic acid in addition to the products described (loc. cit.). Attempts to determine the basicity of (I) by use of NH₃ led to H. W. $p \cdot \mathrm{CO}_2 \mathrm{H} \cdot \mathrm{C}_6 \mathrm{H}_4 \cdot \mathrm{CO} \cdot \mathrm{NH}_2$.

Stereomutation and absorption of β-anisylacrylic acids. (MLLE.) R. M. DA COSTA (Compl. rend., 1934, 198, 1996—1998).—Ultra-violet light changes β -anisyl-, β -anisyl- α - (I) and - β -methylacrylic acids (best if present as Na salts) into the corresponding allo-acids, m.p. 65° (30%), 113° (30%), and 110° (35% yield), respectively. (I) is unchanged by conc. H₂SO₄ at -10°, but the corresponding alloacid gives 6-methoxy-2-methylindone, m.p. 142°, thus proving the cis-structure of the allo-acids. The absorption spectra of the two series are closely similar, but those of the allo-acids are slightly weaker and displaced towards the ultra-violet. R. S. C.

1:6-Reduction of cyclic β -bromobenzoylcrotonic ester. R. E. LUTZ (J. Amer. Chem. Soc., 1934, 56, 1378—1381).— γ -Methoxy- γ -p-bromophenyl- β -methyl- γ -crotonolactone (cyclic Me β -p-bromobenzoylcrotonate) (I) (this vol., 406) is reduced (Zn dust, AcOH at 50—55°) to γ -methoxy- γ -p-bromophenyl- β -methyl- Δ^{β} -butenoic acid (the enol Me ether of β -p-bromobenzoylbutyric acid) (II), m.p. 122·5° (corr.) (ozonolysis products, p-C₆H₄Br·CO₂Me and CH₂Ac·CO₂H). Reduction (Zn dust, boiling AcOH) of (I) gives γ -methoxy- γ -p-bromophenyl- β methyl- γ -butyrolactone (cyclic Me β -p-bromobenzoylbutyrate), m.p. 98° (corr.) [also obtained when (II) is boiled with AcOH], converted by MeOH-H₂SO₄ into Me β -p-bromobenzoylbutyrate. The formation of (II) from (I) is considered to involve 1: 6-addition of H₂ (*i.e.*, to :O and >O) giving

 $C_6H_4Br \cdot C(OMe)$: CMe · CH. $C(OH)_2$, which then rearranges. H. B.

cis- and trans-1: 2-Dimethylcyclopropane-1:2-dicarboxylic acid. K. von Auwers and O. UNGEMACH (Annalen, 1934, 511, 152-168).-The condensation product from Me₂ pyrocinchonate and CH₂N₂ is decomposed by superheating, the ester hydrolysed by HCl, and the mixture of acids thus obtained is treated with AcCl, whereby cis-1: 2-dimethylcyclopropane-1: 2-dicarboxylic acid (I), m.p. 115—117°, is converted into the anhydride (II), b.p. 113—115°/9 mm., m.p. 54—56°, from which it is regenerated by H_2O . trans-1:2-Dimethylcyclopropane-1: 2-dicarboxylic acid (III), m.p. 230-231°, is obtained similarly from the pyrazoline derived from Me_2 dimethylfumarate and CH_2N_2 . Unlike (I), (III) reacts with difficulty with AcCl, by which it is converted into a non-cryst. polymeric anhydride (IV) slowly re-transformed by H_2O into (III). When heated in vac., (IV) passes into y-methyl-a-methyleneglularic anhydride, b.p. 135-136°/9 mm., m.p. 60° corresponding acid (V), m.p. 107°; monoanilide, m.p. 164-164.5°]. Reduction of (V) by Na-Hg affords a mixture of aa'-dimethylglutaric acids (monoanilide, m.p. 157°). Attempts to isomerise (I) by HCl gave partly unsaturated products formed by fission of the cyclopropane ring. Similar difficulties were met in the use of AcCl for the isomerisation of (III), which could be effected in some degree by use of Ac₂O. Treatment of (II) with NH2Ph in C6H6 leads to cis-1:2-dimethylcyclopropanecarboxylanilic acid (VI), m.p. 139-140° when rapidly heated, hydrolysed by NaOH to (I) and NH₂Ph, transformed by NH₂Ph at 100° into the dianilide or, under other conditions, into the corresponding anil, m.p. $131-132^{\circ}$, obtained also from (VI) and AcCl. With NH₂Ph in C₆H₆ (III) gives trans-1: 2-dimethylcyclopropane-1: 2-dianilide

(VII), m.p. $266-267^{\circ}$, accompanied by the transanilic acid, m.p. $195-196^{\circ}$. Excess of NH₂Ph at 100° or its b.p. transforms (III) into (VII) exclusively. (III) is unaffected by heating at $220-230^{\circ}$ or by protracted warming with AcCl. The following derivatives are prepared analogously: cis-p-toluidic acid, m.p. $149-150^{\circ}$; cis-p-tolil, m.p. $120-121^{\circ}$; transp-toluidic acid, m.p. 200° ; trans-di-p-toluidide, m.p. $275-276^{\circ}$. The dissociation consts. of (I) and (III) have been measured at 25° . H. W.

Synthesis in the santene series; complete synthesis of santenic acid. G. KOMPPA and W. ROHRMANN (Ber., 1934, 67, [B], 828-829).—Catalytic reduction of dehydro- π -apocamphoric acid (Skita) yields isosantenic acid (I) and a non-separated mixture of isomeric santenic acids. (I) is transformed into Et_2 bromoisosantenate, b.p. 147-149°/7 mm., converted by hot quinoline into Et_2 dehydrosantenate, b.p. 133-135°/7 mm., which is hydrolysed to a dehydrosantenic acid (II), m.p. 168-169°, identical with that obtained by Aschan from bromosantenic acid. Catalytic reduction of (II) affords mainly cis-isosantenic acid. H. W.

Derivatives of salicylic acid. VII. Interaction of thionyl chloride with esters of aromatic hydroxy-acids in presence of finely-divided copper. II. Synthesis of thio-ether of 4-methoxysalicylic acid and related compounds. N.W. HIRWE, G. V. JADHAV, and Y. M. CHAKHRADEO (J. Univ. Bombay, 1933, 2, No. 2, 128-131).-Treatment of Me 4-methoxysalicylate with SOCl, and Cu powder gives the Me2 ester (I) of bis-(4-hydroxy-2-methoxy-5carboxyphenyl) sulphide (II), m.p. 226° [by hydrolysis of (I) with aq. NaOH] $[Na_2 (+H_2O), K_2 (+2H_2O), Ca$ $(+4H_2O)$, and $Ba(+4H_2O)$ salts; diamide, m.p. 187°; Ac_2 derivative, m.p. 162°; Bz_2 derivative, m.p. 185°]. The constitution of (II) is confirmed by nitration with dil. HNO₃ to 5-nitro-4-methoxysalicylic acid, m.p. 232°. The mechanism of the formation of (I) is discussed. H. N. R.

Action of sulphuric acid in the cold and at slightly raised temperatures on aromatic acids and their esters. J. B. SENDERENS (Compt. rend., 1934, 198, 1655—1658; cf. A., 1928, 881).—BzOH, $o \cdot C_6H_4Me \cdot CO_2H$, and $o \cdot C_6H_4(CO_2H)_2$ are unaffected by conc. H_2SO_4 at room temp. and at 80°. CH_2Ph \cdot CO_2H and CH_2Ph \cdot CH_2 \cdot CO_2H give sulphonic acids slowly at room temp. and rapidly at 80°, whilst $2: 4 \cdot C_6H_3Me_2 \cdot CH_2 \cdot CO_2H$ is immediately sulphonated as it dissolves. $o \cdot OH \cdot C_6H_4 \cdot CO_2H$ is sulphonated in the nucleus at room temp. after some hr. J. L. D.

Aluminium sulphonates and aluminosulphonic acids of the aromatic series, and their application to certain syntheses. M. DOMINIKIEWICZ (Arch. Chem. Farm., 1934, 1, 93—108).—The Al salts of 1:3- and 1:4-C₆H₄(CO₂H)·SO₃H, 1:4:3- and 1:2:5-C₆H₃(CO₂H)(OH)·SO₃H, 2:3:5- and 2:3:7-C₁₀H₅(CO₂H)(OH)·SO₃H are prepared by adding the theoretical amount of Al₂(SO₄)₃ to the aq. Ba salts, filtering, evaporating the filtrate to dryness, dissolving in EtOH, and again evaporating. The above salts are readily sol. in H₂O, EtOH, and AcOH, and are

to (II).

 CO_2H

(II.)

CO₂H

not decomposed by dil. alkalis. $Hg(OAc)_2$ and $Al[1:2:5-C_6H_3(CO_2H)(OH)\cdot SO_3]_3$ give the corresponding 3-acetoxymercuri-derivative, sparingly sol. in H_2O . R. T.

Preparation of phthalimide. C. L. TSENG and M. HU (Sci. Quart. Nat. Univ. Peking, 1934, 4, 191— 235).—A survey of existing methods. W. R. B.

Influence of o-, m-, and p-substituents in organomagnesium carboxylates containing a labile hydrogen on their reaction with Grignard reagents. D. IVANOV and G. PCHENITCHNY (Bull. Soc. chim., 1934, [v], 1, 223-233).-The effect of the nature of the group Ar in CH_Ar CO_MgCl in determining whether the product of its interaction with RMgX gives (1) an arylmalonic acid (A., 1931, 483) or (2) a β -hydroxy- $\alpha\beta\gamma$ -triarylbutyric acid (*ibid.*, 726) has been studied. (1) is the main reaction when Ar =o-, m-, or p-C₆H₄Me, or p-C₆H₄Pr^{β} (group a), o- (b) and m- (c) $-C_6H_4Br$ or $-C_6H_4Cl$, and α - or β - $C_{10}H_7$ (d), and R=alkyl, o- C_6H_4Me or α - $C_{10}H_7$; $Ar=\alpha$ - $C_{10}H_7$ and R=Ph, m- or p- C_6H_4Me , and p- C_6H_4Br ; and thus from appropriate pairs are obtained o-, m.p. 139-140° (decomp.), m., m.p. 130–131° (decomp.), and p-tolyl-, m.p. 143·5–144·5° (decomp.), p-isopropyl-, m.p. 143·5° (decomp.), o-, m.p. 124–125° (decomp.), and m-bromo-, m.p. 125·5–126·5°, and m-chloro-, m.p. 127–128° (decomp.), -phenyl-, and $-\alpha$ -, m.p. 151° (decomp.), and -β-naphthyl-, m.p. 148° (decomp.), -malonic acid. (2) is the main reaction when Ar =group (a), $m \cdot C_6 H_4 Br$, or $\beta \cdot C_{10} H_7$, and R=Ph, mand $p-C_6H_4Me$, or $p-C_6H_4Br$, and thus are obtained the following -butyric acids : \$-hydroxy-ay-di-o-tolylβ-m-tolyl-, m.p. 147-148.5°, -αγ-di-0-tolyl-β-p-tolyl-, p-m-tolyt-, m.p. $147-140^{-5}$, $-\alpha\gamma$ -at-0-tolyt-p-p-tolyt-, m.p. 138° ; $-\beta$ -phenyl- $\alpha\gamma$ -di-o-, m.p. $145-146^{\circ}$, -di-m-, m.p. $137\cdot5-138^{\circ}$, and -di-p-tolyl-, m.p. $172-173^{\circ}$; $-\alpha\beta\gamma$ -tri-m-tolyl-, m.p. $135-136^{\circ}$; $-\alpha\gamma$ -di-m-tolyl- β -p-tolyl-, m.p. $139-140^{\circ}$; $-\alpha\gamma$ -di-p-tolyl- β -m-tolyl- β -p-tolyl- $\alpha\gamma$ -di-p-isopropylphenyl-, m.p. $174-175^{\circ}$; $-\beta$ -m-tolyl- $\alpha\gamma$ -di-p-isopropylphenyl-, m.p. $139-140^{\circ}$; $-\beta$ -p-tolyl- $\alpha\gamma$ -di-p-isopropylphenyl-, m.p. $158-159^{\circ}$: tolyl- $\alpha\gamma$ -di-p-isopropylphenyl-, m.p. 158—140 , -p-p-tolyl- $\alpha\gamma$ -di-p-isopropylphenyl-, m.p. 158—159°; - β -phenyl- $\alpha\gamma$ -di-p-isopropylphenyl-, m.p. 162—163°; - $\alpha\gamma$ -di-m-bromophenyl- β -m-, m.p. 142·5—143·5°, and - β -p-tolyl-, m.p. 142—143°; - β -phenyl- $\alpha\gamma$ -di-m-bromophenyl-, m.p. 157·5—158·5°; - β -phenyl- $\alpha\gamma$ -di-m-bromophenyl-, m.p. 157·5—158·5°; - β -phenyl- $\alpha\gamma$ -di-mm-chlorophenyl-, -β-phenyl-αγ-di-β-naphthyl-, m.p. 165.5—166.5° (decomposed by 20% NaOH to β -C₁₀H₇·CH₂·CO₂H and Ph β -naphthylmethyl ketone, m.p. 122°), -butyric acid. From COPh₂ are obtained β-hydroxy-ββ-diphenyl-α-m-chlorophenyl-, m.p. 161.5°, and -aa-diphenyl-a-a-naphthyl-, m.p. 163-164°, -propionic acid. J. W. B.

Perylene and its derivatives. XLI. Position of the substituents in dinitroperylene. K. FUNKE and G. P. YPSILANTI (Monatsh., 1934, 64, 143—152). —3:10-Dibenzamidoperylene (I) is oxidised (aq. CrO_3) to 6-benzamido-Bz-1-benzamido-1:9-benzanthrone(2)-5:10-dicarboxylic acid (II) (converted by distillation with Zn dust into benzanthrene) and 3:10-dibenzamidoperylene-4:9-quinone (III) (quinol dibenzoate). The production of (II) from (I) establishes the constitution of 3:10-dinitroperylene [from which (I) is prepared]. (III) is best prepared from (I) and HNO₃ (d 1.1); it is oxidised (MnO₂, conc. H₂SO₄)



3:10-di-p-chlorobenzamidoperylene-4:9-quinone. H. B.

Characteristics of opianic and hemipinic acid. V. M. RODIONOV and T. A. ABLETZOVA (Ukrain. Chem. J., 1933, 8, 316—321).—Hemipinic acid (I) can be separated from opianic acid (II) by pptn. as the Ca salt. Good yields of meconine and (I) are obtained by boiling (II) during 3 hr. with 35% KOH. R. T.

Action of acetic anhydride and sodium acetate on the anhydrides of β -arylglutaconic acids. Formation of glutaconylacetic acids. D. B. LIM-AYE and V. M. BHAVE (J. Univ. Bombay, 1933, 2, No. 2, 82-89).-β-Arylglutaconic anhydrides condense in their enolic form, $CH \ll_{C(OH)}^{CHR,CH} > CO$, with Ac_2O and NaOAc to give β -arylglutaconylacetic acids (I), CH $\leq_{C(OH)\cdot O}^{CR=CH}$ >C:CH·CO₂H. Treatment of (I) with aq. NaOH causes ring-fission with production of γ -acetyl- β -aryl- Δ^{β} -butenoic acids, CHAc:CR·CH₂·CO₂H (II). (I) is normally accompanied by the lactone CH₂ CR:CH₂ (III), which may also be obtained from (I) and aq. HCl. (11) is decarboxylated when heated above its m.p. to yield the corresponding ketone, CHAc:CRMe (IV). (II) may also be reduced with Na-Hg, yielding the saturated keto-acid, CH2Ac CHR CH2 CO2H (V). The following are described : β-p-anisyl-, m.p. 132° (gives p-OMe·C₆H₄·COMe with aq. NaOH); β -(4-methoxy-3-methylphenyl)-, m.p. 189°; β -(2-methoxy-5-methylphenyl)-, m.p. 129°; β -phenyl-, m.p. 115°; β -(2-methoxy-4-methylphenyl)-, m.p. 138°; β -o-anisyl-, m.p. 116°, -glutaconylacetic acids [as (I)]. γ -Acetyl-B p anised m p. 125° (docomp) [acetylβ-p-anisyl-, m.p. 125° (decomp.) [semicarbazone, m.p. 155° (decomp.); phenylhydrazone, m.p. 165°; oxime, m.p. 190° (decomp.)]; -β-(4-methoxy-3-methylphenyl)-, m.p. 146° (semicarbazone, m.p. 155°; phenylhydrazone, m.p. 165°); -β-(2-methoxy-5-methylphenyl)-, m.p. 98° (semicarbazone, m.p. 152°; phenylhydrazone, m.p. 122°), and -β-phenyl-, m.p. 109° (semicarbazone, m.p. 152° ; phenylhydrazone, m.p. 145°), $-\Delta^{\beta}$. butenoic acids [as (II)]. β -p-Anisyl-, m.p. 112° ; β -(4-methoxy-3-methylphenyl)-, m.p. 95° ; β -phenylm.p. 96°, -methyleneglutaconides [as (III)]. 4-Methoxy-, m.p. 48° (semicarbazone, m.p. 193°; phenylhydrazone, m.p. 70°; oxime, m.p. 107°; oxidised to p-methoxy-β-methylcinnamic acid); 4-methoxy-3-methyl-, b.p. 145—150°/5 mm. (semicarbazone, m.p. 205°; oxime, m.p. 100°; oxidised to 4-methoxy-3methyl-\beta-methylcinnamic acid, m.p. 145°); and 2-methoxy-5-methyl-, b.p. 135°/5 mm. (semicarbazone, m.p. 200°), -β-methylstyryl Me ketone [as (IV)]. γ-Acetyl-

β-anisyl-, m.p. 104° (semicarbazone, m.p. 190°; oxime, m.p. 169°; *Ét* ester, b.p. 190—195°/5 mm.); -β-(4-melhoxy-3-methylphenyl)-, m.p. 72° (semicarbazone, m.p. 178°); -β-(2-methoxy-5-methylphenyl)-, m.p. 98° (semicarbazone, m.p. 199°), and -β-phenyl-, m.p. 85° (semicarbazone, m.p. 175°), -butyric acids [as (V)]. H. N. R.

Chlorine-containing lichen substance. I, II. G. KOLLER and K. POPL (Monatsh., 1934, 64, 106-113, 126-130).-I. The atranorin extracted (Et₂O) from Pseudevernia furfuracea, L., contains Cl and on acetolysis (AcOH at 140-150°) gives Me β -orcinolcarboxylate, atranol, and an aldehyde (I), C₈H₇O₃Cl, m.p. 143° [m-bromoanil, m.p. 228° (vac.) (decomp.)]. Reduction (H₂, Pd-C, EtOH) of (I) gives β-orcinol (II) and 2-chloro-3: 5-dihydroxy-p-xylene, m.p. 88-89° [reduced (HI in CO₂) to (II)]. The Me₂ ether, m.p. 78° (Me₂SO₄), of (I) is oxidised (alkaline KMnO₄) to an acid (III), C10H11O4Cl, m.p. 158°, reduced (H2, Pd-C, aq. NaOAc) to p-orsellic acid Me, ether (IV). (I) appears to be 2-chloro-3: 5-dihydroxy-p-tolualdehyde.

II. Chloro-p-orsellic acid Me, ether, m.p. 157-158° (Me ester, m.p. 71-72°), from (IV) and Cl₂-H₂O, is



identical with (III) (above). Details are given for the isolation and purification of chloroatranorin (A), CO₂Me m.p. 208° (vac.), which on acetolysis (AcOH at 150°) gives (I). Alcoholysis (MeOH at 155°) of (A) affords Me

3-orcinolcarboxylate and Me chlorohæmatommate (6-chloro-3: 5-dihydroxy-4-aldehydo-0-toluate), m.p. 90°. H. B.

XXXVIII. Protocetr-Lichen substances. aric acid and its alkyl ethers. Y. ASAHINA and Norstictic acid, a new Y. TANASE. XXXIX. lichen acid, and occurrence of *d*-arabitol in lichens. Y. ASAHINA and M. YANAGITA. XL. Occurrence of volemitol in lichens. Y. ASAHINA and M. KAGITANI. XLI. Constitution of physodic acid (I). Y. ASAHINA and H. NOGAMI (Ber., 1934, 67, [B], 766-773, 799-803, 804-805, 805-811). -XXXVIII. Successive extraction of the thalli of Parmelia Zollingeri, Hepp, with boiling Et₂O and COMe₂ yields atranorin, m.p. 196°, lecanoric acid, m.p. 180° (decomp.) [Me ester Mc₃ ether, m.p. 147°], mannitol, and considerable amounts of protocetraric acid (I), decomp. 245-250° after darkening at about 220° [Ac₅ derivative (II) m.p. 113°]. Hydrogenation of (I) (Pd-C) affords hypoprotocetraric acid (III), decomp. 241° after darkening at 220°, best identified by conversion by CH2N2 into Me hypoprotocetrarate Me₂ ether (IV), m.p. 170°. Mild treatment of (IV) with KOH-MeOH leads to a compound, $C_{18}H_{14}O_4(OMe)_4$ (due to opening of lactone ring), transformed by CH₂N₂ in COMe₂ into the Me₅ derivative of hypoprotocetraric acid hydrate,

^C₁₈H₁₃O₃(OMe)₅, m.p. 115-116°. (I) or fumar-protocetraric acid and Pr^aOH at 100° afford protocelraric acid Pro ether, decomp. 240° after darkening at 200°, hydrogenated (Pd-C in AcOH) to (III) and converted by Ac.O containing a little conc. H₂SO₄ into (II). The Bua, m.p. 178-179° (decomp.), isoamyl, m.p. 173° (decomp.), and CH.Ph, m.p. 201° (decomp.) after darkening at 198°, ethers of (I) are prepared similarly and undergo similar transformations.

XXXIX. Extraction of the thalli of Lobaria pulmonaria from Sakhalin with Et20 and COMe2 and treatment of the extracts with NH2Ph in COMe2 leads to the isolation of gyrophoric acid, m.p. 228° (decomp.) (Ac4 derivative, m.p. 228°), and norstictdianil, m.p. about 265° (decomp.) after softening at about 240°, hydrolysed by conc. HCl in COMe, at room temp. to norstictic acid (I), C₁₈H₁₂O₉, decomp. 283° after darkening at 240° (penta-acetate, m.p. 212°). Catalytic hydrogenation (Pd-C in AcOH) converts (I) into hyposalazic acid, decomp. 280° after darkening at 240° (Me ester Me, ether, m.p. 164°). The COMe, extract (see above) contains d-arabitol (II), m.p. 103°, $[\alpha]_{p}^{2}$ +7.82° in saturated Na₂B₄O₇ (penta-acetate, m.p. 76°). 1- and r-Arabitol penta-acetate have m.p. 76° and 95°, respectively. (II) is also obtained from \hat{L} . pulmonaria from Central Japan and from Ramalina geniculata. Extraction of R. scopulorum (Retz), Nyl, leads to the isolation of usnic acid, (II), and salazic acid.

XL. Volemitol, m.p. 153.5° [(:CHPh)3 derivative, m.p. 222-223°), is obtained from Dermatocarpon miniatum and Primula officinalis, Jacq.

XLI. Extraction of the thalli of Parmelia physodes with Et₂O leads to atronorin and physodic acid (I), with Et₂O leads to atronorm and physodic acid (1), $C_{26}H_{30}O_8$, m.p. 205°. (I) does not contain OMe, gives a monoxime, m.p. 209—210°, and an Ac_2 derivative (II), m.p. 153—155.5°. Treatment with CH_2N_2 affords successively the Me_1 ester, m.p. 156—157°, Me_1 ester Me_1 ether (III), m.p. 117—119°, and Me_1 ester Me_3 ether (IV), m.p. 123—125°. In presence of bromo-thymol-blue and phenolphthalein (I) neutralises I and Q_2 emission of MOI 2 equivs. of KOH, respectively, indicating thus the presence of a highly sensitive lactone ring. Dis-solution of (I) in cold KOH followed by immediate acidification of the solution leads to isophysodic acid (V), m.p. 191—192°, converted by short treatment with CH_2N_2 into the *Me* ester, m.p. 197°, and by prolonged action into (IV). CH_2N_2 transforms (II) successively into Me diacetylphysodate, m.p. 114-115°, and its non-cryst. Me_1 ether. When boiled with HCO_2H or with quinoline and Cu-bronze (I) or (V) loses CO₂ and yields *physodone* (VI), C₂₅H₃₀O₆, m.p. 198-199°, which does not react with NH₂OH and gives an amorphous product with CH₂N₂. Fusion of (I) with KOH gives n-hexoic acid, orcinol, and *n*-amylresorcinol. (III) with $KMnO_4$ yields oliveton-ide Me₁ ether, m.p. 57°. The transformations of (I), (V), and (VI) are readily explained by the following constitutions:



Y.

Lichen substances. XLII. Components of certain Usnea types with special consideration of compounds of the salazic acid group (II). ASAHINA and T. TUKAMOTO (Ber., 1934, 67, [B], 963-971).-Extraction of Usnea articulata v. asperula,

Müll. Arg., leads to d-usnic acid, m.p. 203° , $[\alpha]_{15}^{16} + 483^{\circ}$ in Me OR" ČНО OR"'.CH.O (A.)

CH₂·OR' CHCl₃, salazic acid α -Me ether (I) (A; R'=Me; OR'' R'' = R''' = R''' = H), CO m.p. 210° (decomp.), and salazic acid B-Me ether (II) [A; R'''=Me; R'=R''=R'''=H],

m.p. 250-252° (decomp.) after becoming discoloured at 240°. (I) is transformed by H₂ (Pd-C in AcOH) into hyposalazic acid, decomp. about 280° (Me ester Me_2 ether, m.p. 165°). (I) affords a dianil $C_{31}H_{24}O_8N_2$. m.p. 169° (decomp.), and is converted by Ac₂O containing a trace of conc. H₂SO₄ into an amorphous material. (II) yields a penta-acetate, m.p. 228° (decomp.), and a dianil, m.p. 231° (decomp.). Dry distillation of (II) gives atranol Me₁ ether, m.p. 78°, whilst reduction (Pd-C) affords hypostictic acid, m.p. 264° (decomp.) after darkening at 240°. Treatment of salazic acid (III) with CH_2N_2 in $COMe_2-Et_2O$ yields Me salazate (A; R''=Me; R'=R''=R'''=H), m.p. 229° [acetate, m.p. 103-104°; monoanil, Co5H10O9N, m.p. 218-219° (decomp.)], transformed by H₂ (Pd-C-AcOH) into Mehyposalazate, m.p. 273°. Treatment of (III) with boiling AcOH gives a acetylsalazic acid, decomp. 275-276° after darkening at about 220°. Triacelylhyposalazic acid has m.p. 234° (slight decomp.). Possibly the salazic acid Me ether (A., 1933, 1161) is A (R"=Me; R'=R""=R""=H), but the material does not appear homogeneous. Extraction of U. japonica, Wain, leads to usnic acid, norstictic acid, m.p. 284-285° (decomp.) after becoming discoloured at 260° (penta-acetate, m.p. 212°; dianil, decomp. 260-262° after becoming discoloured at 240°), reduced and methylated to trimethylhyposalazic acid, m.p. 165°; and (III). H. W.

Ring change by deamination of 2-aminocycloparaffin alcohols. M. GODCHOT and M. MOUS-SERON (Compt. rend., 1934, 198, 2000-2002).-The H oxalate and H tartrate of 2-aminocyclohexanol and NaNO₂ at 0° give NH₄NO₂ and cyclopentanealdehyde (80% yield), b.p. 42-43°/18 mm. (NaHSO3-compound ; semicarbazone, m.p. 123-124°; with HNO3 gives $CO_2H \cdot [CH_2]_3 \cdot CO_2H$). 2-Aminocycloheptanol gives similarly cyclohexanealdehyde (semicarbazone, m.p. 167-168°; oxidised to adipic acid), but 2-aminocyclopentanol forms N2, cyclopentane 1: 2-oxide, b.p. 102-103°), and trans-cyclohexane-1: 2-diol (unchanged by COMe,-HCl). R. S. C.

Separation of the components of lignin. H. PAULY [with A. FOULON, O. HANSEN, O. HABER-STROH. H. BAILOM, and J. SEXTL] (Ber., 1934, 67, [B], 1177—1199).—The complete analysis of winter rye straw gives the following results, the % being calc. on the dry initial material. The portion sol. in MeOH contains cerotic acid (0.7%), fats etc. (0.23%), HCO₂K+(HCO₂)₂Mg (0.2%), a gum, sol. in H₂O, (urunic acid and galactose) (0.95%), native lignin A_1 (0.36%), and native lignin A_2 (0.74%). Extraction

of the residue with cold, 1.5% NaOH removes a fraction containing (HCO₂), Ca (0.9%), AcOH (from Ac) (1.3%), pentoses (due to hydrolysis) (2.8%), alkalilignin B_1 (1.54%), alkali-lignin B_2 (4.67%), and xylan (11.59%). Treatment of the residue with 85% AcOH containing 0.3% of H₂SO₄ gives 18.55% of substances sol. in H₂O with 85% of monoses (xylose, methylpentose, glucose, mannose, galactose), 3.22% of lignol C_1 , 4.68% of lignol C_2 , and 3.50% of lignol C_3 . Residual cellulose amounts to 38.56%. The separation of A_1 from A_2 depends mainly on the difference in solubility in CHCl₃. A_1 has m.p. about 160° after softening at 100° and shrinking strongly at 140°, I val. 40.4%, $[\alpha]_{p} \pm 0^{\circ}$ in AcOH. It dissolves readily in dil. NaOH. It does not reduce Fehling's solution before or after hydrolysis. A_2 has m.p. >250° after softening at 190°, I val. 22.4%; in general phenolic and lignin properties it closely resembles A_1 , from which it differs in composition, mol. wt., and solubility. B_1 and B_2 are separated from one another mainly by CHCl₃. B_1 is non-cryst., has m.p. 120° after softening at 102°, $[\alpha]_D \pm 0^\circ$ in AcOH, and gives the usual colour reactions of lignins. B_2 softens at about 190°, but does not melt at a higher temp. Apart from mol. wt. and m.p., the differences between B_1 and B_2 are less marked than those between A_1 and A_2 . It appears probable that B_1 and B_2 are derived from material in which an acetylxylan is esterified by the aromatic lignin components. C_1 , C_2 , and C_3 appear analogous to similar materials isolated from various woods, in which A_1, A_2, B_1 , and B_2 are not present. The term "lignol" is applied to the phenolic components of difficultly produced lignins completely free from polysaccharides. The C_1 fraction from all sources is characterised by solubility in C_6H_6 , C_2 by solubility in CHCl₃, whereas C_3 is generally sol. in AcOH, fatty acids, etc., but not in C_6H_6 or CHCl₃. C_1 fractions have low m.p. (about 90°), whereas the m.p. of C_2 fractions are higher and C_3 fractions cannot be melted. All are optically inactive and non-cryst. They do not contain Ac. They give all the colour and other reactions of lignin and behave as typical phenol derivatives. The mol. wt. of fraction C_2 from any given source is double that of fraction C_1 , but individual vals. of the mol. wt. of fraction C_1 or C_2 from various sources differ greatly. Fraction C_3 exhibits very high mol. wt. It therefore appears incorrect to consider a single lignin in nature or a single fundamental unit from which all lignins are derived. The widely varying yields of vanillin obtained by oxidising lignins of differing origin with CrO_3 -AcOH or by oxidising C_1 , C_2 , and C_3 are explicitly only by oxidising C_1 , C_2 , C_3 , C_3 are explicitly only by C_3 . plicable only by assuming a differing structure; this view is supported by the I vals. The supposed presence of piperonyl residues in lignin is negatived by the complete absence of piperonal from the products of large-scale oxidation which yielded several hundred g. of vanillin.

The examination of the absorption of I from 0.1N-I-KI at 15-20° in absence of light shows that no action is observed in 10-14 days with eugenol, CHPh:CH·CH₂·OH, coniferin, coniferaldehyde, fumaric acid, styryl Me ketone, p-hydroxystyryl Me ketone, CO(CH:CHPh)2, dipiperonylideneacetone, cinnamylidene-acetophenone, -benzylideneacetone, -acrylic acid, -pyruvic acid, -lævulic acid, piperic acid, piperin, and furfuracrylic acid. Almost exactly 2 atoms are added by isoprene, isoprenedicarboxylic acid, limonene, terpinene, cyclopentadiene, pinene, indene, and kawaic acid, whereas menthene, phellandrene, dicyclopentadiene, and caoutchouc absorb < 2 atoms. It is shown that the action of I on lignin is strictly chemical and additive. The method consists in allowing the finely-divided material to remain in contact with at least twice the requisite amount of 0.1N-I for 4-5days. The method is well suited for purposes of comparison, but the exact point of addition is not obvious and the presence of conjugated double linkings is suggested. H. W.

Nitration of phenacyl chloride and bromide. C. BARKENBUS and J. P. CLEMENTS (J. Amer. Chem. Soc., 1934, 56, 1369–1370).—The % of m-NO₂derivative formed during nitration (no details given) of COPhMe, COPh·CH₂Cl (I), and COPh·CH₂Br is 65-5, 68-5, and 69-4, respectively; determinations are made (essentially) by Yabroff and Porter's modification (A., 1932, 511) of Flürscheim and Holmes' method (A., 1928, 403). m-Nitrophenacyl chloride, m.p. 100-5—102°, is obtained in 77% yield from (I) and HNO₃ (d 1.5) in cold 96% H₂SO₄. H. B.

Action of Grignard reagents on ketoximes. J. HOCH (Compt. rend., 1934, 198, 1865—1868).— CPhEt:N·OH (I) and MgPhBr (5 mols.) give a little NH₂Ph, (usually) α -hydroxylamino- $\alpha\alpha$ -diphenylpropane (II), m.p. 103° (hydrochloride, m. p. 258°; Bz derivutive, m.p. 189°), and $\alpha\alpha$ -diphenylpropane- $\alpha\beta$ -imine (III), CPh₂->NH, m.p. 74° (hydrochloride, m.p. 170— 175°; phenylurethane, m.p. 149°). The structures of (II) on here been derived for the following remetions and

(II) and (III) are based on the following reactions and on non-identity with the products expected to result from addition of Ph to N in (I). (III) is shown by spectral analysis to be saturated, gives

CHPh₂·CHMe·NH₂ with Na-EtOH, does not react with NH₂OH or semicarbazide, and with hot 20% HCl yields CHAcPh₂ (by isomerisation to the ketimine and subsequent hydrolysis). The formation of NH₂Ph is explained by addition of some Ph to N yielding MgBr·CPhEt·NPh·OMgBr, which hydrolyses to CPhEt:NPh, and finally NH₂Ph and COPhEt. MgEtBr gives only γ -ethylpentane- $\beta\gamma$ imine (60% yield), b.p. 102°/13 mm. (hydrochloride, m.p. 180—185°; phenylurethane, m.p. 11°; picrate, +C₆H₆, m.p. 135—136°), stable to HCl. R. S. C.

Hydroxylamine derivatives of hydroxymethyleneacetophenone. K. VON AUWERS and H. WUN-DERLING (Ber., 1934, 67, [B], 1062—1077).—The spectrochemical behaviour of benzoylacetaldoxime (I) excludes the possibility that it has the structure CHBz:CH·NH·OH, but the sp. exaltations are low for a true oxime. (I) is converted into 5-phenylisooxazole (II) by AcCl or by acidification of its alkaline solutions by mineral acids, but not by AcOH. (II) is the main product formed when (I) is distilled in vac. (I) is transformed by PCl₅ into (II) and CH₂Bz·CN (III), whereas (III) is exclusively obtained when an alkaline solution of (I) is preserved. It is not considered that a fundamental difference exists in the mode of withdrawal of H₂O from (I) by acid and alkali. Dissolution of (I) in cold Ac_2O and removal of the excess of anhydride gives the Ac_1 derivative, transformed by distillation in vac. or treatment with Ac_2O at 100° into a mixture of (II) and (III), whereas (III) is the sole product of hydrolysis by cold NaOH-CH₂Bz-C H₂O. An Ac₂ derivative, m.p. 114-115°, OR N is described. (I) is therefore A (R=H) and the monoximes of CH₂BzAc and CH₂Bz₂ for similar reasons are as A, with R=Me and Ph, respectively. (III), b.p. 160°/10 mm. (prep. from CH₂BzCl described), is converted by boiling Ac₂O into β -acetoxycinnamonitrile, b.p. 170-171°/10 mm.

The "sesquioxime" (IV) of hydroxymethyleneacetophenone is converted by hot alkali into 3-phenylisooxazole (V) and 5-amino-3-phenylisooxazole. At room temp., 5-hydroxylamino-3-phenylisooxazoline (VI), m.p. 108-109° (sulphate), is formed; it slowly reduces cold Fehling's solution and AgNO3-EtOH and passes when treated with dil. HCl at 15-20°, with AcOH, or boiling H₂O into (IV). The reactions CPh·CH₂>CH·NH·OH (VI) may be represented : $+ \mathrm{OH} \cdot \mathrm{NH} \cdot \mathrm{CH} <_{\mathrm{O}}^{\mathrm{CH}_{2} \cdot \mathrm{CPh}} = \mathrm{OH} \cdot \mathrm{N} \left(\mathrm{CH} <_{\mathrm{O}}^{\mathrm{CH}_{2} \cdot \mathrm{CPh}} \right)$ $(IV) + NH_2OH$. The possibility that (VI) is present as OH·N:CPh·CH, CH:N·OH in alkaline solution is excluded for the following reasons. It is oxidised by $K_{a}Fe(CN)_{6}$ in alkaline solution to the *azoxy*-compound $\overset{CPh \cdot CH_{2}}{\underset{N \longrightarrow O}{\longrightarrow}} CH \cdot NO.N \cdot C \ll \overset{CH \cdot CPh}{\underset{O \longrightarrow N}{\longrightarrow}}, \text{ m.p. 184° (slight)}$ decomp.), thus resembling NHPh·OH. All the replaceable H atoms of oximes or hydroxylamino-oximes can be substituted by Ac by means of Ac, O and Ac attached to O, but not to N, is removed by cold MeOH-KOH, giving N-Ac derivatives which yield a characterisric red colour with FeCl₃. (VI) yields a non-cryst. Ac_2 derivative from which a N-Ac compound, cryst. Ac_2 derivative from which a N-Ac compound, m.p. 172—174°, is obtained. With BzCl it affords a monobenzoate (VII), m.p. 136—137°, an ON- Bz_2 com-pound (VIII), m.p. 157—158°, and a N- Bz_1 derivative, m.p. 175—176°. Since (VII) and (VIII) are obtained by the Schotten-Baumann and C_5H_5N methods, (VI) must contain •NH•OH and its ring remain intact in alkaline solution. (VI) is transformed by warm BzCl into dibenzhydroxamic acid and (V). Attempts to prepare benzoylacetaldehydedioxime by the action of an excess of NH₂OH and alkali on hydroxymethyleneacetophenone (IX) led to (VI) in good yield. The action of NH,OH on the condensation product of (IX) NHPhMe gives the hydroxylamino-oxime and OH:N·CPh·CH₂·CH(NH·OH)·NPhMe, m.p. 107°. The following compounds are incidentally described : the Ac₂ derivative of benzylideneacetophenonehydroxylamino-oxime, converted by KOH-MeOH into the N-Ac1 compound, m.p. (indef.) 80°; Ac3 and N-Ac1 compounds of crotonylbenzenehydroxylaminooximine; Ac, derivative of benzoylacetonedioxime. H. W.

Phenanthrene derivatives. I. Reactions of magnesium 9-phenanthryl bromide. W. E. BACHMANN (J. Amer. Chem. Soc., 1934, 56, 1363— 1367).—Mg 9-phenanthryl bromide (I) and PhCN in Et₂O-C₆H₆ give 9-benzoylphenanthrene, m.p. 89·5—90° (cf. Willgerodt and Albert, A., 1911, i, 882), also pre-

pared from 9-cyanophenanthrene and MgPhBr and by the action of PhCHO on the •OMgBr derivative of phenul-9-phenanthrylcarbinol (II), m.p. 139.5-140.5° [from (I) and PhCHO]. Reduction (I, red P, AcOH) of (II) affords 9-benzylphenanthrene, m.p. 153-154° (cf. loc. cit.), also obtained from (I) and CH, PhCl. The following are prepared from the compounds quoted in parentheses and (I): o-tolyl 9-phenanthryl ketone, m.p. 88-90° (o-C₆H₄Me·CN), which when heated at the b.p. for 45 min. and then distilled at atm. pressure gives 1:2:3:4-dibenzanthraceno, m.p. 200-202° (lit. 196-197°); 9-methylphenanthrene, m.p. 90—91° (McI); diphenyl-9-phenanthrylmethane (III), m.p. 175—176° (CHBrPh₂); 9-phenanthryldi-phenylenemethane (IV), m.p. 197—198° (9-bromofluorene); 9-phenanthrylcarbinol, m.p. 149° (CH₂O); 9-phenanthrylmethylcarbinol, m.p. 134-135° (MeCHO); diphenyl-9-phenanthrylcarbinol (V), m.p. 173-174° (COPh2); 9-phenanthryldiphenylenecarbinol (VI), m.p. 189° (fluorenone); phenanthrene-9-carb-oxylic acid, m.p. 251-252° (CO₂), and its Et ester, m.p. 58° (ClCO2Et); di-9-phenanthryl, m.p. 184-185° (CuCl₂), and 9-hydroxyphenanthrene, m.p. 144-146° (O_2) . (I) exhibits chemiluminescence when exposed to air. Reduction (HI-AcOH) of (V) gives (III) and 9-phenyl-1:2:3:4-dibenzfluorene [also obtained by dehydration (AcOH-conc. H₂SO₄) of (V)]. (VI) is similarly reduced to (IV). H. B.

Unsaturated ketones from deoxybilianic and isodeoxybilianic acid. T. SHIMIZU and T. KAZUNO (Z. physiol. Chem., 1934, 224, 155-159).-Distillation of isodeoxybilianic acid yields an oil, which on hydrogenation (PtO2) adds H2 and gives a ketone, C22H34O, m.p. 133—134°, $[\alpha]_{10}^{23}$ —96.8° in EtOH. Distillation of deoxybilianic acid gives a cryst. ketone, C₂₂H₃₂O, m.p. 153°, $[\alpha]_{0}^{22} + 110.8^{\circ}$ in EtOH, which on hydrogenation affords the ketone (I), $C_{22}H_{34}O$, m.p. 136°, $[\alpha]_D$ +182.7° in EtOH, identical with Wieland's product from Borsche's ketone, m.p. 144° (A., 1924, i, 1201; 1925, i, 1066). With Br in AcOH, (I) gives a bromoketone (II), $C_{22}H_{33}OBr$, m.p. 161°, $[\alpha]_{10}^{20} + 15.5^{\circ}$ in EtOH. In C_5H_5N , (II) yields an unsaturated ketone (III), $C_{22}H_{32}O$, m.p. 107°, oxidised by KMnO₄ in AcOH to a hydroxydiketone, $C_{22}H_{32}O_3$, m.p. 170–173°. The Br in (II) must be at C5, the double linking in (III) J. H. B. between $C_{\underline{s}}$ and $C_{\underline{s}}$.

Condensation of cyclopentanone with phenolic aldehydes. B. SAMDAHL and B. HANSEN (J. Pharm. Chim., 1934, [viii], 19, 573-578; cf. A., 1928, 523; 1930, 343).-In presence of HCl phenolic aldehydes condense with cyclopentanone to give 2: 5-dibenzylidene compounds. These may be used as indicators, being greenish-yellow in acid and orange or red in alkaline solution. The following are described, the p_{π} range of the colour change being given in brackets: 2:5-divanillylidene-, m.p. 214-215° 2:5-di-4-hydroxy-3-ethoxybenzylidene-, $[7 \cdot 4 - 9 \cdot 8];$ m.p. 188—189° (decomp.) [7·8—9·8]; 2:5-di-5-bromovanillylidene-, m.p. 268—269° (decomp.) [7·0— 8·1]; 2:5-di-5-nitrovanillylidene-, m.p. 292—294° (decomp.) [insol.]; and 2: 5-di-3: 4-dihydroxybenzylidene-cyclopentanone, m.p. 274-275° [6.6-6.8-11.6]. H. N. R.

Allyl rearrangements in indene series. C. F. KOELSCH (J. Amer. Chem. Soc., 1934, 56, 1337--1339).—1-Hydroxy-1: 2-diphenyl-3-p-tolylindene (I), m.p. 175-177° [from 2-phenyl-3-p-tolylindone (II) and MgPhBr in Et₂O-C₆H₆], and 1-hydroxy-2: 3-diphenyl-1-p-tolylindene [from 2: 3-diphenylindone and p-C₆H₄Me·MgBr (III)] are converted by MeOH-H₂SO₄ into the same Me ether (IV), m.p. 206-207° [probably that of (I)]. 2: 3-Diphenyl-a-hydrindone, m.p. 100-101° (from CHPh, CHPh COCl and AlCl₃ in C6H6), and (III) give 1-hydroxy-2: 3-diphenyl-1-p-tolylhydrindene, m.p. 171—173°, dehydrated (AcOH-H₂SO₄) to 1 : 2-di-phenyl-3-p-tolylindene (V), m.p. 116—117°. 2-Phenyl-3-p-tolyl-a-hydrindone [by reduction (Zn dust, AcOH) of (II)] and MgPhBr afford 1-hydroxy-1: 2-diphenyl-3-p-tolylhydrindene, m.p. 140-160° (? mixture of stereoisomerides), similarly dehydrated to 2:3-diphenyl-1-p-tolylindene (VI), m.p. $154-156^{\circ}$. (IV) is cleaved by 40% Na-Hg in Et₂O to a mixture of approx. equal amounts of (V) and (VI). The Na derivative from (V) or (VI) and 40% Na-Hg is hydro-lysed to the same mixture of (V) and (VI). (V) undergoes 90% conversion into (VI) when boiled with a 5% solution of KOH in 90% EtOH. The anion present in solutions of the metal derivatives of (V) and (VI) is labile; the structure is fixed only after addition of H. Contrary to Earl and Wilson (A., 1932, 382), 9 - phenyl - 9: 10 - dihydrophenanthrene - 10 - carboxylic acid could not be obtained from CHBrPh·CHBr·CO.H, C₆H₆, and AlCl₂; CHPh₂·CHPh·CO₂H results under varying conditions. H. B.

Preparation of 2-hydroxyfluorenone. R. PATRIZIETTI (Anal. Asoc. Quím. Argentina, 1934, 22, 24-27).-The method of Diels is modified, the solution of diazofluorenone being filtered into boiling aq. AcOH. The yield is increased to 80%. R. N. C.

Poly-membered ring systems. III. *m*- and *p*-Ring closure in benzene series. K. ZIEGLER and A. LUTTRINGHAUS (Annalen, 1934, 511, 1-12; cf. A., 1933, 951; this vol., 195).-Crude resorcinol di- ζ -bromohexyl ether [from m-C₆H₄(ONa)₂ and an excess of $\alpha\zeta$ -dibromohexane in EtOH], KCN, KI, and a little $CuSO_4$ in aq. EtOH give resorcinol di- ζ -cyano-hexyl ether, b.p. 238°/0.04 mm., m.p. 53-54°, converted by treatment with NaNPhAlk in Et₂0 (loc. cit.) and subsequently with H₂O into resorcinol 7-imino-8-cyano-1: 13-tridecamethylene ether,

m-C₆H₄ C·[CH₂]₆·C·NH m.p. 97° (53.5% yield), which is hydrolysed (2N-H2SO4 in CHCl3) to resorcinol 7-keto-8-cyano-1: 13-tridecamethylene ether, m.p. 93°. Quinol di-ζ-cyanohexyl ether, m.p. 84-88° (the crude di-ζ-bromohexyl ether has m.p. 91-95°), is similarly converted into quinol 7-imino-8-cyano-1:13-tridecamethylene ether (Î), m.p. 138-139° (52% yield); the corresponding keto-nitrile (II) undergoes ready autoxidation in MeOH and air to HCN and the acid, $p - \text{CO}_2 \text{H} \cdot [\text{CH}_2]_5 \cdot \text{O} \cdot \text{C}_6 \text{H}_4 \cdot \text{O} \cdot [\text{CH}_2]_6 \cdot \text{CO}_2 \text{H}, \text{m.p. 131}^\circ$ (Me_2 ester, m.p. 68°). More energetic hydrolysis (aq. H₂SO₄ in CO₂) of (I) gives [after removal of (II) by autoxidation and subsequent extraction with alkali] quinol 7-keto-1: 13-tridecamethylene ether, m.p. 58-59° (semicarbazone, m.p. 124-126°).

m-C₆H₄(CH₂·CH₂·CO₂H)₂, obtained by reduction (H₂, Pd-BaSO₄, H₂O) of the NH₄ salt of m-C₆H₄(CH:CH·CO₂H)₂ [from m-C₆H₄(CHO)₂ and CH₂(CO₂H)₂ in C₅H₅N at 45–50°], is converted through the obleviate and omida into m di 6 through the chloride and amide into m-di- β -cyano-ethylbenzene, b.p. 165—169°/0·1 mm., which with NaNPhAlk gives much resin and a compound, $(C_{12}H_{12}N_2)_2$, m.p. 266—268°. Hydrolysis (aq. H₂SO₄ in CO_2) of this affords the diketone

 $m \cdot C_6 H_4 < [CH_2]_2 \cdot CO \cdot [CH_2]_2 > C_6 H_4 \cdot m, m.p. 116 -$ 117.5° (disemicarbazone, decomp. 274°). Attention is directed to the possibility of optical isomerism in polymembered ring ethers of 1:5- and 2:6-C10H6(OH)2 and 2:6-disubstituted quinols. H. B.

Action of magnesium phenyl bromide on di-benzoylethylene. R. E. LUTZ and W. R. TYSON (J. Amer. Chem. Soc., 1934, 56, 1341-1342).-Addition of [:CHBZ]₂ (I) to Et₂O-MgPhBr (II) gives 60-65% of $\alpha\beta$ -dibenzoyl- α -phenylethane (III), about 5% of high-melting secondary product (A), and resin; the following reactions probably occur: (COPh·CH:)₂+2MgPhBr \rightarrow [COPh·CHPh·CH:CPh·OMgBr] \rightarrow

 $OMgBr \cdot CPh$: CPh: CPh: CPh · OMgBr \longrightarrow COPh·CH2·CHPh·COPh.

Addition of (II) to (I) gives a little or no (III) and 70-85% of (A); (A) is freed from Mg and Br with difficulty and has m.p. 145-200° (fractional crystallisation has yielded a substance, C₃₈H₂₈O₃, m.p. 272-274°). MgMeI and (I) give (mainly) non-cryst. products and traces of two isomeric compounds, $C_{18}H_{20}O_2$, m.p. 170° and 215—216°. $\alpha\beta$ -Di-2:4:6-trimethylbenzoyl-, m.p. 137° (corr.), and $\alpha\beta$ -di-p-bromobenzoyl-, m.p. 160° (corr.), - α -phenylethanes are prepared [as (III)] from (II) and ab-di-2:4:6-trimethylbenzoyl- and -p-bromobenzoyl-ethylene, re-H. B. spectively.

Derivatives of 9-hydroxy-9-phenyl-10-anthrone. F. F. BLICKE and R. D. SWISHER (J. Amer. Chem. Soc., 1934, 56, 1406-1408; cf. A., 1932, 617). -2-o-Methoxybenzylbenzoic acid and H2SO4-H2O -2-o-Methoxybenzylbenzolc acid and h₂sO₄-H₂O (3:1 by vol.) at 50° give 4-methoxy-9-anthrone, m.p. 134-135°, oxidised (Na₂Cr₂O₇, AcOH) to 1-methoxy-anthraquinone. MgPhBr (3 equiv.) and 2-, 3-, and 4-methoxy-9-anthrones give 2-, m.p. 94-96°, 3-, m.p. 106-108°, and 4-, m.p. 164-166°, -methoxy-9-phenylanthracene, respectively, oxidised (Na₂Cr₂O₇, AcOH) to 9-hydroxy-2-, m.p. 183-185°, -3- (I), m.p. 177-178°, and -4-, m.p. 228-230°, -methoxy-9-phenyl-10-anthrone respectively, which are methylated phenyl-10-anthrone, respectively, which are methylated (MeOH-HCl) to 2:9-, m.p. 115-117°, 3:9-, m.p. 142-144°, and 4:9-, m.p. 194-195°, -dimethoxy-9-phenyl-10-anthrone, respectively. 4':4"-Dimethoxydiphenylphthalein and SOCl₂ in C₆H₆ give 4'-methoxy-2-anisoylbenzophenone and a trace of (probably) 2:5-dianisyl-3:4-benzfuran; 4'-methoxydiphenylphthalein (II) similarly affords (I) and 9-hydroxy-9anisyl-10-anthrone (III). (II) is converted by conc. H_2SO_4 into (probably) 2-phenyl-5-anisylbenzfuran, amorphous, which is oxidised (Na₂Cr₂O₇, AcOH) to H. B. 2-anisoylbenzophenone and (III).

Condensation of 3:4-methylenedioxystyryl methyl ketone with nitrobenzaldehydes. W. KRASZEWSKI and K. GOŁĘBICKI (Rocz. Chem., 1934, 14, 203-206).-The products of condensation of 3:4-methylenedioxystyryl Me ketone with the isomeric nitrobenzaldehydes are : o-, m.p. 154° (4-Brderivative, m.p. 138-140°; phenylhydrazone, m.p. 88-89°), converted on recrystallising from H₂O into β-hydroxy-β-0-nitrophenylethyl 3:4-methylenedioxy-styryl ketone, m.p. 118° [Bz, m.p. 130°, and 2-Br-derivative, m.p. 90° (decomp.); semicarbazone, m.p. 191°]; m-, m.p. 188° (4-Br-derivative, m.p. 155°; phenylhydrazone, m.p. 170°), and p-nitrostyryl 3: 4-methylenedioxystyryl ketone, m.p. 189-190° (4-Br-derivative, m.p. 142°; phenylhydrazone, m.p. 165°). R. T.

Highly activated carbonyl group. Dimesityl tetraketone. A. R. GRAY and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1367-1369; cf. this vol., 525).-Mesitylglyoxal (loc. cit.) and EtOH-KCN give γ -hydroxy - $\alpha\beta\delta$ -triketo - $\alpha\delta$ -di-2:4:6-trimethylphenyl-butane (I), m.p. 188.5—189.5°, oxidised (conc. HNO₃) to di-2:4:6-trimethylphenyl tetraketone (II), (C₆H₂Me₃·CO·CO·)₂, m.p. 133-134°, red. (II) gives an unstable hydrate and is reduced by NHPh·NH, in EtOH to (I). (II) undergoes fission when treated with warm 20% KOH; CO₂, mesityl-glycollic and -glyoxylic acids, and an unidentified compound, m.p. 112·5—113·5°, are isolated on acidification. Attempted prep. of derivatives with NH_2 ·OH, NH_2 ·CO·NH·NH₂, and o-C₆H₄(NH₂)₂ has been unsuccessful (owing to the alkaline reaction medium). H. B.

Reduction of acenaphthenequinone by Clemmensen's method. H. GOLDSTEIN and W. GLAUSER (Helv. Chim. Acta, 1934, 17, 788-789).-Acenaphthenequinone is reduced by Zn-Hg and boiling 20% HCl to acenaphthene in about 35% yield. Similarly, 3-methoxyacenaphthenequinone affords 3-methoxyacenaphthene, m.p. 65.5°, in about 25% H. W. vield.

Application of the electronic theory to organic compounds. VI. Isomerism of sulpho-derivatives of anthracene and anthraquinone. A. M. BERKENGEIM and M. P. ZNAMENSKAJA (J. Gen. Chem. Russ., 1934, 4, 31–58).—SO₃H groups are replaced by H on hydrolysis with 75% H_2SO_4 or on reduction with 2% Na–Hg, whilst OSO_2H groups are unaffected by these reagents. This rule is verified for anthraquinone-1- and -2-mono- and -1:5-, -1:8-, -2:7-, and -2:6-di-sulphonic acids, and for anthracene-1:8-, -2:7-, and -2:6-disulphonic acids. Apparent deviations from the rule are ascribed to impurities, to erroneously allocated orientation (thus, the 1:5-acid is supposed, on the basis of the results of hydrolysis, to be in reality 1:6-), or to isomeric transformation at the temp. of hydrolysis. R. T.

Derivatives of anthraquinone. III. Aminomethylanthraquinones. IV. Dichloroanthraquinones. M. HAYASHI and A. NAKAYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 238-239B, 239-240B).---III. Interaction of 4-nitrophthalic anhydride, excess of PhMe, and AlCl₃ at 75-78° gives 4-nitro-, m.p. 217-218°, and 5-nitro-2-p-toluoylbenzoic acid, m.p. 190-191°, which are reduced to 4-amino- (I), m.p. 224° (Ac derivative, m.p. 244°), and 5-amino-2-p-toluoylbenzoic acid (II), m.p. 181.5-182° (decomp.) (Ac derivative, m.p. $220-221^{\circ}$). (I) is cyclised by conc. H_2SO_4 at 100° to aminomethylanthraquinone-A (III), m.p. $281-281\cdot5^{\circ}$, which is converted (Sandmeyer) into the corresponding *Cl*-compound, m.p. $228\cdot5-229\cdot5^{\circ}$. Under the same conditions (II) gives a mixture apparently containing some (III).

IV. Chloroaminoanthraquinone-A (cf. A., 1933, 612) is converted by Sandmeyer's reaction into 2 : 6dichloroanthraquinone, m.p. $287 \cdot 5 - 288^{\circ}$; chloroaminoanthraquinone-B (loc. cit.) similarly gives 2 : 7-dichloroanthraquinone, m.p. $230 \cdot 5 - 231^{\circ}$. Absorption curves of all the above in EtOH are given. H. A. P.

Mechanism of the asymmetric catalytic race-misation of amygdalin. I. A. SMITH (Ber., 1934, 67, [B], 1307-1317).—The action of KOH-MeOH on amygdalin (I) is similar to its action on Fischer's glucoside, and hence is restricted to the aglucone portion of the mol. The first phase of the change, which is complete in a few min. and is accompanied by a slight increase in lævorotation, involves a catalytic racemisation. At the end of this phase CN is intact and hydrolysis by conc. HCl yields a nearly inactive mandelic acid. The second phase, which requires about 1 day for completion, is accompanied by diminution of lævorotation. The product does not contain OMe and does not give the carmine-red coloration with H2SO4 characteristic of CN·CHPh·OH. Hydrolysis with conc. HCl gives OH·CHPh·CO₂H (II) with moderately high + rotation, whereas similar hydrolysis of (I) yields the homogeneous *l*-acid and hydro-lysis with H_2SO_4 removes the gentiobiose residue, leading thus to optically pure (+)-mandelonitrile. The product of the second phase when treated with H_2SO_4 gives $OH \cdot CHPh \cdot CO_2Me$ (III), $[\alpha]_1^{15} + 33 \cdot 2^{\circ}$ in $COMe_2$ (the pure ester has $[\alpha]_p + 121^{\circ}$). The second phase is considered to be associated with the addition of MeOH to CN giving an imino-ether. Since reaction occurs under the influence of the optically active gentiobiose group, a preferential production of the compound from neoamygdalin (IV) is assumed. The residue consists of (IV) with an excess of (I), and since each component is very sensitive to alkali, the mixture is rapidly transformed into isoamygdalin. In the third phase, which requires about 1 month for completion, the lævorotation increases; OMc is already present in the mol. Hydrolysis with HCl yields nearly inactive (II), whereas treatment with H_2SO_4 affords almost inactive (III) and (II). In this phase reaction is considered to consist in the slow, catalytic racemisation of the imino-ether or Me ester. Confirmation of this view is found in the observation that a third phase does not exist in the action of NH₃-MeOH on (I); at the end of the second phase hydrolysis with H_2SO_4 gives (III), $[\alpha]_D^{16} + 43.3^{\circ}$ in COMe₂, and (II), $[\alpha]_D^{16} + 70.1^{\circ}$ in H_2O . Treatment of (I) with KOH-MeOH for about 1 day and of the product with Ac₂O in C₅H₅N affords Me hepta-acetylamygdalate, m.p. 202- 203.5° , $[\alpha]_{D}^{0} - 66.4^{\circ}$, $[\alpha]_{5461}^{20} - 78.4^{\circ}$ in CHCl₃, and Me hepta-acetylneoamygdalate, m.p. 187–189, $[\alpha]_{5461}^{20}$ -6.6° in CHCl₃. H. W.

Cerebronic acid. Reply to Levene and Yang. E. KLENK (J. Biol. Chem., 1934, 105, 467–468; cf. this vol., 78).—Polemical. The view is restated that lignoceric acid obtained by Levene and Yang by oxidation of cerebronic acid (I) is present as an impurity in the (I). H. A. P.

Dehydrogenation of gitogenin. W. A. JACOBS and J. C. E. SIMPSON (J. Amer. Chem. Soc., 1934, 56, 1424—1425).—Dehydrogenation (Se) of gitogenin gives the same ketone, $C_8H_{16}O$ (semicarbazone, m.p. 144·5—145°) (cf. Ruzicka and van Veen, A., 1929, 1305), and hydrocarbon, m.p. 123·5—124° (not depressed by Diels' hydrocarbon, $C_{18}H_{16}$), as are obtained from sarsasapogenin (I). (I), the *Digitalis* sapogenins, and the cardiac aglucones appear to be alicyclic derivatives of the sterol and bile acid ring-system.

H. B. Sarsapogenin and gitogenin. W. A. JACOBS and J. C. E. SIMPSON (J. Biol. Chem., 1934, 105, 481– 510).—Dehydrogenation of sarsapogenin (I) with Se at 230—240° gives a ketone, $C_8H_{16}O$ (semicarbazone, m.p. 143—144°), which is not necessarily Me *iso*hexyl ketone (semicarbazone, m.p. 153—154°), as stated by Ruzicka and van Veen (A., 1929, 1305), and methylcyclopentanophenanthrene, m.p. 123·5—124°; it therefore probably contains a nuclear structure similar to that of cholesterol. With AcOH-HCl (I) gives a *Cocompound*, $C_8H_{14}O_3$ (*semicarbazone*, m.p. 119·5—120°), which appears to be unsaturated [C(NO₂)₄]. A similar result is obtained with gitogenin. H. A. P.

Saponins and sapogenins. I. Echinocystic acid. I. BERGSTEINSSON and C. R. NOLLER (J. Amer. Chem. Soc., 1934, 56, 1403—1405).—Successive extraction of the root of *Echinocystis fabacea* with MeOH, 50% MeOH, and MeOH and evaporation of the combined extracts to dryness gives the crude saponin, hydrolysed (aq. MeOH-HCl at 60°) to the sapogenin (*echinocystic acid*) (I), $C_{30}H_{48}O_4$, m.p. 305—312° (corr.; decomp.), $[\alpha]_{546}^{38}$ +40.6° in 95% EtOH [diacetate (II), m.p. 272—275° (corr.); Me ester, m.p. 213—215° (diacetate, m.p. 200—201°)]. The rate of hydrolysis (EtOH-KOH) of (II) indicates the occurrence of primary and sec. OH groups in (I). (I) and (II) give a yellow colour with C(NO₂)₄ in CCl₄; neither could be reduced (H₂, PtO₂, AcOH). H. B.

Plant pigments. LX. Astacin. II. P. KAR-RER and L. LOEWE (Helv. Chim. Acta, 1934, 17, 745– 747).—Astacin (I) is $C_{40}H_{48}O_4$ and its Ac derivative is $C_{40}H_{46}O_4Ac_2$. (I) yields a *dioxime*, $C_{40}H_{50}O_4N_2$, which contains four active H (Zerevitinov). (I) evolves little CH₄ when treated with MgMeI in C_5H_5N . Catalytic hydrogenation of (I) discloses the presence of thirteen active double linkings, two of which are due to enolisation; this is in accord with the established presence of 2 OH in perhydroastacin. The 4 CO of (I) are present in pairs, since (I) and $o-C_6H_4(NH_2)_2$ yield a *diphenazine* derivative, $C_{52}H_{56}N_4$. (I) is therefore 4:5:4':5'- or 5:6:5':6'-tetraketo- β carotene. H. W.

Modified rubbers. IV. Oxidation of rubber with aqueous hydrogen peroxide-acetic acid mixtures. G. F. BLOOMFIELD and E. H. FARMER (J.S.C.I., 1934, 53, 121–1257).—The oxidation of rubber with H_2O_2 in presence of AcOH and H_2O yields partly-acetylated OH-acids of considerable mol. wt. By varying the proportions of reagents in the
oxidation the proportion of OAc groups entering the mols. of the rubber may be regulated. Since the oxidation product (A) closely resembles those resulting from AcO₂H oxidation of rubber, it is inferred that oxidation proceeds through the intermediate agency of AcO₂H. The influence of proportion of reagents, temp., catalysts, etc. on the oxidation is studied. A can undergo further acetylation (free OH groups); its saponification gives a OH-acid (B) which can be reacetylated to yield a material similar to A. The composition of B appears to remain const. in spite of considerable changes in the proportions of reagents used in the formation A or when the AcOH in the oxidising mixture is replaced, e.g., by HCO₂H.

Natural and synthetic rubber. XIII. Mol. wt. of sol-rubber. T. MIDGLEY, jun., A. L. HENNE, A. F. SHEPARD, and M. W. RENOLL. XIV. Structural formula for ebonite. T. MIDGLEY, jun., A. L. HENNE, and A. F. SHEPARD (J. Amer. Chem. Soc., 1934, 56, 1325-1326, 1326-1328).-XIII. A solution of sol-rubber (I) (B., 1931, 853; 1933, 200), tetramethylthiuram disulphide, and a little Zn stearate in C_6H_6 is evaporated at room temp. in a high vac. and the resulting skin heated at 100° (bath) until approx. 0.06% S is combined. Repeated fractional pptn. of the product from EtOH-C6H6 gives fractions containing 0.058 ± 0.003 , 0.116 ± 0.003 , and $0.179 \pm$ 0003% S. Assuming that these are mono-, di-, and tri-sulphur derivatives (RS, RS2, RS3), the mol. wt. of (I) is about 54,000.

XIV. The structure (A) assigned to chonite explains

the production (B., 1932, 902) of the following pyrolysis products: 2-methylthiophen (by fission at bc), 2-methyl-5-ethylthiophen (fission at ac), 2:3-dimethylthiophen (fission at bd; migration of Me). Fission at ad should occur most frequently; the resulting frag-C-C

ment may cyclise to C·C S >C, which can give

rise to m-C₆H₄Me₂ (loss of H₂S) or 2:4-dimethylthiophen (loss of 2C). H. B.

Citronellol and rhodinol. ANGLA (Compt. rend., 1934, 198, 2241—2244).—d-Citronellol (I) and *l*hodinol from the Bourbon geranium (II) and from the Algerian geranium (III) are isolated with BzCl (cf. 4, 1896, i, 445) to give (cf. A., 1928, 1113) mixtures containing 45% of the α - and 55% of the β -form. (I) and (II) have the same numerical rotatory dispersion; (III) has a higher val. The results of Lagneau (cf. B, 1934, 301) are untrustworthy because his measurements were carried out on commercial samples of (I) and (II), which contain the α - and β -forms in varying proportions. His vals. for rhodinol from the rose (isolated as above) agree with the vals. now obtained. J. L. D.

Pyrolysis of carveol. J. DŒUVRE (Bull. Soc. chim., 1934, [v], 1, 198—206).—Pyrolysis of *d*-carveol (I) [from *d*-carvone and Al(OPr^{β})₃ or Al(OBu^{α})₃] at 560[°]/170 mm. affords uncondensed (-75°) gaseous products 10%, Δ^{β} -butene, MeCHO 0.5%, isoprene 6%, tiglaldehyde 5% [2:4-dinitrophenylhydrazone, m.p. 222° (block)], a mixture of hydrocarbons, b.p. 55—90°/40 mm., 10% (probably containing $C_{10}H_{14}$ or $C_{10}H_{16}$), a C_{10} aldehyde, b.p. 88—92°/15 mm., 5% (probably CH₂:CMe·CHMe·CH₂·CH:CMe·CHO), a ketone fraction, b.p. 98—109°/15 mm., 15%, unchanged (I) 40%, and a viscous residue 3%.

J. W. B.

Synthesis of myrtenol and myrtenal. G. DUPONT, W. ZACHAREWICZ, and R. DULOU (Compt. rend., 1934, 198, 1699-1701; cf. A., 1933, 1166).--Pinene with SeO₂ in boiling EtOH during 4 hr. does not afford verbenol and verbenone, but myrtenol (I), b.p. $106-108^{\circ}/14 \text{ mm.}, [\alpha]_{D} + 44 \cdot 11^{\circ}$ [phthalate, d- or l-form, m.p. 114-115°; dl-form, m.p. 120-120.5°], which is oxidised (CrO₃) to (II); and reduced (H₂-Pt) to myrtanol (III), b.p. $113-114^{\circ}/14$ mm., and myrtenal (II), b.p. 99-100°/15 mm., [a]_p +14.75° [semicarbazone, d- or l-form, m.p. 225° and 216° (two forms), dl-form, m.p. 206°; oxime, d- or l-form, m.p. 70.5-71.5°, dl-form, m.p. 101°], which gives d-pinic acid (dl-form, m.p. 101-102.5°) with KMnO₄, is reduced (H₂-Pd) to myrtanal (semicarbazone, m.p. 155°) and by H2-Pt to (III). Interaction of d-pinene with Co abietate and O, during 24 hr. affords d-verbenone (IV) (oxime, m.p. 163° ; semicarbazone, m.p. $206-207^{\circ}$), oxidised by KMnO₄ to d-pinonic acid, m.p. $130-131^{\circ}$. Raman spectra measurements show (I), (II), and (IV) to be different. J. L. D.

10-Hydroxycamphor and its derivatives. Y. ASAHINA and M. ISHIDATE [with T. SANO] (Ber., 1934, 67, [B], 1202—1204).—d-Ketopinic acid is converted by CH_2N_2 into Me d-ketopinate, b.p. 137°/16 mm., m.p. 45—46° [semicarbazone (I), m.p. 216°]. (I) is transformed by Na-EtOH and subsequent hydrolysis with HCl into d-10-hydroxycamphor (II), m.p. 220°, $[\alpha]_1^{6}$ +48.6° in EtOH [semicarbazone (III), m.p. 200° (decomp.); d-10-acetoxycamphor, b.p. 148°/16 mm.]. (II) with Na₂Cr₂O₇ and H₂SO₄ affords the corresponding aldehyde, m.p. 210—213°, readily oxidised by air. (III) with NaOEt-EtOH at 160—180° gives 10-hydroxycamphor (ω -borneol), m.p. 200—201°, $[\alpha]_D \pm 0^\circ$, oxidised to the aldehyde, m.p. 187—189° (semicarbazone, C₁₁H₁₉ON₃, m.p. 220—221°). H. W.

Diterpene oxides of the resin of Dacrydium Colensoi. I. J. R. HOSKING and C. W. BRANDT (Ber., 1934, 67, [B], 1173-1177).-Extraction of the wood of D. Colensoi with boiling C6H6 yields 7% of brown resin containing 10% of acidic products, mainly resin acids, and 90% of neutral material, not volatile with steam. Distillation of the neutral portion under diminished pressure gives manoyl oxide (I), $C_{20}H_{34}O$, b.p. 135—137°/0·3 mm., m.p. 29°, $[\alpha]_D^{13} + 19\cdot6^\circ$ in abs. EtOH, ketomanoyl oxide (II), C₂₀H₃₂O₂, b.p. 174—178°/ 0.5 mm., m.p. 76—77°, [a]¹³₁+440.4° in abs. EtOH, and a trihydroxyditerpene oxide (III), C₂₀H₃₂O₄, m.p. 208-209°, $[\alpha]_{10}^{23}$ -12.5° in EtOH. (I) is unsaturated and is hydrogenated (PtO2 in EtOAc at 15-20° or AcOH at 50°) to dihydromanoyl oxide, b.p. 148°/0.2 mm., m.p. 19°. (I) does not react with o-C₆H₄(CO)₂O, NH2 CO NH NH2, NHPh NH2, or NH2OH. It cannot be acetylated. OH and OMe are absent. It remains unchanged when heated with Na. (II) affords an oxime, m.p. 146—147°, and a semicarbazone, m.p. 135°; it is hydrogenated (PtO₂ in EtOAc) to dihydroketomanoyl oxide, m.p. 89—90°. (II) forms the main component of the cryst. deposit found in the wood. (III) contains 3 OH (Zerevitinov) and yields an Ac_3 derivative. It is hydrogenated (PtO₂ in EtOH and EtOAc) to a H_2 -derivative, m.p. 211°. H. W.

Hydrogenation of a mixture of two α -ethylenic aldehydes. WIEMANN (Compt. rend., 1934, 198, 2263—2264; cf. A., 1933, 255).—Furfuraldehyde (I) with Zn-Cu-H₂ in AcOH affords some furfuryl alcohol, resins, and products which distil with decomp. Equimol. quantities of (I) and crotonaldehyde give dipropenyl glycol (10%) and furfurylpropenyl glycol, b.p. 125°/2·8 mm. (phenylurethanes, m.p. 222—223°, and much below 222°, respectively). (I) (3 mols.) and acraldehyde (4 mols.) afford divinyl glycol (15%) and furfurylvinyl glycol (40%), b.p. 115—116°/3 mm. (phenylurethanes, m.p. 189° and 116—118°).

J. L. D. Condensations of furan derivatives. III. Condensation of furfuraldehyde with acetone in acid and alkaline media. Determination of small quantities of furfuraldehyde. V. V. TSCHELINCEV and E. K. NIKITIN (Bull. Soc. chim., 1934, [v], 1, 184–189).—The orange colour formed when solutions of furfuraldehyde (I) are condensed with excess of COMe₂ in 50% H₂SO₄ at 50° \propto concn. of (I), but when condensation is effected with N-KOH at 20°, the colour obtained by subsequent addition of 50% H₂SO₄ \propto [concn.]² of (I). Details of colorimetric methods for the determination of (I) based on these reactions are given, sensitivity being 0.001%.

J. W. B.

strepto- and heterocyclo-Polymethine dyes from furfuraldehyde and their vinylene homologues. W. KÖNIG [with K. HEY, F. SCHULZE, E. SILBERKWEIT, and K. TRAUTMANN] (Ber., 1934, 67, [B], 1274—1296).—Azomethine salts could not be obtained from the aldehydes

 $CH-CH > C \cdot [CH:CH]_n \cdot CHO$ (I) (n=0, 1, 2, or 3) and sec. bases. Addition of $HClO_4$ to the Schiff's base derived from (I) and primary aromatic amines yields azomethine perchlorates

 $\begin{bmatrix} \mathbf{C}\mathbf{H} \cdot \mathbf{C}\mathbf{H} \\ \mathbf{C}\mathbf{H} \cdot \mathbf{O} \\ \mathbf{C}\mathbf{H} \\ \mathbf{C}\mathbf$

which increases with increase of n. When n=1, 2, and 3, respectively, the colours of the salts are yellow to red, red to bluish-red, and violet or, in solution, orange-yellow, orange-red, and dark ruby-red. Furfurylidene-p-anisidine, m.p. 68°, yields a perchlorate, m.p. 156°. The azomethine perchlorates from 2streptovinylenefurfuraldehyde (I; n=1) and the requisite bases are as follows: from NH₂Ph, m.p. 184°; from p-OMe·C₆H₄·NH₂, m.p. 211° (Schiff's base, m.p. 70°); from p-OMe·C₆H₄·NHMe, m.p. 191°; from tetrahydroquinoline (II), decomp. 177°; from 2methyldihydroindole (III), m.p. 223°. From 2-streptodivinylenefurfuraldehyde (I; n=2) azomethine perchlorates are obtained by use of the bases: NH₂Ph, decomp. 167°; p-OMe·C₆H₄·NH₂, decomp. 179° (Schiff's base, m.p. 102°); from NHPhMe, m.p. 159°; from p-OMe·C₆H₄·NHMe, decomp. 180°; from (II), m.p. 165°; from tetrahydro-*p*-toluquinoline (IV), m.p. 196°; from thallin, m.p. 191°; from (III), m.p. 199°. From 2-streptotrivinylenefurfuraldehyde (I; n=3) and *p*-OMe·C₆H₄·NH₂ or (IV) are derived *perchlorates*, m.p. 198° and m.p. 189°, respectively. Treatment of (I) with 2 mols. of a sec. amine in little MeOH and with 1 mol. of HClO₄ or HBr in EtOH leads to dyes of the type

 $[\operatorname{ArNR} \cdot \operatorname{CH} \cdot \operatorname{NArR}] X^{-}.$

The following compounds, in which n=0, are described: The following compounds, in which n = 0, are described. Ar=Ph, R=Me, X=ClO₄, m.p. 104°; Ar= $C_6H_4 < \frac{CH_2 \cdot CH_2}{N - CH_2}$, X=ClO₄, m.p. 159°; Ar= OMe·C₆H₃ < $\frac{CH_2 \cdot CH_2}{N - CH_2}$, X=ClO₄, indef. m.p.; Ar= C₆H₄ CH₂ CHMe, X=ClO₄, m.p. 185°; the anhydrobases, $O\langle CH(NArR) - CH \\ C(:CH\cdot NArR) \cdot CH$ or $O\langle CH \cdot NArR \\ C(:CH \cdot NArR) \cdot CH$ from (IV) and (III) have m.p. 131° and m.p. 139°, respectively. Analogous compounds in which n=2 are described : $Ar = C_6H_4 < \stackrel{CH_2 \cdot CH_2}{\underset{N \cdot CH_2}{\overset{CH_2}{\xrightarrow{}}}, X = ClO_4, m.p. 141^\circ;$ $Ar = C_{\theta}H_{3}Me < \stackrel{CH_{2} \cdot CH_{2}}{N \cdot CH_{2}}, X = ClO_{4}, m.p. 139^{\circ}; Ar =$ $OMe \cdot C_6H_5 < \stackrel{CH_2 \cdot CH_2}{\underset{N \longrightarrow CH_2}{\overset{CH_2}{\overset{}}}}, X = ClO_4, m.p. 119^\circ; Ar =$ $C_{6}H_{4} < CH_{-N} > CHMe$, X=ClO₄, m.p. 149°. Acetylation of the furfuraldehyde dyes and their vinylene homologues is effected with warm Ac₂O, with AcCl usually in the cold, less frequently in the warm, or by treatment with Ac2O or AcCl (BzCl) in C5H5N with good cooling, the last-described process being most generally applicable. The following compounds are described derived from $[ArNH \cdot CH \cdot CH \cdot CH \cdot C(OAc) \cdot [CH \cdot CH]_n \cdot CH \cdot NArR]X^-$: n=0: Ar=Ph, R=Me, X=ClO₄, decomp. 168°; Ar= C₆H₄< $\frac{CH_2 CH_2}{N-CH_2}$, X=ClO₄, decomp. 142°; Ar= $C_6H_3Me < CH \cdot CH_2$, X=ClO₄, ill-defined m.p.; Ar= OMe· $C_6H_3 < CH_2 \cdot CH_2$, X=ClO₄, ill-defined m.p.; Ar= $C_6H_4 < CH_2 > CHMe$, X=ClO₄, ill-defined m.p.; n=1: $\begin{array}{l} \text{Ar=Ph, R=Me, X=ClO_4, decomp. 108°; Ar=Ph,} \\ \text{R=Et, X=ClO_4, m.p. 170°;} \\ \text{Ar=C_6H_4} < \stackrel{\text{CH}_2\text{`CH}_2\text{'CH}_2\text{'}}{\text{N}\text{·CH}_2\text{'}} \\ \text{decomp. 181°; Ar=OMe·C_6H_4} < \stackrel{\text{CH}_2\text{`CH}_2\text{'}}{\text{N}\text{·CH}_2\text{'}} \\ \text{Ar=ClO_4, Mercellar} \\ \text{CH}_2\text{'} \\ \text$ decomp. 196°; Ar= $C_6H_4 < CH_2 > CHMe$, X=ClO₄, decomp. > 200°; $Ar = C_6 H_4 < \frac{CH_2 \cdot CH_2}{N - CH_2}$ X=Cl (Bz in place of Ac); n=2: Ar= $C_6H_4 < CH_2 CH_2, X = ClO_4, m.p. 175^\circ; Ar = OMe \cdot C_6H_2 CH_2 CH_2, X = ClO_4, m.p. 174^\circ; Ar = OMe \cdot C_6H_2 CH_2 CH_2, X = ClO_4, m.p. 174^\circ; Ar = CH_2 CH_2 CH_2 CH_2$ $C_6H_4 < CH_2 > CHMe$, X=ClO₄, m.p. 185°. The optical properties of the dyes are described in detail. H. W.

898

Dibenzfuran. [Diphenylene oxide.] I. Sulphonation. H. GILMAN, E. W. SMITH, and H. J. OATFIELD. II. Metalation. H. GILMAN and R. V. YOUNG (J. Amer. Chem. Soc., 1934, 56, 1412-1414, 1415-1416).-I. Diphenylene oxide (I) and ClSO₂H in CCl_4 at about 25° give the 3-sulphonic acid (II), decomp. > 300° (*Ba* salt); the *sulphonyl chloride*, m.p. 140°, is reduced (Zn dust, H₂O followed by NaOH and Na₂CO₃) to Na diphenylene oxide-3-sulphinate, which with aq. HgCl₂ affords 3-chloromercuridiphenylene oxide (III), m.p. 236.5—237°, also obtained from Mg 3-dibenzfuryl bromide and HgCl₂ in Et_2O . (III) is converted (usual methods) into 3-bromo- and 3-iododiphenylene oxide. Disulphonation (conc. H2SO4) of (I) or further sulphonation (conc. H_2SO_4) of (II) gives the 3:6-disulphonic acid; the disulphonyl chloride, m.p. 219°, is reduced (as above) to Na diphenylene oxide-3: 6-disulphinate, which is then converted into 3:6-di(chloromercuri)-, and thence into 3:6-dibromoand 3: 6-di-iodo-diphenylene oxide.

II. Hg(OAc)₂ and (I) at 150° give 1-acetoxymercuridiphenylene oxide, m.p. 199-200°, converted into 1-chloromercuri-, m.p. 235-238°, and 1-iodo-diphenylene oxide, m.p. 71-72° [the Grignard reagent and CO₂ afford diphenylene oxide-1-carboxylic acid (IV), m.p. 208–209°]. (I) with Et_2O -LiMe, Na+ HgBua₂ in light petroleum, and Na-K alloy in light petroleum gives the 1-Li, 1-Na, and 1-K derivative, respectively; treatment with CO2 affords (IV) in each tase. H. B.

Natural coumarins. XIII. **Synthesis** of ingelicin (from Angelica archangelica). E. SPATH and M. PAILER (Ber., 1934, 67, [B], 1212-1213; cf. this vol., 779).-Na umbelliferone is converted by CH₂Br·CH(OEt)₂ in xylene at 175-180° into angelicin and almost homogeneous umbelliferone Et ether. H. W.

Synthesis of 7-methoxy-8-isoamylcoumarin (dihydro-osthol). H. L. HALLER and F. ACREE, Jun. (J. Amer. Chem. Soc., 1934, 56, 1389-1390).-2:6-Dihydroxy1soamylbenzene (tetrahydrotubanol), malic acid, and conc. H2SO4 at 70-80° and then at 130-140° give 7-hydroxy-8-isoamylcoumarin (I), m.p. 104-106°, methylated (CH_2N_2) to the Me ether, m.p. 55° (cf. Späth et al., this vol., 416). Tetrahydrotubaic acid similarly affords 7-hydroxy-8-isoamylcoumarin-6-tarboxylic acid, m.p. 224-225° (Ac derivative, m.p. 173-175°), decarboxylated (Cu-bronze, quinoline) to (1) in poor yield. H. B.

Synthesis of anthocyanins. R. ROBINSON (Ber.,

1834, 67, [A], 85—105).—Mainly a lecture. [With J. RESUGGAN.] The following synthesis of manin is cited as an example of successful operation in the absence of protective groups. 3: 4-Dihydroxy-p-glucosidoxyacetophenone (I), m.p. 158°, is obtained is 70% yield by hydrolysing its Ac derivative with $B_4(OH)_2$. O^2 - β -Glucosidyl- (II), m.p. 192° (decomp.) after softening at 170°, and O^2O^4 -di- β -glucosidyl-, m.p. 163-164° (decomp.), -phloroglucinaldehyde are preared similarly. A mixture of (I) and (II) is dried at 150° high vac. and dissolved in EtOAc containing $Mg(ClO_4)_2$. The solution is saturated with HCl and preserved at 0°, thereby giving cyanin chloride.

H. W.

Synthesis of anthocyanins. XVIII. Cyanidin 3-xyloside and 3:7- and 5:7-diglucosides. R. H. MACDOWELL, R. ROBINSON, and A. R. TODD. XIX. 5-Glucosidylapigeninidin, believed to be identical with gesnerin, an anthocyanin of Gesnera fulgens. (MRS.) G. M. ROBINSON, R. ROBINSON, and A. R. TODD. XX. Synthesis of malvidin 3-galactoside and its probable occurrence as a natural anthocyanin. (MISS) J. C. BELL and R. ROBINSON (J.C.S., 1934, 806-809, 809-812, 813-818).-XVIII. ω-O-Triacetylβ-xylosidoxy-3: 4-diacetoxyacetophenone (I), m.p. 162°, prepared from ω -hydroxy-3: 4-diacetoxyacetophenone and triacetyl-a-xylosidyl bromide, with HCl and 2-O-benzoylphloroglucinaldehyde followed by picric acid, gives 3-β-xylosidylcyanidin picrate. The chloride could not be obtained owing to hydrolysis to cyanidin chloride. The xyloside shows similar colour reactions to chrysanthemin. (I) and HCl with 2-O-benzoyl-4tetra-acetylglucosidylphloroglucinaldehyde affords cyanidin chloride 3-xyloside 7-glucoside $(+3H_2O)$, whilst ω-O-tetra-acetyl-β-glucosidoxy-3: 4-diacetoxyacetophenone similarly yields cyanidin chloride 3:7-di- β -glucoside (+5.5H₂O). ω -3:4-Trihydroxyacetophenone and 2:4-di-(O-tetra-acetyl-B-glucosidyl)phloroglucinaldehyde give the flavylium salt, hydrolysed to cyanidin chloride 5:7-di- β -glucoside (+2H₂O). The 3:7- and 5:7-diglucosides are readily distinguished from cyanin, especially by the colour reactions.

XIX. 2 - O - Benzoylphloroglucinaldehyde (II), 4-hydroxyacetophenone, and HCl give benzoylapi-geninidin chloride, decomp. 203°, debenzoylated to apigeninidin chloride, identical with the product obtained by demethylation of acacetinidin chloride (cf. Pratt et al., A., 1927, 1083; Asahina and Inibuse, A., 1928, 1256). 2-O-Tetra-acetyl-β-glucosidylphloro-glucinaldehyde (III) and 4-hydroxyacetophenone afford 7:4'-dihydroxy-5-O-tetra-acetyl-B-glucosidoxyflavylium chloride ($+2H_2O$), hydrolysed to 5- β -glucosidylapigeninidin chloride (+8H2O). Acetovanillone and (III) yield 7: 4'-dihydroxy-3'-methoxy-5-β-glucosidoxyflavylium chloride (3'-methoxygesnerin chloride) $(+2H_2O)$, hydrolysed to a diglucoside $(+1.5H_2O)$, which resembles gesnerin chloride in many of its The second anthocyanin isolated from properties. natural gesnerin is probably 3': 5'-dimethoxygesnerin.

ω-Hydroxy-4-acetoxy-3: 5-dimethoxyaceto-XX. phenone, O-tetra-acetyl-a-galactosidyl bromide, and Ag₂O give ω-O-diacetyl-β-galactosidoxy-4-acetoxy-3:5dimethoxyacetophenone, which with (II) forms a flavylium salt. This salt with picric acid yields 3- β -galactosidylmalvidin picrate (+2H₂O), which is converted into malvidin chloride 3-galactoside (IV). (IV) behaves similarly to œnin in colour reaction, but differs in distribution numbers. A re-examination of cyclamin and cenin has shown them to be identical. Primulin from P. sinensis and (IV) are identical. ω-Hydroxy-4-acetoxy-3: 5-dimethoxyacetophenone, triacetylxylosidyl bromide, and Ag₂O give ω-O-triacetyl- \beta-xylosidoxy-4-acetoxy - 3: 5-dimethoxyacetophenone, which with (II) forms a flavylium salt and 5-O-benzoyl-4'-O-acetylmalvidin chloride. The flavylium salt is hydrolysed to malvidin chloride 3-xyloside, F. R. S. which readily decomposes.

E. S. CHOTINSKI, B. Z. AMITIN, and D. A. KORNIENKO. (b) Distillation of ammonium mucate. E. S. CHOTINSKI and V. S. BOGOMOLOV (Ukrain. Chem. J., 1933, 8, 297-303, 304-306).-(a) Chiefly pyrrole (I) is obtained by the destructive distillation of NH₄ mucate (II), with pyrrole-2-carboxylamide (III) as a secondary product, whilst with NH, mucamate (IV), (III) is the principal product.

(b) The yield of (I) from (II) increases, and that of (III) diminishes, when the distillation is performed rapidly; slow heating has the opposite effect. It follows that (III) is produced from (IV), which is formed from (II) during the reaction. R. T.

1-Phenylpiperidine-4-carboxylic acid. V. PRE-LOG and V. HANOUSEK (Coll. Czech. Chem. Comm., 1934, 6, 225-230).-ac-Dibromopentane-y-carboxylic acid heated with NH2Ph gives 1-phenyl-3-(B-phenylaminoethyl)pyrrolidone, m.p. 128-129° (hydrobromide, m.p. 182—183°), and the anilide, m.p. 210°, of 1-phenylpiperidine-4-carboxylic acid (I), m.p. 131° [hydrobromide, m.p. 218—219°; picrate, m.p. 207° (decomp.)]. The methiodide, decomp. 180°, of (I) gives a betaine, m.p. 266°, converted by heat into the Me ester, m.p. 46°, of (I). A. A. L.

Synthesis of the two isomeric N-methylconicines. R. LUKES and (MME.) M. SMETACKOVA (Coll. Czech. Chem. Comm., 1934, 6, 231-240).-N-Methylpiperidone with MgProBr gives 1-methyl-2: 2-dipropylpiperidine, b.p. 102-103°/9 mm. [isolated as the picrate, m.p. 163-164°; aurichloride, m.p. 162-164°; platinichloride, m.p. 220-222° (decomp.)], and N-methyl-y-coniceine, b.p. 182°/760 mm., 72°/10 mm. [hydrochloride (+ H_2O), m.p. 89°; aurichloride, m.p. 80°; perchlorate, m.p. 130—133°; picrate, m.p. 170—171°]. The latter is reduced electrolytically or with H, and colloidal Pd to N-methylconicine (platini-chloride, m.p. 197°; picrate, m.p. 112-114°), which is resolved by crystallisation of the H tartrate. The *d*-base has $[\alpha]_{11}^{23} + 82.4^{\circ}$ (hydrochloride, m.p. 192– 193°, $[\alpha]_{D} + 27.8^{\circ}$; hydrobromide of the *l*-base, m.p. 188–191° $[\alpha]_{D} - 21.9^{\circ}$). Physical consts. of the bases are recorded. A. A. L.

Action of Grignard reagents on 4-diphenylyl piperidinomethyl ketone and on N-methyl-cinchotoxine. (MISS) B. R. CARPENTER and E. E. TURNER (J.C.S., 1934, 869-872).—Ph₂, CH₂Br-COBr, and AlCl₃ afford 4-diphenylyl CH₂Br ketone (I), m.p. 126-127°, which with NPhMe₂ gives phenyl-4-phenylphenacyldimethylammonium bromide, m.p. 144-145°. (I) is also obtained by bromination of 4-diphenylyl Me ketone, and is different from 4'-bromo-4-diphenylyl Me ketone, m.p. 131°, from AlCl₃ and 4-bromodiphenyl. 4-Diphenylyl Pr^{β} ketone, m.p. 61-62° (lit. 56°; p-nitrophenylhydrazone, m.p. 143-144°), is brominated to the a-Br-compound, m.p. 99-100°, obtained by Friedel-Crafts reaction, whilst the Bu^{\$} ketone, m.p. 77-78° (lit. 63°), gives the a-Br-compound, m.p. 131-132°. 4-Phenylacetyl-4'-acetyldiphenyl has m.p. 118-119°. Ph 4-diphenylyl ketone and MgMeI give phenyl-4-diphenylylmethylcarbinol, m.p. 102-103°. 4-Diphenylyl Me ketone and MgPreI yield 4-diphenylylmethylisopropylcarbinol, m.p. Ph2, $63-64^{\circ}$. CH₂Cl·COCl, and AlCl₃ give 4:4'-di(chloroacetyl)di-phenyl, m.p. 226-227°, which with C₅H₁₁N gives

4:4'-di(piperidinoacetyl)diphenyl, m.p. 143-144°. 4-Diphenylyl piperidinomethyl ketone, m.p. 93-94° (methiodide, m.p. 184-185°), obtained from the bromomethyl ketone, with MgMeI affords 4-diphenylylmethylpiperidinomethylcarbinol, m.p. 89-90° (methiodide, m.p. 186-187°). N-Methylcinchotoxine does not react with MgPhBr or MgMeI, and hence tends to avoid the ketonic structure. F. R. S.

3-Quinolylazo-2:6-diaminopyridine and its derivatives. M. M. KATZNELSON and I. L. KNUNIANZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 415-418).-Diazotisation of 8-aminoquinoline and coupling with 2:6-diaminopyridine (I) yields 3-(8'quinolylazo)-2: 6-diaminopyridine, m.p. 191—193° (hydrochloride), unaccompanied by any bisazo-com-pound. 3-(6'-Methoxy-8'-quinolylazo)-2: 6-diaminopyridine, m.p. 168°, is similarly obtained from 8-amino-6-methoxyquinoline and (I). H. N. R.

Substituted amides of pyridinecarboxylic acids. E. GRYSZKIEWICZ-TROCHIMOWSKI (Arch. Chem. Farm., 1934, 1, 65-71).-Nicotinoyl chloride condenses with 2-aminopyridine in C₆H₆ in presence of C₅H₅N to yield the 2-pyridylamide, m.p. 138-139°, with d-2-aminocamphor in Et₂O to yield the d-2-camphorylamide, m.p. 144-145°, and with d-bornylethylamine (without solvent) to afford the 2-d-N-ethylbornylamide, m.p. 89-90°, of nicotinic acid. The bis-N-diethylamide of pyridine-2: 6-dicarboxylic acid, m.p. 122-123°, is prepared from NHEt2 and iso-R. T. cinchomeronoyl chloride.

Ease of formation of cyclic imines. II. G. SALOMON (Helv. Chim. Acta, 1934, 17, 851-862).-Conditions favourable for the synthesis of polymembered cyclic imines are examined in connexion with possible side changes which are detected by kinetic measurements. The velocity coeffs. of the formation of hexamethylenemine (I) have been measured between 37° and 58° and the proportion of multimol. reactions calc. from the relationship of rate of reaction to initial concn. Undisturbed ring closure occurs in $\Rightarrow 0.005M$ solution. Examination of the readiness of formation of hexadecamethyleneimine in alkaline BuOH is complicated by the side changes caused by an involved relationship to $p_{\rm H}$ in these media. Comparison of the heats of activation and reaction consts. of the formation of (I) and $[CH_2]_2 > NH$ shows that the poor yields frequently observed in the synthesis of (I) are due essentially to the insolubility of CH₂Br·[CH₂]₄·CH₂·NH₂ in H₂O, and not to smaller ease of formation. The readiness of production of cyclic imines in solution depends mainly on the spatial structure of the rings and the thermodynamically caused, chemical relationship between halogeno-H. W. alkylamine and solvent.

Poly-membered heterocyclic compounds. III. Preparation of hexamethyleneimine and hexadecamethyleneimine from the aliphatic bromoamines. L. RUZICKA, G. SALOMON, and K. E. MEYER (Helv. Chim. Acta, 1934, 17, 882-886).-CH₂Br·[CH₂]₄·CH₂·NH₂,HBr and NaOH in much H₄O at 50° and then at 80° yield hexamethyleneimine, b.p. 130°/723 mm., in 50% yield.

[With M. HURBIN.] an-Dibromohexadecane and

o-C₆H₄(CO)₂NK at 170—180° give phthal- π -bromohexadecylimide, m.p. 74°, hydrolysed to π -bromohexadecylamine hydrobromide (I), m.p. 165°. In H₂O, (I) does not appear to yield hexadecamethyleneimine (picrolonate, m.p. 208—210°), which is obtained by means of NaOH in BuOH. These and other polymembered, cyclic imines have the characteristic odour of musk. H. W.

Synthesis of isatin. M. DOMINIKIEWICZ and M. Киеwsка (Arch. Chem. Farm., 1934, 1, 71-81).-In the Sandmeyer synthesis of isatin from NHPh·CS·NHR $(R=p-tolyl and 1-C_{10}H_7)$, of the two possible isomerides of the nitriles only NPh:C(CN)·NHR is (I) obtained, and of the thioxamides only NPh:C(CS·NH₂)·NHR, whilst when $R = p - C_6 H_4 Br$ the corresponding compounds are NHPh·C(CN):N·C,H,Br and $\dot{N}HPh \cdot C(CS \cdot \dot{N}H_2): N \cdot C_6H_4Br$ (II). (I) yield the anils of 4-methyl- and 1:2-benzo-isatin on heating with H₂SO₄, whilst (II) affords the p-bromoanil of isatin. The substance NPh:C(CS·NH₂)·NH·C₁₀H₇, m.p. 122-123°, is prepared by heating the corresponding nitrile with NH_4 polysulphide at 32° (96 hr.). R. T.

Condensation of 2-chlorolepidine with anthranilic acid. P. K. BOSE (Current Sci., 1934, 2, 430-431).—Previous views (A., 1932, 66) of the mechanism of the condensation are maintained.

L. S. T.

Syntheses in the hydroaromatic series. XX. Addition of acetylenedicarboxylic esters to hydrazobenzene. O. DIELS and J. REESE (Annalen, 1934, 511, 168—182).— $[\cdot \text{NHPh}]_2$ (I) and $[:C \cdot CO_2 \text{Me}]_2$ (II) in boiling MeOH afford the adduct (III), CO₂Me·C(NHPh·NHPh):CH·CO₂Me, m.p. 138°, which passes in hot AcOH containing dil. HNO₃ into benzidine nitrate and Me 1:2-diphenylpyrazol-5-one-3carboxylate (IV), m.p. 137-138°, obtained directly from (I) and (II) in warm AcOH. Treatment of (III) with KOH-MeOH at 100° leads to 1:2-diphenylpyrazol-5-one-3-carboxylic acid (V), decomp. about 205°. Condensation of (I) with $Et_2C_2O_4$ at 140° and hydrolysis of the product gives (V), transformed by boiling A = O into the product gives (C), transformed by D boiling Ac₂O into 1:2-diphenylpyrazol-5-one, m.p. 130°. In boiling xylene (III) is converted into Me_2 indole-2: 3-dicarboxylate, m.p. 114°, hydrolysed by boiling conc. HCl to Me H indole-2: 3-dicarboxylate, m.p. 256°, and transformed by 30% KOH into indole-2-carboxylic acid, m.p. 203-204° (Me ester, m.p. 152°), which loses CO₂ above its m.p and gives indole. When heated above its m.p. or in boiling C₅H₅N or NPhMe₂, (III) passes into Me 3-anilino-2-hydroxyquinoline-4carboxylate, m.p. 224-225° (Ac derivative, m.p. 276°), hydrolysed by 20% KOH to 3-anilino-2-hydroxyquinoline-4-carboxylic acid (VI), m.p. 257° (Ac derivative, m.p. >345°), which gives 3-anilino-2-hydroxyquinoline (VII), m.p. 219-220° (Ac derivative, m.p. 272°), when heated. (VI) or (VII) is converted by prolonged boiling with conc. HCl-AcOH into 2:3-dihydroxyquinoline, m.p. 258° (Ac derivative, m.p. 214°). H. W.

Nitration of aryloxy-2- and -4-methylquinolines. Synthesis of substances having possible antimalarial action. (MISS) R. M. MURRAY and E. E. TURNER (J.C.S., 1934, 856-860).-KOPh and 30

2-chloro-4-methylquinoline at 190° give 2-phenoxy-4methylquinoline, m.p. 51° [methiodide, m.p. 220° (decomp.); stable to piperidine (I) at 195°, which with HNO₃ (d 1.5) and AcOH at 50° gives 2-(4'-nitro-phenoxy)-4-methylquinoline, m.p. 140-141° (corr.) [gives with (I) at 170-180° 2-hydroxy-4-methylquinoline and p-nitrophenylpiperidine], reduced by Fe-EtOH-HCl to the 4'-NH₂-compound, m.p. 135° (acetylacetone anil, m.p. 109°, hydrolysed by conc. H₂SO₄ at 100°). m-NO₂·C₆H₄·OK and 2-chlorolepidine (II) yield 2-(3'-nitrophenoxy)-4-methylquinoline, m.p. 152°, reduced to the 3'-NH₂-compound, m.p. 170-171° [acetylacetone anil, m.p. 81°, gives with H₂SO₄ at 100° 5- or 7-(4'-methyl-2'-quinolinoxy)-2: 4-dimethylquinoline, m.p. 173°]. 2-p-Tolyloxy-4-methylquinoline (III), m.p. 60°, similarly prepared [meth-iodide, m.p. 197-198° (decomp.)], with KNO₃-H₂SO₄ at $<-5^{\circ}$ gives the 3'-NO₂-derivative (IV), m.p. 121° at <-5 gives the $3 - NO_2$ -derivative (IV), m.p. 121, also obtained from 2-nitro-*p*-cresol and (II), stable to (I) at 160°; the $2' \cdot NO_2$ -derivative, m.p. 148° (prepared from 3-nitro-*p*-cresol) [gives a gum with (I) at 160°], with HNO₃ (*d* 1·5) at 60-70° gives the $2' : 5' \cdot (NO_2)_2$ -derivative, m.p. 186°, reduced to the $2' : 5' \cdot (NH_2)_2$ -derivative, m.p. 204°. (IV) is reduced to the $3' \cdot NH_2$ -derivative, m.p. 174°, the acetyl-acetone anil of which, m.p. 139-140°, is hydrolysed by H.SO. (III) with HNO₂ under certain conby H₂SO₄. (III) with HNO₃ under certain conditions gives 2-(2': 3': 5'[?]-trinitro-4'-methylphenoxy)-4-methylquinoline, m.p. 315°. Quinol Me ether leads to 2-(4'-methoxyphenoxy)-4-methylquinoline, m.p. 103° (corr.) [methiodide, m.p. 182° (decomp.; corr.)], the 3'-NO2-derivative, m.p. 112-113° (corr.), of which is reduced to the 3'-NH₂-derivative, m.p. 138-139° (corr.) (salicylidene derivative, m.p. 127-128°; acetylacetone anil, m.p. 115-116°, hydrolysed by H₂SO₄), and with NH₃-EtOH at 170-180° affords the 3'-nitro-4'-amino-compound, m.p. 156°. Similarly are obtained 2-(4'-ethoxyphenoxy)-4-methylquinoline, m.p. 90-91° [methiodide, m.p. 185-186° (decomp.) after sintering at 130-131°7, 4-phenoxy-2methylquinoline (VI), m.p. 73° {methiodide, m.p. 210° (decomp.); 4'-NO₂-, m.p. 177° [reacts normally with (I) at 170–180°], and 4'-NH₂-derivative, m.p. 168°}, the 3'-NO2-derivative of (VI) (from m-NO2 C6H4 OH), m.p. 135-136°, and the corresponding 3'-NH2-compound, m.p. 101-102°, the acetylacetone anil of which gives 5- or 7-(2'-methyl-4'-quinolinoxy)-2:4dimethylquinoline, m.p. 194—195°; 4-p-tolyloxy-2-methylquinoline, m.p. 89—90° [methiodide, m.p. 207— 208° (decomp.) after sintering at 204°; 3'-, m.p. 163°, and 2'-NO₂-, m.p. 134—135°, and 3'-NH₂-derivative, m.p. 98—99°], 4-(4'-methoxyphenoxy)-2-methylquinol-ine, m.p. 168° [methiodide, m.p. 225—226° (decomp.) after sintering at 223°; 3'- NO_2^{-} , m.p. 205–206°, and 3'- NH_2 -derivative, m.p. 171–172°]. R. S. C.

Structure and synthesis of new anti-malarials. I. Plasmoquin. III. Atebrin.—See B., 1934, 650.

Nitro- and amino-derivatives of acridone. N. S. DROZDOV and S. S. DROZDOV (J. Gen. Chem. Russ., 1934, 4, 1-8).-2-Nitro- and 2-amino-acridone are obtained in good yield by heating the corresponding substituted diphenylaminecarboxylic acids or their salts with $POCl_3$. 2: 4-Dinitrodiphenylamine2'-carboxylic acid (I) yields similarly 2:4-dinitroacridone, whilst its K salt affords the acid chloride of (I), together with its *lactam*, m.p. 224°. R. T.

Monochloroacridine and acridone. N. S. DROZDOV (J. Gen. Chem. Russ., 1934, 4, 117—119).— Acridone is obtained by heating diphenylamine-2carboxylic acid in xylene with the theoretical amount of POCl₃, in presence of a 300% excess of which the product is chloroacridine. R. T.

Preparation of cystinehydantoin. W. C. HESS (J. Amer. Chem. Soc., 1934, 56, 1421).—Cystine (I) and KNCO in dil. HCl give cystinehydantoin, $C_8H_{10}O_4N_4S_2$, decomp. from 310°, which is readily decomposed by alkalis, gives a negative Sullivan reaction for (I), and behaves as (I) in the Okuda (A., 1926, 190) and Folin-Marenzi (A., 1929, 1093) methods of determination of (I). H. B.

5-β-Ethyl-substituted derivatives of barbituric acid. E. F. ROSENBERG, R. F. KNEELAND, and G. S. SKINNER (J. Amer. Chem. Soc., 1934, 56, 1339-1340).—Et n-butyl-β-bromoethyl- (I), b.p. 127—128°/ 0.5 mm., and isoamyl-β-bromoethyl- (II), b.p. 145-147°/2 mm., *-malonates* are prepared from CNaR(CO₂Et)₂ and (·CH₂Br)₂ in Et₂O or C₆H₆; Et isoamyl-β-chloroethylmalonate (III), b.p. 132°/1 mm., is similarly obtained using CH2Cl·CH2I. Et isoamylβ-dimethylaminoethyl-, b.p. 152-154°/10 mm. (hydrochloride, m.p. 78°) [from (III) and EtOH-NHMe, at 100°], isoamyl-β-diethylaminoethyl-, b.p. 141°/1 mm. [from (II) and EtOH-NHEt2 at 100°], and n-butylβ-dimethylaminoethyl-malonate, b.p. 115°/3 mm. [hydrochloride, m.p. 137-138° (corr.)] [from (I) and EtOH-NHMe₂ at room temp.], are described. 5-n-Butyl-5-β-dimethylaminoethyl-, m.p. 118-119° [hydrochloride, m.p. 244-245° (corr.)], and 5-isoamyl-5-β-dimethylaminoethyl-barbituric acid, m.p. 115-116° (scaled tube) [hydrochloride, m.p. 277-280° (scaled tube)], are prepared by a slight modification of the usual procedure. When (II) is distilled slowly at about 20 mm., α -carbethoxy- α -isoamyl- γ -butyrolactone, b.p. 165—166.5°/18 mm., is formed; with CO(NH₂)₂ and EtOH-NaOEt, this gives 5-isoamyl-5-β-hydroxyethylbarbituric acid, m.p. 177.5-178° (corr.).

H. B.

Enolisation of ψ -uric acid. H. BILTZ and L. LOEWE (Ber., 1934, 67, [B], 1199—1202).—Treatment of ψ -uric acid (I) or its 1-Me ether (II) with CH₂N₂ leads to the *Me ether* of *enol*-1: 3-dimethyl- ψ uric acid, decomp. 210° after reddening and softening at about 200°, converted by conc. HCl at 100° into 1: 3-dimethyluric acid. (II) and CHMeN₂ give the *Et ether* of *enol*-methyl- ψ -uric acid, m.p. 205° (decomp.), or, if reaction is prolonged, the *Et ether* of *enol*-methylethyl- ψ -uric acid, m.p. 230° after reddening at 210°, decomp. 232—234°. Reasons are advanced for considering that the conversion of (I) into uric acid uoes not proceed through the enols. H. W.

Mono-N-arylpiperazines and their derivatives. V. PRELOG and Z. BLAZEK (Coll. Czech. Chem. Comm., 1934, 6, 211-224).—The following are obtained by methods previously described (this vol., 196; in some cases MeOH is replaced by Bu^aOH): the monohydrobromides of N-p-bromo-, m.p. 239° (decomp.) {base, m.p. 98.5° [Ac derivative, m.p. 129° , and its hydrochloride, m.p. $215-220^{\circ}$ (decomp.)]} (yield 52° /₀), -m-, m.p. 255° , and -p-nitro- (I), m.p. > 290° (dihydrobromide, m.p. > 290° ; base, m.p. 135°), -o- (II), m.p. 242.5° (yield 90° /₀), and -p-hydroxy-phenyl-(III), m.p. 219° (yield 70° /₀), -p-tolyl-, m.p. 242° (base, m.p. $32-33^{\circ}$, b.p. $112^{\circ}/1$ mm.) (yield 85° /₀), - α -, m.p. > 290° (hydrochloride), and - β -naphthyl-piperazine, decomp. 280° (base, m.p. 78°), Et p-piperazinebenzoate, m.p. 188.5° (hydrobromide of acid, m.p. > 300°), $\beta\beta'$ -di-o-, m.p. $188-189^{\circ}$ (yield 12° /₀), and -p-toluidino-, m.p. 245° (yield 6° /₀), and - α -naphthylaminodiethylamine, m.p. $216-217^{\circ}$ (yield 8.5° /₀); and the dihydrobromides of N-o-, m.p. > 290° , and -m-aminophenyl-, decomp. 305° (base, m.p. $179-180^{\circ}$), and -p-phenylenedipiperazine, m.p. > 300° (tetrahydrobromide, m.p. > 300° ; colour reaction described). (I) is reduced to the dihydrobromide, m.p. > 290° , of the NH_2 -compound, m.p. 126° (colour reaction described). Hydrolysis of (II) and (III) with 48°_{0} HBr gives the dihydrobromides of N-o-, m.p. 289- 290° (decomp.), and -p-hydroxyphenylpiperazine, decomp. 275° . A. A. L.

Uranyl [antipyrine and piperazine] salts.— See this vol., 855.

Pyrimidines. CXLII. Acetylation of 2-ketotetra- and -hexa-hydropyrimidines. K. FOLKERS and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 1374—1377).—Et 2-keto-4-phenyl-6-methyl-1:2:3:4-tetrahydropyrimidine-5-carboxylate (I) is acetylated (Ac₂O) to (probably) the 1-Ac derivative, m.p. 175.5-177° (not obtainable from NHAc·CO·NH₂, PhCHO, and CH₂Ac·CO₂Et), which is readily hydrolysed (EtOH-HCl) to (I) and is converted by POCl₃ into (I). Et 2-keto-4-phenyl-1:6- and -3:6-dimethyl-1:2:3:4-tetrahydropyrimidine-5-carboxylate similarly afford the 3-Ac, m.p. 108-109.5°, and 1-Ac, m.p. 164.5-166°, derivative, respectively, showing that both the 1- and 3-NH groups are sufficiently basic for reaction. The increased basicity of Et 2-keto-4-phenyl-6-methylhexahydropyrimidine-5-carboxylate is manifested by its (partial) solubility in dil. HCl and the formation of its $1:3-Ac_2$ derivative, m.p. 101.5-102.5°. 2-Keto-5-phenyl-4-benzyl-1:2:3:4-tetrahydropyrimidine also gives the 1:3-Ac2 derivative, m.p. 104.5-105°; the increased basicity is ascribed to the absence of a 6-substituent and the displacement of Ph at C4. 2-Keto-4:6-diphenyl-4-methyl-1:2:3:4-tetrahydropyrimidine(11) (A., 1933, 1059) affords (probably) the 3-Ac derivative, m.p. 182-183°, thus favouring the constitution H. B. assigned (loc. cit.) to (II).

Change of 2:4:6-trinitrobenzylideneaniline into an indazolone derivative. S. SECAREANU and I. LUPAS (Bull. Soc. chim., 1933, [iv], 53, 1436—1442).—2:4:6-Trinitrobenzylideneaniline and Na₂CO₃ in hot EtOH give 4:6-dinitro-N-oxy-2-phenylindazolone, $C_6H_2(NO_2)_2 < \underbrace{C(OH)}_{NO} > NPh, m.p. 252^\circ$ [Na salt, m.p. about 240° (decomp.)], the Ag salt, decomp. about 250°, of which with EtI gives the corresponding 3-ethoxy-compound, m.p. 148°. R. S. C. J. L. D.

Isomerism of 4:6-dinitrobenzylideneaniline. S. SECAREANU and I. LUPAS (Bull. Soc. chim., 1934, [v], 1, 373-380).-2:4-(NO₂)₂C₆H₃·N:CHPh with Na₂CO₃ in boiling EtOH affords 6-*nitro*-3-*hydroxy*-2*phenylindazole*, m.p. about 260° (Ac derivative, m.p. 190-191°; Bz derivative, m.p. 171°), together with 6-*nitro*-3-*hydroxy*-2-*phenylindazole* 1-*oxide*, m.p. 166-167° (Ag salt; OEt-derivative, m.p. 64-65°), but less easily than does the corresponding 2:4:6-(NO₂)₃-compound (cf. preceding abstract). o-NO₂·C₆H₄·N:CHPh does not undergo similar re-

Vasicin and peganin. K. S. NARANG and J. N. RAY (Current Sci., 1934, 2, 388—390).—Evidence against the identity of vasicin and peganin and against the structure given by Späth and Nikatwitz (this vol., 310) to the latter is discussed. L. S. T.

2:4:6-Trinitrobenzylideneaniline. S. SECAR-EANU and I. LUPAS (J. pr. Chem., 1934, [ii], 140, 90— 96).—Extension of the previously described reaction (this vol., 308) to the 2:4:6-trinitrobenzylidene derivatives of m-NO₂·C₆H₄·NH₂, m.p. 160—161°, o-, m.p. 143°, and p-NH₂·C₆H₄·CO₂H, m.p. 204° (lit. 147°), and p-NH₂·C₆H₄·OEt, affords the following 4:6-dinitro-2hydroxy-1:3-diaryl(R)benztriazolines:R=m-C₆H₄·NO₂, m.p. 263°, o-, m.p. > 280°, and p-C₆H₄·CO₂H, m.p. > 340°, p-C₆H₄·OEt, m.p. 197°, and CH₂Ph, m.p. 224° [no (NO₂)₃-benzylidene derivative obtained], together, in the last case, with a substance, C₂₈H₂₄O₉N₈, m.p. > 300° (structures suggested). Their more strongly basic character prevents the similar reaction with alkylamines. J. W. B.

Azimido- and N-methylazimido-benzene derivatives. K. FRIES, H. GÜTERBOCK, and H. KÜHN (Annalen, 1934, 511, 213-240).-5-Amino-1:2:3benztriazole (I) [by reduction of the 5-NO₂-compound with H_2 -Ni-Co-Cu at 80°/80 atm.; Ac_2 (II), m.p. 184°, and Ac, m.p. 240°, derivatives; benzeneazocompound, m.p. 207° (Ac derivative, m.p. 243°)] is converted by the Skraup synthesis into 5:6-triazolo-



arrangements.

quinoline (A), m.p. 260°, and by diazotisation into 5-hydroxy-1:2:3benztriazole (III), m.p. 228° (decomp.) [Ac₂ derivative (IV), sinters 115°, m.p. 127°], which with Br-AcOH affords its 4-Brderivative, m.p. 230° (decomp.), converted by AcOH-HNO₃ (d 1.51)

into 4-nitro-5-hydroxy-1: 2: 3-benztriazole, m.p. 236° (decomp.). With Cl₂ (II) in AcOH-NaOAc gives the 5-Ac derivative, m.p. 281° (decomp.), of 4-chloro-5amino-I: 2: 3-benztriazole, m.p. 218°, obtained by aq. EtOH-HCl hydrolysis. (III) in AcOH with Cl₂ affords its 4-Cl-derivative (V), m.p. 246° (decomp.), further converted by Cl₂ in AcOH-NaOAc at 0° into 4:4-dichloro-5-keto-4: 5-dihydro-1: 2: 3-benztriazole, m.p. 132° (decomp.) (hydrochloride, decomp. 72°), reduced by SnCl₂-AcOH to (V). With NaNO₂-H₂SO₄ at 0° (III) gives its 4-NO-derivative, explodes > 360°, reduced (SnCl₂-HCl) to the 4-NH₂-compound, m.p. 217° (decomp.). Diazotisation of 6-amino-1-methyl-1: 2: 3-benztriazole (Brady *et al.*, A. 1931, 239; best obtained by catalytic reduction of the 6-NO₂-compound) affords the 6-OH-derivative

(VI), m.p. 151°, which condenses with 40% CH₂O in EtOH-NaOAc to di-(6-hydroxy-1-methyl-1:2:3-benztriazole-7-)methane, sinters 230°, m.p. 242° (Ac2 derivative, m.p. 236°). With Br-AcOH (VI) gives its 7-Br-derivative, m.p. 159°, converted by CHCl₃-HNO₂ (d 1.52), through the nitrobromo-ketone, into 6:7-diketo-, decomp. > 100°, and by Br-AcOH-NaOAc into 7:7-dibromo-6-keto- (VII), m.p. 117-119°, -1-methyl-6:7-dihydro-1:2:3-benztriazole. (VII) is converted by heating in AcOH-few drops conc. HCl into 5:7-dibromo-6-hydroxy-1-methyl-l:2:3-benztriazole, m.p. 222° (decomp.). With H_2SO_4 -HNO₃ (d 1.4) at < 30°, 1:2:3-benztriazole (VIII) gives its 4-NO2-derivative (IX) (Borsche et al., A., 1911, i, 329), reduced (H₂-Ni-Co-Cu at 100°/80 atm.) to the $4-\dot{N}H_2$ -compound (X), m.p. 149° [Ac, m.p. 241°, and Ac_2 , m.p. 174°, derivatives; benzene-azo-compound, m.p. 244° (Ac₂ derivative, m.p. 284°)], converted by diazotisation into the 4-OH-compound, m.p. 216°, which with Br-AcOH affords its 5:7-Br₂derivative, explodes when heated. Passage of Cl, into (X) in AcOH-fuming HCl and subsequent reduction (SnCl₂-AcOH) of the ketochloride gives 5:6:7-trichloro-4-hydroxy-1:2:3-benztriazole, decomp. > 280°, converted by HNO₃ (d 1.4) into 6:7-dichloro-4:5diketo - 4:5-dihydro - 1:2:3-benztriazole. With HNO₃-H₂SO₄ 1-methyl-1:2:3-benztriazole gives its 7-NO2-derivative (XI), m.p. 203°, the isomeric 4-NO2-derivative, sinters 163°, m.p. 173°, being obtained by Me_2SO_4 from the tautomeric (IX). Catalytic reduction of (XI) gives the corresponding 7- NH_2 -compound, m.p. 121° [4-benzeneazo-compound, m.p. 246° (Ac derivative, m.p. 223°), and, under certain coupling conditions, its 4-(1'-methyl-1': 2': 3'benztriazole-4'-)azo-compound, m.p. 291°]. The corresponding 4-amino-1-methyl derivative with Cl₂ in AcOH-conc. HCl affords 4:4:5:6:6-pentachloro-7keto-1-methyl-4:5:6:7-tetrahydro-, m.p. 176° (decomp.), reduced (SnCl2-AcOH) to 4:6-dichloro-7-hydroxy-1methyl-, m.p. 273° (decomp.), converted by HNO3 (d 1.4) into 4-chloro-6: 7-diketo-1-methyl-6: 7-dihydro-, m.p. 187-188°, which with boiling EtOH-NH₂Ph gives 4-anilo-6-hydroxy-7-keto-1-methyl-4: 7-dihydro-, m.p. 219-221°, -1:2:3-benztriazole. In EtOH-NaOAc, or 2N-HCl, (VIII) condenses with 40% CH₂O to give its 1-hydroxymethyl derivative, m.p. 148° (decomp.) [5-NO₂-derivative, m.p. 133-136° (decomp.), obtained similarly], (III) similarly giving its 1-hydroxymethyl derivative, m.p. 187° (decomp.) [giving (IV) with AcCl-C₅H₅N-CHCl₃], isomerised by 2N-NaOH to the 4-hydroxymethyl derivative, explodes on heating (Ac_3 derivative, m.p. 135°), but when condensation is effected in EtOH-aq. NaOH, the 1:4di(hydroxymethyl) derivative, decomp. 327°, is obtained, whereas in 2N-NaOH the product is di-(5hydroxy-1-hydroxymethyl-1:2:3-benztriazole-4-)methane, decomp. 316-317° (Ac₄ derivative, m.p. 202°),





derivative), probably (B). 5-Hydroxy-1-phenyl-1:2:3-benztriazole with CH₂O similarly gives its 4-hydroxymethyl derivative, m.p. 147°, resolidifying and remelting 220°. β -C₁₀H₇·OH condenses with CH₂O-2N-NaOH to give 2-(1-hydroxymethylnaphthyl) hydroxymethyl ether, m.p. 103—106°, converted by dil. NaOH into di-(2-hydroxynaphthyl)methane.

J. W. B.

N-Phenyl-4-azimidobenzene derivatives. Κ. FRIES, W. FRANKE, and W. BRUNS (Annalen, 1934, 511, 241-267).-2-Phenyl-1:2:3- ψ -benztriazole (I) (A., 1927, 778) with H₂SO₄-KNO₃ at 60° gives its 2-p-NO,-derivative, m.p. 282°, further converted by the same reagent at 70° into its $4-NO_2$ -derivative, m.p. 240° [also by nitration of the 4-NO₂-derivative of (I), and synthesised from 2:6-(NO₂)₂C₆H₃Cl and $p-NO_2 \cdot C_6 H_4 \cdot NH \cdot NH_2$], the 5- NO_2 -derivative of (I) similarly giving its 2- $p-NO_2$ -derivative, m.p. 208°. Reduction of (I) with H₂-Pd-BaSO₄ in AcOH gives its 4:5:6:7-H4-derivative, m.p. 95°. 5-Hydroxy-2-phenyl-1:2:3-4-benztriazole (II) (A., 1912, i, 656; improved prep.) (Me, m.p. 74°, and Et, m.p. 76°, ether) is similarly reduced to 5-keto-2-phenyl-4:5:6:7tetrahydro-1:2:3-4-benztriazole, m.p. 124° (phenylhydrazone, m.p. 190°). With Br-AcOH-NaOAc (II) gives 4: 4-dibromo-5-keto-2-phenyl-4: 5-dihydro-, m.p. 172.5° [reduced by SnCl₂-AcOH or HBr to the 4-Brderivative (III), two forms, yellow, m.p. 128°, and colourless, m.p. 132°, of (II)], converted by HCl-AcOH into (III), 7-chloro-4:4:6-tribromo-5-keto-2phenyl-4:5:6:7-tetrahydro-, m.p. 163° (loses HCl in boiling EtOH to give 4:4:6-tribromo-5-keto-2-phenyl-4:5-dihydro-, m.p. 169°), and 4:6-dibromo-5-hydroxy-2-phenyl-, m.p. 193° (IV) (Ac derivative, m.p. 192°; oxidised by KMnO4 to 2-phenyl-1:2:3-benztriazole-4:5-dicarboxylic acid), $-1:2:3-\psi$ -benztriazole. With CHCl₃-HNO₃ (d 1.52) at 0° (IV) gives 4:6-dibromo-4-nitro-5-keto-, m.p. 191° (decomp.), decomposed by heating in C_6H_6 to 6-bromo-4:5-diketo- (V), m.p. 173°, -2-phenyl-4:5-dikydro-1:2:3- ψ -benztriazole. Heated with NH₂Ph in EtOH (V) gives 6-bromo-7-anilo-5-hydroxy-4-keto-2-phenyl-4:7-dihydro-1:2:3- ψ -benztriazole, m.p. 227°. With CH₂O in N-NaOH (II)gives 2-(4-hydroxymethyl-2-phenyl-1:2:3-4benztriazole) hydroxymethyl ether, m.p. 95°, with loss of CH₂O and H₂O to give di-(5-hydroxy-2-phenyl- $1:2:3-\psi$ -benztriazole-4-)methane, reduced by Zn-NaOH to the 4-Me derivative, m.p. 168°, of (II). The Ac derivative of (II) rearranges with AlCl₃ in CS₂ to $4 \cdot (5 - hydroxy - 2 - phenyl - 1 : 2 : 3 - \psi - benztriazole)$ methyl ketone (VI), m.p. 168° [Ac derivative, m.p. 145° autoxidation in NaOH to a substance, m.p. 340° (decomp.)], the corresponding chloromethyl (VII), m.p. 187° (Ac derivative, m.p. 151°) (using CH₂Cl·COCl), bromomethyl, m.p. 168°, and dibromo-



methyl ketone (VIII), m.p. 189° (Ac derivative, m.p. 191°) [by bromination of (VI)], also being prepared.

With AgOAc-AcOH (VIII) gives the Ac derivative (A, R=OAc), m.p. 218-220° (decomp.), of the 2-OHderivative (A, R=OH), m.p. 174°, of (IX). In boiling EtOH-NaOAc (VII) affords 4:5-(2'-phenyl-1':2':3'triazolo)coumaran-3-one (IX) (A, R=H), m.p. 211°, which condenses with 7-anilo-5-hydroxy-4-keto-2phenyl-4:7-dihydro-1:2:3-4-benztriazole, m.p. 233° (from NH,Ph and the 4:5-diketo-4:5-dihydro-compound), to give the compound (X), m.p. 315°. With Br-AcOH (IX) gives its 2-Br-derivative (A, R=Br), m.p. 206°, converted by NaNO2 into the Na salt of the 2-acinitro-derivative (A, HR=:NO·OH), the corresponding 2-p-dimethylaminoanil (XI) (A, HR= :N·C₆H₄·NMe₂), m.p. 280°, being obtained from (IX) and p-NO·C₆H₄·NMe₂ in aq. EtOH-NaOH. Heated in C_6H_6 with (IX), (XI) gives a compound, $C_{36}H_{26}O_4N_8$, m.p. 207° (decomp.), and with oxythionaphthen in boiling dioxan it gives [4:5-(2'-phenyl-1':2':3'-triazolo)coumaranone]-2-thionaphthen-2-indigo, m.p.285° (decomp.). Reduction of 4-nitro-2-phenyll : 2 : $3-\psi$ -benztriazole with H₂-Ni-Co-Cu at 80 atm. gives the $4-NH_2$ -compound, m.p. 116° (Ac derivative, m.p. 168°), converted by boric acid-2N-H₂SO₄ at 200° into the 4-OH-derivative, m.p. 139° [Ac derivative, m.p. 70° ; 5:7-Br₂-derivative, m.p. 205° (decomp.) (Ac derivative, m.p. 137°)], and the compound, $C_{36}H_{24}N_{10}$, m.p. 280° (best yield if 2N-HCl at 200° is used). Reduction of the o-nitrophenylhydrazone, m.p. 192° (decomp.) (Et_2 ester, m.p. 74°), of CO(CO₂H)₂ with SnCl2-HCl gives the corresponding o-NH2-derivative, m.p. 134° (decomp.) [Ac derivative, m.p. 164° (decomp.)] (reversibly), converted by boiling MeOH into an isomeride, m.p. 141°, and oxidised by $CuSO_4$ -aq. NH_3 to 1:2:3-benztriazole. With o-NO2. C6H4. N2Cl, resorcinol gives its o-nitrobenzeneazo-derivative, m.p. 185°, reduced (Zn-NaOH) to 2-(2': 4'-dihydroxyphenyl)-1:2:3-4-benztriazole, m.p. 200° (Ac2 derivative, m.p. 112°). J. W. B.

Caffeine derivatives. I. 8-Ethers of caffeine. II. Molecular rearrangement of 8-ethers of caffeine. R. C. HUSTON and W. F. ALLEN (J. Amer. Chem. Soc., 1934, 56, 1356—1358, 1358—1359).— I. 8-Chloro- (or -bromo-)caffeine and NaOR (1 equiv.) in ROH give the following 8-ethers : methoxy-, m.p. 172·5—174°, ethoxy-, m.p. 137·5—140°, n-, m.p. 129·5—130·5°, and iso-, m.p. 153·5—154·7°, -propoxy-, n-, m.p. 88·6—89°, sec.-, m.p. 122·5—123·8°, and tert.-, m.p. 158—161·6°, -butoxy-, n-, m.p. 71·8—72·6°, and iso-, m.p. 125—127°, -amyloxy-, n-hexyloxy-, m.p. 52·5—53·6°, n-heptyloxy-, m.p. 61·2—63·6°, allyloxy-, m.p. 124—126°, phenoxy- (I), m.p. 140·4—143°, p-hydroxyphenoxy- (II), m.p. 207—209, benzyloxy-, m.p. 172—173·5°, and phenylethoxy-, m.p. 142—144·5°, -caffeine. Except (I) and (II), all are converted by hot dil. HCl or heating alone at 250—300° into hydroxycaffeine (III) (cf. below).

II (cf. Biltz and Bergius, A., 1917, i, 589). 1:3:7:9-Tetramethyl- and 1:3:7-trimethyl-9. ethyl-, -9-n-propyl-, m.p. $138\cdot8-140\cdot6^{\circ}$, 9-allyl-, m.p. $143-144\cdot5^{\circ}$, and -9-benzyl-, m.p. $187-189\cdot5^{\circ}$, -uric acids are obtained [with (III)] when the requisite ethers (above) are heated in open tubes (cf. loc. cit.) at $170-210^{\circ}$, $245-255^{\circ}$, $250-270^{\circ}$, $170-185^{\circ}$, and $200-205^{\circ}$, respectively. Attempts to rearrange the $\begin{array}{ll} \Pr^{\beta}, \ \mathrm{Bu}^{\alpha}, \ n\text{-} \ \mathrm{and} \ iso\text{-}\mathrm{amyl}, \ \mathrm{hexyl}, \ \mathrm{Ph}, \ \mathrm{p}\text{-}\mathrm{OH}\text{-}\mathrm{C}_{6}\mathrm{H}_{4}, \ \mathrm{and} \\ \mathrm{C}_{2}\mathrm{H}_{4}\mathrm{Ph} \ \mathrm{ethers} \ \mathrm{were} \ \mathrm{unsuccessful}. & \mathrm{H}. \ \mathrm{B}. \end{array}$

Chlorophyll-b. H. FISCHER and S. BREITNER (Annalen, 1934, 511, 183-202).—Rhodin-g-oxime (I) is smoothly converted by Na2CO3-C5H5N into pyrophæophorbide-b-oxime (II) and, similarly, rhodin-g ester into pyrophæophorbid-b (III) thus establishing the presence of the isocyclic ring in chlorophyll-b and of :N.OH in the same positions in (I) and (II). Rhodinporphyrin-g Me₃ ester is transformed by AcOH-HBr at 45-50° into pheoporphyrin- b_4 (Me ester, C₃₄H₃₄O₄N₄, m.p. 262°). Rhodinporphyrin-g is converted by protracted heating with HCO₂H into rhodinporphyrin- g_5 (IV) (Me ester, $C_{35}H_{38}O_5N_4$, m.p. 264°). Energetic degradation of (IV) with alkali leads to phyllo- and rhodo-porphyrin. The oxime of (IV) has m.p. 263°. Rhodin-g and HCO₂H at 80° give neorhodin porphyrin-g₃ (V), C₃₂H₃₂O₃N₄ (Me ester, m.p. 243°, and its oxime, m.p. 245°), and a substance converted by CH₂N₂ into the Me ester C₃₃H₃₆O₄N₄, m.p. 239° (oxime, m.p. 255°). Boiling 20% HCl transforms (V) into a compound (Me ester $C_{33}H_{36}O_4N_4$, m.p. 232°). Subjection of the Fe salt of (V) to the keto-



reaction gives a new porphyrin (Me_2 ester $C_{34}H_{36}O_4N_4$, m.p. 205°), which does not contain CO. The presence of CH is established by its production from rhodin-*g*, its catalytic reduction to phylloporphyrin, and its oxidation to citraconimide, thus indicating the structure given for (V). Rhodin-*g* Me₃ ester and CHN_2 ·CO₂Et give a product which is hydrolysed and re-esterified (CH_2N_2) to a Me_2 tetracarboxylate $C_0H_{44}O_9N_4$, m.p. 231°, in which CO is intact. Since (I) reacts similarly, the CH₂ group is involved. Under like conditions, neorhodinporphyrin- g_3 Me ester and CHN_2 ·CO₂Et afford the Me ester $C_{36}H_{36}O_5N_4$, m.p. 230°. (III) and rhodin-*g* are therefore (III) and (VI).



Chlorophyll. VIII. Pyrophæophorbins-a and -b and their oximes. A. STOLL and E. WIEDE-

MANN (Helv. Chim. Acta, 1934, 17, 837-851).--Methylphæophorbid-a-oxime (I) in C5H5N is converted by short treatment with boiling KOH-MeOH into pyrophæophorbin-a-oxime (II), m.p. > 280°, which very closely resembles (I) in colour and absorption spectrum. (II) is readily transformed by HCl-MeOH at room temp. into the Me ester, softens at 310° (corr.), and is hydrolysed by HCl containing Et₂O to pyrophæophorbin-a, $C_{33}H_{36}O_3N_4$, m.p. 235° (corr.). Similarly, methylphæophorbid-b-dioxime (III) is hydrolysed by alkali to pyrophæophorbin-bdioxime (IV), the colour and spectrum of which in $Et_2O-C_5H_5N$ are closely similar to those of (III). With cold HCl-MeOH (IV) yields the Me_2 ether, of the set softens at 315° (corr.), and is transformed by HCl-Et₂O into pyrophæophorbin-b-monoxime (II) [Me ester, m.p. (indef.) 207° (corr.)]. Protracted acid hydrolysis of (IV) leads to pyrophæophorbin-b, which closely resembles phæophorbid-b in colour and spectrum. H. W.

Bile pigments. VI. Biliverdin, uteroverdin, and oocyan. R. LEMBERG (Biochem. J., 1934, 28, 978-987; cf. A., 1932, 627, 1266).—Improved preps. are described for biliverdin (I), mesobiliverdin (II), and their Me₂ esters. (I) forms the first (green) stage of the Gmelin reaction. The formula C33H34O6N4 for (I) is confirmed. The Me2 ester of (I) crystallises in two forms, one from prep. of pure bilirubin (III) and the other from natural (I) (oocyan and uteroverdin) and from (III) mother-liquors. Crystallographic investigation shows that the two forms are not structurally different substances. Cryst. monochlorides are obtained from (I) (green needles), (II) (green needles), (I) Me₂ ester and (II) Me₂ ester (m.p. 175-176°, sinters). The ester of (II) gives complex salts with Zn and Cu, the Zn salt lacking the typical fluorescence of pyrrole pigment Zn complexes. A formula for (I) is suggested. C. G. A.

Alkaloids of Anabasis aphylla. VIII. Products of the oxidation of anabasine. G. MENSCHIKOV, M. LOSSIK, and A. OREKHOV (Ber., 1934, 67, [B], 1157—1158).—Benzoylanabasine in boiling H₂O is oxidised by KMnO₄ to δ -benzamido- δ -3-pyridyl-n-valeric acid (I), m.p. 145—146°, $[\alpha]_{\rm D}$ $\pm 0^{\circ}$, hydrolysed by 12N-HCl to δ -amino- δ -3-pyridyln-valeric acid dihydrochloride (II), m.p. 172°, which gives the corresponding lactam (III), C₁₀H₁₂ON₂, m.p. 147—147.5°, when heated at 160°. The physiological activity of (I), (II), or (III) is < that of anabasine. H. W.

[Yohimbine.] G. BARGER (Ber., 1934, 67, [B], 1124—1125).—A comment on the publication of Hahn *et al.* (this vol., 667). H. W.

[Yohimbine.] G. HAHN (Ber., 1934, 67, [B], 1211).—A reply to Barger (see above). H. W.

Constitution and synthesis of salsoline. E. SPATH, A. OREKHOV, and F. KUFFNER (Ber., 1934, 67, [B], 1214—1217; cf. Orekhov *et al.*, A., 1933, 727; this vol., 787).—The identity of *ON*-dimethylsalsoline with carnegine is placed beyond doubt. *iso*Vanillin, CH₂PhCl, and KOH in boiling EtOH afford isovanillin benzyl ether, m.p. 62—63°, transformed by MeNO₂ and KOH in EtOH at 0—10° into

 α -nitro- β -3-benzyloxy-4-methoxyphenylethylene (I), m.p. 129-130°. (I) is reduced by Zn dust and AcOH in EtOH to 3-benzyloxy-4-methoxyphenylacetaldoxime, m.p. 120-122°, converted by Na-Hg in AcOH-EtOH into \$-3-benzyloxy-4-methoxyphenylethylamine, m.p. 43-44° (picrate, m.p. 144-146°). The Ac derivative, m.p. 128-128.5°, of the base is transformed by P2O5 in boiling PhMe and subsequent reduction with Sn and HCl into 6-hydroxy-7-methoxy-1-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 223-224° (vac.), identical with natural salsoline. In like sequence vanillin benzyl ether is transformed successively into α -nitro- β -4-benzyloxy-3-methoxyphenylethylene, m.p. 122-123°, 4-benzyloxy-3-methoxyphenylacetaldoxime, \$-4-benzyloxy-3-methoxyphenylethylamine, m.p. $68-70^{\circ}$ [picrate, m.p. $174-176^{\circ}$ (vac.); Bz derivative, m.p. $134-135^{\circ}$], acet- β -4-benzyloxy-3-methoxyphenylethylamide, m.p. $116-117^{\circ}$, and 7-hydroxy-6-methoxy-1-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 174-176° (vac.). H. W.

Rotatory dispersion of the quinine salts of the Codex. E. CANALS, M. MOUSSERON, and S. PER-ROTET (J. Pharm. Chim., 1934, [viii], 19, 578–589).— $[\alpha]_{3790}^{4}$, $[\alpha]_{3461}^{6}$, and $[\alpha]_{479}^{6}$ are tabulated for the basic valerate, hydrobromide, hydrochloride, and formate and the neutral sulphate, hydrobromide, and hydrochloride of quinine. The val. of $[\alpha]$ depends mainly on the $p_{\rm H}$ of the solution; this also influences the rotatory dispersion, which conforms to Drude's expression. H. N. R.

Separation of *d*- and *dl*-lupanines. J. F. COUCH (J. Amer. Chem. Soc., 1934, 56, 1423-1424).— The mixture, b.p. 220-226°/12 mm., m.p. 67-81° (softens at 40°), $[\alpha]_{23}^{ab}$ +32.02° in EtOH, of *d*- (I) and *dl*- (II) -lupanine, obtained from white lupin seeds, is extracted four times with warm light petroleum. Recrystallisation of the insol. material from COMe₂ gives (II). Crude (I), obtained by cooling the extract, is purified through the *d*-camphorsulphonate and hydriodide. H. B.

Alkaloids of Convolvulus pseudocantabricus. II. A. OREKHOV and R. KONOVALOVA (Ber., 1934, 67, [B], 1153—1156).—The crushed seeds are moisted with 25% NH₃ and percolated with C_6H_6 . The solution is extracted with 10% HCl which is made alkaline with NH₃ and extracted with CHCl₃. The dried extract is evaporated and the residual crude alkaloids are transformed into their hydrochlorides, which are separated by 96% EtOH into (mainly) convolvine hydrochloride and convolvamine hydrochloride, m.p. 237—239°. Convolvamine (I),

 $C_{17}H_{23}O_4N$, has m.p. 114—115°, $[\alpha]_D \pm 0^\circ$ [picrate, m.p. 263—264° (decomp.); platinichloride, m.p. 216— 217°; aurichloride, m.p. 201—202°; methiodide, m.p. 257—259°]. (I) is hydrolysed by boiling KOH-EtOH to 3:4-(OMe)₂C₆H₃·CO₂H (II) and tropine (III) and hence is veratroyltropeine. Its synthesis from veratroyl chloride and (III) in boiling PhMe is recorded. Convolvine is also an alkamine ester and affords (II) when hydrolysed. H. W.

Ring closure of (-)-norprotolaudanosine to (-)-tetrahydroprotoberberine and configuration of bases of the type of tetrahydroberberine. W. LIETHE (Ber., 1934, 67, [B], 1261-1263).-dl-1Benzyltetrahydroisoquinoline is resolved into its optical antipodes by NH₄ d- α -bromocamphor- π -sulphonate in very dil. AcOH. (-)-1-Benzyltetrahydroisoquinoline (I) has $[\alpha]_{15}^{**}$ -72° in C₆H₆, -44° in MeOH (d- α -bromocamphor- π -sulphonate, m.p. 173°; hydrochloride, m.p. 192°, $[\alpha]_{15}^{**}$ -45° in H₂O). (I) is converted by successive action of HCO₂H at 200° and P₂O₅ in boiling tetrahydronaphthalene into (-)-tetrahydroprotoberberine. The steric relationship of bases of the type of tetrahydroberberine to laudanosine is thus established and the validity of the optical methods of determining configuration of this class of substances is confirmed. H. W.

LXXX. Strychnos alkaloids. So-called "brucinesulphonic acid II." H. LEUCHS (Ber., 1934, 67, [B], 1082-1085).-Specimens of brucinesulphonic acid II (I), forming apparently homogeneous, rectangular leaflets, when treated with boiling 80% EtOH vield brucinesulphonic acid IV (II) in 40% yield, and a mixture of (II) and brucinesulphonic acid III (III) gives the crystals of (I). Re-examination of the products obtained from (I) proves them to be derived from (II); this is expected, since the products from (III) are less readily formed and more difficult to isolate. The "nitroquinone" (IV) and nitroquinol hydrate II (V) and the " aminoquinol II " are derivatives of (II), as are the semicarbazone of (IV), the Et2 ester and the Ac3 compound from (V), and the benzylidene- and benzyl-brucinesulphonic acids from (I). Oxidation of (I) with KMnO4 causes complete decomp. of (II), while leaving (III) intact. H. W.

Strychnine. II. Constitution of strychnine and of Tafel's base. M. KOTAKE and T. MIT-SUWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 119—134).—Tafel's base $C_{24}H_{30}O_3N_2$ (I), m.p. 156° [benzylidene derivative (II), m.p. 168°], obtained from methylstrychnine and NaOEt-EtOH, and the similar base $C_{23}H_{28}O_3N_2$ (III) (benzylidene derivative, m.p. 210°) formed when NaOMe-MeOH is used, with 6N-HCl on a H₂O-bath afford the same compound $C_{22}H_{25}O_2N_2Cl,H_2O$ (IV), m.p. 265—268°, and with 6-N-HNO₃, (I) gives the compound $C_{22}H_{28}O_4N_2$, m.p. 212—213°. With conc. KOH (IV) is converted into the compound $C_{22}H_{24}O_3N_2,3H_2O$. With MeI at 100° (I) affords a methio-lide, m.p. 304°,



from which alkali liberates a syrupy base which -CH₂ with MeI at 100° gives -CH₂ an isomeric methiodide, -CH₂ m.p. 217°. Oxidation of -CH₂ (II) with KMnO₄-COMe₂ -CH₂ gives the (OH)₄-derivative, m.p. 226°. The

dihydro-base obtained by Pd-H₂ reduction of (I) gives a benzylidene derivative, m.p. 204°, similarly oxidised to the $(OH)_2$ -derivative, m.p. 219°. These reactions are discussed on the basis of the structure (A) which is proposed for strychnine. J. W.B.

Sinomenine. XXXIX. Bimolecular derivatives of true thebainone. K. Goto and H. OGAWA (Annalen, 1934, 511, 202–209).–1-Bromothebainone, m.p. 196°, $[\alpha]_{\rm p}^{16}$ –52.0° in EtOH (from thebame), $[\alpha]_{\rm p}^{16}$ –53.7° (from codeine), is obtained ORGANIC CHEMISTRY.

by the action of Br on thebainone (I) in AcOH. The methiodide, m.p. 200° (decomp.), and oxime, m.p. 235° (decomp.) (hydrochloride, m.p. 261°), are described. Pschorr's "S-free ketone," $[\alpha]_{11}^{h} - 45.7^{\circ}$



's "S-free ketone," [α]₁ⁿ -45.7° in EtOH, or Schöpf's "true thebainone," [α]₁ⁿ -46.5° in EtOH, is reduced by Na-Hg to di-8: S'-dihydrothebainone (II), m.p. 303°, [α]₁ⁿ +15.9° in MeOH-CHCl₃[methiodide, m.p. 310° (decomp.); non-cryst. semicarbazone, m.p. 283° (de-2 (decomp.)]. Admixture with an equal amount of its optical

antipode affords dl-di-8:8'-dihydrothebainone, m.p. 307° . (I) is transformed by AuCl₃ in dil. HCl into di-1:1-thebainone (II), decomp. (indef.) 265° after softening at 210°, $[\alpha]_{16}^{16}$ —219.8° in MeOH-CHCl₃ [hydrochloride, m.p. 295°; methiodide, m.p. 250° (decomp.); non-cryst. oxime, decomp. > 298°]. Di-1:1'-dihydrothebainone, large prisms, m.p. 235°, or short prisms, m.p. 258°, $[\alpha]_{11}^{16}$ —159.8° in EtOH, is obtained by hydrogenation (Pd) of (II) or by oxidation of dihydrothebainone with AgNO₃; the methiodide, m.p. 255° after softening at 210° or (+COMe₂) m.p. 235° after softening at 210° or (+COMe₂) m.p. 235° after softening at 200°, $[\alpha]_{17}^{16}$ +158.5° in EtOH (methiodide, m.p. 278°), is obtained by treatment of tetrahydrodisinomenine with NaOH and Na-Hg or of demethoxydihydrosinomenine with AgNO₃.

H. W.

III. H. Organic compounds of germanium. BAUER and K. BURSCHKIES (Ber., 1934, 67, [B], 1041-1045; cf. A., 1933, 1062).-Prolonged interaction of MgPhBr and GeCl₄ in Et₂O-C₆H₆ leads to GePh₄, m.p. 229-230°, and Ge₂Ph₆ (I), m.p. 336-337°, whilst less highly phenylated compounds cannot be isolated. (I) is also obtained from MgPhBr and GeBr₄ if the reaction is protracted (cf. Morgan et al., A., 1925, i, 1197). Similarly p-C₆H₄Me-MgBr et al., A., 1925, i, 1197). Similarly p-C₆H₄Me·MgBr and GeCl₄ afford Ge(p-C₆H₄Me)₄, m.p. 226°, and germanium hexa-p-tolyl, m.p. 345°, obtained in better yield from p-C₆H₄MeBr, Na, and GeCl₄ in boiling Et₂O. GeCl₄ and CH₂Ph·MgCl in Et₂O-C₆H₆ give Ge(CH₂Ph)₄, m.p. 110°, and Ge tribenzyl chloride (II), m.p. 154—155°. Ge(CH₂Ph)₄ and Br in boiling C₂H₄Br₂ yield Ge tribenzyl bromide (III), m.p. 145°, whence the oxide, C₄₂H₄₂OGe₂, m.p. 134— 135°, by means of AgNO₃ or KOH in boiling EtOH, fluoride, m.p. 96°, iodide, m.p. 141°, and (II). (III) is fluoride, m.p. 96°, iodide, m.p. 141°, and (II). (III) is converted by MgEtI in Et.O into Ge tribenzyl ethyl, m.p. 56-57°, and by Na in boiling xvlene into Ge_2 hexabenzyl, m.p. 183-184°. H. W.

Mercuration of hemipinic acid. V. M. RODIO-NOV and T. A. ABLETZOVA (Ukrain. Chem. J., 1933, 8, 322—332; cf. A., 1933, 729).—Hemipinic acid and Hg(OAc)₂ yield a 2:1 mixture of 3:4-dimethoxy-2and 2:3-dimethoxy-6-anhydrohydroxymercuribenzoic acid (I), together with o-veratric acid, originating from the hydrolysis of (I). R. T.

Preparation of mixed organo-magnesium compounds. V. GRIGNARD (Compt. rend., 1934, 198, 2217—2220).—Grignard's method (this vol., 327) gives better results than that of Urion (*ibid.*, 640) as regards the ease of formation of organo-Mg compounds from bromoveratrole, $p-C_6H_4Br_2$, $p-C_6H_4Br\cdot CH_2Br$, and C_6BrMe_5 . Both methods give the same yield with $C_6Me_5\cdot CH_2Br$ because the Br is labile. Double decomp. (cf. A., 1932, 41) is insufficient to explain these reactions. J. L. D.

Aromatic organo-zinc compounds. K. A. Kozeschkov, A. N. NESMEJANOV, and V. I. POTROSOV (Ber., 1934, 67, [B], 1138–1142).—The following compounds are obtained by heating the requisite Hg diaryl with Zn wool in xylene in CO_2 . The liquid is decanted from pptd. Hg and cooled, when the Zn diaryl separates and is preserved in CO2: ZnPh2, m.p. 107°; Zn di-p-fluorophenyl, m.p. 135-136°; Zn di-p-chlorophenyl, m.p. 212-214°, which does not increase in wt. when covered with Et₂O which is allowed to evaporate and affords $Sn(C_6H_4Cl)_4$, m.p. 200°, when treated with SnBr₄ in boiling xylene; Zn di-o-tolyl, m.p. 207-210°; Zn di-p-dimethyl-aminophenyl, m.p. $135-137^{\circ}$; Zn di- β -naphthyl, m.p. 184-186°. Under similar conditions, Zn and $Hg(\alpha-C_{10}H_7)_2$ do not appear to interact. Reaction between Zn and $Hg(\hat{p}-C_6H_4Br)_2$ does not occur appreciably in boiling xylene, whereas at 220-230° complex change takes place without yielding organo-Zn compounds, which, similarly, are not obtained Hg(p-C₆H₄I)₂ at 200-250°. Zn from and Hg(C₆H₄·CO₂Et-p)₂ do not react at 200-210°. Zn and Hg(CH₂Ph)₂ in boiling xylene or at 110° afford H. W. [CH,Ph]2.

Titration curves of proteins.—See this vol., 842.

Salting-out of amino-acids from protein hydrolysates. I. Isolation of tyrosine, leucine, and methionine. E. M. HILL and W. ROBSON (Biochem. J., 1934, 28, 1008-1013).-A simple procedure is described for the isolation from caseinogen hydrolysates (I), and from ovalbumin, of tyrosine (II), methionine (III), and leucine (IV). The yields of (II) and (III) compare favourably with those obtained by other methods. (II) slowly separates when an aq. solution of the residue from the evaporation of (I) is brought to $p_{\rm H}$ 2.4 by addition of NaOH and decolorised by C. The mother-liquor after separation of (II) is brought to p_{π} 6.0 and evaporated until NaCl begins to separate; (III) and (IV) also separate on cooling and float near the surface. (III) is separated from (IV) by formation of an insol. Hg complex (V) with Hg(OAc)₂ in 3% AcOH. To obtain max. pptn. of (V), saturated NaCl solution must later be added. (V) is decomposed by H₂S, and the liberated (III) is isolated by evaporation and crystallising from EtOH- C_5H_5N at p_{Π} 6.0. (IV) can readily be isolated after removal of Hg from the filtrate from (V). Curves are given showing the solubility of (III) in H₂O and in saturated aq. NaCl; the latter does not exhibit dissymmetry as does the corresponding curve for (IV). The isoelectric point of (III) is at $p_{\rm H}$ 6.

A. E. O.

Autoclave splitting of blood albumin with 2% phosphoric acid. V. S. SADIKOV and D. P. MALIUGA (Compt. rend. Accad. Sci. U.R.S.S., 1934, 2, 418-421).-H₃PO₄ has a weaker effect on

albumin than have other mineral acids, 6 hr. in an autoclave at 180° being necessary with 2% acid. Treatment of 1500 g. of white blood albumin yielded 30 g. of a substance (I), C17H29O3N3, m.p. (recryst.) 271.5°; it is optically inactive and contains no NH2 or CO₂H groups. Hydrolysis with conc. HCl yields 2 mols. of leucine and 1 mol. of proline. (I) is repre-sented as $OH \cdot C \cdot NH \cdot C(CH_2 Pr^{\beta}) : C(OH) \cdot N \cdot CH_2 \rightarrow CH_2$. $C(CH_2 Pr^{\beta}) \cdot NH \cdot C(OH) = C \cdot CH_2$

H. N. R.

Simplified Dennstedt method of elementary analysis without the secondary oxygen supply. E. YAMAGUCHI (J. Soc. Chem. Ind. Japan, 1934, 34, 206B).—2—8 mg. of substance are gently heated in a stream of O2. Combustion occurs on a Pt tube filled with Pt wire contained in a SiO, tube.

R. S. B.

Chromic acid method for determining organic carbon. J. W. WHITE and F. J. HOLBEN (J. Assoc. Off. Agric. Chem., 1934, 17, 334-336).-Improvements of the original method (A., 1925, ii, 240) are E. C. S. described.

Determination of sulphur in organic compounds by oxidation with perchloric acid. E. KAHANE and M. KAHANE (Bull. Soc. chim., 1934, [v], **E**. 1, 280-290).-The substance (0.1-0.2 g.) is heated with 0.5 c.c. of 10% aq. I_2O_5 and 2 c.c. of a mixture of $HClO_4$ (d 1.61, 2 parts) and HNO_3 (d 1.39, 1 part). Any escaping H_2S is trapped in bulbs containing some of the I_2O_5 solution. The oxidised residue and the contents of the bulbs are combined, evaporated to fuming, reduced with N₂H₄,2HCl, and S is determined as BaSO4. D. R. D.

Micro-volumetric determination of sulphur and chlorine in organic compounds with the use of an assay balance. D. W. Cowie and D. T. GIBSON (Analyst, 1934, 59, 388-391).-Improvements in Pregl's method for determining S, and modifications enabling simultaneous determination of halogens to be made, are described. E. C. S.

Determination of arsenic in organic compounds. E. KAHANE (Bull. Soc. chim., 1934, [v], **1**, 190-198).—The substance (0.3-0.4 g.) oxidised with 5 c.c. of a mixture of H_2SO_4 (d 1.81, 7 parts), HClO₄ (d 1.61, 2 parts), and HNO₃ (d 1.39, 1 part). After oxidation the liquid is evaporated to fuming, and contains the As as arsenate which is determined by standard processes. D. R. D.

Colorimetric method for the determination of N-acetylglucosamine and N-acetylchondrosamine. W. T. J. MORGAN and L. A. ELSON (Bio-chem. J., 1934, 28, 988—995).—The method of Zuckerkandl and Messiner-Klebermass (A., 1931, 1081) is modified by the use of 0.5*N*-Na₂CO₃ and a glacial AcOH solution of p-NMe2 ·C6H4 ·CHO to give an C. G. A. accuracy of 1-2%.

Determination of aromatic amines. I. Use of potassium bromide in [nitrite] titration. S. UENO and H. SEKIGUCHI. II. Determination of mixed primary, sec., and tert. arylamines. S. UENO, S. KANESAKA, and H. SEKIGUCHI (J. Soc. Chem. Ind. Japan, 1934, 37, 235–236B, 236–237B).--

NH₂Ph, the toluidines, aminophenols, and their ethers, are rapidly and accurately determined by titration with NaNO, in acid solution in presence of KBr.

II. The above modification of the standard method is equally applicable to mixtures of primary, sec., and tert. arylamines, formation of N- but not of p-nitrosoamine being accelerated equally with diazotisation.

H. A. P. Behaviour of Millon's base. III. M. A. Schwarz (Gazzetta, 1934, 64, 257-260).-With CHPhCl₂ and with CPhCl₃ Millon's base forms compounds analogous, respectively, to those obtained with BzCl and CH, PhCl (A., 1931, 808). T. H. P.

Tetrachlorophthalimide as a reagent in qualitative organic analysis. C. G. F. Allen and R. V. V. NICHOLLS (J. Amer. Chem. Soc., 1934, 56, 1409-1410).-Tetrachlorophthalimide, m.p. 336-337° [from C₆Cl₄(CO)₂O and (NH₄)₂CO₃], and MeOH-KOH in dioxan give the K derivative (I) [the Na derivative, prepared similarly, is less reactive than (1)], which reacts with alkyl halides and halogeno-esters, -ketones, -ethers, and -hydrins at 200° (in sealed tube if b.p. of halide is $< 140^{\circ}$) to give cryst. N-substituted derivatives. The following are described : Me (II), m.p. 210-211°; Et, m.p. 192-193°; Bua, m.p. 153-154°; n-, m.p. 145-146°, and iso-, m.p. 170-171°, -amyl; n-hexyl, m.p. 150-151°; n-heptyl, m.p. 145-146°; n-hexadecyl, m.p. 129-130°; carbo-nbutoxy-, m.p. 151-152°; carbethoxymethyl (III), m.p. 180-181°; carbo-n-butoxymethyl, m.p. 116-117°; αcarbomethoxyethyl, m.p. 165-166°; a-carbethoxyethyl, m.p. 159—160°; α-carbethoxypropyl, m.p. 116—117°; α -carbethoxy-n-butyl, m.p. 113—114°; α -carbethoxy-n-amyl, m.p. 122—123°; β -acetoxyethyl, m.p. 168—169°; amyl, m.p. 122–125; p-acetoxyetnyl, m.p. 100–100, β -hydroxyethyl, m.p. 208–209°; β -phenoxyethyl, m.p. 155–156°; γ -hydroxypropyl, m.p. 165–166°; γ -bromopropyl, m.p. 164–165°; γ -cyanopropyl, m.p. 194–195°; phenacyl, m.p. 258–259°; β -benzoylethyl, m.p. 205–206°. CBr(CO₂Me)₃ and CHBr(CO₂Et)₂ give (II) and (III), respectively; Ph γ -chloropropyl tatone (2:4.dimitronhenylbydrazone m.p. 167°) is ketone (2:4-dinitrophenylhydrazone, m.p. 167°) is H. B. converted into benzoylcyclopropane.

Determination of dihydrocholesterol in presence of coprosterol.-See this vol., 929.

Sensitive and specific reaction for ergosterol. J. BRÜCKNER (Biochem. Z., 1934, 270, 346-348).-Ergosterol (I) is dissolved in 2 c.c. of C₆H₆ or CHCl₃ and 1 c.c. of Ac2O, 0.5 c.c. of COMe2, a crystal of Cu(OAc)₂, and then 0.5-1 g. of anhyd. ZnCl₂ are added. A bluish-violet solution with strong red fluorescence and a characteristic absorption band at 612 mµ is obtained, the reaction being still positive when 1 c.c. of C_6H_6 contains 0.0006 mg. of (1). Vitamin-D (II) under the same conditions gives a reddish-brown solution also showing characteristic absorption. (II) can be detected in irradiated (I) by P. W. C. this reaction.

Truhaut's colour reaction for uric acid. P. K. Bose (Current Sci., 1934, 2, 427).-o-C₆H₄(NO₂)₂ (1), but not pure m-C₆H₄(NO₂)₂(II), produces a violet colour with NaOH and small amounts of uric acid (III). The (II) used by Truhaut (A., 1933, 1314) in testing for (III) probably contained (I), which gave the colour. L. S. T.

Detection of smallest quantities of nicotine. A. WENUSCH (Z. Unters. Lebensm., 1934, 67, 601– 605).—A procedure is described for the isolation of nicotine and its identification by means of tests for the presence of the C_5H_5N nucleus; the absence of the C_4H_4N nucleus (I) before, and its presence after, dehydration; and the presence of a NMe group on (I). E. C. S.

Green coloration of solutions of quinine salts. II. M. BACHSTEZ and G. CAVALLINI (Annali Chim. Appl., 1934, 24, 266—270; cf. this vol., 88).—The Cu content of quinine salt solutions, which under certain conditions makes them green, may be determined photometrically by means of diphenylthiocarbazone, without previous incineration. Usually $4-5 \times 10^{-6}$ g. of Cu per g. is present. The occasional yellow colour of the solutions containing Cu is due to incomplete oxidation caused by lack of O_0 . T. H. P.

Gravimetric and volumetric determination of brucine and strychnine as dichromate. I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Pharm. Assoc., 1934, 23, 404–408).—Brucine (I) and strychnine (II) salts yield ppts. with $K_2Cr_2O_7$, which after drying over deliquescent NaBr have the respective compositions $(C_{23}H_{26}O_4N_2)_2, H_2Cr_2O_7, 5H_2O$ and

 $(C_{21}H_{22}O_2N_2)_2, H_2Cr_2O_7, H_2O.$ (I) and (II) may be detected in concns. > 0.02% by this method, which is suitable for their gravimetric determination. A volumetric method is also described, the EtOH-washed ppt. being dissolved in excess of 0.1N-Fe" solution, and back-titrated with 0.1N-K_2Cr_2O_7. Results for (I) are slightly low, owing to slight oxidation of (I) by K_2Cr_2O_7 even in presence of Fe". A. E. O.

Biochemistry.

Oxygen saturation curves of blood. W. HEROLD (Z. physikal. Chem., 1934, 168, 227–231).— Assuming that the degree of aggregation of the hæmoglobin, α , is uniform in the blood of animals of a particular species, but varies from species to species, and that the heat of binding of an O₂ mol. is const. and independent of the no. of mols. already bound by the complex, an equation is obtained which agrees satisfactorily with many existing data for O₂ and CO absorption curves below about 37° at CO₂ pressures below about 40 mm. The logarithm of the halfsaturation pressure is a linear function of 1/temp. α represents the adjustment of the O₂ absorption to the needs of the particular organism. R. C.

Gas and electrolyte equilibria in blood. XVIII. Solubility and physical state of atmospheric nitrogen in blood-cells and -plasma. D. D. VAN SLYKE, R. T. DILLON, and R. MARGARIA. XIX. Solubility and physical state of uncombined oxygen in blood. J. SENDROY, jun., R. T. DILLON, and D. D. VAN SLYKE (J. Biol. Chem., 1934, 105, 571-596, 597-632).—XVIII. The solubility coeffs. (I) of N₂ at 38° in plasma and cells are 0.0117 and 0.0146, whereas the val. for whole blood depends on the hæmoglobin (II) content and in normal cases is $1-2\% > in H_2O$. Dissolved (II) takes up approx. 13 times as much N₂ as H₂O, and the lipins also dissolve measurable amounts which, in non-lipæmic blood, is 1-2%. There is no evidence of adsorption of (II), as the N₂ taken up follows Henry's law.

XIX. (I) of \tilde{O}_2 at 38°^2} are : $H_2O \ 0.02323$, plasma 0.0209, cells 0.0260, whole blood 0.0230. (II) takes up approx. 1.2 times as much O_2 as does H_2O , and in the whole blood this balances the depressing effect due to dissolved salts and inert protein. When formation of oxyhæmoglobin is prevented, dissolution follows Henry's law. H. G. R.

Biochemistry of respiratory pigments. J. Roche (Bull. Soc. Chim. biol., 1934, 16, 793-821).— A lecture. Oxygen to iron ratio in oxychlorocruorin and the total quantity of oxygen carried by the pigment in Spirographis. H. M. Fox (Proc. Roy. Soc., 1934, B, 115, 368—373).—One mol. of labile O_2 corresponds with one atom of Fe. Large variations were noted in the vals. for chlorocruorin-Fe per g. of worm. H. G. R.

Blood-serum as a hæmoglobin-destroying agent. L. DOLJANSKI and O. KOCH (Virchow's Arch., 1933, 291, 401-409).—Blood-serum of man, rabbit, and fowl can convert hæmoglobin into methæmoglobin and also split off the hæm part of the mol. NUTR. ABS. (b)

Elimination of iron from blood-pigment and hæmatin by means of sulphurous acid and action of light. R. ZEYNEK and S. KITTEL (Z. physiol. Chem., 1934, 224, 233—243).—Hæmatin and hæmochromogen are not affected by SO_2 in the dark, but in the light lose Fe and yield substances resembling hæmatoporphyrin (I), but differing from Nencki's (I) in S content and solubility. Nencki's (I) is similarly affected, so that (I) may be the first product. Blood-pigments similarly lose Fe, but give porphyrinproteoses of varying protein content (40-60%). The sensitisation of white mice by these light-SO₂ products differs little from that obtained with Nencki's (I). J. H. B.

Oxidation and phosphorylation in hæmolysed horse blood-corpuscles. J. RUNNSTRÖM, A. LENNERSTRAND, and H. BOREI (Biochem. Z., 1934, 271, 15—21; cf. Warburg and Christian, A., 1932, 74).—Cozymase (I) from yeast greatly accelerates the oxidation of hexose-mono- and -di-phosphoric acid in hæmolysed horse-blood corpuscles in presence of $PO_4^{\prime\prime\prime}$ buffer and methylene-blue (II), the degree of acceleration depending on the activity of (I) and the condition of the blood. When there is weakening or insufficiency of respiratory co-enzyme (I) acts as substitute. Adenylpyrophosphoric acid (III) sometimes acts like (I), but less effectively. During the accelerated oxidation inorg. P enters into org. combination, but this does not occur if (II) is absent, and dephosphorylation, retarded by (I), takes place. The phosphorylation is inhibited by CH₂I·CO₂H, but not by NaF. The decomp. of added (III) is also retarded by (I). Ascorbic acid does not act like (I). W. McC.

Physico-chemical correlations in the blood and criteria for application to clinical study. M. SIGON (Arch. Ist. Biochim. Ital., 1934, 6, 195-242).--R. N. C. Theoretical.

Mechanism of methylene-blue action on blood. M. M. BROOKS (Science, 1934, 80, 15-16).-A L. S. T. discussion.

Physical properties of blood-serum. M. DOLA-DILHE (Compt. rend., 1934, 198, 1884-1886).-The pptn. of globulin (I) in serum occurs over a zone of p_{Π} with a max. of total pptn. at a definite p_{Π} (II) depending on the degree of dilution. (II) increases with increasing dilution. Heating, by increasing the dispersive power of the albumin, restricts the pptn. zone of (I). C. G. A.

Mol. wt. of the globulins of blood-serum. A. ROCHE and J. BRACCO (Compt. rend., 1934, 199, 98-99).-The mol. wts. (cf. A., 1925, ii, 965) of the serum-globulins of the horse and man are 150,000 and 130,000, respectively. Incubation of horse serum at 0° and 37° during 1-2 months changes the mol. wt. to 136,000 and 226,000, respectively (cf. this vol., 93). The val. for antidiphtheria serum is 213,000.

J. L. D.

Nephelometric determination of the protein fractions of blood-plasma with the step photometer. A. KORANYI and E. B. HATZ (Z. anal. Chem., 1934, 97, 266-270).-Total proteins in 1 c.c. of plasma (8 c.c. of blood +2 c.c. of isotonic Na citrate) are coagulated by 50 c.c. of acid $(NH_4)_2SO_4$ (I) [1·vol. saturated aq. (I) + 1 vol. 0·2N-HCl]. Globulin + fibrinogen are pptd. from 1 c.c. by 25 c.c. of halfsaturated (I), fibrinogen alone by a solution of 27 vols. of saturated (I) + 73 vols. H_2O . The turbidities produced are determined nephelometrically.

J. S. A.

Solubility of serum-proteins in concentrated solutions of neutral salts. A. BONOT (J. Chim. phys., 1934, 31, 301-325).-The solubilities of albumin and pseudo-globulin of ox-serum in aq. $(NH_4)_2SO_4$ have been determined by Sörensen's proportionality method. The limiting solubilities of the different fractions of serum-albumin obtained by pptn. indicate that the protein is a heterogeneous system of which the components are homeomeric. The solubility of a heterogeneous protein may be represented by a modification of Cohn's formula. The structure of the protein micelle is discussed.

M. S. B.

Absolute colorimetry. X. Determination of bilirubin in serum. A. THIEL and O. PETER (Biochem. Z., 1934, 271, 1-8; cf. A., 1933, 1134).-Bilirubin (< 1 unit upwards) is directly determined as azo-derivative by the abs. colorimetric method. W. McC.

Changes in the calcium and magnesium of the serum and in the inorganic phosphorus of the blood of cows at calving and of the calf during early life. W. M. ALLCROFT and W. GODDEN (Biochem. J., 1934, 28, 1004-1007; cf. A., 1932, 1272) .- Serum-Mg (I) tends to increase just before, at, or within 24 hr. of calving, and in general varies inversely with serum-Ca (II). Calves at birth and for the first 8 weeks of life show higher levels of (II) and blood-inorg. P than the normals for the dam. (I) is < normal at birth, but has attained this normal after 3 weeks. A. E. O.

Changes in the p_{π} of the blood of the Japanese beetle (Popillia japonica, Newman) during metamorphosis. D. LUDWIG (Anat. Rec., 1933, 57, No. 4, Suppl., 55-56).-During metamorphosis the $p_{\rm H}$ of the blood changes from an average of 7.07 in the third instar to 6.79 in the late prepupa, whilst pupation is marked by a return to $p_{\rm H}$ 6.94. The increase of acidity during the prepupal stage probably depends on the autolysis of larval tissues.

NUTR. ABS. (b). Determination of p_{π} of plasma using the hydrogen electrode. J. LOISELEUR (Bull. Soc. Chim. biol., 1934, 15, 612-617).-Some modifications of the apparatus of du Nouy (A., 1932, 135) permit the p_{π} determination to be made in 20 min. A.L. with an accuracy of 0.01.

Blood-sugar and -lactic acid during perfusion of the spleen. N. FIESSINGER, H. BENARD, R. CATTAN, and M. HERBAIN (Compt. rend. Soc. Biol., 1933, 114, 479-481).-Perfusion of the spleen with oxalated or defibrinated blood caused a fall in bloodsugar (I), accompanied by a rise in -lactic acid (II). No proportionality existed, however, between the decrease in (I) and the (II) formed. The living cells, supplied by partly oxygenated blood, probably accelerate one or other of two reactions, anaerobic [producing (II)] and aerobic [destroying (II)].

NUTR. ABS. (b) Effect of iodoacetic acid and other substances on the disappearance of glucose from shed blood. D. M. MOWAT and C. P. STEWART (Biochem. J., 1934, 28, 774–778).— $CH_2I \cdot CO_2H$ (I) and $CH_2Br \cdot CO_2H$ prevent glycolysis in shed human blood, the requisite concn. in each case being much > that required for (I) to prevent lactic acid formation in cardiac muscle. CH₂Cl·CO₂H, CHMel·CO₂H, and CH₂I·CH₂·OH (II) have similar though weaker actions, but $CH_2I \cdot CH_2 \cdot CO_2H$ is inactive. The action of (I) but actions, but not of (II) is inhibited by glutathione (III), and (II) does not react with (III) to produce HI. It thus appears that the action of (II) on glycolysis is different from that of (I). Both (I) and (II) inhibit the action W. O. K. of blood-phosphatase.

Antiricin. R. GRUTZNER (Biochem. Z., 1934, 271, 32-53; cf. A., 1931, 507).-Dried sterile sera containing antiricin slowly lose their activity on long keeping, but activity is completely restored by cold treatment for 20 hr. with 0.05-0.01N-NaOH in physiological aq. NaCl and subsequent neutralisation. This process also increases the activity of dry or other sera. Fractional pptn. with COMe2 or EtOH followed by the treatment causes preferential accumulation of active material (I) in the first fraction or fractions. The activity of (I) is reduced but not

destroyed by dil. H_2O_2 and HNO_2 , and unaffected by dil. CH_2O , MeCHO, PhCHO, salicylaldehyde, and furfuraldehyde. H_2SO_3 has no effect, but H_2S , cysteine, and KCN irroversibly reduce the activity. Possibly the sera contain a precursor of antiricin.

W. McC. Swelling of the lens of the eye. F. P. FISCHER (Kolloid-Z., 1934, 67, 317—321).—The degree and velocity of swelling have been determined in acids, alkalis, and salts of different conen. Non-electrolytes diminish the swelling. The capacity of the lens for binding H_2O is < that of the cornea or corium, but the intensity of binding is greater. There is no direct relation between swelling and transparency or permeability of the lens. E. S. H.

Sedimentation constants of muscle-proteins. H. J. DEUTICKE (Z. physiol. Chem., 1934, 224, 216— 228).—By means of the ultra-centrifuge, from extracts of fresh frog's muscle a protein component with sedimentation const. (I) 7.57×10^{-13} was separated from a residue, from which sometimes there was obtained a component with (I) 1.06×10^{-13} . After muscular activity the first (I) is unchanged, indicating the absence of new protein of different mol. size. In extracts from rabbit's muscle, protein components having (I) vals. of 7.70 and 5.39×10^{-13} were obtained, the residue being negligible. The stability region of these proteins is between $p_{\rm H}$ 5-1 and 5-5. J. H. B.

Nucleoprotein-purines in muscle. B. UMSCR-WEIF (Bull. Soc. Chim. biol., 1934, 16, 543—549).— Guanine and adenine are the only purine bases found in the deproteinisation ppt. of muscle obtained by boiling in slightly acid aq. solution, and the ratio of the quantities present is similar to that in nucleic acid. Hypoxanthine is found only in the aq. extract. In muscular metabolism therefore only the adenine of the nucleotides is concerned, and not that of nucleic acid or nucleoprotein. A. L.

Nucleoproteins of fish-testes. H. VON EULER and G. SCHMIDT (Z. physiol. Chem., 1934, 225, 92— 102).—Fish-testes (I) contain only traces of phosphoproteins. Substances rich in P are obtained by pptn. at $p_{\rm H}$ 7 from the nucleoproteins (II) extracted with aq.NH₃from (I); these are probably nucleoprotamines, and are more viscous than the (II) pptd. at acid reaction. The mol. ratio purine-N/P was 5/2, as for thymus-nucleic acid, for all (II) examined. The N distribution indicates that the changes on ripening occur principally in the protein constituents of (II).

J. H. B.

Carotenoids and the vitamin-A cycle in vision. G. WALD (Nature, 1934, 134, 65).—The combined pigment and choroid layers of R. esculenta and R. pipiens (dry wt. approx. 2·2 mg.) contain approx. 4×10^{-6} g. per eye of vitamin-A (I) and approx. 10^{-6} g. of another carotenoid possessing the properties of xanthophyll (II). These amounts are not appreciably altered by light or dark adaptation. The retinas of dark-adapted animals contain no (II) and only a trace of (I), but CHCl₃ extracts a third carotenoid, retinene (III), which shows a small absorption max. at approx. 410 mµ and larger ones at 310 and 280 mµ. (III) gives a strong blue colour with SbCl₃ due to a sharp band at 655 mµ. In light-adapted retinas, (III) disappears and is replaced by (I). The mechanism of this change is described. C_6H_6 and CS_2 extract no (III). (I) is bound in visual purple (IV) and yellow to a colourless mol. insol. in fat solvents, and $CHCl_3$ breaks this complex to yield (III). Visual pigment appears to be a carotenoid protein; (IV) is probably a conjugated protein in which (I) is the prosthetic group. L. S. T.

Yellow feather-pigment of the canary [Serinus canaria canaria (L.)] and the occurrence of carotenoids in birds. H. BROCKMANN and O. VOLKER (Z. physiol. Chem., 1934, 224, 193-215).-On a carotenoid-free diet the plumage of canaries becomes white (after moulting). Addition of lutein (I) or zeaxanthin (II) to the diet restores the yellow colour. Violaxanthin (III), β -carotene (IV), and lycopene (V) have no effect. In many birds the yellow plumage-colour is due to (I), often accompanied by its two degradation products, "canary-xanthophyll" and the "picofulvin" of the woodpecker. Indefinite degradation products of (I) or other carotenoids [(II)] may be present. Similar observations on the yolk of hen's eggs show that only (I) and (II) restore the colour, not (III), (IV), or (V). Thus only the xanthophylls with two OH groups appear to produce pigments. The pigment of the red papillæ around the eye of the pheasant (Phasianus colchicus) is probably astacene. J. H. B.

Body-fats of the hen. T. P. HILDITCH, E. C. JONES, and A. J. RHEAD (Biochem. J., 1934, 28, 786– 795).—The body-fats belong to the group containing 30-35% of saturated acids. About 65% of the fats belong to the C_{18} series (oleic 35-38%, linoleic 20-22%). Small quantities of C_{20-22} unsaturated acids and 7-8% of palmitoleic acid suggest a relationship of these fats to marine-animal fats. Palmitic acid 25-30%, stearic acid 5-7%, and only traces of myristic acid are present. The fats from abdomen, gizzard, and neck were approx. identical, whilst the composition of the diet, which in no case contained > 4% of fat, had little effect. W. O. K.

Fatty acids of pig liver. I. Octadecenoic acids and the desaturation theory. H. J. CHANNON, E. IRVING, and J. A. B. SMITH (Biochem. J., 1934, 28, 840—852).—The unsaturated fatty acids of pig's liver were oxidised by KOH-KMnO₄ (A., 1925, i, 1129, 1234) and the (OH)₂-acids separated. Fractionation by EtOH-Et₂O (I:1) indicated the presence of \leq two octadecenoic acids, of which \leq 80% was oleic acid and the residue mainly an acid, m.p. 117— 120°, probably the Δ^{\times} acid. The Δ^{λ} acid was not evident (cf. A., 1909, ii, 597). The results, together with the inability of the animal to synthesise certain unsaturated acids (A., 1932, 961), appear to invalidate the theory of desaturation of fatty acids by the liver. F. O. H.

Protein-linking of physiologically important substances. Condition of glycogen in liver, muscle, and leucocytes. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem., 1934, 225, 103-124).—The solubility of glycogen (I) of liver, muscle, and leucocytes and the composition of the (I)-protein ppts. obtained from the extracts was examined. Dissolution was attained by heating with H₂O for 15-30 min. and by the action of 2% CCl₃·CO₂H. Goose-liver contains very variable amounts of (I), the (I)-rich liver (II) contains most of the (I) in sol. form, in the (I)-poor liver (III) the greater part is firmly bound. The (I)-protein ppts. from (II) show high (I), from (III) low (I), content. Typical (I)proteins yield 66-75% of glucose. Muscle and leucocytes show similar relations in respect of sol. and insol. (I) content. The respective terms lyo-(I), desmo-(I), and "symplex" are employed for sol. and insol. (I), and any complex such as (I)-protein, formed by the action of residual affinities. J. H. B.

Liver-glycogen. D. J. BELL and F. G. YOUNG (Biochem. J., 1934, 28, 882—889).—Examination of the reducing power, $[\alpha]$, ash content, coloration with I, and polarimetric behaviour on hydrolysis with aq. acids fails to reveal any significant difference between the glycogen (I) from the livers of fasted or fed rabbits, rats, or fish (cod, haddock, whiting). Pptn. from aq. solution by AcOH to 80% concn. affords a highly purified ash-free (I). Treatment with 30% KOH at 100° for 2—3 hr. does not influence the properties of (I) (cf. A., 1932, 1022). F. O. H.

Distribution of glycogen in the organs of Sepia. M. CHAIGNE (Compt. rend. Soc. Biol., 1933, 114, 1103—1105).—Glycogen (I) was found not only in the liver and muscles, but in practically all organs, the amount varying with the time of year. This may be related to the sexual cycle. The (white) nidamental organs of the female in spring contain 10 times as much (I) per g. of tissue as in October.

NUTR. ABS. (b)

Galactogen. V. F. MAY (Z. Biol., 1934, 95, 277-297).—Galactogen [from snails or their eggs (A., 1932, 415)], decomp. $245-250^{\circ}$, gives no colour with I, is not hydrolysed by saliva or yeast, and does not reduce alkaline Cu solutions, but is pptd. as a Cu complex. Oxidation by HNO₃ gives mucic acid. The ash (2.85%) is mainly P and Fe, which are probably intrinsic parts of the mol. Hydrolysis by dil. acids yields galactose, $[\alpha]_p +53^{\circ}$, which exhibits no mutarotation and is probably a modification of β -galactose (A., 1897, i, 391), into which it is converted by treatment with EtOH etc. The differentiation of galactogen from glycogen by staining methods etc. and the quant. separation of the two polysaccharides are discussed. F. O. H.

Variations in copper content of organs of the edible snail. R. GUILLEMET and A. SIGOT (Compt. rend. Soc. Biol., 1933, 114, 1041—1043).—The Cu contentisabout0.003% of the total wt. whether fasted or fed. About half of this Cu is in the blood and most of the residue is in the muscle and teguments. The liver and pancreas do not appear to act as storage organs for Cu. NUTR. ABS. (b)

Iodine survey of New Zealand live-stock. II. Sheep of the Wairarapa district. P. H. SYKES (Trans. Roy. Soc. New Zealand, 1934, 64, 17-34).— The I content of thyroids of sheep grazing on different soil types attained different mean vals. Sex differences in this respect were not observed. A decrease in the relative and abs. amounts of I in the gland is associated with an increase in fresh and dry wts. Use of iodised licks for lambs during 2 months prior to killing increased the I of the glands, but no other effects were apparent. A. G. P.

Improved fixing solution for methylene-blue preparations. E. C. COLE (Stain Tech., 1934, 9, 89—90).—A mixture of 50 c.c. of distilled H₂O, 50 c.c. of glycerol, and 15 drops of conc. HCl is saturated with NH₄ molybdate. H. W. D.

Variations in the reaction of spiders' venom. J. VELLARD (Compt. rend., 1934, 198, 2123—2124).— The venom secretion (after initial emptying of the glands) of *Ctenus*, *Nephila*, and *Lycosa*, kept at 15°, is always acid, whereas that of spiders kept at 33° (other conditions const.) is alkaline, the latter being the more toxic. Species, age, sex, and other physiological factors are without effect. J. W. B.

Colloidal phosphate of milk. G. T. PYNE (Biochem. J., 1934, 28, 940—948).—Ca caseinogenate (I) and the colloidal Ca phosphate (II) in milk are considered to be in chemical combination. The effect of oxalate on the titratable acidity of milk and caseinogen–Ca phosphate complexes indicates that the inorg. colloid constituent is mainly a double salt of (I) and $Ca_3(PO_4)_2$. C. G. A.

Colloidal behaviour of sericin.—See this vol., 842.

Spectrography of ox-bile. C. GAUTIER and R. RICARD (Compt. rend., 1934, 198, 2026—2028).— The ash of ox-bile gives in the C arc lines of Na, K, Ca, Mg, P, Fe, Mn, Cu, and Al, the first five elements being relatively abundant. R. S. C.

Excretion of dyes by the liver. Y. TADA (Japan, J. Gastroenterol., 1933, 5, 191—200).—Dyes are removed from the blood into the bile by the parenchymatous cells of the liver. CH. ABS.

Excretion of dyes after experimental liver injury. E. WAKABAYASHI (Japan. J. Gastroenterol., 1933, 5, 201–235).—Excretion is influenced similarly by chemical or parasitic degeneration of the parenchymatous cells. CH. ABS.

Relation between chemical constitution and excretion of dyes by the liver and kidneys. Y. TADA and K. HISHIKAWA (Japan. J. Gastroenterol., 1933, 5, 187—190).—Monoazo-dyes with one sulphone group are excreted chiefly through the kidneys; with two such groups more is found in the urine, and with three, 41.9% was excreted in the urine and 6.4% in the bile. CH. ABS.

Urinary excretion of total fixed mineral bases and ammonia. M. CHATRON (Compt. rend. Soc. Biol., 1933, 114, 1100—1102).—Urinary excretion of fixed base is independent of excretion of acid radicals. Excretion of NH₃ maintains an approx. const. $p_{\rm H}$ in spite of variations in excretion of fixed base or acid. High NH₃ excretion may indicate a high abs. acid or low fixed base excretion. NUTR. ABS. (b)

for solubility losses. Urea and NH_2 -acids do not interfere. (I) in calculi can be determined directly, also total $PO_4^{\prime\prime\prime}$ by pptn. with MgO mixture.

R. N. C.

Renal elimination of injected urea and creatinine. W. W. KAY and H. L. SHEEHAN (J. Physiol., 1933, 79, 359-415). - In rabbits increase in the concn. of urea or creatinine (I) in the blood causes reduction of the extraction ratio (amount of the substance retained by the kidney expressed as % of the total quantity carried to it by the blood), although the abs. amount removed per unit of blood increases. When the concn. of (I) is increased, the quantity of urea excreted is considerably decreased. Increase in the urea concn. does not affect the excretion of (I). The results confirm neither the secretion nor reabsorption theory of renal activity, but show that under certain conditions a return of urea from the tubules to the blood occurs. NUTR. ABS. (m)

Presence of *d*-allantoin in animals. P. E. THOMAS and P. DE GRAEVE (Compt. rend., 1934, 198, 2205-2207).—*d*-Allantoin, $[\alpha]_{12}^{22}$ +93° in H₂O, was isolated from calves' urine. (I) is fermented by allantoinase at 40° to allantoic acid more rapidly than the *l*-isomeride, which explains the "production" of the latter during fermentation of *dl*-allantoin.

R. S. C.

Renal excretion of carbohydrates in man. E. J. BIGWOOD (Ann. Physiol. Physico-chim. biol., 1932, 8, 401-409).—If all the reduction is due to sugar, urine of fasting normal subjects contains 0.2-2 g. per litre (average 0.8-0.9 g.) of non-fermenting carbohydrates (I). (I) appear to be a mixture, and the reducing power is increased by hydrolysis, the total reduction then corresponding with a physiological excretion of carbohydrate equiv. to 0.1-1.2 g. of C per litre. NUTR. ABS. (m)

Excretion of urine in the dog. VII. Inorganic phosphate in relation to plasma-phosphate level. R. F. PITTS (Amer. J. Physiol., 1933, 106, 1-8).-In normal dogs in which inorg. $PO_4^{\prime\prime\prime}$ has been injected intravenously the $PO_4^{\prime\prime\prime}$ clearance (I) is a curvilinear function of the plasma conen. (II). At low (II) (1.1-1.5 m.-mol.) the urine is $PO_4^{\prime\prime\prime}$ -free, but as (II) is raised the (I) rises and approaches the xylose or sucrose (glomerular) (I) without ever exceeding it. The relationship does not hold in phloridzinised dogs. NUTR. ABS. (b)

Excretion of urinary products by the gastrointestinal tract in nephrectomised dogs. I. Vicarious secretion. G. HESSEL. II. Gastric secretion in nephrectomised dogs. III. Bile secretion in nephrectomised dogs. IV. Withdrawal of gastric and duodenal juice by jejunal fistula. V. Presence in digestive juices of waste products normally excreted in urine and the symptomatology and course of uræmia. G. HESSEL, E. PEKELIS, and H. MELTZER (Z. ges. exp. Med., 1933, 91, 267-273, 274-306, 307-324, 325-330, 331-339).—In nephrectomised dogs (I) with gastric fistula the % of HCl and total Cl show no significant increase in the uræmic state, but waste aubstances (urea, creatinine, indican, phenols) reach high vals., which, however, are < the concns. in the blood at the same time. Hence this is not a true vicarious secretion of urinary waste products. The total amount of urea excreted by the stomach is 12-40 mg. per hr. In (I) with gall-bladder fistula the total vol. of bile and its concns. of total N, nonprotein-N, urea, NH₃, and indican all rise in the uræmic state. The % of urea, non-protein-N, and occasionally indican are slightly greater in the bile than in the blood, possibly due to active secretion or to simple concn. of the bile. The total N in the bile is 19-56 mg. per hr. In (I) with high jejunal fistula the concns. of total N etc. are increased, the % of non-protein-N and urea being > those in the blood. (I) with fistulæ live about 60% longer than those without, and the blood-urea and indican rise much more slowly. NUTR. ABS. (m)

Reduction of the iodo-mercuric reagent of Baudouin by a coloured sulphur compound of normal urine. B. Gwożdź (Bull. internat. Acad. Polonaise, Classe Méd., 1933, No. 2—5, 267—277).— From normal human urine, from which SO_4'' and PO_4''' have been removed, a S compound can be pptd. by the addition of $Cu(OAc)_2$. The yellow ppt. contains neutral S and reduces the alkaline HgI₂ solution of Baudouin, Pénau, and Tanret. 17—25% of the reducing power of this ppt., which changes with the diet of the subject, corresponds with the neutral S contained : 1 mg. of S corresponds with 8 mg. of Hg reduced. NUTR. ABS. (b)

Isolation of crystalline stercobilin. C. J. WATSON (J. Biol. Chem., 1934, 105, 469-472).-Human fæces are ground with abs. AcOH and exhaustively extracted with Et₂O with additions of further AcOH. The Et₂O is removed in vac. and the residue poured into 6-8 vols. of 1% HCl, kept over-night, and filtered from pptd. fatty acids, coprosterol, copronigrin, and chlorin-e. The filtrate is neutralised with NaOAc and extracted first with Et₂O to remove copromesobiliviolin, and then with CHCl₃. The CHCl₃ extract is repeatedly extracted with H₂O, the extract is acidified with HCl, and the stercobilin re-extracted as hydrochloride (I) with $CHCl_3$. The extract is dried (Na_2SO_4) and (I) pptd. by light petroleum and purified by crystallisation from CHCl₃. The free base is liberated by 0·1N-NaOH in presence of CHCl₃. H. A. P.

Effect of the proportions of fat and carbohydrate in the diet on excretion of metabolic nitrogen in the fæces. H. H. MITCHELL (J. Biol. Chem., 1934, 105, 537-546).—Excretion of metabolic N (I) in fæces is not affected by substitution of fat for starch, although the total dry wt. is increased. At low levels of food intake on a low-fat diet, the ratio of (I) to dry matter consumed is increased, due to the prominence of a fraction of (I), which is const. for each organism. At higher levels this fraction is negligible compared with that due to residues of digestive secretions. H. G. R.

Dependence of the quantity of fæcal nitrogen on volume of fæces. W. HEUPKE (Arch. Hyg., 1933, 111, 188—195).—The total amount of N excreted daily in the fæces is directly related to their daily dry wt., 1 g. of N and 1-2 g. of Et₂O extract being found for every 20 g. of dry matter. NUTR. ABS. (m)

Loss of nitrogen and sulphur on drying fæces. D. P. CUTHEERTSON and A. K. TURNBULL (Biochem. J., 1934, 28, 837—839).—The drying of fæces at 100° for 10—14 days produces a marked loss of N (mainly as NH_3) and of S (mainly as H_2S). The latter is prevented by addition of Cu acetate, whilst drying in a current of NH_3 -free air allows liberated NH_3 to be trapped by acid and subsequently determined. F. O. H.

Merino fleece. I. Suint. M. F. FRENEY (J.S.C.I., 1934, 53, 131–1347).—Suint samples vary greatly in composition, but lower fatty acids and hippuric, lactic, and succinic acids were identified in those examined. Bacterial decomp. in the fleece probably accounts for the small amounts of urea and NH_3 found, and for the N bases detected. Suint differs from dry human sweat in containing considerably more K and much less Na and Cl'.

Case of alcaptonuria. A. P. U. CINTRA (Rev. Med.-Cirur. Brazil, 1933, 41, 219).—There were no signs of ochronosis. Homogentisic acid was excreted in the urine at the rate of 7.14 g. in 24 hr. Urinary NH₃ was 1.32%. The alkali reserve of the blood-serum was normal. The patient had been alcaptonuric from birth. NUTR. ABS. (m)

Treatment of severe iron deficiency-anæmia and hæmorrhagic anæmia. V. Preparation of caseinate of iron and copper. G. FONTES and L. THIVOLLE (Le Sang, 1933, 7, 803—806).—Compounds prepared by the treatment of milk with $CuSO_4$ and $Fe(CIO_4)_3$ are recommended in the treatment of Fe deficiency and hæmorrhagic anæmia.

NUTR. ABS. (b)

Significance of iron in anæmia. III. Iron in urine. IV. Effect of food-iron on iron balance in untreated secondary and pernicious anæmia. V. Iron balance in secondary anæmia under the influence of liver-iron therapy. A. H. MULLER (Z. ges. exp. Med., 1933, 91, 463-470, 579-584, 585-592).-III. In health the Fe excreted in the urine over 24 hr. was > 2 mg., being about 2.5% of that present in the fæces. In febrile illnesses (e.g., pneumonia) there was not, but in secondary, and more especially pernicious anæmia, there was, a slightly greater urinary excretion of Fe which did not appear to bear any relationship to the blood-Fe. The Fe of the food or liver or small doses of Fe per os had no effect on urinary Fe, but ingestion of > 1 g. of ferrum reductum led to a rapid increase of Fe in the urine.

IV. A positive retention of Fe was noted in untreated cases of both pernicious and secondary anæmia. The amount of Fe retained had no relation to the clinical condition or blood picture, but was greater with a greater Fe content of the food. In circulatory insufficiency with signs of congestion in the alimentary tract the absorption of Fe seemed to be impaired.

V. Administration of liver and min. doses of Fe in cases of secondary anæmia led to a decrease in Fe retention ; with large doses (\lt 3 g. daily) there was a marked negative balance, although there was great improvement in the blood picture. In hypochromic anæmia there is probably in the liver, spleen, and elsewhere a large store of Fe which is not capable of being utilised for the synthesis of hæmoglobin and is mobilised by medicinal Fe and finally excreted by the gut. NUTR. ABS. (b)

Relation of vitamin-A and -D to urinary calculus formation. A. R. BLISS, jun., G. R. LIVER-MORE, and E. O. PRATHER, jun. (J. Urol., 1933, 30, 639-652).—Calculi were formed in 61.8% of the rats maintained on diets deficient in vitamin-A and -D and in 57.1% of those deficient in -A only. The calculi consisted chiefly of Ca and Mg phosphates. CH. ABS.

Relation between kidney- and bladder-stone formation and nutrition. A. POLAK (Arch. Neerl. Physiol., 1934, 19, 176—190).—Addition of 3% of CaCO₃ to the complete diet resulted in kidney- and bladder-stone formation in rats. KH₂PO₄ had a slight effect in vitamin-A deficiency. R. N. C.

Chemical analysis of new growths correlated with their pathological examination. W. R. MANKIN and A. M. WELSH (Med. J. Austral., 1933, [ii], 718—729).—The K content of tumours was approx. ∞ their cellularity. The N content of tumours was > that of normal tissues. NUTR. ABS. (b)

Cancer problem. VII. Potassium and calcium in the tumour and in the patient's serum. H. GUTHMANN, H. WINKLER, and N. GRZIMEK (Arch. Gynäkol., 1933, 155, 185—196).—In tumour patients K was < normal, K: Ca being 1.93 against 2.03. After X-rays or irradiation serum-K rose towards normal. The K content of tumours increased with malignancy. NUTR. Abs. (b)

 $p_{\rm H}$ of blood in cancer. G. BENETATO and M. BENETATO-MODVAL (Compt. rend. Soc. Biol., 1933, 114, 329—331).—The range of $p_{\rm H}$ of oxalated plasma in normal people is $7 \cdot 32 - 7 \cdot 38$ and in cancer $7 \cdot 21 - 7 \cdot 52$. The early cases are more alkaline.

NUTR. ABS. (b) Cholesterol metabolism in cancer patients. O. KIRGREEN (Arch. klin. Chirurg., 1933, 177, 383– 386).—Cancer patients, except in very advanced stages, show normal or, more often, raised serumcholesterol (I) vals., which fall on complete removal of the tumour. After X-ray irradiation of the tumour or, after removal, of its former site, the (I) rises when the tumour has been apparently completely removed falls when the cancer is inoperable or

removed, falls when the cancer is inoperable or the primary tumour has been removed but gland metastases are present, and rises when the disease is in the very advanced stage showing abnormally low (I) vals. These results indicate a storage of cholesterol in the tumour, in such a condition that it is readily decomposed by irradiation. The removal of the tumour or the destruction of the tumour. cholesterol by irradiation involves a readjustment of the blood-cholesterol. NUTR. ABS. (b)

Reducing activity of the tissues of normal and tumour-bearing rats and mice. A. F. WATSON and M. MITOLO (Biochem. J., 1934, 28, 811-814).-Transplantable rat and mouse tumours contain substances which reduce $(NH_4)_2MoO_4$ in acid solution, whilst $CCl_3 \cdot CO_2H$ extracts reduce 2 : 6-dichlorophenolindophenol. The reducing powers vary for different strains of tumours, but are relatively const. for the same strain, as shown by tumours of the same and different ages, multiple transplantable tumours in the same animal, and progressing and spontaneously regressing tumours. W. O. K.

Action of silver nitrate on normal and cancerous tissue of rats and mice. E. HARDE (Bull. Soc. Chim. biol., 1934, 16, 465—466).—Whilst the pituitary and suprarenal glands, the ovaries, and the spleens of adult cancerous mice reduce aq. AgNO₃, the tumours are inactive in this respect. A. L.

Excretion of chlorides in eczema. P. POP-CHRISTOFF and R. ZORN (Compt. rend. Soc. Biol., 1933, 114, 8—10).—Ten cases of acute eczema were placed on a diet containing 5 g. of NaCl daily and the urinary Cl' excretion was determined. Two cases were in equilibrium. In three cases Cl' retention preceded recurrence of cutaneous eruptions; Cl' balance was again established as cure took place. Cl' retention may form the basis of skin ædema in this condition. NUTR. ABS. (b)

Iodine content of Polish drinking-water, in connexion with goitre. A. SZNIOLIS and H. MARCINKOWSKA-LOPIEŃSKA (Arch. Chem. Farm., 1934, 1, 52—63).—The I content of the drinking-H₂O of various localities varies from 0.005 to 15.5×10^{-6} g. per 100 c.c., being on the whole lower for niver- than for well-H₂O, and diminishing with height above sea-level. $0.85 - 3.5 \times 10^{-6}$ g. of I was found in Warsaw sewage-H₂O, as compared with 0.28×10^{-6} g. per 100 c.c. for tap-H₂O. R. T.

Is the high basal metabolic rate in "hyperthyroidism" due to thyroxine ? J. W. CAVETT, C. O. RICE, and J. F. MCCLENDON (Science, 1934, 80, 19-20). L. S. T.

Liver disease and metabolism. III. Aminoacids. K. TSUSHIMA (J. Chosen Med. Assoc., 1933, 23, 110-111).—There is an increase in the NH₂-N of the blood and urine in cancer and cirrhosis of the liver and in coma hepaticum, but not in icterus. The rise in the NH2-N of blood and urine which normally follows the ingestion of large amounts of peptone or gelatin is prolonged in cases of liver disease. When the bile ducts of animals are ligatured, the NH2-N in the blood and urine is increased, and the further rise following over-feeding with peptone is still present after 6 hr. Eck fistula dogs show the normal rise after peptone over-feeding, and if, in addition, the hepatic artery is tied, the NH2-N of the blood rises markedly further. NUTR. ABS. (m)

Metabolism in liver disease. IV. Uric acid. H. INOUE (J. Chosen Med. Assoc., 1933, 23, 117).— In severe cancer of the liver and leucæmia the uric acid content of blood and urine increases. The similar increase which follows over-feeding with peptone is abnormally protracted in liver disease, because of a lowered power of protein absorption in the alimentary canal. NUTR. ABS. (m)

Peptide content of the blood and of pathological fluids. P. VALDIGUIE (Bull. Soc. Chim. biol., 1934, 16, 498—526).—A study of the N distribution in 14 pathological fluids (I) such as occur in cases of cirrhosis indicates that the polypeptide content (II) is not related to the urea nor to the albumin content. (II) of (I), although a little >, is in most cases comparable with, that of the blood (III). Whilst renal impermeability and hepatic insufficiency both increase (II) of (I) and (III), in the former the increase is not proportional to the extent of the failure to eliminate phenolsulphonephthalein. A. L.

Creatine-creatinine metabolism. Treatment of muscle-diseases with glycine. A. MADER, E. SELTER, and R. SCHELLENBERG (Z. ges. exp. Med., 1933, 92, 151—164).—In infancy and childhood creatinuria normally occurs. The output of creatinine (I) increases with increasing age in children with healthy muscles. In progressive muscular dystrophy the (I) coeff. was reduced and the creatine coeff. raised. Administration of glycine tended to restore (I) and creatine metabolism to normal.

NUTR. ABS. (m)

Fate of intravenous saline in healthy and nephrotic subjects. A. GANDELLINI (Z. ges. exp. Med., 1933, 92, 361—366).—Intravenous injection of saline produces both in healthy and nephrotic subjects (I) an immediate slight rise of blood-Cl and a reduction in protein, red cell-count, and hæmoglobin content. After 24 hr. there is still a slight increase of blood-Cl in (I). Very little of the injected Cl appears in the urine of (I) within 24 hr., whereas in normal subjects 100% or more is excreted when the diet is NaCl-rich and 34—75% with NaCl-poor diet. The NaCl concn. of the urine of (I) reaches high levels in some cases. In all cases the Cl rapidly leaves the blood-stream, but in (I) is held by the tissues, whereas in health it rapidly passes back to the blood to be excreted.

NUTR. ABS. (b)

Mineral metabolism in renal disease. IV. Mineral excretion in normal subjects during prolonged administration of equivalent amounts of sodium and potassium chlorides. V. Mineral excretion in renal disease during prolonged administration of equivalent amounts of sodium and potassium chlorides. H. GLATZEL and W. MECKE (Z. ges. exp. Med., 1933, 91, 504-522, 523-538).-IV. A healthy subject, while on an acid diet, was given KCl or NaCl each for 8 days. Gradually the excretion of the administered alkali reached the level of the intake. There was a greatly increased excretion of the one not given, the Na loss during the KCl period being > the K loss in the NaCl period. During the NaCl period the urinary vol. was increased out of proportion to the output or retention of Na. During the KCl period there was a decrease of the alkali reserve and an increased urinary acidity and output of acid substances.

(Edema and the serum-lipin ratio. H. KURTEN (Z. ges. exp. Med., 1933, 91, 178—192).—In nephritic and pregnancy ædema the increase in plasma-cholesterol is not accompanied by an equal increase (often a decrease) in phosphatide, so that the cholesterollecithin quotient is greatly increased. Hypercholesterolæmia seems to be associated with defective thyroid function. NUTR. ABS. (b)

Biology of the placenta. Blood-picture in the intervillous spaces and metabolism of the placenta. FRANKEN and KREBS (Arch. Gynäkol., 1933, 156, 188-191).-Determination of the isohæmagglutination titre (Saecker) in heterospecific pregnancy revealed that the blood in the intervillous spaces (I) equals the maternal blood (II) in titre, whilst the retroplacental blood has a lower titre because of contamination by amniotic fluid which is rich in fœtal isoagglutinogens. There is less sugar and more non-protein-N in (I) than in venous (II) or foetal blood (III), whilst the NH₂-acids of (I) are in concn. between those of (II) and (III). Urea is equally distributed throughout. No evidence of fat or protein oxidation by the placenta was obtained : carbohydrate appears to be the only material metabolised by the placenta, which explains the low sugar vals. in (I). NUTR. ABS. (b)

Pellagra in Sudanese millet-eaters. N. L. CORKILL (Lancet, 1934, 226, 1387–1390).—The fundamental condition appears to be lack of cholesterol and vitamin-A and -D in the food, lack of -C being a contributory factor. Pellagra is largely allergic. Vitamin-D, and not H₂O-sol. - B_2 , is the anti-dermatitis vitamin. L. S. T.

Blood sedimentation rate and the plasmaproteins. G. R. P. ALDRED-BROWN and J. M. H. MUNRO (Lancet, 1934, 226, 1333–1336).—In rheumatic disease sedimentation rate does not run parallel to the fibrinogen (I) or globulin (II) % of the plasmaproteins; it has no connexion with the globulinalbumin ratio, the fibrinogen-globulin ratio, or the ratios of (I)+(II) to albumin and to total proteins. L. S. T.

Inorganic and organic acid-soluble phosphorus in spontaneous and experimental rickets. V. ANGELINI (Riv. Clin. Pædiat., 1933, 31, 1153— 1171).—Both in rachitic infants and in rats made rachitic by a diet low in P, the total acid-sol. P of blood-serum is diminished. The fall is due to reduction in inorg. P and is closely correlated with the degree of rickets. Org. acid-sol. P shows no significant change, but tends to increase both in infants and in rachitic rats. NUTR. ABS. (b)

Metabolism of healing in celiac rickets. F. J. FORD (Arch. Dis. Childhood, 1933, 8, 355-359).— During antirachitic treatment Ca and P metabolism is similar to that of infantile rickets. CH. ABS.

Effect of the metal on the antirachitic activity of orthophosphates. R. LECOQ and H. VILLETTE (Compt. rend. Soc. Biol., 1933, 114, 1096—1098).— The phosphates of Na, K, Mg, and Sr have antirachitic potency ∞ the PO₄^{'''} present. The Ca^{**} slightly reduced the potency of the PO₄^{'''} in Ca₃(PO₄)₂, whilst the phosphates of Fe, Mn, and Bi showed no antirachitic potency. NUTR. ABS. (b)

Chlorine distribution between the plasma and erythrocytes after injection of sodium chloride in the post-operative period. M. Lévy (Bull. Soc. Chim. biol., 1934, 16, 618—624).—Whilst usually in post-operative hypochloræmia injections of considerable amounts of NaCl increase the erythrocyte-Cl' (I), plasma-Cl' (II), and the ratio (I)/(II), in some cases the increases in (II) are such that the ratio (I)/(II) is lowered. A. L.

Amine production in the intestine of infants: significance of amines in the etiology of toxicosis in infants. D. BRANDES (Jahrb. Kinderheilk., 1933, 141, 128—134).—The fæces of bottle-fed infants are richer in amines (I) than those of breastfed. Since (I) are found in the urine of infants with pyuria but no toxicosis (II), (I) are produced in the urinary tract and (II) does not necessarily result from poisoning with (I). NUTR. ABS. (m)

Action of urea on tissue respiration. B. KISCH (Biochem. Z., 1934, 271, 58-60).—At $p_{\rm H}$ 7.4 tissue (heart, liver, kidney, diaphragm of rat, guinea-pig, sheep, ox, pig) respiration (I) is slightly increased by low concn. of urea, whilst high concn. (0.5M) inhibits (I) in some cases (rat heart, ox retina) only. The stimulating effect is most pronounced with rat and guinea-pig kidney. The optimum concn. varies with the organ concerned. W. McC.

Effect of hypertonic solutions on tissue respiration. I. Effect of chlorides of univalent cations. B. KISCH (Biochem. Z., 1934, 271, 131-141).—The degree of restriction of respiration of tissues (heart, diaphragm, kidney, liver, retina of rat, guinea-pig, ox, sheep) at $p_{\rm H}$ 7.4 by 0.2M solutions of LiCl, NaCl, KCl, CsCl, or NH₄Cl is different for different animals and for different tissues of the same animal, sp. effects being observed in some cases. Variations in the effects occur according to the nutrient material (NH₂-acids, lactate, pyruyate) provided for the tissue. The effects are due to the action of the ions on oxidation catalysis. W. McC.

Effect of oxidation-reduction potential of the medium on growth of tissue cultures. R. E. HAVARD and L. P. KENDAL (Biochem. J., 1934, 28, 1121-1130). —By passing N₂ and traces of O₂ through a culture medium, the E_h can be adjusted to various levels between +300 mv. and -100 mv. Growth of chick heart-tissue decreases with E_h , mitosis ceasing between +20 mv. and -30 mv. L. D. G.

Metabolic activity of the pancreas. E. U. STILL, A. L. BENNETT, and V. B. SCOTT (Amer. J. Physiol., 1933, 106, 509—523).—Activity due to injection of a very active secretin prep. is accompanied and followed by a marked O_2 consumption. The CO_2 which appears in the juice comes at first partly from the blood, but later exclusively from the gland itself. NUTR. ABS. (\dot{o})

Effect of life at high altitude on blood-lactic acid. H. HARTMANN and A. VON MURALT (Biochem. Z., 1934, 271, 74-88).—At low altitudes the lactic acid content (I) of human blood remains const. On moving to high altitudes (3460 m.) (I) first falls and then rises, the deviation from normal being increased after administration of $\rm NH_4Cl$ and much more by that of $\rm NaHCO_3$, which in all circumstances increases (I) > does $\rm NH_4Cl$. The large increase in (I) produced by vigorous bodily exercise is greater at high than at low altitudes, whilst the subsequent fall (after 15 min.) is also greater at high altitudes, the level reached being with $\rm NH_4Cl <$ with $\rm NaHCO_3$ administration. Possibly (I) takes over part of the rôle of the CO₂ of blood at high altitudes. W. McC.

Metabolism in oxygen deficiency. VI. Alteration in protein metabolism at low tension due to administration of glucose. H. ELIAS and J. KAUNITZ. VII. Water metabolism at low oxygen tensions. VIII. Protein content of the liver at low oxygen tension and effect of glucose administration. IX. Nonprotein-nitrogen and its fractions in the liver in oxygen deficiency. Effect of glucose admini-X. Prevention stration. of characteristic changes in protein metabolism at low atmospheric pressures by administration of glucose. XI. Mechanism of effect of carbohydrate at low oxygen tensions (glucose effect). H. ELIAS, J. KAUNITZ, and R. LAUB (Z. gcs. exp. Med., 1933, 92, 397-408, 409-429, 430-435, 436-449, 450-468, 469-479).-VI. The increase in serum-albumin and -globulin produced in rabbits given only H₂O during exposure to diminished O_2 pressure is caused by H_2O loss. Administration of glucose (I) lessens these changes as well as the increase in non-protein-N of the serum, increased electrical excitability, and changes in the blood.

VII. There is an increase in urinary output of H_2O and a decrease in insensible perspiration during exposure of fasting rabbits to lowered O_2 pressure : the reverse is the case when (I) is given. Liver and brain of exposed animals contain slightly more, spleen slightly less, H_2O ; (I) administration has little effect.

VIII. The N content (on dry wt.) and the total wt. of the liver are about 25% greater when rabbits, exposed to low O₂ pressure, are given (I).

IX. Complete starvation, except for H_2O , causes a reduction in the abs. and relative wt. of liver. Administration of (I) maintains the relative but not the abs. wt. The % of non-protein-N in the liver is greatly reduced in all except the animals given (I) during exposure to low O_2 pressure where the reduction is slight. The contents of urea and NH_2 -acid are increased in all, but least when (I) is given; the polypeptide-N shows no significant change except in the (I) animals, where there is a marked diminution.

X. Exposure to low O_2 pressure causes a reduction in the H_2O content of the blood in the hepatic vein. Administration of (I) prevents any difference in the H_2O content of hepatic and portal blood, and also lessens the breakdown of proteins in the liver and tends to promote anabolism.

XI. Administration of sorbitol or galactose during exposure to low O₂ pressure has practically no protective action on the proteins, whereas both fructose and (I) have a marked effect. The reduction 3 P of H_2O content of the liver is largely prevented by (I) or fructose, but only slightly by sorbitol and galactose. NUTR. ABS. (m)

Nutritive effect of ethyl alcohol. T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1933, 9, 1035—1044).— Excess of fat in the diet had a bad effect on the nutrition of rats. Normal growth was obtained when EtOH (optimum 5%) was added. The liver- and body-fat increased considerably on addition of 5% of EtOH. The liver-glycogen was unaffected.

CH. ABS. Physiological behaviour of trioses and related compounds. V. Behaviour of liver- and muscle-glycogen after feeding glyceraldehyde with simultaneous dosage of insulin. R. STÖHR (Z. physiol. Chem., 1934, 224, 229-232; cf. A., 1933, 88).—Administration of glyceraldehyde to fasting rats causes marked deposition of glycogen (I) in the liver, but only slightly in muscle. When insulin is also given the effect is reversed, muscle- but not liver-(I) increasing. J. H. B.

Fructose and galactose tolerance in premature infants. W. FABISCH and F. ETZOLD (Z. Kinderheilk., 1933, 55, 702—707).—The average galactose tolerance is 1.6 g. per kg. body-wt. for premature and 2.2 for full-time infants, and the corresponding average fructose tolerances are 1.5 and 2.6.

NUTR. ABS. (m)

Peculiarities of carbohydrate metabolism in infants and children. II. Keto-antiketogenic ratio of the food of infants and children. Effect of alkaline salts and hormones on ketone metabolism in children. W. HEYMANN and E. MATER (Z. Kinderheilk., 1933, 55, 502—511).—Taking the ketogenic portion (I) of the food as 90% of the fat cal. and 60% of the protein cal. and the antiketogenic (II) as 10% of the fat cal., 40% of the protein cal., and 100% of the earbohydrate cal., a (I)/(II) ratio of 2.5 was found to produce ketosis equally in infants and children; 10—15 g. of NaHCO₃ or citrate per day, which raised the $p_{\rm H}$ of the urine to 8.4, did not increase the ketonic substances in the blood or the urine. Prolan, adrenaline, and thyroxine had no action on the formation and excretion of ketones.

NUTR. ABS. (b)

Ketonæmia in rabbits. L. KALLÓS-DEFFNER (Z. ges. exp. Med., 1933, 92, 389—393).—Hunger leads to the appearance of considerable amounts of ketones in the blood of rabbits. Exposure to reduced atm. pressure (I) produces the same effect, which may be due to poor intake of food, since administration of glucose prevents ketosis. After removal to ordinary (I) the disappearance of ketones runs parallel with increase of wt. NUTR. ABS. (b)

Simultaneous occurrence of sugar and acetone in the urine of non-diabetic children (glycoketonuria). F. ALTMANN (Z. Kinderheilk., 1933, 55, 639—668).—After the administration of 100 g. of glucose (I) a simultaneous appearance of (I) and $COMe_2$ in the urine was observed in six non-diabetic patients with ketosis due to various causes and in twelve children who had previously been given a carbohydrate-poor, high-fat diet; the blood-sugar

curve was diabetic in type except for the low fasting level. No relationship was noted between the bloodor urinary COMe, and the presence of COMe, in the breath. In glycosuria and ketonuria large amounts of sugar must be given. There was a tendency to lose wt. on a high-fat diet with high calorific val.

NUTR. ABS. (b)

Role of the liver in the metabolism of carbohydrate and fat. C. H. BEST (Lancet, 1934, 226, 1155-1160, 1216-1221, 1274-1277).-Lectures. L. S. T.

Digestion of food. III. Synthetic fats. S. SUZUKI (J. Agric. Chem. Soc. Japan, 1933, 9, 1007-1018).-Tristearin (I) and triolein (II) were given to dogs instead of fat. (II) is more digestible than (I). (I), but not (II), retarded the digestion of other components, especially protein. CH. ABS.

Fat metabolism in the fowl. I. Composition of the egg-fat of the fowl as affected by the ingestion of large amounts of different fats. E. M. CRUICKSHANK (Biochem. J., 1934, 28, 965-977).-On normal cereal rations containing protein supplements the mixed fatty acids of the egg-fat (I) contained approx. 31% of solid acids, 47-51% of oleic, 15-19% of linoleic, and 2-3% of linolenic acid. The superficial and internal fat deposits (II) are more uniform in composition in the fowl than in pigs and cattle. The degree of saturation and proportion of components in (I) were modified by ingestion of unsaturated fatty acids (III), but very little by saturated fatty acids (IV). Ingestion of (III) causes a marked and rapid increase of unsaturation in (II); ingestion of (IV) increased saturation. C. G. A.

Fat deposition in the lung. T. OLIARO (Z. ges. exp. Med., 1933, 91, 366-369).-Simultaneous determinations of the fat content (I) of the blood of rabbits from the left and right heart, peripheral veins, and vena cava reveal a reduction of 11.1-25.5% in the blood from the left heart, indicating that fat is stored in the lungs. (I) of the lungs is greater (7.3 as against)6.1%) when the animals are given olive oil 3 hr. before being killed. NUTR. ABS. (m)

Effect of cholesterol and phloridzin on fat metabolism. Fat content of liver of cats and rabbits after intraportal or subcutaneous injection of these substances. H. TSENG (Z. ges. exp. Med., 1933, 92, 108-128).—Intraportal injection of cholesterol into cats and rabbits had no significant effect on the fat of the liver, in disagreement with Remesow's finding of fat-impoverishment and glycogen synthesis in rabbits. Phloridzin caused a great increase of liver-fat. NUTR. ABS. (b)

Rôle of the liver in cholesterol and phosphatide metabolism. H. HEINLEIN (Z. ges. exp. Med., 1933, 91, 638-682).-In both full-grown and young dogs on normal diet only 50-70% of the cholesterol (I) and 3-6% of the phosphatide (II) of the food was excreted. Analysis of the organs indicated that (I) is synthesised in the growing animal but not in the adult, (II) in neither. Absorption of (I) took place even in the absence of bile, whilst (II), although hydrolysed, was not absorbed in the absence of bile.

The excretion of (I) and (II) takes place chiefly through the intestinal wall, since it was but little affected by the exclusion of bile from the gut by means of a fistula. NUTR. ABS. (b)

Cerebroside storage. H. BEUMER and H. FASOLD (Z. ges. exp. Med., 1933, 90, 661-664).-Cerebrosides are contained in the nervous system and suprarenals, probably due to the medullary portion of the latter being rich in nerve-substance. Cerebroside (I) ingested by a breast-fed infant appeared in toto unchanged in the faces (II): in a boy of twelve only 20% of 0.5 g. appeared in the (II) probably on account of bacterial action. Sphingosine did not appear in the urine after ingestion or subcutaneous or intravenous injection. Large amounts of (I) are stored unchanged in the liver and other organs after injection into dogs or rabbits. NUTR. ABS. (b)

Significance of the liver in the metabolism of lipins. Change in the amounts of blood- and bile-lipin in parenteral administration of lecithin to normal rabbits. Metabolism of lipins in hepatic disturbance in rabbits. Y. OSODA (Japan. J. Gastroenterol., 1933, 5, 115-123, 124-131).-After injection of lecithin into rabbits the blood- and bile-lecithin, -cholesterol, and -total fatty acids increase. On intravenous injection of lecithin after hepatic injury the blood-lipin is high if the parenchymatous cells are blocked and normal if only the hepatic stellate cells are blocked. CH. ABS.

Production of ketones and ammonia in different species of animals. H. TRIMBACH (Compt. rend. Acad. Sci., 1933, 197, 708-710).-In man, calves, pigs, dogs, rabbits, cats, and rats, on diets of cow's milk or carbohydrates alone, ketone and NH₃ excretion were very variable, per unit of wt., in the different species on the same diet, and did not vary together in the different species. NUTR. ABS. (b)

Deamination of alanine in the liver. E. AUBEL (Ann. Physiol. Physico-chim. biol., 1933, 9, 929-933).-AcCO₂H was obtained from alanine but not from Na lactate. The medium must be well aërated. The reaction appears to be due to diastase.

NUTR. ABS. (b) Intermediary metabolism of histidine. IV. S. EDLBACHER and M. NEBER (Z. physiol. Chem., 1934, 224, 261-272; cf. A., 1931, 513).-The probable course of the action of histidase is as follows. The glyoxaline ring is opened, with entry of 2H20 and loss of NH_3 , yielding the enol or keto-form of ω -formylglutamine (I). With NaOH, (I) affords NH₃, HCO₂H, and glutamic acid (II), shown to be identical with the protein degradation product obtained by oxidative deamination (III) with kidney slices (Krebs), as both yield α -ketoglutaric acid (2:4dinitrophenylhydrazone, m.p. 220°). With H2O2 the enzymic fission mixture, probably containing (1), gives succinic acid semi-aldehyde (2: 4-dinitrophenyhydrazone, m.p. 201-202°) [also obtained with H₃O₂ from (II)]. a Aminobutyric acid (IV) by (III) gives a-ketobutyric acid (2: 4-dinitrophenylhydrazone, m.p. 196°; p-nitrophenylhydrazone, m.p. 203°). With H2O2, alanine and (IV) give MeCHO and EtCHO, J. H. B. respectively.

Oxidation of sulphur of homocystine, methionine, and S-methylcysteine in the animal body. V. DU VIGNEAUD, H. S. LORING, and H. A. CRAFT (J. Biol. Chem., 1934, **105**, 481–488; cf. this vol., 322).—Homocystine (I), S-methylcysteine (II), decomp. 248°, $[\alpha]_{12}^{\infty}$ -32° in H₂O [formyl derivative, m.p. 118– 119° (corr.), $[\alpha]_{12}^{\infty}$ -13.5° in H₂O], and dl-methionine (III) were fed to rats, and the total S, SO₄", and unoxidised S in the urine determined. The % of the extra total S excreted appearing as SO₄" is practically the same for both (I) and (III). (II) is also readily oxidised. H. D.

Proteins of the liver of frogs after fasting. C. GAUTIER (Bull. Soc. Chim. biol., 1934, 16, 414—418).—The right lobes of the livers of frogs were removed and compared with the remaining portions (I) of the livers of the same animals after fasting for some weeks. (I) decreased little in wt. and their protein content remained almost const. A. L.

Nitrogenous extractives of muscle in protein inanition. A. ROCHE (Compt. rend. Soc. Biol., 1933, 114, 1185—1187).—In rats, death from protein (I) starvation leads to extensive changes in muscle-(I), the H₂O-sol. N increasing by about 21%. In complete starvation the increase is 39%. Thus the H₂O-sol. N is intermediary in the equilibrium, circulatory N == extractable muscle-N == muscle-(I)-N, comparable with Voit's "circulatory (I)."

NUTR. ABS. (m) NUTR. ABS. (m) Nitrogen reserves in animals. A. ROCHE (Ann. Physiol. Physico-chim. biol., 1933, 9, 933—938).— In the absence of food protein, N requirement is met by partial mobilisation of muscle- and not of reserveprotein. Hence muscle-protein does not consist of mols. of fixed constitution, but is of vary variable composition. NUTR. ABS. (m)

Morphology of protein metabolism of animal cells. B. V. KEDROVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 312—316).—Observations have been made of the distribution of stained granules in various stages of development of tadpoles grown in dil. neutral-red, and the rôle of the chromophilic protein material is discussed. R. K. C.

Nutritive value of proteins of lucerne and clover hay when fed alone and with maize proteins. K. L. TURK, F. B. MORRISON, and L. A. MAYNARD (J. Agric. Res., 1934, 48, 555—570).—With growing lambs, the apparent digestibilities of the proteins of clover hay (I), lucerne hay (II), (I)+maize, and (II)+ maize are 50, 56, 55, and 63%, respectively; the true vals. show the same relative differences. The efficiency of utilisation is indicated by the biological vals. of 81, 79, 80, and 77, respectively; with (II) alone the val. is 50, whilst addition of starch and sugar increases it to 72. When fed in a balanced diet, (II) is probably not deficient in the quality of its proteins. F. O. H.

Increase of food value of proteins in wheat and rye bread by the admixture of pea meal. Z. MARKUZE (Zdrowie, 1933, Nos. 19—20).—The biological val. of the food proteins is increased from about 1 for wheat bread, 1.1 for rye bread, and 1.21— 1.38 for peas, to 1.6—1.9 with 80% wheat+20% peas, or 60% rye+40% peas, and to 2 for 60% wheat +40% peas. NUTR. ABS. (m)

Comparative digestive utilisation of protein by different animals. P. LELU (Compt. rend., 1934, 198, 2022—2024).—N utilisation (determined by a modified formula) by pigs, dogs, and rats is for milk 96.7, 95.4, and 96.4, and for meal of peas 95.9, 79.4, and 77.1, of barley 94.2, 71.9, and 65.6, and of soyabeans 89.6, 80.6, and 68.6%, respectively. R. S. C.

Effects on metabolism of a diet consisting chiefly of protein, egg-white, ox or fish muscle, or milk protein. A. GALAMINI (Problema alimentare, 1933, 3, 41-79).- A high-protein dict (I), in which the protein is in the form of egg-white or dried codfish, fed to rats, causes the appearance in the urine, after 25-30 days, of a green pigment (II) which does not appear on an exclusive meat diet. (II) appears earlier if EtOH is given with the egg-white or if the rats have previously been for some time on (I). During exclusive protein feeding urinary N excretion increases to 10-20 times the normal. When part of the egg-white is replaced by starch or butter in the proportion 1:6, the loss is greatly reduced and (II) disappears from the urine. On an exclusive meat diet little or no growth occurs in rats, and dried cod will not maintain body-wt. Milk-protein permits maintenance of wt. and health for a long time.

NUTR. ABS. (m)

Value of protein degradation products in silage for the nitrogen metabolism of milch cows and wethers. W. KIRSCH and H. JANTZON (Futterkonservierung, 1933, 4, 79—92).—In silage, true protein is broken down to amides. In clover silage (I), made by the cold process with addition of sugar, decomp. of 34.4% of true protein occurs. In milch cows and wethers fcd on (I) containing amides sufficient for N requirement, the amides are utilised. The N balance is always positive. NUTR. ABS. (m)

Production of purines in exogenous protein metabolism. C. DEGAN (Ann. Physiol. Physicochim. biol., 1933, 9, 481-493).—In rapidly growing pigs (wt. 14-20 kg.) addition of considerable quantities of starch to a diet of skim milk causes a marked increase in N retention and a simultaneous decrease in excretion of purines and of allantoin+purine derivatives. This indicates synthetic production of purines from dietary proteins. NUTR. ABS. (m)

Constancy of the level of endogenous purine excretion in the individual. C. DEGAN (Ann. Physiol. Physico-chim. biol., 1933, 9, 451-468).— The total urinary excretion (I) of purines is const., per unit wt., in animals of the same species, and of approx. the same size (pigs, rabbits, dogs), on a diet of carbohydrates only, this level representing the min. level of sp. endogenous N metabolism. On a diet free from purines but containing protein, (I) varies from individual to individual and is always > on a carbohydrate diet, indicating purine synthesis. The ratio of allantoin-N+total purine-N: total N, which is const. in adult rabbits from one individual to another, varies in growing pigs. NUTR. ABS. (m)

Dependence of the excretion of endogenous purines on the quantity and energy value of the diet. C. DEGAN (Ann. Physiol. Physico-chim. biol., 1933, 9, 469–480).—With young pigs (wt. 15–20 kg.) on a diet without protein and consisting almost entirely of carbohydrates, fed in varying amounts, increases up to four times the lowest level cause no increase in the excretion of endogenous purines (I). Purine excretion parallels total N excretion and falls when the supply of carbohydrate and fat is insufficient to ensure the min. level of (I) metabolism. It is unlikely that processes connected with the work of the digestive tract and the associated glands play any important rôle in the production of (I). NUTR. ABS. (m)

Effect of amino-acids on purine metabolism. C. DEGAN (Ann. Physiol. Physico-chim. biol., 1933, 9, 494—507).—In pigs addition to the diet of glycine, glutamic acid, or asparagine in large quantities causes no increase in purine excretion. NUTR. ABS. (m)

Purine metabolism in hypophysectomised dogs. B. BRAIER (Compt. rend. Soc. Biol., 1933, 114, 1209—1212).—In normal and hypophysectomised dogs fed (a) for 6—10 days on lean beef free from bone, (b) for 10 days on a progressively decreasing N intake, and (c) on a N-free diet for 5 days, the N output is least from the operated dogs during protein starvation (I). Whilst normal and operated dogs have comparable outputs of total purine, the latter eliminate less uric acid and purine bases but more allantoin. The ratio allantoin-N : total N is higher in these dogs in all three periods than in controls. The ratio total purine-N : total N is similar in both groups. The coeffs. of purine oxidation during (I) is 72% for normal and 88% for operated dogs. NUTR. ABS. (m)

Nuclein metabolism. XXXIII. Adeninedeoxyriboside. W. KLEIN. XXXIV. Ribodeoseadenylic acid from thymus-nucleic acid. W. KLEIN and S. J. THANNHAUSER (Z. physiol. Chem., 1934, 224, 244—251, 252—260; cf. A., 1933, 981).— XXXIII. Ag' selectively inhibits the action of deaminase in the intestinal enzyme system and permits the isolation of cryst. adeninedeoxyriboside (+H₂O), m.p. 181°, $[\alpha]_{11}^{n}$ —26° in H₂O (*picrate*), from the enzymic hydrolysis products of thymus-nucleic acid.

XXXIV. The EtOH-sol. fraction from the enzymic hydrolysis of thymus-nucleic acid in presence of arsenate was fractionated by means of brucine. It gave *ribodeoseadenylic acid* [cryst. *Ca* salt (I) $(+H_2O)$, decomp. without melting, $[\alpha]_{19}^{19} - 38^{\circ}$ in H_2O]. Intestinal phosphatase hydrolyses (I), yielding adenine- and hypoxanthine-deoxyriboside.

J. H. B.

Muscle contraction. K. LOHMANN (Naturwiss., 1934, 22, 409—411).—The energy changes in muscle contraction are discussed with particular reference to the creatinephosphoric acid cleavage. H. D.

Utilisation of yeast in man. F. M. KUEN and K. PURINGER (Biochem. Z., 1934, 271, 152—167).— Utilisation of the N and energy (calories) provided by fresh press yeast (dead) amounts to 52.5 and 37.1%. With dried yeast the vals. are 90.4 and 89.05%. The difference is due to the alteration in the walls of the yeast cells and consequent increased capability for diffusion caused by the drying. W. McC. Hippuric acid. IV. Synthesis in the animal body. I. KANZAKI (Sei-i-kwai Med. J., 1933, 52, No. 1, 85-96).—In rabbits the kidneys are not the only organs concerned. Experimental P or CHCl₃ poisoning shows that the liver participates in the synthesis. CH. ABS.

Origin of phenols in the organism. A. D. MARENZI (Compt. rend. Soc. Biol., 1933, 114, 800– 801).—After complete excision of the intestinal tract in two dogs, the phenol content of the urine decreased from 490 to 189 mg. per litre. After bilateral nephrectomy (I) the total phenol content of the blood increased from 1.8 to 5.6 mg. per 100 c.c. in 3 days. After (I) and excision of the gastro-intestinal tract, the bloodphenol increased less rapidly, from 1.5 to 3.3 mg. per 100 c.c. in 34 hr. Part of the blood-phenol is of endogenous origin. NUTR. ABS. (m)

Metabolism of naphthalene in rabbits. M. C. BOURNE and L. YOUNG (Biochem. J., 1934, 28, 803– 808).—The urine of rabbits to which $C_{10}H_8$ has been fed contained (a) a sol. compound of unknown constitution which yields $C_{10}H_8$ when warmed with dil. HCl, and (b) 1- α -naphthylmercapturic acid, m.p. 170– 171°, $[\alpha]_{77}^{37}$ —25° in EtOH (cf. this vol., 888). When heated with acid it yields β -1-naphthylthiolpropionic acid, decomp. 160—165°, and AcOH, whilst with dil. NaOH, NH₃ is evolved and α -C₁₀H₇·SH is formed. W. O. K.

Effect of apple diet on nitrogen and mineral metabolism. H. HÜTKER (Arch. Kinderheilk., 1933, 100, 2—15).—During a raw apple-diet period the N balance became negative and the non-protein-N of the serum reduced; serum-Cl was reduced and alkali reserve increased. S and P retentions were diminished due to reduced intake. The Ca balance was also reduced due to increased excretion through the gut. The good effect of the diet in renal disease is probably the result of increased excretion of nitrogenous waste substances. NUTR. ABS. (b)

Nutritive value of the mountain apple, Eugenia malaccensis or Jambosa malaccensis. C. D. MILLER, R. C. ROBBINS, and K. HAIDA (Philippine J. Sci., 1934, 53, 211—221).—In comparison with ordinary apples mountain apples have approx. the same proportion of Ca, P, and Fe, higher H_2O contents, lower (50%) sugar, and somewhat lower vitamin- $A, -B_1, -B_2$, and -C contents. A. G. P.

Effect of acidified silage on digestibility, nitrogen, calcium, and phosphorus balances in cattle, sheep, and dogs. F. GRAMATZKI (Z. Tierzuchtung Züchtungsbiol., 1933, 28, 433—450).—In ruminants, utilisation of N was reduced by addition of acids, and the P- and, to a smaller extent, the Ca-balance reduced. In pigs the results were similar, the P and Ca balances being most affected when free mineral acid was present in the silage. NUTR. ABS. (b)

Effect of hot-fermentation silage from grass containing Equisetum on composition of milk and butter-fat. J. KESELING (Milch. Forsch., 1933, 16, 148—154).—Feeding silage containing Equisetum causes a fall in total protein, cascinogen, and albumin and a rise in the n of the milk, whereas feeding hay changes these vals. in the opposite direction. All the other vals. show changes in the same direction, but of different orders, with the two types of feeding, except the P_2O_5 content, which is unaltered. The acidity of the butter-fat and its I val. are raised and the Reichert-Meissl, Polenske, and sap. vals. are lowered by feeding either the silage or the hay. NUTR. ABS. (b)

Iodine metabolism in man. W. ELMER (Polska Gaz. lekarska, 1932, No. 49; 1933, Nos. 4 and 11).— In normal persons an increase in blood-I was observed up to 6 hr. after intravenous injection of KI containing 1.3 mg. of I; the increase lasted longer in hypothyroid persons (I). In hyperthyroidism (II) the original level was reached in 24 hr. Elimination of the injected I was greatest during the first 6 hr. and amounted in 24 hr. to 20–30% of the amount injected. In (I) the amount excreted was much > in (II), much < in normal subjects. There was no increase in the I of bile. It appears that hyperthyroid tissues absorb I with more avidity than normal. NUTE. ABS. (b)

Iodine excretion in the bile during fasting and after food. A. W. ELMER and Z. LUCZYNSKI (Compt. rend. Soc. Biol., 1933, 114, 1340—1342).— The I content of the bile in fasting rabbits was 4—14× 10^{-6} g., in rabbits after feeds of beetroot and oats, $27-69 \times 10^{-6}$ g. per 100 c.c. The liver probably plays an important part in the metabolism of I, excreting it in the bile after meals. NUTR. ABS. (b)

Chlorine impoverishment and regulation of osmotic pressure. E. KERPEL-FRONIUS (Z. ges. exp. Med., 1933, 90, 676—683).—In young puppies a carbohydrate-rich, NaCl-free diet led to great reduction of the Cl contents of blood and tissues, but no increase in non-protein-N or alkali reserve. There was an increased H₂O content of brain sufficient to cause cerebral disturbances. Addition of 3% of protein to the diet delayed the onset of osmotic disturbances (I) and hydramia (II), whilst addition of NaCl prevented (I), but had no effect on (II).

NUTR. ABS. (b)

Changes in calcium content of the embryo and egg of the hen during incubation. P. SACCARDI and P. LATINI (Arch. Sci. biol., 1933, 19, 55-61).— The Ca content of the egg (white+yolk) increases more during incubation than in the unincubated egg. The Ca is derived from the shell for the growth of the embryo. The increase becomes marked about the twelfth day of incubation and thereafter increases rapidly. NUTR. ABS. (b)

Calcium tolerance in cats. J. L. D'SILVA (J. Physiol., 1933, 80, 6P).—Intravenous injection of CaCl₂ in Ringer solution (18 mg. of Ca per c.c.) into chloralosed cats caused a rise in serum-Ca (I) in some animals > in others, apparently due to a difference in capacity of the tissues to assimilate Ca. In cases where very high (I) vals. are obtained, the Ca may be in an inactive form, since Ca rigor of the heart would otherwise result. NUTR. ABS. (b)

Mineral metabolism. XXVII. Effect of two different calcium-phosphorus ratios on the growth of calves. P. J. DU TOIT, A. I. MALAN, and J. W. GROENEWALD (Onderstepoort J. Vet. Sci., 1933, 1, 421-424).-No difference in growth rate was observed when the calves received 10 lb. of wholo milk per day, whether the CaO: P_2O_5 ratio of the diet was kept at 1:1.4 (as in milk) or at 1:0.3 (by feeding CaCO₃). NUTR. ABS. (b)

Retention of calcium and phosphorus in rations with a wide CaO: P_2O_5 ratio. J. H. W. T. REIMERS (South African J. Sci., 1933, 30, 447-451).---No harmful results were observed with young pigs on a ration with a CaO: P_2O_5 ratio of 1:2 or 1:3. Extra P_2O_5 , supplied as Na_2HPO_4 , did not affect the Ca but increased the P balance. The excess P was almost all voided in the urine. NUTR. ABS. (b)

Influence of some acids on the calcium, phosphorus, and nitrogen metabolism and acid-base equilibrium in fowls. H. BURCKHARDT (Rept., Versuchsanst. Liebefeld-Bern).—The retention of Ca and P by two cockerels was increased by the addition of skim-milk to a basal ration, but was unaffected by the further addition of 1.2% of lactic acid (I). Addition of 0.5% of HCl had no effect on one cockerel, but in the other resulted in increased NH₃-N content of the urine, a negative Ca balance, and decreased P and N retention. This addition is probably about the crit. level. With young chicks, (I) and AcOH were without harmful effect. The same amount of HCl was detrimental. NUTE. ABS. (b)

Water exchange in the body of the fish. G. von HEVESY and E. HOFER (Z. physiol. Chem., 1934, 225, 28—34).—The H₂O in the body of fish immersed in H₂O containing 0.45% of H₂²O takes up H²O until equilibrium (*i.e.*, equal H₂²O content) is reached with the external H₂O (about 1 hr. for goldfish, longer for larger fish). If the fish is then transferred to H₂O, an exchange again occurs. With dead fish the exchange is slower. H¹ attached to C is not exchanged for H². J. H. B.

Iron in the diets of pre-school children. H. McKAY (Ohio Agric. Exp. Sta. Bimo. Bull., 1934, 19, 73—77).—Data showing the daily intake of Fe by children are recorded and discussed. A. G. P.

Intermediary iron metabolism in children. F. THOENES (Klin. Woch., 1933, 12, 1686-1688).-Barkan's "easily eliminated Fe" of whole blood (action of 0.4% HCl) is about 5% hæmoglobin-Fe (I) In serum or plasma very small quantities occur, about 0.4% of (I). Serum-Fe of children is highest at birth, 1.72×10^{-3} mg. per c.c. To the end of the second month the average is 1.29; later 0.80. For older children it is 1.21. It therefore approx. parallels (I). Under-nutrition and starvation increase and posthæmorrhagic or nutritional anæmia reduces it. Scarlet fever, diphtheria, measles, and septic infections greatly reduce it. Whooping cough and tuber-culosis have no effect. Medicinal Fe does not increase it regularly or definitely. Blocking the reticuloendothelial system or diphtheria toxin reduces it. Hence serum-Fc is a measure of blood destruction which the reticulo-endothelial system controls.

NUTR. ABS. (b) Ethyl alcohol. IV. Distribution of alcohol in tissues. M. NICLOUX. V. Diffusion of ethyl alcohol. M. NICLOUX and G. GOSSELIN (Bull. Soc. Chim. biol., 1934, 16, 330-337, 338-354).—IV. The penetration of EtOH into tissue may be analogous to that of $CHCl_3$, but the H_2O , instead of the lipin content, will be the determining factor.

V. EtOH penetrates into biological fluids placed in collodion dialysing vessels surrounded by dil. aq. EtOH until the [EtOH] outside is equal to the concn. in the H_2O inside. When live fish, however, are placed in dil. aq. EtOH the ratio of [EtOH] in the H_2O of the tissue to that in the external medium is 0.86 for the whole gudgeon, 0.94 for the tadpole, 0.83 for the liver, 0.86 for muscle, and 0.92 for the blood of the carp. A. L.

Occupational poisoning by the vapours of some esters employed as solvents. P. DUQUENOIS and P. REVEL (J. Pharm. Chim., 1934, [viii], 19, 590-601).—HCO₂Me, HCO₂Et, MeOAc, and EtOAc are toxic to man. The symptoms induced in frogs and guinea-pigs are described. H. N. R.

Chemical and pharmacological studies on mixtures of sodium halides with quinine salts. G. MARTIGNETTI (Arch. Farm. sperim., 1934, 58, 14—33).—The min. concn. of quinine mono- (I) or di-hydrochloride (II) solution required to form a ppt. with solutions of NaCl varies approx. inversely as the min. [NaCl]. The ppt. is shown to consist of (I) or (II), the solubility of which is lowered by the Cl' of the NaCl. Rabbits injected intravenously with NaCl are not killed by the min. lethal dose of (I), and only after some considerable time by that of (II), unless NaCl is so conc. as to be itself toxic. R. N. C.

Destruction of *l*-, *d*-, and *dl*-hyoscine by eggwhite and rabbit serum. W. F. VON OETTINGEN and I. H. MARSHALL (Proc. Soc. Exp. Biol. Med., 1933, 31,224—225).—*l*-Hyoscine, *dl*-hyoscyamine, and their isomerides are destroyed at the same rate on incubation with egg-white, but with rabbit serum the relative amount of destruction differs according to the period. The differences reside in the tropic acid radical.

CH. ABS.

Reaction given by urine after ingestion of novalgin or melubrin. S. DEZANI and A. M. B. SEMERIA (L'Ind. Chimica, 1934, 9, 764—767).— Following ingestion of novalgin (Na 4-sulphonylmethylamino-1-phenyl-2:3-dimethylpyrazolone) or melubrin (the sulphonylamino-compound), the urine gives a ruby-red colour with I, probably owing to hydrolysis of the two compounds in the organism to 4-amino-1-phenyl-2:3-dimethylpyrazolone (aminoantipyrin) or a related compound. T. H. P.

Comparative pharmacological studies on calcium gluconate and camphorsulphonate. I. L. DONATELLI (Arch. Farm. sperim., 1934, 58, 34— 48).—The actions of Ca gluconate (I) and camphorsulphonate (II) on the isolated frog's heart are similar. The effect of (II) on the isolated mammalian heart persists longer than that of (I) after washing out. (II) augments blood-pressure (HI) and respiration (IV) steadily; (I) has no effect on (III), and causes unsteadiness in (IV). Cryoscopic measurements show that (II) is almost completely dissociable, but (I) only partly, their solutions isotonic with blood being, respectively, 4.75% and 9%. R. N. C. Extraction of the active principle of Acocanthera Abyssinica. C. BRAGA (Arch. Farm. sperim., 1934, 58, 1—13).—The active principle (I) has been obtained by extraction of the powdered leaves with H_{20} , neutralisation with aq. NH_3 , pptn. as tannate, decomp. of this with ZnO, extraction with EtOH, and successive dissolution in H_2O and EtOH and filtration. (I) is difficult to separate from resins, and has not been obtained quite pure; it is apparently a glucoside, is dialysable, and arrests the heart in systole.

R. N. C. Blood-sugar regulation as affected by psychic secretion of the glands of the digestive system. G. SANPAOLESI (Riv. Clin. Pediat., 1933, 31, 1076– 1080).—In infants, after a fast of 7—8 hr., the sight of food, sucking an empty bottle, or sham feeding with an empty spoon in presence of food causes a 20% increase in blood-sugar. NUTR. ABS. (m)

Carbohydrate metabolism and the effect of decapitation and decerebration under nitrous oxide anæsthesia. J. S. L. BROWNE and C. L. EVANS (J. Physiol., 1933, 80, 1—20).—Anæsthesia with N₂O containing 5—12% of O₂ results in a rise of blood-sugar and -lactate in cats. Decapitation or decerebration under N₂O results in a fall of liverglycogen followed by a rise, the fall being less in animals with inactivated adrenal glands. In the decapitate cat glyconeogenesis usually proceeds at the rate of at least 0.6 g. per hr. NUTR. ABS. (m)

Liver-glycogen during decerebration hyperglycæmia : influence of atropine and ergotamine on this condition. M. L. LONG (J. Physiol., 1933, 80, 296—304).—Intravenous injection of atropine (1-11 mg. per kg.) into rabbits with a high liver-glycogen (I) 0—4 hr. after pontine puncture, only slightly retards, whilst ergotamine (0.4—0.9 mg. per kg.) under the same conditions, and also when (I) is low, almost entirely prevents, decerebration hyperglycæmia. Atropine does not influence the breakdown of (I), whilst in most experiments with ergotamine (I) and blood-lactic acid remain practically unchanged. No correlation could be found between decrease in (I) and increase in blood-sugar following decerebration.

NUTR. ABS. (m)

Effect of splanchnicotomy and phloridzin on decerebration hyperglycæmia. M. G. FORSTER (J. Physiol., 1933, 80, 323—328).—Pontine decerebration of fasted rabbits is not followed by the usual rise of blood-sugar if the splanchnic nerves are tied several days before, or if phloridzin is administered during, the experiment, provided the renal vessels are not ligated. NUTR. ABS. (m)

Autonomic cell regulation after administration of phloridzin. A. PARTOS and A. HERZOG (Z. ges. exp. Med., 1933, 91, 602-607).—After subcutancous injections of phloridzin into rabbits and dogs there are increase and decrease of the sugar of the whole blood, plasma, and corpuscles. The corpuscular sugar varies inversely with the cholesterol concn., which appears therefore to be an important regulator of the cellular content of sugar. NUTR. ABS. (m)

Action of phloridzin on sugar absorption. E. WERTHEIMER (Pflüger's Archiv, 1933, 233, 514528).—Subcutaneous or oral administration of phloridzin (I) to rabbits reduces the absorption (II) of sugars from the alimentary tract. The reduction runs parallel with the rapidity of (II) demonstrated by Cori for the various sugars, being greatest with galactose and glucose and least with the pentoses. The rate of (II) of glucose with (I) is the same as that of arabinose alone. The (II) of sugars from the peritoneal cavity is not affected by (I), nor is (II) of NH_2 -acids from the intestine. (I) has as elective action, preventing the active (II) by, but not diffusion of sugar through, the bowel wall and renal tubules. The prevention of active (II) is possibly due to inhibition of hexose phosphate production by (I). NUTR. ABS. (m)

Determination of phloridzin in the liver and kidneys after intravenous injection into the dog. A. LAMBRECHTS (Compt. rend., 1934, 198, 2029— 2030).—The amount of phloridzin in the liver and kidneys of the dog 25—80 min. after intravenous injection is found by ultra-violet spectrography to be small. R. S. C.

Influence of the autonomic nerves on alimentary hyperglycæmia and the absorption of glucose. E. A. HORNE, E. J. MCDOUGALL, and H. E. MAGEE (J. Physiol., 1933, 80, 48-64).—Ergotoxine (I) and atropine (II) suppress hyperglycæmia (III) in normal rabbits after oral administration of glucose partly by delaying absorption (IV), whilst in amytalised animals splanchnicotomy, vagotomy, or injection of atropine increases the rate of (IV) of glucose and the degree of (III); (I), or (I) + (III), stimulate (IV), but temporarily suppress (III). The promotion of (IV) by (I) and (II) is due to inhibition of impulses passing down the autonomic nerves. The results favour the view that alimentary (III) is due to an overflow of absorbed glucose through the liver. NUTR. ABS. (m)

Experimental tolerance to some poisons. J. LÉVY (Bull. Soc. Chim. biol., 1934, 16, 631-709).—A lecture.

Protective action of various antidotes on poisoning by α -aminopropionitrile. C. SANNIÉ (Bull. Soc. Chim. biol., 1934, 16, 562—580).—Cysteine and glutathione have a preventive but no curative effect, glucose and methylene-blue are without action, NaNO₂, NaH₂PO₂, and sulphates of NH₂OH and N₂H₄ have curative but not preventive effect when used as antidotes for poisoning in guinea-pigs injected with lethal doses of NH₂·CHMe·CN. A. L.

Neuro-muscular action of amides and cyanides. R. BONNET (Compt. rend., 1934, **198**, 1880–1881).— MH_2Ac and urea (I) at a concn. of 0.093 g. N per 100 c.c. are not toxic to nerve (II) or muscle (III). At a concn. of 0.7 g. per 100 c.c. they poison (III) only. At much lower concn. $(1^{\frac{1}{2}}$ and $\frac{1}{8}$, respectively) HCN and KCN poison both (II) and (III). (I) thus behaves as an amide and not as a cyanide. C. G. A.

Clinical significance of traces of fluorides in water. N. J. AINSWORTH (Analyst, 1934, 59, 380– 385).—H₂O in areas associated with the clinical condition of "mottled teeth" contained $4\cdot5-5\cdot5$ p.p.m. of F. E. C. S.

Effect of sulphide, sulphite, and sulphate compounds on metabolism. M. KOJIMA (Z. ges. exp. Med., 1933, 91, 257–266).—Administration of S" to rats increased the C/N ratio in the urine and lowered the vacat-O/N and vacat-O/C ratios, *i.e.*, decreased the oxidation of C, but increased that of N compounds. The effect of SO_3 " and SO_4 " was much less. A transient hyperglycamia was produced in rabbits, greatest with S" and least with SO_4 ". NUTR. ABS. (b)

Glutathione and ascorbic acid content of the liver of rats poisoned with phosphorus. S. LANG and A. SCHÉDA (Biochem. Z., 1934, 271, 180—184).— Starvation has no effect on the (very variable) glutathione (I) content of the rat liver, on the ratio oxidised (I) : reduced (I), or on the ascorbic acid (II) content. The (I) content of the liver is much < that of the adrenals (III). Administration of P is also without effect on these vals. and on the (II) content of (III). There is no relation between the carbohydrate and the (I) contents of the liver. W. McC.

Pharmacology of lead. IX. Distribution of lead by the autohistoradiographic method. X. Relationship of lead deposition to calcium metabolism. B. BEHRENS and A. BAUMANN (Z. ges. exp. Med., 1933, 92, 241-250, 251-264).-Injection of radioactive Pb (Th - B) was followed by deposition of the metal in various organs and tissues, especially the bones. Large amounts were found in liver and spleen, and Pb was demonstrated in the bile a few min. after the injection. Pb was deposited in those areas of the bones where Ca was being deposited. When pathological calcification was produced (arterial degeneration, hypervitaminosis-D) Pb was always deposited in the calcified zones. Administration of acid reduced the deposition of Pb in all organs except the kidneys. Previous administration of Ca gluconate also decreased the retention of Pb. The parallelism between Ca and Pb is attributed to their affinity for $PO_4^{\prime\prime\prime}$, that of Pb NUTR. ABS. (b) being the greater.

Copper balance in normal rats after ingestion of different amounts of copper. R. GUILLEMET (Compt. rend. Soc. Biol., 1933, 114, 1038—1040).— Practically all the Cu ingested as a sol. salt by a rat over a period of 34 days was excreted in the fæces, and there was no indication of storage of Cu when the animal was killed after a post-period of 20 days. The very small amount of Cu excreted in the urine was independent of the amount ingested.

NUTR. ABS. (b)

Extent of the retention of ingested aluminium. E. W. SCHWARTZE, G. J. COX, R. B. UNANGST, F. J. MURPHY, and H. B. WIGMAN (J. Amer. Med. Assoc., 1933, 101, 1722-1725).-Fresh tissues of guinea-pigs, receiving no added Al, contained about 0.4 p.p.m. Al, the carcases of growing animals containing > those of the adult animal. Feeding large amounts of sol. Al salts (lactate or chloride) produced a scarcely detectable deposition of Al in the soft tissues and somewhat larger amounts in bone. Al does not appear to be cumulative in the tissues and no systemic pharmacological effect can be ascribed directly to absorbed Al. No harmful effects can be expected from sol. Al occurring in foods or introduced by utensils into a diet of normal P content. NUTR. ABS. (b)

Biological separation of heavy water. W. W. STEWART and R. HOLCOMB (J. Amer. Chem. Soc., 1934, 56, 1422—1423).—The d of H₂O obtained (repeated distillation with KMnO₄) from cow's milk and urine and tap-H₂O is the same in each case. H. B.

Relation of materials of the cell nucleus to the lethal action of ultra-violet radiation. J. R. LOOFBOUROW and F. F. HEYROTH (Nature, 1934, 133, 909).— λ 2950 Å. is approx. the longest effective in destroying thymus-nucleic acid, adenine, uracil, etc. Materials of the cell-nucleus appear to play an important part in the lethal action of ultra-violet radiation for many kinds of micro-organisms. When rays < approx. 2900 Å. are filtered out, irradiation of nuclear compounds brings about absorption changes indicative of the formation of isomerides or more complex compounds. L. S. T.

Geochemistry of living matter. B. P. UVAROV (Nature, 1934, 134, 11-12). L. S. T.

Dehydrases. A. BERTHO (Angew. Chem., 1934, 47, 497-501).—A review.

Action of inhibitors on potato pyrocatecholoxidase. D. RICHTER (Biochem. J., 1934, 28, 901-908).-Pyrocatechol-oxidase preps. (I) from different sources (potato, lilac, elder, mushroom, Polyporus hispidus, mealworm) show marked sp. differences in their behaviour towards the inhibitory effect of varying concns. of resorcinol. The conditions under which (I) effect the secondary oxidation of $o-C_6H_4(NH_2)_2$ and of AcSH were determined. The rate of oxidation of *p*-cresol by potato (I) is markedly accelerated by substances which produce o-quinones (e.g., adrenaline, glycine, dihydroxyphenylalanine) and inhibited by substances which combine with o-quinones (e.g., NaHSO3, KI, NH2Ph); hence o-quinones play an essential part in the oxidation of monohydric phenols. F. O. H.

Flavin respiration. T. WAGNER-JAUREGG, H. RAUEN, and E. F. MÖLLER (Z. physiol. Chem., 1934, 225, 145—146; cf. this vol., 807).—Since cryst. lactoflavin shows a lower redox potential than the succinate-fumarate-succinodehydrogenase system, the actual H donator is probably formed from succinic acid during the experiment. O_2 is concerned in its production, which explains the inhibition of the reaction by HCN and CO. J. H. B.

Thermostability of fumarase. J. P. JACOBSOHN and F. B. PEIREIRA (Bull. Soc. Chim. biol., 1934, 16, 550—561).—Determinations of the const. of inactivation of fumarase for varying temp. indicate that the rate of inactivation (I) does not correspond with that of a unimol. reaction. (I) in more conc. is > in dil. solutions of the enzyme, and increases with $p_{\rm H}$ of the solution and with age of the enzyme material. The presence of malate retards (I). A. L.

Inactivation of catalases from certain marine animals by oxygen. G. W. MARKS (J. Biol. Chem., 1934, 105, 489–500; cf. this vol., 109).—For catalases from various sources the inactivation in air is >in N₂. Assuming the quantity of H₂O₂ decomposed is directly \propto the enzyme concn. a unimol. equation expresses the inactivation. H. D. Oxidation of thiosulphate to sulphate by tissue slices in vitro. N. W. PIRIE (Biochem. J., 1934, 28, 1063—1075).—Na₂S₂O₃ is oxidised to SO₄^{''} by ratliver, -kidney, and -chorion and goose-kidney without increase in O₂ consumption. This will not take place anaërobically, and the tissue is irreversibly inactivated by anaërobic incubation. Na₂S₄O₆ is also oxidised, but there is no evidence that it is an intermediate in the above reaction. H. G. R.

Interferometric method [applied to Abderhalden's reaction]. A. DURUPT (Bull. Soc. Chim. biol., 1934, 16, 461-464).—A reply to Guillaumin (this vol., 428). A. L.

Propepsin and prorennin. S. P. L. SØRENSEN, H. HOLTER, and B. ANDERSON (Biochem. Z., 1934, 271, 199—205).—Recent papers (A., 1932, 881; 1933, 1081, 1203; this vol., 450) contain many contradictions because insufficient care is taken to distinguish between the substances concerned and to take into account the peculiarities of coagulation. W. McC.

Determination of pepsin. L. UTKIN (Biochem. Z., 1934, 271, 127—130).—As in Robertson's method of trypsin determination (A., 1912, ii, 819) caseinogen (I) (about 2%) in 0.25N-HCl is treated with pepsin at 30°. After pptn. of (I) with aq. 0.133N-NaOAc n is determined. A second determination is made after 30 min. ($p_{\rm H}$ 1.6—1.7). The amount of pepsin which changes n by 0.0005 is a pepsin unit. The error is $\pm 2.5\%$. W. McC.

Plant proteases. XVII. Aminopolypeptidase of yeast. W. GRASSMANN, L. ENDEN, and H. SCHNELLER (Biochem. Z., 1934, 271, 216–228; cf. A., 1931, 393; 1933, 1081).—Increased purity and yield are attained by liberating the enzyme from yeast with papain, pptg. with AcOH (avoiding excess), dissolving the ppt. in aq. NH₃, removing impurities (including most of the nucleic acid) by adding NaOAe and $(NH_4)_2SO_4$ to saturation, and dialysing. The yield obtained by grinding yeast with liquid air is almost as high; hence the enzyme is probably present as such in the cells. The purcest samples contain about 1% of P, exhibit protein reactions, and have activity equiv. to > 400 units. W. McC.

Nucleotidase and its relationship to the deamination of nucleotides in the heart and in muscle. J. REIS (Bull. Soc. Chim. biol., 1934, 16, 385-399).-A study of the phosphatase content of various tissues of the frog, rat, dog, man, pig, rabbit, calf, hen, goose, and pigeon using adenylic (I) and inosic (II) acids and adenine nucleotide as substrate, indicates that there exists a nucleotidase (III) sp. for purineriboside 5-monophosphates which is distributed in varying amounts throughout the tissues, but is not found in the skeletal muscle (IV). Whilst in (IV) of the frog no nucleotidase is present, with that of the rat only (I) and (II) yield H₃PO₄. The influence of Mg , $p_{\rm H}$, and substrate concn. on (III) is the same as that on bone-phosphatase. A parallel study of deamination (V) and dephosphorylation (VI) using (1) as substrate indicates that in the skeletal muscle of the frog and rabbit and in the heart-muscle of the pigeon, where the nucleotidase content is small or nil, (V) can take place independently of (VI). $PO_4^{""}$ inhibits (V)

only in the heart-muscle of the pigeon. (V) may therefore take place directly without previous (VI). A. L.

Glycolysis. E. LUNDSGAARD (Angew. Chem., 1934, 47, 495–497).—A review.

Influence of the hydrogen-ion concentration of the medium on the hydrolysis of α - and β -glycerophosphoric acids by maltase. J. COURTOIS (Compt. rend., 1934, **199**, 95–97).—The optimum $p_{\rm H}$ for the hydrolysis of α -glycerophosphoric acid (I) of conces. 0·01, 0·1, and 0·333N is 4·7, 4·5, and 5·2, respectively, and 3·9, 4·0, and 5·2 for the β -form (II). The rate of hydrolysis of both isomerides is higher for lower concess. of substrate and smaller $p_{\rm H}$ than for higher concess. and greater $p_{\rm H}$. The rate of hydrolysis of (II) is > that of (I) because (II) has (a) a larger affinity for maltase (cf. A., 1913, i, 540) than (I), and (b) because of the greater speed of hydrolysis of its maltase-substrate complex. The $p_{\rm H}$ influences (a) and (b) in opposite senses. J. L. D.

Specificity of β -glucosidase and enzymic equilibria. C. N. IONESCU and A. KIZYK (Ber., 1934, 67, [B], 990—996).—Repetition of the work of Bourquelot (J. Pharm. Chim., 1914, [vii], **10**, 361) on the hydrolysis/synthesis of β -methylglucoside (I) by emulsin in MeOH-H₂O confirms his results, and is supported by a similar series of experiments in OEt·CH₂·CH₂·OH-H₂O. The discrepancy between the const. calc. from the ratio of the velocities and from the conens. is not due, as supposed by von Euler and Josephson (A., 1924, i, 1266), to the greater affinity of β -glucosidase for glucose than for (I), but to their failure to take into account the different conen. of MeOH and H₂O. The general laws of chemistry are applicable to these reactions, which do not form exceptions to the law of mass action. H. W.

Specificity of glucosidases in moulds and bacteria. E. HOFMANN (Naturwiss., 1934, 22, 406-409).—EtOH-Et₂O-treated *B. Delbrücki* and *B.* coli decomposed 60% in 48 hr. and 97% in 24 hr., respectively, of solutions of β -phenylgalactoside (I), whilst β -phenylglucoside (II) was unattacked under the same conditions. Enzyme preps. from *A. niger* hydrolysed both (I) and (II) in proportions varying with the substrates on which they were reared. Preps. from *Mucor javanicus* hydrolysed (I) only.

H. D.

Function of phosphates in the fermentations of sugars. W. J. YOUNG (J. Proc. Roy. Soc. N.S.W., 67, 1-17M).—A lecture. C. M. B.

Equilibrium between hexosediphosphoric acid and dihydroxyacetonephosphoric acid [in biological fluids]. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1934, 271, 89–110; cf. this vol., 560).— Dialysed muscle extract (rabbit) or yeast extract contains a H₂O-sol. enzyme, zymohexase (I), which is not readily adsorbed and is relatively thermostable (destroyed in 30 min. at 60°, in 10 min. at 70°). (I) is unaffected by CH₂I-CO₂H, NaF, and Na₂C₂O₄, is most active at $p_{\rm H}$ 6—10, and rapidly (a few min. at room temp.) converts hexose diphosphate or dihydroxyacetonephosphoric acid into an equilibrium mixture of the two. K varies from 22×10⁻³ at 70° to 0.18×10⁻³ at -7° . W. McC. Conversion of diphosphoglyceric acid into pyruvic acid. C. NEUBERG, W. SCHUCHARDT, and A. VERCELLONE (Biochem. Z., 1934, **271**, 229—232).— At p_{π} about 6.7 fresh top yeast or maceration juice from botton yeast converts diphosphoglyceric acid into AcCO₂H. W. McC.

Decomposition of lactic acid by yeast enzymes. III. A. HAHN and M. DÜRR (Z. Biol., 1934, 95, 298—306; cf. this vol., 110).—Formation of lactic acid (I) in yeast suspensions in PO₄^{'''} buffer digested for 3 hr. at p_{Π} 7 occurs in vac. but not in O₂. In presence of CH₂Br·CO₂H, formation of (I) in vac. is inhibited, whilst a decrease in the content of (I) occurs in O₂, a process inhibited by KCN. In presence of washed muscle, 0.008% of CH₂Br·CO₂H suppresses the increase of (I) in vac., no oxidation of (I) occurring in O₂. This absence of O₂ carrier is due to inactivation by EtOAc used in the prep. of the yeast. Addition of the cell-residues of the extract produces a marked oxidation of (I), which is also shown by suspensions of dried yeast and, to a smaller extent, by yeast macerates. F. O. H.

Cozymase. I. Mol. wt. K. MYRBACK. II. Isolation. K. MYRBACK and H. LARSSON (Z. physiol. Chem., 1934, 225, 125—130, 131—140).—I. The mol. wt. of purified cozymase (I) by the free diffusion method is probably about 500, certainly < 450. The (I) in the various layers was determined by fermentation. Ionic dissociation is repressed by NaCl, which, however, inhibits the fermentation and tends to give high vals. for mol. wt.

II. (I) solutions were purified by pptn. of impurities with Pb(OAc)₂, pptn. of (I) with Hg(NO₃)₂, and liberation by H₂S. Pb(OAc)₂+Ba(OH)₂ may also be used in place of Hg(NO₃)₂, Pb being removed by H₂SO₄. Other precipitants used consecutively for further purification are phosphotungstic acid, picric acid (to remove impurities), and AgNO₃. The best fraction, $[\alpha] -70^{\circ}$, had an activity of 180,000 units. Various colour reactions are given. (I) contains 15% of N, of which 80-85% is purine (adenine)-N, the remainder a different form. J. H. B.

Cozymase as co-enzyme in enzymic dehydrogenations. B. ANDERSSON (Z. physiol. Chem., 1934, 225, 57—68).—In addition to the enzymic dehydrogenation of malic, lactic, citric, and glutamic acids and EtOH, that of HCO_2H and glucose is also activated by cozymase (I), but not by succinic dehydrogenase. The enzymic oxidation of EtOH and lactic acid by O_2 and washed, dried top yeast or washed heart-muscle is activated by (I). The co-enzyme of lactic acid- and probably of glucose-dehydrogenase is identical with cozymase. J. H. B.

Resistance of micro-organisms, particularly yeasts, to ultra-violet light. J. BEAUVERIE (Compt. rend., 1934, 198, 2017—2019).—Individuals of Saccharomyces cerevisiæ have varying resistance to ultraviolet light, some being killed, some unable to reproduce, and some unaffected after the same exposure.

R. S. C. Biochemistry of micro-organisms. XXXVIII. Metabolic products of *Penicillium minioluteum*, Dierckx. Minioluteic acid. J. H. BIR- KINSHAW and H. RAISTRICK (Biochem. J., 1934, 28, 828—836).—P. minio-luteum grown on Czapek-Dox medium with glucose as the sole source of C yields spiculisporic acid (γ -hydroxy- $\beta\delta$ -dicarboxypentadeco- γ -lactone (cf. Clutterbuck et al., A., 1931, 1094), and minioluteic acid (I), $C_{14}H_{24}O_3(CO_2H)_2$, m.p. 171°, [a]] +108·1°, [a]] $\frac{\pi}{2700}$ +94·5° (in COMc₂), [a]] $\frac{\pi}{290}$ +62·4°, [a]] $\frac{\pi}{2700}$ +54·6° (Na_2 salt in H₂O) (Me_2 ester, m.p. 86·5°; trihydrazide, sinters 157—160°, m.p. 201°). When fused with KOH (I) yields $H_2C_2O_4$, n-dodecoic acid (hydrazide, m.p. 104—105°), and decylsuccinic acid (II), m.p. 90—91° [anhydride (III), m.p. 66—67°), the constitution of which is proved by condensing Et α -bromo-n-dodecoate with Et sodiomalonate to give Et $\alpha\beta$ -dicarbethoxytridecoate, b.p. 172°/1 mm., hydrolysed to $\alpha\beta$ -dicarboxytridecoic acid, m.p. 148°, vac. distillation of which yields (III), hydrolysed to (II). (I) with Na-Hg gives the γ -lactone of α -hydroxy- γ carboxy-n-tetradecoic acid (IV), m.p. 119°, also obtained by condensing Et₂ decylsuccinate, b.p. 155— 159°/2 mm., with Et₂C₂O₄ in NaOEt to impure α -keto- γ -carboxy-n-tetradecoic acid (2 : 4-dinitrophenylhydrazone, m.p. 180°), reduced (Na-Hg) to (IV). (I) is therefore the γ -lactone of $\alpha\beta$ -dihydroxy- $\beta\gamma$ -dicarboxy-n-tetradecoic acid.

Formation of urease by Aspergillus niger. T. MIWA and S. YOSHII (Sci. Rep. Tokyo Bunrika Daigaku, 1934, 1, 243—270).—A. niger and Penicillium glaucum produce both urea and urease when grown in media containing NH_4NO_3 or protein fission products (hydrolysates of silk, fibrin, or ovalbumin). The production of urease is accelerated by addition of glucose or fat to peptone cultures and, except when NO_3' is used as a source of N, by increase of [H'], whilst it is less marked with old cultures. F. O. H.

Hydrocyanic acid as a nitrogen source for the growth of Aspergillus niger. N. N. IVANOV and L. K. OSNIZKAJA (Biochem. Z., 1934, 271, 22—31).— In a N-free medium containing sugar, N, in a form which cannot be utilised by the mould, is given up to the medium, despite the N-insufficiency, by A. niger. When KCN is added its N is assimilated, the N content of the mycelium increasing almost five-fold.

W. McC.

Fermentation of sugar by the root nodule bacteria. A. I. VIRTANEN, M. NORDLUND, and E. HOLLO (Biochem. J., 1934, 28, 796—802).—Fermentation of glucose by heavy suspensions of *Rhizobium* trifolii (I) gives rise to $PrCO_2H$, considerable quantities of lactic acid being found as intermediate. CO_2, H_2 , and small amounts of AcOH and EtOH are also produced, the mol. ratio of $PrCO_2H$ to CO_2 and H_2 being 1:2:2. Similar fermentation of glucose is also caused by crushed nodules from plants grown in sterile quartz sand cultures. An aq. extract of Aspergillus niger mycelium stimulates the growth of (I). The catalase content of (I) is comparatively low. W. O. K.

Isoelectric point of bacteria. G. YAMAHA and S. ABE (Sci. Rep. Tokyo Bunrika Daigaku, 1934, 1, 221-229; cf. A., 1933, 1334).—Flocculation and micro-cataphoresis in 0.9% NaCl-HCl or 0.02M-PO₄^{'''} buffer give, respectively, the $p_{\rm H}$ vals.: B. pseudodiphtheriæ (?), 1.6 and 4.3, 1.8; B. subtilis, 2.2, 3.6; B. pertussis, 1.9, 2.5; B. proteus, 2.4, 2.1; B. anthracis, 2.5, 3.1; Sarcina lutea, 2.7, 2.6; Diplococcus gonorrhoæ, 3.3, 2.5; Staphylococcus aureus, 3.5, 3.4; B. pyocyaneus, 3.8, 3.1. As with caseinogen, the isoelectric point depends on the suspension medium. F. O. H.

Effect of hypertonic sugar solutions on the thermal resistance of bacteria. A. C. FAY (J. Agric. Res., 1934, 48, 453–468).—The increased resistance to heat shown by bacteria in the presence of sugar solutions is influenced by the permeability of the cells. The protective action increases with the osmotic pressure of the sugar solution, but is not the same for equimol. solutions of different sugars. Maltose and lactose have small activity in this respect. The protective effect is paralleled by the ability of the sugar solutions to retard the coagulation of ovalbumin and the inactivation of rennin by heat. The mechanism of these changes is discussed. A. G. P.

Influence of flavins on the respiration of lactic acid bacteria (*Thermobacterium helveticum*). E. ADLER and H. VON EULER (Z. physiol. Chem., 1934, 225, 41-45).—Lactoflavin, ovoflavin, and a prep. of "lumiflavin" from liver increase the respiration of lactic acid bacteria in glucose solution and are not inhibited by 0.001*M*-KCN. J. H. B.

Preparation of *l*-sorbose. K. MAURER and B. SCHIEDT (Biochem. Z., 1934, 271, 61–63).—Sorbitol in aq. yeast extract is treated at 28—30° in shallow glass vessels with *B. xylinum*. When max. reducing power has been attained (about 6 weeks) the liquid is treated with Pb acetate, filtered, freed from Pb with H_2S , and evaporated to a thin syrup. Cryst. *l*-sorbose is deposited and is recryst. from MeOH. Yield 50-70%. W. McC.

Respiration and fermentation of pathogenic bacteria. II. B. diphtherice. A. FUJITA and T. KODAMA (Biochem. Z., 1934, 271, 185-198; cf. this vol., 698).—The effect of [H], temp., time, salt concn. (PO4""), kind of substrate (glucose, maltose, mannose, fructose, galactose, lactose, sucrose, rhamnose, arabinose, NH2-acids, AcOH, AcCO2H, glycerophosphoric, succinic, malic, propionic acids, glycerol), methylene-blue, and $CH_2I \cdot CO_2H$ on the respiration (I) and for-mentation (II) is described. The p_{Π} optimum is 7.1—7.7 for (I) and 7.47 for (II). (I) increases with rise of temp., but the % increase per 1° is the greater the lower is the temp. (I) and (II) decrease rapidly with time except when the temp. is low (0°), the decrease then being slow. PO_4''' has no effect on (11). Of the substrates glucose is the most easily fermented and the best supporter of (I). Lactose, sucrose, and the pentoses scarcely support (I) at all. Asparagine and glutamic acid support (I) well, some of the other NH2 acids (e.g., leucine, glycine) not at all. Lactic acid and AcOH are completely, AcCO2H and glycerol incompletely, oxidised. In a growth-supporting medium (I) of the bacteria increases 100-200%. (I) of asparagine is greatly increased, (I) of glucose and AcOH is not affected, by addition of cystine. (I) and (II) are equally restricted by CH₂I-CO₂H, but the degree of restriction varies with the substrate. Anaërobic (II) of 1 mol. of glucose produces 2.2 equivs. of acids, chiefly HCO₂H and lactic acid with little W. McC. AcOH and succinic acid.

Autolysis of B. pneumococcus. B. BORGHI (Z. physiol. Chem., 1934, 225, 69-78) .- On autolysis of the cultures for periods up to 80 days, the total N decreased slightly, the residual N (after CCl₃·CO₂H pptn.) and the acidity by CH2O titration increased. The autolysed material was dialysed. The dialysate from "young" autolysates caused fever and leuco-cytosis when injected into rabbits. From older autolysates the pyrogenic, dialysable substances had disappeared and the dialysate now acted on the leucocytes and reticulo-endothelial system. The nondialysable products were always strongly pyrogenic and toxic. J. H. B.

Toxic and immunising substance isolated from Bacillus ærtrycke. A. BOIVIN, L. MESROBEANU, and I. MESROBEANU (Compt. rend., 1934, 198, 2124-2126).—The toxic substance isolated from this bacillus by CCl₃·CO₂H is capable of immunising mice against injections of the living bacillus. J. W. B.

Toxic and immunising substance isolated from Bacillus ærtrycke. A. BOIVIN and L. MESROBEANU (Compt. rend., 1934, 198, 2211-2212).-Evaporation in vac. of an aq. solution from the bacillus gives a yellow substance (I), sol. in H₂O, insol. in org. solvents, which with hot 0.2N-AcOH gives a less toxic, white ppt. On acid hydrolysis it becomes non-toxic and vields a polysaccharide (about 40%) and fatty acids (about 22%). (I) contains a little N, P, S, and Ca, and is probably the Ca salt of a phosphatide-polyaccharide complex. R. S. C.

Formation of coprosterol in the intestine. I. Possible role of dihydrocholesterol, and a method of determining dihydrocholesterol in presence of coprosterol. II. Action of intestinal bacteria on cholesterol. H. DAM (Biochem. J., 1934, 28, 815-819, 820-825).-I. A method for the determination of dihydrocholesterol (I) in presence of coprosterol (II) depends on the difference of solubility of the digitonides in dry MeOH. (I) administered to man is recovered in the fæces, and is therefore not converted in the intestine into (II).

11. During the putrefaction of fæces, the total sterol content remains const., but the degree of saturation rises unless it is initially very high. The product of reduction is (II) and not (I). The reaction is not accelerated by the presence of formates. Putrefaction of the contents of the small intestine does not result in reduction of the unsaturated sterols. Cholesterol added before putrefaction in the form of eggyolk, sol. esters, or colloidal suspensions is not significantly reduced. W. O. K.

Tubercle bacillus. I. Extraction and separation of lipin substances. M. MACHEBEUF, G. LEVY, N. FETHKE, J. DIERYCK, and A. BONNEFOI (Bull. Soc. Chim. biol., 1934, 16, 355-384).-Tubercle bacilli (1 kg.) sterilised by heating to 120° and washed free from glycerol with H₂O were extracted consecutively with COMe. (I), cold EtOH (II), hot EtOH (III), Et₂O (IV), and CHCl₃ (V). Extract (I) (11 g.) contained no P or haptene and had no acid-resistant power. Extract (II) (7.1 g.) contained much P and had a high haptene content; phosphatides and glycerides were present. Extract (III) (5.4 g.) contained

little P and had a high acid-resistant power. Extracts (IV) (5.2 g.) and (V) (1.8 g.) contained P and gave on hydrolysis reducing sugars, including a pentose in (IV). The total glycerol content of the lipins, mainly present in extract (I), was < 12%. A.L.

Inhibiting action of phloridzin on the fermentation of sugar by B. coli. L. CALIFANO (Biochem. Z., 1934, 271, 123-126).-The fermentation of glucose, fructose, and mannose by B. coli is restricted by phloridzin (I) presumably because it inhibits phosphorylation. Fermentation of glucose is restricted 25% and 80% when the concn. of (I) is 0.0067M and 0.0133M, respectively. W. McC.

Reversible dehydrogenase systems. I. Reversibility of the hydrogenase system of B. coli. D. E. GREEN and L. H. STICKLAND (Biochem. J., 1934, 28, 898-900).-The equilibrium between H₂ and H' [as measured colorimetrically with methylviologen (A., 1933, 958) or electrometrically is attained in the presence of B. coli exactly as in the presence of Pt-black (A., 1931, 525). The catalysis by B. coli is completely reversible, the hydrogenase system being the most negative reversible oxidation-reduction system as yet described in living cells. F. O. H.

Influence of heavy water on the biological processes of bacteria. G. LOCKEMANN and H. LEUNIG (Ber., 1934, 67, [B], 1299-1302).-Increase in the concn. of H_2^2O between 0.02% and 0.54% has a favourable influence on the life of B. coli and B. pyocyaneus, since more AgNO₃ is required for their destruction as the concn. increases. H. W.

Decomposition of sodium formate by B. coli in the presence of heavy water. A. FARKAS, L. FARKAS, and J. YUDKIN (Proc. Roy. Soc., 1934, B, 115, 373-379).-Decomp. of HCO₂Na by hydrogenolyase of B. coli and by Pd-black occurs through at. reactions and the primary formed H1 and H2 exchange with those of H₂O and H₂O before formation of H₂ and H. G. R. H^3 .

Action at a distance of staphylococcal bacteriophage on staphylococcus. I. LOMINSKI (Compt. rend., 1934, 199, 168-170).—The bacteriophage has a mitogenetic effect on the bacteria. Induction is probably due to chemical reactions, as evidenced by the progressive disappearance of a catalase from the filtrates on exposure to air. J. L. D.

Increase in the resistance of protozoa to Xradiation caused by lecithin in colloidal solution. B.S. LEVIN and C. PIFFAULT (Compt. rend., 1934, 198, 2024-2026).-Lecithin (I) in colloidal solution increases the resistance of Paramecium aurelia to X-rays, the effect increasing if contact with (I) occurred 3-8 days before exposure, and thereafter decreasing. R. S. C.

Effect of hormones on creatine-creatinine metabolism: total nitrogen, uric acid, and allantoin. S. BUADZE (Z. ges. exp. Mcd., 1933, 90, 762-804).—In a bitch fed on a completely creatine (I)-free diet, injection of thyroxine (2 mg. daily) caused an increase in total creatinine (II) (especially preformed), uric acid (III), and allantoin (IV) and a slight rise in total N (V). During œstrus thyroxine (1 mg.) produced a greater increase of (II) with very slight rise

of (V) and insignificant change in (IV). Injection of l-adrenaline (3 mg. daily for 2 days) led to definite rise of (I), (II), (IV), and occasionally (III), but little change in (V). Smaller doses had practically no effect. Injection of phloridzin caused an increased output of (V) but no other significant change. Injection of 1 c.c. of menformone (40 units of folliculin) caused an increased output of (II) but no other change. Anterior pituitary hormone occasionally produced slight rise in (II) output, whilst after posterior lobe hormone no change was noted. Injection of insulin (20 units) caused a reduction of (II), (IV), and (V). 30 units of insulin produced an increased output of (II), (III), and (IV), but not of (V). Injection of parathormone led to an increased output of (II) and (V), but variations in (III) and (IV). Injection of guanidine carbonate (0.4 g. previously neutralised) caused a marked reduction in output of (II), (IV), and (V). When parathormone was given with guanidine there was no change from the normal, indicating some relationship between these two substances. NUTR. ABS. (m)

Effect of thyreotropic hormone and of desiccated thyroid on creatine and creatinine excretion. L. I. PUGSLEY, E. M. ANDERSON, and J. B. COLLIP (Biochem. J., 1934, 28, 1135—1140).—Feeding of thyreotropic hormone (I) and desiccated thyroid to normal rats produces increased creatine exerction (II). Extracts of adrenotropic and growth hormones, and of boiled thyreotropic extract, have no effect. (I) causes a greater rise in (II) with hypophysectomised than with normal rats, and also causes increased (II) in the dog. Increased (II) is not prevented by addition of antithyreotropic substance. L. D. G.

Influence of thyroid preparations on the plumage of birds. R. PRAWOCHEŃSKI and B. SLIZYŃSKI (Nature, 1934, 133, 950; cf. A., 1933, 1199). L. S. T.

Effect of splenic hormone, prosplen, on chlorine metabolism. H. PROBST (Z. ges. exp. Med., 1933, 92, 311—323).—Injection of splenic hormone into healthy fasting subjects changes the [Cl'] of the urine in one of three ways : steady reduction, reduction with temporary increases before the min. val. is reached in about 3 hr., or increase for 30—45 min., then reduction. The Cl content of the blood moves in an opposite direction to that of the urine. Injection of hormone prior to administration of saline causes a fall in blood-Cl, whilst previous administration of saline produces a rise. NUTR. ABS. (b)

Spleen and carbohydrate metabolism. F. RATHERY and R. COSMULESCO (Ann. Physiol. Physicochim. biol., 1933, 9, 939—942).—The effect of splenectomy (I) on blood-sugar and alimentary hyperglycæmia in the normal and depancreatised dog and of (I) followed by pancreatectomy (II) is variable. Most often (I) causes or increases hyperglycæmia, causes loss or prevents production of liver-glycogen, and aggravates the effect of (II). NUTR. ABS. (m)

Specific dietary factor for lactation. W. NAKA-HARA, F. INUKAI, and S. KATO (Proc. Imp. Acad. Tokyo, 1934, **10**, 268—270).—Extracts (I) prepared from ox liver by acidified 60% EtOH have a lactationpromoting action (II) in rats when added to diets adequate for growth, pregnancy, and parturition, but inadequate for lactation. Treatment of (I) with acid clay yields an adsorbed fraction which is poor in (II), whilst the non-adsorbed material has a marked (II). Hence the (II) of (I) is apparently not related to the content of vitamin-*B* complex. The factor to which (II) is due is designated "lactation factor" or "factor-L" (cf. A., 1932, 1174). F. O. H.

Lactation. II. Lactation-promoting substance in liver extract. W. NAKAHARA and F. INUKAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 33—38).—Female albino rats maintained on a certain diet (this vol., 317) failed to suckle their young. The young were often suckled after feeding with liver extract (prep. described), their growth was above the average, and in every case there was evidence of milk secretion. J. L. D.

Effect of vagotonin on adrenaline hyperglycæmia. D. SANTENOISE, G. FUCHS, L. MERKLEN, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1933, 114, 1021—1023).—Adrenaline, injected into dogs in physiological amounts after administration of vagotonin, exerts no hyperglycæmic action. The parasympathetic system appears to be involved.

NUTR. ABS. (m) Adrenalectomised, depancreatised cats. C. N. H. LONG and F. D. W. LUKENS (Science, 1934 79, 569—571).—Details of sugar metabolism in cats in which both adrenals and the pancreas have been removed in stages are given. Unilateral adrenalectomy does not appear consistently to prevent or alleviate the course of pancreatic diabetes, but complete adrenalectomy markedly ameliorates the usual results of complete pancreatectomy whether or not the diabetes has already developed. L. S. T.

Mode of action of the contra-insular hormone of the anterior pituitary. IV. Effect of the hormone when active extracts are introduced into cerebrospinal fluid. V. Effect of sympathetic poisons and narcosis on the blood-sugar reaction following administration of the hormone. Possibility of biological demonstration of VI. the hormone in cerebrospinal fluid. H. LUCKE and H. HAHNDEL (Z. ges. exp. Med., 1933, 91, 689-695, 696-703, 704-709).-IV. Suboccipital injection of active contra-insular hormone of the anterior pituit. ary produces immediately a marked and lasting rise of blood-sugar (I). Injection of normal saline has no effect, and boiling of the active pituitary extract lessens the intensity and duration of the hyperglycamic action.

V. Injection of ergotamine during the hyperglycæmic effect of the hormone quickly nullifies it, the (I) falling to normal : as the ergotamine effect on the sympathetic passes there is a very slight rise in (I). The action of somnifen on the central nervous system inhibits or prevents the action of the hormone even when injected directly into the cerebrospinal fluid (II).

VI. (II), whilst normally having no contra-insular effect, contains large amounts of the hormone after its intramuscular administration, the highest conen. being found in the second half hr. after injection.

The hormone is produced in the anterior pituitary,

passes into (II), acts on the sugar centre, and thence through the sympathetic and adrenals on the (I). NUTR. ABS. (m)

Anterior pituitary extract and hyperglycæmia due to adrenaline or morphine. B. A. HOUSSAY and E. DI BENEDETTO (Compt. rend. Soc. Biol., 1933, 114, 82—83).—After several days of treatment with large doses of anterior pituitary extract, prepared by the method of Evans and Simpson (Amer. J. Physiol., 1931, 98, 511), dogs exhibit an enhanced hyperglycæmic reponse to injections of morphine or adrenaline. NUTR. ABS. (m)

Nervous system in the production of posterior pituitary hyperglycæmia. B. A. HOUSSAY and E. DI BENEDETTO (Compt. rend. Soc. Biol., 1933, 114, 795—797).—The hypoglycæmic action of posterior pituitary extracts is lacking in the absence of the liver and adrenal glands, but pancreatectomy does not enhance it. It is slightly less after section of the splanchnic nerves, but is unaffected by vagotomy and may be due, in part, to a hypersecretion of adrenaline as well as to a direct action of the extract.

NUTR. ABS. (m)

Relation of the anterior pituitary to carbohydrate metabolism. B. O. BARNES and J. F. REGAN (Endocrinol., 1933, 17, 522—528).—A dog deprived of both pancreas and hypophysis showed glycosuria (I) only when injected with anterior pituitary extracts (II); it was very sensitive to insulin. Of Il normal dogs, 7 exhibited (I), reduced glucose tolerance, and raised fasting blood-sugar when injected with (II), but thyroidectomised dogs did not respond in this way. The injection of female sex hormone into dogs increased their sensitivity to insulin.

NUTR. ABS. (m)

Pituitary and nitrogen excretion in the toad. B. BRAIER (Compt. rend. Soc. Biol., 1933, 114, 80— 82).—Hypophysectomised toads on a N-frce diet excrete less N in the urine than do normal toads. Grafting of the glands on to such animals increases the Noutput to normal. NUTR. ABS. (m)

Hyperglycæmic action of posterior pituitary extract. B. A. HOUSSAY and E. DI BENEDETTO (Compt. rend. Soc. Biol., 1933, 114, 793—795).— Following intravenous injections, spread over 1 hr., of different amounts of a neutralised AcOH extract of a standard posterior pituitary powder, the curve connecting rise of blood-sugar and amount of extract injected is S-shaped. NUTR. ABS. (m)

Preparation of the homogeneous hormone from the corpus luteum. K. H. SLOTTA, H. RUSCHIG, and E. FELS (Ber., 1934, 67, [B], 1270-1273).-With the aid of suitable ketonic reagents, the following ketones have been isolated from the purified oils of the corpus luteum of the swine or from the active, cryst. products derived therefrom : luteosterone-A, m.p. 185-186° (crystallographical data), physiologically inactive; luteosterone-B, also inactive, and, like A, does not show a max. between 200 and 300 mµ characteristic of the absorption spectrum of the follicle hormone; luteosterone-C, C20H28O2 or C21H30O2, m.p. 127-128° (corr.), and luteosterone-D, m.p. 118-119° (corr.), which are physiologically active and very similar to one another. H. W.

Effect of sex hormones on the metabolism of the sex organs. S. ASCHHEIM and H. GESENIUS (Arch. Gynakol., 1933, 153, 434—446).—The O_2 quotient (I) of immature mouse-uterus was raised by previous injection into the animal of the urine of pregnant women. This is due to its content of æstrin, not to prolan. The response is not sp., being elicited by aolan, cantharidin, yohimbine, and male hormones. The injection of male hormone preps. into immature male mice increased the (I) of the testes. This effect is sp. The increases in tissue respiration occur very rapidly after the injections. NUTR. ABS. (b)

Carotene. VIII. Separation of carotenes by adsorption. H. H. STRAIN (J. Biol. Chem., 1934, 105, 523-535).— α - and β -Carotenes may be isolated from natural products by adsorption on MgO without previous crystallisation. They occur as such in plants. H. G. R.

Substance A', intermediate between vitamin-Aand β -ionone. A. CHEVALIER, Y. CHORON, and J. GUILLOT (Compt. rend., 1934, 198, 2207—2208).— When vitamin-A is irradiated in 95% EtOH, the absorption max. at 3280—3250 Å. remains unchanged until a late stage in the decomp., but changes occur between 3000 and 2700 Å. There is formed a *sub*stance, sparingly sol. in EtOH, provisionally named A', having an absorption max. in hexane at 3125 Å., and giving β -ionone when further irradiated. R. S. C.

Substance inhibiting the Carr-Price reaction. O. RYGH (Bull. Soc. Chim. biol., 1934, 16, 609-611). Cod-liver oil contains a substance, saponified with difficulty, which inhibits the Carr-Price reaction for vitamin-A.

Relation of growth response to dosage of vitamin-A. K. H. COWARD (Biochem. J., 1934, 28, 865-869).—The validity of the previously established curve (I) relating response to dosage of vitamin-A (II) (A., 1931, 269) was confirmed by testing (II) in doses of known ratio. (I) is applicable to various sources of (II) (butter, fish-meal, cod-liver oil, dried milk, wheat germ, etc.) in doses from that just sufficient to maintain wt. in rats to that 50 times as great. Comparison with (I) from other laboratories indicates differences, probably due to the basal diet used.

F. O. H.

Simplification of vitamin tests. [Vitamin-A and -D.] K. H. COWARD and K. M. KEY (Biochem. J., 1934, 28, 870-874).—With vitamin-A tests on rats, the increase in wt. is approx. the same for either daily or half-weekly doses, whilst the accuracy of the test is not significantly decreased. Similarly with vitamin-D (cod-liver oil or international standard) the whole dose can be administered at the beginning of the 10 days' curative period instead of in ten daily doses. F. O. H.

Influence of solvent on the vitamin-A activity of carotene and cod-liver oil. F. J. DYER, K. M. KEY, and K. H. COWARD (Biochem. J., 1934, 28, 875-881).—The biological activity of the provisional international vitamin-A standard (I) (a carotene prep.) depends on the nature of the solvent used. Thus solutions in arachis or coconut oil have a potency 5-6 times that of equal (wt./vol.) solutions in hardened cotton-seed oil or Et laurate. Similarly the activity of cod-liver oil depends on the diluent used. No correlation appears to exist between the yellow colour of different solutions and their activity. β -Carotene has a potency 175% of that of (I). F. O. H.

Relation of the colour and vitamin-A content of butter to the nature of the ration fed. I. Influence of the ration on the yellow colour of the butter. S. J. WATSON, G. BISHOP, and J. C. DRUM-MOND. II. Carotenoid and vitamin-A contents of the butter. A. E. GILLAM and I. M. HEILBRON (Biochem. J., 1934, 28, 1076-1085).-The yellow colour (I) of cow-butter (II) is increased by the addition of 50% of artificially dried grass to winter rations. Although there is considerable difference in the "ceiling "val. of (I) for Shorthorn and Ayrshire (II) when equiv. amounts of carotene (III) are fed, there is very little difference in vitamin-A content (IV). (IV) in goat-butter is similar to that of (II), although (III) was <5% of that in (II). H. G. R.

Long-duration experiments on the fat-soluble vitamins. L. RANDOIN and R. NETTER (Bull. Soc. Chim. biol., 1934, 16, 595-608).-Small amounts of maize-gum oil administered to young rats, fed on a diet complete in all respects except that it kept the animals sterile, permitted reproduction, but not the survival of the young. Wheat-germ oil (I), however, which contained only traces of vitamin-A (II), whilst unable to promote reproduction, permitted the survival of the young of older rats when administered before weaning. (I) administered to rats fed on a diet which contained no (II) promoted better growth over long periods than that obtained with supplements of comparable amounts of carotene or cod-liver oil. Hence (I) probably contains a growth factor different from the known forms of (II). A. L.

Comparative antirachitic efficiency of irradiated ergosterol and cod-liver oil for the chicken. Determination of rachitic leg-weakness. M. J. L. DOLS (Arch. Néerland. Physiol., 1934, 19, 290—294). —The observations of Steenbock and others, that irradiated ergosterol in peanut oil is less effective against rachitic leg-weakness (I) in chickens than the rat equiv. of cod-liver oil, are confirmed. The radiographic examination of the ribs is recommended as a shorter and more trustworthy method for the determination of (I). R. N. C.

Calcifying properties of green, artificially dried, and sun-cured pasture herbage. R. E. HODGSON and J. C. KNOTT (J. Agric. Res., 1934, 48, 439—446).—The degree of calcification (I) in rats was practically the same whether herbage was fed fresh, hayed, or artificially dried. Optimum (I) was attained by inclusion of 3% of herbage (dry wt.) in the ration. A. G. P.

Vitamin-D international standard. Determination of the biological activity. L. RANDOIN (Bull. Soc. Chim. biol., 1934, 16, 428-439).—The curing of young rats (30-32 g. wt.) made rachitic by the feeding of a vitamin-D-free diet requires a daily dose of 0.0005 mg. of the 1932 standard solution of irradiated ergosterol, *i.e.*, 5 international units of vitamin-D. A. L. Antisterility vitamin and the fat-soluble growth vitamins. L. RANDOIN and R. NETTER (Bull. Soc. Chim. biol., 1934, 16, 581—594).—The relationship in occurrence and properties between the carotenoid substances (auxematols) possessing vitamin-A and -Eactivity is pointed out. A. L.

Realisation of alimentary equilibrium permitting growth in rats in the absence of all known fat-soluble vitamins. L. RANDOIN and R. NETTER (Compt. rend., 1934, 198, 2120—2122).— A diet consisting of caseinogen 15%, brewer's yeast 5%, lard 20%, dextrin 56%, salts 4%, cellulose (filter paper), and distilled H₂O, but free from vitamin-A,-D, and -E, maintains normal life and growth in rats, and acts as a curative diet for avitaminosis-A.

J. W. B.

Vitamin- B_1 international standard. Determination of the biological activity. L. RANDOIN (Bull. Soc. Chim. biol., 1934, 16, 440—447).—Adult pigeons fed on a diet containing no vitamin-B require a min. daily dose of 75 mg. of the international standard prep. (I) of vitamin- B_1 , *i.e.*, 7.5 international units, to prevent the appearance of symptoms of polyneurits. (I) also contains vitamin- B_2 and $-B_3$. A. L.

Comparative determinations of the antineuritic vitamin content of rice, made by experiments on the rice-bird, and by the rat tests. J. P. SPRUYT (Arch. Néerland. Physiol., 1934, 19, 295-300).—Determinations of the vitamin- B_1 contents of six samples of rice gave identical results with rice-birds and rats. R. N. C.

Antineuritic vitamin. V. Preparation of vitamin concentrate suitable for parenteral use. E. H. STUART, R. J. BLOCK, and G. R. COWELL (J. Biol. Chem., 1934, 105, 463-466).—Rice polishings are extracted with $CHCl_3-H_2O$ and Lloyd's reagent (I) is added at $p_{\rm H}$ 4.5. Vitamin- B_1 is eluted from (I) with warm EtOH-HCl. Further purification is obtained by repeating the adsorption on (I). H. D.

Action of crystalline vitamin- B_1 on the respiration of polyneuritic tissues in vitro. R. H. S. THOMPSON (Biochem. J., 1934, 28, 909–915).—Addition of vitamin- B_1 to minced muscle, heart, and liver tissue from polyneuritic pigeons has no effect on their O₂ uptake, but with kidney it causes a large increase, restoring the val. almost to normal. C. G. A.

Pyruvic acid as an intermediary metabolite in the brain tissue of avitaminous and normal pigeons. R. A. PETERS and R. H. S. THOMPSON (Biochem. J., 1934, 28, 916—925).—Disappearance of AcCO₂H (I) accompanies the increased O₂ uptake induced by cryst. vitamin-B₁ in pigeon-brain tissue (II) in vitro, 2 O₂ corresponding approx. to 1 mol. of (I). It is thought that (I) is a normal intermediate in the metabolism of (II). (I) accumulates in normal (II) in presence of CH₂I-CO₂Na, but not of NaF C. G. A.

Reduction-oxidation potential of lactoflavin and its derivatives. R. KUHN and G. MORUZZI (Ber., 1934, 67, [B], 1220-1223).—The normal potentials of lactoflavin (I) and its tetra-acetate, lumilactoflavin and its N-Me and NN'-Me₂ deriv-

atives, and of the degradation acid (II), C12H12O3N2, have been measured against the normal H_2 electrode at $p_{\pi} 5.9$ and $p_{\pi} 7.0$. The redox behaviour is very little affected by acetylation, methylation, or removal of the sugar-like side-chain. Since the behaviour of (II) is also closely similar to that of the flavins, it follows that the unexplored fundamental unit of the flavin mol. with 2 N is entirely responsible for the oxidation-reduction behaviour. Addition of the alkali-labile ring system and, further, of the sugar-like side-chain is practically without influence. The ring system containing :N·CO·NH·CO· determines the colour and absorption spectrum of the flavins, which is not influenced by addition of the sugar-like side-chain and only slightly affected by subsequent union with protein. The sugar-like side-chain is causative of the vitamin nature of (I), which is retained on further addition of protein. The presence of the latter imparts enzymic character to the pigment. H. W.

Alkali-labile ring of lactoflavin ; monomethyl and dimethyl compounds. R. KUHN and H. RUDY (Ber., 1934, 67, [B], 1125—1130).—Treatment of the Ag salt of lumilactoflavin (I) with MeI at room or slightly elevated temp. yields N-methyl-lumilactoflavin (II), m.p. 326° (decomp.), which contains one active H (Zerevitinov). The absorption spectra of (I) and (II) are identical. The brilliant green fluorescence of (II) is reversibly destroyed by dil. alkali. Treatment of (I) with NaOH and Me₂SO₄ yields NN'dimethyl-lumilactoflavin (III), C₁₅H₁₆O₂N₄, m.p. 286° (corr.), which does not contain active H. Its fluorescence is irreversibly destroyed by NaOH owing to hydrolysis. When heated with NaOH (III) loses 2NMe and yields the carboxylic acid, C₁₂H₁₂O₃N₂, m.p. 215°, identical with that obtained from (I). (I) is therefore C₁₁H₁₀N₂{ \cdot NH·CO \cdot CO·NH^{*} H. W.

Constitution of lumilactoflavin. R. KUHN and H. RUDY (Ber., 1934, 67, [B], 1298—1299).—Lumilactoflavin yields about 0.5 mol. of alkyl iodide, and therefore consists of about equal parts of an alkylimide-free (α) and alkylimide-containing (β) pigment. The Na₂CO₃-sol. portion obtained by alkaline hydrolysis is free from NAlk and therefore derived from α -lumilactoflavin. The carboxylic acid (I) C₁₂H₁₂O₃N₂, the product C₁₁H₁₂ON₂ of its decarboxylation, and the 0-free base obtained from (I) by energetic alkaline degradation contain NAlk. H. W.

1:3-, 6:7-, 7:8-, and 6:8-Me₂ derivatives, with exception of those substituted in the alloxan ring, give compounds closely similar to but not identical with photoflavin. H. W.

Vitamin- B_3 . J. R. O'BRIEN (Biochem. J., 1934, 28, 926-932).—Supplements of 20-30 doses of vitamin- B_1 (I) failed to restore the wt. of pigeons (II) on a diet of polished rice (III) or autoclaved whole wheat. Extracts (IV) obtained by hydrolysis of wheat germ with boiling $N-H_2SO_4$ restore the wt. of (II) on (III)+(I). (IV) is inactivated by oxidation. (II) on (III)+6 to 12 doses of (I) do not regain wt. when given 2 g. of caseinogen daily. Vitamin- B_3 is regarded as a wt.-restoring factor. C. G. A.

Maintenance nutrition in the pigeon and its relation to heart block. C. W. CARTER (Biochem. J., 1934, 28, 933—938).—The failure of restoration of wt. of pigeons on a polished rice diet supplemented by a yeast concentrate is partly due to inadequate protein allowance which can be made good by addition of caseinogen. Such regain in wt. may, however, be accompanied by cardiac arhythmia, which can be climinated by wheat-germ extract (see preceding abstract). C. G. A.

Vitamin-C in the human pituitary. J. GOUGH (Lancet, 1934, 226, 1279—1281).—The Szent-Györgyi test shows that the reaction for ascorbic acid is less intense in old than in young individuals (I), that it is intense in the anterior lobe of young or middle-aged (I) in whom general body nourishment had been normal, and that it is slight or negative in (I) who had died of prolonged illness with severe emaciation. L. S. T.

Ascorbic acid content of certain citrous fruits and manufactured citrous products. A. L. BACHARACH, P. M. COOK, and E. L. SMITH (Biochem. J., 1934, 28, 1038-1047).-Titration of ascorbic acid (I) in fruit juice with 2:6-dichlorophenol-indophenol gives slightly but appreciably more reproducible results than titration with I, the two methods giving results usually in good agreement. Extreme and mean vals. of (I) per ml. of juice were : for oranges (II), 0.22, 0.89, 0.51 mg.; for tangerines, 0.10, 0.78, 0.37 mg.; lemons (III), 0.47, 0.73, 0.64 mg. Variations were often found even between fruits from the same consignment. Storage for 1 month caused, on the average, nearly 20% loss of (I) in (II), but only 6% in (III). Concn. and subsequent storage of (II) juice leads to no appreciable loss of (I). Marmalades containing most peel are richest in (I) (up to 0.14 mg. per g.). In all types of citrous fruits, the flavedo is richest and the albedo next richest in reducing power; the juice was poorer in (I) than the peel, whilst the pips contained no demonstrable amount. A. E. O.

Nature of the precursor of vitamin-C in the vegetable kingdom. I. Vitamin-C in the growing pea seedling. S. N. RAY (Biochem. J., 1934, 28, 996-1003).-Pea seedlings were grown on nutrient gelatin containing a possible precursor of ascorbic acid (I). The rate of production of (I) bore no direct relation to the rate of growth. Hexoses (II), especially mannose (a growth inhibitor), favoured greatly increased production of (I) (up to 0.5 mg. per g. wet tissue) over the control (0.05 mg. per g.); dissacharides were less effective; arabinose and xylose (good growth-promoters), starch and dextrin, sugar alcohols, glycerol, AcCHO, and AcCO₂Na, Na glutamate, lactate, and glycerophosphate were all ineffective. The (I) content fell steadily during prolonged cultivation. (II) may serve as precursors of (I) in germinating seeds. A. E. O.

Synthesis of vitamin-C.—See this vol., 869.

Influence of vitamin-C on plant and animal amylases. A. PURR (Biochem. J., 1934, 28, 1141— 1148).—Vitamin-C (ascorbic acid) (I) is a sp. activator for β -amylase (II) of animal origin. With barleyamylase, (I) has an inhibiting effect on (II), but no effect on α -amylase (III); the oxidised form of (I) has no effect on (II), but inhibits (III). L. D. G.

Effect of ascorbic acid on fatty acid oxidations in the liver. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1934, 28, 1014-1027).-In presence of liver slices (I), ascorbic acid (II) is only partly oxidised at 37° at $p_{\rm II}$ 7.4 in presence of O₂. Presence of (II) results in increase in Q_{o} , and in the production of CH₂Ac·CO₂H (III) when rat (I) or scorbutic guinea-pig (I) [but not normal guinca-pig (I)] are placed in a glycerophosphate-Locke medium containing Na butyrate or crotonate. (II) also prolongs the steady rate of O_2 uptake by (I). It is suggested that the effects of (II) on production of (III) are due to the oxidation of fatty acids, being inherently connected with the general respiratory metabolism of (I). (II) appears not to affect the oxidation of dl-OH·CHMe·CH₂·CO₂H in presence of rat (I). The large inhibitory effect of 0.0002N-CH₂I·CO₂H on the production of (III) is reduced by presence of (II), the reduction not being due to a chemical reaction between these compounds. There is no distinct correlation between production of (III) and the glycogen content of the liver (cf. this vol., 210). A. E. O.

Physiological action of ascorbic acid and some related compounds. V. DEMOLE (Biochem. J., 1934, 28, 770-773).—Large doses of ascorbic acid (I) (up to 5 g. per kg. in one dose or up to 12 g. per kg. over a no. of days) administered to various warm- and cold-blooded animals produced no toxic effect. Of 0.1 g. of (I) per kg. administered subcutaneously to a dog 75% was excreted in the urine. Synthetic *l*-(I) (A., 1933, 1035) behaved biologically identically with *l*-(I) from paprika, but synthetic *d*-(I) as well as *l*erythro-3-ketohexonic acid, *d*-lyxo-3-ketoheptonic acid, *l*-xylo-3-ketoheptonic acid, and *d*-arabo-3-ketohexonic acid were without biological activity. *d*-Erythro-3-ketohexonic acid had an activity about 1/20 of that of *l*-(I). W. O. K.

Hæmorrhages in chicks reared on artificial diets; a new deficiency disease. H. DAM (Nature, 1934, 133, 909—910).—Extensive subcutaneous or intramuscular hæmorrhages (I) occur in chicks fed on a diet of vitamin-A-free caseinogen, marmite, salt mixture, starch, and cod-liver oil concentrates. Vitamin-C (II) as lemon juice or as ascorbic acid has no effect on the symptoms, but with a diet of cereals or seeds+salts (I) do not occur. The disease is due to an antihæmorrhagic factor different from (II) and present in cereals or seeds. L. S. T.

Chemical aspects of carbon assimilation. N. R. DHAR (J. Indian Chem. Soc., 1934, 11, 145– 178).—A lecture, mainly historical. F. R. S.

Relationship between nitrogen and chlorophyll content in the natural and morbid yellowing of leaves. R. S. HILPERT and K. HEIDRICH (Ber., 1934, 67, [B], 1077-1081).—Data are given for the % of N and chlorophyll (I) determined by the authors' method and according to Willstätter for the strong, green leaves, the lower leaves from incipient to complete fading, the stalks and pale green, lower portions of leaves, and the cars including the grains of wheat. It appears that (I) is united with a certain portion of the protein (" mobile protein ") in contrast to the fixed portion which remains after fading. The relationship is quant. when taken over the complete period of vegetation. Acute poisoning (SO₂ or Cl₂) causes little alteration in the % of N, whilst different vals. for (I) are given by the two methods of determination, indicating that much (I) exists in a colourless or slightly coloured form which yields a coloured Cu compound. Necrosis and rust cause diminution of % N to 1.09% and 1.94%, respectively, the latter val. corresponding with the presence of (I) in considerable amount. H. W.

Adsorption of sunflower oil by the hulls. J. KOLPAKOV (Masloboino Zhir. Delo, 1933, No. 4, 19-22).-16.6-18.5% of the oil may be adsorbed. CH. ABS.

Absorption by plants. VI. Urea and its comparison with ammonium salts. F. DIAZ AGUE-RECHE and A. CASTILLO (Anal. Fis. Quím., 1933, 31, 669-671; cf. B., 1932, 653).—Urea shows a pronounced toxic effect, causing loss in wt. comparable with that caused by NH₄Cl, but more intense with small conens. The effects of urea, NH₄Cl, and NH₄NO₃ (in which the toxicity of NH₄⁻ is partly neutralised by NO₃⁻) are directly compared. R. K. C.

Variations of the apparent $r_{\rm H}$ of soil during growth of plants. L. MEYER (Compt. rend., 1934, 198, 2199—2201).—Beans (I) and *Lolium* growing in soil, or (I) in Knop's liquid, induce an $r_{\rm H}$ in the soil or liquid independent of the initial $r_{\rm H}$, but dependent on the plant and nature of the soil. R. S. C.

Effect of yeast extract on the growth of plants. B. V. NATH and M. SURYANARAYANA (Nature, 1934, 134, 27).—A claim for priority (cf. this vol., 463). L. S. T.

Effect of folliculin on plant growth. H. VON EULER and B. ZONDEK (Biochem. Z., 1934, 271, 64– 73; cf. A., 1931, 1337; 1932, 1068).—Although folliculin (I) added to nutrient media of growing hyacinths (II) disappears and cannot be recovered from plant or medium, no acceleration of growth or development of (II) can be observed. Living or pulped roots of (II) rapidly inactivate (I) which cannot then be re-activated by boiling with HCl. No inactivation of (I) is caused by fresh or dried yeast or by boiled root pulp from (II). W. McC.

Influence of hormones on foliage and development of vegetables. D. V. HYKES (Compt. rend. Soc. Biol., 1933, 113, 629-632).—Adrenaline (I), thyroxine (II), and hypophysin have either a stimulatory or inhibitory action on plant growth, according to the concn. in which they are applied. The action of (II) is mainly on the leaves, and of (I) and (III) on root development. Insulin and tricresol favourably affected growth at all concns. examined. A. G. P.