## BRITISH CHEMICAL ABSTRACTS

## A.--PURE CHEMISTRY

**OCTOBER**, 1934.

## General, Physical, and Inorganic Chemistry.

Origin of anomalous displacements in the Stark effect of hydrogen. W. STEUBING and P. JAKEL (Z. Physik, 1934, 90, 112-132).

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A. B. D. C.

Demonstration of the axiality of light emission of the ultra-violet hydrogen lines 1025 and 1215 A. R. FRERICHS and H. BOMKE (Physikal. Z., 1934, 35, 549-551).—For the 1025 A. line, with parallel emission, the ratio of the intensity of the longwave to that of the short-wave component is 1:2. An approx. val. of 1:1.5 is obtained for opposite emission. For the 1215 Å. line, the components have the same intensity in both parallel and opposite emission. A. J. M.

Nuclear spin of deuterium. G. M. MURPHY and (MISS) H. JOHNSTON (Physical Rev., 1934, [ii], 46, 95-98).-Determination of the alternating intensities in emission of the  $\Delta v = 0$  sequence of the Fulcher bands leads to a nuclear spin of unity. N. M. B.

Direct proof of the existence of metastable molecules in active nitrogen. J. KAPLAN (Nature, 1934, 134, 289).-The bands 2760.6 and 2603.8 Å. appear in the N afterglow and provide direct proof of the existence in it of metastable mols. L. S. T.

Situation of the A  $({}^{3}\Sigma)$  level in the nitrogen molecule. E. T. S. APPLEYARD, N. THOMPSON, and S. E. WILLIAMS (Nature, 1934, 134, 322-323).

L. S. T.

Measurements of intensity distribution and width of predissociation lines of the AlH molecule. II. H. C. BURGER and P. H. VAN CITTERT (Z. Physik, 1934, 90, 70).-Polemical against Farkas and A. B. D. C. Levy (this vol., 823).

Further band systems of aluminium hydride. W. HOLST (Nature, 1934, 134, 322).-The band system at 4950 Å. (this vol., 715) belongs to a  ${}^{1}\Sigma^{***} \longrightarrow {}^{1}\pi$ L. S. T. transition.

Continuous emission spectra of atomic origin. G. BALASSE (J. Phys. Radium, 1934, [vii], 5, 304-308).—Spectra excited by electrodeless discharge have been photographed for the neutral atoms of K, Rb, Cs, Zn, Hg, P, As, Bi, S, and I, and for the ionised atoms of Hg, S, and I. Properties and mechanism of emission are discussed. The coincidence of certain lines with the continuous spectrum is explained by anomalous dispersion (see this vol., 935).

N. M. B.

Deepest terms in ions of the isoelectronic sequences Ni I to Kr IX and Pd I to Xe IX. P. G. KRUGER and W. E. SHOUPP (Physical Rev., 1934, [11], 1051

46, 124-129).-Radiations corresponding with energy differences between terms have been found, and new lines of Kr IX and Xe IX are predicted. N. M. B.

Spectrum of nickel hydride. A. G. GAYDON and R. W. B. PEARSE (Nature, 1934, 134, 287).-Details of a spectrum attributed to the mol. NiH are given. L. S. T.

Spectrum of zinc. L. BLOCH and E. BLOCH (J. Phys. Radium, 1934, [vii], 5, 289-298).-The spark spectrum in vac. revealed the new Zn IV order of <120 lines in the range 4000-2500 Å. The highfrequency electrodeless discharge allowed the separation of the orders Zn II, giving < 50 new lines, Zn III, and Zn IV. Data for about 800 lines are tabulated.

N. M. B.

1 62

Band spectrum of Se<sub>2</sub>. E. OLSSON (Z. Physik, 1934, 90, 138-144).—Bands near 3700 and 3900 Å. were investigated; Se<sup>80</sup> has no nuclear spin.

A. B. D. C.

Second spark spectrum of tellurium. S. G. KRISHNAMURTY (Nature, 1934, 134, 255).—The funda-mental intervals  $5p^3P_0$ — $5p^3P_1$ ,  $5p^3P_2$ — $5p^3P_2$ , and  $5p^3P_2$ — $5pD_2^1$  are 4751, 3410, and 9198 cm.<sup>-1</sup>, respec-tively. The calc. third ionisation potential of Te is approx. 29.5 volts. L. S. T.

Excitation and ionisation of mercury atoms in columns of the rare gases containing mercury. F. M. PENNING (Physica, 1934, 1, 763-769).-From spectrograms of the positive columns of the rare gases at a pressure of 10 mm. and at 0° and 19°, in presence and absence of Hg, it is concluded that at 19° the positive ions are mainly Hg<sup>+</sup> formed by direct electron collision, whilst at 0° excitation of rare gases is H. S. P. necessary.

Initial stages of spark discharges in gases. H. J. WHITE (Physical Rev., 1934, [ii], 46, 99-106).-Using the electro-optical shutter, a study in N<sub>2</sub>, H<sub>2</sub>,  $O_2$ ,  $CO_2$ , He, and A at atm. pressure and gaps < 1 cm. shows four types of spark breakdown characterised by the appearance and growth of luminous streamers; the velocity of the latter in H<sub>2</sub> and N<sub>2</sub> is approx.  $10^7$ cm. per sec., agreeing with calc. electron velocities under breakdown conditions. Results indicate that the current at breakdown is carried mainly by electrons, which come from the cathode rather than from ionisation in the gas. The space charges causing breakdown arise from differences in mobility velocity of N. M. B. electrons and positive ions.

Interior radiation of the electric arc. T. PECZALSKI (Compt. rend., 1934, 199, 405-407).-Using hollow C electrodes it has been shown that the spectrum of the internal layers of an arc salted with  $CaF_2$  includes Ca, C, N<sub>2</sub>, and O<sub>2</sub> bands, whilst the radiation from the exterior consists principally of  $CaF_2$  bands. J. W. S.

Thermal mechanism in the column of the arc. L. S. ORNSTEIN and H. BRINKMAN (Physica, 1934, 1, 797—824).—Theoretical. The formation and destruction of excited particles in the ordinary arc is due chiefly to collisions between atoms and mols. Near the electrodes and at low pressures, excitation and ionisation due to electron collision may occur, so that the thermal mechanism of the arc changes into the electron mechanism of the glow discharge. H. S. P.

Formation of hydrogen in a vacuum. M. POSEJPAL (Compt. rend., 1934, 199, 186–188; cf. this vol., 236, 471).—It has been shown that  $H_2$  preexisting in the discharge tube cannot account for the development of  $H_2$  in a vac. during discharge, described previously. Measurable vols. of  $H_2$  are developed in a vac. tube which contains 30 thin Pt wires (12 connected to the cathode and 18 to the anode), but  $H_2$  is not developed when the same current is passed but with no wires in the tube. The vols. produced are about twice those which are formed by the same current during electrolysis, in agreement with the author's theory. J. W. S.

Emission of low-penetrating radiation by charged insulators. G. REBOUL (J. Phys. Radium, 1934, [vii], 5, 329—343).—Charged insulators emit, in losing their charge, a highly absorbable radiation which ionises gases, affects a photographic plate, and gives rise to invisible phosphorescence phenomena. Certain anomalies which are shown by insulators and can be explained by the emission, and the properties, nature, and origin of the radiation are examined and discussed. N. M. B.

X-Ray dispersion in nickel by the method of total reflexion. A. J. LAMERIS and J. A. PRINS (Physica, 1934, 1, 881–888; cf. A., 1931, 1105).—The hump found by Kiessig in the dispersion curve near to the Ni K edge is not confirmed. The results obtained do not agree with Honl's theoretical curve.

H. S. P.

Fine structure of X-ray absorption edges of the polyatomic vapours  $GeCl_4$  and  $AsCl_3$ . D. COSTER and G. H. KLAMER (Physica, 1934, 1, 889— 894).—The fine structure of the K absorption edge of Ge and As in the vapours of  $GeCl_4$  and  $AsCl_3$ , respectively, has been measured, and found to extend for several hundred volts from the edge. For  $GeCl_4$  fine structure agrees with theory (see following abstract); for  $AsCl_3$  it indicates that the distance of the Cl atoms from the As atom is about 2.20 Å. H. S. P.

Theoretical calculation of the fine structure for the *K* absorption band of Ge in GeCl<sub>4</sub>. D. R. HARTREE, R. DE L. KRONIG, and H. PETERSEN (Physica, 1934, 1, 895-924).—Mathematical.

H. S. P.

K Series X-ray emission lines of iron in several compounds. S. TANAKA and G. OKUNO (Japan. J. Physics, 1934, 9,75—79).— $K\alpha_1, K\alpha_2, K\beta$ , and  $K\beta'$  lines of Fe were investigated for Fe, Fe<sub>2</sub>O<sub>3</sub>, FeS, FeS<sub>2</sub>, and K<sub>3</sub>Fe(CN)<sub>6</sub> by means of the secondary method. Separation of  $K\beta'$  from  $K\beta_1$  was obtained for  $\text{Fe}_2O_3$  and FeS. Displacement of the  $K\beta_1$  lines of the compound relative to that of the pure element was detected especially for  $\text{FeS}_2$ . With Fe and the other compounds investigated  $\Delta\lambda$  for the  $K\alpha$  doublet is 4, whereas  $\text{FeS}_2$ has the corresponding  $\Delta\lambda 3.82$ . W. R. A.

Quadrupole lines in the K series of ruthenium. E. WILHELMY (Physical Rev., 1934, [ii], 46, 130–132). —The Ru  $K\beta_4$  (K— $N_{IV}N_V$ ) and  $K\beta_5$  (K— $M_{IV}M_V$ ) lines have been observed with a double crystal spectrometer; the wave-lengths are 0.55974 and 0.56668 Å., respectively.  $K\beta_5$  appears to be a doublet; the width of the single components is < 11 volts;  $K\beta_4$  is 28 volts. The intensity ratios are:  $K\beta_4/K\alpha_1=1/160, K\beta_5/K\alpha_1=1/400$ . A very faint line ( $K\beta_6/K\alpha_1=1/2000$ ) of  $\lambda$  0.558 Å, has been observed. N. M. B.

Intensity measurements of X-ray spectral lines. M. BÖTZKES (Z. Physik, 1934, 89, 667–681). —Relative intensities are given for Ta L lines.

A. B. D. C. Determination of atomic scattering factors for X-rays in the region of L absorption edges. J. BRENTANO and A. BAXTER (Z. Physik, 1934, 89, 720-735).—Observations were made for W and Al. A. B. D. C.

L Absorption discontinuities of bismuth. L. H. CARR (Physical Rev., 1934, [ii], 46, 92–95).– Using balanced cells containing  $Bi(NO_3)_3, 5H_2O$  in dil.  $HNO_3$ , and dil.  $HNO_3$ , respectively,  $\mu/\rho$  was measured at 20 wave-lengths in the range 0.56-1.54 Å. Equations to the branches of the curve and the magnitudes of discontinuities were deduced. N. M. B.

Experiment showing the dark current of alkali cells due to a glow electron current. R. SCHULZE (Z. Physik, 1934, 90, 63-69).—The dark current is shown as exponentially dependent on temp., and must be due to a glow electron current.

A. B. D. C.

Form of discharge in gas-filled photo-cells. F. ROTHER and H. BOMKE (Physikal. Z., 1934, 35, 703—705).—In the gas-filled cell a form of discharge occurs well below the breakdown potential. It is not a glow discharge, but is an accompaniment of the increase in the photo-current brought about by ionisation by collision. The nature of the discharge does not vary with the type of anode. A. J. M.

Secondary emission of tantalum. R. WAR-NECKE (J. Phys. Radium, 1934, [vii], 5, 267–282).— The variation of the no. of secondary electrons ejected from a Ta target as a function of the speed of the primary electron in the range 0—1000 volts has been investigated. Distribution curves show that secondary electron speeds lie between zero and that of the primary electron. N. M. B.

Ratio of the dia- and para-magnetism of an electron gas as a function of the strength of field. K. F. NIESSEN (Physica, 1934, 1, 783—796).—Mathematical. This ratio is not const. With stronger fields the Landau diamagnetic effect increases relatively to the Pauli paramagnetic effect. H. S. P.

Proton production in the low-voltage arc. E. S. LAMAR and O. LUHR (Physical Rev., 1934, [ii], 46, 87—91).—An improved design of tube gave proton current/total current as high as 98% at 0.3—0.4 mm. pressure. N. M. B.

Diffusion of positive ions of salts through copper, silver, and gold at high temperature. Mass spectrograph analysis of emitted ions. J. CICHOCKI (Ann. Physique, 1934, [xi], 2, 160).—A correction (cf. this vol., 125). N. M. B.

Effect of the electric field on alkali metal atoms in atomic ray experiments. H. SCHEFFERS and J. STARK (Physikal. Z., 1934, **35**, 625–627).—Experiments with at. rays of K, Li, and Cs in electrical fields of various strengths show that a moment is produced  $\infty$ the field strength, the proportionality factors being  $4\cdot 2$ ,  $3\cdot 4$ , and  $1\cdot 2$  (all  $\times 10^{-23}$ ), respectively.

A. J. M.

Revision of at. wt. of niobium. Analysis of niobium pentachloride. O. HÖNIGSCHMID and K. WINTERSBERGER (Z. anorg. Chem., 1934, 219, 161— 177).—Methods for the prep. of pure Nb<sub>2</sub>O<sub>5</sub> are described. Nb<sub>2</sub>S<sub>5</sub> was prepared by the action of H<sub>2</sub>S and CS<sub>2</sub> on Nb<sub>2</sub>O<sub>5</sub> at 1000°. NbCl<sub>5</sub> was formed by the action of Cl<sub>2</sub> on Nb<sub>2</sub>S<sub>5</sub> and purified by fractional sublimation in vac. The at. wt. of Nb is 92.91 (Ag 107.880, Cl 33.457), in good agreement with the val. obtained by the mass spectrograph. M. S. B.

Thermal data and at. wt. of xenon. W. HEUSE and J. OTTO (Physikal. Z., 1934, 35, 628-629).—The 0° isotherm and the expansion and potential coeffs. of Xe have been determined. The at. wt. determined from the density of the gas is  $131\cdot22\pm0\cdot02$ .

A. J. M.

Radioactivity of samarium. HERZSFINKIEL and A. WRONCBERG (Compt. rend., 1934, 199, 133—135). —The max. penetration of  $\alpha$ -particles emitted by Sm<sub>2</sub>O<sub>3</sub>, measured by an ionisation chamber and electroscope method, was 1.67 cm., confirming the val. found by Curie and Joliot (Mäder, this vol., 713). 1 g. of Sm emits 67 particles per sec. B. W. B.

Actinium-uranium ratio in radioactive minerals. (MLLE.) E. GLEDITSCH and E. FOEYN (Compt. rend., 1934, 199, 412—414).—The mean Ac: Io ratio for a no. of minerals from different sources is calc. as 0.243:1. This, combined with the accepted val. for Io: U (0.53:1), indicates Ac: U 0.128:1. For every 100 atoms of U, 4 disintegrate into Ac. It is concluded that if Ac is derived from an isotope of U the half-life period of the latter should not differ from that of U-I. J. W. S.

Ultimate origin of the actinium series. H. J. WALKE (Phil. Mag., 1934, [vii], 18, 256-262; cf. this vol., 471).—It is suggested that the Ac series arises from the disintegration of the heavy U isotope (called protactino-uranium PrAcU) of at. wt. 239, and not as a result of branching of the main U series. PrAcU is stated to lose an  $\alpha$ -ray to form a product (U-Z<sub>1</sub>) of mass 235, at. no. 90, which loses a  $\beta$ -ray to yield U-Z. The latter by a  $\beta$ -ray change yields AcU and thence by another  $\alpha$ -ray change U-Y. The latter passes to Pa and thence to Ac by  $\beta$ - and  $\alpha$ -ray changes, respectively. J. W. S.

Ionisation curves for polonium  $\alpha$ -radiation in pure xenon and krypton. R. NAIDU (J. Phys.

Radium, 1934, [vii], 5, 343–346).—Bragg curves and data are given. The ranges at  $15^{\circ}$  are :  $R_{\rm Kr} 3.03 \pm 0.01$ ,  $R_{\rm Xc} 2.17 \pm 0.01$  cm. The absorbing powers relative to air are Kr 1.227, Xe 1.785. The total ionisation relative to air is Kr 1.45, Xe 1.40, and relative to He, Kr 1.263, Xe 1.221, air 0.873. The % ionisation energy losses are 30 in Kr, 40 in Xe, and 49 in air. N. M. B.

Measurements of the absorption of  $\gamma$ -rays by the method of coincidences. Radiation from excited beryllium. P. AUGER (Compt. rend., 1934, 199, 414—416).—The radiation from a tablet of Be bombarded with  $\alpha$ -rays from a 10-millicurie Po source has been studied with oxidised steel and Al counters, mounted in coincidence. The variation of the no. of impacts with the nature and thickness of interposed metallic screens is shown graphically. 21 mm. of Pb reduced the intensity to one half, corresponding with an absorption coeff. of 0.34 cm.<sup>-1</sup> J. W. S.

Theory of nuclear transformations and the classification of light elements. G. PETIAU (J. Phys. Radium, 1934, [vii], 5, 426-430).—A more detailed consideration of work already noted (this vol., 323, 578).

Range- and resonance-groups of protons from nuclear transformations by  $\alpha$ -particle collisions. H. POSE (Physikal. Z., 1934, 35, 633-636).—The excitation functions of nuclear proton groups of Al, Na, F, N, and B have been investigated. The absorption curves indicate definite range groups, and resonance groups occur for protons from all the above with the possible exception of B. The facts can be explained by Gamow's theory. A. J. M.

Ranges of nuclear protons produced by the transformation of nitrogen by polonium  $\alpha$ -rays. H. STEGMANN (Physikal. Z., 1934, **35**, 636–637).— Three groups of protons are liberated; two groups, with ranges of 56 and 101.5 mm., respectively, are due to a resonance effect, whilst the third, with a range of \$1.5 mm., is due to a normal excitation process.

A. J. M.

*H*-Rays from aluminium using radium-B+Cas source. G. ORTNER and G. STETTER (Z. Physik, 1934. 89, 708—712).—Artificial disintegration with this source gives four broad groups of *H*-rays.

A. B. D. C.

"Nuclear photo-effect ": disintegration of the diplon by  $\gamma$ -rays. J. CHADWICK and M. GOLD-HABER (Nature, 1934, 134, 237—238).—Exposure of H<sup>2</sup> to  $\gamma$ -radiation from Ra-Th produces an effect which must be attributed to protons (I) resulting from the splitting of the diplon, probably according to the scheme  $_{1}H^{2}+h\nu \longrightarrow _{1}H^{1}+_{0}n^{1}$ . The mass of the neutron calc. from an estimate of the energy of (I) is  $1.0080\pm0.0005$  and the binding energy of the diplon is  $2\cdot1 \times 10^{6}$  ev. The cross-section for disintegration of a diplon by a  $\gamma$ -ray of  $2\cdot62 \times 10^{6}$  ev. is  $10^{-28}$  cm.<sup>2</sup> Lea's suggestion of the capture of neutrons by (I) (this vol., 235) is criticised. L. S. T.

Intense sources of protons, applicable to [the study of] transmutations. H. HULUBEI (Compt. rend., 1934, 199, 199-201).—Hydrogenated Pd forms a convenient source of protons, the wall of a Pd tube being introduced between a source of  $H_2$  and the vessel for acceleration of the protons, and being kept warmed either by the Joule effect alone or with auxiliary heating. J. W. S.

Radioactivity induced by neutron bombardment. T. BJERGE and C. H. WESTCOTT (Nature, 1934, 134, 286).—Using neutron sources of Rn+Be many of Fermi's results have been confirmed. Additional results are : F gives an approx. 40-sec. period; the longer period exhibited by Zn is approx. 6 hr. and the active body is an isotope of Cu; Cu gives a 6-hr. period and the active body is probably the same as that obtained from Zn; Na gives a weak effect of the same period (approx. 10 hr.) as the long periods of Mg and Al; the active body in each case is probably  $_{11}Na^{24}$ . L. S. T.

Spontaneous emission of neutrons from radioactive isotopes. H. J. WALKE (Nature, 1934, 134, 215).—A discussion. Goldhaber's view (this vol., 826) is supported.  $\gamma$ -Radiation of high energy, the neutron, and the positron emission observed by Curie, Joliot, and Preiswerk (*ibid.*) all result from the  $\beta$ -ray activity of the unstable nuclei,  ${}_{13}\text{Al}{}^{28}$  and  ${}_{14}\text{Si}{}^{31}$ , produced (cf. this vol., 939). L. S. T.

Complex neutron. H. MARGENAU (Physical Rev., 1934, [ii], 46, 107—110).—The unsatisfactory results of assuming that the neutron is a combination of a proton and an electron, with a modified potential near the proton, are demonstrated on the basis of the theories of Dirac and of Schrödinger. N. M. B.

Induced positron radioactivity. F. H. NEWMAN and H. J. WALKE (Nature, 1934, 134, 288–289).— Theoretical. Radioactivity induced by proton, diplon, neutron, and  $\alpha$ -particle bombardment can be explained on the hypothesis that the nuclear structure of stable isotopes consists of  $\alpha$ -particles, neutrons, and diplons. L. S. T.

Experimental proofs of the annihilation of positive electrons. F. JOLIOT (J. Phys. Radium, 1934, [vii], 5, 299-303; cf. this vol., 126, 127).

N. M. B.

Limits of the energy spectra of positrons and electrons from artificial radio-elements. A. J. ALICHANOV, A. J. ALICHANIAN, and B. S. DŽELEPOV (Nature, 1934, 134, 254—255).—The end-points of the spectra of radio-N, radio-P, and radio-Al are 1450, 3700, and 3050 kv., respectively. L. S. T.

Photographic investigations with positrons. L. BEWILOGUA and K. R. DIXIT (Physikal. Z., 1934, **35**, 699—702).—A photographic method for the identification of positrons, similar to that used by Rutherford for the investigation of the secondary  $\beta$ -radiation, is described. The distribution of electrons and positrons was investigated, the ratio of positrons to electrons increasing with the at. no. The absorption of electrons and positrons at Ag and Pb foils was also investigated by this method. A. J. M.

Estimated electron affinities of the light elements. G. GLOCKLER (Physical Rev., 1934, [ii], 46, 111—114).—Empirical extrapolation of the Moseley  $I^{1/2}$ -Z curves gives for the affinities, in e.v.: H (+0.7), He (-0.5), Li (+0.3), Be (-0.6), B (+0.1),  $\begin{array}{l} C \ (+1\cdot37), N \ (+0\cdot04), O \ (+3\cdot8), F \ (+3\cdot9), Nc \ (-1\cdot20), \\ Na \ (+0\cdot1), Mg \ (-0\cdot9), Al \ (-0\cdot2), Si \ (+0\cdot6), P \ (+0\cdot2), \\ S \ (+2\cdot1), Cl \ (+3\cdot7), A \ (-1\cdot0), Ni \ (+0\cdot3), Cu \ (+1\cdot2), \\ Ag \ (+1\cdot0), Hg \ (+1\cdot8). \\ \end{array}$ 

Radiation emitted by the retardation of fast electrons. F. SAUTER (Ann. Physik, 1934, [v], 20, 404-412).—Theoretical. Wave-mechanical formulæ, which include the relativity correction, have been derived for the spectral intensity of the radiation emitted when an electron collides with an at. nucleus, and for the total energy radiated. R. S. B.

Diamagnetism of the Dirac electron. T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 165—170).—Mathematical. J. W. S.

Classical theory of the spinning electron. H. A. KRAMERS (Physica, 1934, 1, 825-828).— Mathematical. The ratio e/mc of the magnetic moment and angular momentum of the electronic spin is classically derived without reference to a detailed classical model of the constitution of the electron.

H. S. P. Exchange in the Thomas-Fermi atom. H. JENSEN (Z. Physik, 1934, 89, 713-719).—Theoretical. A. B. D. C.

Wave equation of the photon. L. DE BROGLIE (Compt. rend., 1934, 199, 445-448; cf. this vol., 236).—Mathematical. J. W. S.

Is the Lorentz contraction dependent on refractive index ? L. COURVOISIER (Z. Physik, 1934, 90, 48-62).—This contraction of a ponderable body is independent of the refractive index of itself or of its medium. A. B. D. C.

Reflecting power of aluminised surfaces. B. K. JOHNSON (Nature, 1934, 134, 216).—Data for reflexion throughout the ultra-violet spectrum are given for Al deposited on glass by the new evaporation method. L. S. T.

Simple and general relationship between molecular spectra and the electrons and electron rings of the constituent atoms. H. DESLANDRES (Compt. rend., 1934, **199**, 393—397; cf. this vol., 828).—The theory previously put forward is extended and shown to be in accordance with the Raman spectra of  $H_2$ (gas),  $C_2$  (crystal), and  $C_2H_2$  (gas), the absorption spectra of  $H_2$  (gas),  $Li_2$  (gas), and  $C_2H_2$  (gas), and the Swan spectrum of  $C_2$  (gas). J. W. S.

Transparency of the lower atmosphere and its content of ozone. D. CHALONGE and E. VASSY (J. Phys. Radium, 1934, [vii], 5, 309—319).—Using an improved spectrograph the coeffs. of atm. absorption in the ultra-violet were obtained by photometric measurement of the absorption of 1200—1400 m. of air for continuous H radiation. Two spectra compared, photographed at distances of 400 and 1600— 1800 m., show for wave-lengths >2700 Å. absorption attributed to  $O_2$ , and consisting of bands, followed below 2421 Å. by a continuous spectrum. Outside the region of absorption the  $O_3$  content is deduced. Data for simultaneous determinations at two localities are given. N. M. B.

Suppression of certain bands of the ozone spectrum under the action of cold. (MME.) L.

LEFEBRE (Compt. rend., 1934, 199, 456–457).—The ultra-violet absorption spectrum of  $O_3$  is much sharper at  $-80^{\circ}$  than at 20°. The spectrum can be classified into bands which become more intense, and those which almost disappear, these bands being attributed to electron jumps from a state of zero vibration and finite vibrational states, respectively. J. W. S.

Significance of the  $O_4$  spectrum and existence of polyatomic polarisation molecules. W. FIN-KELNBURG (Z. Physik, 1934, 90, 1—10).—Solid, liquid, and high-pressure  $O_2$  spectra are shown, similar to those of diat. polarisation mols., and give dissociation energies for excited  $O_4$  states to corresponding  $O_2$ states, as several hundredths of a volt.

A. B. D. C. Significance of the  $O_4$  spectrum and existence of polyatomic polarisation molecules. H. SALOW (Z. Physik, 1934, 90, 11).— $O_2$  absorption between 2400 and 2900 Å. increases progressively in presence of He, Ne, A, N<sub>2</sub>, and CO<sub>2</sub>. A. B. D. C.

Zeeman effect in triplet bands. Influence of magnetic fields on lines of the third positive carbon monoxide bands. R. SCHMID (Z. Physik, 1934, 89, 701-707). A. B. D. C.

**Band spectrum of CO<sup>+</sup>.** H. BULTHUIS (Physica, 1934, 1, 873—880).—The rotational structure of the combination bands  $B^2\Sigma \longrightarrow A^2\Pi$ , (0, 3), and (0, 4) has been analysed. With the aid of these and of the  $B^2\Sigma \longrightarrow X^2\Sigma$  and  $A^2\Pi \longrightarrow X^2\Sigma$  band lines, the combination principle was tested and the intensity relations were found to agree qualitatively with theory.



Spectrum of gallium oxide. (MISS) M. L. GUERNSEY (Physical Rev., 1934, [ii], 46, 114—116).— The spectrum has been photographed and a band system in the region 3800-4200 Å. is identified as a  ${}^{2}\Sigma \rightarrow {}^{2}\Sigma$  transition. Wave-nos., quantum assignments, and intensities are tabulated, and an equation for the band heads is given. N. M. B.

Absorption and fluorescence spectra of some hydrocarbons with two benzene nuclei. R. TITEICA (Compt. rend., 1934, 199, 458–460).—Data are recorded for EtOH solutions of Ph<sub>2</sub>, CH<sub>2</sub>Ph<sub>2</sub>, [CH<sub>2</sub>Ph]<sub>2</sub>, and CH<sub>2</sub>Ph·C<sub>6</sub>H<sub>4</sub>Ph. The spectra frequently show a periodicity of 400–500 cm.<sup>-1</sup>, this frequency difference decreasing with increasing complexity of the mol. The heavier is the mol., the further is the fluorescence spectrum displaced towards the visible region. J. W. S.

Absorption spectra of single crystals of polynuclear hydrocarbons. K. S. KRISHNAN and P. K. SESHAN (Current Sci., 1934, 3, 26–27).—The absorption of single crystals of anthracene, phenanthrene, 1:2-benzophenanthrene, 1:2:5:6-dibenzanthracene (I), fluorene, fluoranthene, and pyrene is more intense when the incident light vibrations are parallel to than when normal to the  $C_6H_6$  planes in the mols. Details are given for (I). L. S. T.

Ultra-violet absorption spectra of gen-alkaloids. V. BRUSTIER and P. BLANC (Bull. Soc. chim., 1934, [v], 1, 702—712).—The N-oxides of atropine, hyoscyamine, and scopolamine have seven absorption bands (maxima between 2410 and 2715 Å.) which are less intense and of slightly shorter  $\lambda$  than the corresponding bands of the parent alkaloids. The absorption of morphine N-oxide (I) is similar to that of morphine (II), but the band of (I) is at a slightly shorter  $\lambda$  and the intensity is < that of (II). The absorption systems of strychnine and its N-oxide (III) are almost identical, but that of the benzoate of (III) is modified, the bands being more intense and at longer  $\lambda$ . J. G. A. G.

Spectrum of heavy water in the photographic infra-red. G. HERZBERG and H. VERLEGER (Physikal. Z., 1934, 35, 622).—Four bands were found, two due to HH<sup>2</sup>O and two to H<sup>2</sup><sub>2</sub>O. The HH<sup>2</sup>O band at 9400 Å. and the H<sup>2</sup><sub>2</sub>O band at 11,600 Å. were very strong. The former corresponds approx. with the strong H<sup>2</sup><sub>2</sub>O band at 9400 Å. A. J. M.

Infra-red spectrum of magnesium oxide. J. Fock (Z. Physik, 1934, 90, 44–47).—Investigation of this spectrum from 2.8 to 200  $\mu$  gives a fundamental at 17.3  $\mu$ , near the val. deduced from sp. heat.

A. B. D. C.

Short-wave infra-red [spectra] of silicates. K. WIRTZ (Physikal. Z., 1934, 35, 649–651).—The structure of the silicates is considered. There is similarity between the short-wave infra-red spectrum of a sulphate and a silicate such as titanite,  $(CaO,Ti)SiO_4$ , both giving two bands. Similar spectra are given by diopside and albite, and can be ascribed to the SiO<sub>4</sub> group. Silicates containing single Si·O groups with metal atoms in the crystal lattice give essentially similar spectra. A. J. M.

Transformation of ammonium salts: influence of the  $NH_4$  radical on anions. J. FOCK (Z. Physik, 1934, 90, 38–43).—The transformation effect observed in the 9  $\mu$  band of SO<sub>4</sub> in  $(NH_4)_2$ SO<sub>4</sub> does not occur in Na<sub>2</sub>SO<sub>4</sub> or in K<sub>2</sub>SO<sub>4</sub>, and is due to a coupling effect of the NH<sub>4</sub> radical. A. B. D. C.

Infra-red absorption spectrum of formaldehyde. I. H. H. NIELSEN (Physical Rev., 1934, [ii], 46, 117—121; cf. Patty, A., 1932, 558; Dieke, this vol., 238).—Further investigation to beyond 11.0  $\mu$ revealed additional bands at 5.7, 6.7, 7.5, 8.6, and 9.6  $\mu$ . Data and resolution into rotational components are tabulated and plotted. N. M. B.

Normal frequencies of sulphur hexafluoride. A. EUCKEN and H. AHRENS [with E. BARTHOLOME and L. BEWILOGUA] (Z. physikal. Chem., 1934, B, 26, 297—311).—In measurements with gaseous and liquid  ${
m SF}_6$  the Raman lines 775, 645, and 525 cm.<sup>-1</sup> have been observed (cf. this vol., 830). These are taken to correspond with the simple totally symmetrical frequency,  $v_1$ ,  $v_2$ , and  $v_3$ , respectively. The infra-red spectrum exhibits the frequencies 617 ( $v_5$ ) and 965 cm.<sup>-1</sup> ( $\nu_6$ ). The last of the frequencies theoretically to be expected has been found by measurement of the mol. heat,  $C_p$ , of the gas at 210-340° abs. to be 363 cm.<sup>-1</sup> ( $v_4$ ), which is optically inactive. The other bands in the infra-red spectrum are accounted for as combination vibrations of the above by applying the selection rules for an octahedral model. R. C.

Raman spectrum of water. I. M. MAGAT (J. Phys. Radium, 1934, [vii], 5, 347-356).-Bands at 500 and 200 cm.<sup>-1</sup> were found and separated from the satellite lines of Hg in the range 30-240 cm.<sup>-1</sup> No band was found at  $\lambda$  3630. Intramol. vibrations of H<sub>2</sub>O and of complex quasi-mols. were identified. Full data and frequencies are tabulated. N. M. B.

Intensity measurements in the Raman spectrum of carbon dioxide. (MISS) I. HANSON (Physical Rev., 1934, [ii], 46, 122–123).—A simple photographic method of measuring Raman intensities is described. The ratio of the intensities of the strong  $CO_2$  doublet is corr. to 0.572. An exposure of 24 days brought out three new lines corresponding with shifts  $1244\pm10$ ,  $1426\pm8$ ,  $1528\pm15$  cm.<sup>-1</sup>, as predicted by Dennison (cf. A., 1933, 661). N. M. B.

Rotational Raman effect in liquids. I. Benzene. S. BHAGAVANTAM and A. V. RAO (Indian J. Physics, 1934, 8, 437–443; cf. this vol., 345).—The intensity of the diffuse wings accompanying the Rayleigh lines in  $C_6H_6$  starts from a max. at or near the centre and decreases rapidly for about 20 cm.<sup>-1</sup>, thence gradually for about 130 cm.<sup>-1</sup> Discussion of results indicates that the wing cannot be explained as due only to mol. rotation. N. M. B.

Dispersion of polarisation of Raman lines. S. C. SIRKAR (Indian J. Physics, 1934, 8, 415-423).— The dependence of polarisation of Raman lines of some liquids on the frequency of the exciting radiation has been investigated. Liquids having their absorption bands in the near ultra-violet show considerable dispersion in the polarisation. If  $\rho$  is the ratio of the intensity of the weak to the strong component, the val. of  $\rho$  for excitation by  $\lambda\lambda$  5461 and 4358 is 4 : 5 in the case of PhNO<sub>2</sub>, and for CS<sub>2</sub> the ratio of vals. of  $\rho$ for excitation by  $\lambda\lambda$  5461, 4358, and 4046 is 1:0.85:0.75. For liquids having absorption bands farther in the ultra-violet,  $\rho$  is practically independent of the frequency of the exciting line. N. M. B.

Raman spectra of isomeric alcohols. G. V. NEVGI and S. K. K. JATKAR (Indian J. Physics, 1934, 8, 397-414).-Full data are tabulated for various isomerides of butyl, amyl, and octyl alcohols. An explanation of the large shifts 2870-2930 cm.<sup>-1</sup> is suggested. The frequency 1450 cm.<sup>-1</sup> is probably due to the transverse vibration of H in  $\cdot$ CH<sub>2</sub> ; 1300 cm.<sup>-1</sup> is attributed to the bending vibration of H in straight C chains. The shifts 750-1030 cm.<sup>-1</sup> are due to the outer vibrations of OH against the rest of the mol. groups, decreasing as homologous series are ascended, and in passing from primary and sec. to tert. alcohols; these assignments are confirmed by thermal data. Heats of dissociation tend to decrease in a homologous series, and more markedly in passing from primary to tert. alcohols. N. M. B.

Raman effect and constitution of molecules. VII. Depolarisation of Raman frequencies of cis- and trans-isomeric compounds. Raman frequencies of  $CH_2Br_2$  and their polarisation. B. TRUMPY (Z. Physik, 1934, 90, 133–137; cf. this vol., 583).—Polarisation of Raman lines of cis- and trans- $C_2H_2Cl_2$  distinguish between the two isomerides. Data for  $CH_2Br_2$  are compared with those for  $CH_2Cl_2$ (loc. cit.). A. B. D. C. Raman effect of the hydroxyl radical. L. MEDARD (Compt. rend., 1934, **199**, 421–423; cf. this vol., 583).—With an Hg arc, filtered through a solution of CoCl<sub>2</sub> and a Corning No. 306 filter, and by further filtering the scattered light from the liquid under test through a solution of NaNO<sub>2</sub>, the continuous background normally encountered with org. OH-compounds is suppressed. HCO<sub>2</sub>H shows a weak Raman band at 2950–3300 cm.<sup>-1</sup>; [CH<sub>2</sub>·OH]<sub>2</sub> shows a broad band at 3300–3500 cm.<sup>-1</sup> and a narrower, more intense band at 3700 cm.<sup>-1</sup> NH<sub>2</sub>OH freshly prepared shows a broad band at 3300 cm.<sup>-1</sup> superimposed on the NH<sub>2</sub> bands. Anhyd. glycerol yielded only continuous backgrounds. J. W. S.

Raman effect. XXXV. Raman spectra of some acetyl and acetonitrile compounds. H. C. CHENG (Z. physikal. Chem., 1934, B, 26, 288—296).— Ten compounds have been studied. The behaviour of the frequencies of the CH and CCl linkings in the groups CH<sub>2</sub>Cl, CCl<sub>3</sub>, and CHCl<sub>2</sub> and the effect of Cl substitution on the CO frequency are discussed. The CN group has an inner vibration frequency at 2250 and a second frequency at 150—200 cm.<sup>-1</sup> R. C.

Light scattering by binary liquid mixtures. S. PARTHASARATHY (Indian J. Physics, 1934, 8, 275– 313).—A mol. theory of the scattering of light by binary liquid mixtures is developed, in which account is taken of the optical anisotropy of the mols. and of the influence of the Lorentz polarisation field on the effective mol. optical anisotropy. Tabulated data for 25 binary liquid mixtures giving the variation of the depolarised scattering with concn. are in agreement with the theory. Anisotropic and density scattering and magnetic and electric birefringence are discussed in relation to the theory. N. M. B.

Polarisation of fluorescence. II. Dyes in solution. S. M. MITRA (Indian J. Physics, 1934, 8, 445-450).—In order to determine whether variations of polarisation of substances previously reported (cf. this vol., 346) were due to the solvent, investigations were repeated for the solid dyes and in sugar solutions, castor oil, glycerol-H<sub>2</sub>O mixtures, and gelatin as solvents. The % polarisation differed in each case, and its sign continued to be negative for  $\lambda$  3131 excitation. N. M. B.

Sensitisation of phosphors. S. ROTHSCHILD (Physikal. Z., 1934, 35, 557—560).—A CaS-Sm phosphor can be sensitised by a trace of Bi; Cu, Pb, and Mn are not effective. The explanation is discussed. A. J. M.

Electrical conductivity of Ag<sub>2</sub>HgI<sub>4</sub>. Mechanism of conduction in solids of high conductivity. J. A. A. KETELAAR (Z. physikal. Chem., 1934, B, 26, 327-334).—Conductivity measurements at 18-93<sup>°</sup> have shown that  $\alpha$ -Ag<sub>2</sub>HgI<sub>4</sub> is a good conductor, and transport measurements that conduction is purely cationic, principally by Ag<sup>°</sup>. The high conductivity of the  $\alpha$ -form, by far the highest yet observed in a solid with solely electrolytic conductivity, and its small temp. coeff. are ascribed to the energy of release of the metal ions being zero owing to 25% of the points in the metal ion lattice being vacant. The same explanation may be extended to other similar solid conductors, e.g., a-AgI and a-CuI. The transformation  $\alpha = \beta \cdot Ag_2 HgI_4$  may be partly continuous. R. C.

Dipole moments and physico-chemical properties. IV. A. E. VAN ARKEL (Chem. Weekblad, 1934, 31, 470-474).-The observed b.p. of many liquids agree closely with the vals. calc. on the basis of London's views. The influence of structure, and in particular of the presence of dipoles, on b.p. is discussed; calc. and observed influences of dipoles in various CH<sub>4</sub> derivatives are in agreement. Unsaturated hydrocarbons are considered, and the influence of the nature and orientation of substituents in the C6H6 ring is discussed. H. F. G.

Anomalous absorption and dispersion of primary alcohols in the ultra-short wave range. K. KRAUSE (Physikal. Z., 1934, 35, 684-691).-The absorption and dispersion of alcohols (BuªOH, Bu<sup>\$</sup>OH, n-amyl alcohol) and ethereal oils (eugenol, bay oil, linalool) and of alcoholic solutions with various viscosities were determined in the wave-length range 2-5 m. A new differential process for the absorption experiments, and a modified Drude's method for the determination of the dielectric const., are described. The dependence of the absorption max. on viscosity confirms theory. The dielectric const. of the three oils is independent of frequency. A. J. M.

Dipole moment of non-associated gaseous hydrogen fluoride. C. H. D. CLARK (Physikal. Z., 1934, 35, 622-623).-The dipole moments of the hydrogen halides are considered. The moment of non-associated HF is calc. as 1.58 Debye units, and the nuclear separation 0.864 Å. A. J. M.

Effect of solvent on the moment of a molecule containing movable dipoles. A. E. STEARN and C. P. SMITH (J. Amer. Chem. Soc., 1934, 56, 1667-1670).—The dipole moment of EtCl in heptane,  $C_{g}H_{g}$ , CS<sub>2</sub>, CCl<sub>4</sub>, CHCl<sub>3</sub>, and Et<sub>2</sub>O and their binary mixtures has been determined at temp. between  $-70^{\circ}$  and 90°. Complexes appear to be formed in Et<sub>2</sub>O and  $C_6H_6$ . A dipole in the interior of a mol. may have no detectable effect on the internal potential energies of adjacent mols., although the mol. field may alter the moment of an adjacent EtCl mol. E. S. H.

Dipole moments of phosgene, hydrogen cyanide, and certain substituted methanes. C. P. SMITH and K. B. MCALPINE (J. Amer. Chem. Soc., 1934, 56, 1697-1700).—The dipole moments calc. from measurements of the dielectric consts. of COCl<sub>2</sub>, HCN, MeNO<sub>2</sub>, and CCl<sub>3</sub>·NO<sub>2</sub> vapours conform with those calc. on the assumption of a central tetrahedral C atom. E. S. H.

Variations in refractive index of CO<sub>2</sub>-free dry air, and a statistical correlation with solar activity. L. W. TILTON (J. Res. Nat. Bur. Stand., 1934, 13, 111-124).-Examination of published data has shown a correlation of refractivity of air with E. S. H. sunspot no.

Refractive index of gaseous "heavy water." C. CUTHBERTSON (Nature, 1934, 134, 251).-- 45462.23 for gaseous heavy  $H_2O$  (approx. 30%  $H_2^*O$ ) is 1.000256 compared with 1.000255 for ordinary H<sub>2</sub>O. L. S. T.

Molecular refractivity and association of liquids containing the hydroxyl group. R. P. ALLARD and H. H. WENZKE (J. Amer. Chem. Soc., 1934, 56, 1693-1694).-Changes in mol. refractivity of AcOH on dilution with  $C_6H_6$  or dioxan show that such changes do not constitute a simple test of association of OH compounds. E. S. H.

Principal optical polarisabilities of the naphthalene molecule. K. S. KRISHNAN (Indian J. Physics, 1934, 8, 431-436; cf. A., 1933, 10).-From the Lorentz refraction const., the depolarisation factor of light scattering, and the Cotton-Mouton const., the calc. vals. of the polarisabilities along the three principal axes are  $26.\hat{8}$ , 14.1, and 11.5 (all  $\times 10^{-24}$ ) c.g.s., N. M. B. e.s.u.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. VIII. Magneto-optical dispersion of n-butyl, methyl, and ethyl acetate. G. E. JONES and E. J. EVANS (Phil. Mag., 1934, [viii], 18, 386-400; cf. A., 1931, 24; this vol., 349).—Ordinary dispersion and magnetooptical dispersion data are tabulated for the region 2700-7000 Å. Verdet's const. and the vals. of e/m are calc. and their variation with mol. wt. is J. W. S. discussed.

Paramagnetic rotation in a variable magnetic field. G. ZANOTELLI (Atti R. Accad. Lincei, 1934, [vi], 19, 718—722).—The paramagnetic part of Verdet's const. in an oscillating field (frequency, n,  $3\cdot 2-5\cdot 5\times 10^6$  cycles per sec.) does not differ by > one sixth from the val. in a steady field. With aq. CeCl<sub>3</sub>, the rotation at any given field strength is independent of n and there is no detectable hysteresis. D. R. D.

Complexes between metals of the first transitional series and dipyridyl and phenanthroline. L. CAMBI and A. CAGNASSO (Atti R. Accad. L. CAMBI and A. CAGNASSO (Att I. Actal. Lincei, 1934, [vi], 19, 458–461).—The suscepti-bility-temp. curves, between 291° and 84° abs., of [Ni(dipyridyl)<sub>3</sub>]Br<sub>2</sub>,3H<sub>2</sub>O and [NiR<sub>3</sub>]Br<sub>2</sub>,2H<sub>2</sub>O, and of [CoR<sub>3</sub>]Br<sub>2</sub>,2H<sub>2</sub>O and [MnR<sub>3</sub>]Cl<sub>2</sub> (R=phenanthroline) are practically coincident. H. F. G.

Structure of the nitro-group. H. O. JENKINS (Nature, 1934, 134, 217).—The finite vals. found for the differences  $\infty P_2 - E_2$  are due in the case of  $p \cdot C_6 H_4(NO_2)_2$  (I) and  $s \cdot C_6 H_3(NO_2)_3$  (II) to sp. solvent effects of  $C_6 H_6$  and  $C_{10} H_8$  on the dissolved nitro-compounds. The vals. of  $\infty P_2 - E_2$  for (I) and (II) in CHCl<sub>3</sub> are zero. Hence both (I) and (II) are non-polar and the NO, group is symmetrical a resonance polar and the  $NO_2$  group is symmetrical, a resonance existing between  $-N \bigtriangledown_0^0$  and  $-N \bigtriangledown_0^0$ . L. S. T.

Magneto-chemical investigations. IX. Nickel oxide. W. KLEMM and K. HAAS (Z. anorg: Chem., 1934, 219, 82-86).-Variable vals. for the magnetic susceptibility, x, of NiO are due to partial splitting up into Ni and a higher oxide at  $> 400^{\circ}$ . Above an O content between  $NiO_{1.003}$  and  $NiO_{1.008}$  % is practically const. independently of field strength. In apparently pure NiO the proportion of metallic Ni is 0.3-0.6%.  $\chi$  for the NiO phase increases linearly with rise of temp., contrary to the Curie or Weiss law. At low temp. the vals, are much < those for salts, and the relation between those for NiO and NiS is similar to that found for Cu. M. S. B.

Magnetic properties of rare-earth salts. E. H. WILLIAMS (Physical Rev., 1934, [ii], 46, 133—134).— The susceptibility reciprocal-abs. temp. curve for  $GdCl_3$ ,  $NdCl_3, 6H_2O$ , and  $Gd_2(SO_4)_3, 8H_2O$  is a broken line; the last named, when carefully dried, gives a straight line through the origin. N. M. B.

Diamagnetism of organic compounds and influence of temperature and constitution. II. R. CABRERA and H. FAHLENBRACH (Z. Physik, 1934, 89, 682-700; cf. A., 1933, 1233).-Susceptibilities are given between  $-50^{\circ}$  and  $140^{\circ}$  for laboratory glass, Jena apparatus glass 20, uviol and quartz glass, cetyl alcohol (I), hexane, C<sub>6</sub>H<sub>6</sub>, AcOH, o- and p-cresol, o-, m-, and p-C6H4Me-NO2, and p-C6H4Cl-OH, and at room temp. for isoamyl alcohol and sugar charcoal. Abrupt change of susceptibility was observed at each m.p., the magnitude of the change being exponentially related to the dipole moment of the substance, and probably brought about by deformation of the electron cloud. Apart from this change only (I) showed variation of susceptibility with temp. Pascal's A. B. D. C.  $\lambda$ -theory is discussed.

Diamagnetism of organic liquid mixtures. S. R. RAO (Indian J. Physics, 1934, 8, 483–501; cf. A., 1932, 678).—Using an improved method, data are tabulated and plotted for  $COMe_2$ -CHCl<sub>3</sub>,  $COMe_2$ -PhNO<sub>2</sub>,  $COMe_2$ -C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>-AcOH, C<sub>6</sub>H<sub>6</sub>-PhNO<sub>2</sub>,  $COMe_2$ -AcOH, and  $COMe_2$ -NH<sub>2</sub>Ph. In all cases the additive law of mixtures is obeyed. Evidence indicates that for  $COMe_2$ -CHCl<sub>3</sub> and  $COMe_2$ -PhNO<sub>2</sub> association produced no change in the sp. diamagnetic susceptibility. N. M. B.

"Electron motion" in limited crystal lattices. S. RIJANOV (Z. Physik, 1934, 89, 806-819).—The energy spectrum and proper functions for a twodimensional lattice are discussed. A. B. D. C.

Determination of the variation of the inner potential of a crystal lattice from the deviations from Bragg's law of electron diffraction. II. V. E. LASCHKAREV (Z. Physik, 1934, 89, 820–825; cf. this vol., 126).—The periodic variation of this potential through the lattice is estimated for MoS<sub>2</sub>. A. B. D. C.

Distance between micelles in viscose rayon. N. MATSUMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 356B).—The X-ray val. 65 Å. was given by several fibres spun under similar conditions but with diameters ranging from 7 to  $36 \mu$ . G. H. C.

Study of chemical systems by variations of weight during regular temperature variation. M. GUICHARD (Compt. rend., 1934, 199, 138—140).— The interpretation of wt.-temp. curves of substances undergoing thermal decomp. or dehydration is complicated by the occurrence of fusion or solidification.

B. W. B.

Valency angle of oxygen. G. M. BENNETT, D. P. EARP, and S. GLASSTONE (J.C.S., 1934, 1179–1180).— It is inferred from measurements on solutions in  $CCl_4$ , cyclohexane, and  $C_6H_6$  that the dipole moment of diphenylene dioxide is 0, indicating an angle of 120° between the O valency linkings in this compound. R. S. B.

Chemical linking. I. Interpretation of valency on the basis of wave-mechanics and band spectra. R. F. HUNTER and R. SAMUEL (J.C.S., 1934, 1180-1186).-Current theories of valency are criticised in the light of spectroscopic and wavemechanical evidence. In particular it is emphasised that the "lone pair" of electrons  $(s^2)$  cannot form a chemical linking without fission and transference of at least one electron to a p group. The octet rule leads to incorrect formulation (e.g., in O2 the octet is actually not closed, the lowest level is  ${}^{3}\Sigma$ , and the mol. should be written  $\equiv 0 \equiv 0$ ), and in many cases stable structures are formed with incomplete octets. A theory is proposed in which there is only one type of chemical linking (covalent) the polarisation of which may vary between 0 (in H<sub>2</sub>) and the val. in a true salt. Chemical union results in the formation of a closed group or sub-group, which may or may not contain 8 electrons. Any atom may act as the + partner, and the max. no. of + valencies = the no. of electrons in the outer shell. The formulæ  $-N \zeta_0^0$  and  $-N \zeta_0^0$  are

regarded as physically inadmissible, the 5 links in  $-N(=O)_2$  (correct formulation) arising from 5 identical p electrons (excited N). . KF, HF, and complexes formed by B and Al trihalides and Be dihalides with amines etc. are considered to be formed by dipole association. It is inferred that CO contains a double linking. R. S. B.

Energy relations in the periodic system of chemical compounds of the type  $A_m B_n$ . H. G. GRIMM (Angew. Chem., 1934, 47, 594—601).—It is shown for several substances (halogens, alkali halides, CuCl, C, N<sub>2</sub>, alkali metals, etc.) that the type of mol. actually formed is the one to be expected from energetics, other types of mol. requiring the absorption of additional energy. Valency is similarly treated. A. G.

Parachor and ring structure. S. K. RAY (J. Indian Chem. Soc., 1934, 11, 499—501).—From measurements on 15 compounds it is found that  $C_5H_5N$  derivatives have the same structural contribution as the corresponding  $C_6H_6$  derivatives, and that in 5-membered rings unsaturated N lowers the contribution due to the ring by about 5.5 units, but not when saturated. The mutual condensation of 5- and 6-membered rings lowers the parachor by 2.5 units. D. R. D.

Nature of the recrystallisation process. H. G. MULLER (Physikal. Z., 1934, 35, 646-649).—Recrystallisation is a self-diffusion process. For the origination of recrystallisation nuclei, a special centre-formation is not required. A. J. M

Kinetic deduction of rate of formation of nuclei. R. KAISCHEV and I. N. STRANSKI (Z. physikal. Chem., 1934, **B**, 26, 317–326).—Expressions giving the rate of formation of liquid nuclei from supersaturated vapour, crystal nuclei (with the simple cubic lattice) from supersaturated vapour, and gas nuclei from superheated liquid have been derived. All contain the factor  $e^{-F\sigma/3kT}$ ,  $F\sigma/3$  being the work of formation of a nucleus. R. C.

Mechanism of equilibrium of small crystals. III. I. N. STRANSKI and R. KAISCHEV (Z. physikal. Chem., 1934, B, 26, 312—316; cf. this vol., 946).— The Gibbs-Wulff condition for the equilibrium of a small crystal, *i.e.*, that the central distances for the equilibrium form shall be proportional to the corresponding sp. surface energies, is equiv. to the condition that the mean work of separation,  $\overline{\phi}$ , shall be the same for each face of the equilibrium form. Only those faces can appear in the equilibrium form for which  $\overline{\phi}$  depends on the extent of the face. The possible faces in the equilibrium form of a cubic face-centred and closest-packed hexagonal lattice are enumerated. R. C.

Investigation of surface area and lattice changes of crystalline salts by Hahn's emanation method. F. STRASSMANN (Z. physikal. Chem., 1934, B, 26, 353—361; cf. A., 1931, 890).—The val. for the surface area of a specimen of cryst.  $Ba(NO_3)_2$ deduced from its emanating power agrees with the val. obtained by direct microscopic measurement, although there is appreciable diffusion of Rn from within the crystals through the surface. The emanation method may also be used qualitatively to follow the formation of  $Ba(NO_3)_2$ , 2KNO<sub>3</sub> in the solid eutectic mixture of KNO<sub>3</sub> and  $Ba(NO_3)_2$  at room temp. R. C.

Investigation of connexion between lattice structure and permeability to gases of organic salts by Hahn's emanation method. F. STRASS-MANN (Z. physikal. Chem., 1934, **B**, 26, 362—372).— The emanating power, *E*, of org. Ba salts is independent of the hardness and *d* of the crystals, but is decisively influenced by the constitution of the salt. It is deduced that a considerable proportion of the emanation (Rn or thoron) given off diffuses from within the crystal and that the diffusibility is influenced by the structure of the crystal. Diffusion seems to occur particularly readily along glide-planes. A method of determining a very small *E* for thoron with a precision of  $\pm 5\%$  is described. R. C.

Crystallisation of metals from sparse assemblages. E. N. DA C. ANDRADE and J. G. MARTINDALE (Nature, 1934, 134, 321-322).—When Au or Ag crystals grow slowly from a film in which the amount of available material is small, the first stage of crystallisation appears to be the formation of an aggregate of spherulitic nature, in which the individual cryst. fibres behave as if uniaxial. L. S. T.

Helicoidally rolled spherolites of the allantoins and their artificial coloration. P. GAUBERT (Compt. rend., 1934, 199, 213—215)—These spherolites are formed when supersaturated solutions of l- or r-allantoin are placed in a thin layer on glass. The rolling of the cryst. particles forming the radial fibres occurs around the b crystallographic axis. Addition of a trace of coal-tar dye favours the formation of this structure. Spherolites coloured with methylene-blue are polychroic. J. W. S. Diffuse scattering of X-rays from sodium fluoride. III. Using sensibly monochromatic radiation. P. S. WILLIAMS (Physical Rev., 1934, [ii], 46, 83—86; cf. A., 1932, 979).—A comparison of the classical scattering of Mo  $K\alpha$  lines by NaF with that by paraffin is in agreement with previous results using a band of wave-lengths, but shows appreciable divergence from the predictions of quantum theory. N. M. B.

Powder figures of magnetised single iron crystals. S. KAYA (Z. Physik, 1934, 89, 796-805). —Powder figures on the cubic face are directly related to the condition of magnetisation.

A. B. D. C. X-Ray researches on thin nickel films. R. RIEDMILLER (Ann. Physik, 1934, [v], 20, 377-403).—d for thin films of Ni evaporated in a vac. on to a microscope cover-slip has been calc. from the wt. and thickness, l (X-ray interferometric), and is 20-25% < the val. for Ni in bulk for most of the films of l=400-1750 Å., owing to loosening in the crystallite structure, or to increase in the lattice const. The sp. electrical resistance in vac. decreases rapidly as *l* increases, and then reaches a const. val. 35-40 times the normal for l > 1000 Å., up to 2250 Å. The refraction coeff.,  $\delta = 1 - n$ , has been measured by means of X-rays;  $\delta/d = approx. \text{ const.} = 2.66 \times 10^{-6}$ (theoretical val.  $2.58 \times 10^{-6}$ ). Calculation shows that in two cases  $1 O_2$  mol. is present with 4 and 10 Ni R. S. B. atoms.

X-Ray investigation of calcium at higher temperatures. II. L. GRAF (Physikal. Z., 1934, 35, 551-557).—The change taking place in the structure of Ca at 450° was investigated. The phase stable above 450° may occur either as space-centred cubic or hexagonal close-packed lattices. The purity of the Ca decides the form of the lattice, which is hexagonal with pure Ca. Another transition occurs at 300°, where sudden changes occur in some of the properties of the metal. With very pure Ca a further transition point at 218° seems probable. A. J. M.

Lattice structure of the oxides, sulphides, selenides, and tellurides of lithium, sodium, and potassium. E. ZINTL, A. HARDER, and B. DAUTH (Z. Elektrochem., 1934, 40, 588—593).—The following vals. for lattice const. and ionic distance, respectively, are given (in Å.): Li<sub>2</sub>O 4.619, 2.00; Li<sub>2</sub>S 5.708, 2.47; Li<sub>2</sub>Se 6.005, 2.60; Li<sub>2</sub>Te 6.504, 2.82; Na<sub>2</sub>O 5.55, 2.40; Na<sub>2</sub>S 6.526, 2.83; Na<sub>2</sub>Se 6.809, 2.95; Na<sub>2</sub>Te 7.314, 3.17; K<sub>2</sub>O 6.436, 2.79; K<sub>2</sub>S 7.391, 3.20; K<sub>2</sub>Se 7.676, 3.32; K<sub>2</sub>Te 8.152, 3.53.

E. S. H. Lattice constant of OsS<sub>2</sub>. K. MEISEL (Z. anorg. Chem., 1934, 219, 141–142).—X-Ray measurements on OsS<sub>2</sub> give a  $5.6075 \pm 0.0006$  Å. and  $d 9.57 \pm 0.01$ . M. S. B.

Structure of the pseudo-halogens and their compounds. I. Thallous thiocyanate. M. STRADA (Gazzetta, 1934, 64, 400-409).—TICNS is of the tetragonal system, ditetragonal pyramidal class, group  $\Gamma_t$ , symmetry  $C_4$  or  $C_{2v}$ ; a 4.766, c 3.78 Å.; one mol. per unit cell,  $d_{calc.}$  5.06. The electronic structure of the CNS ion is similar to that of the halogen ions, and in TICNS the C, N, and S atoms are in a straight line forming the polar axis of the crystal. H. F. G.

Fibrous structure in ionic lattices. II. G. R. LEVI and M. TABET (Atti R. Accad. Lincei, 1934, [vi], 19, 723—725; cf. this vol., 479).—Threads of AgCl and AgBr formed under pressures of 2000— 7500 atm. show fibrous structure, the crystallites being oriented along the (111) axis at room temp. and along the (100) at higher temp. (e.g., 280°). The transition temp. varies with the pressure and is lower for AgBr than for AgCl. Breaking stresses of the threads have been measured. Laminæ of AgCl and AgBr show marked fibrous structure. D. R. D.

Crystal structure of nickel bromide and iodide. J. A. A. KETELAAR (Z. Krist., 1934, 88, 26-34).—The sublimed salts have the CdCl<sub>2</sub> structure with  $a_0$  3.71<sub>5</sub>,  $c_0$  18.30, and  $a_0$  3.89<sub>5</sub>,  $c_0$  19.63 Å., respectively, referred to hexagonal cells. Nonsublimed NiBr<sub>2</sub> exhibits the "alternating" structure (cf. this vol., 16). The difference between these structures and those of the corresponding Co compounds is unexpected. B. W. R.

Crystal structure of the low-temperature modification of ammonium bromide. J. A. A. KETE-LAAR (Nature, 1934, 134, 250–251).—At low temp. NH<sub>4</sub>Br has a tetragonal lattice and at  $-100^{\circ}$  a is  $6\cdot007\pm0\cdot006$  Å. and  $c 4\cdot035\pm0\cdot004$  Å.; probable space-group  $D_{4h}^{\circ}$ . L S. T.

Quantitative spectrometric studies of ammonium and potassium cupric chloride dihydrate,  $(\mathbf{NH}_4)_2\mathbf{CuCl}_4, \mathbf{2H}_2\mathbf{O}$  and  $\mathbf{K}_2\mathbf{CuCl}_4, \mathbf{2H}_2\mathbf{O}$ . L. CHROBAK (Z. Krist., 1934, 88, 35–47).—Fourier projections, based on intensity measurements from shaped crystals and corr. for extinction, are used to differentiate between the conflicting suggestions which have been made for the structure of these compounds. No conclusion is reached for the  $\mathbf{NH}_4$ salt; for the K salt, definite evidence in favour of one is obtained. B. W. R.

Crystal structure of the alums. C. A. BEEVERS and H. LIPSON (Nature, 1934, 134, 327).—Details are given. L. S. T.

Atomic arrangement in ammonium and cæsium persulphate,  $(NH_4)_2S_2O_8$  and  $CS_2S_2O_8$ , and the structure of the persulphate group. W. H. ZACHARIASEN and R. C. L. MOONEY (Z. Krist., 1934, 88, 63—81).—The X-ray data from these two isomorphous compounds, in relation to the very different scattering powers of the constituent atoms, allow the at. parameters to be separately determined. The cell consts. are  $a_0$  7.83,  $b_0$  8.04,  $c_0$  6.13 Å.,  $\beta$  95° 9', and  $a_0$  8.13,  $b_0$  8.33,  $c_0$  6.46 Å.,  $\beta$  95° 19', respectively; space-group  $C_{2h}^{*}$ . The persulphate group appears as two tetrahedral SO<sub>4</sub> groups (S at the centre) joined by an oblique covalent linking. B. W. R.

Fine-structure researches on boracite. M. MEHMEL (Z. Krist., 1934, 88, 1–25).—Above 265°  $\alpha$ -boracite (Mg<sub>6</sub>Cl<sub>2</sub>B<sub>14</sub>O<sub>26</sub>) is cubic;  $a_0$  12·1 Å., 4 mols. in the cell. Below this temp. the  $\alpha$ -modification is rhombic,  $a_0$  17·07,  $b_0$  17·07,  $c_0$  12·07 Å., 8 mols. in the cell. The space-group cannot be fixed. The  $\beta \rightarrow \alpha$  transition is exhibited by a discontinuity in the expansion coeff. B. W. R.

Crystal structure of enargite, Cu<sub>3</sub>AsS<sub>4</sub>. L. PAULING and S. WEINBAUM (Z. Krist., 1934, 88, 48-53).—The structure is orthorhombic,  $a_0$  6.46,  $b_0$  7.43,  $c_0$  6.18 Å., space-group  $C_{2r}^*$ , analogous to that of wurtzite (ZnS), each As and Cu being tetrahedrally surrounded by S. B. W. R.

**Crystal structure of binnite**,  $(Cu,Fe)_{12}As_4S_{13}$ . L. PAULING and E. W. NEUMAN (Z. Krist., 1934, 88, 54-62).—The cell is cubic with  $a_0$  10·19 Å., spacegroup  $T_d^s$ . From intensity considerations satisfactory at. positions are found, which are probably also applicable to the tetrahedrite minerals  $(CuZn)_{12}Sb_4S_{13}$ . B. W. R.

Effect of temperature on the crystalline spacing of certain normal diacids. F. D. LA TOUR and A. RIEDBERGER (Compt. rend., 1934, 199, 215— 217; cf. A., 1932, 1192).—The interplanar distance  $a/2 \sin \beta$  (A., 1929, 126) for the higher dibasic acids with an even no. of C atoms increases rapidly with rise of temp. This is due principally to expansion along the *a* axis. Expansion along the *b* axis is very slight. Discontinuities in the temp. coeff. of expansion along the *a* axis occur between  $C_{12}$  and  $C_{14}$  and between  $C_{18}$  and  $C_{20}$ . The abnormal variation of the interplanar distance  $c \sin \beta$  is attributed to a variation in  $\beta$  depending on the attractions between the  $CO_2H$  groups. J. W. S.

Structure of thin celluloid films. III. E. T. JONES (Phil. Mag., 1934, [vii], 18, 291-302; cf. A., 1933, 1236).—Structures of celluloid films are discussed with reference to the patterns obtained by passing cathode rays through them. J. W. S.

Casein.—See this vol., 1119.

Variation of the thermal and electrical conductivity of a single bismuth crystal in a magnetic field. H. REDDEMANN (Ann. Physik, 1934, [v], 20, 441—448).—The thermal ( $\Lambda_T$ ) and sp. electrical ( $\Lambda_E$ ) conductivities of a single Bi crystal (rod) have been determined from  $-193 \cdot 92^{\circ}$  to  $23 \cdot 3^{\circ}$ ; the Wiedemann-Franz-Lorenz no.  $L=\Lambda_T/T\Lambda_E$  varies from  $10 \cdot 99 \times 10^{-8}$  to  $4 \cdot 17 \times 10^{-8}$ . In a magnetic field (H) of 5900 gauss transverse to the axis of the crystal rod at  $-183 \cdot 5^{\circ} \Lambda_E$ , for the most favourable angle (6) between the field and the axis of the rod, is approx.  $0 \cdot 1$  its former val.  $\Lambda_T$  is unaffected by a variation in 0, and in H is  $0 \cdot 83$  its former val. The high val. of L is due to the contribution of lattice conduction to  $\Lambda_T$ . R. S. B.

[Electrical] conductivity of tellurium. C. H. CARTWRIGHT and M. HABERFELD (Nature, 1934, 134, 287—288).—Curves showing the decrease in resistance of Te produced by the addition of Cu or Sb are discussed. The addition of 0.2% of Sb or Biincreased the conductivity of Te 100-fold and changed the temp. resistance coeff. from negative to positive.

L. S. T.

Dependence of the conductivity of very thin metallic layers on the electrostatic field. R. DEAGLIO (Naturwiss., 1934, 22, 525-526).—Thin metallic layers sputtered or vaporised show a considerable increase in conductivity on application of an electrostatic field. With vaporised layers, the effect is symmetrical, and independent of the sign of the charge, but for layers formed by sputtering the effect is unsymmetrical, and the increase in conductivity is > when the layer is positively charged.

A. J. M.

Change of resistance of thin metallic layers on charging. A. DEUBNER (Ann. Physik, 1934, [v], 20, 449—462).—An apparatus for determining very small changes of resistance is described. For Ag layers about 40 atoms thick, and a charge of 5000 volts, a change of 10<sup>-4</sup> of the resistance was measurable (cf. this vol., 588). For Au about 0·1 of this could be found, whilst for Cu and Bi there was no detectable change. The connexion between the resistance change and the optical absorption of the layers is discussed. A. J. M.

Thermal variation of the structural demagnetisation factor in nickel and cobalt. T. KAHAN (Compt. rend., 1934, 199, 349—351).—The structural demagnetisation factor decreases with rise of temp., being distinguished in this way from the geometrical factor, which does not vary with temp. A. J. M.

Magnetic properties of iron-cobalt single crystals. J. W. SHIH (Physical Rev., 1934, [ii], 46, 139-142).—The direction for easiest magnetisation changes from <100> to <111> as the amount of Co increases, the transition occurring at about 42%Co. The theory of Fowler and Powell is contradicted (cf. A., 1931, 791). The magnetisation curve of a 70% Co specimen agrees with Akulov's theory.

N. M. B.

Unsymmetrical hysteresis loop. S. S. SIDHU (Indian J. Physics, 1934, 8, 451-467).—A general investigation of the magnetic properties of different grades of Sisteel and 50% Ni steel, when symmetrically and unsymmetrically magnetised, is described.

N. M. B. Magnetism of tin. S. R. RAO (Nature, 1934, 134, 288).—As the particle size of colloidal white Sn decreases, the small paramagnetic susceptibility (I) changes to diamagnetic which then increases as particle size decreases. The (I) of white Sn appears to depend on the crystal structure and not to be an at. property. L. S. T.

Dependence of magnetic induction on the magnetic field in superconducting lead. G. N. RJABININ and L. W. SHUBNIKOW (Nature, 1934, 134, 286-287). L. S. T.

Refractive index of thin films of potassium. B. MUKHOPADHYAY (Current Sci., 1934, 3, 25).—A discussion of the discrepancy between calc. (this vol., 231) and experimental (A., 1933, 1096) vals.

L. S. T.

Optical properties of thin films. M. BLACKMAN (Phil. Mag., 1934, [vii], 18, 262–272).—Theoretical. J. W. S.

Dispersion of the phase jump for reflexion of hight at thin metallic layers. J. BAUER (Ann. Physik, 1934, [v], 20, 481-501).—The experiments were carried out by Fabry and Buisson's method (J. Physique, 1908, [iv], 7, 417), with Ag, Au, and Pt obtained by cathodic sputtering or vac. vaporisation. The phase-jump increases as the absorption coeff. of the layer decreases. For non-homogeneous layers, the course of the phase-jump varies over the layer. The two modifications of Ag found by Fabry and Buisson are identical with those of Ritschl (A., 1931, 888). A. J. M.

Condensation of thin metallic films : some reflecting observations. T. V. STARKEY (Phil. Mag., 1934, [vii], 18, 241-256).-A method for correlating structural characteristics with reflecting power is developed, and is applied to films condensed from a mol. beam of Cd vapour on a target cooled with liquid air. Owing to surface irregularities and uneven contamination, active centres exist on the target and become occupied in a time short in comparison with the time of growth of the film, the final vols. of the aggregates formed at these centres ranging about a mean vol. according to the Gaussian law of errors. Because of mechanical trapping, a permanent sensitisation of the surface occurs, which persists in spite of acid cleaning of the surface and increases on each repetition of the process. The growth of the aggregates is favoured by the migration of small particles, probably mols., to the active centres, and the no. of aggregates per unit area is independent of the rate of growth of the film and of the residual air pressure. J. W. S.

Velocity of propagation of sound in carbon dioxide near the critical state. V. SCHPAKOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 26— 34).—Measurements were made at 15—50° at pressures from 1 to 85 atm. in a gas column by the method of resonance. An increase in the mol. thermal capacity at const. vol. was observed with increasing pressure, attributed to the formation of cybotactic groups in the gas. H. J. E.

Norbury relationship for thermal resistance of metals. H. REDDEMANN (Ann. Physik, 1934, [v], 20, 502—512).—The extent to which the law of the linear isothermal ( $\Delta w = \Delta \rho/ZT$ ), connecting thermal resistance (w), electrical resistance ( $\rho$ ), and temp. (T), holds for alloys of Cu, Al, Au, Ag, Pt, and Pd with other metals is investigated. The const. Z is almost independent of the added metal up to a certain val. of  $\rho_{sp}$ . The law holds satisfactorily up to this limit, and may be used to calculate w from  $\rho$ . As long as  $\rho \propto w$ , the Norbury relationship (connecting the increase of resistance of alloys with the positions of the metals in the periodic system) holds for both. A. J. M.

Theory of liquids. T. S. WHEELER (Current Sci., 1934, 3, 23-24).—Theoretical. Vals. of surface tension and internal latent heat calc. for He,  $H_2$ , Ne, A, and  $N_2$  are in agreement with those observed for the liquid state. L. S. T.

Calorimetric studies at very low temperatures. W. H. KEESOM (J. Phys. Radium, 1934, [vii], 5, 373-384).—A lecture. N. M. B.

Specific heats of zinc and silver at liquid helium temperatures. W. H. KEESOM and J. A. KOK (Physica, 1934, 1, 770-778).—It is shown experimentally that the rapid descent of the  $TC^{-1/3}-T$  curve below  $5^{\circ}$  abs. is not due to absorption of He at the surface of the metal. The effect is attributed to the heat capacity of the free electrons (I), and below  $3 \cdot 0^{\circ}$  abs. the supplementary at. heat for Ag agrees with (I) calc. by Sommerfeld's formula. With Zn the agreement is less satisfactory. H. S. P.

Specific heats of gases at high temperatures. W. T. DAVID and A. S. LEAH (Phil. Mag., 1934, [vii], 18, 307—321).—From the temp. reached in explosions of H<sub>2</sub> and O<sub>2</sub> and CO and O<sub>2</sub> in various proportions and diluted with other gases, and from the known vals. of the sp. heats at lower temp., it is concluded that the theoretical vals. of the sp. heats of CO, N<sub>2</sub>, and CO<sub>2</sub>, and probably those of H<sub>2</sub> and O<sub>2</sub>, are accurate up to 2500°. The theoretical vals. for H<sub>2</sub>O show inaccuracies only above 2000°. J. W. S.

Determinations with condensed heavy hydrogen. K. CLUSIUS and E. BARTHOLOMÉ (Naturwiss., 1934, 22, 526—527).—The sp. heat of pure  $H_2^*$  in the solid and liquid states at 10° and 23° abs., the heat of fusion, triple point pressure, and density of the liquid  $H_2^*$  have been determined. In the solid state,  $H_2$  and  $H_2^*$  have practically the same sp. heat below 14° abs. The mol. vol. of  $H_2^*$  at the triple point is about 11.5% < that of  $H_2$ , a difference which remains at 0° abs. A statistical calculation of the abs. entropy of  $H_2^*$  at 298.2° abs. gives 38.98 entropy units, in sufficiently good agreement with the experimental val. (38.76). A. J. M.

Isotopic ratio in hydrogen : general survey by precise density comparisons on water from various sources. H. J. EMELEUS, F. W. JAMES, A. KING, T. G. PEARSON, R. H. PURCELL, and H. V. A. BRISCOE (J.C.S., 1934, 1207-1219) -d for various samples of rigorously purified  $H_2O$  has been determined to within  $2 \times 10^{-7}$  g. per c.c. by observing the flotation temp. of a SiO<sub>2</sub> float. London tap-H<sub>2</sub>O (I) of const. d served as a standard. The following results for d relative to (I) at 20.335° were obtained for the sources given; the unit  $=1 \gamma d = 10^{-6}$  g. per c.c., heavier than the standard = +: natural waters, -0.63 to +2.52; minerals, +2.52 to +6.30; fruits, -0.8 to +4.41; sucrose, +8.61; Salix caprea, sap +3.67, wood, +3.15; animal fluids, -0.84 to +2.52; electrolyte baths, +30.4 to +19.9; other industrial liquids, -5.04 to +4.62. The H<sub>2</sub>O from rasorite (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>,4H<sub>2</sub>O  $\Delta\gamma d = \pm 6.30$ ) is distinctly heavier than that from tincal  $(Na_2B_4O_7, 10H_2O \Delta \gamma d = +2.73)$ mean). Thermophilic cotton fermentation gives no change in d. On freezing H<sub>2</sub>O, H<sub>2</sub>O crystallised preferentially, which may explain the difference in d between natural and artificial ice. The crystallisation of K alum and of Na2SO4 caused no separation between the two isotopes. H<sub>2</sub>O adsorbed on SiO, gel and charcoal gave  $\Delta \gamma d = +0.4$  and +0.2. Distillation effected a considerable concn. of H<sub>2</sub>O. It is inferred that in the absence of local influences the abundance ratio of the two isotopes is const. over the earth's surface. R. S. B.

Adiabatic cooling of magnetic substances. W. J. DE HAAS and E. C. WIERSMA (Physica, 1934, 1, 779-780).—A method of obtaining a homogeneous temp. as low as  $0.031^{\circ}$  abs. in 66 g. of K Cr alum is described. H. S. P.

Phenomenon of fusion in relation to a new equation of state and the lattice structure of solids. I. S. FRANCHETTI (Atti R. Accad. Lincei, 1934, [vi], 19, 713—718).—Theoretical. An equation of state is evolved from the relationships previously deduced by the author. D. R. D.

Vapour pressures of metals of high b.p. I. Determinations by b.-p. method. J. FISCHER (Z. anorg. Chem., 1934, 219, 1-16).-Experiments with Hg in a graphite crucible show that, in Greenwood's method for the determination of the b.p. of a metal, a disturbance of the molten metal has been mistaken for boiling at a temp. much < the true b.p. The extent of the deviation depends on the nature of the gas flowing through the outer vessel containing the porous crucible (graphite, sintered corundum, or ZrO<sub>2</sub>) and, above a certain min., is not affected by the velocity of flow of the gas, but the phenomenon does not occur in the absence of the gas stream. The effect is due to effusion. By heating to const. temp. the true b.p. may be obtained. The b.p. found for Pb is  $1750 \pm 10^{\circ}$  and for Ag  $2150 \pm 20^{\circ}$ . The v.p. const. for Pb is in good agreement with the theoretical val. and the Trouton const. is normal. The shape, size, and distribution of the pores in graphite have been studied. M. S. B.

Formula and tables for the pressure of saturated water vapour in the range 0-374°. N. S. OSBORNE and C. H. MEYERS (J. Res. Nat. Bur. Stand., 1934, 13, 1-20).—The tables are computed from a formula which represents an adjusted composite appraisal of the available published data.

E. S. H. Continuation of the vapour-pressure curve above the critical point. A. EUCKEN (Physikal. Z., 1934, 35, 708—711; cf. this vol., 723).—Theoretical. It is shown that it is possible to demonstrate the continuation of the v.-p. curve above the crit. point on the basis of certain analytical criteria.

A. J. M.

Dependence of "vapour pressure" on temperature above the critical point. M. TRAUTZ (Physikal. Z., 1934, 35, 711).—A reply to Eucken (preceding abstract). A. J. M.

Vapour pressure of solid and liquid deuterium and the heats of sublimation, of fusion, and of vaporisation. G. N. LEWIS and W. T. HANSON, jun. (J. Amer. Chem. Soc., 1934, 56, 1687–1689).—V.-p. data for  $H_2^2$  (containing < 0.03% H<sub>2</sub>) are recorded between 20° and 15° abs. The presence of small amounts of H<sub>2</sub> affects the vals. markedly. The following are some of the data : heat of vaporisation 308.3 (liquid), 357.2 (solid); heat of fusion 48.9 g.-cal. per mol.; triple point 18.66° abs.; b.p. 23.6° abs. E. S. H.

Vapour pressure of hydrogen and deuterium fluorides. W. H. CLAUSSEN and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1934, 56, 1820).—The v.p. of H<sup>1</sup>F between 5 and 76 cm. is given by  $\log_{10} P_1$  (cm.) =6.3739—1316.79/T and of H<sup>2</sup>F by  $\log P_2$  (cm.) =6.2026—1261.16/T. E. S. H. Thermal expansion of artificial graphite and carbon. P. HIDNERT (J. Res. Nat. Bur. Stand., 1934, 13, 37-51).—Over the range 20—1000° the expansion coeffs. of transverse sections are > those of longitudinal sections of artificial graphite, and the vals. increase with rising temp. The coeffs. appear to be influenced by the grain size. The expansion coeffs. of C rods made with lampblack are > those made with petroleum coke, indicating that the latter is more suitable for the low-expanding element of temp. regulators. E. S. H.

Viscosity of esters of saturated aliphatic acids. A. H. GILL and F. P. DEXTER (Ind. Eng. Chem., 1934, 26, 881).— $\eta$  for various esters from MeOAc to  $C_5H_{11}$ ·CO<sub>2</sub> $C_5H_{11}$  has been determined at 25°, and is approx. the same for esters containing the same no. of C atoms. It is suggested that a satisfactory substitute for porpoise-jaw oil (I), used for delicate machinery, could be made from an isomeride of Bu<sup>g</sup>CO<sub>2</sub>C<sub>12</sub>H<sub>25</sub> contained in (I), and a saturated fatty acid. R. S. B.

Problems of the liquid state. H. KUDAR (Physikal. Z., 1934, 35, 560-563).—Theoretical. The phenomena of melting, temp. coeff. of fluidity, thermal expansion of liquids, and self-diffusion and conductivity of solid electrolytes are considered.

A. J. M.

Thermal diffusion in gas mixtures. G. BLÜH and O. BLÜH (Z. Physik, 1934, 90, 12—37).—An interferometer has been used to follow diffusion in  $H_2$ -CO<sub>2</sub> and  $H_2$ -N<sub>2</sub> mixtures at -185°, -80°, and 170°. In addition to attractive forces there are repulsive forces inversely  $\propto$  at least the 5th power of the mol. separation. A. B. D. C.

Chart for the rapid calculation of mixtures. J. S. BAKER (Ind. Eng. Chem., 1934, 26, 910).—A chart is described by which the amounts of mixtures of two components required to give a desired concn. may be read off. R. S. B.

V.p. of binary systems. I. Benzene and acetic acid. F. HOVORKA and D. DREISBACH (J. Amer. Chem. Soc., 1934, 56, 1664–1666).—Theoretical considerations show that the system  $C_6H_6$ -AcOH is not azeotropic. E. S. H.

Tests for accuracy of vapour-liquid equilibrium data. H. A. BEATTY and G. CALINGAERT (Ind. Eng. Chem., 1934, 26, 904-909).—Simple rules, derived from the Duhem-Margules equation (I), are given for testing the accuracy of v.-p. data for nonideal binary systems. The partial pressures  $p_1$  and  $p_2$  are plotted against the mol. fractions x and 1-x; then the ratio of the slope of the curve  $(dp_1/dx$  for component 1) to the slope of the line joining the point to the origin  $(p_1/x)$  will be the same for the two components at the same val. of x, or  $(dp_1/dx)/$  $(p_1/x) = [dp_2/d(1-x)]/[p_2/(1-x)]$ . If for a particular val. of x the tangent to one partial pressure curve passes through the origin, the same relation will be shown by the tangent to the second curve. Linear portions of the curves which extrapolate to the origin lie over the same range for the two curves. Other rules involving activity coeffs. are deduced, and data which have passed these tests may be further examined by graphical integration of (I), using activity coeffs.; one partial pressure curve is calc. from the other and then compared with experiment. Examples from isobaric and isothermal data are given. R. S. B.

X-Ray studies on the diffusion of metals in copper. C. MATANO (Japan. J. Physics, 1934, 9, 41-47).—The coeffs. of diffusion of Al, Zn, Mn, Ni, Sn, Pd, Pt, and Au in Cu have been determined at 400° and 950°. Previous treatment influences the coeff. greatly at 400° but not at 950°. W. R. A.

Dipole theory and the size of molecules. J. W. WILLIAMS (Trans. Faraday Soc., 1934, 30, 723-728; cf. A., 1933, 447).—Theoretical. The Debye equations are developed to apply to a binary mixture.

H. J. E.

Dipole moments of the halogen hydrides in solution. F. FAIRBROTHER (Trans. Faraday Soc., 1934, 30, 862–870).—The dipole moment of HCl, HBr, and HI has been measured in  $C_6H_6$  and  $CCl_4$  solution. In each case the val. is > that in the gaseous state. The solute mol. is changed from its covalent state (as gas) to a mol. of the ion pair type under the polarising influence of the dipoles induced in the solvent by the fields of the solute dipoles.

H. J. E.

Polarity and the association of liquids. A. R. MARTIN (Trans. Faraday Soc., 1934, 30, 759–762).— The dielectric consts. of mixtures of  $C_6H_6$  with PhCl, PhCN, and BzOH have been measured, and are correlated with the partial v.p. For the  $C_6H_6$ -PhCl and  $C_6H_6$ -PhCN mixtures deviations from the ideal v.-p. relation are accounted for by interdipole forces (I) and van der Waals forces. In  $C_6H_6$ -BzOH mixtures (I) is the predominating factor. H. J. E.

Temperature solution method and the atom polarisation. H. O. JENKINS (Trans. Faraday Soc., 1934, 30, 739—745).—The polarisation of PhNO<sub>2</sub> in decahydronaphthalene has been measured at 25° and 142.4°. The experimental val. at 142.4° is > that calc. from the Debye linear law. The discrepancy is attributed to the influence of temp. on the dielectric const. of the solvent, and, as a result, on its interaction with the solute. The accuracy of estimates of at. polarisation based on the temp.-solution method is questioned. H. J. E.

Dielectric behaviour of concentrated solutions of dipole substances. A. E. VAN ARKEL and J. L. SNOEK (Trans. Faraday Soc., 1934, **30**, 707–719).— Measurements have been made for PhNO<sub>2</sub> in  $C_6H_6$ . PhMe, and  $CS_2$ , for  $C_5H_5N$  in  $C_6H_6$ , and for MeCN and its Cl-derivatives in  $C_6H_{14}$ ,  $CCl_4$ , and  $C_6H_6$ . The polarisation decreases with increasing concn., especially when the dipole moment is large. H. J. E.

Influence of the solvent on dipole moments. F. H. MÜLLER (Trans. Faraday Soc., 1934, 30, 729– 734).—The total polarisation of various mols. has been measured in a range of solvents of different dielectric const. (I). Only the polarisation due to orientation changes with the solvent. Mols. without moment (e.g.,  $CCl_4$  or  $CS_2$ ) show no change. The total moment causes the solvation effect. Generally the dipole moment decreases regularly with increasing (I) of the solvent. This is true when (I) for a given solvent is varied by change of temp.  $C_2H_4Cl_2$ , I, and some ketones are exceptional. H. J. E.

Energy absorbed in dielectrics with polar molecules. P. DEBYE (Trans. Faraday Soc., 1934, 30, 679-684).—A crit. discussion. The relaxation times (I) of m-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, PhNO<sub>2</sub>, and CHCl<sub>3</sub> in C<sub>6</sub>H<sub>14</sub>, CS<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, CCl<sub>4</sub>, and C<sub>10</sub>H<sub>18</sub> are 1·2-3·6, 1·9-5, and 2·3-3·9 (all ×10<sup>-12</sup>) sec., respectively. The vals. of (I) for a given polar substance in different non-polar solvents are not  $\infty$  their viscosities. H. J. E.

Dielectric constant measurements in aqueous solution and *cis-trans* isomerism. G. DEVOTO (Z. Elektrochem., 1934, 40, 641; cf. this vol., 1093).— Measurements are recorded for aq. solutions of betaines of the cinnamic acid series. The elevation of the dielectric const. of  $H_2O$  per mol. of dissolved *trans-m-*<sup>+</sup>NMe<sub>3</sub>·C<sub>6</sub>H<sub>4</sub>·CH:CPh·CO<sub>2</sub><sup>-</sup> is > that for the *cis* compound. For *m*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH:CH·CO<sub>2</sub>H there is an equilibrium between the polar and non-polar forms. H. J. E.

Dielectric investigations of cellulose derivatives in organic liquids. I. Dipole moment and solvation of glucose penta-acetate and cellobiose octa-acetate. II. Dipole moments of cellulose acetates and their solvation. I. SAKURADA and S. LEE (J. Soc. Chem. Ind. Japan, 1934, 37, 331-334B, 334-337B).—I. The dipole moments of  $\beta$ -glucose penta-acetate (I) in C<sub>6</sub>H<sub>6</sub> and in CHCl<sub>3</sub>, and of cellobiose octa-acetate (II) in CHCl<sub>3</sub> are 2·43, 1·99, and 2·40 e.s.u., respectively. The mol. polarisation of (I) in CHCl<sub>3</sub> is < in C<sub>6</sub>H<sub>6</sub>, and the solvation with CHCl<sub>3</sub> is 0·74 or 1·48 mol. per mol., according to whether the fall in orientation polarisation is ascribed wholly to the CHCl<sub>3</sub> or to both the CHCl<sub>3</sub> and to (I).

II. The dipole moments (on  $C_6$  basis) in CHCl<sub>3</sub> of two preps. of cellulose acetate of widely different viscosities were found to be 1.98 and 1.95, respectively. Their solvation is probably about the same as that of (I) and (II) (0-0.3 c.c. per c.c.) and the high viscosity is due to mechanical trapping of solvent. A. G.

Dielectric capacity of albumin solutions. W. J. SHUTT (Trans. Faraday Soc., 1934, 30, 893-897).---A Pt ellipsoid of rotation with mirror attached is suspended from a torsion head (I) in the liquid between two external Pt discs. Application of an alternating field rotates the suspended system, which is then adjusted to zero by (I). The effect with an unknown solution is compared with that for H<sub>2</sub>O, from which the dielectric const. (II) of the former is cale. The val. of (II) for  $2\cdot5\%$  aq. albumin has a max. at  $p_{\rm H}$  4.9, and min. at  $p_{\rm H}$  4.4 and 5.25. The val. of (II)  $\propto$  albumin conen. H. J. E.

Dipole moments and physico-chemical properties. V. A. E. VAN ARKEL (Chem. Weekblad, 1934, 31, 490—492).—Dissolution is too complicated a phenomenon for the influence of dipoles to be calc. quantitatively, but it is shown qualitatively that, e.g., the solubilities of Cl-derivatives of  $CH_4$  and  $C_2H_6$ are in accordance with theory. H. F. G.

Influence of viscosity on the decrease in fluorescent power of the solutions of certain dyes as a function of concentration. J. BOUCHARD (Compt. rend., 1934, 199, 460-462).—The fluorescent power of solutions of dyes in  $H_2O$ -glycerol mixtures has been studied as a function of conen. and viscosity,  $\eta$ . The fluorescent power for infinite dilution is independent of the  $\eta$ . The fluorescence in aq. sucrose or glucose solution is equal to that in aq. glycerol solution of equal  $\eta$ . The results are in agreement with the view that the variation of fluorescence with conen. is due to the velocities of diffusion in the solution. J. W. S.

Relation between the dissolution properties of organic liquids and the viscosity of cellulose ester solutions. I. SAKURADA and M. SHOJINO (Kolloid-Z., 1934, 68, 300-305).—The solvent power of 11 org. liquids for cellulose esters has been examined by comparing the form of the solubility curves of the esters in liquid mixtures, of which one component is a non-polar, indifferent liquid, such as  $C_6H_6$ . Parallel viscosity measurements show that  $\eta$  decreases as solvent power increases. E. S. H.

System aluminium-zinc. E. SCHMID and G. WASSERMANN (Z. Metallk., 1934, 26, 145-150).-X-Ray measurements at 20-400° show that the composition of the saturated  $\gamma$ -phase varies from 5% Zn at 160° to 48% Zn at 350°, and that the  $\beta$ -phase has a similar face-centred cubic structure to the  $\gamma$ -phase. No evidence of the existence of Al<sub>2</sub>Zn<sub>3</sub> at any temphas been obtained. The  $\beta$ -phase appears to be a continuation of the  $\gamma$ -phase, the two regions being separated by a miscibility gap, although it is possible that at > 350° the two phases merge into one another without interruption, which would indicate that the accepted solidus line needs modification. The eutectoidal structure produced by the decomp. of  $\beta$  is the result of recrystallisation caused by a far-reaching diffusion process. A. R. P.

Thermal analysis of the system rubidiummercury. Mercurides of the alkali metals. W. BILTZ, F. WEIBKE, and H. ECGERS (Z. anorg. Chem., 1934, 219, 119—128).—The phase diagram shows the existence of RbHg<sub>6</sub>, m.p. 132°, and the compounds RbHg<sub>2</sub>, m.p. 256°, almost black; Rb<sub>2</sub>Hg<sub>7</sub>, m.p. 197°; Rb<sub>7</sub>Hg<sub>8</sub>, peritectic decomp. 157°, and Rb<sub>3</sub>Hg<sub>4</sub> (brass-coloured), Rb<sub>5</sub>Hg<sub>18</sub>, Rb<sub>2</sub>Hg<sub>9</sub>, and RbHg<sub>9</sub> with peritectic or eutectic points at 170°, 194°, 162°, and 67°, respectively. Comparison with the other alkali metals indicates that the thermal stability of compounds with Hg increases from Li to Cs, and that the lower mercurides of the lighter metals and the higher mercurides of the heavier metals are those more readily formed. M. S. B.

Equilibrium diagrams of the systems leadthallium and lead-thallium-cadmium. E. JANECKE (Z. Metallk., 1934, 26, 153—155).—From a review of the evidence obtained in recent work the existence of the compound PbTl<sub>2</sub> is indicated.

A. R. P. Cadmium-lithium alloys. A. BARONI (Z. Elektrochem., 1934, 40, 565).—Polemical (cf. this vol., 356). E. S. H.

Crystallographic structure of the intermediate phase Au<sub>2</sub>Pb. H. PERLITZ (Keemia Teated, 1934, 2, 11-16).—From X-ray examination of Au-Pb alloys the existence is inferred of an intermediate phase with a narrow range of homogeneity in the region 66.6 at.-% Au. The lattice is face-centred cubic, and the unit cube of edge 7.910 Å. contains 24 atoms. It is inferred that 16 Au atoms occupy the positions 16b, and 8 Pb atoms the position 8g, of Wyckoff's tables, a structure identical with that of MgCu<sub>2</sub> and KBi<sub>2</sub>. R. S. B.

Electrical conductivity and equilibrium diagram of binary alloys. XIII. Formation of solid solutions in the system magnesium-tin. G. GRUBE and H. VOSSKUHLER. XIV. System lithium-thallium. G. GRUBE and G. SCHAUFLER (Z. Elektrochem., 1934, 40, 566—570, 593—600; cf. this vol., 724).—XIII. Measurements of electrical conductivity and thermal expansion in Mg-rich alloys show a sharp fall in the solid solution region as the Sn content is increased, reaching a min. at the composition Mg<sub>2</sub>Sn. The solubility limit is 3.5% Sn at the eutectic temp. and 0.5% Sn at 440°.

XIV. Thermal analysis and conductivity-temp. curves indicate the existence of LiTl,  $\text{Li}_2\text{Tl}$ ,  $\text{Li}_5\text{Tl}_2$ ,  $\text{Li}_3\text{Tl}$ , and  $\text{Li}_4\text{Tl}$ . E. S. H.

Formation of metallic hydrides by atomic hydrogen. II. System tantalum-hydrogen. E. PIETSCH and H. LEHL (Kolloid-Z., 1934, 68, 226–230; cf. A., 1933, 1020).—By the action of at. H on Ta a new solid phase is formed, having a cubic bodycentred lattice with a 3.42 Å. Excess of H produces a solid solution in which a increases to 3.44 Å.

E. S. H.

Continuous transition and critical point be-tween two solid phases. U. DEHLINGER (Z. physikal. Chem., 1934, B, 26, 343-352; cf. A., 1933, 896).—Theoretical. It is deduced that in the transformation (cubic  $\longrightarrow$  tetragonal) of the superstructure of the alloy AuCu, the connexion between the regularity of the at. distribution and the tetragonal axial ratio will depend on the pressure. Calculation of the thermodynamic equilibria, introducing an entropy term depending on the lattice symmetry, shows that at low pressures a discontinuous transition, and at high pressures a continuous transition, which is a phase change of the second order, are to be expected; between the two will be a crit. point. The possibility of continuous transition depends on the presence of electrons not necessary either for the general electron gas or the co-ordination of the first R. C. sphere.

Temperature-structure-composition behaviour of certain crystals. M. J. BUERGER (Proc. Nat. Acad. Sci., 1934, 20, 444–453).—Theoretical considerations relating to two-component crystals are discussed. H. F. G.

Adsorptive inclusion and mixed crystal formation. A. SMEKAL (Physikal. Z., 1934, 35, 643— 646).—The conditions for the formation of mixed crystals of two substances are discussed. The decisive factor for complete miscibility is the energy, and not necessarily a similarity of lattice dimensions. Criteria for distinguishing between the inclusion of small quantities of a foreign substance in a crystal by adsorption or by the formation of mixed crystals are examined. The first or second of these methods will occur according as there is, or is not, a localisable electron linking in the foreign atom. Various applications are described. A. J. M.

Principles of gas exsorption. II. A. GUYER, B. TOBLER, and R. H. FARMER (Chem. Fabr., 1934, 7, 265-269; cf. this vol., 592).-The rate of loss of gas from saturated H<sub>2</sub>O droplets moving downwards is very great compared with stationary drops and stirred solutions, owing probably to eddies within the drops. The fractional loss A and apparent "evasion coeff." B (loss of gas in mg. per min. per sq. cm. from a 0.1%solution at zero external partial pressure of the gas) are nearly linear functions of the time of formation of the drops. With increase of the size of the drops A diminishes rapidly but B is unchanged, whilst with increase of the distance of fall A increases; B is independent of the distance and the rate of fall. With rise of temp. A increases, but only  $\infty$  the change in the rate of diffusion of the gas within the liquid. Reduction of pressure increases the rate of loss of gas to a greater degree than in the case of bulk solutions. H. F. G.

Permeability to hydrogen of nickel, copper, and some of their alloys. W. BAUKLOH and H. KAYSER (Z. Metallk., 1934, 26, 156–158).—Curves showing the permeability to H<sub>2</sub> (I) at 600–900° are given for Ni, Ni + 1% Cr, Ni + 2% Cr, 33·3:66·6 Ni-Cu alloy, 75:25 Cu-Ni alloy, Armco Fe, and pure Cu. (I) decreases in the order given and the slope of the curves (except that of Fe) also decreases in this order. A. R. P.

Diffusion of water in a zeolite crystal. Mobility of adsorbed molecules. A. TISELIUS (Z. physikal. Chem., 1934, 169, 425-458; cf. this vol., 249).—In the diffusion of  $H_2O$  in single crystals of heulandite the diffusion coeff., D, is not const., except for very small conen. gradients, but falls rapidly with the concn. (c). From the variation of D with temp. the energy of activation of diffusion has been calc., and this indicates that the diffusing mols. even in positions intermediate between the two lattice points are bound to the lattice by strong forces. The variation of D with c seems to be a consequence of the deviation of the sorbed state from the ideally dissolved state. D varies considerably with direction, which is partly explained by what is known of the lattice structure. Sorption isobars and the variation of the double refraction and angle of extinction with the H<sub>2</sub>O content have been determined. R. C.

Penetration of copper into rock salt by electrolysis and diffusion. S. ARZIBISCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 20-26).—Cu diffuses into a NaCl crystal pressed between two copper plates and heated to 760°. Diffusion of other metals could not be detected. The effect with Cu is attributed to the approx. equality of the ionic radii of Cu and Na. Similar diffusion with resultant red coloration of the crystal occurs in an electric field, or in a NaCl crystal coloured blue by immersion in Na at 700°. From absorption measurements the red-coloured crystals are shown to contain colloidal Cu. H. J. E.

Liquid-liquid equilibria involving heavy water. N. F. HALL, H. R. WENTZEL, and T. SMITH (J. Amer. Chem. Soc., 1934, 56, 1822).—Addition of  $H_2^{2O}$  depresses the lower crit. solution temp. of nicotine- $H_2O$  mixtures and raises the crit. solution temp. of PhOH- $H_2O$  mixtures. In the latter case the temp. rise  $\infty$  the amount of  $H_2^{*O}$  added. E. S. H.

Separation of crystals and gases from supersaturated solutions. R. FRICKE (Kolloid-Z., 1934, 68, 165–168).—A review of published work.

Solubility of calcium lævulate in water. G. J. Cox, M. L. DODDS, and C. CLASPER (J. Amer. Pharm. Assoc., 1934, 23, 662—664).—The solubility is given by  $p=27\cdot58+0\cdot173t+0\cdot0031t^2$ , where p is g. of Ca(C<sub>5</sub>H<sub>7</sub>O<sub>3</sub>)<sub>2</sub>,2H<sub>2</sub>O per 100 g. of solution and t is temp. in °C. C. G. A.

Cinchonine solubility. R. A. HATCHER (Amer. J. Pharm., 1934, 106, 244–249).—The solubility of cinchonine in  $H_2O$  is said to depend on the method of measurement. R. S. B.

Solubility of magnesium ammonium phosphate in some salt solutions. K. L. MALJAROV and V. B. MATSKIEVITSCH (Z. anal. Chem., 1934, 98, 31–33).— The solubility of MgNH<sub>4</sub>PO<sub>4</sub> increases with the conen. of NH<sub>4</sub> or Na' salt present; this is particularly marked with  $(NH_4)_2C_2O_4$ . The solvent effect of salts increases in the order NaCl, NH<sub>4</sub>NO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>Cl,  $(NH_4)_2SO_4$ ,  $(NH_4)_2C_2O_4$ . The use of NH<sub>4</sub>NO<sub>3</sub> instead of NH<sub>4</sub>Cl in separating Ca and Mg is therefore recommended. A. R. P.

Solubility of the phosphoric acid of different phosphates. F. MACH and P. LEDERLE (Z. Pflanz. Düng., 1934, A, 34, 323—340).—Various Ca phosphates are more sol. in  $H_2O$  than in aq.  $Ca(HCO_2)_2$  (I) containing free CO<sub>2</sub>. The solubility is lowered if the (I) is substantially free from CO<sub>2</sub>, and is still lower in soil extracts. The conclusion of Wilhelmj (B., 1931, 455) could not be substantiated. SiO<sub>2</sub> sol increases the solubility of phosphates, but SiO<sub>2</sub> gel is without effect. A. G. P.

Influence of salt- or acid-type hydrophilic colloids on the solubility of sparingly soluble acids and bases. I. Gum arabic and its free acid. H. BRINTZINGER and H. G. BEIER (Kolloid-Z., 1934, 68, 271—275).—The solubility of BZOH, salicylic and sulphanilic acids is increased by gum arabic, but not by arabic acid (I), whilst the solubility of strychnine and of o-, m-, and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> is increased by (I). These influences are attributed to salt formation. E. S. H.

Solubility of gluten. W. H. COOK and R. C. ROSE (Nature, 1934, 134, 380–381).—Gluten (I) is completely dispersed by 10 and 12% solutions of Na salicylate (II). Higher conens. are slower in their action. 8% (II) and 24% CO(NH<sub>2</sub>)<sub>2</sub> are min. conens. for complete dispersion of (I). L. S. T.

Distribution of chloroacetic acids between two non-miscible liquid phases. N. A. DE KOLOSOVSKI and F. S. KULIKOV (Z. physikal. Chem., 1934, 169, 459-471).—The distribution ratio of the chloroacetic acids between H<sub>2</sub>O and twelve org. solvents has been determined at 25° over a wide range of concn. R. C. Formation of fog in the absorption of hydrogen chloride by liquids. H. REMY [with W. OWE] (Kolloid-Z., 1934, 68, 246—253).—The absorption of fumes of moist SO<sub>3</sub> and of HCl (obtained by passing air through a conc. solution or by passing H<sub>2</sub> over heated AgCl) in H<sub>2</sub>O, EtOH, aq. 1% gelatin, aq. KOH, BaCl<sub>2</sub>, or AgNO<sub>3</sub> has been determined. Absorption of HCl is almost complete, although in some cases a slight fog remains above the absorbent liquid. Absorption of SO<sub>3</sub> is  $\leq 67\%$  in any of the systems examined, and varies with the concn. of SO<sub>3</sub> in the fumes. E. S. H.

Sorption of sulphur dioxide by active charcoal. I. Relation between sorption, temperature, and pressure. K. ARII (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 853—867).—The adsorption isotherms of SO<sub>2</sub> on active coconut charcoal have been determined at  $0-50^{\circ}$ , the results being in agreement with Freundlich's formula. The relation between amount adsorbed per c.c. (a), pressure (p), and temp. (t) is given by  $\log a = \log a_0 - (0.006790 - 0.0006742$   $\log p)t$ , where  $a_0$  is the amount adsorbed at 0°. The differential isosteric heat of adsorption is also calc.

J. W. S. Adsorption of ether vapour from vapourair mixture by active charcoal powder [in relative motion]. E. BOYE (Kolloid-Z., 1934, 68, 367—371). —Adsorption isotherms at 20° have been determined, using two kinds of finely-divided active C.

E. S. H.

Adsorption of acids by animal charcoal. S. CASPE (J. Indian Chem. Soc., 1934, 11, 439-440).— The loss in acidity of aq. HCl and AcOH on treatment with animal C is due to reaction between these acids and phosphates present in the C, and not to adsorption as is commonly supposed. D. R. D.

Influence of acidity on the adsorption of metal salts by active charcoal. H. LEUNIG (Z. anorg. Chem., 1934, 219, 178—180).—Adsorption of  $Hg(NO_3)_2$ from aq.  $HNO_3$ ,  $FeCl_3$  from aq. HCl, and  $K_2Cr_2O_7$ from aq.  $H_2SO_4$  of different concn. shows that increasing acidity reduces the amount of salt adsorbed, but that, above a certain definite concn., the acid has no further influence. M. S. B.

Effect of  $p_{\rm H}$  on the adsorption and deamination of alanine by charcoal. E. BAUR and K. WUNDERLY (Biochem. Z., 1934, 272, 1—8; cf. this vol., 594).— Low acidity stimulates and high acidity restricts the adsorption and deamination of alanine by charcoal, the quant. relationships being exactly similar to those between activity and  $p_{\rm H}$  in fermentation. The production of complex ions which are expelled from the adsorbent by [H'] is assumed. W. McC.

Absorption of alkali metals on metal surfaces. I. Formation and adsorption of ions; potential curves. J. H. DE BOER and C. F. VEENEMANS (Physica, 1934, 1, 753-762).—Theoretical. Alkali metal atoms are transformed into positive ions by adsorption at a metal surface, if the sum of the energies of adsorption of the ions  $(Q_i)$  and of escape of electrons from the metal  $(\epsilon \phi_0) >$  energies of adsorption  $(Q_a)$  and of ionisation  $(I_a)$  of the atoms. If in addition  $e\phi_0 > I_a$ , the absorbed ions are vaporised

E. S. H.

at higher temp. The adsorption phenomena may be compared with the formation of chemical compounds as is shown by the potential curves. H. S. P.

Activated adsorption of water vapour by alumina. H. S. TAYLOR and A. J. GOULD (J. Amer. Chem. Soc., 1934, 56, 1685—1687).—Pptd.  $Al_2O_3$  has a very high adsorptive capacity for  $H_2O$  vapour at high temp. The lower temp. at which activated adsorption of  $H_2O$  vapour occurs and the lower heat of adsorption, as compared with the corresponding data for  $H_2$ , explain the dehydrating characteristics of  $Al_2O_3$ . E. S. H.

Adsorption of sulphate ion by thorium hydroxide sol dialysed to different degrees. N. V. KAREKAR and A. M. PATEL (Kolloid-Z., 1934, 68, 286—289).—Using  $K_2SO_4$ , MgSO<sub>4</sub>, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as the added electrolytes the adsorption of the cations increases with increasing valency and decreases with progressive dialysis of the sol. The adsorption of  $SO_4''$  in  $K_2SO_4$  and MgSO<sub>4</sub> is reduced, but in Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is slightly increased, by the addition of MeOH, EtOH, or Pr<sup>g</sup>OH. E. S. H.

Absorption of acetone by cellulose nitrates. M. MATHIEU and C. KURYLENKO (Compt. rend., 1934, 199, 427—428).—The absorption spectrum of cellulose trinitrate-COMe<sub>2</sub> combinations is quantitatively influenced by the amount of  $H_2O$  in the COMe<sub>2</sub> used and is markedly different if  $H_2O$  is rigidly excluded. Further, absorption of COMe<sub>2</sub> is reversible without loss of structure. It is concluded that no definite compounds are formed. R. S. C.

Exchange adsorption and adsorption indicators. I. M. KOLTHOFF (Kolloid-Z., 1934, 68, 190– 200).—A discussion of the conditions for exchange adsorption and for true adsorption. The action of adsorption indicators is explained on the basis of exchange adsorption. E. S. H.

Theory of phenomenon of liquid drops on the surface of the same liquid. M. KATALINIĆ (Kolloid-Z., 1934, 68, 372-373).—Polemical (cf. A., 1933, 1113). E. S. H.

Reciprocal solubility and surface tension. V. SEMENTSCHENKO and E. DAVIDOVSKAJA [with S. GRATSCHEVA] (Kolloid-Z., 1934, 68, 275–286).— The influence of additions of  $BuCO_2H$ ,  $C_5H_{11}$ · $CO_2H$ ,  $C_6H_{13}$ · $CO_2H$ ,  $C_7H_{15}$ · $CO_2H$ , and amyl alcohol on the interfacial tension and crit. solution temp. of the system MeOH-hexane has been determined at 2°, 7°, 12°, 17°, and 22°. Similar data have been obtained for the system nicotine-H<sub>2</sub>O with the above and other additions. The results show that substances which lower the interfacial tension cause the region of partial miscibility to contract, and vice versa.

E. S. H.

Spreading of cellulose and its derivatives on solids and liquids. I, II. T. NAKASHIMA and M. NEGISHI (J. Soc. Chem. Ind. Japan, 1934, 37, 327— 331B).—The spreading coeff. of solutions of cellulose nitrate or acetate (I) in COMe<sub>2</sub> or of (I) in MeOAc depends greatly on the quality of the prep. and on the concn. It is only slightly affected by the surface tension, but is probably a function of the viscosity. A. G.

4 A

Mechanical properties of unimolecular films. I. LANGMUIR (J. Franklin Inst., 1934, 218, 143-171). —A lecture, dealing mainly with the author's own work and including unpublished work [with (MISS) K. B. BLODGETT] on unimol. films of stearic acid at a H<sub>2</sub>O-hydrocarbon interface. Bimol. and more composite films are dealt with in addition to unimol. films. D. R. D.

Surface films of ergosterol and its irradiation products. J. F. DANIELLI and N. K. ADAM (Biochem. J., 1934, 28, 1583—1591).—Surface pressure and potential measurements on unimol. films of ergosterol and its irradiation products show considerable changes in the tilt of the mols. as irradiation proceeds, probably due to stereochemical changes altering the angle of tilt of the OH group to the ring system. The position of the double linking probably alters, also, during irradiation. Position 3 for OH is favoured.

C. G. A.

Mechanism of deformation of thread-like materials. II. Arrangement of the micelles of films. O. KRATKY (Kolloid-Z., 1934, 68, 347-350; cf. A., 1933, 902).—Consideration of published work on the double refraction of stretched cellulose nitrate films suggests that the micelles exist either as groups of parallel units or as bundles. E. S. H.

Wetting phenomena with hydrophilic and hydrophobic powders in a system of two immiscible liquids. IV. Influence of acids on the wetting of lead glance powder with different flotation reagents. E. BERL and B. SCHMITT (Kolloid-Z., 1934, 68, 350-361; cf. A., 1933, 1114).-The wetting curves of sulphated PbS in presence of different inorg. and org. acids and K Et xanthate are described. The cause of the observed max. is ascribed to preferential adsorption of the acid in dil. and conc. solutions at active, sulphated centres. With increasing degree of sulphation of PbS the max. is displaced in the direction of higher acid concn.; in absence of sulphate, org. acids having no hydrophilic groups can act as flotation reagents. E. S. H.

Heat of wetting charcoals of graded activity, in relation to adsorptive capacity and retentivity. S. H. BELL and J. C. PHILIP (J.C.S., 1934, 1164-1169).—The increase of available surface of either birchwood or sugar charcoal, and the decrease of bulk density on activation by air at 700-900°, are accompanied by a steady rise in the heat of wetting, which seems to be more definitely related to the retentivity than to the adsorption. Air treatment seems to reduce adsorptive power in the early stages, probably due to clogging by hydrocarbons which are removed by the subsequent treatment. No appreciable adsorption of dissolved substances of large mol. dimensions, e.g., methylene-blue, occurs with sugar C until a late stage in the air-activation of the C. The rise in the adsorption val. with increase in period of activation is then comparatively rapid. M. S. B.

Precipitation phenomena in the drying of dilute solutions. H. FLOOD and L. TRONSTAD (Kolloid-Z., 1934, 68, 333-335).—The formation of annular and spiral periodic structures in the evaporation in vac. of very dil. NaOH-Na<sub>2</sub>CO<sub>3</sub> solutions is described. E. S. H.

BRITISH CHEMICAL ABSTRACTS.-A.

Mosaic structure of crystals and heterogeneous equilibrium. D. BALAREV (Kolloid-Z., 1934, 68, 266—271).—A discussion of the effect of the heterogeneous structure of crystals on equilibrium in reactions involving a solid phase, with reference to sp. examples. E. S. H.

Compressibility of dilute solutions of electrolytes. A. SZALAY (Physikal. Z., 1934, 35, 639-643). —The compressibility was investigated by the Debye-Sears optical diffraction method employing ultrasonic waves. A linear increase in the velocity of sound with the ionic conen. in  $H_2O$  was found. The compressibility decreases linearly with increasing conen. Ions with the same charges produce approx. the same effect, but the effect increases with valency > corresponds with a linear law, but < for a quadratic law. A. J. M.

Viscosity of solutions of strong electrolytes. V. D. LAURENCE and J. H. WOLFENDEN (J.C.S., 1934, 1144—1147).—The relative viscosities of aq. LiCl, LiBr, LiI, LiIO<sub>3</sub>, LiOAc, Li picrate, KI, KIO<sub>3</sub>, KOAc, AcOH, NEt<sub>4</sub>Br, and NEt<sub>4</sub> picrate have been determined at 25° at conens. down to approx. 0.005N in some cases. The A and B coeffs. of the Jones-Dole equation  $\eta=1+A\sqrt{c+Bc}$  have been calc. The A vals. are in good agreement with the Falkenhagen-Dole equation. The B vals. for the inorg. salts are approx. additive, being made up of independent components characteristic of the two ions, but this is not so for salts containing the NEt<sub>4</sub> and picrate ions. Comparison of B for OAc' and AcOH shows that the val. of B is increased by an electric charge.

M. S. B. Surface tension of Debye-Hückel electrolytes. L. ONSAGER and N. N. T. SAMARAS (J. Chem. Physics, 1934, 2, 528—536).—Wagner's formula for the surface tension of electrolytes is simplified. The limiting law  $\sigma = \sigma_0 + \text{const.} \times c \log (\text{const.}/c)$  is obtained. The theory accounts fairly well for the observed  $\sigma$  up to concns. of 0.2N. The available data for uni-univalent electrolytes indicate that Coulomb's law is valid for distances > a mol. diameter (3×10<sup>-8</sup> cm.) from the surface. M. S. B.

Superficial electric moments of particles [dispersed] in a liquid medium. (MLLE.) N. CHOUCROUN (Compt. rend., 1934, 199, 36–38; cf. A., 1933, 461).—A micro-electrophoresis apparatus is described for use on a microscope stage, with which superficial electric moments of gamboge, mastic, and powdered glass were measured as functions of  $p_{\rm H}$ . The double layers were found to cover only approx. 0.01% of the surfaces. The surfaces of bacteria and of yeasts were found to be non-uniformly electrified, definite orientation occurring in the applied field. Groups of bacteria may be separated by differential electrophoresis. The charges on yeasts varied periodically with time, and may be related to the vital processes. B. W. B.

Mechanical properties of disperse systems and surface layers. II. Elastic properties and dispersity of foams. Experimental test of theory. D. DERJAGUIN and E. OBUCHOV (Kolloid-Z., 1934, 68, 243-246; cf. A., 1933, 777).—Data for 0.02% aq. saponin are in complete agreement with the theory previously outlined. E. S. H.

Limits of applicability of ultrafiltration to the recognition of the colloid state. B. ERSCHLER (Kolloid-Z., 1934, 68, 289–298).—Collodion membranes have the power to retain crystalloids. With non-electrolytes the amount retained is independent of the concn. and is generally  $\geq 2-3\%$ . With electrolytes the amount retained is greater for dil. solutions, but less for conc. solutions. The charge on the membrane is discussed as a factor. E. S. H.

Anomalous turbulence in sols. Wo. OSTWALD [with V. TRAKAS and collaborators] (Kolloid-Z., 1934, 68, 211—226).—In sols of Congo-red, benzopurpurin 4B, cotton-yellow, geranin, and 2% gum arabie turbulence is observed at very low velocities of flow. E. S. H.

Preparation of colloidal manganese dioxide. E. CHIRNOAGĂ (Kolloid-Z., 1934, 68, 298—300).— MnO<sub>2</sub> sols are prepared by the slow reduction of 0.01N-KMnO<sub>4</sub> at room temp. with EtOH, Et<sub>2</sub>0, CHCl<sub>3</sub>, CS<sub>2</sub>, PhMe, xylenc, etc. The sol is negatively charged and is readily coagulated by electrolytes, but is remarkably stable after boiling. E. S. H.

Cohesion in the system sand + colloidal silicic acid and ferric hydroxide, dried at 110°. A. GLAZUNOV and V. PETAK (Chem. Listy, 1934, 28, 191-194).—Grains of sand are agglutinated by heating at 110° with colloidal Fe(OH)<sub>3</sub>(I); cohesion augments with (I) content up to 4%, thereafter diminishing. This effect is due to saturation of the sand surface with (I) at 4%, above which excess of (I) remains unadsorbed, and yields a non-cohesive powder on drying. SiO<sub>2</sub> gel has no agglutinative action, and if present together with (I) prevents cohesion. R. T.

Magnetic birefringence in mercurisulphosalicylic acid sols. S. PRAKASH and L. N. BHAR-GAVA (J. Indian Chem. Soc., 1934, 11, 449–454).— Addition of KCl causes a decrease in the magnetic birefringence (B) of these sols;  $Ba(NO_3)_2$  and  $KNO_3$ increase B, and with KBr B passes through a min. For FePO<sub>4</sub> and Zr(OH)<sub>2</sub> sols, B=0. D. R. D.

Vanadium pentoxide jellies. A. RABINERSON (Kolloid-Z., 1934, 68, 305—316).—Thixotropic  $V_2O_5$ gels containing electrolytes, especially at higher concns., become non-thixotropic on keeping. The change is accelerated by shaking. Thixotropic gels are attributed to oriented coagulation. The setting time is retarded by previously heating the sol. Fresh thixotropic gels are liquefied by warming, probably through destroying the oriented coagulation.

E. S. H. Formation of a ruby-red jelly of zirconium sulphosalicylic acid. S. PRAKASH and L. N. BHARGAVA (J. Indian Chem. Soc., 1934, 11, 419– 420).—If Zr sulphosalicylic acid gel (cf. A., 1933, 1011) is allowed to set in presence of  $Al(NO_3)_3$  or  $HNO_3$ , it acquires a ruby-red colour. With NaNO<sub>3</sub>, the colour is bright yellow. The rate of development of colour in presence of  $Al(NO_3)_3$  has been followed using a Nutting photometer. D. R. D.

Ageing of gel-like basic zinc salts. Topochemical reactions of compact disperse systems. W. FEITRNECHT (Kolloid-Z., 1934, 68, 184–190). X-Ray examination of gelatinous basic Zn salts, produced by hydrolysis, shows that (a) with basic  $\text{ZnCl}_2$ a definite diagram for a  $\text{Zn}(\text{OH})_2$ -rich form is given together with other variable forms, (b) with basic ZnBr<sub>2</sub> three characteristic forms are shown, and (c) with basic ZnSO<sub>4</sub> the structure varies with the Zn(OH)<sub>2</sub> content. E. S. H.

Structure of cellulose solutions. S. GLIKMANN (J. Chim. phys., 1934, 31, 458—468).—The viscosity of solutions of cellulose nitrate (I) and acetate and of ethyl- and benzyl-cellulose in different org. solvents, the pptn. of COMe<sub>2</sub> solutions of (I) by aq. CaCl<sub>2</sub>, the variation of the  $\zeta$ -potential of (I) with concn., and the appearance of (I) under the ultramicroscope after fractionation, may all be explained by assuming the existence of reversible aggregates of the cellulose derivatives which dissociate almost entirely in dil. solution, and form a gel-like structure in conc. solution. M. S. B.

Kinetics of slow coagulation. S. GHOSH (Kolloid-Z., 1934, 68, 316—324).—A crit. review of published work. E. S. H.

Action of "zwitterions" on colloids. E. WEITZ and W. CONRAD (Kolloid-Z., 1934, 68, 230– 233).—Zwitterions of the nature of aliphatic or aromatic  $NH_2$ -acids have little or no coagulating effect on positively-charged  $Fe(OH)_3$  sols or negatively-charged Au sols. The zwitterions stabilise  $Fe(OH)_3$  sols, but sensitise Au and  $As_2S_3$  sols, towards coagulation by other electrolytes. E. S. H.

Lyotropic effects. E. M. BRUINS (Chem. Weekblad, 1934, 31, 479—480).—It is shown graphically that there is a crit. cation (anion) for which the lyotropic series of the anions (cations) comes to an end; for di-univalent salts the crit. lyotropic nos. are 14.9 and 0.01 for the anion and cation, respectively. H. F. G.

Lyophilic colloids. II. Solvation problem. S. LIEPATOV and S. PREOBRASHENSKAJA (Kolloid-Z., 1934, 68, 324—333; cf. this vol., 144).—Measurements of the viscosity and osmotic pressure at different concn. and temp., and of the heat of dissolution of cellulose acetate in MeOAc have been made. The results are discussed in relation to the main theories of lyophilic colloids, and the conclusion is reached that solvation is a complex phenomenon which cannot be explained on purely chemical grounds. E. S. H.

Lyophilic colloids. XXII. Heat-coagulation of ovalbumin. H. R. KRUYT and J. R. DE JONG (Kolloid-Beih., 1934, 40, 55–86; cf. this vol., 27).— Sols of ovalbumin undergo a decrease of viscosity ( $\eta$ ) between 0° and 20°, which is attributed to a diminution of the degree of hydration. Between 20° and 90°  $\eta$  increases, especially in the case of isoelectric sols; the change is less as the  $p_{\rm H}$  diverges from the isoelectric point, and when a sufficient charge on the particles is attained the sol obeys the Hagen-Poiseuille law; these phenomena are attributed to changes in the degree of aggregation. At const. temp. > 20° some decomp. occurs, causing a decrease of  $\eta$ . The effect of adding EtOH is similar to that of raising the temp. E. S. H. Rôle of lipins in the changes of state of proteins. W. PAULI and M. A. OMAR (Kolloid-Z., 1934, 68, 203—211).—The prevention of the heat-coagulation of ovalbumin by removal of lipins is due to a strong displacement of  $p_{\rm H}$  in the alkaline direction, and can be overcome by electrodialysis. The lipin content does not affect the behaviour of albumin towards H<sup>\*</sup>, OH', CO(NH<sub>2</sub>)<sub>2</sub>, or Na salicylate.

E. S. H.

Structural changes taking place during the ageing of freshly-formed precipitates. II. Free mobility of lead ions in amicroscopic crystals of lead sulphate. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1934, 56, 1658—1661; cf. this vol., 840).—Rates of exchange between ageing inactive PbSO<sub>4</sub> and radioactive Pb<sup>\*\*</sup> solution and between radioactive PbSO<sub>4</sub> and inactive Pb<sup>\*\*</sup> solution are identical. The rate of exchange is diminished by a large excess of Pb(NO<sub>3</sub>)<sub>2</sub> in the supernatant liquid. The homogeneous distribution of Th-*B* throughout the system is explained by the assumption that the Pb<sup>\*\*</sup> ions can move freely in the primary amicroscopic PbSO<sub>4</sub> crystals, even in a ppt. 50 min. old.

E. S. H. Colloidal behaviour of sericin. III. H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 283-302; cf. B., 1934, 878).—The cataphoretic velocity (v) of sericin particles has been measured over a range of  $p_{\rm H} 3.6-5$ . From 10° to 40° log v=a+bt, where t is temp. and a and b are consts. The influence of salts and of preheating the sericin on v has been studied. v decreases on keeping owing to gelatinisation. Two forms of sericin have been prepared by adding to a lukewarm solution an equal vol. of saturated  $(NH_4)_2SO_4$ ; on keeping sericin-A (transparent, long fibres) flocculates on the surface and sericin-B (white, granular) slowly ppts. from the solution. Other precipitants, and separation by an electric current and by freezing, are described. The average N contents of sericin-A and -B are 16.36 and 16.11%. Flocculation vals. have been determined for many salts, the controlling factor being the charge on the cation; pptn. with alcohols and  $COMe_2$  has also been studied. In an electric field the A form predominates at the anode and the B form at the cathode. In all cases batches from different silk cocoons are compared. R. S. B.

Ostwald's isocolloid theory and the explanation of the fine structure of resins. R. HOUWINK (Kolloid-Z., 1934, 68, 371—372).—A correction. E. S. H.

Physical chemistry of the dehydration processes of bakery colloids. Physico-chemical foundations of moisture determination. A. I. GERSCHSON (Kolloid-Z., 1934, 68, 361—366).—A study of the dehydration of flour, dough, and bread at different temp. shows that the moisture content is a linear function of temp., whilst at const. temp. the rate of dehydration follows an unbroken curve, which at lower temp. is in accordance with a unimol. reaction. No clear distinction between the free and bound H<sub>2</sub>O can be made. E. S. H.

Physical chemistry of starch and breadmaking. XX. Connexion between the changes in starch in the staling of bread and the changes

in the retrogression of starch paste. J. R. KATZ. XXI. Connexion between changes in the X-ray diagram, on the one hand, and changes in the swelling capacity and amount of soluble amylose, on the other, in the retrogression of wheat starch in the first stage of peptisation (judged by experiments on the retardation of the staling of bread). J. R. KATZ and A. WEIDINGER (Z. physikal. Chem., 1934, 169, 321-338, 339-360; cf. this vol., 961).-XX. In the staling of bread and the ageing of starch paste the same process occurs, but not with the same intensity. In staling, the change in the starch is retrogression from the first stage of peptisation, whilst in the ageing of starch the change is retrogression from the second stage. In both cases a substance with a B X-ray diagram is formed. In the first stage of peptisation a V diagram is obtained, in the second an amorphous diagram. Wheat starch heated with 20-50% of H<sub>2</sub>O yields an A with a superimposed V diagram, but with < 20% of H<sub>2</sub>O an unchanged A diagram only, and heated with 50-60% of  $H_2O$  a pure V diagram. The starch in fresh bread is attacked more rapidly by malt diastase than that in stale bread, and the latter more rapidly than native

starch not heated with  $H_2O$ . XXI. Heating at 40—70°, cooling at -185°, the presence of too little or too much  $H_2O$ , and the presence of aldehydes or certain alkaline substances, but not of ketones, delay or prevent the staling of bread. The effect of each of these factors on the X-ray diagram runs parallel with the effect on the swelling capacity, as measured by the vol. of decantate, and usually with the effect on the amount of sol. amylose (I). It seems that the decline on staling in the amount of (I) and in swelling capacity are closely related, but are not manifestations of the same fundamental change. These results confirm the hypothesis that in retrogression from the first stage of the peptisation of starch the fall in swelling capacity is due to transformation of the starch into a modification of lower swelling capacity. R. C.

Theory of the equation of state. I. G. SCHWEIKERT (Z. Physik, 1934, 90, 355—372).—An equation of state of the van der Waals type has been derived from a consideration of mol. vol. and time of collision. The equation is utilised in the calculation of sp. heats. A. B. D. C.

Thermodynamical theory of the equation of state. V. JACYNA, S. DEREVJANKIN, A. OBNORSKI, and T. PARFENTJEV (Z. Physik, 1934, 90, 331—341).— Experimental data show almost complete agreement with the thermodynamic equation. A. B. D. C.

The liquid state. J. H. HILDEBRAND (Science, 1934, 80, 125-133).—A lecture. L. S. T.

Spectral physics and thermodynamics. Calculation of free energies, entropies, specific heats, and equilibria from spectroscopic data and the validity of the third law. H. ZEISE (Z. Elektrochem., 1934, 40, 662—669).—A further review (cf. A., 1933, 1245).

Activities of life and the second law of thermodynamics. F. G. DONNAN and E. A. GUGGENHEIM (Nature, 1934, 134, 255; cf. this vol., 733). L. S. T. Thermodynamic properties of steam at high temperatures. A. R. GORDON (J. Chem. Physics, 1934, 2, 549).—Vals. for the thermodynamic properties of steam, calc. from Mecke's spectroscopic data, are given for temp. 1500—3000° abs. M. S. B.

Exchange reaction of hydrogen and deuterium oxide. R. H. CRIST and G. A. DALIN (J. Chem. Physics, 1934, 2, 548).—New corr. vals. are given for the equilibrium const. of the reaction  $H^{1}H^{2}O + H^{1}_{2} =$  $H^{1}_{2}O + H^{1}H^{2}$ . For temp. 300—900° abs. K is 0.35— 0.83 (cf. this vol., 962). M. S. B.

Equilibrium  $H_2O+HD=HOD+H_2$  and its rôle in the separation of the hydrogen isotopes. A. FARKAS and L. FARKAS (J. Chim. Physics, 1934, 2, 468-469).—The separation of H<sup>1</sup> and H<sup>2</sup> by various processes, such as electrolysis, decomp. of dil. acids by metals etc., is governed by the vals. of the possible equilibria, especially  $H_2O+H^1H^2 = H^1H^2O+H_2^1$ by the rate of establishment of the equilibria which may be catalysed by different substances, especially metals, and by the rate of reaction of the different individuals,  $H_2O$ ,  $H'H^2O$ , and  $H_2^2O$ . M. S. B.

Equilibrium constants of the vapour-phase hydration of ethylene, propylene, and the butylenes. H. M. STANLEY, J. E. YOUELL, and J. B. DYMOCK (J.S.C.I., 1934, 53, 205-208T).—Equilibrium consts. for the following gaseous reactions have been determined at latm. by a flow method in the temp. range specified: (1) CH<sub>2</sub>:CH<sub>2</sub>+H<sub>2</sub>O  $\Longrightarrow$  EtOH (145-250°); (2) CHMe:CH<sub>2</sub>+H<sub>2</sub>O  $\Longrightarrow$  CHMe<sub>2</sub>·OH (175-250°); (3) [:CHMe]<sub>2</sub> or CHEt:CH<sub>2</sub>+H<sub>2</sub>O  $\rightleftharpoons$ CHMeEt·OH (150-250°); (4) CMe<sub>2</sub>:CH<sub>2</sub>+H<sub>2</sub>O  $\rightleftharpoons$ CMe<sub>3</sub>·OH (150° and 175°). In every case, the vals. of  $K_p [=p_{\text{alcohol}}/(p_{\text{olefine}} \times p_{\text{H},0})]$  diminish with rising temp. The heat of hydration of C<sub>2</sub>H<sub>4</sub> is calc. as +9600 g.-cal. per mol. At a given temp. the equilibrium is most favourable for alcohol production in the case of C<sub>2</sub>H<sub>4</sub> and least favourable in the case of the *n*-butylenes, whilst C<sub>3</sub>H<sub>6</sub> and *iso*butylene occupy an intermediate position.

Calculation of the equilibria in keto-enol tautomerism. G. W. WHELAND (J. Chem. Physics, 1934, 2, 482).—A correction (cf. this vol., 28).

M. S. B.

Acid-base function in non-aqueous solvents. I. Colorimetric investigations in m-cresol. J.N. BRÖNSTED, A. DELBANCO, and A. TOVBORG-JENSEN (Z. physikal. Chem., 1934, 169, 361-378).-From measurements of extinction spectra of solutions of indicators in *m*-cresol (I) and extinction of mixed solutions of indicators and protolytic buffers the scale of strength consts. of electroneutral and cation acids in (I) has been determined. The graph of the rational acid const. in (I) against the conventional acid const. in H<sub>2</sub>O consists of two parallel straight lines, one corresponding with neutral carboxylic acids of the AcOH type, the other with cation acids of the NH<sub>3</sub>Ph type, such that if a simple positive acid and an electroneutral acid are equally strong in H<sub>2</sub>O, the former is > 1000 times as strong as the latter in (I). This ratio agrees qualitatively with theory (this vol., 962). Piperidine and certain aliphatic amines are more or less completely protolysed in dil. (I) solution. Judged by these results (I) is a much more strongly acid medium than  $H_2O$  and the alcohols. R. C.

Dissociation constants of boric acid from 10° to 50°. B. B. OWEN (J. Amer. Chem. Soc., 1934, 56, 1695-1697).-The first dissociation const. of H<sub>3</sub>BO<sub>3</sub> and the corresponding heat of dissociation have been determined at 10-50°. At 25°,  $K=5.80\times10^{-10}$  and  $\Delta H = 3360$  g.-cal. E.S.H.

Thermodynamics of aqueous barium chloride solutions from electromotive force measure-E. A. TIPPETTS and R. F. NEWTON (J. ments. Amer. Chem. Soc., 1934, 56, 1675—1680).—E.m.f. measurements of cells of the type Ba (two-phase amalgam)|BaCl<sub>2</sub>(m)|Hg<sub>2</sub>Cl<sub>2</sub>|Hg have been made at 0°, 15°, 25°, 35°, and 45°, and the activity coeffs. relative partial mol. heat contents, and heat capacities of BaCl<sub>2</sub> in aq. solution calc. therefrom. E. S. H.

Iodine cations. W. A. NOYES (J. Amer. Chem. Soc., 1934, 56, 1819).-Evidence for the existence of I+ in aq. solution is adduced. E. S. H.

Activity of sodium and potassium dissolved in gallium. E. S. GILFILLAN, jun., and H. E. BENT (J. Amer. Chem. Soc., 1934, 56, 1661-1663).-The solubility of Na in Ga at 30° is about 0.001 wt.-%; the activity of Na corresponds with an e.m.f. of 0.70 volt. The solubility of K in Ga at 32° is about  $4 \times 10^{-6}$  wt.-%; the activity corresponds with an e.m.f. of 0.76 volt. E. S. H.

Physico-chemical studies of complex acids. XII. Precipitation of the normal and complex tungstates and molybdates of the alkaline earths and of silver. H. T. S. BRITTON and W. L. GERMAN (J.C.S., 1934, 1156-1160).-The reaction between the hydroxides of Ca, Sr, and Ba and aq. NaWO3 containing HCl has been studied conductometrically and electrometrically, and the ppts. formed at different stages have been analysed. Normal tungstates are formed in presence of excess of tungstic acid. The action of normal, para-, and meta-tungstates and -molybdates on BaCl, and AgNO3 has also been examined. The solubility products of  $Ag_2WO_4$  and  $Ag_2MOO_4$  have been determined. In general ppts. obtained with the para- and meta-salts vary in composition with the amount of precipitant employed, and there seems no evidence for the existence of complex M. S. B. para- and meta-salts.

Symbols in the phase rule and in electrochemistry. E. LANGE (Z. Elektrochem., 1934, 40, 655-661).-- A system of nomenclature is developed to represent phase conditions and equilibria.

H. J. E.

System mercuric chloride-potassium chloride-ethyl alcohol. M. PERNOT (Compt. rend., 1934, 199, 478-480).-KCl and HgCl<sub>2</sub> in 95% or 100% EtOHat 34° afford the compound, 5HCl,6HgCl2,2EtOH, which when exposed to air yields the substance, H. W. 5KCl,6HgCl<sub>2</sub>,4H<sub>2</sub>O.

Systematic relationships. LXI. Osmium sulphides. R. JUZA (Z. anorg. Chem., 1934, 219, 129-140).-The reversible decomp. of  $OsS_2$  has been studied tensimetrically. No stable lower sulphide exists and Os and OsS2 are only very slightly sol. in one another. The g.-mol. heat of formation from Os and

S, vapour is 62 kg.-cal. at 1020°. On heating the amorphous pptd. OsS<sub>2</sub> in vac. it glows at 560-570° and crystallisation suddenly takes place. Oxysulphides are produced by the action of H<sub>o</sub>S on OsO, solutions. M. S. B.

Heat of dilution of heavy water. E. DOEHLE-MANN, E. LANGE, and H. VOLL (Naturwiss., 1934, 22, 526).—The heat of dilution of H<sub>2</sub>O containing varying amounts of H<sup>1</sup>H<sup>2</sup>O has been measured by means of a differential calorimeter. The concess. were deter-mined by a refractometer. The strong intermol. forces of H<sub>2</sub>O are shown in the negative vals. of the heat of dilution. The heat of dilution is approx.  $\infty$ the initial concn. of H<sup>1</sup>H<sup>2</sup>O. A. J. M.

Determination of gradation of polarity of amino-nitrogen in organic compounds. D. RADULESCU and O. JULA (Z. physikal. Chem., 1934, B, 26, 390-394; cf. A., 1930, 1087).—The heat of neutralisation, U, of several org. bases with three anhyd. org. acids and two aq. mineral acids has been determined. For each acid the bases fall into approx. the same order in respect of the gradation of U, which is taken to be the order of polarities. Sp. heats of the acids and bases are recorded. R. C.

Heats of combustion and of formation of the normal paraffin hydrocarbons in the gaseous state, and the energies of their atomic linkings. F. D. ROSSINI (J. Res. Nat. Bur. Stand., 1934, 13, 21-35).—From vals. obtained for the heats of combustion (I) of simple *n*-paraffins (A., 1931, 433, 1236; this vol., 966) the (I) of all other *n*-paraffins in the gaseous state are deduced. When the no. of C atoms (n) is >5, at 25° and 1 atm. (I)= $60\cdot40+n(157\cdot00\pm 0\cdot08)$  kg.-cal. per mol. In any org. mol. containing a *n*-alkyl group (n > 5), the addition of CH<sub>2</sub> increases (I) by  $157\cdot00\pm0\cdot08$  kg.-cal. per mol. The heats of formation of all the n-paraffins in the gaseous state at 25° C. and 0° abs. from  $H_2$ ,  $\beta$ -graphite, and diamond, respectively, have been calc. The energy of dissociation of gaseous n-paraffins into gaseous C and H at  $0^{\circ}$  abs. is a linear function of n, when n is > 6. The energy evolved in the reaction C (gas) +2H (gas)+  $C_nH_{2n+2}$  (gas)= $C_{n+1}H_{2n+4}$  (gas) at 0° abs., when n is > 5, is  $(20.8\pm0.9)+D_{c0}$  kg.-cal. per mol., where  $D_{\rm co}$  is the energy of dissociation of CO at 0° C.

E. S. H. Hydration of normal Mg", Ca", Sr", and Ba" solutions. J. BABOROVSKY and O. VIKTORIN (Chem. Listy, 1934, 28, 188-191).-Measurements of the transport nos. of N-chloride solutions indicate Mg 20, Ca" 16-17, Sr" 16, and Ba" 11H<sub>2</sub>O. R. T.

Conductivity of methoxides and ethoxides. G. E. M. JONES and O. L. HUGHES (J.C.S., 1934, 1197-1207).—The electrical conductivity of the methoxides and ethoxides of Li, Na, and K has been determined in MeOH and EtOH at 25°; in order to ascertain the effect of impurities, the conductivity of the Me and Et carbonates of Li, Na, and K, and of CO<sub>2</sub> and NH<sub>3</sub> in both alcohols, and finally of Ca(OMe)<sub>2</sub> in MeOH has also been measured. The following mobilities are recorded : OMe' 53.3; OEt' 24.5; MeCO3' 45.4; EtCO3' 20.7. The dissociation consts. of CO2 and NH3 in MeOH are  $2 \times 10^{-10}$  and  $2 \times 10^{-6}$  and in EtOH

 $6 \times 10^{-12}$  and  $1.5 \times 10^{-7}$ , respectively. A method for the correction of the conductivity data for bases on account of the presence of CO<sub>2</sub> is worked out.

M. S. B.

Velocity of establishment of potential. J. J. BIKERMAN (Compt. rend., 1934, 199, 453-455).--Assuming that the effects of applying a potential between two electrodes immersed in an electrolyte are (a) displacement of charges within the mols., (b) orientation of the mols., and (c) accumulation of anions and dissipation of cations at the anode, and vice versa at the cathode, it is concluded that the e.m.f. should show a dispersion at frequencies of 10<sup>7</sup> to 10<sup>8</sup> per sec. The anomalies observed in electrode capacities under a.c. cannot be due, therefore, to the slowness of the formation of the double layer, but are more probably due to alteration in the dielectric const. and viscosity of the solvent in the electrolyte-electrode interface or to J. W. S. secondary causes.

Potentials of bismuth oxides and the alkaline bismuth cell. E. BAUR and W. LATTMANN (Z. Elektrochem., 1934, 40, 582—585).—Measurements of potential of the electrode  $Bi|Bi_2O_3,N$ -NaOH in presence of oxidising agents reveal the existence of  $B_2O_4$ and  $B_4O_7$ . The cell  $Bi|Bi_2O_3,N$ -NaOH, $Bi_2O_4|Ni$  has e.m.f. 1.035 volts. E. S. H.

Periodic changes of potential of iron in chromicsulphuric acid solutions. II. M. KARSCHULIN (Z. Elektrochem., 1934, 40, 559—564; cf. this vol., 601).—Addition of HCl, NaCl, CuSO<sub>4</sub>,  $K_2SO_4$ , or KNO<sub>3</sub> reduces the frequency and amplitude of the periods and causes the Fe to become more active. When the system is in a steady state, the potential of Fe being positive to the calomel electrode, periods are induced by adding the above salts or by cathodic polarisation. During such "positive " periods the Fe is covered with a black, magnetic oxide. E. S. H.

Reduction of permanganate in buffered solution: potentiometric titration with hydrogen peroxide. W. PUGH (J.C.S., 1934, 1150—1151).— Using silicofluorides as buffers the potentiometric titration of  $KMnO_4$  with  $H_2O_2$  can be carried out completely to the Mn<sup>\*\*</sup> stage in neutral solution. Typical titration curves indicating definite stages in the reduction are given. M. S. B.

Reversibility in the oxidation of certain derivatives of carbohydrates, especially ascorbic acid. R. WURMSER and J. A. DE LOUREIRO (J. Chim. phys., 1934, 31, 419-432; cf. this vol., 367).-An oxidationreduction system, with a potential in the neighbourhood of the reduction potential of indophenols, is present in cellular tissue. For a similar system in reduced carbohydrates the name "redoxine" is proposed. The substance has not been isolated, but its potential in neutral and acid media has been determined. The ultra-violet absorption spectrum has a band at 2780 Å. in a solution of  $p_{\rm H}$  7 and at 2650 Å. in  $p_{\rm H}$  1. The structure of ascorbic acid is discussed and the potential in acid, neutral, and alkaline solution has been determined. The instability of the oxidised form increases considerably with increase of  $p_{\rm H}$ . Reductone also forms a reversible oxidation-reduction system. M. S. B.

Influence of polarisation on photo-voltaic effects. (MLLE.) M. THEODORESCO (J. Chim. phys., 1934, 31, 433-438).-The variations of photosensitivity observed on polarising Cu electrodes covered with CuO, Cu<sub>2</sub>O, or a mixture of the two, in solutions of different electrolytes, have been studied. The effect is reversible, and after suppression of the polarising current the electrode returns gradually to the initial condition. Stirring has no influence. The polarisation e.m.f. corresponding with the max. effect depends on the concn. of electrolyte in the same way as the electrolytic decomp. potential. Inversion of the photovoltaic behaviour of Cu<sub>2</sub>O occurs after a sufficiently positive polarisation. The formation of a deposit of Cu on the Cu<sub>2</sub>O plate has been observed after negative polarisation. The results are discussed in relation to Audubert's theory of the photovoltaic M. S. B. effect.

Theory of passivity. XXIV. Film passivity and chemical passivity [caused] by anodic treatment of iron in sulphuric acid. W.J. MULLER and E. Löw. XXV. Chemical passivity and its electronic interpretation. W. J. MULLER (Z. Elektrochem., 1934, 40, 570-577, 578-582; cf. this vol., 602).—XXIV. An Fe anode goes into solution in  $H_2SO_4$  at 0.7 volt as Fe<sup>•</sup>, at 0.8—1.4 volts as Fe<sup>•</sup>, whilst at 1.4 volts  $O_2$  is discharged. At < 0.5 volt a white, non-birefringent film, probably of basic salt, forms on the anode, whilst at higher potentials a transparent oxide film forms. The time required for the film transformation varies with initial c.d. in an analogous way to the time required for formation of the primary film. There is a small time interval between the formation of the oxide film and the evolution of  $O_2$ .

O<sub>2</sub>. XXV. An explanation of the difference between the author's concepts of film passivity (in which the metal goes into solution at its lower valency) and chemical passivity (in which the ions entering the solution have a higher valency). E. S. H.

Passage of current in an electrolyte without electrolysis. V. KARPEN (Compt. rend., 1934, 199, 480-483).—The e.m.f. of polarisation for different permanent currents passing between Pt electrodes in a solution of KI (50 g.) and I (30 g.) in H<sub>2</sub>O (1000 c.c.) has been measured. For a given e.m.f. of polarisation the currents passing are incomparably > in the absence of I. The atoms of I in contact with the cathode receive an electron, and the resultant ions pass to the anode, where they become atoms with resulting increase of [I]. The view that the movement of I from cathode to anode is due to diffusion is supported by the observed effect of the relative positions of anode and cathode and of the temp. H. W.

Crystal structure and conductivity of silver mercuric iodide. J. A. A. KETELAAR (Chem. Weekblad, 1934, 31, 442-445; cf. this vol., 1056). H. F. G.

Change of velocity of an explosion wave with pressure. A. SOKOLIK and K. SCHTSCHELKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 102–105). —In a  $2H_2+O_2$  mixture the velocity of explosion, measured photographically, changes from 2630 to 2830 m. per sec. with a pressure change from 200 to 760 mm.; for  $CH_4+2O_2$  from 2040 to 2350 m. per sec. for a pressure change of 80 to 760 mm. In a  $H_2+Cl_2$  mixture the velocity was const. at 1730—1740 m. per sec. at 200—760 mm. The change with pressure is attributed to dissociation in the wave front. H. J. E.

Kinetics of the thermal decomposition of acetaldehyde vapour. M. LETORT (Compt. rend., 1934, 199, 351–353).—The true order of the reaction  $MeCHO = CH_4 + CO$  is 1.5. The val. 2, usually given, is obtained when the walls of the quartz containing vessel have become poisoned. A. J. M.

Flame temperatures in methane-air mixtures. W. T. DAVID and J. JORDAN (Phil. Mag., 1934, [vii], 18, 228—236; cf. A., 1932, 25; this vol., 258).—The temp. obtained by the Na-line reversal method (A., 1932, 127) are much > those from a Pt-Rh resistance thermometer, probably owing to the Na atoms being raised to a temp. > that corresponding with the mean mol. translational energy of the flame gases. The temp. obtained by the latter method show a max. at about 9.4%  $CH_4$ , but, as with CO, they are 250—300° < the calc. temp., indicating a latent energy of about 15% of the heat of combustion. J. W. S.

Kinetics of the reduction of hydrogen peroxide by the halides. A. MOHAMMAD and H. A. LIEB-HAFSKY (J. Amer. Chem. Soc., 1934, 56, 1680—1685).  $-H_2O_2$  is reduced by Cl' or Br' according to the rate law  $-d[H_2O_2]/dt = k_1^{\circ}[H_2O_2][X'] + k_1[H_2O_2][X'][H^*]$ , which is known also to hold for reduction with I. The effects of  $k_1^{\circ}$  and  $k_1$  on temp. variation have been determined. The mechanism is discussed.

E. S. H.

**Reactivity of thiol group. III.** N. HELLSTRÖM (Z. physikal. Chem., 1934, 169, 416—424; cf. A., 1933, 259).—The rate of reaction of  $Zn(S \cdot CH_2 \cdot CO_2Na)_2$ (I) with  $CH_2I \cdot CO_2Na$  (II) and  $CH_2Br \cdot CO_2Na$  (III), and of  $Hg(S \cdot CH_2 \cdot CO_2Na)_2$  with (II) in aq. solution at 25° has been measured. Thiodiglycollic acid is formed, and the reduction-oxidation reaction which occurs in the action of  $CH_2I \cdot CO_2H$  or (II) on the SH group of  $SH \cdot CH_2 \cdot CO_2H$  (IV) is absent. The velocity coeffs. for the reaction of (II) with the Hg SH linking, the SH group, and the SH ion of (IV) are approx. in the ratio 1.5:1:10,000, whilst for the Zn compound the ratio is 150:1:10,000. R. C.

Kinetics of hæmoglobin. IV. General methods and theoretical basis for the reactions with carbon monoxide. V. Combination of carbon monoxide with reduced hæmoglobin. VI. Competition of carbon monoxide and oxygen for hæmoglobin. VII. Reactivity of freshly reduced hæmoglobin. F. J. W. ROUGHTON (Proc. Roy. Soc., 1934, B, 115, 451-464, 464-473, 473-495, 495-503).—IV. The Hartridge-Roughton rapid reaction technique is extended to the study of (a) the combination of CO with reduced sheep hæmoglobin (Hb), (b) the displacement of  $O_2$  by CO from combination with Hb, and (c) the displacement of CO by  $O_2$  from combination with Hb. The velocity equations deduced for reaction (a) from the Hüfner theory (I) and Adair's intermediate compound theory (II) (A., 1925, i, 851) are identical, but differ from that based on Hill's equation (III). When  $\leq$  three of the four available groups of Hb are already occupied by O<sub>2</sub> or CO, theory (II) leads to the velocity equation  $d[\text{COHb}]/dt = m'[\text{CO}][O_2\text{Hb}]/[O_2] - m[\text{COHb}]$  for reactions (b) and (c).

V. The velocity of reaction (a) is approx. 0.1 of that of the O<sub>2</sub>-Hb reaction under similar conditions, and this observation is utilised in a more accurate method especially applicable to dil. solutions. Even beyond the early stages of the reaction d[COHb]/dt =l[CO][Hb] is obeyed, and the effects of varying the concess. of reactants are inconsistent with (III). The velocity at  $p_{\text{H}}$  10 is 50% > at  $p_{\text{H}}$  5.6—7.2, and the temp. coeff. is 1.8 (approx.) in the range 7.2—33.3°. Light displaces the equilibrium CO+Hb == COHb to the left, but does not accelerate the forward reaction.

VI. The trustworthiness of the methods used in this and earlier work is confirmed and the absence of significant photochemical "after-effects" in the "light method" is demonstrated. In the  $p_{\mu}$  range 5.6-10.0, the data for reaction (b) accord with the equation  $d[\text{COHb}]/dt = m'[\text{CO}][O_2\text{Hb}]/[O_2]$  over a twenty-fold range of concn. (< 0.6 millimol. per litre), and m' increases only slightly with decrease of  $p_{\mu}$ . The data for reaction (c) conform to the equation -d[COHb]/dt = m[COHb] at high  $[O_2]$ . Change of  $p_{\rm H}$  has little effect on m, but the temp. coeff. is 4 (approx.) per 10°. The unexpectedly small variations of m' and m with change of  $p_{\mu}$  are discussed, especially with reference to the view that in the exchange of O, for CO, three of the four available linkings of Hb are already saturated with gas mols., and the possibility that Hb and its compounds when freshly formed have different reactivities from the "old" mols. The kinetic data are inconsistent with (III), and since theory (I) is not in accord with dissociation curve data, theory (II) is adopted as the best working hypothesis.

VII. The rate of combination at  $p_{\rm H}$  10 and 15° of CO with Hb freshly reduced from O<sub>2</sub>Hb by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is twice as great as with Hb > 2 sec. old. The difference disappears at 33° and at  $p_{\rm H}$  6.6 (room temp.). The O<sub>2</sub>-Hb reaction does not show a similar phenomenon. The dissociation, by dilution, of 90% O<sub>2</sub>Hb at  $p_{\rm H}$  6.3 leads to an equilibrium established 0.5-0.7 sec. after mixing with 45% O<sub>2</sub>Hb followed by a slowly established equilibrium with 20% O<sub>2</sub>Hb. This was not due to inactivation of the Hb. At  $p_{\rm H}$  10 the equilibrium val. does not fall below the initial val. of 50-60% O<sub>2</sub>Hb. These results are consistent with the above anomalies (Part VI).

J. G. A. G.

Change of reactivity and dissolution velocity of sulphur at the transition temperature. J. A. HEDVALL, A. FLOBERG, and P. G. PALSSON (Z. physikal. Chem., 1934, 169, 75—80; cf. A., 1931, 582).—The reactivity and rate of dissolution in AcOH of S are much greater during the transition rhombicmonoclinic than at temp. either below or immediately above the transition temp. R. C.

Active oxides. LXXVI. Kinetics of thermal decomposition of magnesite and the chemical

compounds intermediately formed. G. F. HUT-TIG, W. NESTLER, and O. HNEVKOVSKY (Ber., 1934, 67, [B], 1378-1387).-Study of the rate of decomp. of MgCO<sub>3</sub> in vac. when used in powder form, as a film obtained by spreading a paste of MgCO<sub>3</sub>-MeOH (or EtOH) on glass and subsequently heating, or mixed with a metallic powder of high thermal conductivity, shows that the true rate of decomp. (dissociated from factors such as thermal conductivity and diffusion of gas) is best measured under the conditions last named, provided so much powder is used that the particles of it are in contact with one another throughout the mass. At 530° equal weights of MgCO<sub>3</sub> are decomposed in equal intervals of time, and the change cannot be represented as of the 2/3 order. At 510° breaks in the decomp. isotherm occur corresponding with the compounds 4MgCO<sub>3</sub>,3MgO, (?)  $2MgCO_{3,}3MgO$ , and  $MgCO_{3,}3MgO$ . At  $520^{\circ}$  the existence of the substance  $MgCO_{3,}2MgO$  is indicated. At 490°, decomp. is slow, but the characteristics of the 510° isotherm are probably emphasised. H. W.

Topochemical processes in materials. H. STAGER (Kolloid-Z., 1934, 68, 137—146).—A discussion including examples of the corrosion of metals. E. S. H.

Topochemical aspect of the corrosion of metals. U. R. EVANS (Kolloid-Z., 1934, 68, 133-137).—A review. E. S. H.

Transmission of detonations in a vacuum. A. BELIAEV and J. B. CHARITON (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 166—167).—The initiating crystal of PbN<sub>6</sub> (wt. 1—2 mg.) was placed over a small hole in a metal disc (I) 1 mm. thick at the centre of a glass bulb. The initiated crystal was placed below (I) on a mica slip. In air at normal pressure the detonation was transmitted approx. 1.5 cm. In vac. the lower crystal of PbN<sub>6</sub> could be detonated when at 40—45 cm. from (I), the energy reaching its surface being approx. 500 ergs per sq. cm. H. J. E.

Application of the laws of chemical kinetics to secondary processes of electrolysis. S. A. PLETE-NEV and V. N. Rosov (Z. Elektrochem., 1934, 40, 600-604).—The velocity of dissolution of Cu in aq. CuCl<sub>2</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and the velocity of anodic oxidation of FeSO<sub>4</sub> have been measured. The results are discussed in relation to the kinetic laws. E. S. H.

Hydrolysis of starch by acid. A. P. SCHULZ and W. HÖNSCH (Chem.-Ztg., 1934, 58, 640—642, 671).— Results are given of 4 hydrolyses with HCl of 2 different concns. and at 2 different temp. The products were analysed in terms of amyloses (I), glucose (II), and maltose (III), and the results, represented according to both rectangular (IV) and triangular co-ordinates, are compared especially with those of Rolfe and Defren (A., 1898, i, 7). All the curves (IV) show a marked max. in the (III) content. Under approx. technical conditions, formation of (III) is more rapid than its decomp. The intersection points of the (I) and (II) curves give measures of the hydrolysis and show that at 100° the velocity of reaction approx.  $\infty$  the acid concn., whilst at higher temp. (pressure boiling) the increased effect is  $< \infty$  the increase in acid concn. T. H. P.

Rate of reaction between organo-magnesium halides and esters. G. VAVON, M. BARBIER, and G. THIEBAUT (Bull. Soc. chim., 1934, [v], 1, 806-814). -The benzoates of the following are described: CHPra, OH, b.p. 146-147°/14 mm., CHPra, OH, b.p. 141-142°/15 mm., methylpscudobutylcarbinol, b.p. 125°/12 mm., neomenthol, b.p. 181°/16 mm. The rate of reaction, x, of ROBz (R=Et, Bu) with MgEtBr > MgPr<sup>g</sup>Br > MgBuBr > MgPhBr, and MgBuCl>MgBuBr>MgBuI. With MgR'Br, the val. of x when R is a primary grouping > sec. > tert. and  $\operatorname{CHPr}_{2^{\alpha}} > \operatorname{CHPr}_{2^{\alpha}}, \quad \operatorname{CHMeBu} > \operatorname{CHMe}_{\psi} - \operatorname{Bu},$ and menthyl>neomenthyl, thus demonstrating the effects of the structure of R. The vals. of x for Et esters increase with the strength of the acid; thus, with substituted EtOBz, o-Cl>o-Br>o-I and o-MeO (I)> m > p, and a steric factor is involved, since the x for Et valerate>Et pivalate, EtOBz>o-C<sub>6</sub>H<sub>4</sub>Me·CO<sub>2</sub>Et  $>s-C_6H_2Me_3\cdot CO_2Et$ , and  $\beta->\alpha$ -naphthoate. The exceptionally high val. of x for (I) is attributed to a complex Mg oxonium compound being formed with the O of the OMe. J. G. A. G.

Solubility of cadmium in some organic acids. P. FORTNER and H. LUKAS (Pharm. Zentr., 1934, 75, 557-562).—The rates of dissolution of Cd (I) in 0·1N-lactic, -succinic, -tartaric, -citric, and -oxalic acids have been determined at room temp., 35°, and 60°. Dissolution is approx. four times as rapid in Pt as in glass, owing to electrolytic action. The solubility of (I) in wine is > that calc. from the acidity. The following new normal salts are described, the solubilities % at 40° being given in parentheses: lactate (10·11), succinate (0·367), tartrate (0·100), citrate (0·23), oxalate (0·009).

Inter-relations of hydrogen and deuterium molecules. A. J. GOULD, W. BLEAKNEY, and H. S. TAYLOR (J. Chem. Physics, 1934, 2, 362—373).— $H_2O$ in a Pyrex or soft-glass vessel does not affect the concn. of  $H_2$ - $H_2^*$  mixtures. No effect is produced by stop-cock grease. Diffusion through Pd without circulation produces very little change, but diffusion with circulation results in a residual mixture containing  $H_2^1$ ,  $H^1H^2$ , and  $H_2^2$  in approx. equilibrium proportions, indicating that the diffusion process is at. Desorption from charcoal at liquid air temp. is a mol. process, and there is no reaction between H and H<sup>2</sup>. Hg and glass at room temp. also produce no reaction.  $Cr_2O_3$ and a Ni-kieselguhr surface promote reaction between -190° and 110° and a Pd surface at 270°. Any surface promoting the reaction between H<sup>1</sup><sub>2</sub> and H<sup>2</sup><sub>2</sub> will also promote the ortho-para conversion of  $H_2$ , but the converse is not true. The vals. of the equilibrium const.  $[H^{1}H^{2}]^{2}/[H^{1}_{2}][H^{2}_{2}]$  between  $-190^{\circ}$  and  $270^{\circ}$  are in good agreement with those calc. from statistical mechanics. The calc. val. at 270° is 3.67.

M. S. B.

Explosion of mixtures of combustible gases with air by nuclear drops of water and other nuclei and by X-rays. I. Explosion of gaseous combustible mixtures passing through vitreous and steel combustion tubes, by nuclear drops of water. II. Explosion of hydrogen-air mixtures by X-rays. R. O. KING. III. Explosion of hydrogen-air mixtures by stone dust. IV. Explosion by nuclear drops of water of ethylene-air mixtures passing through a nickel-steel com-bustion tube. R. O. KING and G. MOLE (J. Inst. Petroleum Tech., 1934, 20, 791-805, 806-812, 812-815, 816-820).-I. H<sub>2</sub>O droplets were injected axially down a rising column of gas in a heated vertical tube 1.25 in. diam. The ignition and explosion of the central stream of H2-air mixture by H2O droplets ["nuclear" ignition (I)] occur at temp.  $> 585^{\circ}$ , and hence the length of tube heated by the furnace (6 in.) and the rate of gas flow (F=100 c.c. per min.) were so chosen that the boundary layer did not ignite [" self. ignition " (II)] at lower temp. and that flameless surface combustion was, relatively, not so rapid as to deplete the central core of gas sufficiently to make it non-inflammable. In Pyrex tubes, the nuclear ignition temp.,  $T_N$ , coincided with that of (II),  $T_S$ , with mixtures containing 12-50% H<sub>2</sub>, but with richer mixtures  $T_N$  was  $< T_S$  and such explosions were feeble and localised. With a new Cr-Ni-steel tube (II) was limited to 18-45% H<sub>2</sub>-air mixtures at  $< 700^{\circ}$  and 50 c.c. per min., but H<sub>2</sub>O injected into richer mixtures produced (I). Ageing of the tube catalysed surface combustion and the central column of gas became too impoverished to explode. The effect was diminished by increasing F, and  $T_N$  was then  $< T_S$ . (I) is due to H<sub>2</sub>O droplets and not steam passing through the gas phase. The process is physical, since injected refractory particles lowered the ignition temp., T.

II. X-Rays lowered the T of air-H<sub>2</sub> rich mixtures in new Pyrex tubes to vals.  $< T_S$ , but the effect disappeared when the tube had been exposed to O<sub>2</sub>-rich mixtures. The lowering by X-rays is attributed to increased electrification of the layers of gas moving slowly over the surface, and this effect is counterbalanced by rapid steam formation when the surface becomes oxidised. X-Rays produced no significant effects when the Fe tube was used, since surface oxidation-reduction equilibria were rapidly established.

III. Dust (chieffy  $Al_2O_3$ ) depressed  $T > did H_2O$ droplets, but  $T_N$ ,  $T_S$ , and the dust T decreased and converged as F was increased. The phenomenon is contrasted with the action of dust in inhibiting explosions in coal mines.

IV. The effect of the surface of the Fe tube on the 5-10% C<sub>2</sub>H<sub>4</sub>-air mixture was < and more reproducible than with H<sub>2</sub>-air mixtures. At 50 c.c. per min. (II) was not observed, but H<sub>2</sub>O injections produced (I) with > 6% C<sub>2</sub>H<sub>4</sub>.  $T_N$  decreased linearly with increase of [C<sub>2</sub>H<sub>4</sub>]. With F > 100 c.c. per min., (II) was observed, and as F was further increased  $T_S$  decreased to the approx. const. vals. of  $T_N$ . The results are interpreted in terms of the fog produced during hydrocarbon oxidations providing a sufficient concn. of nuclei to cause explosion. J. G. A. G.

Acid-base reactions involving deuterium. W. F. K. WYNNE-JONES (J. Chem. Physics, 1934, 2, 381-385).—Measurements have been made of the rate of neutralisation of the  $\psi$ -acid nitroethane in H<sub>2</sub>O. The results indicate that the rates of ionisation of H<sup>1</sup> and H<sup>2</sup> are as 10:1. The importance of this in the catalysis of sucrose inversion by acids and bases in H<sup>2</sup><sub>2</sub>O is discussed. The effect of H<sup>2</sup><sub>2</sub>O on the acid catalysis of the mutarotation of  $\alpha$ -glucose has been studied, and the results show that the catalytic activity of  $H_2O$  is 3.8 times that of  $H_2^2O$ , whilst the activity of  $(OH_5^4)$  is only 1.33 times that of  $(OH_5^4)$ . The mechanism of the reaction is discussed. It is suggested that the exchange of  $H^2$  and  $H^4$  atoms in a homogeneous phase at room temp. is essentially an acid-base-catalysed reaction, and is probably most readily brought about by adding acid and alkali alternately. M. S. B.

Catalytic activity of deuterium ion  $(H_3^*O^{\circ})$ . E. A. MOELWYN-HUGHES (Z. physikal. Chem., 1934, B, 26, 272–280; cf. this vol., 607).—The ratio of the catalytic coeff. of  $H_3^*O^{\circ}$  for the mutarotation of glucose in  $H_2^*O$  to the catalytic coeff. of  $H_3O^{\circ}$  for the mutarotation in  $H_2O$  is < 1 and rises with the temp., T, whilst the corresponding ratio for the inversion of sucrose is > 1 and falls with rising T. Arrhenius' equation is valid for the mutarotation, the energy of activation for  $H_3^*O^{\circ}$  being > for  $H_3O^{\circ}$  by 1250 g.-cal.; both vals. agree with the theoretical vals. To explain the greater activity of  $H_3^*O^{\circ}$  compared with that of  $H_3O^{\circ}$  in the sucrose inversion it is suggested that the intermediate sugar-catalyst complex is more stable. R. C.

Iodide ion catalysis of hydrogen peroxide in heavy water. E. ABEL, O. REDLICH, and W. STRICKS (Naturwiss., 1934, 22, 525).—The catalytic decomp. of  $H_2O_2$  in a solution containing  $H_2O$  by KI was investigated by an interferometric method. For a solution containing 60 mol.-% H<sub>2</sub>O there is a decrease in the velocity coeff. of 20% compared with the val. for pure  $H_2O$ . Similarly the velocity coeff. of the reaction between  $H_2O_2$  and HI is decreased when  $H_2^*O$  is used. A. J. M.

Action of inhibitors on the decomposition of hydrogen peroxide. D. RICHTER (J.C.S., 1934, 1219—1224).—The inhibition by 18 substances (I) of the photochemical decomp. of 0.1M-H<sub>2</sub>O<sub>2</sub> at  $p_{\rm H}$  6.8 by light of  $\lambda$  300 m $\mu$  did not, in general, increase in direct proportion to the concn. of inhibitor. 33—38 mols. of H<sub>2</sub>O<sub>2</sub> were decomposed per quantum absorbed in the presence of 5—10×10<sup>-4</sup>M-CH<sub>2</sub>Ph·OH, -resorcinol, and -PhOH. (I) have only small inhibiting effects on the decomp. of H<sub>2</sub>O<sub>2</sub> catalysed by liver catalase, yeast catalase, and hæmatin, and it is therefore inferred that the enzymic decomp. does not involve reaction chains of the type occurring in the photochemical decomp. J. G. A. G.

Catalysed decomposition of nitroamide. V. Catalysis in m-cresol. J. N. BRONSTED, A. L. NICHOLSON, and A. DELBANCO (Z. physikal. Chem., 1934, 169, 379-387; cf. A., 1933, 471).-The decomp. in protolytic buffers in m-cresol solution at 20° proceeds in accordance with the protolytic theory of acidic and basic catalysis. With electroneutral bases (I) the velocity is not affected by addition of acid, but with anion bases (II) the velocity coeff. falls with increasing acid concn. The graph of the logarithm of the mol. catalysis const., k, against the logarithm of the protolytic strength const., K, of the base in m-cresol consists of two straight lines, one corresponding with (I), the other with (II), and the equations connecting k and K are exactly similar to those for the decomp. in aq. and C<sub>5</sub>H<sub>11</sub>.OH solutions. The catalysis is determined, not by the hypothetical "internal basicity" of the catalyst, but by the practical scale of basicity corresponding with the medium. R. C.

Temperature coefficient of the sucrose inversion. E. A. MOELWYN-HUGHES (Z. physikal. Chem., 1934, B, 26, 281-287) .- The unimol. law is valid for the acid-catalysed inversion only within certain limits of temp. and acid concn. At higher temp. there are deviations indicating that there is a further reaction, which becomes increasingly evident as the temp., T, rises. The nature of this reaction is unknown. The apparent heat of activation calc. by Arrhenius' equation falls as T rises, and it is suggested that corresponding with the possibility of several simultaneous reactions the sucrose mol. has several heats of activation (cf. A., 1933, 910). At higher temp. sucrose reacts with pure H<sub>2</sub>O giving org. acids and unidentified products. R. C.

Oxidation of thiol compounds by hydrogen peroxide at room temperatures in presence of inorganic catalysts. I. Oxidation of cystine and dithioglycollic acid in presence of molybdic acid and tungstic acid sols. J. C. GHOSH and B. C. KAR (J. Indian Chem. Soc., 1934, 11, 485-497).-These sols exert a strong catalytic action particularly in presence of small concus, of Cu<sup>II</sup>, Fe<sup>II</sup>, Cr<sup>III</sup>, or Ce<sup>III</sup> sulphates or MnCl<sub>2</sub>. KCN has no effect; this shows that catalysis is not due to traces of Fe salts etc. The reaction follows a unimol. law in any single experiment, but the velocity coeff. (I) increases with the initial concn. of  $H_2O_2$ ; the temp. coeff. of (I) is 2-2.3 per 10°. With molybdic acid, (I) increases with  $p_{\rm H}$ ; with tungstic acid it has a max. at low  $p_{\rm H}$  $(p_{\rm H} 1.13$  for cystine, 1.62 for dithioglycollic acid), a min. at 2.5, and then rises again. Beyond  $p_{\rm H}$  5, spontaneous decomp. of the H<sub>2</sub>O<sub>2</sub> prevented measurements. (I) also increases with the concn. of the sol, the deviation from direct proportionality being ascribed to the change in the surface/mass ratio with the larger particles in the conc. sols. D. R. D.

Action similar to that of oxidase with metallic complex salts. X. Y. SHIBATA and K. YAMASAKI (Bull. Chem. Soc. Japan, 1934, 9, 273—283).—The  $O_2$  uptake of p-OH·C<sub>6</sub>H<sub>4</sub>·NHMe sulphate (I) in slightly alkaline solution has been measured at 25°, alone (x), in the presence of cobaltammines (II), and Cr complex salts (III). (II) form a black ppt. with (I) and decrease x, (III) form no ppt. and scarcely affect x. In the case of (II) the stronger oxidisers of the polyphenols give the smallest  $O_2$  uptake, and the ppt. appears sooner than in the case of the weaker oxidisers. (III) do not affect the polyphenols. The addition of KCN and (III) to (II) tends to remove the retarding influence of (II) on x. NH<sub>2</sub>OH considerably increases, but only slightly influences the effect of (II) on, x. R. S. B.

Synthesis of esters by castor seed lipase.—See this vol., 1033.

Exchange reaction between deuterium and water vapour on surfaces. H. S. TAYLOR and H. DIAMOND (J. Amer. Chem. Soc., 1934, 56, 1821— 1822).—In contact with catalytic hydrogenating surfaces, such as  $Cr_2O_3$  and ZnO,  $H_2^3$  reacts with adsorbed  $H_2O$  and may be replaced completely by  $H_2$ . E. S. H.

Hydrogenation-dehydrogenation catalysts. K. PACKENDORFF and L. LEDER-PACKENDORFF (Ber., 1934, 67, [B], 1388-1391).-A powerful dehydrogenating catalyst results when  $H_2$  is passed over the carrier, impregnated with  $H_2PtCl_6$ , at 100–150°. Such catalysts are unsuitable for hydrogenation. Typical dehydrogenating catalysts can dehydrogenate at 170-180°, that is at a temp. lower than that usually regarded as the optimum for hydrogenation. Conversely, a typical hydrogenating catalyst can convert C<sub>6</sub>H<sub>6</sub> into C<sub>6</sub>H<sub>12</sub> to the extent of 30% at 310°. Since dehydrogenating catalysts are obtained at  $150-180^{\circ}$  and hydrogenating agents at  $0-10^{\circ}$ , the characteristic properties of the former are ascribed to its lower activity. In confirmation, a hydrogenating can be converted into a dehydrogenating catalyst by P, but not by S. Activity in a catalyst is probably associated with a small granule irregularly formed and inactivity with coarse, regularly formed granules. H. W.

Optical asymmetric catalysis at quartz crystals. G. M. SCHWAB, F. ROST, and L. RUDOLPH (Kolloid-Z., 1934, 68, 157—165).—Ppts. of Ni or Pt on optically active quartz have the power to catalyse preferentially the dehydration or oxidation of one of the optical isomerides of racemic sec.-BuOH. A "specificity" of 10% has been observed, the optimal condition being a loose, monat. coating of metal.

E. S. H.

Active oxides. LXXIX. Kinetics of dehydration of Kohlschutter's topochemical aluminium hydroxide. G. F. HUTTIG and O. STEFFEL [with O. HNEVKOVSKY] (Kolloid-Z., 1934, 68, 178– 184; cf. this vol., 606).—Dehydration isotherms at 120°, 150°, and 180° show that the loss of  $H_2O$  proceeds as a zero order reaction to the composition  $Al_2O_3$ , whilst the dependence of velocity coeff. on temp. is in accordance with Arrhenius' equation. Further dehydration is in accordance with a unimol. reaction. E. S. H.

Active oxides. LXXVII. Dependence of the catalytic activity of different magnesium oxides on their mode of preparation and previous history. B. STEINER and G. F. HUTTIG (Kolloid-Z., 1934, 68, 253-260; cf. this vol., 850).-The catalytic effect of 18 different preps. of MgO on the reaction  $2CO + O_2 \longrightarrow 2CO_2$  has been investigated at 240-495° and with different amounts of catalyst. The results show that the catalysts are characterised by the quantity and quality of active centres. MgO prepared from Mg(OH)<sub>2</sub> ages slowly, the no. of active centres increasing while the quality decreases; MgO from MgC<sub>2</sub>O<sub>4</sub> ages more rapidly with the same result: MgO from basic MgCO<sub>3</sub> has a small no. of highly active centres. The sources of MgO fall in the following order with regard to the catalytic activity of MgO at 460°: magnesite, MgC<sub>2</sub>O<sub>4</sub>, Mg(OH)<sub>2</sub>, basic MgCO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>. E. S. H.

Formation of ammonia at highly dispersed metals. D. P. DOBYTSCHIN and A. V. FROST (Z. Elektrochem., 1934, 40, 585-587).—Polemical (cf. this vol., 371). E. S. H. Poisoning of ammonia catalysts by gases containing oxygen. P. V. USSATSCHEV, V. I. TARA-KANOVA, and V. A. KOMAROV (Z. Elektrochem., 1934, 40, 647—653).—On poisoning technical NH<sub>3</sub> catalysts by small additions of  $CO_2$ , CO,  $SO_2$ ,  $N_2O$ , NO, or  $H_2O$ to the  $N_2$ -H<sub>2</sub> mixture, the NH<sub>3</sub> concn. in the issuing gas first rose and then fell, due to displacement of adsorbed NH<sub>3</sub> from the catalyst surface. The no. of active centres on the catalyst and the time of contact of NH<sub>3</sub> mols. with the surface are greater at lower temp. The reaction rate is controlled by the rate of NH<sub>3</sub> desorption. H. J. E.

Catalytic interchange of hydrogen between water and ethylene and between water and benzene. J. HORIUTI and M. POLANYI (Nature, 1934, 134, 377–378).—After  $H_2O$  containing 3 at.-% of  $H^2$  is heated with  $C_2H_2$  or  $C_6H_6$  in a sealed tube in presence of a Ni catalyst, the  $C_2H_2$  and  $C_6H_6$  contain  $H^2$ . L. S. T.

Kinetics and mechanism of the catalytic exchange of chlorine for the amino-group. N. N. VOROSHCOV and V. A. KOBELEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 108—114).—In the reaction between PhCl and aq. NH<sub>3</sub> at 200° with CuCl as a catalyst, the rate  $\propto$  [CuCl] and, over a limited range,  $\propto$  [NH<sub>3</sub>]. The rate is determined by the formation of the complex PhCl,Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>, which reacts rapidly with NH<sub>3</sub>, OH', and NH<sub>2</sub>Ph. H. J. E.

Passivation and activation of cadmium. T. PIERZCHALSKI (Rocz. Chem., 1934, 14, 295–300).— HCNS,  $CS(NH_2)_2$ ,  $CS_2$ , I, and As catalyse the dissolution of Cd in 7N-HCl, whilst HCN and  $CO(NH_2)_2$  are without effect. HCNS exerts a max. action at 0.0025N concn., whilst that of the remaining catalysts increases with their concn. R. T.

Contact method of conversion of acetylene into acetone.—See B., 1934, 792.

Catalysis by liquid metals. E. W. R. STEACLE and E. M. ELKIN (Canad. J. Res., 1934, 11, 47—52).— There is no abrupt change in the rate of decomp. of MeOH on a Zn surface when the Zn is melted nor in the order (0-0.5) of the reaction, and it is therefore doubtful whether the catalysis can be ascribed to a limited part of the solid surface. The products of decomp. are mainly H<sub>2</sub> and CO, and the heat of activation is 30,000 g.-cal. A. G.

Influence of certain organic hydroxy-compounds on the oxidation of ferrous hydroxide by dissolved oxygen. W. S. PATTERSON (J.S.C.I., 1934, 53, 298-299T).—EtOH,  $[CH_2 \cdot OH]_2$ , glycerol, erythritol, and mannitol inhibit the oxidation  $Fe(OH)_2 \longrightarrow Fe(OH)_3$  by dissolved  $O_2$ . The effect increases for equimolar proportions of inhibitor with increasing % OH in the org. compound. A possible explanation is suggested due to the adsorption of the org. compound in the Fe(OH)\_2 gel, which is thus in some measure protected.

Oxidation of glucose by air in presence of iron pyrophosphate. A. GOERNER (J. Biol. Chem., 1934, 105, 705—709).—Bacterial contamination was eliminated by the use of germicides and shown not to be the cause of the oxidation. Glucose solutions containing pyrophosphate (I) or phosphate buffers do not yield appreciable amounts of  $CO_2$  in absence of Fe. Increasing amounts of (I) do not inhibit the catalytic action of Fe. C. G. A.

Electrolytic concentration of the heavy hydrogen isotope in water. L. TRONSTAD and J. BRUN (Z. Elektrochem., 1934, 40, 556—558).—Contrary to a recent report (this vol., 612)  $H_2^{\circ}O$  can be conc. by electrolysing  $H_2SO_4$  solutions with Pb electrodes. Failures are attributed to the formation of spongy Pb at the cathode, whereby diffusion of fresh electrolyte is hindered. E. S. H.

Concentration of deuterium by electrolysis of sulphuric acid solutions. T. TITANI, K. KURANO, and M. HARADA (Bull. Chem. Soc. Japan, 1934, 9, 269–271).—Commercial H<sub>2</sub>SO<sub>4</sub> diluted to 10% with tap H<sub>2</sub>O has been electrolysed in fractions using Pb electrodes ( $10 \times 4$  cm.) and 4 amp. d.e. The loss of H<sup>1</sup> and H<sup>2</sup> by electrolysis is expressed by  $-dN_1 = (k_1+k)N_1dt, -dN_2 = (k_2+k)N_2dt$ , where  $N_1$  and  $N_2$  are the total mols. of H<sup>1</sup> and H<sup>2</sup>,  $k_1$  and  $k_2$  are consts. for the electrolysis proper, and k is a const. for the loss due to evaporation and spray. It follows that the total separation factor a,  $(\log N_{10} - \log N_1)/(\log N_{20} - \log N_2)$ , where  $N_{10}$  and  $N_{20}$  refer to the start, is related to the electrolytic separation factor  $\alpha$ ,  $=k_1/k_2$ , according to  $\alpha = a/[1-b(a-1)]$ , where  $b=k/k_1$ . The final concn. of H<sup>2</sup> varies from 0.08 to 0.9%,  $\alpha$  from 2.2 to 2.7, a from 1.50 to 1.58, and b from 0.62 to 0.78. The results are compared with those of other workers, and it is suggested that  $\alpha$  may depend on the initial content of H<sup>2</sup>. R. S. B.

Concentration of deuterium by electrolysis of neutral salt solutions. I. T. TITANI, K. OKABE, and M. HARADA (Bull. Chem. Soc. Japan, 1934, 9, 272-273).-0.25*M*-Na<sub>2</sub>SO<sub>4</sub> has been electrolysed in fractions between a Ni cathode and a Pb anode  $(10 \times 4 \text{ cm.})$  using 2.5 amp. a=1.58 (cf. preceding abstract), b=0.58, and  $\alpha=2.3$ ; the product contains 0.085% of H<sup>2</sup>. When Na<sub>2</sub>SO<sub>4</sub> is replaced by 0.5M-NaOH with Ni electrodes and 3 amp., a=1.52, b=0.88, and  $\alpha=2.8$ ; the product contains 0.08% of H<sup>2</sup>. The use of Na<sub>2</sub>SO<sub>4</sub> dispenses with neutralisation, and the same electrolyte can be used throughout. R. S. B.

Alkaline storage battery. V. Alkali zincate storage battery.—See B., 1934, 802.

Electrolysis of methyl alcohol solutions of zinc and cadmium chlorides. E. GUILLERMET (Compt. rend., 1934, 199, 191-193; cf. this vol., 154).-Electrolysis of a 5% MeOH solution of ZnCl<sub>2</sub> with a c.d. of 1.3-5 amp. per sq. dm. yields compact deposits adhering well to a Pt cathode. At 3-5 amp. per sq. dm. there is a tendency for treeing at the edges of the cathode. The deposit is almost pure with c.d. 3-5 amp. per sq. dm., with c.d. 1 amp. per sq. dm. during 4 hr. runs, or with acid solutions, but in other cases it is contaminated with oxychloride. The yields reach 95% with a Zn anode, but are less with a Pt anode, decreasing with increasing time of electrolysis, or c.d., and decreasing distance between the electrodes. Use of a diaphragm increases the yield. The Zn anode is attacked uniformly, but there is chemical as well as electrochemical attack. Electro-

lysis of 0.7-0.9% MeOH solutions of CdCl<sub>2</sub> with a c.d. of 0.5-3 amp. per sq. dm. yields, not an adherent deposit, but a black spongy mass. With a Cd anode this deposit contains white particles of an oxychloride containing MeOH, and the same material is formed in suspension in the solution. With a Pt anode the solution becomes acid and the white compound disappears, the deposit turning greyish and cryst. Since the total yields with a Cd anode are 100%, the formation of the white product is attributed to an electrochemical process, probably discharge of CdCl ions. With a Pt anode the yields are < 100%, are increased by use of a diaphragm, and decreased by using an acid solution. There is no chemical, as distinct from electrochemical, attack on a Cd anode. J. W. S.

Electrolytic deposition of iron-nickel alloys.— See B., 1934, 801.

Electrometallurgy of aluminium. P. DROSS-BACH (Z. Elektrochem., 1934, 40, 605—608).—Evidence is adduced to show that the primary process in electrolysing molten cryolite is the decomp. of NaF. E. S. H.

Substitute for platinum as anode material in electrolytic oxidation processes. I. Tungsten anodes. G. ANGEL (Z. Elektrochem., 1934, 40, 641-647).—In the electrolysis of cone. aq. NaClO<sub>3</sub> (with or without addition of aq. Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) with a W or Mo anode, a protective oxide film forms. Electrolysis occurs with > 70 volts applied potential, the anodes being strongly attacked. If a Pt lead is used for the W electrode, practically all of the current is carried by the Pt, NaClO<sub>4</sub> being formed normally, with high current efficiency. The W is unattacked. H. J. E.

Electrodeposition of rhodium.—See B., 1934, 801.

Kinetics of photosynthesis. R. EMERSON and L. GREEN (Nature, 1934, 134, 289–290).—A crit. discussion (cf. this vol., 497). L. S. T.

Measurement of doses of very soft X-rays (limit rays). R. JAEGER (Physikal. Z., 1934, 35, 665-682).—Modifications in the method for hard X-rays make it applicable for soft rays. A. J. M.

Limit of the variation of the relation between intensity and velocity of photochemical reactions. W. V. BHAGWAT (J. Indian Chem. Soc., 1934, 11, 443—447).—The velocity of the reaction usually  $\infty$ , or else increases less rapidly than, the intensity of illumination. In the few cases where it increases more rapidly, the effect is due to the destruction of inhibitors by the light. Proportionality to the square root of the intensity is more probable with high than with low frequency. D. R. D.

Kinetics of reactions of heavy hydrogen. I. H. W. MELVILLE (J.C.S., 1934, 1243-1250).—The data refer to the Hg-photosensitised reduction by H<sub>2</sub> and 66% H<sup>2</sup> of O<sub>2</sub>, N<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub>. At 20°, when H<sub>2</sub> is in excess, the zero order reaction velocities are not affected by isotopic composition, but when O<sub>2</sub> is in excess, the reaction becomes of first order with respect to H and the velocity with H<sub>2</sub> is < with H<sub>2</sub> owing to a collision frequency factor. A similar effect would

be expected with excess of  $N_2O$  and  $C_2H_4$ . Consistent with  $H+N_2O \longrightarrow N_2+OH$  (slower) and  $OH+H_2$ -- H<sub>o</sub>O+H, there is no isotope effect in the reaction with excess of H<sub>2</sub> at appropriate pressure and 250°, and hence quantum-mechanical leakage of H atoms is negligible. In 2H2: O2 mixtures at 4.6 mm. and 246-421°, chain lengths of about 30 were found and the reaction velocity with  $H_2^2$  is < with  $H_2$ , but this difference diminishes as the temp. is raised. This is consistent with the initial formation of HO2 followed by  $HO_2+H_2 \longrightarrow H_2O+OH$ , to the activation of which the different zero-point energies of H<sub>2</sub> and H; contribute. In presence of Pd-black and excess of H, the reactions at 20° are of zero order at pressures > sp. limiting vals. Experiments at 20° and 339° show that the quantum yield in the hydrogenation of C<sub>2</sub>H<sub>4</sub> is independent of temp. and the H isotope used; hence a chain mechanism is excluded and the second step in the reaction is probably between Et and H. In no case could the difference between the rates of reaction of the two isotopes be attributed to the leakage of atoms through potential barriers.

J. G. A. G.

Initiation of the hydrogen-chlorine reaction by X-rays. S. GOTZKY and P. GUNTHER (Z. physikal. Chem., 1934, B, 26, 373-389).-The relation between reaction velocity and concns. is represented by Bodenstein and Dux's equation (A., 1913, ii, 1039). The reaction chains are initiated by dissociation of  $Cl_2$  and 7.8 g.-cal. of energy of secondary electrons is required for the formation of 1 mol. of HCl. The energy of the secondary electrons is insufficient to cause concurrently chemical excitation and ionisation in the reaction mixture; the act of excitation is causally related to the appearance of ions. Each ion is associated with three or four acts of excitation. The energy of recombination of the ions seems to be of no account for the excitation of the reaction. These results agree with Lind's cluster theory (cf. this vol., 975). Cu surfaces irradiated with X-rays retard the reaction, whilst Ag surfaces have no effect. R. C.

Mercury-photosensitised decomposition of the deuteroammonias. J. C. JUNGERS and H. S. TAYLOR (J. Chem. Physics, 1934, 2, 373-380).-Samples of  $N(H^{1}H^{2})_{3}$  in which  $H^{1}$  was replaced by  $H^{2}$  to the extent of 68, 90, and 99%, respectively, have been prepared by treating different samples of  $Mg_3N_2$ with H.O vapour. These varying compositions showed that stable amido- and imido-compounds had been present in the original Mg<sub>3</sub>N<sub>2</sub>. The physical properties of NH; (99% H2) have been determined and contrasted with those of NH3 (in parentheses): d 1.174 (1); f.p. 199° (195.2°) abs.; b.p. 242.3° (239.75) abs.; v.p. at 238.6° abs. 628 (714) mm.; latent heat of vaporisation from v.-p. curve 5990 (5797) g.-cal. Substitution of H<sup>2</sup> for H<sup>1</sup> displaces the ultra-violet absorption bands towards shorter wave-lengths. The absorption curves also give an indication of the three possible N(H<sup>2</sup>,H<sup>1</sup>)<sub>3</sub> present. The Hg-photosensitised decomp. of  $NH_3$  is > 10 times slower than that of NH3 by H2. It is also inhibited more strongly by H<sub>3</sub> than that of  $NH_3$  by  $H_2$ . There is a qual., but not quant., resemblance in the kinetics of decomp. of NH, and NH. The nature of the collisions involved

on decomp. is discussed on the basis of the data on the quenching of Hg resonance radiation by  $N(H^2H^1)_3$ . M. S. B.

Influence of water on the photolysis of ozone at  $\lambda 280, 254, \text{ and } 210 \text{ m}\mu$ . G. S. FORBES and L. J. HEIDT (J. Amer. Chem. Soc., 1934, 56, 1671—1675).— In the photolysis of O<sub>3</sub> at partial pressures 10 mm.— 1 atm. in presence of saturated H<sub>2</sub>O vapour at 2° and 20°, the quantum yields,  $\phi$ , range from 1.6 to 130, indicating a chain mechanism.  $\phi$  is raised by increase in  $p_{0,*}$ , but depressed by increase in total pressure or in  $p_{0,*}$ , and at any given wave-length is inversely proportional to a fixed power of the light intensity;  $\phi \propto \sqrt{[H_2O]}$ . E. S. H.

Photochemical reduction of carbon dioxide on surfaces. M. QURESHI and S. S. MUHAMMAD (J. Osmania Univ. Coll., 1933, 1, Reprint; cf. A., 1932, 1006).—CO<sub>2</sub> was bubbled at 25—30° through an irradiated aq. suspension of electrolytic NiCO<sub>3</sub>, activated by heating at 120—140° or by irradiation. No CH<sub>2</sub>O or carbohydrate was formed. H. J. E.

Formation of silver bromide emulsion for photography. VII—X. M. MIYATA (J. Soc. Chem. Ind. Japan, 1934, 37, 299—303B).—Washing the emulsion results in the removal of adsorbed Br' and its replacement by Cl' derived from the  $H_2O$ . The sensitivity (I) of an emulsion increases with the [Cl'] of the wash  $H_2O$  up to 0.01N, and it is also increased by the addition of AgCl by other methods. AgCl is more sensitive to light than AgBr, and its (I) is increased by a small proportion of AgBr or of AgI, which behave like optical sensitisers. The increase in (I) during digestion is probably due to the nuclei of AgCl increasing in size and approaching the AgI within the grains.

A. G.

So-called photochemical antagonism. M. TRAUTZ and H. E. HAAS (Z. wiss. Phot., 1934, 33, 81-93).—A crit. survey is given of the theories of reactions which are reversible (I), or variable in equilibrium point (II), by exposure to light or to lights of different  $\lambda$ . For (I), the action of infra-red light approximates to the thermal equilibrium, but the behaviour to ultra-violet light depends on the intensity. For (II), particularly when contrasting reactions in the dark and in the light, a difference in mode of reaction (although producing the same end-products) is postulated. J. L.

Herschel effect. O. BARTELT and H. KLUG (Z. Physik, 1934, 89, 779—785).—This is due to re-formation of Ag ions from Ag atoms of the latent image. A. B. D. C.

Theory of photographic development. I. Adsorption theory.—See B., 1934, 813.

Theory of photographic development. II. Adsorption of quinol on colloidal silver. A. J. RABINOWITSCH and S. PEISSACHOWITSCH (Z. wiss. Phot., 1934, 33, 94—104; cf. B., 1934, 813).—Mixtures of Ag sols containing gelatin with varying amounts of quinol (I) were analysed by titration with I, before and after ultra-filtration. Some of the (I) is adsorbed on the Ag particles, and some is oxidised, the remainder being found in the filtrate. The surface of the Ag particles must be larger than expected from counting the no., as an average of 5 mols. of (I) are adsorbed per Ag atom. J. L.

Photodissociation of molecules in the Schumann ultra-violet. A. TERENIN and H. NEUJMIN (Nature, 1934, 134, 255).—In photochemical reactions induced in gases by light in the Schumann region the emission of OH and CN accompanying the photodissociation of more complex mols. has been observed. The observed processes are  $h\nu+H_2O \longrightarrow H+OH^*$ ,  $h\nu+MeOH \longrightarrow Me+OH^*$ , and  $h\nu+MeCN \longrightarrow Me+$ CN\*, where OH\* and CN\* are excited radicals emitting the bands at 3062 and 3883 Å., respectively.

L. S. T.

Influence of circularly polarised light on the velocity of mutarotation of some sugars. P. SOUTY (Compt. rend., 1934, 199, 198—199).—Relative to lavorotatory circularly polarised light of the same intensity, dextrorotatory circularly polarised light accelerates mutarotations which lead to increased positive rotations (mannose, maltose, etc.), and retards mutarotations which lead to increasing negative rotations (glucose, lactose, etc.). Certain frequencies are more effective than others, monochromatic illumination of  $\lambda$  5461 Å., but not 5890—5896 Å., affecting the mutarotation of glucose. J. W. S.

Photosensitising action of iodine. Isomeric transformation of allocinnamylideneacetic acid into the normal form. I. J. C. GHOSH, D. S. N. MURTHI, and D. N. DAS GUPTA. II. J. C. GHOSH and D. S. N. MURTHI (Z. physikal. Chem., 1934, B, 26, 255-266, 267-271; cf. A., 1931, 180).—I. The velocity coeff. of the transformation in  $C_6H_6$  solution sensitised by I is given by  $(1/t) \log_e[A/(A \times x)]$ , where t is the time and A the initial concn. of allo-acid multiplied by an empirical const. (1·33). It increases with [I], at first rapidly, then more slowly, and  $\infty$  the square root of the energy of the radiation absorbed. These results are accounted for by supposing the primary act to be the photo-dissociation of I mols. into atoms, followed by a chain reaction :  $I+A \longrightarrow IA$ ,  $IA \longrightarrow I+B$ ,  $I+B \longrightarrow IB$ , and  $IB+A \longrightarrow I+B+B$  (A=allo-acid, B=normal acid). The activation energy calc. on the assumption that a collision between two I atoms in presence of  $C_6H_6$  mol. always gives I agrees with the val. calc. from the temp. coeff.

II. The kinetics of the transformation in  $CCl_4$  solution can be accounted for by the above mechanism. R. C.

Induced and photochemical oxidation of sodium tartrate by air and its use in diabetes and prolonged fasting. C. C. PALIT and N. R. DHAR (J. Indian Chem. Soc., 1934, 11, 471—477).—Na tartrate is oxidised directly by air in presence of Na<sub>2</sub>SO<sub>3</sub>,  $Ce(OH)_2$ , NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and Fe(OH)<sub>2</sub>, the activity of the catalyst falling in approx. this order. The activity of  $Ce(OH)_2$  and  $Fe(OH)_2$  is increased by addition of traces of  $Cu(OH)_2$  and decreased by larger quantities. The action is accelerated by light. K oleate and Na tartrate mutually retard the oxidation of each other by air. The results suggest that Na tartrate should be of use in the treatment of diabetes and inanition, and that traces of Cu salts should be added to the Fe salts in the treatment of anæmia.

D. R. D.

Products of irradiation of ergosterol with ultra-violet rays. A. V. TRUFANOV (Khim. Farm. Prom., 1933, 253—256).—Irradiation of a 2% solution in  $C_6H_6$  for 4 hr. gave the best results (50% activated). CH. ABS.

Interchangeability of hydrogen atoms in organic compounds with the hydrogen atoms of water. R. KLAR (Z. physikal. Chem., 1934, B, 26, 335—342).—There is no interchange of H atoms between heavy H<sub>2</sub>O and NaOAc or C<sub>6</sub>H<sub>6</sub>. With MeCHO there is slow interchange and with CH<sub>2</sub>O, COMe<sub>2</sub>, and CH<sub>2</sub>Ac<sub>2</sub> all the H atoms are interchangeable. With COMe<sub>2</sub> interchange occurs by way of enolisation; it is very slow in neutral, more rapid in acid, and very rapid in alkaline solution. The quotient of the ratio H<sup>2</sup>: H in the org. compound by that in the H<sub>2</sub>O is < 1.

R. C.

Heavy water. H. ERLENMEYER and H. GARTNER (Nature, 1934, 134, 327).—By crystallising Na<sub>2</sub>SO<sub>4</sub> from H<sub>2</sub>O containing 4—5 % H<sub>2</sub><sup>3</sup>O, normal and heavy H<sub>2</sub>O are divided practically equally in the H<sub>2</sub>O of crystallisation and the solution. Within this concn. range Et<sub>2</sub>O dissolves H<sub>2</sub><sup>1</sup>O and H<sub>2</sub><sup>3</sup>O in equal quantities. When the Et<sub>2</sub>O drops are allowed to rise through this solution of heavy H<sub>2</sub>O, dissolving mainly H<sub>2</sub>O out of the interfaces H<sub>2</sub>O-Et<sub>2</sub>O, then the interfaces are enriched in H<sub>2</sub><sup>3</sup>O. [Co(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub> but not KH<sub>2</sub>PO<sub>4</sub> exchanges its H for H<sup>2</sup> in this solution. L. S. T.

Separation of heavy water from ordinary water. G. BRUNI and M. STRADA (Atti R. Accad. Lincei, 1934, [vi], 19, 453—458).—Methods of separation based on freezing the H<sub>2</sub>O and on fractional crystallisation of hydrated salts are discussed. From 1500 litres of H<sub>2</sub>O, 21 g. having a H<sub>3</sub>O content of 0.37%, corresponding with an enrichment of about 20 times, were obtained after 7 cycles of freezing. Fields of snow which had been repeatedly thawed and re-frozen exhibited a surface layer about 2 cm. thick containing 0.055% of H<sub>3</sub>O. Large crystals of carnallite from the Stassfurt and Beienrode deposits yielded on distillation H<sub>2</sub>O containing up to 0.0412% of H<sub>3</sub>O, compared with 0.027—0.029% for the adjacent mass of crystals. H. F. G.

Silver difluoride. H. JOCKUSCH (Naturwiss., 1934, 22, 561).—The reaction between powdered Ag and  $F_2$  at room temp. gives rise to yellow AgF<sub>2</sub>, which is rapidly decomposed by  $H_2O$  giving Ag<sub>2</sub>O and an oxidising solution. The easily decomposable fluorate may be formed (A., 1933, 797). It reacts with EtOH forming MeCHO and AcOH, becoming reduced to Ag. It does not react with CCl<sub>4</sub> at 0°, but if dissolved reducing agents, *e.g.*, EtOH, PhMe, are present, it is reduced to AgF. A. J. M.

Reaction between hypophosphorous acid and silver nitrate. T. AJELLO (Gazzetta, 1934, 64, 351— 359).—Contrary to statements in the lit., equimol. quantities of  $H_3PO_2$  and  $AgNO_3$  react without evoluion of gas and with only partial oxidation of the former. The  $AgH_2PO_2$  first formed decomposes to yield Ag and  $H_2PO_2$  groups, and the latter react with  $H_2O$  to form  $H_3PO_2$  and O; finally, the O oxidises, although incompletely, the  $H_3PO_2$  to  $H_3PO_3$  and  $H_3PO_4$ . H. F. G. Combination of silver and copper with fluorine. O. RUFF and M. GIESE (Z. anorg. Chem., 1934, 219, 143—148).—The compound,  $AgF_2$ , has been prepared by the action of  $F_2$  at 150—200° on Ag halide, on mol. Ag prepared by reducing  $Ag_2O$  with  $CH_2O$ , or on fine Ag gauze. It is dark brown, highly reactive, and strongly paramagnetic; X-ray examination shows it to be rhombic, a 6·24, b 5·480, c 4·86 Å., d calc. for 4 mols. 5·4; d (pyknometric in  $CCl_4$ ) 4·57—4·78; the dissociation pressure is 1 atm. at 435—450°. AgF<sub>2</sub> might be used as a fluorinating agent. Its formation explains the catalytic action of Ag salts in the decomp. of gases by F<sub>2</sub>. No fluoride of Cu higher than  $CuF_2$ could be prepared by similar methods. M. S. B.

Preparation and explosion temperatures of some complex cupric chlorates, perchlorates, and nitrates formed with ethylenediamine. Amel (Compt. rend., 1934, **199**, 201–203).—By slow treatment of  $Cu(ClO_3)_2,6H_2O$ ,  $Cu(ClO_4)_2,6H_2O$ , and  $Cu(NO_3)_2,6H_2O$  with 75% ( $CH_2\cdot NH_2)_2$  (en), the com-pounds,  $Cu(ClO_3)_2,2en,H_2O$  (I);  $Cu(ClO_4)_2,3en,H_2O$ (II);  $Cu(ClO_4)_2,2en,H_2O$  (III);  $Cu(ClO_4)_2,3en,H_4O$ (IV);  $Cu(NO_3)_2,2en$  (V); and  $Cu(NO_3)_2,3en,H_4O$ (VI) have been obtained. On keeping for 60 hr. in a vac. desiccator at 20°, (II) loses 10% of its en, (IV) is almost unchanged, and (VI) passes almost completely into (V). All are insol. in Et<sub>2</sub>O and almost so in EtOH. (III) and (IV) are slightly sol. in COMe<sub>2</sub>. The ag. solutions vary in colour from blue to purple; they are decomposed by acids, and excess of KOH ppts. CuO on prolonged boiling. All explode on heating, generally after melting with decomp. The induction periods before explosion are given as functions of the temp. in graphical form. (I) and (II) explode readily, and (III) and (IV) less readily on striking with a hammer; (II) and (VI) also explode on contact with J. W. S.  $H_2SO_4$ .

Thermal dehydration or decomposition of certain minerals and salts. A. F. GILL (Canad. J. Res., 1934, 10, 703—712).—By the use of a combined calcining furnace and weighing balance, data have been obtained for the course of the decomp. up to 800— $1000^{\circ}$  of magnesite, hydromagnesite, magnesitic dolomite, dolomite, serpentine, asbestos, Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, gypsum, MgSO<sub>4</sub>,7H<sub>2</sub>O, AlCl<sub>3</sub>,6H<sub>2</sub>O, pyrites, and coal. H. S. P.

Technical preparation of calcium-silicon alloys. R. WEINER (Z. Elektrochem., 1934, 40, 624–. 629).—A Ca–Si alloy (approx. 30% Ca) has been prepared by heating CaC<sub>2</sub>, SiO<sub>2</sub>, and C in a 20-kw. electric furnace, using mainly resistance heating. The alloy, as formed, should be removed from the hottest zone, in which it is unstable. A similar product is formed from CaO, SiO<sub>2</sub>, and C. H. J. E.

**Crystals of calcium carbonate.** T. NODA (J. Soc. Chem. Ind. Japan, 1934, 37, 319–322B).—When aq.  $(NH_4)_2CO_3$  is added to aq. CaCl<sub>2</sub> the formation of rhombic as opposed to acicular crystals of CaCO<sub>3</sub> is favoured by low temp., low  $[NH_3]$ , and high concn. of reactants. Below 35° spherulitic crystals appear. A. G.

Effects of fluorides on thermal synthesis of calcium silicates. S. NAGAI and M. MIYASAKA (J.

Soc. Chem. Ind. Japan, 1934, 37, 303–306B).—The addition of  $CaF_2$  to mixtures of  $CaCO_3$  or CaO with  $SiO_2$  lowers the temp. of combination by about 200°, and diminishes the proportion of CaO in the silicate when heating is prolonged. A.G.

Effects of fluorides on the thermal synthesis of calcium silicates. II. S. NAGAI and M. MIYASAKA (J. Soc. Chem. Ind. Japan, 1934, 37, 419–421B).—The presence of increasing amounts of CaF<sub>2</sub> increases the rate of the reaction  $2\text{CaO} + \text{SiO}_2 \longrightarrow 2\text{CaO}, \text{SiO}_2$  at 1200°; at 1300° the conversion produces some 3CaO,SiO<sub>2</sub>. Part of the CaF<sub>2</sub> is removed by evaporation during the reaction. T. W. P.

Disperse structure of the real crystal system, and the temperature of the beginning of grey glow. D. BALAREV and N. KARABASCHEV (Kolloid. Z., 1934, **68**, 261—266).—The temp. at which the grey glow appears on heating  $BaSO_4$  is lowered by the presence of impurities in the crystals. The result is attributed to the liberation of free energy from the inhomogeneous crystal structure. E. S. H.

Action of mercuric oxide on ferric chloride solutions. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 814—815).—By agitating HgO with aq. FeCl<sub>3</sub>, HgCl<sub>2</sub> and Fe(OH)<sub>3</sub> are formed, the last being soluble in excess of FeCl<sub>3</sub>. With increase of HgO, HgCl<sub>2</sub> is deposited, and finally Hg oxychlorides appear.

Ĵ. G. A. G.

Hydrated phosphates and arsenates of tervalent elements. I. Hydrates of boron phosphates and arsenates. E. GRUNER (Z. anorg. Chem., 1934, 219, 181-191).-X-Ray examination shows that sol. BPO4 and the insol. form obtained by heating this at 1000° are identical. By isothermal dehydration at 20° hydrates with 6, 5, 4, and 3H<sub>2</sub>O have been shown to exist. The only hydrates of BAsO<sub>4</sub> indicated by isobaric decomp. at 11 mm. are BAsO<sub>4</sub>,6H<sub>2</sub>O and 3H<sub>2</sub>O. No ammoniates have been obtained, but the compounds BPO4,3H2O,NH3 and BAsO<sub>4</sub>,3H<sub>2</sub>O,NH<sub>3</sub>, prepared by extracting any of the hydrates with liquid NH3, appear to be acid salt complexes of phospho- and arseno-boric acid,  $H_2[BPO_3(OH)_4]$  and  $H_2[BAsO_3(OH)_4]$ . The higher hydrates appear to be hydrates of these acids. Potentiometric titration indicates that, in aq. solution, a mixture of H<sub>2</sub>BO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> or H<sub>3</sub>AsO<sub>4</sub> is obtained. M. S. B.

Boric acid and alkali borates. VI. Nature and thermal decomposition of ammonium perborate. W. KRETZSCHMAR. VII. Constitution of perborates and polyborates. H. MENZEL (Z. anorg. Chem., 1934, 219, 17-34, 35-41).--VI. NH<sub>4</sub>BO<sub>3</sub>,0.5H<sub>2</sub>O, dried in the air, can be kept unchanged in a closed vessel at room temp. for a considerable time. Long exposure causes a very gradual loss of NH<sub>3</sub> and active O, and a slight increase of H<sub>2</sub>O. By drying in vac. the anhyd. salt is obtained without decomp. X-Ray analysis of the two compounds shows that there are definite differences of crystal structure which indicate that they are separate chemical individuals. The constitutional formula of NH<sub>4</sub>BO<sub>3</sub> is discussed. NH<sub>4</sub>BO<sub>3</sub> is decomposed by heat, and the proportions of the products at different temp. between 120° and 250° have been determined. The chief products are  $\rm NH_3$ ,  $\rm N_2$ ,  $\rm O_2$ , and (above 150°)  $\rm N_2O$ . The character of the decomp. process is discussed and, in connexion with it, the thermal decomp. of  $\rm NH_4NO_3$ , regarded as an intermediate product, has been investigated.

VII. There is no reason to regard  $NH_4BO_{3,0}\cdot 5H_2O$ and  $KBO_{3,0}\cdot 5H_2O$  as fundamentally different from  $NaBO_{3,0}\cdot 5H_2O$  and  $LiBO_{3,0}\cdot 5H_2O$ . They are all substitution products of  $H_2O_2$ . Different structural formulæ, put forward for the polyborates, are discussed. M. S. B.

Change of true specific gravity of kaolin by heating. T. NAKAI and Y. FUKAMI (J. Soc. Chem. Ind. Japan, 1934, 37, 430–432B).—The changes in *d* of two samples of kaolin on heating to increasingly higher temp. were measured by Yoshida's method. Over the ranges, room temp. to 400°, and 1200– 1500°, the samples differed through small differences in impurities. In both the *d* fell sharply over the range 400–600°, corresponding with the conversion kaolinite  $\longrightarrow Al_2O_{3(amorph.)}+Si_2O_{(amorph.)}+H_2O$ , but rose from 600° to 1200°. The conversion  $Al_2O_{3(amorph.)}$  $\longrightarrow \gamma -Al_2O_3$  between 900° and 1000°, and the reaction  $3Al_2O_3+2SiO_2 \longrightarrow 3Al_2O_3,2SiO_2$  (mullite) between 1100° and 1200°, cause changes of slope in *d*-temp. curve. T. W. P.

X. The existence and methods of prep. of the oxides and sulphides of Ga and In already recorded have been confirmed. By the thermal analysis of the systems Ga-Te and In-Te the existence of the following tellurides is demonstrated : GaTe, m.p.  $824\pm2^{\circ}$ , black, soft, friable leaflets; Ga<sub>2</sub>Te<sub>3</sub>, m.p.  $790\pm2^{\circ}$ , hard, brittle, and black; InTe, m.p.  $696\pm2^{\circ}$ , silver-grey fused mass when hot, steel-blue when cold; In<sub>2</sub>Te<sub>3</sub>, m.p. 667 ± 2°, hard, brittle, and black. The following selenides have been prepared by synthesis : Ga<sub>2</sub>Se, black; GaSe, m.p. 960±10°, dark reddish-brown leaflets;  $Ga_2Se_3$ , m.p. probably > 1020 $\pm$ 10°, black, hard, and brittle, red on grinding; In<sub>2</sub>Se, black and soft; InSe, m.p.  $660 \pm 10^\circ$ , black and friable,  $In_2Se_3$ , m.p. 890  $\pm 10^\circ$ , black and rather soft. d, magnetic susceptibilities, and m.p. of many of the compounds of Ga, In, and Tl are recorded. Gradations of colour and other properties are discussed. Ionic vols. have also been compared. M. S. B.

Change of form of graphite crystals on burning. N. BACH and I. LEVITIN (Kolloid-Z., 1934, 68, 152– 157).—The appearance of etch-like figures on the surface of graphite when heated in  $CO_2$  is described. Addition of HCl to the atm. transforms the rounded figures into hexagonal. The reaction with  $CO_2$  at 1000° is catalysed by the ash components of the graphite or by adding K. In pure C, only the unsaturated outer atoms in the hexagonal basal planes are able to react. E. S. H.

Reduction of graphite oxide by hydrogen sulphide. U. HOFMANN and A. FRENZEL (Kolloid-Z., 1934, 68, 149—151).—H<sub>2</sub>S penetrates between the layers of C atoms and substitutes S for O. The product decomposes rapidly with separation of S. E. S. H.

Primary processes in the oxidation of graphite. L. MEYER (Z. Elektrochem., 1934, 40, 640-641).--Polemical against Sihvonen (cf. this vol., 978). H. J. E.

Morphology and mode of reaction of natural organic growths. (Topochemical reactions.) K. HESS and C. TROGUS (Kolloid-Z., 1934, 68, 168— 175).—Published work on the chemical, X-ray, and microscopical examination of the reaction of ramie threads with various reagents is discussed from the topochemical viewpoint. E. S. H.

Mineral colours. J. HOFFMANN (Z. anorg. Chem., 1934, 219, 197–202).—The natural quartz colours are ascribed to the presence of silicates, e.g., Na<sub>2</sub>O,3SiO<sub>2</sub> and Na<sub>2</sub>O,4SiO<sub>2</sub>, grey, and Na<sub>2</sub>O,SiO<sub>2</sub>, amethyst. CO<sub>2</sub> and CO from Na<sub>2</sub>CO<sub>3</sub> may also give a grey colour. Citrine colouring is probably due to Na<sub>2</sub>O,Fe<sub>2</sub>O<sub>3</sub>. The coloration of rock-salt is attributed to the formation of various NaCl complexes through the action of light. M. S. B.

Corrosion figures on glass. J. HERBERT (Compt. rend., 1934, 199, 369—371).—The resemblance of the corrosion figures obtained by etching glass with HF to the silicofluorides of Na and Ca is very marked. Figures having the form of crystals of  $CaSiF_6$  have been obtained by depositing crystals of this salt on glass not containing Ca, and etching the glass with HF. Chemical composition of the glass has a great effect on the form of the figures, as has also the concn. of the corrosive liquid. The rapidity with which the molten glass has been cooled is without effect on the form of the figures. A. J. M.

Preparation of cerium and its alloys. A. KARL (Bull. Soc. chim., 1934, [v], 1, 871-877).-Anhyd. CeCl<sub>3</sub> has been prepared (1) by heating the hydrous chloride (I) in a current of dry HCl (traces of oxychloride remain), (2) by passing COCl<sub>2</sub> at 350-400° over (I) previously heated until dry, (3) by passing HCl over dry Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> at 450°, and (4) by dehydrating (I) mixed with CaCl<sub>2</sub>, the final stage being in an atm. of HCl. Ce is not obtained by heating CeO2 with CSi, but a reactive Ce-Mg alloy is obtained with Mg. About 85% of the calc. yield of 97% Ce is obtained by lowering 70 g. of Ca into a molten mixture of 1 part by wt. of CeCl<sub>3</sub> with 2.5 parts of CaCl<sub>2</sub> in a vertical Fe tube. Fe added to the melt yields an Fe-Ce alloy. CeF<sub>3</sub> and Ca do not afford Ce; Al does not react with CeCl<sub>3</sub>, but Mg forms a Ce-Mg alloy. J. G. A. G.

Synthesis of ammonia under very high pressures above 1000 kg. per sq. cm. J. BASSET (Compt. rend., 1934, 199, 205–208).—The reaction of a  $N_2+3H_2$  mixture has been studied at pressures of 1000–4500 kg. per sq. cm. and at 0–1000°. Above 2000 kg. per sq. cm. the reaction occurs irrespective of the material of the container, and the velocity of the reaction is so increased that the presence of a special catalyst is no longer required. At const. partial pressure the formation of  $\rm NH_3$  is independent of the presence of impurity. The optimum temp. is 800—1000°. Under the experimental conditions used, the production capacity is 10 g. per hr. per c.c. of space at 850° and 4500 kg. per sq. cm., only 2—3% of the gases not combining. J. W. S.

Hydrolytic fission of amines. W. J. HICKIN-BOTTOM (J. Amer. Chem. Soc., 1934, 56, 1820–1821). —The induced polarity theory of Lapworth and Robinson is applied to reactions of this type.

E. S. H.

Reactions between nitrogen compounds and phenols. II. Solubility product and complex formation. R. LABES and T. BREITENSTEIN (Arch. exp. Path. Pharm., 1934, 175, 372-395; cf. this vol., 446).-The combination between a phenol (I) and a N compound (II) is mainly governed by the affinity between the acidic phenolic OH and a suitable basic N. (II) which are strong bases readily forming cations in aq. solution, take up H' and consequently do not unite readily with (I); similarly the influence of a proximate CO·NH·CO group (e.g., veronal and luminal) or of a free NH<sub>2</sub> (e.g., NH<sub>2</sub>Ph) decreases the affinity. Many heterocyclic (II) (e.g., C<sub>5</sub>H<sub>5</sub>N, quinoline, antipyrine, pyramidone, caffeine, alkaloids) are very active. Combination is influenced by the no. and hydrophobic character of lipophilic groups which produce a high Langmuir residual affinity and thereby form complexes at low concns. of the components. The solubility of the complexes formed partly depends on the degree of dissociation of groups not participating in the combination. The bearing of the data obtained on the pharmacological action of drugs is F. O. H. discussed.

Oxygen isotope separation by chemical reaction. H. S. TAYLOR and A. J. GOULD (J. Amer. Chem. Soc., 1934, 56, 1823).—Fractional thermal decomp. of PbO<sub>2</sub> does not cause any appreciable separation of O<sup>16</sup> and O<sup>18</sup>, but by treating 30% H<sub>2</sub>O<sub>2</sub> at room temp. with colloidal Pt the first fractions of O<sub>2</sub> collected are enriched in O<sup>16</sup>. E. S. H.

Action of hydrochloric acid on sulphates and alums. N. D. COSTEANU and A. S. COCOȘINSCHI (Bull. Acad. Sci. Roumaine, 1934, 16, 122—130).— Na<sub>2</sub>SO<sub>4</sub> and  $K_2$ SO<sub>4</sub> when evaporated with HCl and dried at 200—210° increase in wt. to an extent which does not alter on repetition of the treatment, the product being, probably,  $3M_2$ SO<sub>4</sub>, 2HCl. With K and NH<sub>4</sub> alums the increase of wt. increases with each repetition of the evaporation. H. F. G.

Polythionates. IV. Function of arsenic compounds in the formation of polythionates from thiosulphates and acids. C. J. HANSEN (Ber., 1934, 67, [B], 1418—1420).—Mainly a reply to Kurtenacker *et al.* (this vol., 160). H. W.

Formation of sulphuric acid and hydrogen sulphide by the decomposition of sodium thiosulphate. P. W. SCHENK (Z. anorg. Chem., 1934, 219, 87-88).—The views put forward by Foerster and Umbach (this vol., 616) as to the mode of decomp. of  $H_2S_2O_3$  are not in accordance with the properties of SO. M. S. B.

Preparation of sodium tungstate free from molybdate and a simplified process for the preparation of a correct uric acid reagent. O. FOLIN (J. Biol. Chem., 1934, 106, 311-314).-MoO<sub>4</sub>" is removed by conversion into sulphomolybdates which are sol. in EtOH, the WO<sub>4</sub> being insol.

C. G. A.

**Rhenium fluorides (especially \operatorname{ReF}\_6, \operatorname{ReOF}\_4, \operatorname{ReO}\_2\operatorname{F}\_2, \operatorname{ReF}\_4, and \operatorname{K}\_2\operatorname{ReF}\_6). O. RUFF and W. KWASNIK (Z. anorg. Chem., 1934, 219, 65-81).—Pure \operatorname{ReF}\_6, m.p. 18.5°, b.p. 47.6°, has been prepared. It is chemically reactive and readily reduced to \operatorname{ReF}\_4 at comparatively low temp. (e.g., H<sub>2</sub> 200°, CO 300°, \operatorname{SO}\_2 400^\circ, etc.). At higher temp. Re may be obtained. d and v.-p. measurements have also been made. Other compounds have been prepared, viz., \operatorname{ReOF}\_4, m.p. 39.7^\circ, \operatorname{ReO}\_2\operatorname{F}\_2, m.p. 156°, \operatorname{ReF}\_4, m.p. 124.5°, and \operatorname{K}\_2\operatorname{ReF}\_6. Their chemical and physical properties have been examined. It has not been found possible to prepare \operatorname{ReF}\_7, and the reasons for this are discussed. The m.-p. diagram for \operatorname{ReF}\_6 and oxyfluorides indic ates no other oxyfluorides as a solid phase. During attempts to prepare \operatorname{ReF}\_7 there were indications of the formation of \operatorname{ReOF}\_2 and \operatorname{ReO}\_3\operatorname{F}. M. S. B.** 

Action of potassium hydroxide on iodides. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 692—696).— By agitating PbI<sub>2</sub> with aq. KOH a mixture of insol. white oxyiodides (I) of Pb, K plumbite (II), and PbKI<sub>3</sub> are formed. With increasing [KOH] > N, the concn. of (II) increases only very slowly, whilst the % of I in (I) becomes const. and the % of Pb varies within narrow limits. With 0.02—0.375*M*-KOH, BiI<sub>3</sub> affords orange BiOI (III). With > 0.375*M*-KOH, the (III) first formed is transformed into the white oxyiodide, BiOI,2Bi<sub>2</sub>O<sub>2</sub>, which is formed immediately with > 3*M*-KOH and affords BiI<sub>3</sub> with dil. acid. KOH does not affect TII in the dark, but in the light, yellow TII is changed into the green form. This change is reversed by boiling with dil. acid. J. G. A. G.

**Pseudomorphic ferric hydroxide. I.** H. SIECKE (Kolloid-Z., 1934, 68, 175—178).—Forms of Fe(OH)<sub>3</sub> prepared under different conditions from K and Na ferrites have been characterised by their equilibrium composition in a  $H_2O$ -saturated atm. and by their catalytic effect on the decomp. of  $H_2O_2$ . E. S. H.

Heat content and lattice structure of active ferric oxide. R. FRICKE and P. ACKERMANN (Z. Elektrochem., 1934, 40, 630—640; cf. this vol., 133).— The energy content of active Fe<sub>2</sub>O<sub>3</sub>, prepared by dehydration of  $\alpha$ -FeO<sub>2</sub>H under various conditions, and measured by the heat of dissolution in 40.5% HF, is the higher the lower is the dehydration temp. From X-ray measurements the active oxide consists of colloidal particles with imperfect lattices. The catalytic activity of the oxides is related to these lattice imperfections. They are removed by heating.

Silver ferrite. X.  $\gamma$ -FeO<sub>2</sub>H from ferrous carbonate and the transformation of  $\gamma$ -FeO<sub>2</sub>H into  $\alpha$ -FeO<sub>2</sub>H. A. KRAUSE, K. MORONIÓWNA, and E. 4 B PRZYBYLSKI (Z. anorg. Chem., 1934, 219, 203—212).— By oxidising pptd. FeCO<sub>3</sub> with a current of air, preferably at 8°,  $\gamma$ -FeO<sub>2</sub>H (I) is formed. This, like  $\gamma$ -FeO<sub>2</sub>H (II) from Fe(OH)<sub>2</sub>, is a practically pure, cryst. ferrous acid which forms a positive sol in acids and a negative sol in alkalis. The conditions for the transformation  $\gamma$ -FeO<sub>2</sub>H  $\longrightarrow$  amorphous HFeO<sub>2</sub>  $\longrightarrow \alpha$ -FeO<sub>2</sub>H (goethite) differ in the two compounds and indicate that (I) forms smaller ring mols. than (II).

M. S. B.

Amorphous and crystallised hydrated oxides and oxides. XX. Ageing of ortho-ferric hydroxide to goethite as a discontinuous crystallisation or devitrification. A. KRAUSE, W. SWIAT-KOWSKA, H. TORNO, and J. STOCK (Z. anorg. Chem., 1934, 219, 213-224).-The ageing of two differently prepared Fe<sup>III</sup> orthohydroxides has been studied at 20° under N-NaOH. The formation of cryst. goethite is preceded by the formation of an amorphous gel which is comparable with a supercooled glass. The amorphous stage is most stable at the isoelectric point. The chain mols. formed by the amorphous hydroxide give ring mols. of amorphous HFeO2 which are the nuclei of goethite. The whole process is accelerated by rise of temp. M. S. B.

Complex salts of 2:2'-dipyridyl with bivalent iron.—See this vol., 1113.

Complex cobaltic salts with acid esters. J. MEYER [with H. MARX and C. REUTER] (Z. anorg. Chem., 1934, 219, 149—160).—By the action of EtHC<sub>2</sub>O<sub>4</sub> on [Co(NH<sub>3</sub>)<sub>4</sub>CO<sub>3</sub>]HCO<sub>3</sub>,H<sub>2</sub>O the compounds, [Co(NH<sub>3</sub>)<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>Et)<sub>2</sub>]C<sub>2</sub>O<sub>4</sub>Et (I),

 $[Co(NH_3)_4(C_2O_4Et)_2]C_2O_4Et$  (I),  $[Co(NH_3)_4C_2O_4]C_2O_4H$ ,  $[Co(NH_3)_4(C_2O_4H)_2]_2C_2O_4$ , and  $[Co(NH_3)_2(H_2O)_2(C_2O_4H)_2]_2C_2O_4$  have been obtained. All but (I) have probably the acid residue in the 1:6- instead of the 1:2-position. The malonic ester mol. could not be introduced into the tetrammine and diethylammine complex owing to its size. By the use of MeHSO<sub>4</sub> the compounds  $[Co(NH_3)_4CO_3]SO_4Me$  and  $[Co(NH_3)_4(H_2O)MeSO_4](SO_4Me)_2$  have been obtained. Two MeSO<sub>4</sub> groups in the 1:2-position in the tetrammine complex are not possible owing to steric effects. The second group must be H<sub>2</sub>O or MeOH.

M. S. B.

I. Action of mercuric oxide on nickel chloride and of nickel oxide on mercuric chloride. II. Action of mercuric oxide on chromous chloride. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1,697—698,699).—I. NiCl<sub>2</sub>,8NiO (I) is pptd. when HgO is agitated with aq. NiCl<sub>2</sub>, and when the wt. of HgO is > a limiting val., HgCl<sub>2</sub> is also pptd. A mixture of NiO and aq. HgCl<sub>2</sub> changes partly into HgO, NiCl<sub>2</sub>, and (I).

II. With little HgO, a sol.  $Cr^{II}$  oxychloride is formed, but with greater quantities all of the Cr is pptd. as  $Cr(OH)_3$  together with HgCl<sub>2</sub> and HgO. J. G. A. G.

Influence of substituents in bases and anions on the co-ordination index of a metal. V. Additive products of pyridine with the nickel salts of substituted acetic acids. A. ABLOV (Bull. Soc. chim., 1934, [v], 1, 731-738).—The following compounds are described : Ni(OAc)<sub>2</sub>,2C<sub>5</sub>H<sub>5</sub>N,2H<sub>2</sub>O; Ni(OAc)<sub>2</sub>,2C<sub>5</sub>H<sub>5</sub>N,0·5H<sub>2</sub>O;

H. J. E.

 $\begin{array}{c} Ni(CH_{2}Ph\cdot CO_{2})_{2}, 2C_{5}H_{5}N, 2H_{2}O; \\ Ni[CHPh(OH)\cdot CO_{2}]_{2}, 2C_{5}H_{5}N, 2H_{2}O; \\ Ni[CPh_{2}(OH)\cdot CO_{2}]_{2}, 2C_{5}H_{5}N, 2H_{2}O; \\ Ni(CH_{2}Cl\cdot CO_{2})_{2}, 6H_{2}O; Ni(CH_{2}Cl\cdot CO_{2})_{2}, 3C_{5}H_{5}N, 2H_{2}O; \\ Ni(CHCl_{2}\cdot CO_{2})_{2}, 4C_{5}H_{5}N; Ni(CCl_{3}\cdot CO_{2})_{2}, 4C_{5}H_{5}N; \\ Ni(Ch\cdot CH_{2}\cdot CO_{2})_{2}, 4C_{5}H_{5}N, H_{2}O; \\ Ni(2H_{2}-C_{10}H_{7}\cdot SO_{3})_{2}, 3C_{5}H_{5}N, 3H_{2}O. \\ The existence of constraint of the lit, was not confirmed \\ \\ \end{array}$ 

Ni $(2-C_{10}H_{7}\cdot SO_{3})_{2}, 3C_{5}H_{5}N, 3H_{2}O$ . The existence of several salts recorded in the lit. was not confirmed. There is a parallelism between the strength of the acid and the no. of mols. of base co-ordinated, and in the comparison with the corresponding Cu salts (cf. this vol., 13) the effect of the sp. affinity of Cu for  $\cdot$ CN is emphasised. The results are interpreted in terms of a sp. affinity of the acid residue (I) for the metal arising from a polarisation of the cation by (I). The term "index of co-ordination" loses its precise significance in so far as it is not always possible to distinguish whether the anion is in the interior or exterior zone of the central cation. J. G. A. G.

Amphoteric hydroxides as isopoly-bases. K. JAHR (Przemysł Chem., 1934, 18, 127–129).—A lecture. R. T.

Significance of isopoly-acids in the formation and structure of isopoly-compounds. Hydrolysis and aggregation of isopoly-bases. G. JANDER (Przemysł Chem., 1934, 18, 125–126, 126– 127).—Lectures. R. T.

X-Ray method of chemical analysis. E. WAINER (J. Amer. Chem. Soc., 1934, 56, 1653—1657).—A crit. study of procedure and the variables involved. The log time-density is a more suitable function for defining the plate characteristic for X-ray exposure than the usual log intensity-density. E. S. H.

Determination by extraction methods. P. BALAVOINE (Mitt. Lebensm. Hyg., 1934, 25, 82—86). —Errors and their elimination are discussed. Woy's formula is modified mathematically, the wt. of substance sought which is removed from x g. of sample being 4b-a; thus, 2x and x g. of sample are well mixed separately with the same sufficient vol. of solvent, the residues after evaporation of half of the supernatant liquid being weighed (a and b, respectively). An application to fat in chocolate is described. J. G.

Calculation of the results of conductometric titrations. J. MIKA (Z. anal. Chem., 1934, 98, 3— 12).—Mathematical expressions are given by the use of which more accurate results can be obtained than by the graphical method. A. R. P.

Measurement of hydrogen-ion concentration. I. SORAGTO (Ind. Sacc. Ital., 1933, 26, 511—517).— The Hellige comparator method is suitable for colourless and slightly coloured solutions where an accuracy of 0.2— $0.3 \ p_{\rm II}$  suffices; for darker solutions, and where higher accuracy is required, the potentiometric method must be used. Sb rods cooled slowly after casting are more suitable than plates obtained by the electrolysis of the chloride in COMe<sub>2</sub> solution.

Improvement of Mohr's titration by changing the form of the silver chloride precipitate. A. LOTTERMOSER and W. LORENZ (Kolloid-Z., 1934, 68, 201-203).—Addition of 5-10 c.c. of 0.1% agar solu-

J. P. O.

tion to the titrated liquid prevents the formation of large clots of AgCl in conc. Cl' solutions. E. S. H.

Determination of free iodine. P. LISBOA E COSTA (Bol. assoc. brasil. pharm., 1934, 15, 57—65).— 5% aq. PhOH is added and the HI formed is titrated with 0.1N-Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. CH. ABS.

Determination of small quantities of fluorides in water.—See B., 1934, 782.

Determination of sulphate in waters and mineral waters. O. HACKL (Z. anal. Chem., 1934, 98, 1—3).—Removal of  $SiO_2$  by evaporation is unnecessary before pptn. of the SO." with  $BaCl_2$ .

A. R. P. Automatic detection and control of hydrogen sulphide.—See B., 1934, 755.

Potentiometric determination of selenocyanate in presence of thiocyanate. P. SPACU (Z. anal. Chem., 1934, 98, 26—31).—In neutral solution using a Ag-wire indicator electrode KCNSe and KCNS can be determined successively by titration with AgNO<sub>3</sub>, but a small positive error is always obtained for KCNSe and a corresponding negative error for KCNS. A. R. P.

Devarda's method. E. CATTELAIN (J. Pharm. Chim., 1934, [viii], 20, 118—121).—Details are given for the exact determination of NO<sub>3</sub>' as NH<sub>3</sub> by Devarda's method. C. G. A.

Iodometric determination of nitric oxide by Mayrhofer's method.—See B., 1934, 798.

Gasometric micro-determination of phosphoric acid. E. KIRK (J. Biol. Chem., 1934, 106, 191-201).— $H_3PO_4$  (0.005-0.02 mg. of P) is determined (within  $\pm 0.5\%$  for > 0.01 mg. of P) by a modified pptn. as strychnine phosphomolybdate, purification by washing, dissolution in COMe<sub>2</sub>, and evaporation, and gasometric determination of C in the residue by Van Slyke's wet combustion method. R. S. C.

Production of arsenic mirrors in Marsh's apparatus and the determination of small amounts of arsenic. J. GANGL and J. V. SÁNCHEZ (Z. anal. Chem., 1934, 98, 81–96).—The wide mirror deposition tubes used in the standard apparatus may lead to loss of As. In a new apparatus the metal is deposited in a spiral capillary of quartz; it is dissolved out with a solution of ICl and the liberated I titrated with HCN and KIO<sub>3</sub> (cf. Kubina, A., 1929, 163). D. R. D.

Electrolytic conductivity method for determining carbon dioxide dissolved in water.—See B., 1934, 767.

Continuous determination and recording of the carbon dioxide content of gas mixtures.—See B., 1934, 798.

Potentiometric determination of cyanate. R. RIPAN-TILICI (Z. anal. Chem., 1934, 98, 23–26). The solution is titrated very slowly at 0° with 0·1N-AgNO<sub>3</sub> using a Ag-wire indicator electrode and applying a correction factor for the solubility of the AgCNO. A. R. P. Purification and physical properties of organic compounds. Specific heat of solids just below the m.p. as a criterion of purity. E. L. SKAU (J. Chim. phys., 1934, 31, 366—382).—Theoretical. The sp. heats of mixtures of  $C_6H_6$  with small amounts of  $C_{10}H_8$  are calc. The vals. increase rapidly near the m.p., whereas the sp. heat of pure  $C_6H_6$  shows little variation until the m.p. is attained. Traces of impurity can be detected in this way, but a eutectic mixture would show the same behaviour as a pure solid. R. S.

Determination of potassium as perchlorate. J. D'ANS [with T. KANAKOWSKY] (Angew. Chem., 1934, 47, 583—586).—The sample is dissolved in dil. HCl and treated at 20° with conc. aq. NaClO<sub>4</sub> nearly saturated (at 20°) with KClO<sub>4</sub>. The cryst. ppt. is washed with 1% HClO<sub>4</sub> in EtOH followed by EtOH, dried, and weighed. A small correction factor for the amount of KClO<sub>4</sub> sol. in the final mixture is applied. The maintenance of a const. temp. is important. NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, or MgSO<sub>4</sub> does not interfere; hence the method is applicable to kainite etc. When NH<sub>4</sub> salts are present the sample is treated with aq. NaOH or, alternatively, NH<sub>4</sub>ClO<sub>4</sub> is quantitatively removed from the ppt. by heating at 380—450° for 20—30 min. A rough technique suitable for mines is described. F. O. H.

Separation of barium from calcium by the sulphate method. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anal. Chem., 1934, 98, 12—22).— BaSO<sub>4</sub> can be pptd. free from CaSO<sub>4</sub> from solutions of the two chlorides containing 2—5 c.c. of N-HCl in 200 c.c. by slow addition of  $0.2N-H_2SO_4$  at room temp. with vigorous stirring; the ppt. should be filtered next day, washed with hot 1% H<sub>2</sub>SO<sub>4</sub>, then with H<sub>2</sub>O, and ignited apart from the paper.

A. R. P.

Determination of magnesium in aluminium and duralumin.—See B., 1934, 800.

Determination of zinc in presence of uranium. W. R. WIGGINS and C. E. WOOD (J.S.C.I., 1934, 53, 254T).—Two methods for the determination of Zn, viz., pptn. of Zn–8-hydroxyquinoline in alkaline tartrate or in alkaline malate solution, were compared. In each case the ppt. was brominated to the 5 : 7-Br<sub>2</sub>derivative volumetrically, and close agreement between experimental and theoretical vals. obtained.

[Electrolytic] determination of zinc.—See B., 1934, 764.

Application of quantitative spectrographic analysis to metallurgical problems.—See B., 1934, 764.

Determination of copper with [ammoniacal] potassium cyanide solution. HARBAUER and GEORGI (Chem.-Ztg., 1934, 58, 712-713).—In the titration of Cu<sup>••</sup> with KCN results are low unless at least 5 g. of  $\rm NH_4$  salt are present in 150-200 c.c. of the solution. A large excess of free  $\rm NH_3$  must be avoided and the KCN solution standardised on a known Cu solution. It will then remain unaltered for some weeks if kept in a cool, dark place. Metals which form CN complexes or insol. metal salts must be absent. With care as to these points the method is almost equal to the electrolytic one for accuracy. C. I.

Mercurimetry and its applications in chemical and biochemical analyses. A. IONESCO-MATIU (Bull. Soc. Chim. biol., 1934, 16, 970–992).—Alecture.

Volumetric determination of mercuric and mercurous iodides. D. Köszeci and N. Tomori (Pharm. Zentr., 1934, 75, 532–535).—1—1·3 g. are boiled with 10 c.c. of 2N-KOH and 3 c.c. of 40% aq. CH<sub>2</sub>O; the mixture is cooled, diluted to 200 c.c., and filtered. In the approved method, 10 c.c. of filtrate (I) are acidified with AcOH, treated with 30 c.c. of Cl-H<sub>2</sub>O, boiled for 20 min., and the resulting KIO<sub>3</sub> is determined by titration with 0·1N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> after adding 0·5 g. of KI and excess of HCl. Alternatively, the I' in (I) may be determined titrimetrically with AgNO<sub>3</sub> or KBrO<sub>3</sub> solutions. S. C.

Electrometric titration of manganese according to Volhard. E. I. ACHUMOV and B. B. VASILIEV (Zavod. Lab., 1934, 3, 407–409).—Minor modifications of Brann and Clapp's method (A., 1929, 286) are proposed. R. T.

Determination of the "true" and apparent manganese dioxide content of pyrolusite. H. DITZ (Z. anorg. Chem., 1934, 219, 113—118).—The methods proposed for the determination of the different stages of oxidation of Mn in pyrolusite, and the influence on the result of the amount and nature of the oxides of Fe present, are discussed. M. S. B.

Vogel's thiocyanate test for cobalt in presence of iron. H. DITZ and R. HELLEBRAND (Z. anorg. Chem., 1934, 219, 97—104).—By substituting  $COMe_2$ for  $C_5H_{11}$ ·OH-Et<sub>2</sub>O mixtures in Vogel's reaction the test for Co becomes much more sensitive, but the sensitivity in presence of a little Fe is much < for Co alone, independently of the method used for the preliminary separation of Fe. M. S. B.

Rapid determination of small amounts of tungsten in ores etc.—See B., 1934, 800.

Measurement of strong polonium preparations. G. ORTNER and G. STETTER (Physikal. Z., 1934, 35, 563-564).—The method uses an ionisation chamber filled with pure  $N_2$ . A. J. M.

Volumetric determination of titanium. E. TSCHIECH (Pharm. Zentr., 1934, 75, 513—515).—The solution containing  $Ti(SO_4)_2$  and  $H_2SO_4$  is run through a Jones reductor into aq.  $Fe_2(SO_4)_3$ , and the  $Fe^{II}$  produced titrated with aq.  $KMnO_4$ . Fe in the Ti is determined by reducing a separate portion with NaHSO<sub>3</sub> or SnCl<sub>2</sub> and titrating back, and its equiv. is deducted from the Ti found. A. G.

Determination of bismuth in copper.—See B., 1934, 764.

Determination of niobium and tantalum in wolframite. J. A. TSCHERNICHOV and (MISS) M. P. KARSAJEVSKAJA (Z. anal. Chem., 1934, 98, 97–107). —The usual method of removing W by aq. NH<sub>3</sub> is not satisfactory, since appreciable amounts of W are found with the earth acids. In the new procedure, heavy metals are removed by successively digesting the mineral with HCl, aqua regia, and aq. NH<sub>3</sub>-NH<sub>4</sub>NO<sub>3</sub>, then evaporating the residue with  $H_2SO_4$  and HF, followed by treatment with aq.  $NH_3$  and washing with  $NH_4NO_3$ ; it is then fused with  $K_2S_2O_7$ , and extracted with tartaric acid. The solution is pptd. with  $H_2S$  and then with cupferron. This ppt. is fused with  $Na_2CO_3$ , W extracted with  $H_2O$ , and the residue fused with  $K_2S_2O_7$ . It is then treated by the method of Schoeller (A., 1929, 1160; 1932, 356). D. R. D.

Construction of thermostats and cryostats. A. LALANDE (J. Chim. phys., 1934, 31, 439-457).—The principles which should govern the construction and regulation of baths of const. high or low temp. are discussed. M. S. B.

Automatic cryostat. A. I. SCHATTENSTEIN (Z. Elektrochem., 1934, 40, 653—655; cf. A., 1930, 1394). —A 2·5-litre Dewar vessel containing EtOH, fitted with stirrer and thermo-regulator (I), is cooled by a thick Cu strip, one end of which is in a large insulated vessel containing solid CO<sub>2</sub>. An electric heating coil operates in conjunction with (I). A temp. const. to  $0.005^{\circ}$  is attained down to  $-70^{\circ}$ . H. J. E.

Micro-burner. W. STAHL (Chem.-Ztg., 1934, 58, 682). E. S. H.

Kerr effect, and light distribution with the Kerr cell. A. NARATH (Kinotech., 1933, 15, 395–399).—Theoretical deductions are supported by experiment. The Kerr const. for PhNO<sub>2</sub> (546·1 m $\mu$ ; 20°) is  $3\cdot61 \times 10^{-5}$ . CH. Abs.

Technique of measurement of radiation by the rectifying layer selenium cell. R. SEWIG (Physikal. Z., 1934, 35, 564—565).—The use of rectifying layer Se cells for meteorological investigations is discussed (cf. this vol., 272). A. J. M.

Technique of measurement of radiation by the rectifying layer selenium cell. W. GRUNDMANN and L. KASSNER (Physikal. Z., 1934, 35, 566—567; cf. preceding abstract).—Reasons for the unsuitability of these cells for meteorological work are given.

A. J. M.

amounts.

Metal contact photo-electric cell. P. SELENYI (Physica, 1934, 1, 781-782).—A question of priority (cf. de Boer and van Geel, this vol., 624). H. S. P.

Optical factors in cæsium-silver oxide photoelectric cells. H. E. IVES and A. R. OLFIN (J. Opt. Soc. Amer., 1934, 24, 198—205).—The emissive power is greater at the red end of the spectrum. The photoelectric emission behaves as though it originates in a thin surface layer. C. W. G.

Valve action and photo-effect of the silicon carbide detector. P. SPECHT (Z. Physik, 1934, 90, 145—165).—The barrier layer effect which appears only with small currents has a large valve action, whilst the vol. effect is small. The photo-effect, which shows saturation with increasing light intensity, is a max. at points of max. valve action. A. B. D. C.

Design and construction of photo-electric cells. R. V. JONES (J. Sci. Instr., 1934, 11, 247-257).—The principles of design are discussed, and the construction of a simplified form is described. C. W. G. Quantitative photographic photometry. W. H. E. BANDERMANN (Z. Physik, 1934, 90, 266– 278). A. B. D. C.

Reflectivity of intermetallic systems. J. WULFF (J. Opt. Soc. Amer., 1934, 24, 223—226).--Measurements on a no. of Mg systems are recorded. C. W. G.

Source of ultra-violet continuous radiation. O. S. DUFFENDACK and J. H. MANLEY (J. Opt. Soc. Amer., 1934, 24, 222).—A low-voltage arc in  $H_2$  is satisfactory. C. W. G.

Determination of the dielectric constant of dilute aqueous solutions by means of highfrequency oscillations. F. P. HENNIGER (Ann. Physik, 1934, [v], 20, 413—440).—The dielectric const. ( $\varepsilon$ ) of aq. solutions of CuSO<sub>4</sub>, La(NO<sub>3</sub>)<sub>3</sub>, and K<sub>4</sub>Fe(CN)<sub>6</sub> has been determined at 20° by means of a resonance method for a range of concess. The electrolyte solution is compared with aq. KCl of equal conductivity. The frequency,  $2 \times 10^{-7}$  ( $\lambda$ =15·02 $\pm$ 0·02 m.), falls in the region of greatest variation of  $\varepsilon$ with  $\lambda$ . Results are in good agreement with the theory of Debye and Falkenhagen. R. S. B.

Mass spectrograph. J. MATTAUCH and R. HERZOG (Z. Physik, 1934, 89, 786-795).

A. B. D. C.

Investigation of ionisation chambers and production of rays of given range. G. DIECK (Z. Physik, 1934, 90, 71—111). A. B. D. C.

Crystal detectors. J. N. FRERS (Z. Elektrochem., 1934, 40, 612—624).—Current-voltage characteristics were studied for the systems Pt|CuBr; Pt|Ag<sub>2</sub>S; Pt|Cu<sub>2</sub>S; Pt|PbS; Pt|MoS<sub>2</sub>; Pt|FeS<sub>2</sub>; Pt|ZnO; FeS<sub>2</sub>|PbS; ZnO|PbS; ZnO|FeS<sub>2</sub>, the detector being heated, if necessary, to secure conduction. The mechanism of crystal detector action is discussed.

H. J. E. Apparatus for exact dosage of volatile liquids in gaseous form. O. EICHLER (Arch. exp. Path. Pharm., 1934, 175, 399–400).—The liquid (e.g.,  $CHCl_3$ ) is heated in an apparatus whereby the source of heat is controlled by the v.p. of the volatilised fluid. The vapour escapes through a capillary tube of known dimensions and mixes with air in calculable

F. O. H.

Oxidation of sulphurous acid. I. Dilatometric technique. R. C. HOATHER and C. F. GOODEVE (Trans. Faraday Soc., 1934, **30**, 626–629). —A dilatometric apparatus is described for following the reaction  $SO_2$  (aq.)  $+0.5O_2$  (aq.)  $=SO_3$  (aq.) by observing the diminution in vol. R. S. B.

Efficiency of laboratory condensers. J. FRIED-RICHS and H. VON KRUSKA (Chem. Fabr., 1934, 7, 284—287).—Details are given of the cooling surfaces, heat transfer coeffs., k, and limiting rates of condensation of Et<sub>2</sub>O vapour of a no. of different types of laboratory condenser (I). The West (I) has the highest k (0.85) of those studied, and although large sizes are not practicable it is excellent for fractionations. The Dimroth (I) (k=0.75) may be made with a very large surface, but fractions easily mix; it is recommended for extraction. Other vals. of k
are: spiral 0.62, Allihn 0.56, Mach 0.55, Liebig 0.47. H. F. G.

Use of mica in place of platinum wire in analytical work. V. I. PODGORBUNSKI and I. F. SCHTSCHEPETUNIN (Sovetsk. Zolotoprom., 1933, No. 3-4, 20-22).—Muscovite and phlogopite micas arc satisfactory. CH. Abs.

Vapour density determinations by an optical method. M. WEISS (Ann. Physik, 1934, [v], 20, 557-568).—A method of determining v.d. of gases and vapours to within 0.1% is based on the fact that the mol. refractivity of a gas is independent of pressure, within wide limits. It has been used to determine the v.d. of air, CO<sub>2</sub>, Et<sub>2</sub>O, EtCl, and EtNO<sub>2</sub> at 20° and 100°. The mol. refractions and polarisabilities of these substances and C<sub>6</sub>H<sub>6</sub> were also determined. A. J. M.

Sensitive float method for the determination of small changes in the density of liquids, particularly water. H. MOSER (Physikal. Z., 1934, 35, 682-683).—A trustworthy and comparatively rapid method for determining changes in d, accurate to  $\pm 6 \times 10^{-7}$ , is described. The method requires 140 c.e. of the liquid, and has been chiefly used in the examination of the isotopic constitution of H<sub>2</sub>O.

A. J. M.

Measurement of deposited dust from the atmosphere. H. W. GONELL (Chem. Fabr., 1934, 7, 300-303).—Rain-H<sub>2</sub>O drains off a slightly inclined Zn tray into a 1-litre vessel in which entrained dust deposits. The tray is painted internally with lubricating oil; this is finally dissolved in  $C_6H_6$ , which is added to the H<sub>2</sub>O. The apparatus is finally cleaned with Et<sub>2</sub>O. A wire gauze of 2 mm. mesh over the

tray keeps off leaves, insects, etc. An exposure of 1-2 weeks affords sufficient dust for microscopical study. C. I.

Copper apparatus for the determination of m.p. C. F. LINSTRÖM (Chem. Fabr., 1934, 7, 270).— The block is so designed that the substance may be observed from a direction perpendicular to the direction of the incident light, which is provided by a small electric lamp and focussed through a hole in the block by means of a condenser. Evolution of gas, changes of colour, etc. during heating may be clearly detected. H. F. G.

Use of dioxan as solvent in the determination of mol. wt. by the cryoscopic method. A. E. OXFORD (Biochem. J., 1934, 28, 1325—1329).— Specially purified dioxan (b.p.  $101.4^{\circ}$ , f.p.  $11.67^{\circ}$ ) is suitable for use as solvent in the cryoscopic determination of mol. wt. (K=47) of many cryst. org. compounds, but cannot accurately be used for sugars and NH<sub>2</sub>-acids owing to low solubility, for substances containing H<sub>2</sub>O of crystallisation (these sharing their H<sub>2</sub>O with the solvent), or for carolic acid. A semimicro-method of determination has been devised.

Micro-determination of mol. wt. of volatile liquid compounds. A. F. COLSON (Analyst, 1934, 59, 529-531).—The method is based on that of Blackmann (A., 1910, 643). E. C. S.

Nomenclature of the hydrogen isotopes and their compounds. E. J. CRANE (Science, 1934, 80, 86-89). L. S. T.

Ancient Indian iron. S. C. BRITTON (Nature, 1934, 134, 238-240, 277-279). L. S. T.

## Geochemistry.

Atmospheres of the stars. H. N. RUSSELL (J. Franklin Inst., 1934, 218, 127–142).—A review of existing knowledge of stellar spectra and of the deductions which can be made therefrom concerning the composition, temp., and general conditions prevailing in the atm. of stars. D. R. D.

Vertical distribution of ozone in the atmosphere. F. W. P. GÖTZ, A. R. MEETHAM, and G. M. B. DOBSON (Proc. Roy. Soc., 1934, A, 145, 416—446).— Spectroscopic observations of the light from the zenith blue sky while the sun is rising or setting have been made at Arosa for a year. The height and distribution of the  $O_3$  have been found under various meteorological conditions for different seasons of the year. The average height of the  $O_3$  in Switzerland is about 22 km. above sea-level, and this is distributed mainly between the ground and 35 km. The main changes in  $O_3$  content are centred at a height of about 10— 20 km. The form of the vertical distribution depends chiefly on the total  $O_3$  present. L. L. B.

Transparency of the lower atmosphere and its content of ozone.—See this vol., 1054.

Waters of Mt. Meru, Tanganyika. D. STURDY, W. E. CALTON, and G. MILNE (J. E. Africa Uganda Nat. Hist. Soc., 1932, No. 45-46, 1-38).—Analytical data for the H<sub>2</sub>O and for lake-edge salt deposits are recorded. CH. ABS.

Absorption of light by sea-water. E. B. STEPHENSON (J. Opt. Soc. Amer., 1934, 24, 220—221). —In the formula  $I=I_0\times10^{-\gamma D}$ , where I is in footcandles and D is in ft.,  $\gamma=0.008\pm0.001$  for clear open sea, and 0.030 in Panama Bay. C. W. G.

Mud of Lake Canieris. J. KUPZIS (Latvij. Univ. Raksti, 1934, 2, 357–382).—The mud is strongly alkaline and is rich in  $CaSO_4$ , Fe, Al, sulphide-S, and amines. A. G.

San Francisco Mountains meteorite. S. H. PERRY (Amer. J. Sci., 1934, [v], 28, 202–218).—An analysis (Fe 91.91, Ni 7.83%) and full description are given. C. W. G.

Quantitative study of pleochroic haloes. I. G. H. HENDERSON and S. BATESON. II. G. H. HENDERSON and L. G. TURNBULL (Proc. Roy. Soc., 1934, A, 145, 563—581, 582—591).—I. A recording microphotometer has been constructed for measuring the amount of darkening in pleochroic haloes. Records of U haloes in biotite are given. The ranges of all

I. A. P.

the  $\alpha$ -particles, including U-I, agree with the features of the halo.

II. A biotite from Renfrew, Ontario, has been studied by the above method. The ring radii agree with the known ranges of the  $\alpha$ -particles of the U and Ac families. No evidence is found of any change in the ranges of the  $\alpha$ -particles in the course of geological time. L. L. B.

Dickite in the Rôseki deposits in Shôkôzan. B. YOSHIKI (Proc. Imp. Acad. Tokyo, 1934, 10, 417— 420).—An analysis and dehydration phenomena are recorded. C. W. G.

Chemical formula of basaltic hornblende. Y. KAWANO (Proc. Imp. Acad. Tokyo, 1934, 10, 349– 352).—Analyses of hornblende from Korea and Lukow lead to the formulæ  $(O,OH,F)_{2\cdot0}(Ca,Na,K)_{2\cdot8}(Mg,Fe^{II},Mn,Fe^{III},Ti)_{5\cdot1}[(Si,Al)_{4\cdot0}O_{11\cdot0}]_2$  and  $(O,OH,F)_{2\cdot0}(Ca,Na,K)_{3\cdot1}(Mg,Fe^{II},Mn,Fe^{III},Al,Ti)_{5\cdot0}[(Si,Al)_{4\cdot0}O_{11\cdot0}]_2$ . C. W. G.

Escape of helium from minerals and rocks. B. G. CHLOPIN, E. K. GERLING, and E. M. JOFFE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 121– 127).—He is given off more readily from the minerals uraninite and chlopinite by heating to  $400-600^{\circ}$  in presence of H<sub>2</sub>, which penetrates into the mineral and is adsorbed. The results suggest that the He is held in the mineral in at least two forms. CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and their homologues are more effective than H<sub>2</sub> at  $600-700^{\circ}$ . They probably form active H. A gas reacting chemically with the mineral and changing its structure should also accelerate the loss of He. H. J. E.

Chromium. III. Occurrence of chromium in certain soils and plants in the province of Quebec. A. DINGWALL and H. T. BEANS (J. Amer. Chem. Soc., 1934, 56, 1666—1667). E. S. H.

Distribution of chromium and manganese. G. von HEVESY, A. MERKEL, and K. WURSTLIN (Z. anorg. Chem., 1934, 219, 192—196).—The Cr and Mn content of a no. of rocks has been determined by X-ray spectroscopy. Deep-lying rocks have the largest Cr content and essexite the least. The mean val. for volcanic rock is 1 part in 2000. Essexite is also poorest in Mn and diorite richest, the mean val. being 1 part in 1000. M. S. B. Determination of the age of certain minerals. G. H. HENDERSON (Proc. Roy. Soc., 1934, A, 145, 591-598).—The presence of Ac in pleochroic haloes of the U types leads to a new method of determining the age of certain minerals. The method is applied to three biotites. L. L. B.

Microscopical study of the siliceous sand of Kliwa; its origin and the conditions of deposition. M. G. FILIPESCO (Bull. Acad. Sci. Roumaine, 1932, 15, 141—146).—The sand consists of a mixture (10:1) of angular and rounded particles, the former being marine and the latter air-borne. The heavy minerals are derived from metamorphic rocks, and the quartz grains are associated with fragments of quartzite. The quartz and grits of Kliwa are all derived from the Dobruja ridge, which contains, *inter alia*, quartzitic rocks and schists. H. F. G.

X-Ray and colloid-chemical study of clay. W. HOFMANN, K. ENDELL, and D. WILM (Angew. Chem., 1934, 47, 539—547).—A detailed review of work carried out during the past decade. H. F. G.

X-Ray diagrams of different peranthracites and true anthracites. P. CORRIEZ (Compt. rend., 1934, 199, 410—412).—Anthracites show a foliated structure similar to that of graphite, but the separation between successive layers is slightly > in the latter case. A few of these layers form the unit cell of anthracite. The development of the lattice in other directions, however, varies from sample to sample, the degree of organisation increasing as the amounts of gas developed from the sample on heating decrease, finally reaching graphite structure in peranthracite from Arèches. X-Ray methods afford a method of distinguishing between anthracites and peranthracites.

J. W. S.

Free alumina in soils. F. HARDY (Nature, 1934, 134, 326-327).—Further evidence of the presence of free gibbsitic alumina in bauxites, laterites, and lateritic soils and its absence from most tropical red earths and kaolinitic earths has been obtained by determinations of heats of wetting. This test may be a quicker and simpler alternative to the alizarin test for detecting free  $Al_2O_3$  in the products of rock weathering and in soils. L. S. T.

## Organic Chemistry.

Physico-chemical problems of organic chemistry. E. HERTEL (Z. Elektrochem., 1934, 40, 405– 413).—A lecture. E. S. H.

Spacial configuration of organic molecules and molecular aggregates. H. MARK (Z. Elektrochem., 1934, 40, 413–424).—A lecture. E. S. H.

Experimental problems resulting from a rational system of organic compounds. H. G. GRIMM (Z. Elektrochem., 1934, 40, 460-462).—A lecture (cf. Naturwiss., 1929, 17, 535, 557).

E. S. H.

Symmetrical disubstituted methanes from members of optically active homologous series of disubstituted carboxylic acids and their derivatives. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1934, 106, 173—178; cf. this vol., 55).— The conversion of *l*- $\beta$ -methylhexoic acid into  $\delta$ -methylheptane (I) is described. Optically inactive (I) is also obtained from *d*- $\alpha$ -bromo- $\delta$ -methylheptane. Optically inactive  $\varepsilon$ -methylnonane is derived from (—)- $\beta$ methylheptoic acid and from (—)- $\alpha$ -bromo- $\varepsilon$ -methylnonane. 1- $\Delta^{\beta}$ -Hepten- $\delta$ -ol, b.p. 157°/760 mm., [ $\alpha$ ]b —0-8° (H phthalate, [ $\alpha$ ] $\overline{\beta}$ <sup>3</sup>—1.25° in C<sub>6</sub>H<sub>6</sub>), is converted into inactive *di*-n-propylcarbinol, b.p. 152— 153°/760 mm. H. D.

Peroxide effect in addition of reagents to unsaturated compounds. VIII. Addition of hydrogen iodide to ethylene compounds. M. S. KHARASCH and C. HANNUM (J. Amer. Chem. Soc., 1934, 56, 1782—1784).—Addition of anhyd. HI to  $C_3H_6$  in presence of ascaridole (I) or NHPh<sub>2</sub> (in a vac.) gives  $Pr^{\beta}I$  (the "normal product," *i.e.*, the product analogous to that obtained using HBr in presence of antioxidant) in each case. Similarly,  $\Delta^{\alpha}$ -butene affords sec.-BuI, whilst  $\delta\delta$ -dimethyl- $\Delta^{\alpha}$ pentene gives (cf. Whitmore and Homeyer, this vol., 54)  $\beta$ -iodo- $\delta\delta$ -dimethylpentane. Allyl bromide and HI at  $-38^{\circ}$  or room temp. in presence of (I) give a good yield of CH<sub>2</sub>Br·CHMeI (II); at  $-38^{\circ}$  in presence of NHPh<sub>2</sub> and in a vac., addition does not occur, whilst at 0° a poor yield of (II) (accompanied by much tar and some  $Pr^{\beta}I$ ) results. H. B.

Rearrangement during pyrolysis of butenes. C. D. HURD and A. R. GOLDSBY (J. Amer. Chem. Soc., 1934, 56, 1812–1815).—When  $\Delta^{a}$ -butene (I) is passed through a Pyrex tube (contact time 9-12 sec.) at 600°, 650°, and 700°, the extent of decomp. is 10, 57, and 87%, respectively. The gaseous products formed are  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_3H_6$ , butadiene (trace), and (at 650° and 700°, but not at 600°)  $\Delta^{\beta}$ -butene (II) (63: 37 mixture of cis- and trans-forms). The extent of decomp. of (II) at  $650^{\circ}$  and  $700^{\circ}$  is 44 and 80%, respectively, with contact time 12-13 sec. Rearrangement into (I) occurs, and the recovered (II) has the same composition as the original material; the other gaseous products are as above. isoButene is not produced from (I) or (II). Mixtures of  $C_4H_{10}$ , C<sub>4</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>6</sub> are separable with a Frey-Hepp column (B., 1933, 581). H. B.

Polymerisation of butadiene, isoprene, dimethylbutadiene, and cyclohexadiene. N. D. ZELINSKI, Y. I. DENISENKO, M. S. EVENTOVA, and S. I. KHROMOV (Sintet. Kauchuk, 1933, No. 4, 11— 14).—In contact with AlCl<sub>3</sub>,  $\beta\gamma$ -dimethylbutadiene polymerises in 24 hr. to a substance different from that obtained on slow polymerisation. Isoprene behaves similarly. Pure butadiene (I) does not polymerise readily, but (I) containing 20—50% of other hydrocarbons polymerised rapidly. 1:3- and 1:4cycloHexadiene polymerise only when heated.

CH. ABS.

Oxygen additive compounds of acetylenes. C. A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 1822—1823).—CH:CR, CR:CR', and CR:CHal (R and R' are alkyl and aryl) acquire oxidising properties after contact with air or  $O_2$ ; peroxide formation probably occurs. H. B.

Addition of methyl alcohol to vinylacetylene. D. B. KILLIAN, G. F. HENNION, and J. A. NIEUW-LAND (J. Amer. Chem. Soc., 1934, 56, 1786–1787).— CH<sub>2</sub>:CH·C:CH and MeOH in presence of BF<sub>3</sub> (prep.: A., 1933, 932), HgO, and CCl<sub>3</sub>·CO<sub>2</sub>H give the  $Me_2$ acetal, b.p. 63–65°/25 mm., of  $Me \beta$ -methoxyethyl ketone, b.p. 139–140°/745 mm. H. B.

Addition of organic acids to alkylacetylenes. G. F. HENNION and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 1802—1803).—CH:CAlk and RCO<sub>2</sub>H in presence of BF<sub>3</sub>,Et<sub>2</sub>O (prep.: A., 1933, 932), HgO, and MeOH give CH<sub>3</sub>:CAlk·O·COR (I) and varying amounts of COMeAlk (II). (I) are hydrolysed (EtOH-KOH) to (II). The following are described:  $\alpha$ -methylvinyl, b.p. 92—94°/736 mm., and  $\alpha$ -n-amylvinyl, b.p. 92—94°/40 mm., acetates;  $\alpha$ -n-butylvinyl acetate, b.p. 74—75°/39 mm., chloroacetate, b.p. 100— 101°/20 mm., and benzoate, b.p. 147—149°/21 mm. H. B.

Chlorofluoro-ethanes and -ethylenes. E. G. LOCKE, W. R. BRODE, and A. L. HENNE (J. Amer. Chem. Soc., 1934, 56, 1726—1728).—Pentachlorofluoroethane (I), b.p. 137.9° (corr.)/760 mm., m.p. 101.3°, s-tetrachlorodifluoroethane (II), b.p.92.8° (corr.)/ 760 mm., m.p. 24.65°,  $\alpha\alpha\beta$ -trichloro- $\alpha\beta\beta$ -trifluoroethane (III), b.p. 47.7° (corr.)/760 mm., m.p.  $-36.4^{\circ}$ , s-dichlorotetrafluoroethane (IV), b.p. 3.8° (corr.)/760 mm., CCl<sub>2</sub>F·CF<sub>3</sub>, b.p. about  $-2^{\circ}$  (corr.)/760 mm., and CClF<sub>2</sub>°CF<sub>3</sub>, b.p.  $-38^{\circ}$  (corr.)/760 mm., are obtained from C<sub>2</sub>Cl<sub>6</sub> and SbCl<sub>2</sub>F<sub>3</sub> (Midgley and Henne, B., 1930, 651). CCl<sub>3</sub>·CClF<sub>2</sub>, b.p. 91.5° (corr.)/760 mm., m.p. 40.6° (lit. 52°), and  $\alpha\alpha\alpha$ -trichloro- $\beta\beta\beta$ -trifluoroethane, b.p. 45.8° (corr.)/760 mm., m.p. 13.2°, are prepared by chlorination of CHCl<sub>2</sub>·CHF<sub>2</sub> and CH<sub>2</sub>Cl·CF<sub>3</sub>, respectively. (I) and Zn in EtOH give trichlorofluoroethylene, b.p. 72·1° (dibromide, m.p. 122·5°); (II) similarly affords cis., b.p. 21·1°, m.p.  $-130.5^{\circ}$ , and trans., b.p. 22°, m.p.  $-110.3^{\circ}$ ,  $-\alpha\beta$ -dichloro- $\alpha\beta$ -difluoroethylenes; (III) yields CCIF:CF<sub>2</sub>, m.p.  $-23^{\circ}$  (dibromide, bromide, b.p. 46·4°, m.p.  $-112^{\circ}$ ). s-Dichlorodibromodifluoroethane has b.p. 139·7°, m.p. 32·5°. Numerous other physical data are given. H. B.

Allylic transformations. III. Dichloropropylenes. A. KIRRMANN, PACAUD, and H. DOSQUE (Bull. Soc. chim., 1934, [v], 1, 860-871; cf. A., 1932, (Duff. Soc. enhance, 1994, 1995, 1996, 1997, 1996, 1997, 600).—The following reactions indicate that com-pounds, CHX:CH·CH<sub>2</sub>X, are tautomeric with, but more stable than, CH<sub>2</sub>:CH·CHX<sub>2</sub> (X=halogen), but that the latter have an independent existence. Acraldehyde and PCl<sub>5</sub> give  $\gamma$ -chloroallyl chloride (I) (229%) acrylidence dichloride (II) (169%) come Actationly de and 1 Cl<sub>5</sub> give  $\gamma$ -chlorodaly chloride (1) (32%), acrylidene dichloride (II) (16%), some CHCl<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>Cl (III), b.p. 143—144° (also obtained from CH<sub>2</sub>Cl·CH<sub>2</sub>·CHO and PCl<sub>5</sub>), and (?) ace-trichloro- $\beta$ -chloromethylpentan- $\gamma$ -ol, b.p. 135—137°/19 mm. (I) with hot NaOMe or NaOEt gives  $\gamma$ -chloroallyl Me ether (IV), b.p. 107—108°, and Et ether; b.p. 126— 127° respectively. (II) gives (IV) more slowly with 127°, respectively. (II) gives (IV) more slowly, with traces of derivatives of (II). CHCl:CH·CH<sub>2</sub>I and MgPrBr at  $-10^{\circ}$  give a mixture, containing probably a little cyclohexene. (II) with MgPhBr gives a poor yield of the mixture obtained from (I). (I) with NHEt<sub>2</sub> in cold Et<sub>2</sub>O gives slowly dimethyl- $\gamma$ -chloro-allylamine, b.p. 57—58°/17 mm. (picrate, m.p. 91°; platinichloride, m.p. 169—170°); (II) gives a poor yield of a base (picrate, m.p. 91°). (I) or (II) with NaOAc in AcOH at 110° gives a 50% yield of ?-chloropropenyl acetate, b.p. 57 /15 mm., hydrolysed by cold NaOH to y-chloroallyl alcohol (V), b.p. 57°/14 mm. (phenylurethane, m.p. 75°), which with  $PCl_3$  gives (I). (I) and Ag<sub>2</sub>O in cold H<sub>2</sub>O give (V) and di- $\gamma$ -chloroallyl ether, b.p. 88-91°/15 mm. (tetrabromide, b.p. 197°/ 19 mm.), obtained in lower yield also from (II) and CHBr:CH·CH<sub>2</sub>Br. CaBr<sub>2</sub> and hot (I) give much CHCI:CH·CH<sub>2</sub>Br (VI). CaI<sub>2</sub> reacts more rapidly with (I) than with (II). y-Chloroallyl iodide has b.p. 157°/ 760 mm., 51°/16 mm. (I) does not react with Zn in hot COMe2 or Mg, but with " mol." Na violently gives

gaseous products. (VI), however, reacts with Mg to give a mixture. (III) with NaOAc in AcOH gives  $\gamma\gamma$ -dichloropropyl acetate (78%), b.p. 85°/18 mm., hydrolysed by cold 0.2N-NaOH to  $\gamma\gamma$ -dichloropropyl alcohol, b.p. 82—83°/20 mm. R. S. C.

Saturated solid alcohol from the urine of pregnant mares.—See this vol., 1126.

Synthesis of higher alcohols from water-gas under pressure. E. M. BOTSCHAROVA and B. N. DOLGOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 115—120).—41% of oily products (higher alcohols 67, esters 7.2, acids 4.7, hydrocarbons 1%) are obtained by passing  $1:1 \text{ CO-H}_2$  over  $4ZnO-V_2O_5$ -KOH catalyst at  $350-450^{\circ}/220$  atm. Many other catalysts gave less satisfactory results. R. T.

Action of polyhydric alcohols on periodic acid and alkali periodates. L. MALAPRADE (Bull. Soc. chim., 1934, [v], 1, 833-852).-For elucidation of these reactions the following analytical methods are used. Org. and mineral acids are titrated with NaOH in presence of HIO<sub>4</sub> using thymolphthalein, as this changes to blue when the HIO<sub>4</sub> is converted into Na<sub>2</sub>H<sub>3</sub>IO<sub>6</sub>. Aldehydes are determined by a modification of Dœuvre's method or by the NaHSO<sub>3</sub> method using KIO<sub>3</sub> in dil. AcOH for oxidation of the excess SO<sub>3</sub>" (aldehyde-H sulphite compounds do not reduce KIO<sub>3</sub>-dil. AcOH). The accepted course of the HIO<sub>4</sub> oxidation is verified by these methods for inositol, tartaric, gluconic, and saccharic acids, glucose, and dihydroxyacetone. By use of a deficiency of  $HIO_4$  it is shown that the reaction proceeds stepwise, thus : (a) OH·CHR·CHR'·OH  $\longrightarrow$  RCHO+R'CHO; (b) if R or R'=R''·CH·OH, then OH·CHR''·CHO  $\rightarrow$ R''CHO+HCO<sub>2</sub>H, and so on. HIO<sub>4</sub> also oxidises ketones, which is interpreted by means of the hydrated forms of the latter. HIO4 oxidation is thus generalised in the equation  $O\dot{H} \cdot CRR' \cdot CR'R'' \cdot O\ddot{H} + O \longrightarrow R \cdot CO \cdot R' + R'' \cdot CO \cdot R' + H_2O$ , in which R and R''=H or alkyl, and R'=H or OH. NaIO<sub>4</sub> and K<sub>2</sub>H<sub>3</sub>IO<sub>6</sub> (I) react similarly to HIO, in all respects, but more slowly, and, being readily purified, can be used for determination of polyhydric alcohols (II). (I) may form additive compounds with (II). R. S. C.

Rapid qualitative test for ethylene glycol and its application in presence of glycerol. A. W. MIDDLETON (Analyst, 1934, 59, 522–524).—The aq. alcohols are treated with HNO<sub>3</sub>, whereby  $[CH_2 \cdot OH]_2$ (I) yields  $H_2C_2O_4$ , isolated as the Ba salt and detected by decolorisation of warm aq. KMnO<sub>4</sub>. 0.1 g. of (I) can be detected in the absence of glycerol (II), and 0.3 g. in the presence of 0.7 g. of (II), but the test fails when (II) forms > 75% of the mixture. E. C. S.

d-Sorbitol. New source, method of isolation, properties, and derivatives. H. H. STRAIN (J. Amer. Chem. Soc., 1934, 56, 1756—1759).—Details are given for the isolation (in about  $2\cdot5\%$  yield) of *d*sorbitol (I), m.p. 91—93° (corr.),  $[\alpha]_{5461} - 2\cdot5°$  in H<sub>2</sub>O (compound, m.p. 89°, with 1 mol. of  $C_5H_5N$ ), from the fruit of *Photinia arbutifolia*, Lindl. The following derivatives of (I) are described : hexa-acetate, m.p. 101-102° (corr.) (lit. 99°),  $[\alpha]_{5461} + 10\cdot6°$  in COMe<sub>2</sub>; benzylidene, m.p. 195—196.5°; truisopropylidene, b.p. 140°/1-2 mm., m.p. 45—46°,  $[\alpha]_{5461} + 15\cdot8°$  in EtOH; tri(methylene), m.p. 213—214° (corr.) (lit. 206—209°),  $[\alpha]_{5461}$  -32·8° in  $C_5H_5N$ . (I) is not epimerised by heating with  $C_5H_5N$ . H. B.

Tests for purity of ether. II. A.  $W_{\Theta}$ HLK (Dansk Tidsskr. Farm., 1934, 8, 226–232).—Aldehydes in Et<sub>2</sub>O can be best detected by Ag<sub>2</sub>O-aq. NH<sub>3</sub>, and removed by adding solid KOH to the moist Et<sub>2</sub>O. R. P. B.

Autoxidation of diethyl ether and chemistry of its decomposition products. II. R. NEU (Pharm. Zentr., 1934, 75, 529—532; cf. A., 1932, 1017).—Et<sub>2</sub>O free from aldehydes undergoes rapid autoxidation in presence of colloidal Fe or blood charcoal (Fe<sub>2</sub>O<sub>3</sub>) and in clean sheet-Fe containers in the dark. The action of light is of secondary importance. S. C.

Unsaponifiable matter from oils of elasmobranch fish. X. Structure of batyl alcohol and synthesis of  $\beta$ -octadecyl glyceryl ether. W. H. DAVIES, I. M. HEILBRON, and W. E. JONES (J.C.S., 1934, 1232-1235).-Crystallisation of the crude solid ay-benzylideneglycerol (Hill et al., A., 1928, 1213) after keeping affords a geometrical isomeride (I), m.p. 62.5-63° (labile Bz derivative, m.p. 80-81°, readily passing into the stable form, m.p. 103°), which with Ag2O-Mel affords a \$-Me ether, b.p. 145-148°/5 mm., hydrolysed to Hill's glyceryl  $\beta$ -Me ether. With n-C<sub>18</sub>H<sub>37</sub>I the K derivative of (I) in C<sub>6</sub>H<sub>6</sub> gives its  $\beta$ -octadecyl ether. m.p. 43-44°, hydrolysed by aq. EtOH-HCl to glyceryl β-octadecyl ether (II), m.p. 62-63° [di(phenylurethane), m.p. 83-84°], depressed by admixture with batyl alcohol (III) (the  $\alpha$ -ether). Condensed films of (II) on H<sub>2</sub>O occupy approx. 6 Å.<sup>2</sup> more area at all pressures than do those of natural or synthetic (III) (Adam and Harding). Similar reactions afford the  $\beta$ -cetyl ether of (I), m.p. 34-35°, hydrolysed to glyceryl β-celyl ether, m.p. 60-61° [di(phenylurethane), m.p. 82-83°]. J. W. B.

Methyl hydrogen phosphates. V. HARLAY (J. Pharm. Chim., 1934, [viii], 20, 160—167).—The prep., isolation, and properties of  $MeH_2PO_4$  and  $Me_2HPO_4$  and their determination in presence of  $H_3PO_4$  are described.

Determination of aliphatic nitrates by titration. J. W. H. OLDHAM (J.S.C.I., 1934, 53, 236T).— A method for the determination of org. nitrates by means of aq.  $Ti_2(SO_4)_3$  is described and examples are given.

Preparation and properties of  $\beta$ -monoglycerides. B. F. STIMMEL and C. G. KING (J. Amer. Chem. Soc., 1934, 56, 1724—1725).— $\alpha\gamma$ -Benzylideneglycerol and the appropriate acyl chloride in C<sub>5</sub>H<sub>5</sub>N at 20° give  $\alpha\gamma$ -benzylideneglyceryl decoate, m.p. 32.5°, laurate, m.p. 46.6°, myristate, m.p. 62°, palmitate, m.p. 63.5°, and stearate, m.p. 69°, which when reduced (H<sub>2</sub>, Pd-black, EtOH) (cf. Bergmann and Carter, A., 1930, 1555) afford glyceryl  $\beta$ -decoate, m.p. 40.4°,  $\beta$ -laurate, m.p. 51.1°,  $\beta$ -myristate, m.p. 61°,  $\beta$ -palmitate (I), m.p. 68.5°, and  $\beta$ -stearate, m.p. 74.4°, respectively. (I) rearranges to the  $\alpha$ -palmitate in 0.05N-EtOH-HC during 24 hr. at room temp.; little or no change occurs in solutions < 0.005N. Similar results are found with aq. EtOH-NH<sub>3</sub> (concn. about twice that of HCI). Prolonged heating of (I) induces a change which does not involve complete transition; short heating has little or no effect. H. B.

Acetoacetic ester condensation. VII. Condensation of alkyl acetates. N. FISHER and S. M. MCELVAIN (J. Amer. Chem. Soc., 1934, 56, 1766-1769).—The yields of CH<sub>2</sub>Ac·CO<sub>2</sub>R obtained in 2-32 hr. from 1.2 mols. of ROAc (R=Me, Et, Pr<sup>a</sup>, Pr<sup> $\beta$ </sup>, Bu<sup>a</sup>, Bu<sup> $\beta$ </sup>, Bu<sup> $\gamma$ </sup>, sec.-Bu) and 0.2 mol. of NaOR (preps. described) at a temp. (57-115°) capable of maintaining, where possible, homogeneity of the reaction mixture are usually 50-80%. The high yields indicate (cf. A., 1931, 1035) that NaOR is the active condensing agent. NaOPh fails to condense PhOAc; the enolic form of the  $\beta$ -CO-ester cannot decompose the salt of the more acidic phenol, thus preventing condensation (cf. this vol., 756). Pra, b.p. 78°/11 mm., Prβ, b.p. 69°/11 mm.,  $Bu^{\alpha}$ , b.p. 90°/11 mm.,  $Bu^{\beta}$ , b.p. 84.5°/11 mm., sec.-Bu, b.p. 79.1°/11 mm., and Buy, b.p. 71.5°/11 mm., acetoacetates are new. H. B.

Action of iodoacetic acid on mercaptans and amines. L. MICHAELIS and M. P. SCHUBERT (J. amines. L. MICHAELIS and M. 1. BORGERS Biol. Chem., 1934, 106, 331–341).—Tri(carboxy-methyl)amine (I) is prepared from glycine and KOH solution at 80° The CH<sub>2</sub>I·CO<sub>2</sub>H (II) in aq. KOH solution at 80°. The titration curve of (I) shows two pK, one at 3 and one near 10.  $K_2$  salts of di(carboxymethyl)- $(\alpha$ -carboxyethyl)amine, carboxymethyldi-(a-carboxyethyl)amine, tri-(acarboxyethyl)amine, and tetracarboxymethyl-p-phenyl-enediamine, m.p. 165°, are prepared similarly. K tetracarboxymethylcystine diacetate (III) is prepared from cystine and (II) in aq. KOH at 90° by pptn. with EtOH. (III) gives dicarboxymethylcysteic acid with Br. Reduction of (III) with Sn in HCl and pptn. of the product from AcOH with EtOH gives K dicarboxymethylcysteine acetate. Cysteine and CH2Cl·CO2H in aq. KOH give S-carboxymethylcysteine, and thiolacetanilide and (II) give carboxymethylthiolacetanilide, m.p. 99-100°. Glutathione and (II) neutralised with Na2CO3 form S-carboxymethylglutathione at room temp. The rate of reaction of (II) with SH is > that with NH2. At H. D. physiological  $p_{\rm H}$  the reaction is slow.

Constitution of linoleic acid.—See this vol., 1046.

Synthesis of ascorbic acid and its analogues : addition of hydrogen cyanide to osones. W. N. HAWORTH, E. L. HIRST, J. K. N. JONES, F. SMITH, and (in part) R. W. HERBERT and C. E. WOOD (J.C.S., 1934, 1192—1197).—Mainly a more detailed account of results already published (this vol., 633). The mechanism of the formation and reactions of iminoglucoascorbic acid is given. Similarly from galactosone and NaCN is obtained *iminogalactoascorbic* acid, m.p. 190° (decomp.),  $[\alpha]_D^m -95^\circ$  in H<sub>2</sub>O, +25° in N-HCl (absorption band at 275 mµ,  $\varepsilon$  approx. 18,000), hydrolysed by N-HCl at 15° to galactoascorbic acid. J. W. B.

Physiological activity of synthetic ascorbic acid. W. N. HAWORTH, E. L. HIRST, and S. S. ZILVA (J.C.S., 1934, 1155-1156).—In comparative tests (guinea-pigs) the physiological, physical, and chemical properties of highly purified natural ascorbic acid and of the synthetic material (A., 1933, 936) are identical. J. W. B.

Reversibility in the oxidation of certain derivatives of carbohydrates, especially ascorbic acid.—See this vol., 1072.

Derivatives of glycuronic acid. IV. Synthesis of methyl  $\alpha$ - and  $\beta$ -tetra-acetylglycuronates and of methyl 1-chlorotriacetylglycuronate. W. F. GOEBEL and F. H. BABERS (J. Biol. Chem., 1934, 106, 63—69; cf. A., 1933, 808).—Me *d*-glycuronate, from MeI and the Ag salt, gives a mixture of Me  $\alpha$ - (I), m.p. 111—112° (corr.),  $[\alpha]_{14}^{24}$  +98.0° in CHCl<sub>2</sub>, and  $\beta$ - (II), m.p. 178° (corr.),  $[\alpha]_{14}^{24}$  +8.7° in CHCl<sub>3</sub>, -tetra-acetylglycuronate. With Ac<sub>2</sub>O and ZnCl<sub>2</sub> or C<sub>5</sub>H<sub>5</sub>N (I) and (II) give Me 1-chlorotriacetylglycuronate, m.p. 150.5—151.5° (corr.),  $[\alpha]_{14}^{24}$  -16.7° in CHCl<sub>3</sub>, with AcCl and HCl. H. D.

Keten. I. Preparation and reactions. F. O. RICE, J. GREENBERG, C. E. WATERS, and R. E. VOLBRATH (J. Amer. Chem. Soc., 1934, 56, 1760-1765).—Secondary factors in the prep. of keten (I) from COMe<sub>2</sub> (by passage through a quartz tube) are : (i) packing the tube with quartz or Pyrex glass, (ii) furnace temp. (if  $\leq 600^{\circ}$ ), (iii) contact time, (iv) dilution of the COMe2 vapour with an inert gas. The essential condition for a good yield (based on COMe<sub>2</sub> decomposed) is the decomp. of only a small fraction of the COMe<sub>2</sub> used. The yield is diminished considerably by the presence of 0.1 mol.-% of MeI, Me<sub>2</sub>S, Me<sub>2</sub>SO<sub>4</sub>, PbEt<sub>4</sub>, and *iso*amyl nitrite, and to a slight extent by McCHO, NH<sub>3</sub>, CHPh<sub>3</sub>, and azo*iso*-propane. As usually prepared, (I) contains 5-10%of  $\hat{C}_2H_4$ , which is separable by distillation in a vac.jacketed still. Pure (I), b.p.  $-41^{\circ}/760$  mm., m.p.  $-134 \cdot 6^{\circ}$ , is stable at  $-80^{\circ}$  provided it is freed (by distillation) from C particles and resinous material. (I) is a powerful acetylating agent; Ac derivatives are obtained from various alcohols, ArOH, and NH2Ar, provided these can be liquefied or dissolved in an inactive [to (I)] solvent. Polymerisation of the (I) can usually be avoided by slow passage into the compound (kept relatively conc.) at as high a temp. as possible. BuyOH reacts very slowly;

m-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (at 225°) gives resinous material and Ac<sub>2</sub>O; NH<sub>2</sub>Bz (at 180°) affords PhCN and Ac<sub>2</sub>O. H. B.

Crystalline methyl-d-riboside. J. MINSAAS (Annalen, 1934, 512, 286–289).—Methyl-d- $\beta$ -riboside, m.p. 83—84° (corr.),  $[\alpha]_{10}^{20}$  —113.6°, is obtained by heating ribose with 0.25% HCl-MeOH. H. W.

Acetone [isopropylidene] derivatives of dribose. II. P. A. LEVENE and E. T. STILLER (J. Biol. Chem., 1934, **106**, 421–429).—Methylribopyranoside (I) on acetonylation (A., 1933, 1145) gave an isopropylidene derivative (II), b.p. 84–86°/0.05 mm. Methylisopropylidenemethylriboside, b.p. 68–69°/0.04 mm., on hydrolysis with 0.02N-HCl at 100° shows a change of  $[\alpha]_{\rm p}$  from -64.5° to -22° in 30 min. and the product (III) contains 46% of a monomethylpentose. Exhaustive methylation of (III) gave trimethylmethylriboside, which with 0.02N-HCl at 100° showed a fall in  $[\alpha]_{\rm p}$  and an increased reducing power to a max. of 52%. p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Cl with (II) gave a mixture of 2:3-isopropylidenemethylribofuranoside 5-p-toluenesulphonate (IV), m.p. 83—84°,  $[\alpha]_{25}^{25}$ —35·5° in EtOH, and isopropylidenemethylribopyranoside 4-ptoluenesulphonate (V), m.p. 144—145°,  $[\alpha]_{25}^{25}$ —114·9° in EtOH, separated by recrystallisation from EtOH. (V) is hydrolysed by 5% H<sub>2</sub>SO<sub>4</sub> to methylribopyranoside 4-p-toluenesulphonate, m.p. 124°,  $[\alpha]_{27}^{25}$ —40° in CHCl<sub>3</sub>. (IV) gave an I-derivative with NaI (Oldham, A., 1932, 254), whilst (V) did not. It is concluded that on acctonylation (I) partly rearranges to furanoside. H. D.

Reactions of carbohydrates. II. Reactions with *m*-dinitrobenzene and alkali hydroxides. L. EKKERT (Pharm. Zentr., 1934, 75, 515—516).— Reducing carbohydrates (I) give a violet colour when a few drops of the solution are added to 5 mg. of  $m \cdot C_6 H_4(NO_2)_2$  in 5 drops of EtOH and warmed after adding 1—3 drops of *N*-NaOH. Non-reducing (I) remain colourless. A. G.

Synthesis of aldehydo-sugar acetates. M. L. WOLFROM, L. W. GEORGES, and S. SOLTZBERG (J. Amer. Chem. Soc., 1934, 56, 1794-1797).-The product from β-glucose tetra-acetate and EtOH-NH, OH is acetylated (Ac<sub>2</sub>O, C<sub>5</sub>H<sub>5</sub>N at room temp.) to aldehydoglucoseoxime hexa-acetate (A., 1931, 467), hydrolysed (H2C2O4,2H2O in MeOH) to the penta-acetate (loc. cit.), which is converted by HNO<sub>2</sub> (cf. Claisen and Manasse, A., 1889, 584) into aldehydoglucose penta-acetate (I),  $[\alpha]_{p} + 10.6^{\circ}$  in MeOH. Acetylation (Ac<sub>2</sub>O, C<sub>5</sub>H<sub>5</sub>N) of glucosesemicarbazone dihydrate gives (mainly) aldehydoglucosesemicarbazone pentaacetate (II), m.p. 154.5-155.5°, [a]<sup>23</sup> +96.6° in CHCl<sub>3</sub> (cf. A., 1929, 1043), and smaller amounts of an isomeric penta-acetate (III), m.p. 236-237°, [a]<sup>25</sup><sub>1</sub>, -16° in CHCl<sub>3</sub>, a tetra-acetate, m.p.  $171-172^{\circ}$ ,  $[\alpha]_{D}^{25}-9^{\circ}$  in CHCl<sub>2</sub> [acetylated further to (III)], and a hexa-acetate, m.p. 110—111.5°,  $[\alpha]_{15}^{25}$ —100° in CHCl<sub>3</sub>. (II) is converted by HNO<sub>2</sub> into (I). Acetylation (Ac<sub>2</sub>O, C<sub>5</sub>H<sub>5</sub>N) of galactoseoxime gives  $\beta$ -galactoseoxime hexa-acetate and a H<sub>2</sub>O-insol. product, which is hydrolysed (MeOH- $H_2C_2O_4$ ) to a mixture (A), m.p. 92–96°,  $[\alpha]_p + 36\cdot6°$ in CHCl<sub>3</sub>, of approx. equal amounts of aldehydogalactoseoxime penta-acetate hydrate (IV) and galactonitrile penta-acetate (V).  $HNO_2$  converts (A) into a mixture of (V) and aldehydogalactose pentaacetate (VI), which are more easily separated than are (IV) and (V). (VI) is also obtained by the action of HNO<sub>2</sub> on the mixture obtained by acetylation (Ac<sub>2</sub>O, C<sub>5</sub>H<sub>5</sub>N at 55°) of galactosesemicarbazone.

H. B.

Comparative action of periodic acid on hexoses and the artificial heterosides derived therefrom. H. HÉRISSEY, P. FLEURY, and (MLLE.) M. JOLY (J. Pharm. Chim., 1934, [viii], 20, 149–160; cf. A., 1933, 596).—Hexoses treated with HIO<sub>4</sub> consume 5 O and liberate 1 mol. of CH<sub>2</sub>O. The derived  $\alpha$ - and  $\beta$ heterosides require only 2 O and no CH<sub>2</sub>O is formed. E. H. S.

Additive compounds of the carbohydrates. I. Potassium hydroxide-glucose and related compounds. E. G. V. PERCIVAL (J.C.S., 1934, 1160—1164).—With NaOR in dry ROH glucose (I) forms compounds,  $C_6H_{12}O_6$ , NaOR (R=Me or Et), but if a trace of  $H_2O$  is present or with aq. EtOH-KOH the compound (II),  $C_6H_{12}O_6$ , KOH is obtained. With dry  $Me_2SO_4$  at 45—70°, (II) affords much unchanged (I) and, after acetylation, cryst.  $\beta$ -methylglucoside tetra-acetate together with its syrupy mixture with the  $\alpha$ -compound. (II) is assigned the structure  $OH \cdot CH < CH(CH_2 \cdot OH) = O > CH \cdot OH \leftarrow OH' \} K^*$ .

With dil. aq. EtOH-KOH cellobiose (III) forms the compound  $C_{12}H_{22}O_{11}$ ,KOH [similarly converted by Me<sub>2</sub>SO<sub>4</sub> into unchanged (III), β-methylcellobioside hepta-acetate and its α-isomeride], but in more conc. solutions there is evidence that  $C_{12}H_{22}O_{11}$ ,2KOH (giving a monomethylmethylcellobioside with Mc<sub>2</sub>SO<sub>4</sub>) is formed. Maltose appears to give  $C_{12}H_{22}O_{11}$ ,3KOH in conc. alkaline solution. J. W. B.

Optical rotatory dispersion in the carbo-III. Tetramethyl-a-methylhydrate group. glucopyranoside and tetramethyl-a-methylmannopyranoside. R. W. HERBERT, E. L. HIRST, and C. E. WOOD (J.C.S., 1934, 1151-1155).—Although α-methylmannopyranoside exhibits complex rotatory dispersion, its Me<sub>4</sub> derivative (I) shows simple dispersion in H<sub>2</sub>O, EtOH, and CHCl<sub>3</sub>, the rotation being controlled by an absorption band in the region of  $\lambda$  1600. In agreement with this, (I) shows no selective absorption down to  $\lambda 2100$ . The complex rotatory dispersion of a-methylglucopyranoside is enhanced in its Me<sub>4</sub> derivative (II), which can be represented by a two-term Drude equation with terms of opposite sign,  $k_1$  of the high-frequency term (contributed by a band at approx.  $\lambda$  1500) being >  $k_2$  of the low-frequency term ( $\lambda$  2500 for H<sub>2</sub>O and CHCl<sub>3</sub>; 2300 for EtOH). The absorption curve of (II) is characterised by a stepout in the region of  $\lambda$  2600, the cause of which is discussed. The ratio  $k_2/k_1$  is dependent on the solvent, being -0.0198 for H<sub>2</sub>O, -0.0484 for EtOH, and -0.0248 for CHCl<sub>3</sub>. J. W. B.

of  $2:3:6-tribenzoyl-\alpha-methyl-$ Synthesis glucoside. D. J. BELL (J.C.S., 1934, 1177-1179).- $\alpha$ -Methylglucoside 2:3-dibenzoate (I) with 1.2 mol. of BzČl in  $C_5H_5N$  affords the 2:3:6-tribenzoate (II), m.p. 132–133°,  $[\alpha]_{1}^{ls}$  +141·1° [4-p-toluenesulphonyl derivative (III), m.p.  $158-160^\circ$ ,  $[\alpha]_n$ +104.2°, unattacked by NaI in COMe,], the constitution of which is established by the following observations. With excess p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Cl and C<sub>5</sub>H<sub>5</sub>N, (1) affords its 2 : 6-di-p-toluenesulphonyl derivative, m.p. 122—124°,  $[\alpha]_{b}^{10}$  +94.58°, converted by NaI-COMe, into 6-iodo-a-methylglucoside 2: 3-dibenzoate 4-p-toluenesulphonate, m.p. 136°,  $[\alpha]_{b}^{19}$  +90.9°, which with AgNO<sub>3</sub>-MeCN followed by Zn-Fe-AcOH gives  $\alpha$ methylglucoside 2:3-dibenzoate 4-p-toluenesulphonate, m.p. 179—180°,  $[\alpha]_{11}^{16}$  +106.3°, benzoylation of which gives (III). a-Methylglucoside 2:3:4-tribenzoate 6-p-toluenesulphonate [Helferich et al., A., 1925, i, 9; depresses m.p. of (III)] is similarly converted into the 6-1-compound, and α-methylglucoside 2:3:4-tribenzoate, m.p. 140-142°, depressed by (II). All [a]o J. W. B. vals. are in CHCl<sub>2</sub>.

Reaction between fructose and arsenic acid.— See this vol., 1034.

Structure of *d*-glucoheptulose hexa-acetate. M. L. WOLFROM and A. THOMPSON (J. Amer. Chem. Soc., 1934, 56, 1804-1806).-Glucoheptulose (I) is acetylated [Austin's method (A., 1932, 724); Ac<sub>2</sub>O and ZnCl<sub>2</sub> at room temp.; Ac<sub>2</sub>O (excess) and cold  $C_5H_5N$ ] to the hexa-acetate (II), m.p. 115—116°,  $[\alpha]_1^{s5} + 87^8$  in CHCl<sub>3</sub>, converted by HBr in AcOH-Ac<sub>2</sub>O into a-acetobromo-d-glucoheptulose (III), m.p.  $97-98^{\circ}$ ,  $[\alpha]_{D}^{22}+134\cdot5^{\circ}$ in CHCl<sub>3</sub>, Acetylation [Ac<sub>2</sub>O and C<sub>5</sub>H<sub>5</sub>N (excess) at 0° and then at room temp.] of (I) gives the penta-acetate, m.p. 114—115°,  $[\alpha]_{15}^{26}$  + 49° in CHCl<sub>3</sub> [acetylated (Ac<sub>2</sub>O, NaOAc) to (II)], which contains glucosidic OH, since it is also obtained from (III) and Ag<sub>2</sub>CO<sub>3</sub> in aq. COMe2. (II), EtSH, ZnCl2, and sol. anhydrite (Hammond and Withrow, A., 1933, 1266) give a compound, C<sub>11</sub>H<sub>18</sub>O<sub>5</sub>S<sub>2</sub>Ac<sub>4</sub>, m.p. 92-93°, [α]<sup>25</sup> +65° in CHCl<sub>3</sub> [in which 2 OAc groups of (II) have been replaced by 2 EtS], which is a thioglycoside. This result shows (cf. this vol., 636) that (II) is a cyclic compound (cf. Austin, loc. cit.). H. B.

Karakin, the glucoside of Corynocarpus lavigata. M. S. CARRIE (J.S.C.I., 1934, 53, 288–289T). —The alcoholic extract of karaka kernels contains sugars, consisting of 95% of sucrose and 5% of glucose (I), an oil, hydrolysed to stearic and oleic acids, and karakin (II),  $(C_5H_7O_5N)_3$ , m.p. 122°. (II) is hydrolysed by HCl in cold COMe<sub>2</sub> to 1 mol. of (I) and 3 mols. of heptagenic acid. H. W.

Strophanthin. XXX. Ultra-violet absorption spectra of trianhydrostrophanthidin and trianhydroperiplogenin derivatives. R. C. ELDER-FIELD and A. ROTHEN (J. Biol. Chem., 1934, 106, 71-78).-The curves for ultra-violet absorption (I) of mono- (II) and di- (III) -anhydrodihydrostrophanthidin in EtOH show max. at 3030 Å. due to CHO. At shorter  $\lambda$  (I) increases rapidly and continuously. Octahydrotrianhydrostrophanthidin shows slight (I). The (I) of dihydrotrianhydrostrophanthidin (IV) has a strong band between 2790 and 2500 Å. absent in (II) and (III) if the presence of the CHO is allowed for, indicating a  $C_6H_6$  ring in (III). The (I) of trianhydrostrophanthidin (V) is similar to that of (IV) indicating the presence of an allylbenzene linking (Hillman, A., 1934, 345). The (1) of trianhydroperiplogenin has a band from 2600 to 3000 A., but in the higher  $\lambda$  the curve is displaced from those of (IV) and (V). H. D.

**Ivory-nut** mannans. II. Constitution of mannan-B. F. KLAGES (Annalen, 1934, 512, 185— 194; cf. this vol., 514).—Mannan-B gives by methylation and hydrolysis the same products as does mannan-A (I), and is thus similarly constituted. Oxidation of methylated (I) by I is a secondary reaction, since tetramethyl- $\beta$ -methylglucoside is similarly oxidised. R. S. C.

Size and structure of the cellulose molecule. A. AF EKENSTAM (Svensk Kem. Tidskr., 1934, 56, 157-167).—Cellulose (I) may be dissolved in aq. HCl,  $H_2SO_4$ , or  $H_3PO_4$  for mol. wt. determinations by Staudinger's viscosity method. On account of the decomp. which occurs, the vals. must be extrapolated to zero time. The vals. agree with those obtained by other methods. If (I) is dissolved in conc.  $H_2SO_4$ , the electrical conductivity increases with time.

R. P. B.

Adsorption of acetone by cellulose nitrates.— See this vol., 1067.

Reaction of amines with ethyl β-bromopropionate and n-butyl bromide. W. V. DRAKE and S. M. MCELVAIN (J. Amer. Chem. Soc., 1934, 56, 1810-1812).-The extent and course of the reaction of CH<sub>2</sub>Br·CH<sub>2</sub>·CO<sub>2</sub>Et (I) and Bu<sup>a</sup>Br (II) with various NHR<sub>2</sub> (III) and NR<sub>3</sub> (IV) are determined at 90°, essentially as previously described (A., 1931, 494). The basicity of (III) is the factor controlling elimination of HBr from (I), but there is a considerable difference [undoubtedly due to steric factors associated with the structure of (III)] in the subsequent addition of (III) (of similar strength) to the resulting  $CH_2:CH:CO_2Et$ . The formation of  $NBuR_2$  from (II) and (III) is not related to the basicity of (III); thus, for the same time, NHPhMe reacts to a greater extent than 2-methylpiperidine and  $\text{NHEt}_2$ . The variation in reactivity is probably due to steric factors. The extent of the reaction between (I) and (IV) is related to the basicity of (IV); some steric factor appears to be involved in the elimination reaction, since the N-alkylpiperidines (approx. the same basicity) show widely differing amounts of reaction (the reactivity decreases with increase in the size of alkyl). Considerable amounts of quaternary salt are obtained from (I) and C<sub>5</sub>H<sub>5</sub>N and NPhMe<sub>2</sub>. Quaternary salt formation from (II) and (IV) is also independent of the basicity of (IV). H. B.

Determination of hexamethylenetetramine by precipitation of its uranyl double sulphate. FOUCRY (J. Pharm. Chim., 1934, [viii], 20, 168-170). —The pptn. is quant. and occurs in a solution containing 0.04 mg. of  $(CH_2)_6N_4$  in 2 c.c. E. H. S.

Application of dielectric constant measurements in aqueous solution to organic chemistry. G. DEVOTO (Z. Elektrochem., 1934, 40, 490–493).— A review of published work. E. S. H.

Synthesis of glycine from glyoxylic acid. P. DESNUELLE and C. FROMAGEOT (Bull. Soc. chim., 1934, [v], 1, 700—702).—Hydrogenation (colloidal Pd) of CHO·CO<sub>2</sub>H in an excess of aq. NH<sub>3</sub> gives an 8% yield of glycine. R. S. C.

Synthesis of *dl*-lysine. J. C. ECK and C. S. MARVEL (J. Biol. Chem., 1934, 106, 387—391). cycloHexanone (I) is converted into the oxime and rearranged by Ruzicka's reaction (A., 1921, i, 591) to 2-ketohexamethyleneimine. Hydrolysis and benzoylation gives  $\varepsilon$ -benzamidohexoic acid, which is converted into *dl*-lysine (II) by the method of von Braun. 500 g. of (II) are prepared from 1000 g. of (I). H. D.

Labile hydrogen (Wieland) in the catalytic oxidation of thiol compounds by heavy metals. R. BRDIČKA (Biochem. Z., 1934, 272, 104—112).— The existence of labile H in complex compounds of cysteine with Co and Ni is demonstrated by Heyrovský's method. The activation of H of SH results from co-ordination of SH with Co or Ni, a dipole containing loosely bound H being formed. An explanation is thus provided of the mechanism (I) of the catalysis by heavy metals of the oxidation of SH compounds, direct transference of the activated H of these compounds to the H acceptor being assumed. The views of Warburg and Wieland concerning the inhibition of autoxidation of cysteine by substances containing Fe in complex combination are harmonised by (1). W. McC.

Determination of cystine. Use of the Zeiss photometer. J. H. BUSHILL, L. H. LAMPITT, and L. C. BAKER (Biochem. J., 1934, 28, 1293–1304).— Using light of  $\lambda$  530 mµ the extinction coeff. with the Sullivan technique (A., 1926, 1266) varies up to  $\pm 25\%$  and the Lugg modification (I) (A., 1933, 814), taking precautions to prevent oxidation, to  $\pm 8\%$ . Cystine can be determined with an error of  $\pm 4\%$ , indicating that an error is introduced in its reduction in the process. The colour is affected considerably by O<sub>2</sub>, particularly in (I). H. G. R.

Synthesis of cystinyldiglycine and cystinyldialanine. J. WHITE (J. Biol. Chem., 1934, 106, 141-144).—Dicarbobenzyloxycystinyl dichloride, prepared by the action of PCl<sub>5</sub> on dicarbobenzyloxycystine in  $\text{Et}_2\text{O}$ , gives dicarbobenzyloxycystinyldiglycine (II), m.p. 161-163°, on treatment with glycine in N-NaOH at 0° and subsequent acidification. (II) on hydrolysis with conc. HCl gave cystinyldiglycine (III). Cystinyldialanine (IV) is prepared similarly. The Sullivan reaction is positive for both (III) and (IV).

Synthesis of pentocystine and homomethionine. V. DU VIGNEAUD, H. M. DYER, C. B. JONES, and W. J. PATTERSON (J. Biol. Chem., 1934, 106, 401-407).-Et<sub>2</sub> sodiophthalimidomalonate and trimethylene bromide condense to give Et<sub>2</sub> phthalimidoy-bromopropylmalonate (I). Refluxing an EtOH solution of (I) with NaSH and extracting the evaporated residue with Et<sub>2</sub>O yields Et<sub>2</sub> phthalimido-y-thiolpropylmalonate, which on alkaline hydrolysis gives Na phthalimido-y-thiolpropylmalonate. Oxidation of the Na salt with FeCl<sub>3</sub> gives bis-8-phthalimidoδ-dicarboxybutyl disulphide (II). Hydrolysis of (II) with conc. HCl and extraction with 0.5N-HCl gives δδ'-diaminodi-n-butyl disulphide-δδ-dicarboxylic acid (pentocystine), m.p. 269—272° (decomp.) (III). Di-formylpentocystine has m.p. 122°. (III) gives negative 'SH and Sullivan tests and positive 'S·S' and nin-hydrin tests. Reduction of (III) with Na in liquid NH<sub>3</sub> and addition of CH<sub>2</sub>PhCl gives S-benzylpento-cysteine, m.p. 219-222° (decomp.). α-Amino-δmethylthiolvaleric acid (homomethionine) (IV), m.p. 272-274° (formyl derivative, m.p. 122-123°), is produced by addition of Na to a liquid NH<sub>3</sub> solution of (III) and addition of MeI. Excess of NH<sub>3</sub> is removed, the residue dissolved in H<sub>2</sub>O, and the solution neutralised with 10% HI. Pptn. of (IV) is completed with EtOH. H. D.

Formation and synthetic use of amido- and imido-chlorides. J. VON BRAUN (Angew. Chem., 1934, 47, 611-615).—A crit. summary of the reactions of imidochlorides NR:CR'Cl (R and R'=aryl or alphyl). J. W. B.

Diazomethanes. I. Action of sodium triphenylmethyl on aliphatic diazo-compounds. E. MULLER and H. DISSELHOFF. II. Action of acids on the sodium derivative of diazomethane. E. MULLER and W. KREUTZMANN (Annalen, 1934, 512, 250–263, 264–275).—I. Addition of a small excess of  $CH_2N_2$  to a solution of  $CPh_3Na$  causes immediate decolorisation and formation of a white ppt. (I) which could not be analysed on account of its explosive nature, but is regarded as  $CHN_2Na$ . Hydrolysis of (I) with  $H_2O$  gives up to 35% of  $CH_2N_2$ .  $N_2H_4$ , CN', or  $HCO_2H$  could not be detected. With BzBr at >20° (I) gives a compound  $BzN < CH^3$ .

N—N CPh, or NHBz·N:C, m.p. 35—37°, hydrolysed by alkali through NH<sub>2</sub>·NHBz to N<sub>2</sub>H<sub>4</sub>, BzOH, and HCO<sub>2</sub>H. I in Et<sub>2</sub>O is immediately decolorised by (I) with evolution of a small amount of C<sub>2</sub>H<sub>2</sub>, but not N<sub>2</sub>, and production of CHI<sub>3</sub> with minor amounts of liquid I-compounds. CHPhN<sub>2</sub> causes decolorisation of CPh<sub>3</sub>Na, but gives only smeary products. With Na<sub>2</sub> Ph diphenylyl ketone CHPhN<sub>2</sub> yields 3 : 4-diphenylosotriazole, m.p. 138—139°, the initial formation of CPhN<sub>2</sub>Na being followed by addition of a second mol. of CHPhN<sub>2</sub> and liberation of Ph diphenylyl ketone. CHN<sub>2</sub>·CO<sub>2</sub>Et and CPh<sub>3</sub>Na react with evolution of gas and formation of ill-characterised products. CPh<sub>2</sub>N<sub>2</sub> caused immediate decolorisation of CPh<sub>3</sub>Na without evolution of N<sub>2</sub>. Hydrolysis of the product with H<sub>2</sub>O gives triphenylmethylbenzhydrylidenehydrazine, m.p. 171° (also obtained from CPh<sub>3</sub>Cl and benzophenonehydrazone in C<sub>5</sub>H<sub>5</sub>N at 100°), hydrolysed to COPh<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>, and CPh<sub>3</sub>·OH.

II. Treatment of the compound derived from  $CH_2N_2$  and  $CPh_3Na$  with anhyd. AcOH in presence of  $Et_2O$  gives the expected amount of NaOAc, but no  $CH_2N_2$  or MeOAc; the ethereal solution becomes yellow due to an unstable material regarded as isodiazomethane (I), (CH:N-NH), (I) and BzOH afford benzoylformylhydrazine (II), m.p. 158—159°, also obtained from NHBz·NH<sub>2</sub> and boiling anhyd. HCO<sub>2</sub>H. (II) is transformed by successive treatment with boiling KOH-MeOH and PhCHO into benzoylbenzylidenehydrazine, m.p. 204°, and HCO<sub>2</sub>H. It contains 2 active H (Zerevitinov). With PhNCO it affords the compound  $C_{15}H_{13}O_3N_3$ , m.p. 141° (turbid), becoming clear at 170°. It does not react with aldehydes. (I) and m-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H yield m-nitrobenzoylformylhydrazine, m.p. 208° (also derived from m. NO 4: CH = WHANH

m-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·NH<sub>2</sub> and HCO<sub>2</sub>H), hydrolysed and converted by PhCHO into benzaldazine and *m*-nitrobenzoylbenzylidenehydrazine. *Picrylformylhydrazine*, m.p. 188.5° (decomp.), obtained similarly by both methods, affords a *semicarbazide* derivative

methods, another a semicarbatile dorivative  $C_{14}H_{10}O_8N_6$ , m.p.  $157\cdot5-158^\circ$  (decomp.). (I) and o- $C_6H_4(CO_2H)_2$  give a substance  $C_9H_8O_4N_2$ , m.p. 160. BzBr and (I) yield a compound  $C_8H_7ON_2Br$ , m.p. 192° (slight decomp.), transformed by successive action of NaHCO<sub>3</sub> and PhCHO into benzaldehydebenzoylhydrazone, m.p. 206°. (I) and saccharin give the product  $C_8H_7O_3N_3S$ , m.p. 229° (decomp.). Formylhydrazine and BzOH in boiling Et<sub>2</sub>O do not afford (II).

Magnesium for Grignard reagents. N. W. CUSA and F. S. KIPPING (J.S.C.I., 1934, 53, 213-214T).—Attention is directed to the great influence of the quality of the Mg on the yields of Grignard reagents obtained with cyclohexyl chloride and bromide. H. W.

Preparation of thallium triethyl, triisobutyl, and triphenyl. S. F. BIRCH (J.C.S., 1934, 1132— 1136).—A simplified apparatus is described for the prep. of Tl triaryls and trialkyls by the action of the appropriate Li alkyl or aryl (prep. by the method of Gilman et al., A., 1932, 728) on TIR<sub>2</sub>Cl in Et<sub>2</sub>O or  $C_5H_{12}$ , or on TlCl direct :  $3\text{LiR}+3\text{TlCl} \longrightarrow \text{TIR}_3+$ 2Tl+3LiCl, all operations being carried out in N<sub>2</sub>. Thus from the appropriate pairs are obtained *Tl* triphenyl (60% yield), m.p. 188—189°, decomp. 215— 216°, giving TlPh<sub>2</sub>O in air, and TlPh<sub>2</sub>·OAc with AcOH- $C_6H_6$  : *Tl triethyl*, b.p. 50—51°/1·5 mm. (66%), similarly converted into TlEt<sub>2</sub>·OAc, which with aq. KCN gives the corresponding cyanide, darkens 240°, not melting at 310°; and *Tl triisobutyl*, b.p. 74—76°/ 1·6 mm. (73%), converted into dissobutylthallium acetate, m.p. 215° (decomp.). From LiBu<sup>β</sup> and TlEt<sub>2</sub>Br a compound, b.p. 50—65°/3·2 mm., probably TlEt<sub>2</sub>Bu<sup>β</sup>, was obtained, but was not purified.

## J. W. B.

Rupture of pentamethylene rings with conversion into paraffin hydrocarbons by platinum catalysts in presence of hydrogen. N. D. ZELIN-SKI and B. A. KAZANSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 168—170).—When heated with H<sub>2</sub> at 305—310° (Pt-C) methyl-, ethyl-, and propylcyclopentane yield mixtures of paraffin hydrocarbons, consisting chiefly of the *iso*-isomerides. R. T.

Reaction between sulphur dioxide and olefines. cycloHexene. D. S. FREDERICK, H. D. COGAN, and C. S. MARVEL (J. Amer. Chem. Soc., 1934, 56, 1815— 1819).—cycloHexene (I) and liquid SO<sub>2</sub> in a little 95% EtOH and 2% H<sub>2</sub>O<sub>2</sub> at 25— $30^{\circ}$  give (cf. Seyer and King, A., 1933, 1013) an amorphous compound (II; n=about 39), softens and decomp. > 200°, which is sol. only in CHCl<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, PhNO<sub>2</sub>, and dioxan. Other methods of prep. of (I) are investigated. The presence of OH in (II) is proved by the prep. of Ac, m.p. 210—215°, and chloroacetyl, OH

m.p. 215—220°, derivatives, both of which have Mabout 6000. (II) is degraded by 17% NaOH to (I), dicyclohexenyl sulphone, m.p. 75°, and complex Scompounds, by 5% NaOH to dodecahydrophenoxthine dioxide (III), m.p. 138°, and a little (I), and by 90% KOH at 250° to (I), a dicyclohexenvl, b.p. 234° (tetrabromide, m.p. 158°) [reduced (H<sub>2</sub>, PtO<sub>2</sub>) to dicyclohexyl], cyclohexene-sulphinic or -sulphonic acid (Ag salt), and K<sub>2</sub>SO<sub>3</sub>; these compounds are probably formed from the intermediate di-2-hydroxycyclohexyl sulphone. H. B.

Influence of negative groups on reactions between nitrosobenzene and unsaturated compounds. A. POLVERINI (Gazzetta, 1934, 64, 409— 415).—A change of colour to chestnut-yellow when a compound is mixed with PhNO in a neutral solvent occurs with compounds containing two double linkings (citral, geraniol, pyrrole, isoprene,  $\alpha$ -ionone, linoleic acid), more slowly when negative groups are present in crit. positions (sorbic acid). Compounds with only one double linking also react (CMe<sub>2</sub>:CHMe, oleic acid, ricinoleic acid, pinene, terpineol), more slowly when one negative group is present (dihydrocarvone, atropic acid, CHPh:CHAc, cinnamaldehyde, coumarin), or not at all when two such groups are present (piperic, cinnamic, crotonic, fumaric acids, stilbene).

R. K. C.

Molecular rearrangements involving spontaneous cleavage. C. B. WOOSTER and R. A. MORSE (J. Amer. Chem. Soc., 1934, 56, 1735—1737).— CNaPh<sub>3</sub> in liquid NH<sub>3</sub> and OEt·CH<sub>2</sub>·CH<sub>2</sub>Br in Et<sub>2</sub>O give  $\gamma\gamma\gamma$ -triphenylpropyl Et ether, m.p. 111·5—112°, which with HI (const. b.p.) in N<sub>2</sub> affords  $\gamma\gamma\gamma$ -triphenylpropyl iodide (I), m.p. 174·5—175°. Treatment of (I) with Na in liquid NH<sub>3</sub>, decomp. of excess of Na with NH<sub>4</sub>NO<sub>3</sub>, and subsequent hydrolysis (H<sub>2</sub>O) gives some CHPh<sub>3</sub>; a mol. rearrangement involving spontaneous cleavage appears to take place. The probable mechanism is discussed. (I) and CPh<sub>3</sub>·CH<sub>2</sub>Cl (cf. A., 1930, 762; 1932, 838) are unaffected by NaNO<sub>3</sub> in liquid NH<sub>3</sub>. H. B.

Influence of solvent on the course of reactions of organic molecules. H. LUTGERT (Z. Elektrochem., 1934, 40, 499-501).—A discussion of published work on the influence of dielectric const. and dipole moment. E. S. H.

Magneto-chemistry and the biradical formula. E. MULLER (Z. Elektrochem., 1934, 40, 542).—A discussion of magnetic susceptibility as a means of characterising substances of the type R<sub>2</sub>. E. S. H.

Supposed isomerisation of retene by sulphur. J. R. HOSKING and W. T. MCFADVEN (J.S.C.I., 1934, 53, 195—1967).—The suggestion (Beath, B., 1934, 43) that retene is isomerised by heating with S is shown to be without foundation. The hydrocarbon obtained from crude retene (from abietene or colophony) is pimanthrene (I), m.p. 86° (picrate, m.p. 131°; styphnate, m.p. 159°), and not an isomeride of retene. It is suggested that the "*iso*retene," m.p. 86—87° (picrate, m.p. 127°), obtained by S dehydrogenation of rimuene (*loc. cit.*), and considered to be 1-methyl-6-*iso*propylphenanthrene, is (I). The production of (I) is ascribed to the presence of *d*-pimaric acid or a congener in the crude resin acid products (cf. Rimbach, A., 1897, i, 254).

Preparation of s-acylarylcarbamides. N. PALIT (J. Indian Chem. Soc., 1934, 11, 479–483).— NH<sub>2</sub>·CO·NHAc and NH<sub>2</sub>Ph at 170–175° (5 hr.) give NH<sub>3</sub>, s-acetylphenylcarbamide (I), m.p. 183° (68·5%), CO(NHPh)<sub>2</sub> (11·4%), and NH<sub>2</sub>Ac (14·2%). p-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> gives similarly (3 hr.) nearly pure sacetyl-p-tolylcarbamide (II), m.p. 199–200°, but longer heating gives much di-p-tolylcarbamide. p-Anisidine gives (2 hr.) s-acetyl-p-anisylcarbamide, m.p. 220–221° (69%), di-p-anisylcarbamide, m.p. 235– 237° (10%; more after longer heating), anisylcarbamide, and a substance, C<sub>18</sub>H<sub>13</sub>O<sub>3</sub>N<sub>2</sub>, m.p. 220–221°. NH<sub>2</sub>·CO·NHBz and NH<sub>2</sub>Ph at 170° give NH<sub>3</sub> and s-benzoylphenylcarbamide (III), m.p. 204–205°; longer heating gives much CO(NHPh), s-Benzoyl-p-tolyl-, m.p. 228-229°, and -p-anisyl-carbamide, m.p. 219°, were similarly prepared. (I), (II), and (III) were pre-R. S. Ĉ. viously assigned as-formulæ.

Thio-o-toluidine. Preparation by synthesis and by the action of sulphur on o-toluidine in presence of litharge. H. H. HODGSON and H. V. FRANCE (J.C.S., 1934, 1140-1141).-o-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> (I) and S yield mainly products in which S is ortho to NH2, whereas if PbO is present the chief product is (dihydrochloride, m.p. 248—249°; dipicrate, m.p. 186°;  $Ac_2$ , m.p. 220°, and  $Bz_2$ , m.p. 233°, derivatives; bisazo-compound with  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH, m.p. 258°); highly-coloured by-products are kept at a min. by using an excess of (I) and keeping the temp. as low as possible. 5-Bromo-2-nitrotoluene (III) and the Na salt of 2-amino-5-tolyl mercaptan in EtOH yield 2'-nitro-2-amino-5:5'-ditolyl sulphide, m.p. 104° (hydrochloride, m.p. 187°; Ac, m.p. 143°, and Bz, m.p. 119°, derivatives; corresponding -azo-\Beta-naphthol, m.p. 194°), reduced by Fe dust and very dil. HCl to (II). (III) and Na2S in boiling H2O give 2 : 2'-dinitro-5 : 5'-ditolyl sulphide, m.p. 164°. 2:2'-Dinitro-5:5'-ditolyl disulphide, m.p. 163°, is obtained from (III) and Na2S2 in EtOH.  $\overline{2}$ : 2'-Diamino-5: 5'-ditolyl disulphide is unchanged when boiled with (I) alone or in presence of PbO. 5-Bromotoluene-2-azo-β-naphthol has m.p. 172°. Ĥ. W.

Chemistry of the Knoevenagel and similar reactions. L. H. SMITH and K. N. WELCH (J.C.S.,

1934, 1136—1140).—CH<sub>2</sub>Bz<sub>2</sub> and p-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·OH (I) at 155—170° in presence of a trace of NEt<sub>3</sub> yield  $\alpha\alpha$ -dibenzoyl- $\beta$ -p-dimethylamino-phenylethane, m.p. 132—133°. (I) and the respective phenol afford 4-dimethylamino-4'-hydroxydiphenylmethano, m.p. 107—108°, -2': 4'-dihydroxydiphenyl-methane, m.p. 172.5°, 1-dimethylaminobenzyl-β-naphthol, m.p. 143°, and 4-dimethylaminobenzyl-a-naphthol, m.p. 148-149°. Condensation with m-2-xylenol led only to a glassy solid, whilst quinol did not react. Reactions with phenols do not proceed in this direction in the presence of a trace of acid, probably owing to autocondensation of the alcohol; change does not proceed smoothly in C5H5N. With p-C6H4Me·NH2 and NHPh2, (I) yields p-tolyl-p-dimethylaminobenzylamine, m.p. 101°, and diphenyl-p-dimethylaminobenzylamine, m.p. 80-81°, respectively, whereas o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub> affords methylenebis-o-nitroaniline, m.p. 195°. NPhMe<sub>2</sub> and (I) readily give 4:4'-tetramethyldi-aminodiphenylmethane (II); contrary to von Braun *et al.* (A., 1912, i, 968) (I) is probably an intermediate in the formation of (II) from NPhMe<sub>2</sub> and CH<sub>2</sub>O. The experiments suggest that the function of sec. bases as catalysts in Knoevenagel's reaction is due to the formation of substances of the type NR2 CHR'OH and an electronic theory is discussed. H. W.

Derivatives of 4:4'-tetramethyldiaminodiphenylmethane. D. C. R. JONES and F. A. MASON (J.C.S., 1934, 1190-1192).-Chlorination of  $CH_2(C_eH_4\cdot NMe_2 \cdot p)_2$  (I) in AcOH containing NaOAc gives the  $3:3'-Cl_2$ -derivative, b.p.  $265^{\circ}/20$  mm. (picrate, m.p. 173°). The corresponding 2-Cl-, m.p. 63°, and 2-Br-, m.p. 68°, -derivatives are obtained from

the very unstable 2-diazonium compound by the Sandmeyer-Gattermann reaction. The 2:2'-Cl2-, m.p. 96°, and  $2: 2' \cdot Br_{2}$ , b.p. 265°/20 mm., m.p. 103°, -derivatives are derived from the 2: 2'-bisdiazonium compound. The I- or I2-compounds could not be prepared similarly. Bromination of (I) in AcOH affords the 3: 3'-Br2-derivative (II), b.p. 274-279°/20 mm. (*picrate*, m.p. 188°), whereas attempted monobromin-ation in AcOH, CHCl<sub>3</sub>, CCl<sub>4</sub>, or  $C_2H_2Cl_4$  led to (II) and unchanged (I). ClSO<sub>3</sub>H and (I) in  $C_2H_2Cl_4$  yield 4:4'-tetramethyldiaminodiphenylmethane-2:2'(?)-disul-phonic acid (Na salt). CH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>-m)<sub>2</sub>, Me<sub>2</sub>SO<sub>4</sub>, and NaOH give diphenylmethane-3:3'-bistrimethyl-ammonium iodide w p. 228°. ammonium iodide, m.p. 228°. H. W.

Reduction of some oximes and their acetyl derivatives by aluminium amalgam. V. CER-CHEZ and (MME.) DUMITRESCO-COLESIU (Bull. Soc. chim., 1934, [v], 1, 852-856).-Oximes or their Ac derivatives (I) with Al-Hg give > 50% yields of the amines or acetamides. In some cases partial hydrolysis of Ac occurs, because (I) exists partly as O-Ac compound. In this way are obtained heptyl-, benzyl-(and its Ac derivative), o-hydroxy- and o-methoxybenzyl- (and its Ac derivative), and benzhydryl-amine (and its Ac derivative).  $CPh_2:N\cdot OH$  has m.p. 71° (cf. R. S. C. lit.).

Compounds of ethyl iodoacetate with benzyldimethylamine and ethylpiperidine. (MLLE.) M. CHALEIL (Bull. Soc. chim., 1934, [v], 1, 738-742).-The gel forms of the methiodide, m.p. 129-130° (decomp.), of Et benzylmethylaminoacetate [from CH2Ph·NMe2 and CH2I·CO2Et (I)] and ethiodide, hygroscopic, cryst. (not obtained pure), of N-carbethoxymethylpiperidine [from (I) and ethylpiperidine] do not give Liesegang rings. NHMc, removes halogen acids from cyclohexyl bromide (II) or iodide. 4-Methylcyclohexyl iodide (from the alcohol and  $PI_3$ ), b.p. 86.5—87.5°, loses HI slowly when heated with NNaAcPh in xylene. cycloHexylcarboxylamide (III) and NaOCl give a poor yield of cyclohexylamine. also obtained in poor yield from (III) by way of the cyclohexylmethylurethane, m.p. 75°. The Grignard reagent from cyclohexyl chloride (obtained with much cyclohexene from the alcohol and  $SOCl_2$ ) with  $CO_2$ gives a poor yield of an acid, m.p. 141-142°. (II), however, gives a good yield of cyclohexylcarboxylic acid and a neutral substance, m.p. 65°. (III) is obtained in good yield from the  $NH_4$  salt in gaseous  $NH_3$  at 120–180°. The 2- and 4-methyl homologues are similarly prepared, the former giving only the R. S. C. cis-amide, m.p. 152-153°.

D. VOR-Isomeric *p*-aminoazoxybenzenes. LANDER and H. SCHUSTER (J. pr. Chem., 1934, [11], 140, 193-208).—The separation of the a-, m.p. 138-139°, and b-forms, m.p. 136° (corr.) (cf. lit.), of p-aminoazoxybenzene (I) is improved. The following derivatives are prepared, the m.p. given first being that of the a-form : benzylidene, m.p. 108, 134°; anisylidene (II), m.p. 132° (215°), 124° (207°); cinnamylidene (III), m.p. 126°, 133°; p-phenylbenzyl-idene (IV), m.p. 174° (274°), 179° (273°); p-terephthalyl-idene (bis-derivative) (V), m.p. 227° [293° (decomp.)], 200° [282° (decomp.)]. (II), (III), (IV), and (V) form

-liquid crystals, the m.p. given in parentheses being those of anisotropic melting. The corresponding *derivatives* of *p*-aminoazobenzene have m.p.  $131^{\circ}$ ,  $151^{\circ}$ (185°), 143°, 208° (250°), and 251° (285°), respectively, the last four forming liquid crystals. Both forms of (I) give colourless hydrochlorides, wherefore formulæ

of the type,  $\frac{NR}{NR}$  >0, are suggested. R. S. C.

Normal aryl sulphates. L. DENIVELLE (Compt. rend., 1934, 199, 211—213).—CISO<sub>2</sub>·OPh and PhOH in  $C_5H_5N$  at 120° yield  $Ph_2$  sulphate, b.p. 144—146°/1 mm.; guaiacyl, b.p. 98°/1 mm., m.p. 54°, p-tolyl, b.p. 114—116°/14 mm., m.p. 64—65°, m-tolyl, b.p. 115°/14 mm., m.p. 58·5°, and Ph p-tolyl, m.p. 57°, sulphates are similarly obtained. H. W.

Preparation of *p*-iodophenol and its derivatives. F. B. DAINS and F. EBERLY (Trans. Kansas Acad. Sci., 1933, 36, 114—117).—Noelting and Wrzesinsky's method (Ber., 1875, 8, 820) has been modified. Benzyl, m.p. 62°, and *p*-nitrobenzyl, m.p. 145°, *p*-iodophenyl ethers; methylene, m.p. 114°, ethylene, m.p. 175—177°, and trimethylenc, m.p. 149°, di-*p*-iodophenyl ethers are described. CH. ABS.

Derivatives of s- and as-m-xylenols. E. KAT-SCHER and H. LEHR (Monatsh., 1934, 64, 236-246).-The orientation of the m-5-xylenoldisulphonyl chloride (I), m.p. 117-119° (A., 1931, 83), as the 2:4-disulphonyl chloride (disulphonamide, m.p. 206-208°) is shown by the following data. (I) with 20% aq. NaOAc in COMe2 gives m-xylene-2 : 5-sulphoquinone-4-sulphonyl chloride, decomp. > 300°. Addition of HCl and 30% H<sub>2</sub>O<sub>2</sub> to the filtrate from the prep. of (I) from m-5-xylenol and OH·SO<sub>2</sub>Cl affords a trichloro-m-xylenol (II), m.p. 175-177°; similar treatment of the KOH hydrolysis product of (I) gives (II) and the K salt, decomp.  $> 300^{\circ}$ , of a dichloro-m-xylenolmonosulphonic acid. Reduction of (I) with Zn-AcOH-HCl affords 2: 4-dithiol-m-5-xylenol (III), m.p. 75° [ $Bz_3$  derivative, m.p. 160—161°;  $Ac_3$  derivative, m.p. 124—125°, also by boiling Zn-AcOH-Ac<sub>2</sub>O-NaOAc on (I)], converted by picryl chloride in EtOH at 100° into a dipicryl derivative, m.p. 237-238° (positive FeCl<sub>3</sub> reaction), converted by treat-ment with KOH-EtOH in situ into bis-2: 4-dinitro-



 $Me Me = \begin{bmatrix} 5:7-dimethylphenoxthin 6:6'-\\disulphide (IV), m.p. 255-\\257^\circ. With aq. CH_2Cl·CO_2Na (V) at 100^\circ the K salt of (III) affords m-5-xylenol-2:4-di (thioglycollic acid), m.p. 151^\circ. m - 4 - Xylenol - 5 - sulphonyl$ 

chloride (loc. cit.) [O-Ac derivative, m.p.  $62^{\circ}$ ; sulphonanilide, m.p.  $142-143^{\circ}$  (O-Ac derivative, m.p.  $105^{\circ}$ ), converted by CH<sub>2</sub>N<sub>2</sub> into the sulphonmethylanilide, m.p. 111-112°] with 2N-KOH, with dry NH<sub>3</sub> in Et<sub>2</sub>O solution, or with 20% NaOAc in COMe<sub>2</sub> affords 1:3:1':3'-tetramethyldiphenyl-4:5:4':5'-sulphonylide, no decomp. at 300°. Reduction (Zn-HCl-AcOH) of (VI) affords 5-thiol-m-4-xylenol, m.p. 91-93° (Bz<sub>2</sub>, m.p. 72°, liquid Ac<sub>2</sub>, and monopicryl, m.p. 164°, derivatives). (VI) with 1 mol. of (V) gives m-4-xylenol-5-thioglycollic acid, m.p. 155° (VII), the 4-carboxymethyl ether, m.p. 190-192°, of which is obtained when an excess of (V) is used. With  $OH \cdot SO_2 \cdot CI$ (VII) gives a substance which is probably a thioindigotin derivative. J. W. B.

Molecular rearrangements involving optically active radicals. V. Rearrangement of optically active radicals. V. Rearrangement of optically active phenyl alkyl ethers. M. M. SPRUNG and E. S. WALLIS (J. Amer. Chem. Soc., 1934, 56, 1715— 1720).—PhOBu<sup> $\beta$ </sup> and H<sub>2</sub>SO<sub>4</sub>-AcOH at 105—108° give (cf. Niederl and Natelson, A., 1932, 510) C<sub>4</sub>H<sub>8</sub>, Bu<sup> $\beta$ </sup>OAc, PhOH, C<sub>6</sub>H<sub>4</sub>Bu<sup> $\beta$ </sup>·OH (I) (yield about 8.5%) (acetate, m.p. 112°), o- and p-OH·C<sub>6</sub>H<sub>4</sub>·COMe, and OH·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H; a better yield of (I) is obtained when rearrangement is effected with ZnCl in AcOH when rearrangement is effected with ZnCl<sub>2</sub> in AcOH. m-C<sub>6</sub>H<sub>4</sub>Me·OBu<sup>β</sup> and H<sub>2</sub>SO<sub>4</sub>-AcOH afford C<sub>4</sub>H<sub>8</sub>, m-C<sub>6</sub>H<sub>4</sub>Me·OH, m-cresolsulphonic acid, (probably) 4acetyl-m-cresol, 4-sec.-butyl-m-cresol, and phenolic material of b.p. 260-275°/760 mm.; p-tolyl Bu<sup>g</sup> ether, b.p. 97-99°/14 mm., similarly affords C4H8, BuBOAc (trace), p-C6H4Me.OH, p-cresolsulphonic acid, 3acetyl-p-cresol, 3-sec.-butyl-p-cresol, m.p. 44-44.5° (acetate, m.p. 80-81°), and (probably) some dibutylcresol. Similar rearrangement of d-PhOBu<sup>\$</sup>, b.p. 86-90°/16 mm., [a]<sup>25</sup><sub>5893</sub> +30.02°, d-m-C<sub>6</sub>H<sub>4</sub>Me·OBu<sup>β</sup>, b.p. 103–108°/17 mm.,  $[\alpha]_{3503}^{27}$  +27.35°, and d-p-C<sub>6</sub>H<sub>4</sub>Me·OBu<sup>β</sup>, b.p. 97–100°/14 mm.,  $[\alpha]_{25}^{26}$  +23.14° [prepared from Bu<sup>β</sup>Br,  $[\alpha]_{11}^{22}$  –19.77°, and the (hydrated) NaOAr at 110–120°], gives dextrorotatory alkylphenols; partial racemisation occurs. Possible mechanisms are discussed. H. B.

I. Influence of the position of thiol and methylthiol groups on the colour of monosubstituted  $\beta$ -naphtholazo-dyes. E. JUSA and G. BREUER. II. Influence of position isomerism and S-methylation on the colour of thiol-anaphtholazo-dyes. E. JUSA and L. GRUN (Monatsh., 1934, 64, 247-266, 267-286).-I. Reduction (Zn-HCl-EtOH) of O-carbethoxy-\beta-naphthol-8-sulphonyl chloride gives the corresponding 8-thiol compound, b.p.  $225-235^{\circ}/20$  mm. [picryl derivative, m.p.  $164^{\circ}$ ; Me thioether (I), b.p.  $235-245^{\circ}/25$  mm.], oxidised by FeCl<sub>3</sub> to the 8:8'-disulphide (II), m.p.  $95^{\circ}$ , and hydrolysed by aq. EtOH-KOH to 8-thiol- $\beta$ -naphthol (III), m.p. 92° (Ag and picryl, m.p. 179°, derivatives), converted by CH<sub>2</sub>Cl·CO<sub>2</sub>Na-KOH into  $\beta$ -naphthol-8converted by  $CH_2CI^{*}CO_2Na-KOH$  into  $\beta$ -maphinol-s-thioglycollic acid, m.p. 146°. Hydrolysis (aq. EtOH-KOH) of (II) gives bis- $\beta$ -maphthol 8:8'-disulphide, m.p. 196°, and (I) gives 8-methylthiol- $\beta$ -maphthol (IV), m.p. 96°. (III) and (IV) when coupled with p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Cl give, respectively, 1-p-nitrobenzene-azo-8-thiol- and -8-methylthiol- $\beta$ -naphthol. By similar methods from O-carbethoxy-B-naphthol-7-sulphonyl chloride (PCI<sub>5</sub> on the K sulphonate) are obtained the chloride (PCl<sub>5</sub> on the K sliphonate) are obtained the corresponding 7-thiol compound, m.p. 109° (picryl derivative, m.p. 152°; Me thioether, m.p. 87°), the 7:7'-disulphide, m.p. 129°, 7-thiol-β-naphthol, m.p. 148° (Ag, picryl, m.p. 203°, and Bz<sub>2</sub>, m.p. 159°, derivatives; Me thioether, m.p. 109°), β-naphthol-7-thioglycollic acid, m.p. 149°, bis-β-naphthol 7:7'-di-sulphide, m.p. 205°, and 1-p-nitrobenzeneazo-7-thiol-and -7-methylthiol-β-naphthol. Similarly are obtained 6 thiol-Q-carbethoxy-β-naphthol. Gircul derivative 6-thiol-O-carbethoxy-\$-naphthol (picryl derivative, m.p. 159°), 6-thiol-\$-naphthol (picryl, m.p. 243°, and Bz2, m.p. 211°, derivatives), β-naphthol-6-thioglycollic

acid, m.p. 157°, and 1-p-nitrobenzeneazo-6-thiol- and -6-methylthiol- $\beta$ -naphthol.

II. By application of similar methods to various  $\alpha$ -naphtholsulphonic acids are obtained, from  $\alpha$ naphthol-3-sulphonic acid (Gebauer-Fülnegg et al., A., 1929, 1440), Et O-carbethoxy-x-naphthol-3-sulphonate, m.p. 66° [3-sulphonanilide, m.p. 119°, from the sulphonyl chloride (V), hydrolysed by boiling KOH-EtOH to a-naphthol-3-sulphonanilide, m.p. 172°]. Reduction (Zn-HCl-AcOH) of (V) gives 3-thiol-O-carbethoxy-a-naphthol, b.p. 178°/4 mm. (Me thioether, b.p. 200°/15 mm. ; picryl derivative, m.p. 167°), hydrolysed by aq. EtOH-KOH (N2) to 3-thiol-a-naphthol, m.p. 108° (Me thioether, m.p.  $63^{\circ}$ ), and oxidised by FcCl<sub>3</sub> to the 3:3'-disulphide, m.p. 113°, hydrolysed to bis- $\alpha$ -naphthol 3: 3'-disulphide, decomp. 240°.  $\alpha$ -Naphthol-3-thioglycollic acid, m.p. 133°, 2-p-nitrobenzeneazo-3-thiol- and -3-methylthiol-a-naphthol are also obtained. Similarly from a-naphthol-4-sulphonic acid and the derived 4-thiol-O-carbethoxy- $\alpha$ -naphthol (VI) (picryl derivative, m.p. 160°) and 4-thiol- $\alpha$ -naphthol (1:4-Bz, derivative, m.p. 154°) are obtained : anaphthol-4-thioglycollic acid, m.p. 125°, and [with excess of CH2Cl·CO2Na on (VI)] 1-carboxymethoxy. naphthalene-4-thioglycollic acid,

 $CO_2H \cdot CH_2 \cdot O \cdot C_{10}H_6 \cdot S \cdot CH_2 \cdot CO_2H$ , m.p. 223°, 2-p-nitrobenzeneazo-4-thiol- and -4-methylthiol- $\beta$ -naphthol. From  $\alpha$ -naphthol-5-sulphonic acid are prepared Et O-carbethoxy- $\alpha$ -naphthol-5-sulphonate, m.p. 77°, and the corresponding 5-thiol compound (picryl derivative, m.p. 158°), the Bz<sub>2</sub> derivative, m.p. 193°, of 5-thiol- $\alpha$ -naphthol,  $\alpha$ -naphthol-5-thioglycollic acid, m.p. 135°, 2-p-nitrobenzeneazo-5-thiol- and -5-methylthiol- $\alpha$ naphthol. The tinctorial properties of these azo-dyes are tabulated, methylation of SH deepening the colour tone. J. W. B.

Formation of an intermediate product in the nitration and simultaneous demethylation of 6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene. H. J. LEWIS and R. ROBINSON (J.C.S., 1934, 1253-1255).-6: 7-Dimethoxy-1:2:3:4-tetrahydronaphthalene, b.p. 125°/1 mm., m.p. 53-54°, obtained by reduction of 6:7-dimethoxy-1-keto-1:2:3:4tetrahydronaphthalene with Zn-Hg and HCl, is converted by HNO<sub>3</sub> (d 1.4) in AcOH at  $> 10^{\circ}$  into 9-nitro-6-keto - 7 - methoxy - 1:2:3:4:6:9-hexahydronaphthalene (I), m.p. 92-93° (decomp.) according to the rate of heating. In boiling EtOH (I) passes rapidly into 5(or 8)-nitro-6-hydroxy-7-methoxy-, m.p. 133°, transformed by Me<sub>2</sub>SO<sub>4</sub> into 5-nitro-6: 7-dimethoxy-, m.p. 88-89°, -1:2:3:4-tetrahydronaphthalene. The bearing of this observation on theories of the mechanism of aromatic substitution is discussed. H. W.

Aromatic sulphides. C. LEFEVRE and C. DES-GREZ (Compt. rend., 1934, 199, 300–302; cf. this vol., 886).—Application of the authors' method to polyhydroxy-compounds containing two  $C_6H_6$  rings at about 150° generally gives disulphides in which the  $\cdot$ S·S· group unites the two aromatic nuclei at positions para to OH or NH<sub>2</sub>. Trihydroxybenzophenone, however, gives the compound, [OH· $C_6H_4$ ·CO· $C_6H_2$ (OH)<sub>2</sub>·S·]<sub>2</sub>. o-OH· $C_6H_4$ ·SO<sub>3</sub>H with PhOH and m· $C_6H_4$ (OH)<sub>2</sub> affords dihydroxy- and trihydroxy-diphenylsulphone, respectively, whilst aminohydroxy- and aminodihydroxy-diphenylsulphone are obtained by similar treatment of m-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H. H. W.

Transpositions in the cyclohexane series. The aptitude of the wandering radical towards migration is influenced by its position in space. M. TIFFENEAU and B. TCHOUBAR (Compt. rend., 1934, 199, 360-362).-2 - Chloro - 1 - methylcyclohexanol - A, b.p. 75-76°/14 mm. (from MgMeI and chlorocyclohexanone), and -B, b.p. 87-88°/14 mm. (from methylcyclohexene and HOCl), are de-halogenated by Mg to 2-methylcyclohexanone with a little acetylcyclopentane (I), and (I), respectively. 2-Chloro-1: 4-dimethylcyclohexanol-A, b.p. 92-94°/17 mm. (from MgMeI and 2-chloro-4-methylcyclohexanone), and -B, b.p. 101-102°/18 mm. (from HOCl and 1 : 4-dimethyl- $\Delta^{1}$ -cyclohexene), similarly afford 2:4-dimethylcyclohexanone with a little 1-acetyl-3-methylcyclopentane (II), and (II), respectively. 2-Chloro-1: 5-dimethyl-cyclohexanol-A, b.p. 88-90°/14-15 mm. (from MgMeI and liquid 2-chloro-5-methylcyclohexanone), and -B, b.p. 83-84°/13-14 mm. (from MgMeI and cryst. 2-chloro-5-methylcyclohexanone), give 2:5-dimethylcyclohexanone with a little 3-acetylmethylcyclopentane (III), and (III), respectively. The aptitudes of the CH<sub>2</sub> and Me towards migration are thus influenced by H. W. their position in space.

Oxidation of 1-methyl- $\Delta^1$ -cyclohexene by selenium dioxide. E. URION (Compt. rend., 1934, 199, 363-365).—The main product of the oxidation of 1-methyl- $\Delta^1$ -cyclohexene, b.p. 110—111°/760 mm., by ScO<sub>2</sub> in AcOH is 2-methyl- $\Delta^2$ -cyclohexenyl acetate, b.p. 84°/23 mm. (2-methyl- $\Delta^2$ -cyclohexenol, b.p. 80°/18 mm.), whilst in EtOH 1-ethoxy-2-methyl- $\Delta^2$ -cyclohexene, b.p. 61—62°/15 mm., mainly results. In H<sub>2</sub>O 2-methyl- $\Delta^2$ -cyclohexenone, b.p. 69—70°/16 mm., 178—179°/760 mm., is the chief product. H. W.

Synthesis of hydroxyalkyl- (a-hydroxyethyl-) benzenes and of the corresponding ethers. R. QUELET (Compt. rend., 1934, 199, 483-485).-Compounds,  $C_6H_4R$ ·CHClMe, are converted into sub-stances,  $C_6H_4R$ ·CHMe·OH, when heated with a dil. solution of NaOH or KOH in H2O-COMe2 or when transformed by NaOAc in AcOH into the corresponding acetates, which are subsequently hydrolysed.  $C_6H_4R$ ·CHCIMe is converted into  $C_6H_4R$ ·CHMe·OEt by gradual addition to a solution of KOH in EtOH at 80° and subsequent boiling. The following are new:  $p-\alpha$ -acetoxyethyl., b.p. 136–138°/16 mm., 5 method 2 methods and 125–136°/10 mm. 5-methyl-2-a-acetoxyethyl-, b.p. 135-136°/10 mm., 2-methyl-5-a-acetoxyethyl-, b.p. 128-129°/8 mm., and 2-methyl-4-a-acetoxyethyl-, b.p. 131-132°/10 mm., -anisole : methoxy-4-a-methoxyethyl-, b.p. 105°/15 mm., -4-α-ethoxyethyl-, b.p. 114-115°/15 mm., -4-α-isopropoxyethyl-, b.p. 118-119°/16 mm., 3-methoxy-1methyl-4-a-methoxyethyl-, b.p. 116-117°/16 mm., 3methoxy-1-methyl-4-a-ethoxyethyl-, b.p. 126°/18 mm., 2methoxy-1-methyl-4-a-methoxyethyl-, b.p. 126°/16 mm. 2-methoxy-1-methyl-4-a-ethoxyethyl-, b.p. 128-129 /17 mm., 1-methoxy-2-methyl-5-a-methoxyethyl-, b.p. 113 16 mm., 1-methoxy-2-methyl-5-a-ethoxyethyl-, b.p. 119% 18 mm., 2-methoxy-1-methyl-5-α-methoxyethyl-4-isopropyl-, b.p. 139-140°/16 mm., and 2-methoxy-1methyl-5-α-ethoxyethyl-4-isopropyl-, b.p. 132-133°/9 mm., -benzene. H.W.

Mechanism of anionotropic change and the fate of the mobile anion. H. BURTON (J.C.S., 1934, 1268—1269).—Under the same conditions of temp., time, and concn. as those used for the production of cinnamyl acctate (I) and *p*-nitrobenzoate (II) from  $\alpha$ -phenylallyl *p*-nitrobenzoate (III), and NMe<sub>4</sub>·OAc (IV) in Ac<sub>2</sub>O (A., 1928, 880), (II) and (IV) in Ac<sub>2</sub>O afford very little (I), thus proving that (II) is not an intermediate in the change (III)  $\rightarrow$  (I) and confirming the mechanism previously deduced for anionotropic change (*loc. cit.*). J. G. A. G.

Tetraphenylmethane dyes. II. R.N. SEN and M. M. GHOSH (J. Indian Chem. Soc., 1934, 11, 455-461; cf. A., 1931, 840).-By condensation of malachite-green or crystal-violet with NaOAc and the appropriate amine, phenol, or ether at 160-180° are prepared hexa- (I), m.p. 115-116° (Ac derivative, m.p. 66-68°), and octa-methyltetra-amino-, m.p. 102-104°, hexamethyltriamino-p-hydroxy-, m.p. 102° (Ac derivative, m.p. 84-85°), -2:4-dihydroxy-, m.p. > 270° (Bz2 derivative, m.p. 117-119°), -p-methoxy-, m.p. 140-144°, -2 : 4-dimethoxy-, m.p. 122°, and -4-hydroxy-3-methyl-, m.p. 95° (Ac derivative, m.p. 64-65°), tetra- (II), m.p. 102° (Ac derivative, m.p. 90°), and hexa-methyltriamino-, m.p. 107—110°, tetramethyldi-amino-p-hydroxy-, m.p. 75° (Ac derivative, m.p. 93— 95°), -2 : 4-dihydroxy-, m.p. 124—126° ( $Bz_2$  derivative, m.p. 113°), -p-methoxy-, m.p. 90—95°, -2 : 4-dimethoxy-, m.p. 85—87°, and -4-hydroxy-3-methyl-tetraphenyl-methane, m.p. 113—115° (Ac derivative, m.p. 90—91°). (I) and (II) led to p-(hexamethyltri-, m.p. 116-117°, and p-(tetramethyldi-aminotriphenylmethyl)benzeneazo- $\beta$ -naphthylamine, m.p. 160—162°. The colours pro-B. S. C. duced on dyeing are listed. R. S. C.

Cholesterols. T. RUEMELE (Pharm. Zentr., 1934, 75, 562—565).—A review. S. C.

Merino fleece. II. Rapid method of separating cholesterol and "isocholesterol" of wool wax. M. R. FRENEY (J.S.C.I., 1934, 53, 289–2907). —The Tswett method of separating closely related coloured compounds by chromatographic adsorption in an  $Al_2O_3$  column has been applied to the separation of the colourless sterols of wool wax. By this method preps. with characteristics closely resembling those of cholesterol (I) and isocholesterol (II) were obtained with comparative ease. The lævorotatory (I) was retained in the upper portions of the column, whilst the dextrorotatory (II) was washed down into the lower layers.

Salts of ergosteryl sulphate : preparation and antirachitic activity on irradiation in aqueous medium. S. NATELSON, A. E. SOBEL, and B. KRAMER (J. Biol. Chem., 1934, 105, 761-765).—K, m.p. 225° (decomp.), Na, m.p. 186° (decomp.), and Li, m.p. 170° (decomp.), ergosteryl sulphates and Li cholesteryl sulphate, m.p. 150° (decomp.), were prepared by the action of the corresponding hydroxide on the pyridine steryl sulphate. The Li salts are the most sol., giving soapy solutions in  $H_2O$ . The ergosteryl salts become antirachitic on irradiation. An aq. solution of the irradiated Li salt, administered sub-

4 c

cutaneously, intravenously, or orally, cures rickets in rats. C. G. A.

Constitution of olivil. Products of oxidation of isoolivil. B. L. VANZETTI and P. DREYFUSS (Gazzetta, 1934, 64, 381-399; cf. A., 1929, 1064).-Oxidation of the alkyl derivatives of isoolivil with KMnO<sub>4</sub>+KOH (11 0) yields two classes of substances, (a) neutral substances (phthalides) and (b) sparingly sol. acids. Certain of these and derived products have been identified in the case of dimethylisoolivil with compounds previously synthesised (A., 1931, 226), and in the case of the Me Et and Et, derivatives with compounds now described. Ethylvanillic acid and SO<sub>2</sub>Cl<sub>2</sub> yield the chloride (I), m.p. 73°, b.p. 173-174°. Condensation of (I) with veratrole in presence of  $AlCl_3$  yields 3:4:3'-trimethoxy-4'-ethoxybenzophenone (II), m.p. 107.5— $108^{\circ}$ , whilst with ethylguaiacol it yields 3:3'-dimethoxy-4:4'-diethoxybenzophenone, m.p. 108—109°, and 4:3'-dimethoxy-3:4'-diethoxybenzo-phenone (III), m.p. 125°. Ethylisovanillic acid (improved prep.) yields the chloride, b.p. 275-280°, which condenses with veratrole to give 4:3':4'-trimethoxy-3-ethoxybenzophenone (IV), m.p. 129-129.5°, or with ethylguaiacol to give (III) and 4:4'-dimethoxy-3:3'diethoxybenzophenone, m.p. 135-136.5°. Dimethylisoolivil yields (a) 4:5-dimethoxy-2-(3':4'-dimethoxyphenyl)phthalide, m.p. 188° (not 238°, as previously given), and (b) 4:5:3':4'-tetramethoxy-2benzoylbenzoic acid, m.p. 223° (Me ester, m.p. 161.5°). The latter yields the corresponding benzylbenzoic acid (c) by reduction, 3:4:3':4'-tetramethoxybenzophenone (d) when heated with Cu powder, and 2:3:6:7-tetramethoxyanthraquinone (e) on treatment with 80%  $H_2SO_4$ . Ethylated methylisoolivil, m.p. 189°, yields the homologous 5 : 3' : 4'-trimethoxy-4-ethoxy-derivatives: (a), m.p. 176-177°, (b), m.p. 184°, (c), m.p. 158.5-159.5°, (d), (IV), and (e) 2:3:6trimethoxy-7-ethoxyanthraquinone, m.p. 290° (V). Methylated ethylisoolivil, m.p. 168°, yields the homologous 4:5:3'-trimethoxy-4'-ethoxy-derivatives: (a), m.p. 148°, (b), m.p. 219-220°, (c), m.p. 167°, (d) (II), and (e) the anthraquinone derivative (V). Diethylisoolivil yields the homologous 5: 3'-dimethoxy-4: 4'-diethoxy-derivatives : (a), m.p. 169°, (b), m.p. 213°, (c), m.p. 187°, (d), (III), m.p. 128—128.5°, and (e) 2 : 6-dimethoxy-3 : 7-diethoxyanthraquinone, m.p. 288°. Provisional formulæ are suggested for olivil (A) and



Cyanohydrins. H. T. BUCHERER and W. BRANDT (J. pr. Chem., 1934, [ii], 140, 129–150).—cyclo-Hexanonecyanohydrin (I) is partly decomposed by distillation at 27–49 mm. With conc. HCl at room

temp. and then at 100° it gives an 83% yield of 1hydroxycyclohexane-1-carboxylic acid (II), or, under other conditions, 39.2% of (II), 19.6% of the amide (III) of (II), and 26.5% of a compound,  $C_{13}H_{21}O_2N$ , m.p. 195°. The  $NH_4$  salt, m.p. 178—198° (closed tube), of (I) gives at 150—160° NH<sub>3</sub>, (I), and (III). (II), cyclohexanone, and hot cone. HCl give a poor yield of a substance, m.p. 39°, b.p.  $160-167^{\circ}/20$  mm. [probably  $\Delta^1$ -cyclohexenyl 1-hydroxycyclohexanecarboxylate, since it is insol. in cold NaOH, but hydrolysed by hot KOH-EtOH to (I)], also obtained as a by-product in the hydrolysis of (I). (II) with SOCl<sub>2</sub> gives a poor yield of (?) 1-carboxycyclohexyl 1-hydroxycyclo-hexanecarboxylate, m.p. 156-158°, but with PBr<sub>3</sub> only an oil. (I) and dry NH<sub>3</sub> give the amino-nitrile, m.p. 186—195° (50% yield), hydrolysed by hot 50%  $H_2SO_4$ to 1-aminocyclohexanecarboxylic acid, m.p. 320° (closed tube) (lit. 334-335°), and giving, when diazotised, (II) and an oil. (I) and solid (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> give 1: 1-pentamethylenehydantoin, m.p. 215° (see following abstract); similar substances, m.p. 210-214°, and 174-175°, are obtained from 3-methylcyclohexanoneand acetone-cyanhydrins, respectively. 1-Phenylhydrazino-1-cyanocyclohexane and H2SO4, under certain conditions only, give a 16% yield of the amide, tail conditions only, give a 10% yield of the anide, m.p. 124—128°, and with hot conc. HCl give tetra-hydrocarbazole. 1- $\beta$ -Naphthylaminocyclohexyl cyan-ide and H<sub>2</sub>SO<sub>4</sub> give the *amide*, m.p. 184—187° (*hydro-chloride*, m.p. 210—222°). (I) and NH<sub>4</sub>HS under various conditions give an oil, an indefinite substance, m.p. about 70–75°, or a substance, m.p.  $225^{\circ}$  (hydro-chloride, m.p.  $270-271^{\circ}$ ), probably (A) or (B), which with conc.  $H_{2}SO_{4}$  at 50-60° gives the substance (C),

$$\begin{array}{ccc} \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{NH} \cdot \mathbf{C} & \mathbf{NH} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{C}_{5}\mathbf{H}_{10} > \mathbf{C} \cdot \mathbf{NH} \cdot \mathbf{C} < \mathbf{C}_{5}\mathbf{H}_{10} \\ & \mathbf{N} = \mathbf{N} \cdot \mathbf{C} \cdot \mathbf{N} + \mathbf{N} \cdot \mathbf{C} + \mathbf{N} \cdot \mathbf{N} \cdot \mathbf{C} + \mathbf{N} \cdot \mathbf{N} \cdot \mathbf{C} + \mathbf{N} \cdot \mathbf{N} \cdot \mathbf{C} + \mathbf{N} \cdot \mathbf{N} \cdot \mathbf{N} + \mathbf{N} \cdot \mathbf{N} + \mathbf{N} \cdot \mathbf$$

m.p. 105°, and with hot 10% H<sub>2</sub>SO<sub>4</sub> gives 1-aminocyclohexanecarboxylic acid. Substances similar to (A) or (B), m.p. 169—176°, 155—156°, and 58—63° (hydrolysed to the corresponding NH<sub>2</sub>-acid), were obtained from 3-methylcyclohexanone-, acetone-, and Me Et ketone-cyanohydrins, respectively. R. S. C.

Hydroxy-nitriles from cyclic ketones. H. T. BUCHERER and H. BARSCH (J. pr. Chem., 1934, [ii], 140, 151-171; cf. preceding abstract).-cyclo-Hexanonecyanohydrin (1) and cumidine at 80° give N-1-cyanocyclohexylcumidine, m.p. 78°, but Na naphthionate and sulphanilate do not react. cyclo-Hexanone (II), KCN, and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (III) in C<sub>6</sub>H<sub>6</sub> give the hydantoin (IV), m.p. 215°, also obtained from (I) and hot, solid (III) or warm or cold, aq. (II), but not with solid or aq. NH4OAc or aq. NH3. (IV) is unaffected by cold, conc. H<sub>2</sub>SO<sub>4</sub> or hot, fuming HCl, but with boiling 50% H2SO4 gives 1-aminocyclohexanecarboxylic acid. (I) and NHPh·NH2 gives s-I-phenylhydrazinocyclohexyl cyanide, m.p. 98°, not obtained from cyclohexyl bromide and NHPh·NH2. 1-Anilinocyclohexyl cyanide and 50%  $H_2SO_4$  at  $90-100^\circ$  give the anilino-acid, the hydrochloride of which gives amorphous substances with Ac<sub>2</sub>O, but at 211-220° yields NH<sub>2</sub>Ph. (I) and cold, fuming HCl give a substance (V),  $C_{13}H_{21}O_2N$ , m.p. 195.5—196°, the 1-OHacid (VI), and a compound, m.p. 85° (probably a mixture), which with aq. Na<sub>2</sub>CO<sub>3</sub> gives a substance, m.p. 130°. (I) and cold EtOH-HCl give (V) and (VI). (V) is also obtained from (I) and cold, conc.  $H_2SO_4$ , is stable to conc.  $H_2SO_4$ , but with hot, conc. HCl gives (VI). (VI) and NH<sub>2</sub>Ph or NHPh·NH<sub>2</sub> at 100° give the anilide, m.p. 167°, and phenylhydrazide, m.p. 185°, respectively. (VI) and SOCl<sub>2</sub> give a substance, m.p. 153°. The NH<sub>4</sub> salt of (VI) at 140—160° gives a substance, m.p. 85—92°. 3-Methylcyclohexanone affords a cyanohydrin, which with NH<sub>2</sub>Ph with or without KCN yields resins; 2-methylcyclohexanonecyanohydrin, however, affords 1-anilino- (both methods), m.p. 126°, and 1-p-toluidino-2-methylcyclohexyl cyanide, m.p. 135°, and with solid (III) a substance, m.p. 207°, but yields indefinite substances with fuming HCl. R. S. C.

Polar structure of aromatic betaines. G. DEVOTO (Gazzetta, 1934, 64, 371-380).—Measurements are recorded of the dielectric const. of the following betaines: o., m., and  $p.NMe_3+C_6H_4\cdotCO_2^-$ , o., m., and  $p.NMe_3^+\cdot C_6H_4\cdot O^-$ , trans-p- $NMe_3^+\cdot C_6H_4\cdot CH:CH:CO_2^-$ , m. and  $p.NMe_3^+\cdot C_4H_4\cdot SO_3^-$ , and of  $o.NMe_2\cdot C_6H_4\cdot CO_2H$  (I),  $NHPh\cdot CH_2\cdot CO_2H$ , and  $NMe_2Ph^+\cdot CH_2\cdot CO_2^-$ . The results confirm the amphoteric polar formulæ for the betaines and (I) is predominantly in the polar form [ $K_2$  (ratio zwitterion/ uncharged mols.)=10]. For o., m., and  $p.NH_2\cdot C_6H_4\cdot CO_2H$  (cf. A., 1933, 777) vals. of  $K_2$  are

0.6-0.8 (?), 3-4, and 0.1-0.2, respectively. There is no evidence of deformation of the mols. in solution. R. K. C.

Preparation of amylbenzoic acids.—See B., 1934, 752.

Derivatives of *m*-cresotic acid. N. M. SHAH and R. L. ALIMCHANDANI (J. Indian Chem. Soc., 1934, 11, 467—469).—5-Carboxy-4-methoxy-2-methylmandelic acid (I), CCl<sub>3</sub>·CH(OH)<sub>2</sub> (II), and H<sub>2</sub>SO<sub>4</sub> give the *chloralide* (III), m.p. 178—179°, the structure of which is proved by hydrolysis by

 $\begin{array}{c} \text{Me} & \text{hs proved by hydrogeneration} \\ \text{hot, aq. Ba(OH)_2 to (I),} \\ \text{hot, aq. Ba(OH)_2 to (I),} \\ \text{oxidation to } \alpha \text{-coccinic} \\ \text{acid, and reduction (Zn dust-AcOH) to } \beta\beta \text{-}dic chloroethoxy - 5 - carboxy-4-} \end{array}$ 

methoxy-2-methylphenylacetic acid, m.p. 195-196°, stable to Br, but giving with conc.  $H_2SO_4$  at 100° HCl and 5-carboxy-4-methoxy-2-methylbenzaldehyde. 5-Carboxy-4-hydroxy-2-methylmandelic acid gives with (II) a product which could not be purified. Condensation of *m*-cresotic acid with (II) in the *m*-position is thus improbable (cf. A., 1921, i, 111). R. S. C.

Condensation of pyruvic acid with aldehydes. R. N. SEN and B. K. SEN (J. Indian Chem. Soc., 1934, 11, 411—418).—AcCO<sub>2</sub>H and the appropriate aldehyde, best with 20% KOH-EtOH, give rapidly good yields of the following benzylidenepyruvic acids: benzylidene- (K salt; dibromide and phenylhydrazone, cryst.; with Ac<sub>2</sub>O and NaOAc at 180—190° gives  $\beta$ -naphthaquinone), p-, yellow (I) [changes at 160— 165° to a red form, which reverts to (I) in hot, aq. EtOH and at 175—180° gives a neutral ring com-

pound, m.p. >  $230^{\circ}$  (also obtained by hot Ac<sub>2</sub>O) (K salt; dibromide, softens at 95°; phenylhydrazone, m.p. 186°)], m-, m.p. > 260°, red (K salt, hygroscopic; dibromide and phenylhydrazone, cryst.), and o-nitrobenzylidene-, cryst. (formed with 10% of indigotin and a small amount of a red substance), cinnamylidene-, orange-red, m.p. 74°, changes to yellow form, m.p. 104° when kept [K salt; dibromide, m.p. 114°; phenylhydrazone, m.p. 152°; with Ac<sub>2</sub>O and NaOAc at 200—210° gives the diketone, R < CH.CH.CH (II; R = CO.CO-CH $C_6H_4$ ), red, m.p. 223°], 3:4-methylenedioxy-, yellow, at 70° or with cold HCl gives an orange-red form, m.p. 162-163° [K salt; dibromide, m.p. 102°; phenylhydrazone, m.p. 174°; gives the diketone (II; R = 3:4-CH<sub>2</sub>O<sub>2</sub>:C<sub>6</sub>H<sub>2</sub>), m.p. 160°], p-methoxy-benzylidene-(K salt; dibromide, m.p. 82—85°; phenylhydrazone, m.p. 158°; gives a red ring compound, C<sub>11</sub>H<sub>8</sub>O<sub>3</sub>), furfurylidene-, m.p. 110° [K salt; phenylhydrazone, m.p. 162° (decemp.)] p. (by HCl) an oil and o hydra m.p. 162° (decomp.)], p- (by HCl), an oil, and o-hydr-oxybenzylidene-pyruvic acid (by HCl or KOH), yellow, decomp. 185—190° (obtained with much red lactone, m.p.  $> 235^{\circ}$ ).  $\beta$ -Resorcylaldehyde (conc. HCl at 200–220°) gives the derived *lactone*, red. Glucose (HCl-EtOH; room temp.) gives slowly a 90% yield of  $\delta \epsilon \zeta_{\eta} \theta$ -pentahydroxy- $\alpha$ -keto-n- $\Delta^{\beta}$ -noneno- $\delta$ -lactone  $(6 - \alpha \beta \gamma \delta - tetrahydroxybutyl - 3 - keto - 3 : 6 - dihydro - \alpha - pyr$ one), m.p. > 240°. R. S. C.

Synthesis of kynurenine. I. Decarboxykynurenine. T. YORITAKA (Z. physiol. Chem., 1934, 226, 29—31).—Reduction of the oxime, m.p. 129— 130°, of o-nitrobenzylidenepyruvic acid with SnCl<sub>2</sub> gave o-aminostyryl-α-aminoacetic acid (hydrochloride; sulphate; picrate, decomp. 195°; picrolonate, m.p. 232—236°; phosphotungstate; platinichloride).

J. H. B. Stereochemistry of diphenyls. XXXV. Effect of 3'-substituents on rate of racemisation of 2-nitro-2'-methoxydiphenyl-6-carboxylic acid. S. L. CHIEN and R. ADAMS (J. Amer. Chem. Soc., 1934, 56, 1787-1792).-Me 2-bromo-3-nitrobenzoate (I), 3-iodopyrocatechol Me2 ether, b.p. 124-125°/ 4 mm. (from the 3-NH2-derivative), and Cu bronze at 220-250° give (after hydrolysis) 2:2'-dinitrodiphenyl-6:6'-dicarboxylic acid (II) and 17.2% of 2-nitro-2': 3'-dimethoxydiphenyl-6-carboxylic acid, m.p. 199–200° (all m.p. are corr.), resolvable into the l-acid, m.p. 199–201°,  $[\alpha]_D^{2i7}$  –66.7° (initial) in EtOH [strychnine salt (+1.5H<sub>2</sub>O), m.p. 143.5–147.5°, m.p. (anhyd.) 208–210°]. 2-Chloro-6-iodoanisole, m.p. 94-95° [from 6-chloro-o-anisidine, m.p. 179-180° (decomp.), obtained by reduction (H<sub>2</sub>, PtO<sub>2</sub>, 95% EtOH) of the NO<sub>2</sub>-compound], and (I) similarly afford (II) and 7.9% of 3'-chloro-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 172—173°, resolvable into d-, m.p. 170·5—172°,  $[\alpha]_{15}^{25}$  +14·2° in EtOH (strychnine salt, m.p. 149·5—162°,  $[\alpha]_{15}^{25}$  -51·7° in CHCl<sub>3</sub>), and 1-forms, m.p. 171·5—173°,  $[\alpha]_{15}^{25}$  -41·5° (initial) in EtOH [strychnine salt, m.p. 150·5—153·5° (decomp.),  $[\alpha]_{15}^{25}$  +42·8° in CHCl<sub>3</sub>]. 2-Bromo-6-iodo-misole m p. 92 - 92° [from 6 brows-0 anisidine b p. anisole, m.p. 92-93° [from 6-bromo-o-anisidine, b.p. 157-159°/30 mm., prepared by reduction (Fe powder, dil. HCl) of the NO2-compound (from the bromonitrophenol, Me<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>CO<sub>3</sub> in xylene)], and (I)

give (II) and 3.7% of 3'-bromo-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 182-183°, resolvable into the l-acid, m.p. 180.5—182.5°, [a]25 -38° (initial) in EtOH (cinchonine salt, m.p. 201-206°). 6-Iodo-2-nitroanisole (from the phenol, Me<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>CO<sub>3</sub> in xylene) and (I) afford (II) and 15.5% of 2:3'-dinitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 173-173.5°, resolvable into d-, m.p. 169.5-171.5°, [a] +12.9° in EtOH [brucine salt (+2H2O), m.p. 192-195.5°,  $[\alpha]_{15}^{15} - 116.4^{\circ}$  in CHCl<sub>3</sub>], and 1-forms, m.p. 170.5-172.5°,  $[\alpha]_{15}^{25} - 13.4^{\circ}$  (initial) in EtOH [brucine salt (+2.5H<sub>2</sub>O), m.p. 140-147.5° (decomp.),  $[\alpha]_{17}^{27}$ +100° in CHCl<sub>3</sub>]. 6-Iodo-2-methylanisole, b.p. 124-126°/22 mm. (cf. Robinson, J.C.S., 1916, **109**, 1084), and (I) at 240-280° similarly give (II) and 18.7% of 2-nitro-2'-methoxy-3'-methyldiphenyl-6-carboxylic acid, m.p. 189-193°, resolvable into the l-acid, m.p. 191-193°,  $[\alpha]_{n}^{\infty}$  -100.2° (initial) in EtOH [cinchonine salt, 193,  $[a]_{\rm B} = 100.2$  (initial) in Each [clustering in m.p. 226—229° (decomp.)]. The half-life periods of the *l*-acids in EtOH and COMe<sub>2</sub> at 25° increase in the order: 3'-substituent=OMe, Me, Cl, Br, NO<sub>2</sub>; the acids are much more stable than the isomeric 5'-derivatives (A., 1933, 63). The Na salts racemise more readily in EtOH than in H<sub>2</sub>O; in both cases racemisation usually occurs more readily than with the acids in org. solvents. H. B.

Action of magnesium phenyl bromide on the anhydride and phenylimide of cyclobutane-1:2dicarboxylic acid. E. ELLINGHOE and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1777—1779).—cyclo-Butane-1:2-dicarboxylic anhydride and MgPhBr (I) (1 mol.) in Et<sub>2</sub>O give trans-2-benzoylcyclobutane-1carboxylic acid; with 2 mols. of (I), the lactone (II), m.p. 116—117°, of 2- $\alpha$ -hydroxybenzhydrylcyclobutane-1-carboxylic acid results. (II) and NH<sub>2</sub>Ph,HBr at 160—170° afford the lactam (III), m.p. 136—137°, of 2- $\alpha$ -anilinobenzhydrylcyclobutane-1-carboxylic acid. N-Phenylcyclobutane-1:2-dicarboxylimide and (I) (1 mol.) in Et<sub>2</sub>O give cis-2-benzoylcyclobutane-1-carboxylanilide, m.p. 149·5—150·5°, converted by cold dil. EtOH-NaOH into the trans-form (A., 1932, 746). 2- $\alpha$  - Hydroxybenzhydrylcyclobutane-1-carboxylanilide (IV), m.p. 193·5—194·5°, is obtained from 2 mols. of (I). (IV) is dehydrated in boiling xylene containing a little KHSO<sub>4</sub> to (III) and is converted by Ac<sub>2</sub>O, EtOH-H<sub>2</sub>SO<sub>4</sub>, or EtOH-NaOH into (II). H. B.

Syntheses of cyclic compounds. XI. Thermal decomposition of trans-hexahydrohydrindene- and of trans-decahydronaphthalene-2:2diacetic acids. R. J. TUDOR and A. I. VOGEL (J.C.S., 1934, 1250-1253).-Thermal decomp. of trans-cyclohexane-1: 2-diacetic acid (improved prep.) gives trans-hexahydro-2-hydrindone (83%) and trans-I-methylcyclohexane-2-acetic acid (Ag salt), whilst somewhat higher yields of ketone are obtained by catalytic decomp. in presence of cryst. baryta. Thermal decomp. of trans-decahydronaphthalene-2:2diacetic acid and trans-hexahydrohydrindene-2: 2-diacetic acid under comparable conditions affords 48% and 35.5% of the corresponding :CH2 compounds (A., 1933, 1049), indicating a real difference in the condition of strain of the parent systems. H. W.

Synthesis of 5-chloro-3:4-dimethoxybenzoic acid. R. M. HANN (J. Washington Acad. Sci., 1934,

329-331).-With NH<sub>2</sub>OH,HCl-NaHCO<sub>3</sub>, 5-24, chloroveratraldehyde (by methylation of 5-chlorovanillin) affords its anti-oxime, m.p. 90° (Ac derivative, m.p. 84°), the unstable hydrochloride, m.p. 117°, of which is converted by HCl into the syn-oxime, m.p. 112°, converted by Ac<sub>2</sub>O into 5-chloroveratronitrile, m.p. 103°, from which the corresponding acid, m.p. 191°, is obtained by hydrolysis with 20% NaOH. All m.p. are corr. J. W. B.

Action of chlorosulphonic acid on naphthalene. G. WALTER (Monatsh., 1934, 64, 287-288).—When C<sub>10</sub>H<sub>8</sub> is heated with ClSO<sub>3</sub>H at 180°, tetrachlorophthalic anhydride, m.p. 255°, is obtained. It gives a "glyptal" resin when heated with glycerol at 100– 170°. J. W. B.

Action of maleic anhydride on anthracene derivatives. E. DE B. BARNETT, N. F. GOODWAY, A. G. HIGGINS, and C. A. LAWRENCE (J.C.S., 1934, 1224-1227).-The formation of an adduct from maleic anhydride (I) and an anthracene derivative is independent of the presence of Bz substituents, but may be hindered by the presence of two meso-substituents, and does not occur with dianthranyl or with heterocyclic compounds formally similar to anthra-Although adducts are easily formed from cene. anthranyl acetates and anthranyl Me ethers, the corresponding OH compounds appear incapable of existence, since attempted hydrolysis is accompanied by loss of maleic acid, and the halogen atoms in the adducts from 9-bromo- and 9:10-dichloro- and -dibromo-anthracene are unaffected by KOH-EtOH. (I) adds to an anthrone giving the anthronylsuccinic anhydride. If Cl is in the peri position to the succinic acid residue, this residue is lost on reduction; otherwise the anthranyl succinic acid is formed, although the anthronylsuccinic acids are exceptional in the facile reduction by Zn and alkali to the  $H_2$ -acids. The fol-lowing are described :  $\alpha\beta$ -endo-9 : 10-dihydroanthra-quinyl-9 : 10-succinic anhydrides (cf. II); 9-Ph, m.p. *quangle 9*: 10-succinic anagariaes (cl. 11), 5-1 h, m.p. 252°; 9-CH<sub>2</sub>Ph, m.p. 223°; -9-Br-, m.p. 255°; -9-OAc-, m.p. 240°; -9:10-(OMe)<sub>2</sub>-, m.p. 259°; -1:5-Cl<sub>2</sub>-9-OAc, m.p. 244°; -1:8-Cl<sub>2</sub>-9-OAc, m.p. 227°; 4:5-Cl<sub>2</sub>-9-OAc, m.p. 249°; β-benzoyl-αβ-endo-9:10dihydroanthraquinylpropionic acid (cf. III), m.p. 234°; anthronylsuccinic anhydride (cf. IV), m.p. 215°; its anithrongisactivity annual (ci. 1v), m.p. 215°; 4:5° $Cl_2$ -, m.p. 215°; 4:5° $Cl_2$ -, m.p. 237°; 1:3° $Me_2$ , m.p. 197°; 1:4° $Me_2$ , m.p. 210°; 2:3° $Me_2$ , m.p. 240—260°; 2:4° $Me_2$ , m.p. 230—235°, derivatives ; anthranyl succinic acid, m.p. 210°; 1:4° $Me_2$ , m.p. 220° 2:4° $Me_2$ , m.p. 225° 219°; its  $1:4-Me_2$ , m.p. 228°,  $2:4-Me_2$ , m.p. 235°,  $2:3-Me_2$ , m.p. 235°, derivatives and the corresponding anhydrides, m.p. 200°, 235°, 240°, and 192-194°, respectively; 9:10-dihydroanthranylsuccinic acid,



m.p. 211° (decomp.) [anhydride, m.p. 169°]; 10-bromoanthranylsuccinic acid, m.p. 255° (decomp.) [anhydride,

m.p. 247° (decomp.)]. 10-Methoxyanthrone, KOH, and p-C6H4Me·SO3Me yield anthraquinyl Me2 ether. Anthraquinyl diacetate is obtained by gradual addition of Zn dust to a boiling solution of anthraquinone in C<sub>5</sub>H<sub>5</sub>N and Ac<sub>2</sub>O. 1:5- and 1:8-Dichloroanthraquinyl diacetate have m.p. 310° (decomp.) and m.p. 249°, respectively. H. W.

Synthesis in the cestrin group. J. C. BARDHAN (Nature, 1934, 134, 217).—Condensation of  $\beta$ -l-naphthylethyl bromide with methyl sodio- $\beta$ -ketoadipate gives a keto-ester, cyclised in presence of H<sub>2</sub>SO<sub>4</sub> to 2-carboxy-3: 4-dihydrophenanthrene-1-propionic acid, m.p. about 226-227°. Distillation with Ac<sub>2</sub>O gives an  $\infty$ strus-producing product, C<sub>17</sub>H<sub>14</sub>O, m.p. 210°. L. S. T.

Synthesis of dicyclic terpenes. Synthesis of ethyl cyclohexanone-2:6-dicarboxylate. P. C. GUHA and N. K. SESHARDIENGAR (Current Sci., 1934, 3, 20-21).-Et cyclohexanone-2 : 6-dicarboxylate, b.p. 140-142°/1-1.5 mm. (hydrolysed and decarboxylated to cyclohexanone), is obtained by the action of NaOEt on Et trimethylenedimalonate (I). (I) and COBr<sub>2</sub> afford Et<sub>4</sub> cyclohexanone-2:2:6:6-tetracarboxylate, b.p. 175°/2-3 mm. (acid, m.p. 246°). By use of Et ethylene- and methylene-dimalonates derivatives of cyclopentanone and cyclobutanone are obtained.

H. W.

Tetraphenylcyclopentadienone in the diene synthesis. C. F. H. ALLEN and L. J. SHEPS (Canad. J. Res., 1934, 11, 171-179; cf. A., 1933, 1164).-The endo-ketonic substances obtained by diene syntheses from tetraphenylcyclopentadienone (I) readily lose first CO to yield derivatives of tetrahydrophthalic acid, and then H<sub>2</sub>, giving substituted phthalic acids.

CPh (IV).

Maleic anhydride (II) and (I) (cf. Dilthey et al., this vol., 62) PhC<sup>6</sup>  $\stackrel{1}{\sim}$  CD<sup>2</sup> CH·CO<sub>2</sub>H hydride (III), m.p. 220°, of PhC<sup>5</sup>  $\stackrel{1}{\sim}$  CH·CO<sub>2</sub>H *cis*-1:4-*endo*keto-1:4:5:6tetraphenyl - 1:2:3:4-tetrahydrophthalic acid (IV), m.p. 190-191° (decomp.) [Ag salt,

decomp. 185-190°; Me2 ester, decomp. 155°]. At 240° (III) gives 3:4:5:6-tetraphenyl-1:2-dihydrophthalic anhydride (V), m.p.  $255^{\circ}$  (corresponding cis-Me<sub>2</sub> ester, m.p.  $149-150^{\circ}$ ). Prolonged heating at  $250^{\circ}$  of (I) and (II) or of (III) or (V) at  $270^{\circ}$ , alone or with S, yields 3:4:5:6-tetraphenyl-o-phthalic acid, m.p. 287° [Na salt;  $Me_2$  ester (VI), m.p. 250-251°, also from Me maleate and (I)]. With Me fumarate at 170°, (I) yields trans-Me2 1:4-endoketo-1:4:5:6tetraphenyl-1:2:3:4-tetrahydrophthalate, m.p. 214-215° (decomp.); prolonged heating at 225° gives trans-Me2 3:4:5:6-tetraphenyl-1:2-dihydrophthalate, m.p. 157°. (I) and  $[:C \cdot CO_2 Me]_2$  give (VI); with  $[:C \cdot CO_2 Et]_2$ (I) yields Et 3:4:5:6-tetraphenylphthalate, m.p. 187-188°. (I) and CBz:CPh at 195° vield 2:3:4:5:6-pentaphenylbenzophenone, m.p. 340-341°. (I) does not react with Ph styryl ketone, transdibenzoylethylene, or CPh<sub>2</sub>:CO. Anhydroacetone-benzil and (II) at 131° give 1:4-endoketo-5:6-di-phenyl-1:2:3:4-tetrahydrophthalic acid, (VII), m.p. 186-187° (Ag salt, m.p. 198-199°; K salt; oxime, m.p. 210, 220°) On best from (VII) m.p. 219-220°). On heating (VII) passes into 4:5diphenyl-1: 2-dihydrophthalic acid (VIII), m.p. 235-243° (decomp.) (Ag salt, m.p. 205°). With (II), (VII) and (VIII) yield the dianhydride previously described (loc. cit., IX). All of the endoketonic products described are unaltered by treatment with  $PhN_3$ . H. N. R.

Bile acids. XLIII. M. SCHENCK (Z. physiol. Chem., 1934, 226, 45-52; cf. this vol., 653).-Elimination of the ketoxime group from the oximinolactamhydroxamic acid (I) (loc. cit.) by 20% HCl at 100° affords a ketolactamhydroxamic acid (II), C24H36O8N2, decomp. 238°. With HNO3, (II) gives a ketolactamtricarboxylic acid,  $C_{24}H_{35}O_8N$ , two forms, m.p. 200—205°, and decomp. 262°, respectively (cf. A., 1928, 1007). When (II) is hydrolysed with HCl and the solution evaporated to dryness, the NH<sub>2</sub>OH recombines yielding the oximinoaminotetracarboxylic acid,  $C_{24}H_{38}O_9N_2$ , decomp. 228°. Reduction of the nitro-oximinohydroxamic acid,  $C_{24}H_{35}O_9N_3$ , with Zn



dust and aq. NH<sub>3</sub> yields a dioximinohydroxamic acid (III),  $C_{24}H_{37}O_8N_3$ , decomp. 270°. Beckmann inversion (90%  $H_2SO_4$ ) of (III) gives (I). (III) did not give the expected blue nitroso-compound, C<sub>24</sub>H<sub>33</sub>O<sub>3</sub>N, with HNO2 H. B.

Two syntheses of norpinic acid. K. N. GAIND and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 421-425).-Kerr's synthesis (A., 1929, 445) of norpinic acid does not give the yield claimed. The Na2derivative of Et4 isopropylidenedimalonate (improved prep.) and CH<sub>2</sub>I<sub>2</sub> or the Na<sub>2</sub>-derivative of Et<sub>4</sub> methylenedimalonate (improved prep.) and CMe2Cl, in dry  $C_6H_6$  (8 hr.) at 140° give, after hydrolysis, 1:1-di-methylcyclobutane-2:2:4:4-tetracarboxylic acid, m.p. 200°, which at 220–240°, or, better, in hot 50%H<sub>2</sub>SO<sub>4</sub>, gives norpinic acid, m.p. 146° (softens at R. S. C. 137°).

Knoevenagel reaction and synthesis of unsaturated nitro-compounds. D. E. WORRALL (J. Amer. Chem. Soc., 1934, 56, 1556-1558; cf. Hann and Lapworth, J.C.S., 1904, 85, 46).—β-Nitro-α-phenyl-ethyl alcohol (I) is formed from PhCHO, MeNO<sub>2</sub>, and a little NEt<sub>3</sub>. Reaction occurs much more slowly when NH<sub>2</sub>Bu or n-amylamine (II) is the condensing the Schiff base is first produced, but agent: CHPh.CH·NO2 (III) is the final product. This is probably formed by way of (I) [which is shown to decompose in presence of NH2Alk into (III) and H2O]. sec. Amines are least suitable for the condensation. o-C6H4Cl·CHO and m-NO2·C6H4·CHO react much more readily than PhCHO in presence of NEt3; reaction occurs very slowly in presence of (II), probably owing to the greater stability of the intermediate Schiff base. (III) is also formed from PhCHO,  $MeNO_2$ , and  $NH_2Ph$  [which has no action

on (I)] or other NH<sub>2</sub>Ar; the following mechanism is suggested (cf. A., 1927, 761): CHPh:NPh+MeNO2

 $\rightarrow$  NO<sub>2</sub>·CH<sub>2</sub>·CHPh·NHPh  $\xrightarrow{\text{PhOHO}}$  CHPh:CH·NO<sub>2</sub>+ CHPh:NPh+H2O. (III) is decomposed rapidly by mol. equivs. of NH<sub>2</sub>R and NHR<sub>2</sub>. H. B.

Jute lignin. III. Action of nitric acid on lignin. P. B. SARKAR (J. Indian Chem. Soc., 1934, 11, 407-410; cf. A., 1933, 1050).-Jute lignin with HNO<sub>3</sub> (0.25N-fuming) gives H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (more with conc. than with dil. acid, and at 100° than at 30°), a mixture of  $NO_2$ -compounds (I), and a little AcOH. (I) has 8.27 - 10.2% of OMe. CO(NH<sub>2</sub>)<sub>2</sub> reduces, but does not destroy entirely, the oxidising power of HNO<sub>2</sub>. R. S. C.

Chemical formula of lignin. P. KLASON (Svensk Kem. Tidskr., 1934, 46, 140, 168-169; cf. this vol., 408).—A reply to criticisms. R. P. B.

Many-membered ring-systems. IV. Svnthesis of *dl*-muscone. K. ZIEGLER and K. WEBER (Annalen, 1934, 512, 164-171; cf. this vol., 894) .ακ-Dibromodecane and CHNa( $CO_2Et$ )<sub>2</sub> (I) in EtOH give  $Et_2$  κ-bromodecylmalonate, b.p. 123°/0.02 mm., which with MeI and NaOEt yields  $Et_2$  methyl- $\kappa$ -bromodecylmalonate, b.p. 128°/0.02 mm. This with (I) forms Et<sub>2</sub> tridecane-aaµµ-tetracarboxylate, an oil, yielding by KOH-McOH and subsequent heating at 100° tridecane-au-dicarboxylic acid, m.p. 83-84°, the 100 triaecane-aμ-atcarocagice uta, h.p. 65–67, the Et<sub>2</sub> ester, b.p. 176°/0.9 mm., of which with Na and amyl alcohol gives β-methyltetradecane-aξ-diol (30%) yield), m.p. 46–47°. This afforded aξ-dibromo-β-methyltetradecane, b.p. 135°/0.002 mm., and thence β-methyltetradecyl aξ-dicyanide, b.p. 165°/0.3 mm., which is cyclised to dl-muscone, b.p. 128°/1.2 mm. (semicarbazone, m.p. 133.5-134.5°). R. S. C.

Addition reactions of phenyl vinyl ketone. IV. Termolecular products. C. F. H. ALLEN and A. C. BELL (Canad. J. Res., 1934, 11, 40-46; cf. A., 1933, 950).-Owing to the reactivity of the primary products CN·CH2·CO2Me, CN·CH2·CO·NH2, and CH<sub>2</sub>(CN)<sub>2</sub> give termol. additive products with Ph vinyl ketone (I), whilst 1 mol. of MeNO<sub>2</sub> condenses with 3 mols. of (I). CN·CH<sub>2</sub>·CO<sub>2</sub>Me (even in excess) with (I) in presence of NaOMe in MeOH gives Medi- $\beta$ -benzoylethylcyanoacetate (II), m.p. 144° [disemi-carbazone, m.p. 220° (decomp.)]. (II) and HBr in AcOH yield Me di-( $\beta$ -benzoylethyl)malonamate (III), ACOH yield the ar-(p-orthogotal optimization (11), m.p. 224°, reconverted into (II) by  $P_2O_5$ ; (III) cannot be converted into the Me<sub>2</sub> ester, but yields di-( $\beta$ -benzoylethyl)malonamic acid (IV), m.p. 280°, with aq. KOH followed by HCl. With HBr in CHCl<sub>3</sub>, (II) gives the imide-bromide,  $(CH_2Bz\cdot CH_2)_2C(CO_2Me)\cdot CBr\cdot NH$ , m.p. 165° (decomp.), readily hydrolysed to (IV). (IV) with AcOH yields Me 2-bromo-6-phenyl-3-β-benzoylethyl-3: 4-dihydropyridine-3-carboxylate, m.p. 144°; this is also hydrolysed to (IV) by HBr.  $Di\cdot(\beta-$ benzoylethyl)cyanoacetic acid, m.p. 161°, from (II), on heating loses CO<sub>2</sub>, giving  $\gamma$ -cyano- $\alpha\epsilon$ -dibenzoylpentane (V), m.p. 100° [monosemicarbazone, m.p. 202° (de-comp.)]. This yields a dimeride, m.p. 265°, with HBr in AcOH, conc. HCl, or 50% H<sub>2</sub>SO<sub>4</sub>; with conc.  $H_2SO_4$  (V) isomerises to  $\Delta^5$ -2-keto-6-phenyl-3- $\beta$ benzoylethyltetrahydropyridine, m.p. 141°, sometimes accompanied by a substance, C20H21O3N2, m.p. 137°.

With Br in AcOH (V) is dibrominated and isomerised to 2-bromo-6-phenyl-3- $\beta$ -bromo- $\beta$ -benzoylethylpyridine, m.p. 151°. With CH<sub>2</sub>(CN)<sub>2</sub> (I) gives di-( $\beta$ -benzoylethyl)malononitrile, m.p. 215°; (I) and CN·CH<sub>2</sub>·CO·NH<sub>2</sub> yield di- $\beta$ -benzoylethylcyanoacetamide, m.p. 200—201°. McNO<sub>2</sub> with (I) gives nitrotri- $\beta$ -benzoylethylmethane, m.p. 132°. The prep. of Et 4-benzoylpyrazoline-5carboxylate, m.p. 140°, is described. H. N. R.

Properties of adipoin, a cyclic sugar. G. P. G. MOEYS and 'N. SCHOORL (Pharm. Weekblad, 1934, 71, 1026—1029).—Adipoin, 2-hydroxycyclohexanone, gives all the analytical reactions for a sugar. It reduces Trommer's, Luff's, and Fehling's solutions in the cold, gives a positive test with Bose's reagent (A., 1932, 499) at a dilution of 1:2000, and forms phenylosazones [p-bromo-, m.p. 183—185° (decomp. at 170°), p-nitro-, m.p. 236—237°]. S. C.

Phenanthrene series. VII. 3-Hydroxyacetylphenanthrenes and amino-ketones and -alcohols derived from them. Aminohydroxyphenanthrenes. A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1934, 56, 1745-1747).-3-Hydroxy-6-acetylphenanthrene (I) (cf. A., 1933, 951) is converted (no details) into 3-methoxyphenanthrene-6-carboxylic acid [hydrazide, m.p. 193-194° (all m.p. are corr.)] and thence (Curtius degradation) into 6-amino-3-methoxyphenanthrene, m.p. 125° [N-CO2Et derivative, m.p. 134-135° (the main reaction product is a substance, m.p. 117°); hydrochloride, m.p. 263-264° (decomp.)]. 6-Hydroxy-3-methoxyphenanthrene, m.p. 135-136°, is methylated to 3:6-dimethoxyphenanthrene [picrate, m.p. 154.5° (decomp.)], thus establishing the constitution of (I). 3-Methoxy-9-acetylphenanthrene (II) (cf. loc. cit.) is similarly converted into 3-methoxyphenanthrene-9-carboxylic acid [hydrazide, m.p. 234° (decomp.)] and thence into 9-amino-3-methoxyphenanthrene, m.p. 117-118° {N-CO2Et, m.p. 147°, Cl-, m.p. 128-129° (Ac2 derivative, m.p. 134-135°), and Ac. derivative, m.p. 148.5-150° [described by Werner (A., 1902, i, 437) as the Ac derivative]}, thus establishing the structure of (II). ? Chloro-9-amino-3-ethoxyphenanthrene (Ac, derivative, m.p. 122°) has m.p. 120-123°. 9-Nitro-3-acetoxyphenanthrene, m.p. 159° [from the 3-OAc-derivative and HNO<sub>3</sub> (d 1.5) in AcOH], is hydrolysed (dil. NaOH) to the 3-OH-derivative, m.p. 188-189°, reduced (alkaline Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) to 9-amino-3-hydroxyphenanthrene, m.p. 265-267° (decomp.) (hydrochloride). 10-Amino-3-methoxyphenanthrene, m.p. 116-116.5° (Ac2, m.p. 122.5-123.5°, and N-CO2Et, m.p. 136.5-137.5°, derivatives), is obtained by Curtius degradation of 3-methoxyphenanthrene-10-carb-oxylic acid (Me ester, m.p. 93°; hydrazide, m.p. 243-244°). The Ac derivative, m.p. 249-250°, of 9amino-10-methoxyphenanthrene, m.p. 68-69°, is prepared by methylation (CH<sub>2</sub>N<sub>2</sub> or Me<sub>2</sub>SO<sub>4</sub>) of 9-acetamido-10-hydroxyphenanthrene (Et ether, m.p. 247°). 4-Acetamido-3-hydroxyphenanthrene, m.p. 197° (Me, m.p. 208-209°, and Et, m.p. 159°, ethers), is obtained by hydrolysis of the Ac<sub>2</sub> derivative (Fieser, A., 1929, 930). (II) and Br in Et<sub>2</sub>O and sunlight give 3-methoxy-9-bromoacetylphenanthrene, m.p. 115.5-116.5°, which with NHMe2 in C6H6 and H2 affords 3-methoxy-9-dimethylaminoacetylphenanthrene [hydrochloride (III), m.p. 190-191° (decomp.); perchlorate, m.p.

198—199°]. (III) is reduced  $(H_2, PtO_2, EtOH)$  to the hydrochloride, m.p. 207—208° (decomp.), of 3-methoxy-9 -  $\beta$  - dimethylamino -  $\alpha$  - hydroxyethylphenanthrene [picrate, m.p. 229° (decomp.); benzoate hydrochloride, m.p. 168—170° (decomp.)]. 3-Acetoxy-6-bromoacetyl-, m.p. 160°, -6-diethylaminoacetyl- (perchlorate, m.p. 199—200.5°), and -6- $\beta$ -diethylamino- $\alpha$ -hydroxyethylphenanthrene [hydrochloride, m.p. 173—174° (decomp.)] are similarly prepared. 3-Hydroxy-6- $\beta$ -diethylamino- $\alpha$ -hydroxyethylphenanthrene [hydrochloride, m.p. 186—187° (decomp.); dibenzoate hydrochloride, m.p. 190—191°] has m.p. 125°. H. B.

1:2-Dibenzoylcyclobutanes. E. ELLINGBOE and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1774-1777).—Successive treatment of the mixture of cis- (I) and trans-cyclobutane-1: 2-dicarboxylic acids obtained from cyclobutane-1:1:2-tricarboxylic acid (modified prep.; cf. A., 1929, 794) at 150°, with SOCl, and  $C_6H_6$ +AlCl<sub>3</sub> gives about 75% of trans-1:2-di-benzoylcyclobutane (II), m.p. 96—97.5° [previously described (A., 1932, 746) as the  $\alpha$ -form]. Similar treatment of (I) affords 2-benzoylcyclobutane-1-carboxylic acid, m.p. 127—128° [also obtained from the anhydride of (I),  $C_6H_6$ , and  $AlCl_3$ ], the chloride of which with  $C_6H_6$  and  $AlCl_3$  gives (II). Prolonged exposure of (II) (in  $C_6H_6$ ) to ultra-violet light has little or no effect. (II) and Br in CCl. since in (III) or no effect. (II) and Br in CCl<sub>4</sub> give cis- (III), m.p. 111-112°, and trans- (IV), m.p. 155-156°, -Br,-derivatives (cf. loc. cit.), both of which are converted (at differing rates) by KI in EtOH into 1 : 2-dibenzoyl- $\Delta^2$ cyclobutene (V), m.p. 96–97.5°. (V) and Br in  $CCl_4$ afford (III) only. Reduction (H2, PtO2, EtOH) of (V) gives cis-1: 2-dibenzoylcyclobutane (VI), m.p. 121-122° (dioxime, m.p. 174-175°), previously described (loc. cit.) as the  $\beta$ -form, and a compound, m.p. 222-223°. (VI) is readily converted into (II) by warm conc. HCl or cold EtOH-NaOH; bromination gives H. B. (III) and (mainly) (IV).

Isomeric forms of 3-phenyl-2:3:5:6-tetramethyl- $\Delta^5$ -cyclohexene-1:4-dione. H. M. CRAW-FORD (J. Amer. Chem. Soc., 1934, 56, 1803—1804).— 3-Phenyl-2:3:5:6-tetramethyl- $\Delta^5$ -cyclohexene-1:4dione, m.p. 142° (A., 1928, 523), is converted by heating with fused NaOAc in EtOH into a geometrical isomeride, m.p. 72° (cf. loc. cit.), which is oxidised (KMnO<sub>4</sub>, COMe<sub>2</sub>) to the more fusible form of  $\alpha$ -phenyl- $\alpha\alpha'$ -dimethylsuccinic acid (this vol., 294). H. B.

Perylene derivatives. XLII. Degradation of 3: 9-dibenzoylperylene. O. BENNDORF and W. SORNS (Monatsh., 1934, 64, 167—172).—Oxidation of 3: 9-dibenzoylperylene with  $CrO_3$ -AcOH affords its 4: 10-quinone (I), m.p. 279° (previous darkening) (diodiazine with N<sub>2</sub>H<sub>4</sub>,H<sub>2</sub>O in PhMe), reduced to the hydroquinol, m.p. 266—267°, together with 2:6-dibenzoylanthraquinone-1: 5-dicarboxylic acid +2EtOH and solvent-free, m.p. 315° [also by direct oxidation of (I)], decarboxylated by sublimation in a vac. (CO<sub>2</sub>) to 2: 6-dibenzoylanthraquinone, m.p. 283—284°. J. W. B.

Tautomerism of anthraquinone- $\alpha$ -carboxyl chlorides. V. Tautomerism of anthraquinone-1:4-dicarboxyl dichloride and synthesis of the ring-system of the homocoerdianthrone series

(4:5:6:7:8:9-tribenzopyrene-3:10-quinone). R. SCHOLL and K. MEYER [with A. KELLER]. VI. Tautomerism of 3-methyl- and 2:4-dimethylanthraquinone-1-carboxyl chloride. R. SCHOLL, J. DONAT, and O. BOTTCER (Annalen, 1934, 512, 112-124, 124-130; cf. this vol., 1006).-V. 1:4-Dimethylanthraquinone and MgPhBr (1 mol.) in cold Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> give a little 9-phenyl-1: 4-dimethyloxanthrone, m.p. 198°, whereas 10 mols. of MgPhBr and subsequent heating afford a 55% yield of 9:10-dihydroxy - 9: 10 - diphenyl - 1: 4 - dimethyldihydroanthra cene, m.p. 221-222°. Anthraquinone-1: 4-dicarboxyl dichloride (I) (best from the acid and boiling SOCl<sub>2</sub>), m.p. 203-205°, with C<sub>6</sub>H<sub>6</sub> and AlCl<sub>3</sub> in PhNO<sub>2</sub> at 50–60° gives 9-phenyloxanthrone-1:4-dicarboxylic acid (40% yield) (probably cyclised by  $H_2SO_4$  and Cu acid (40%) yield) (probably cyclised by  $H_2^{0,0}$  and out powder), also obtained in poorer yield together with 1:4-dibenzoylanthracene (7%), m.p. 225°, by use of FeCl<sub>3</sub>. (I), PhMe, and a little FeCl<sub>3</sub>, when heated, give 9-hydroxy-9-p-tolyloxanthrone-1:4-dicarboxylic acid, m.p. 194—195° (stable to hot AcOH or Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, but undergoes ring-closure with H2SO4-Cu), and 1:4di-p-toluoylanthraquinone, cryst. (I), PhMe, and AlCl<sub>3</sub> in cold PhNO<sub>2</sub>, however, afford 9:10-dihydroxy-9: 10-di-p-tolyl-9: 10-dihydroanthracene-1: 4-dicarboxylomonolactone (II), m.p. about 260° (rapid heating), converted by hot Ac<sub>2</sub>O into the dilactone (III), m.p. 253°, also obtained from (II) at the m.p. and reconverted into (II) by hot AcOH. (II) or (III) with conc.  $H_2SO_4$ , faster with Cu powder, undergoes ring-closure,



and with HI-AcOH gives 9:10-di-ptolylanthracene-1: 4-dicarboxylic acid, eryst., which with conc. H<sub>2</sub>SO<sub>4</sub> at 70-80° rapidly affords 5':5''-dicomethylhomocærdianthra -7':7'' - dione (5':5''-dimethyl-4:5:6:7:8:9-tribenzopyrene - 3:10 - quinone) (IV), blue, cryst., is oxidised by CrO<sub>3</sub> to the colourless 9:10 - (OH)<sub>2</sub> - compound, which is rapidly auto-reduced to (IV). Similarly are prepared 1:4-di-(2':4'dimethylbenzoyl)- (by FeCl<sub>3</sub> or AlCl<sub>3</sub>), m.p. 237-238°, 1:4-di-(2':4':6'trimethylbenzoyl)- (by AlCl<sub>3</sub>), m.p.

Me (IV.) dimethylbenzoyl)- (by FcCl<sub>3</sub> or AlCl<sub>3</sub>), Me (IV.) m.p. 237-238°, 1:4-di-(2':4':6'trimethylbenzoyl)- (by AlCl<sub>3</sub>), m.p. 209-210°, and 1:4-di-p-anisoyl-anthraquinone (by FeCl<sub>3</sub>), m.p. 243-245°, 9:10-di-p-anisylanthracene-1:4-dicarboxylic acid, cryst. (obtained by HI from the dihydroxydihydrolactone or dilactone, which were not isolated pure), and 5':5''-dimethoxyhomocœrdianthrone, cryst.

VI. 1:3-Dimethylanthracene and pptd.  $MnO_2$  in  $H_2SO_4-H_2O$  at 60—80° give 3-methylanthraquinone-1carboxylic acid (87% yield), m.p. 277° (cf. lit.), the constitution of which is proved by reduction (Zn dustaq. NH<sub>3</sub>), distillation, and oxidation to 2-methylanthraquinone. This acid with PCl<sub>5</sub> in C<sub>6</sub>H<sub>6</sub> affords the chloride, which with C<sub>6</sub>H<sub>6</sub> and FeCl<sub>3</sub> yields 3benzoyl-1-methylanthraquinone, m.p. 224·5—226°, and the lactone of 9-phenyl-3-methyloxanthrone-1-carboxylic acid (not obtained pure), reduced by Zn dust and KOH to 9-phenyl-3-methylanthracene-1-carboxylic acid, m.p. 295·5—297°. m-Xylene affords similarly 84% of 1-(2': 4'-dimethylbenzoyl)-3-methylanthraquinone, m.p. 196·5—198°, and a little amorphous lactone. Anthraquinone-1: 3-dicarboxylic acid (modified prep.)

gives (SOCl<sub>2</sub>) the dichloride, cryst., which with C<sub>6</sub>H<sub>6</sub> and FeCl<sub>3</sub> affords 1:3-dibenzoylanthraquinone, m.p. 212-214°, and the lactone of 3-benzoyl-9-phenyloxanthrone-1-carboxylic acid, not obtained pure. 1-Cyano-2: 4-dimethylanthraquinone (62% yield from the 1-NH2-compound), m.p. 225-226°, affords 2:4-dimethylanthraquinone-1-carboxylic acid, m.p. 241.5-242.5°, the chloride, m.p. 155-158°, of which leads to 9-phenyl-, m.p. 198-199°, and 9-m-xylyl-2: 4-dimethyloxanthrone-1-carboxylolactone, m.p. 202-204°, and 1-(2': 4'-dimethylbenzoyl)-2: 4-dimethylanthraquinone, m.p. 193-194°. The lactones with H<sub>2</sub>SO<sub>4</sub>-Cu gives coeranthranols. The relative yields of lactones and diketones accord with expectation. 2-Methylanthraquinone-1-carboxyl chloride has m.p. 196—198° (no decomp.; cf. lit.). R. S. C.

The "hydrosulphides" of carvone and 1:4isopropyl- $\Delta^2$ -cyclohexen-1-one. P. L. HOOPER, A. K. MACBETH, and J. R. PRICE (J.C.S., 1934, 1147— 1150).—d-Carvone hydrosulphide forms a bis-2:4-dinitrophenylhydrazone, m.p. 222°,  $[\alpha]_{1}^{\infty}$  —172·2° in CHCl<sub>3</sub>. 1:4-isoPropyl- $\Delta^2$ -cyclohexen-1-one (2:4-dinitrophenylhydrazone, m.p. 137·5—138°) in EtOH with H<sub>2</sub>S gives a hydrosulphide, m.p. 206—207°,  $[\alpha]_{1}^{\infty}$ —127·6° in CHCl<sub>3</sub> (bis-2:4-dinitrophenylhydrazone, m.p. 238—239°,  $[\alpha]_{1}^{\infty}$  +6·35° in CHCl<sub>3</sub>). The hydrosulphide dinitrophenylhydrazones caunot be oxidised and with MeI in Et<sub>2</sub>O-HgCl<sub>2</sub> yield those of the parent ketone. The structure of the compounds is discussed; the presence of two keto-groups is indicated. F. R. S.

Norcamphor group. I. G. KOMPPA and S. BECKMANN (Annalen, 1934, 512, 172-185) .-- a-Norborneol (I), m.p. 149-150° (phenylurethane, m.p. 159-160°), is obtained from norcamphor by hydrogenation (colloidal Pd) in HCl-aq. EtOH or reduction with Na-EtOH. 1:2:2-dicycloHeptanecarboxyl chloride (II), b.p.  $200-202^{\circ}/750$  mm.,  $80-81^{\circ}/8$  mm. (obtained from the acid by PCl<sub>3</sub>), with NaN<sub>3</sub> in xylene  $\begin{array}{c} \mathrm{CH}_2 \cdot \mathrm{CH} - \mathrm{CH}_2 \\ \mid & \mathrm{CH}_2 \mid \\ \mathrm{CH}_2 \cdot \mathrm{CH} - \mathrm{CH} \cdot \mathrm{COCl} \end{array}$ CH2·CH-CH  $CH_2 \cdot CH - CH_2$ CH<sub>2</sub>  $CH_2 \parallel$ CH2·CH-CH·OH ĊH2·ĊH-ĊH (V.) (II.) (I.)

at 120-140° gives \$-norbornylcarbimide, b.p. 71-72°/ 9 mm. [NN'-di-β-norbornylcarbamide, m.p. 257-259° (decomp.)], hydrolysed by conc. HCl to β-norbornylamine, b.p. 156-157°, m.p. 75-80° [hydrochloride, m.p. about 260° (decomp.); aurichloride, m.p. 211-212° (decomp.); platinichloride, decomp. >  $200^{\circ}$ ; carbamide, m.p. 196—197°; phenylthiocarbamide, m.p. 154—155°; picrate, m.p. 174—175°], also obtained less well by Hofmann degradation of the amide from (II). This base with  $HNO_2$  yields  $\beta$ -norborneol (III), m.p. 127—128°, b.p. 176—177° (phenylurethane, m.p. 145-146°; H phthalate, m.p. 102-103°; acetate, b.p.  $89-90^{\circ}/20$  mm.), oxidised by  $K_2Cr_2O_7-H_2SO_4$  to norcamphor. The corresponding chloride (obtained by PCl<sub>5</sub>), b.p. 160-162°, or bromide (IV), b.p. 81-83°/ 30 mm., with Na and EtOH gives norbornylane (1:2:2-dicycloheptane), m.p. 86-87°. (III) and  $P_2O_5$  or (IV) and boiling quinoline give norbornylene (V), m.p.  $51-53^{\circ}$  (dibromide, an oil; nitrosochloride, m.p.  $157-158^{\circ}$ ;  $PhN_3$ -compound, m.p.  $101-102^{\circ}$ ), which is oxidised only by KMnO<sub>4</sub>. R. S. C. R. S. C.

Terpenes. I. Action of oxalic acid on d- $\alpha$ -pinene. T. KUWATA (J. Soc. Chem. Ind. Japan, 1934, 37, 312-315B).—d- $\alpha$ -Pinene and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in COMe<sub>2</sub> at 50—90° afford d-borneol, d-isoborneol, d- $\alpha$ -terpineol (and their oxalates), dipentene, and a small amount of polyterpenes. The acid is assumed to attack the 1- and 7-positions. R. S. C.

Preparation of camphene from bornyl chloride. T. KUWATA (J. Soc. Chem. Ind. Japan, 1934, 37, 389–392B).—The activity of phenols in the removal of HCl from bornyl chloride by  $NH_2Ph$  (I) increases with the no. of OH groups. In presence of  $NH_2Ph$ ,HCl, the condensation of camphene (II) and (I) to give bornylaniline (III) is reversible. When bornyl chloride is distilled with (I), (II) is removed and (III) decomposes into (I) and (II). A. L.

Preparation of camphorquinone. J. ALLARD (Bull. Inst. Pin, 1934, 127–128; cf. this vol., 299).—Borneol and  $SeO_2$  at a high temp. afford camphorquinone (60%). J. L. D.

Use of nitrogen dioxide in the terpene series. R. DULOU (Bull. Inst. Pin, 1934, 129–139).— Mainly a review. Benzylidenecamphor (cf. A., 1891, 1498) with  $N_2O_4$  in Et<sub>2</sub>O below 0° affords a *nitrosite*, m.p. 185–186°, which is hydrolysed (KOH) to camphorquinone. J. L. D.

Rotatory powers of disubstituted camphoranilic acids. M. SINGH and B. SINGH (J. Indian Chem. Soc., 1934, 11, 433—440).— $[M]_{5780}$  and  $[M]_{5461}$ in McOH, EtOH, COMe<sub>2</sub>, and COMeEt are given for 2'-methyl-5'-, m.p. 206° (211·8°), -4'-, m.p. 221—222° (174·7°), and -3'-chloro-, m.p. 219° (145·5°), 4'-methyl-2'-chloro-, m.p. 206—207° (76·3°), and 2'-methoxy-5'chloro-camphoranilic acid, m.p. 176—177°, the figures quoted in parentheses being  $[M]_{5780}$  in MeOH.

R. S. C.

cis- and trans-Isomerides of myrtanol. G. DUPONT and W. ZACHAREWICZ (Compt. rend., 1934, 199, 365-367).-Catalytic hydrogenation (PtO<sub>2</sub>) of d-myrtenol (I) or d-myrtenal (II) leads to d-isomyrtand (III), b.p.  $122^{\circ}/20$  mm.,  $[\alpha]_{\rm D} + 20.67^{\circ}$  [from (II]) or b.p.  $113 - 113 \cdot 8^{\circ}/14$  mm.,  $[\alpha]_{\rm D} + 18 \cdot 0^{\circ}$  [from (I)]. 1-isoMyrtanol has  $[\alpha]_{\rm D} - 24 \cdot 48^{\circ}$  (H phthalate of active alcohol, m.p.  $124 - 124 \cdot 5^{\circ}$ ,  $[\alpha]_{\rm D} - 5 \cdot 6^{\circ}$ , and of r-alcohol, m.p.  $126 \cdot 5 - 127 \cdot 5^{\circ}$ ). d-isoMyrtanyl acetate has b.p. 132.5-133.5°/26 mm., [a]<sub>D</sub> +15.30°. Reduction of the requisite myrtenol by Na in xylene affords 1-myrtanol (IV), b.p. 126.5-127.5°/22 mm.,  $[\alpha]_{D} - 26.06^{\circ}$  (*H phthalate*, m.p. 108.5-109°,  $[\alpha]_{D}$ -15.0°; acetate, b.p. 127.5-128.5°/19 mm., [a]p -21.51°), and r-myrtanol, b.p. 122-123°/19 mm. (H phthalate, m.p. 114.5-116°). Comparison of the Raman spectra indicates that (III) and (IV) are cisand trans-forms, respectively, when the results are considered in conjunction with those obtained for bornel and isoborneol etc. H. W.

Colour reactions of blue sesquiterpenes. S. SABETAY and H. SABETAY (Compt. rend., 1934, 199, 313—316).—Hydrolysis of Bourbon geranium oil followed by fixation of the alcohols as borates and distillation leads to a *sesquiterpene*, b.p.  $117-120^{\circ}/$ 5 mm.,  $\alpha$  +11.40° (*l*=1), which gives a yellow colour with SbCl<sub>3</sub> and an intense blue with Br-CHCl<sub>3</sub>, with  $HNO_3$ -AcOH, or when heated with S. The reaction with Br-CHCl<sub>3</sub> appears sp. for "blue" sesquiterpenes which give less satisfactory colorations with I, HI,  $H_2SO_4$ , or  $HNO_3$ . H. W.

Opianic acid and its derivatives. V. M. Rodio-NOV and S. J. KANEVSKAJA with (in part) M. SCHEM-JAKIN, DAVANKOV, and (MLLES.) FEDOROVA, ABLET-ZOVA, and KUPINSKAJA (Bull. Soc. chim., 1934, [v], 1, 653-678).-The separation of opianic acid (I) from hemipinic acid (II) is modified (two methods). K opianate with CH2Cl·COMe or CH2Cl·CO2Et at 100° gives acetonyl (III), m.p. 104-106°, and carbethoxymethyl opianate [both a-(carboxylic) esters], m.p. 86-87° (semicarbazone, m.p. 186°). Me a-opianate with KOH-MeOH at 0° gives the  $\psi$ -ester. (I)and PhOH at 120° form the  $Ph \psi$ -ester, m.p. 145– 147°; (III) with KOH, piperidine, or NaOAc in hot EtOH gives  $Et \psi$ -opianate. (I), NH<sub>3</sub>, and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in hot EtOH yield meconinacetic acid and β-amino- $\beta$ -2-carboxy-3: 4-dimethoxyphenylpropionic acid, m.p. 132-134°, which at 140-150° gives 3 : 4-dimethoxyphthalimidoacetic acid, m.p. 174-175°, but

CH2(CO2Et)2 gives Et2 meconinmalonate [Et2 dimethoxyphthalidomalonate], m.p. 74-75°. (I) gives (Cannizzaro) meconin (IV) and (II). Hemipinimide, KOH, and KOCl at 15-60° give a mixture of 2-aminoveratric and 3: 4-dimethoxyanthranilic acid, m.p. 98-99°. The latter acid yields 2:3-dimethoxybenzoic (o-veratric) acid (V), m.p. 120-123°. Et guaiacol-o-carboxylate and  $p-C_6H_4Me\cdotSO_3Me$  yield, after hydrolysis, an *acid*, m.p. 184–187°, and (V). (II), NaOH, and Hg(OAc), in hot, dil. AcOH give a mixture of 6-anhydrohydroxymercuri-2: 3-dimethoxyand 2-anhydrohydroxymercuri-5: 6-dimethoxy-benzoic acid, hydrolysed to o- and m-veratric acid, respect-ively. (IV) and KCN at 180–185° give MeCN, a substance, m.p. 86–88°, and "methylnormeconin" (3-hydroxy-4-methoxyphthalide), m.p. 125°, converted into (IV) by p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>Me and by p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>Et and KOH-MeOH into 4-methoxy-3-ethoxyphthalide, m.p. 68-69°, oxidised by KMnO<sub>4</sub> to 4-methoxy-3ethoxyphthalic acid, m.p. 175-176° (anhydride, m.p. 105°). **R**. S. C.

Esterification in presence of alkali. Esterification of nitro-opianic acid by means of silver oxide. M. SCHEMJAKIN (Bull. Soc. chim., 1934, [v], 1, 689-691).—Nitro-opianic acid and Ag<sub>2</sub>O or the pre-formed Ag salt in 55% aq. MeOH at room temp. give the Me  $\psi$ -ester, probably by way of the  $\alpha$ -(carboxylic) ester. R. S. C.

Mechanism of geometrical inversion in regard to coumarins and coumaric acids. T. R. SESHADRI (Current Sci., 1934, 3, 19-20).—Two factors control the *cis* to *trans* inversion from coumarin (I) to coumaric acid (II), viz., addition at the double linking which renders rotation of the groups into the required position possible, and repulsion between the negatively-charged O and CO<sub>2</sub> which forms the driving force of the change. For the reverse change sunlight appears as effective as ultra-violet light and a mechanism is suggested. In the conversion of acids and esters into (I) by HCl, HBr, or  $H_2SO_4$  at 100°, the removal of  $H_2O$  or EtOH is the first stage; the dipole that is formed supplies the necessary energy for the inversion, and the rotation of the groups is facilitated by the temporary addition of the acids at the double linking. Transformation at the m.p. is initiated by loss of alcohol, and the combined effect of CO and the positive charge on the C atom occasioned by loss of OR eliminates the effect of the double linking. H. W.

Influence of substituents on the mercuration of coumarins. K. G. NAIK and A. D. PATEL (J.C.S., 1934, 1043—1047).—Substituted coumarins are only mercurated by Hg acetamide and acetate in presence of 5% NaOH, the results being mainly alike. Hg enters positions 6 and 8, monomercuration taking place if one position be occupied. NO<sub>2</sub> in position 6 is removed. Other groups also influence the course of reaction. Mercuration (Hg acetate) of coumarin gives 6:8-bishydroxymercuricoumarin, which with HCl forms the *chloromercuri*-compound, and with H<sub>2</sub>SO<sub>4</sub> yields the *sulphatomercuri*-compound. Coumarin and Hg acetamide afford 6:8-*bisacetoxymercuricoumarin*, which with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> gives a *compound*, C<sub>18</sub>H<sub>8</sub>O<sub>4</sub>Hg<sub>2</sub>. 7-Hydroxy-6:8-bisacetoxymercuri-4methylcoumarin and I afford a *product*, m.p. 172°.

F. R. S.

Synthesis of 5-hydroxyflavone. S. SUGASAWA (Proc. Imp. Acad. Tokyo, 1934, 10, 338–340).— 2:6-Dimethoxybenzonitrile is converted by MgMeI in PhOMe into 2:6-dimethoxyacetophenone, b.p. 135— 136°/2 mm., m.p. 68—69°, demethylated by AlCl<sub>3</sub> in PhMe to 2:6-dihydroxyacetophenone (I), m.p. 156— 157°, also obtained in better yield but poorer quality from 6-methylumbelliferone acetate. (I), NaOBz, and Bz<sub>2</sub>O at 180—190° yield 5-hydroxyflavone, m.p. 156—157° (acetate, m.p. 145°), whereas at 205—210°, 2-benzoyl-5-hydroxyflavone, m.p. 173—174° (acetate, m.p. 189—190°), is the main product. H. W.

Synthesis of anthocyanins. XXI. 3-β-Glucosidyldelphinidin chloride. (MISS) T. M. REYNOLDS and R. ROBINSON (J.C.S., 1934, 1039–1043).—Tri-benzoylgalloyl chloride and  $CH_2N_2$  give  $\omega$ -diazo-, m.p. 169° (decomp.), converted by HCO<sub>2</sub>H into  $\omega$ -formoxy-, m.p. 116—117°, and by AcOH into  $\omega$ -acetoxy-3:4:5-tribenzoyloguaged on heaven m.p. 128–140°: the form tribenzoyloxyacetophenone, m.p. 138-140°; the formoxy-compound could not be hydrolysed. w-Diazo-3:4:5-triacetoxyacetophenone (I) with p-toluenesulphonic acid forms w-p-toluenesulphonoxy-, m.p. 134°, and with Br in COMe<sub>2</sub> yields  $\omega$ -bromo-3:4:5-triacetoxyacetophenone, m.p. 123°: the  $\omega$ -Cl-derivative has m.p. 114.5°. These compounds do not condense satisfactorily with glucose 2:3:4:6-tetra-acetate. (I) and HCO<sub>2</sub>H yield ω-formoxy-3:4:5-triacetoxyacetophenone, m.p. 99–100°, hydrolysed to the  $\omega$ -OH-compound, m.p. 87–88°. The OH-compound condenses with tetra-acetyl-a-glucosidyl bromide to ω-tetra-acetyl-β-d-glucosidoxy-3:4:5-triacetoxyaceto-phenone, m.p. 87-88° and 141-142°, [α]<sub>H<sub>F</sub> green</sub> -26·0° in CHCl<sub>2</sub>, which with 2-O-benzoylphloro-glucinaldehyde and HCl yields benzoylacetylglucos-idyldelphinidin chloride, hydrolysed by Ba(OH)<sub>2</sub>-MeOH (air-free) to 3-β-glucosidyldelphinidin chloride (±0.8H, Ω) purified through the nicrate (±2.5H<sub>2</sub>Ω). (+0.8 $H_2O$ ), purified through the picrate (+2.5 $H_2O$ ). The anthocyanin has been characterised by colour reactions, absorption spectra, and distribution no. F. R. S.

Constitution of tannins. II. Structure and synthesis of bis-(5:7:3':4'-tetrahydroxy)flavpinacol. A. RUSSELL and J. TODD (J.C.S., 1934, 1066-1070).-Reduction (Zn-AcOH) of chalkone gives a bis-compound the properties of which have been examined. Measurements of H<sub>2</sub> absorbed (2 equivs.) during reduction of 2-hydroxychalkones indicate polymerisation. Phloroacetophenone tribenzoate, protocatechualdehyde dibenzoate, and HCl yield 2:4:6:3':4'-pentabenzoyloxy-chalkone, hydrolysed to the -hydroxy-compound, m.p. 245°, which is reduced to bis-(5:7:3':4'-tetrahydroxy) flavpinacol. The properties of this substance have been compared with those of natural hemlock tannin and show that phlobatannins must be constituted similarly to the reduction products of 2-hydroxychalkones.

F. R. S. Chromone group. XII. Synthesis of 7-hydroxyisoflavone and of  $\alpha$ - and  $\beta$ -naphthaisoflavone. H. S. MAHAL, H. S. RAI, and K. VENKATARAMAN (J.C.S., 1934, 1120—1122).—2:4-Dihydroxyphenyl CH<sub>2</sub>Ph ketone and CH<sub>2</sub>PhCl give 2-hydroxy-4-benzyloxyphenyl benzyl ketone, m.p. 111°, which with HCO<sub>2</sub>Et and Na forms 7-benzoyloxy-, m.p. 171°, hydrolysed to 7-hydroxy-isoflavone, m.p. 215° (Ac derivative, m.p. 139°). 2-Phenylacetyl- $\alpha$ -naphthol, HCO<sub>2</sub>Et, and Na yield 3-phenyl-1:4- $\alpha$ -naphthapyrone, m.p. 187°; the 1-phenylacetyl compound behaves similarly (cf. A., 1932, 1140). F. R. S.

Reactions of o-hydroxybenzylidenediaceto-phenones. I. Reaction with acids. D. W. HILL (J.C.S., 1934, 1255-1258).-o-Hydroxybenzylidenediacetophenone (I) when preserved in cold or treated for a short time with hot AcOH affords 4-phenacylflavene (II), m.p. 96°, whilst it is converted by more prolonged treatment with boiling AcOH into 4-phen-acylideneflavene (III), m.p. 128°, the corresponding substituted hydrochalkone, and COPhMe. The yield of (II) indicates that the transformation of (I) into (III) proceeds entirely through (II). 2-Hydroxy-4-methoxybenzylidenediacetophenone, m.p. 181°, from 2-hydroxy-4-methoxybenzaldehyde, COPhMe, and NaOH in  $H_2O$ -EtOH, is converted similarly into 7-methoxy-4-phenacylflavene, m.p. 85-86°, and 7-methoxy-4-phenacylideneflavene, m.p. 153°, accom-panied by Ph β-2-hydroxy-4-methoxyphenylethyl ketone (semicarbazone, m.p. 177-178°). 2-Hydroxy-5 - methoxybenzylidenediacetophenone (improved prep.) yields 6-methoxy-4-phenacylflavene, m.p. 118-119°, and 6-methoxy-4-phenacylideneflavene, m.p. 146—147°. The analogy between these reactions and the conversion of certain chromanols into chromenes by AcOH suggests that o-OH-derivatives of benzylidenediacetophenone may be formulated

H. W.

Synthesis of anthocyanins. XXII. Isolation of an anthocyanin of Salvia patens termed delphin, and its synthesis. (MISS) T. M. REYNOLDS, R. ROBINSON, and (MISS) R. SCOTT-MONCRIEFF (J.C.S., 1934, 1235—1243).—A delphinidin diglycoside has been isolated as delphin chloride or O-3: 3-diglucosidyldelphinidin chloride (I) from the flowers of S. patens, in which it may occur in an acylated form. In

purification the Ac group is removed and the resulting anthocyanin is named delphin; it is probably widely distributed. (I) is hydrolysed to delphinidin chloride [hydrate  $(+3.5H_2O)$ ] and glucose.  $\omega$ -Tetra-acetyl- $\beta$ glucosidoxy-3:4:5-triacetoxyacetophenone (II) and  $2 - 0 - tetra - acetyl - \beta - glucosidylphloroglucinaldehyde$ (III) condense (HCl) and yield with difficulty (I). 2 - O - Tetra - acetyl - 3 - glucosidyl - 4 - O - benzoylphloroglucinaldehyde, m.p. 72-74°, obtained from (III) and BzCl condenses with (II) to give 7-benzoyloxy-3': 4': 5'triacetoxy - 3:5-di(tetra-acetyl-β-glucosidoxy) flavylium chloride (?). The colour reactions, absorption in the visible region, and distribution no. of (I) have been determined and the natural and synthetic pigments compared. The autocondensation product of 2-Obenzoylphloroglucinaldehyde (EtOAc-HCl) gives a cryst. substance,  $C_{18}H_{15}O_7Cl_3H_2O_3O_1HCl_$ , which after hydrolysis gives a *chloride* and a *picrate*. The condensation product of (III) could not be isolated.



Synthesis of cæroxonones. F. E. KING (J.C.S., 1934, 1064—1066).—The Na salt of resorcinol Me ether (I) and 1-chloroanthraquinone (II) give erythroxyanthraquinone 3'-methoxyphenyl ether, m.p. 130—131°, which with H<sub>2</sub>SO<sub>4</sub> yields cæroxonone-3 : 9, m.p. 310°. (I) and 1 : 5-dichloroanthraquinone (III) similarly form anthrarufin di-3'-methoxyphenyl ether, m.p. 177—178°, and cærdioxonone-3 : 11 (+H<sub>2</sub>SO<sub>4</sub>), a strong vat dye. The Na salt of pyrogallol Me<sub>2</sub> ether (IV) and (II) give erythroxyanthraquinone 2' : 3'-dimethoxyphenyl ether, m.p. 165°, which with H<sub>2</sub>SO<sub>4</sub> gives 4-hydroxycæroxonone [Ac derivative, m.p. 235—240° (decomp.)], a weak green dyc unaffected by NH<sub>2</sub>Ph. (III) and (IV) afford anthrarufin bis-2' : 3'-dimethoxyphenyl ether, m.p. 183°, forming with H<sub>2</sub>SO<sub>4</sub> 4 : 12-dihydroxycærdioxonone-3 : 11 (+0.5H<sub>2</sub>SO<sub>4</sub>), a maroon dye.

F. R. S.

Formation of "Pechmann's dye" and some derivatives thereof. Constitution of "Pechmann's dye,"  $C_{20}H_{12}O_4$ . C. DUFRAISSE and P. CHOVIN (Bull. Soc. chim., 1934, [v], 1, 771—789, 790— 796).—Addition of PCl<sub>5</sub> (2 mols.) to CH<sub>2</sub>Bz·CO·CO<sub>2</sub>Et (1 mol.) at 10°, removal of excess of PCl<sub>5</sub> by cyclohexanone, and subsequent heating at 155° gives Pechmann's dye (I),  $C_{20}H_{12}O_4$ , m.p. 317° (block) (2·5—6·5%) [obtained only in the same yield from CHBz:CH·CO<sub>2</sub>Et (cf. lit.)], characterised by its absorption (max. at  $\lambda$  5050 and 5400). (I) is unchanged by Ac<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, or cold, conc. HCl, but with CrO<sub>3</sub> gives BzOH. (I) with cold 20% KOH-EtOH gives a yellow acid (II),  $C_{20}H_{14}O_5$ , m.p. 332°. (II) is also obtained from (III) by 10% KOH-EtOH; when dissolved in NaHCO<sub>3</sub> and pptd. by acid it gives the yellow acid (IV),  $C_{20}H_{12}O_4$ ,+2H<sub>2</sub>O, m.p. 221°, of Bogert and Ritter. When heated alone or with Ac<sub>2</sub>O, (IV) gives (III), and when dissolved in KOH-EtOH and pptd. by acid gives (II). (III) and HNO<sub>3</sub> (13%) give a neutral, yellow substance (V),  $C_{20}H_{12}O_4$ , m.p. 335°. (I) in  $C_6H_6$  and HNO<sub>3</sub> (13%) give a colourless dicarboxylic acid (VI),  $C_{20}H_{14}O_6$ , m.p. 224° (block), which at 200° gives CO<sub>2</sub> (nearly 1 mol.) and 10% of (I). (V) with Fe–AcOH gives a neutral, yellow substance,  $C_{20}H_{14}O_4$ , m.p. 333° (block). (I) is assumed to be formed by disproportionation.

The following formulæ are assigned, the dilactonic formula for (I) being discarded. The ketonic form is a possible alternative for (IV).



Isomeric derivatives. XXVI. Thiophen bromothiophens and the constitution of thiophendisulphonic acids. W. STEINKOPF, H. JACOB, and H. PENZ (Annalen, 1934, 512, 136-164; cf. A., 1933, 512).—Substituents in the  $\alpha$ -position in thiophen are more labile than those in the β-position. Thus, sulphonation of  $\alpha$ -halogenothiophens leads to some replacement of halogen by SO<sub>3</sub>H,  $\alpha$ -nitrothiophens afford tetrabromothiophen, a-bromothiophens react with Mg (in presence of much MeBr, which is often effective also in the  $C_6H_6$  series), and  $\alpha$ -sulphothio-phens are desulphonated by an excess of Na-Hg. Many data recorded in the lit. are superseded by those given below, where all the constitutions cited are rigidly proved. Mesitylenedisulphonyl chloride and  $o-C_6H_4(SO_2Cl)_2$  with  $o-C_6H_4(NH_2)_2$  give the diparimonanilides, m.p. 200° (decomp.) and 261° (decomp.), respectively. 2-Iodothiophen and CISO3H at -15° give 2-iodothiophen-5-sulphonyl chloride (I), m.p. 51—52° (sulphonamide, m.p. 165°), and thiophen-2-sulphonyl chloride (II). (I) and  $H_2SO_4$ -SO<sub>3</sub> (33%) at < 35° afford 2-iodothiophen-3 : 5-disulphonyl chlor-ide, m.p. 87-88°, converted by a little Na-Hg into thiophen-2: 4-disulphonyl chloride, but by an excess into thiophen-3-sulphonyl chloride. 2-Bromothiophen affords 2-bromothiophen-5-sulphonyl chloride, m.p. 44-46° {sulphonamide, m.p. 144° [converted into (II)]}, and -3: 5-disulphonyl chloride, m.p. 98-101° (disulphonamide, m.p. 214°). Thiophen-2: 4-disulphony chloride and Na-Hg give thiophen-3-sulphonyl chloride. Tetrabromothiophen (III) (modified prep.), m.p. 117-118° (lit. 114°), b.p. 170-173°/13 mm., and Mg-MgMeI give 2:3:4-tribromo- (IV) (50% yield),

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m.p. 43-46°, and some 3:4-dibromo-thiophen, b.p. 221-222°. (IV) affords 2:3:4-tribromo-5-nitrothiophen, m.p. 96-98°. (III) leads similarly to 3:4:5tribromothiophen-2-carboxylic acid, m.p. 259°, and 2:3:4-tribromo-5-iodothiophen, m.p. 126°. Tetra-chlorothiophen gives similarly 2:3:4-trichlorothiophen, b.p. 203-208° (5-NO2-derivative, m.p. 73-76°), and 3:4:5-trichlorothiophen-2-carboxylic acid, m.p. 224° after sintering. 2:5-Dichlorothiophen gives the 3: 4-(NO2)2-derivative, m.p. 88-91°. 3: 4-Dibromothiophen, m.p. 4.5°, b.p. 221-222°, obtained in 30% yield from (III) or as a by-product together with (IV), leads to the 2-NO2- (prepared in Ac2O), m.p. 115—116°,  $2:5 \cdot (NO_2)_0$ -, m.p. 128°, and 2-HgCl-derivatives, m.p. 191°, 3:4-dibromo-2-acetothienone, m.p. 83—85°, Ph 2-(3:4-dibromothienyl) ketone, m.p. 107-109° [oxime, m.p. 155-156°; converted by Br into (III)], 3:4-dibromothiophen-2-sulphonyl chloride, m.p. 118°, and -2: 5-disulphonyl chloride, m.p. 169°, and 3-bromothiophen-4-carboxylic acid, m.p. 150-152°. (IV) leads to 3: 4-dibromothiophen-2-carboxylic acid (poor yield), m.p. 198° (with Br gives the 3:4:5-Br<sub>3</sub>-acid), and 3:4-*dibromo-2-iodothiophen*, m.p. 60°.  $SI_3$ -actual), and S: 4-altoromo-2-ioatintophen, m.p. 60 2:3:5-Tribromothiophen (V) gives (Grignard etc.) 3-bromothiophen (VI), b.p. 157—158°, 2:3-, m.p. -15.5°, b.p. 214° (5-HgCl-, decomp. 240°, and 5- $NO_2$ -derivative, m.p. 75°), and 2:4-dibromothiophen, m.p. -30° to -25°, b.p. 210° [5-HgCl-, m.p. 184—187°, 5- $NO_2$ -, m.p. 79—80°, and 3:5- $(NO_2)_2$ -derivative, m.p. 102°]. These compounds lead to 2:3:2':3'-, nonm and 2:4.2':4' totrabrane 5:5' dishuraments. nom.p., and 2:4:2':4'-tetrabromo-5:5'-dichloromercuridithienyl, m.p. 195-200°, 4:5-, m.p. 85-86°, and 3:5-dibromo-2-acetothienone, m.p. 45°, Ph 5-(2:3-di-bromothienyl) ketone, m.p. 80° (also obtained from Ph 2-thienyl ketone and Br), 2:3-dibromothiophen-5sulphonyl chloride, m.p. 80° (debrominated by Na-Hg), and 2:4-dibromothiophen-3:5-disulphonyl chloride, m.p.  $157^{\circ}$  (debrominated by Na-Hg). (V) gives (Grignard,  $CO_2$ ) 4:5-, m.p. 227-228° (lit. 222°), and 3: 5-dibromothiophen-2-carboxylic acid, m.p. 180-188° (affording the 3:4:5-Br3-acid), and by a Grignard reaction with I 2: 3-dibromo-5-iodothiophen, m.p. 59°. (VI) gives the 2-HgCl-derivative, m.p. 120.5-123°, 3:3'-dibromo-2:2'-dichloromercuridithienyl, m.p. 154°, 3-bromo-(?)2-nitro-, m.p. S1-S3° after sintering, and two ??-dinitro-thiophens, m.p. 110-111° and 167°, respectively, 3-bromo-(?)2-acetothienone, b.p. 130°/11 mm., and 3-bromothiophen-2-carboxylic acid, m.p. 190°. 5-Bromothiophen-2-carboxylic acid, m.p. 141-142°, prepared from 2:5-dibromothiophen (VII) and thioprepared from 2:5-dibromothiophen (VII) and thio-phen-2-carboxylic acid (VIII), yields 4:5-dibromo-thiophen-2-carboxylic acid, m.p. 228-229.5°. (VIII) and Cl<sub>2</sub> in cold AcOH give the 5-Cl-acid, m.p. 146-147°. (VII) and  $H_2SO_4$ -HNO<sub>3</sub> at < 40° give 2:5-dibromo-3-nitrothiophen, m.p. 60-61°, also obtained from 3-nitrothiophen and Br. 2-Bromothiophen with fuming HNO<sub>3</sub> in Ac<sub>2</sub>O gives the (?)2-NO<sub>2</sub>-derivative, m.p. 48-49°. (VII) gives (Grignard, I) 2-bromo-5-iodothiophen, b.p. 116°/13 mm. (IV), (III), and (V) all afford 3:4:5-tribromo-2-acetothienone. and (V) all afford 3:4:5-tribromo-2-acetothienone, m.p. 131°, the yields decreasing in the order given. chloride 2:5-Dibromothiophen-3:4-disulphonyl (modified prep.) gives the dianilide, m.p. 175°. 2:5-Thioxen and fuming H2SO4 form 2:5-thioxen-3:4disulphonic anhydride, decomp. 200° (darkening

at 170°) (disulphonyl chloride, m.p. 146°). Similarly are obtained 2:4-thioxen-3:5-disulphonyl chloride, m.p. 74°, and 2:3-thioxen-5-sulphonamide, m.p. 137— 139° after sintering. The Grignard reagent from (III) with anhyd. CuCl<sub>2</sub> gives (IV) and 2:3:4:2':3':4'hexabromodithienyl, m.p. 125°. Chlorobromothiophens could not be obtained by Grignard reactions.

R. S. C. Diphenylene sulphides. C. COURTOT (Compt. rend., 1934, 198, 2260-2263).-The following sulphones are prepared by interaction of the sulphide with H<sub>2</sub>O<sub>2</sub> in AcOH. 5-Chloro- (I), m.p. 249°; 5bromo- (II), m.p. 266-267° (sulphide, m.p. 126°); 5:5'-dichloro-, m.p. 340° (sulphide, m.p. 212°), and 5:5'-dibromo-diphenylene sulphone, m.p. 361-362° (sulphide, m.p. 229°). Diphenylene sulphone mono- $(+H_2O, \text{m.p.} 276^\circ; sulphonyl chloride, \text{m.p.} 234-235^\circ;$ sulphonyl chloride of sulphide, m.p. 141°), and di-sulphonic acid [disulphonyl chloride, m.p. 333-340° (decomp.)]. The monosubstituted sulphones with NaOH at 195–230° afford hydroxydiphenylene sul-phone, m.p.  $256-258^{\circ}$  (Ac and Bz derivatives, m.p.  $269^{\circ}$  and 176°, respectively), and some hydroxydiphenyl-2-sulphonic acid. The disubstituted sulphones give some dihydroxydiphenylene sulphone, m.p. 331° ( $Bz_2$  derivative, m.p. 227–228°), but mainly dichloro-(sulphonyl chloride, m.p. 202°) and dibromo-diphenyl-2-sulphonic acid (cf. A., 1931, 1406). The orientation of the halogens (cf. A., 1931, 1406; this vol., 900) is shown by the conversion of 5-chloro-2-aminodiphenyl (A., 1927, 236) through the diazonium compound into the sulphonic acid, m.p. 102°, the chloride of which is cyclised in  $PhNO_2$  containing AlCl<sub>3</sub> to (I). Similarly, 5-bromo-2-aminodiphenyl affords (II).

J. L. D.

Preparation and identification of 2:5-dimethylpyrrole. C. F. H. ALLEN and D. M. YOUNG (Canad. J. Res., 1934, 10, 771-773).—A new, convenient method for preparing 2:5-dimethylpyrrole (I) is to reflux  $[CH_2Ac]_2$  with  $(NH_4)_2CO_3$ . The identification of (I) is discussed; (I) with 2:4dinitrophenylhydrazine in aq. EtOH-H<sub>2</sub>SO<sub>4</sub> gives acetonylacetone-2:4-dinitrophenylhydrazone, m.p. 262°, and Et 3-acetyl-2:4-dinitrophenylhydrazone, m.p. 264°. H. N. R.

Bacteriostatic azo-compounds. I. OSTROMIS-LENSKY (J. Amer. Chem. Soc., 1934, 56, 1713-1714). -C<sub>5</sub>H<sub>5</sub>N and NaNH<sub>2</sub> in NPhMe<sub>2</sub> give (cf. Tschitschibabin and Zeide, A., 1915, i, 590) a mixture (A) of 2: 6-(I) and 2:4-diaminopyridines. (A) and diazotised NH<sub>2</sub>Ph afford (cf. B., 1929, 493) a mixture (B) of (probably) 2:4-diamino-5-benzeneazopyridine, m.p. 203°, and 2:6-diamino-3-benzeneazopyridine (II) [the *dihydrochloride*, from (I) and PhN<sub>2</sub>Cl in 8% HCl, passes into the free base when heated to 100°]. 2:6-Diamino-3-p-hydroxy- (III), m.p. 214-215°, -3-p-methoxy-, m.p. 192°, -3-p-ethoxy- (IV), m.p. 176-177°, and -3-o-carboxy-, decomp. slowly at 270°, -benzeneazopyridine are prepared from (I) and  $C_6H_4R\cdot N_2X$ . The bacteriostatic index (max. dilution preventing growth of S. albus, S. aureus, and Str. hæmolyticus on agar media) of the hydrochlorides of (B), (II), (III), and (IV), m-phenylenedisazobis-m-phenylenediamine

4-β-naphthaleneazo-m-phenylenedihydrochloride, amine hydrochloride, and 2:4-diaminoazobenzene hydrochloride has been determined. H. B.

Acetoacetic ester condensation. VIII. Condensation of w-piperidino-esters. W. B. THOMAS and S. M. MCELVAIN (J. Amer. Chem. Soc., 1934, 56, 1806-1809).--Et piperidinoacetate (I) and NaOEt (0.5 mol.) at 110---115°/37 mm. give EtOH (83%) and 52% of Et sodio-ay-dipiperidinoacetoacetate [isolated as the dihydrate (II), softens at about 100° and then

$$\underset{(I.)}{\overset{CH_2 \cdot NC_5H_{10}}{\underset{C=0}{\overset{C-0}{\underset{OH_2}{\times}}}}} N \cdot C \ll \overset{CH_2 \cdot NC_5H_{10}}{\underset{C=0}{\overset{C-0}{\underset{OH_2}{\times}}} Na \underset{OH_2}{\overset{COH_2}{\underset{OH_2}{\times}}}$$

decomposes on further heating, by addition of H<sub>2</sub>O to the Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> solution of the reaction mixture]. (II) is hydro-

lysed (aq. EtOH-NaOH in N<sub>2</sub>) to s-dipiperidinoacetone [dihydrochloride, m.p. 175-195° (decomp.)]. Similar condensation of Et  $\beta$ -piperidinopropionate,  $\gamma$ -piperidinobutyrate(III), b.p. 128-130°/19mm., and 8-piperidinovalerate, b.p. 132-134°/10 mm., followed by hydrolysis (20% HCl), gives 53-68% of di-β-piperidinocthyl ketone (semicarbazone, m.p. 96-97°; dihydrochloride, m.p. 212-214°), di-y-piperidinopropyl ketone, b.p. 188-190°/3 mm. (semicarbazone, m.p. 82-83°; dihydrochloride, m.p. 241-242°), and di-δpiperidinobutyl ketone, b.p. 220-221°/2 mm. (semi-carbazone, m.p. 88-89°; dihydrochloride, m.p. 222-223°), respectively, together with some  $\hat{\beta}$ -piperidinopropionic (hydrochloride, m.p. 206—209°), γ-piperi-dinobutyric (IV), b.p. 162—164°/2 mm., m.p. 71—72° (hydrochloride, m.p. 189—190°), and δ-piperidinovaleric neid (hydrochloride) acid (hydrochloride, m.p. 198-200°), respectively. The above condensations do not proceed satisfactorily at atm. pressure; thus, (III) affords EtOH (71%) and (after treatment with AcOH in  $Et_2O-C_6H_6$ ) (IV) and tarry material. EtOH is also eliminated from Et 3-carbethoxypiperidinoacetate and NaOEt (0.5 mol.) at 110-115°/20 mm.; no condensation occurs (cf. A., 1924, i, 417) with Na at 150° or with Na or NaOEt in xylene. (I) does not react with Na at 150°, whilst (III) does so. The presence of an  $\alpha$ -piperidino-group inhibits the reaction with Na (cf. loc. cit.); in view of the ready condensation with NaOEt, further evidence is thus obtained that Na is not the active condensing agent in the acetoacetic ester condensation. H. B.

2:6-Diamino-4-benzeneazopyridine. A. E. CHICHIBABIN (TSCHITSCHIBABIN) and E. D. OSSET-ROWA (J. Amer. Chem. Soc., 1934, 56, 1711-1713, and Bull. Acad. Sci. U.R.S.S., 1934, 615-622).-4 - Phenylhydrazinopyridine - 2:6 - dicarboxylic acid (+EtOH), m.p.  $231^{\circ}$  (from the 4-Cl-acid and NHPh·NH<sub>2</sub> at 130—133°), is oxidised (air in feebly alkaline solution) to 4-benzeneazopyridine-2: 6-dicarboxylic acid (+0.5AcOH), m.p.  $270^{\circ}$  (decomp.), the Me ester, m.p. 175°, of which with N<sub>2</sub>H<sub>4</sub>,H<sub>2</sub>O at 200° gives the phenylhydrazino-dihydrazide, which on recrystallisation is oxidised to 4-benzeneazopyridine-2:6-dicarboxyhydrazide, m.p. 228°. This is converted into the diazide, m.p. 110°, which with boiling EtOH affords the corresponding diurethane, m.p. 182°, hydrolysed (EtOH-KOH) to 2:6-diamino-4-benzeneazopyridine (I), m.p. 170-171°, and the corresponding monourethane, m.p. 143°. (I) is not obtained from

2:6-diaminopyridine and diazotised NH<sub>2</sub>Ph (cf. Ostromislensky, B., 1929, 493). H. B.

Action of acetylsalicylyl chloride on magnesylindoles. C. TOFFOLI (Gazzetta, 1934, 64, 364-371).-Interaction of Mg 2-methylindolyl bromide (2 mols.) with acetylsalicylyl chloride (1 mol.) yields o-hydroxyphenyl 3-(2-methylindolyl) ketone, m.p. 167°



c-hydroxyphenyl 3-(2-methylindolyl) ketone, m.p. 167° (hydrobromide, m.p. 180°). From equimol. quantities the products are 3-acetyl-2-methylindole, o-3-(2-methylindolyl) ketone, m.p. 197° (hydrobromide, m.p. 187°; picrate, m.p. 190°), and o-1: 3-phenylene-2-methyl-4- 226° (hydrobromide, m.p. 206°)

ketoquinoline (I) m.p. 236° (hydrobromide, m.p. 236°; picrate, m.p. 233°). R. K. C.

reactions of phenylcarbimide. New III. Benzylideneaminoindoles. A. NERI (Gazzetta, 1934, 64, 420-438).-2-α-Anilinobenzyl-3-methylindole (A., 1933, 615) condenses with PhNCO to give  $\alpha$ -(phenyl-2-methyl-3-indolylmethyl) -  $\alpha\beta$ -diphenylcarbamide, m.p. 116°, readily decomposed on attempting recrystallisation or hydrolysed by 20% HCl to benzylidene-2: 2'-dimethyl-3: 3'-di-indole (I), m.p. 246°. 3-a-o-Nitroanilinobenzyl-2-methylindole, m.p. 187°, yields a-(o-nitrophenyl-2-methyl-3-indolylmethyl)-aβ-diphenylcarbamide, m.p. 198-199°. 2-Methylindole (II) and benzylidene-*m*-nitroaniline yield only (I). (II) with NH<sub>3</sub> and 1 or 2 mols., respectively, of o-nitrobenzaldehyde yields 3-a-amino-o-nitrobenzyl-2-methylindole, m.p. 182°, or 3-a-o-nitrobenzylideneamino-o-nitrobenzyl-2-methylindole, m.p. 132°. (II), NH<sub>2</sub>, and PhCHO yield benzylidenedi-indole.

R. K. C.

Modification of Skraup's synthesis of quinoline. G. I. MIKHAILOV (Khim. Farm. Prom., 1933, 344-347).-PhNO<sub>2</sub> (2.32 kg.), NH<sub>2</sub>Ph (0.56 kg.), and glycerol (1.23 kg.) are treated in a special apparatus with  $H_2SO_4$  (0.31 kg.), with stirring. The temp. is kept at 147—149° for 2 hr., 0.94 kg. of  $H_2SO_4$  being slowly added.  $H_2O$  and PhNO<sub>2</sub> begin to distil. When the acid is added the temp is kept at 148— When the acid is added the temp. is kept at 148-149° for 1.5 hr., then slowly raised to  $152^{\circ}$  and kept so for 15 min. The mixture is cooled to  $120^{\circ}$ , freed from PhNO<sub>2</sub>, diluted with H<sub>2</sub>O (4.5 litres), cooled to 10°, and neutralised. The bases are distilled with steam, poured into 0.9 litre of HCl (d 1.14), cooled to  $-5^{\circ}$ , and diazotised with NaNO<sub>2</sub>. The diazonium salt is decomposed, and the quinoline (0.7 kg.) separated with steam from the alkaline liquid.

CH. ABS.

Direct introduction of amino-group into aromatic and heterocyclic nucleus. I. Reaction of quinoline with alkali and alkaline-earth amides in liquid ammonia. F. W. BERGSTROM (J. Amer. Chem. Soc., 1934, 56, 1748-1751).-2-Aminoquinoline (I) is not obtained from quinoline (II) and KNH2 (in liquid NH<sub>3</sub> at 20-130°) or NaNH<sub>2</sub> or LiNH<sub>2</sub> (at 20°), resinous material is formed, not only in liquid NH3, but also in NH2Bua and NEt3. (II) and KNH in liquid NH<sub>3</sub> containing Hg give 5-11% of (I). (I) is obtained in good yield from (II) and Ba(NH2)2 in liquid NH3 at room temp. ; reaction is accelerated by Ba(NO<sub>3</sub>)<sub>2</sub>, Ba(CNS)<sub>2</sub>, LiNO<sub>3</sub>, and Sr(NO<sub>3</sub>)<sub>2</sub>. A little

(I) is produced from (II) and  $Sr(NH_2)_2$ ;  $Ca(NH_2)_2$  is unreactive. Of the various complex ammono-salts investigated, Ba:NK,2NH<sub>3</sub> only reacts with (II) to give (I); slight dissociation into  $KNH_2$  and  $Ba(NH_2)_2$ probably occurs. H. B.

Synthesis of Bz-tetrahydroquinolines. U. BASU (Annalen, 1934, 512, 131-135).-2-Hydroxymethylenecyclohexanone (or its acetate) and Et β-aminocrotonate give Et 2-methyl-5:6:7:8-tetrahydroquinoline-3 carboxylate, b.p. 158°/11 mm. (picrate, m.p. 147°; HgCl<sub>2</sub>-compound, m.p. 116°), hydrolysed to the corresponding acid, m.p. 228° (decomp.), which, when distilled with soda-lime, affords 2-methyl-5:6:7:8-tetrahydroquinoline, b.p. 225°/762 mm. (methiodide, m.p. 121°; picrate, m.p. 157°; platinichloride, m.p. 198°; dehydrogenated by distillation over Pb). Similarly were prepared Et 2:7- (I), b.p. 163°/11 mm., and 2: 6-dimethyl-5: 6:7: 8-tetrahydroquinoline-3-carboxylate, an oil (picrate, m.p. 129°;  $HgCl_2$ -compound, m.p. 122°), the acid from (I), m.p. 243-244° (decomp.), and 2:7-dimethyl-5:6:7:8tetrahydroquinoline, b.p. 237°/762 mm. (methiodide, m.p. 184°; picrate, m.p. 152°; platinichloride, m.p. 195°). 2-Hydroxymethylene-5-methylcyclohexanone and benzoylacetoneimine in hot EtOH give 3-benzoyl-2:7-dimethyl-5:6:7:8-tetrahydroquinoline, m.p. 77° (picrate, m.p. 177°). R. S. C.

Synthesis of *iso*quinoline derivatives. III. Synthesis of corydaldine. L. M. MOHUNTA and J. N. RAY (J.C.S., 1934, 1263—1264).—The azide, obtained from the *hydrazide* of  $\beta$ -3:4-dimethoxyphenylpropionic acid, m.p. 132°, in PhMe solution gives the carbimide (I), cyclised to corydaldine and a neutral substance (II). (I) condenses with various bases to give *carbamides*,

C<sub>6</sub>H<sub>3</sub>(OMe)<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·NH·CO·NHR, which with POCl<sub>3</sub> form bases, 1-arylimino-6:7-dimethoxy-1:2:3:4tetrahydroisoquinolines: carbamide (R = Ph), m.p. 154°, and base, m.p. 139°; carbamide (R = p-C<sub>6</sub>H<sub>4</sub>Me), m.p. 155°, and base, m.p. 126°; carbamide (R = m-C<sub>6</sub>H<sub>4</sub>Me), m.p. 150°, and base, m.p. 188°; carbamide (R = o-C<sub>6</sub>H<sub>4</sub>Me), m.p. 153°; and carbamide (R = p-C<sub>6</sub>H<sub>4</sub>·OEt), m.p. 152°, and base. Condensation of (I) with NHPhMe leads to 1-phenylmethylamino-6:7-dimethoxy-3:4-dihydroisoquinoline, m.p. 150°, reduced (Al-Hg) to a base, m.p. 155—158°. (I) and Ac<sub>2</sub>O in PhMe yield s-bis-(β-3:4-dimethoxyphenylethyl)carbamide, m.p. 152°, identical with (II). F. R. S.

Substituted tetrahydroisoquinoline hydrochlorides. J. S. BUCK (J. Amer. Chem. Soc., 1934, 56, 1769–1771).—6-Methoxy-, m.p. 236°, 5:6dimethoxy-, m.p. 232°, and 6:7-dimethoxy-, m.p. 253°, -tetrahydroisoquinoline hydrochlorides are obtained from the appropriate  $CH_2Ar \cdot CH_2 \cdot NH_2$  and 40%  $CH_2O$ , and subsequent cyclisation (23% HCl) of the

CH<sub>2</sub>Ar·CH<sub>2</sub>·N:CH<sub>2</sub>. They are demethylated (conc. HCl at 170°) to 6-hydroxy-, m.p. 233°, 5 : 6-dihydroxy-, m.p. 246°, and 6 : 7-dihydroxy-, m.p. 262°, -tetrahydroisoquinoline hydrochlorides, respectively. 6-Methoxy-, m.p. 170°, 5 : 6-dimethoxy-, m.p. about 210°, and 6:7-dimethoxy-, m.p. 215°, -N-methyltetrahydroisoquinoline hydrochlorides, prepared similarly from CH<sub>2</sub>Ar·CH<sub>3</sub>·NHMe, are demethylated (52% HI) to 6-hydroxy-, m.p. 236°, 5:6-dihydroxy-, m.p. 255° (decomp. 139°), and 6:7-dihydroxy-, m.p. 276°, -N-methyltetrahydroisoquinoline hydrochlorides, respectively. Application of the above reaction to homopiperonylamine and its N-Me derivative gives (? 5:6)methylenedioxy-, m.p. > 315°, and (? 5:6)-methylenedioxy-N-methyl-, m.p. 315° (to red liquid), -tetrahydroisoquinoline hydrochloride, respectively. 6:7-Dimethoxy-N-methyltetrahydroisoquinoline and N-methyltetrahydroisoquinoline hydrochloride have m.p. 75--77°and 228°, respectively. H. B.

Attempts to find new antimalarials. VIII. Derivatives of 8-aminoalkylaminoquinoline. A. W. BALDWIN and R. ROBINSON. IX. 8-8-Aminobutylamino-6-ethoxyquinoline. W. MEI-SEL and R. ROBINSON (J.C.S., 1934, 1264-1267, 1267-1268).-VIII. 8-Amino-6-ethoxyquinoline and β-bromoethylphthalimide condense to 8-β-phthalimidoethylamino-6-ethoxyquinoline, m.p. 178-179°, hydrolysed to 8-3-aminoethylamino-6-ethoxyquinoline dihydrochloride, m.p. 247°. 8-Aminoquinoline and  $\gamma$ -bromopropylphthalimide (I) yield  $8 \cdot \gamma$ -phthalimido-propylaminoquinoline, m.p. 111°, hydrolysed to  $8 \cdot \gamma$ -aminopropylaminoquinoline dihydrochloride (+H<sub>2</sub>O). 2-Nitro-4-n-butoxyaniline, m.p. 66°, is converted into 8-nitro-6-n-butoxyquinoline, m.p. 92°, reduced to the 8-amino-compound, m.p. 59°, which with (I) gives 8-y-phthalimidopropylamino-6-n-butoxyquinoline, m.p. 75—80°. (CH<sub>2</sub>Cl·CH<sub>2</sub>)<sub>2</sub>O, o·C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NH, and K<sub>2</sub>CO<sub>3</sub> yield ββ'-diphthalimidodiethyl ether, m.p. 157°, and phthalo-β-(β'-chloroethoxy)ethylamide, m.p. 72°, which with KI yields the corresponding *I*-compound, m.p. 83-84°. The I-compound and 8-amino-6-methoxyquinoline (II) give 8-\beta-(\beta'-phthalimidoethoxy)ethylamino-6-methoxyquinoline, m.p. 145°, hydrolysed to  $8-\beta-(\beta'-aminoethoxy)ethylamino-6-methoxyquinoline$ hydrochloride, m.p. 224°. 5-Nitro-2-methoxy-m-xylene, m.p. 91°, is reduced to 2-methoxy-m-5-xylidine, m.p. 61°, which is converted into 6-methoxy-5: 7-dimethylquinoline, m.p. 58°, nitrated to the 8-NO2-compound, m.p. 100.5°. 8-y-n-Propyl-, b.p. 225-230°/0.1 mm., and -butyl-aminopropylamino-6-methoxyquinoline, b.p. 216°/0.1 mm., are obtained from the appropriate amine and (II). The substances have been tested for therapeutic activity.

IX. 8-Amino-6-ethoxyquinoline and  $\delta$ -bromobutylphthalimide give 8- $\delta$ -phthalimidobutylamino-6-ethoxyquinoline, m.p. 114.5—115.5° (hydrobromide, m.p. 143.5—144.5°), hydrolysed to 8- $\delta$ -aminobutylamino-6ethoxyquinoline dihydrochloride (+H<sub>2</sub>O), m.p. 196— 197°, which shows promising results in therapeutic experiments. 8-Amino-6-methoxyquinoline and succinie anhydride condense to 8- $\beta$ -carboxypropionamido-6methoxyquinoline, m.p. 143—144°. F. R. S.

3-Acetylcarbazole and carbazole-3-carboxylic acid. S. G. P. PLANT and S. B. C. WILLIAMS (J.C.S., 1934, 1142—1143).—9-Acetylcarbazole and AlCl<sub>3</sub> give 3-acetylcarbazole (I), m.p. 167°, which with AcCl forms 3: 9-diacetyl-, m.p. 153°, and with Me<sub>2</sub>SO<sub>4</sub> yields 3-acetyl-9-methyl-carbazole, m.p. 102°. (I) is reduced (Zn-Hg and HCl) to 3-ethylcarbazole, m.p. 142°, also obtained by oxidation with S in quinoline of 6-ethyl-1:2:3:4-tetrahydrocarbazole, m.p. 78°, derived by Fischer's reaction from the condensation product of p-C<sub>6</sub>H<sub>4</sub>Et·NH·NH<sub>2</sub> and cyclohexanone. Fusion of (I) with KOH leads to carbazole-3-carboxylic acid, m.p. 276—278° (*Et* ester, m.p. 165°). The compounds obtained by Borsche and Feise (A., 1907, i, 242) are the 2-Ac compounds. 9-Benzoylcarbazole, AlCl<sub>3</sub>, and AcBr give 9-benzoyl-2-acetylcarbazole, m.p. 153°, hydrolysed to 2-acetylcarbazole (II) (oxime, m.p. 278°; lit. 253°). (II) forms 2-acetyl-9-methyl-, m.p. 122° (oxime, m.p. 217°), and 2-ethyl-carbazole, m.p. 225°. F. R. S.

Helicoidally rolled spherolites of the allantoins.—See this vol., 1059.

Condensation of esters and aliphatic nitriles. W. BORSCHE and R. MANTEUFFEL (Annalen, 1934, 512, 97-111).-Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (I), MeCN (II), and KOEt in  $EtOH-Et_2O$  give an improved yield of the K salt of Et β-cyanopyruvate (III) (2:4-dinitrophenylhydrazone, m.p. 128.5°), best identified by coupling with PhN<sub>2</sub>Cl and NaOAc to give the β-benzeneazo-derivative (IV), m.p. 149-150° [2:4-dinitrophenylhydrazone, m.p. 251-252° (decomp.)]. (IV) with NH2 NHPh under various conditions gives 3-cyano-1phenyl-4:5-diketopyrazoline-4-hydrazone, m.p. 189-191°, the osazone, NHPh·N:C(CN)·C(CO<sub>2</sub>Et):N·NHPh, m.p. 132.5° [when kept in EtOH forms (?)3-carbethoxy-5-imino-1-phenyl-4:5-diketopyrazoline-4-phenylhydrazone, m.p.  $105.5-107.5^{\circ}$ ], and a substance, probably (V), m.p.  $149^{\circ}$ . (III) gives similarly the p-bromobenzeneazo-derivatives (VI), m.p. 156-157°

(decomp.) (2: 4-dinitrophenylhydrazone, m.p. 249—250°), the di-p-bromo-osazone, m.p. 156—157°, 3-cyano-1-bromophenyl-4: 5-diketopyrazoline - 4-phenylhydr-azone, m.p. 203°, a substance, m.p. 262—263°, and [from (IV) and NH<sub>2</sub>·NHPh] the ester,

C<sub>6</sub>H<sub>4</sub>Br·NH·N:C(CN)·C(CO<sub>9</sub>Et):N·NHPh, m.p. 156-157°. Et β-cyano-α-ketobutyrate (2:4-dinitrophenylhydrazone, m.p. 149.5-150.5°) is hydrogenated (Adams) to Et β-cyano-α-hydroxybutyrate, b.p. 130-132°/16 mm., and with resorcinol gives mainly Et 7-hydroxy-3-methylcoumarin-4-carboxylate, m.p. 195°, and a small amount of the substance (VII), m.p. 241° (Me<sub>2</sub> ether, m.p. 183-184°). (I) and n-heptonitrile give a 35% yield of Et β-cyano-α-keto-octoate, b.p. 112-114°/2 mm. (2:4-dinitrophenylhydrazone, m.p. 115° after sintering; β-p-anisylazo-derivative, m.p. 96.5-97.5°). Adiponitrile (VIII) gives a 90% yield of βε-dicyano-α-ketohexoate, m.p. 83-84° (K salt; 2:4dinitrophenylhydrazone, m.p. 145°; phenylhydrazone, m.p. 93°; Me ether of the enolic form, b.p. 200-205°/ 17 mm.). (I) and cis- or trans-crotononitrile yield similarly 75-80% of Et  $\delta$ -cyano- $\alpha$ -keto- $\Delta^{\delta}$ -pentenoate, unstable (K salt; Bz derivative, b.p.  $160-165^{\circ}/2$  mm.), probably by way of CH<sub>2</sub>:CH·CH:NK and CO<sub>2</sub>Et·C(OK)(OEt)·CH<sub>2</sub>·CH:CH·C(NK)·OEt. The dinitrile of sorbic acid affords Et  $\zeta$ -cyano-x-keto- $\Delta^{\gamma\epsilon}$ heptadienoate (90% yield), solid, unstable (K salt; Bz derivative, b.p.  $175-178^{\circ}/2$  mm.). (II) and HCO<sub>2</sub>Et give CN·CH<sub>2</sub>·CHO (K and Na salts), which with NH<sub>2</sub>·NHPh yields the phenylhydrazone, m.p.

166—168°, and a substance, m.p. 125—126°, and with  $p-C_6H_4Br\cdot NH\cdot NH_2$  the p-bromophenylhydrazone, m.p. 193—195°, and pp'-dibromophenylformazyl cyanide,  $C_6H_4Br\cdot NH\cdot N:C(CN)\cdot N:N\cdot C_6H_4Br$ , m.p. 259—260° (decomp.), but with  $NH_2Ph$  in AcOH affords by polymerisation the anil,  $CN\cdot CH_2\cdot CH:C(CN)\cdot CH:NPh$ , m.p. 153°. EtCN affords  $\alpha$ -cyanopropaldehyde (Na salt; anil, m.p. 154°; 2:4-dinitrophenylhydrazone, m.p. 145—146°). (VIII) gives similarly  $\alpha$ -dicyano-nvaleraldehyde (Na salt; anil, m.p. 101—102°; 2:4dinitrophenylhydrazone, m.p. 118.5—139.5°; p-bromophenylhydrazone, m.p. 111.5—112.5°). R. S. C.

Derivatives of piperazine. II. Utilisation in identification of fatty acids. C. B. POLLARD, D. E. ADELSON, and J. P. BAIN (J. Amer. Chem. Soc., 1934, 56, 1759-1760).—The following salts of piperazine are described : *H* oxalate, m.p.  $> 300^{\circ}$  (all m.p. are corr.); *H* succinate, m.p.  $205-206^{\circ}$  (decomp.); *H* adipate, m.p.  $244-245^{\circ}$  (decomp.); *H* sebacate, m.p.  $166-168^{\circ}$ ; di(*H* glutarate), m.p.  $152^{\circ}$ ; di(chloroacetate), m.p.  $145-146^{\circ}$ ; ditrichloroacetate, m.p. 121- $121\cdot5^{\circ}$ ; diacetate, m.p.  $208\cdot5-209^{\circ}$ ; dipropionate, m.p.  $124-125^{\circ}$ ; dibutyrate, m.p.  $121-122^{\circ}$ ; disobutyrate, m.p.  $89\cdot5-90^{\circ}$ ; divalerate, m.p.  $112\cdot5 113^{\circ}$ ; disovalerate, m.p.  $139-140^{\circ}$ ; dihexoate, m.p.  $111--111\cdot5^{\circ}$ ; diheptoate, m.p.  $95-96^{\circ}$ ; dilactate, m.p.  $96-96\cdot5^{\circ}$ . H. B.

Optically active barbituric acids. E. C. KLEIDERER and H. A. SHONLE (J. Amer. Chem. Soc., 1934, 56, 1772—1774).—Et d., b.p. 123—124°/10 mm.,  $[\alpha]_{17}^{25}$  +11.62°, and l., b.p. 123—124°/10 mm.,  $[\alpha]_{17}^{25}$  +11.62°, and l., b.p. 123—124°/10 mm.,  $[\alpha]_{17}^{25}$  -11.02°, ethyl-( $\alpha$ -methylbutyl)malonates, prepared (usual method) from d., b.p. 116—118°,  $[\alpha]_{17}^{25}$  +29.9°, and l., b.p. 116—118°,  $[\alpha]_{17}^{25}$  -29°, -CHMePr<sup>a</sup>Br, with CO(NH<sub>2</sub>)<sub>2</sub> and NaOEt give d., m.p. 120—121°,  $[\alpha]_{17}^{25}$  +4.93°, and l., m.p. 120—121°,  $[\alpha]_{17}^{25}$  -4.73°, -5-ethyl-5- $\alpha$ -methylbutylbarbituric acids. dl- $\alpha$ -Cyano- $\alpha$ -ethylhexoic acid, b.p. 145—147°/14 mm. [obtained by hydrolysis (EtOH–KOH) of the Et ester, b.p. 122—123.5°/14 mm. (from Bu<sup>a</sup>Br,

CN-CHEt·CO<sub>2</sub>Et, and NaOEt)], is resolved by Fischer and Flatau's method (A., 1909, i, 628) into d-, b.p. 148—149°/14 mm.,  $[\alpha]_D^{**} + 7\cdot03^{\circ}$ , and *l*-forms, b.p. 148—149°/14 mm.,  $[\alpha]_D^{**} - 6\cdot85^{\circ}$ ; the corresponding Et esters (prepared from the acid chlorides) with NHMe·CO·NH<sub>2</sub> and NaOEt give [after hydrolysis (HCl)] d-, m.p. 75°,  $[\alpha]_D^{**} + 3\cdot5^{\circ}$ , and l-, m.p. 74.5°,  $[\alpha]_D^{**} - 3\cdot4^{\circ} - 1$ -methyl-5-ethyl-5-n-butylbarbituric acids. Differences in the pharmacological action of the above active acids and their dl-forms are noted. dl-a-Cyano- $\alpha$ -ethylisoheptoic acid, b.p. 153·5°/14 mm. (Et ester, b.p. 128—131°/14 mm., from isoamyl bromide and CN·CHEt·CO<sub>2</sub>Et), is similarly resolved into d-, b.p. 156—158°/14 mm.,  $[\alpha]_D^{**} + 6\cdot71^{\circ}$ , and *l*-forms, b.p. 156—158°/14 mm.,  $[\alpha]_D^{**} = 7\cdot73^{\circ}$ , convertible (as above) into d-, m.p. 99°,  $[\alpha]_D^{**} + 1\cdot5^{\circ}$ , and 1-, m.p. 107°,  $[\alpha]_D^{**} = -1\cdot56^{\circ}$ , -1-methyl-5-ethyl-5-isoamylbarbituric acids, which (like the dl-form, m.p. 72°) have no anæsthetic action. H. B.

Correlation of ultra-violet absorption and chemical constitution in various pyrimidines and purines. F. F. HEYROTH and J. R. LOOF-BOUROW (J. Amer. Chem. Soc., 1934, 56, 1728-1734; cf. A., 1931, 1308).—The ultra-violet absorption curves of aq. solutions of the following are given : thymine glycol, alloxantin, *iso*dialuric acid, 5 : 5-diethylbarbituric acid, dialuric acid, alloxan, uracil, thymine, cytosine, *iso*cytosine, *iso*barbituric acid, barbituric acid, pyrimidine, 2 : 6-dichloropyrimidine, 2 : 6-dichloro-4-methylpyrimidine, adenine, adenine thiomethylpentose, and guanine [the absorption of which is affected by  $p_{\rm H}$  (cf. Holiday, A., 1930, 1088)]. Loss of selective absorption accompanies saturation of the nuclear double linkings, whilst the magnitude of the absorption is lessened by introduction of a second or third double linking. The effects of substituents are discussed. The relation of the absorption of the ringcompounds present in nucleic acid to that of the acid itself is discussed. H. B.

Partial synthesis of ribose nucleotides. I. Uridine-5-phosphoric acid. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1934, 106, 113-124).isoPropylideneuridine (I), m.p. 159-160°, [a]<sup>27</sup> -15.8 in MeOH (from uridine,  $H_2SO_4$ , and  $CuSO_4$  in  $COMe_2$ ), with p-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Cl in C<sub>5</sub>H<sub>5</sub>N gives isopropylideneuridine 5-p-toluenesulphonate,  $[\alpha]_{11}^{25} + 17.4^{\circ}$  in COMe<sub>2</sub>, converted into iodoisopropylideneuridine, m.p. 164°,  $[\alpha]_{D}^{\circ} - 16.3^{\circ}$  in COMe<sub>2</sub>. Methylation gives 5-methoxyisopropylideneuridine, m.p.  $223-225^{\circ}$ . It is concluded that (I) is 2:3-isopropylideneuracilribofuranoside (A., 1933, 957). (I) is phosphorylated in  $C_5H_5N$  with POCl<sub>3</sub> at  $-30^{\circ}$  to  $-35^{\circ}$  and the Ba salts are fractionated by their solubility in  $H_2O$ . After hydrolysis with 5N-H<sub>2</sub>SO<sub>4</sub> at 75° for 2 hr. the Ba salt of uridine-5-phosphoric acid (II),  $[\alpha]_{D}^{*} + 3.44^{\circ}$ in 10% HCl, was separated, differing in its solubility in  $H_2O$  from Ba uridylate. The Ba salt of (II) was hydrogenated catalytically to the salt of *dihydro*uridine-5-phosphoric acid (III). The brucine salt of (II) has m.p. 200°,  $[\alpha]_{11}^{24} - 68 \cdot 8^{\circ}$  in C<sub>5</sub>H<sub>5</sub>N. The curves of hydrolysis of the Ba salts of uridine-3-phosphoric acid, (II), and (III) are compared. H. D.

Pyrrole-indole group. XIX. Methane derivatives and methene bases from indoles. B. ODDO and C. TOFFOLI (Gazzetta, 1934, 64, 359-363; cf. A., 1923, i, 715; 1924, i, 1346).—Mg indolyl bromide and MeCHO yield 3:3'-di-indolylmethylmethane, m.p. about 160°, converted in air in presence of HCl into 3-indolyl-3'-indolidenemethylmethane, m.p. 210°. 3:3'-Di-(2-methylindolyl)methylmethane, m.p. 192.5°, and 3-(2-methylindolyl)-3'-(2-methylindolidene)methylmethane, m.p. 222°, are obtained similarly.

R. K. C.

Complex salts of 2:2'-dipyridyl with bivalent iron. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 333-336).— When cryst. FeSO<sub>4</sub> is heated with the theoretical quantities of dipyridyl (dip) (I), and then extracted with boiling MeOH, there are formed three impure salts, probably Fe(dip)<sub>n</sub>SO<sub>4</sub>,mH<sub>2</sub>O, where n=1, 2, 3, and correspondingly m=3, 4, 5. On treatment with BaCl<sub>2</sub> and Ba(OH)<sub>2</sub> to take up any excess of H<sub>2</sub>SO<sub>4</sub> all three salts give predominantly, dark red hexagonal tables of [Fe(dip)<sub>3</sub>]Cl<sub>2</sub>,7H<sub>2</sub>O, rhombic bipyramidal, a:b:c=0.8886:1:0.7717. When the (I) is partly substituted by H<sub>2</sub>O, the cryst. form remains the same. H. S. P.

Residual affinity and co-ordination. XXXIV. 2:2'-Dipyridyl platinum salts. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1934, 965-971).-Bis-2:2'-dipyridyl platinochloride, prepared from 2:2'-dipyridyl, HCl, and K<sub>2</sub>PtCl<sub>4</sub>, with H<sub>2</sub>O at 100° gives 2:2'-dipyridyl hydrochloride and the yellow form of  $\beta$ -2: 2'-dipyridyl platinous chloride (I), which also exists in a red form. Both forms give the same chemical reactions and are probably due to difference of cryst. structure : (I) with  $Cl_2$  affords  $\beta \cdot 2 : 2' \cdot dipyridyl platinic chloride, with AgNO<sub>3</sub> forms <math>\beta \cdot 2 : 2' \cdot dipyridyl$ platinous nitrate, and also gives the bromide, iodide, and hydroxide. A solution of bis-2:2'-dipyridylplatinous chloride is obtained from (I) and excess of 2: 2'-dipyridyl and with KI forms bis-2: 2'-dipyridylplatinous iodide dihydrate and with  $K_2PtCl_4$  yields the platinochloride, oxidised by  $Cl_2$  to bis-2: 2'-dipyridyl-dichloroplatinic platinochloride. With  $C_5H_5N$  and K<sub>2</sub>PtCl<sub>4</sub>, (I) forms a plato-salt, whilst in presence of  $Cl_2, 2: 2'$ -dipyridylpyridinotrichloroplatinic chloride di-hydrate is obtained. With aq.  $NH_3$ , (I) yields 2: 2'dipyridyldiamminoplatinous chloride dihydrate, which with EtOH gives a monohydrate, with KI forms an iodide hydrate, with  $H_2O$  affords 2:2'-dipyridyl-amminoplatinous chloride  $(+2.5H_2O)$  (II), and with  $Cl_2$ leads to 2: 2'-dipyridyldiamminodichloroplatinic chloride dihydrate (monohydrate). (II) with KI forms 2:2'dipyridylamminoplatinous iodide hydrate, and with Cl<sub>2</sub> yields 2:2'-dipyridylamminotrichloroplatinic chloride hydrate, which with Cl2 gives a complex explosive compound in which the H of the  $NH_3$  is partly replaced by Cl. (I) and  $[CH_2 \cdot NH_2]_2$  give 2:2'-dipyridylethylenediaminoplatinous chloride, which with conc. HCl yields the red form of (I), or with dil. HCl the yellow form, with Ag<sub>2</sub>CO<sub>3</sub> and HBr forms 2: 2'-dipyridylethylenediaminoplatinous bromide dihydrate, and with Cl<sub>2</sub> affords 2:2'-dipyridylethylenediaminodichloroplatinic chloride pentahydrate (this gives a complex compound with Cl<sub>2</sub>). (I) and ethylene Me<sub>2</sub> disulphide lead to  $2: \overline{2'}$ -dipyridylethylenedimethyldisulphineplatinous chloride, converted by K2PtCl, into the plato-salt.

F. R. S. Affinity of the arylazo-group. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1934, 64, 415-420).--4-Benzencazo-5-aminoacenaphthene (I) reacts with  $o \cdot C_6H_4(CO)_2O$  to give the *phthalimido*-derivative (II), m.p. 250°, and the Ph·N<sub>2</sub>-group is, therefore, more strongly bound than in 1-benzencazo- $\beta$ -naphthylamine (A., 1929, 181; 1933, 59). Reduction of (II) by Zn and AcOH gives 1': 2'-benzoyleneacenaphtho-4: 5imin-4-azole (III), m.p. 280°. (I) condenses with MeCHO, PhCHO,  $o \cdot C_6H_4$ Me·CHO, and



m-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, respectively, to give the following substituted N(4)-anilidoacenaphtho-4 : 5-iminoazoles :  $\mu$ -methyl-, m.p. 222°,  $\mu$ -phenyl-, m.p. 233°,  $\mu$ -p-tolyl-, m.p. 245°, and  $\mu$ -m-nitrophenyl-, m.p. 252° (as IV). R. K. C.

Preparation of carbocyanine dyes.—See B., 1934, 794.

Conditions and region of validity of the flavin synthesis. R. KUHN and F. WEYGAND (Ber., 1934, 67, [B], 1459—1460).—The production of flavins from alloxan and derivatives of  $o \cdot C_6 H_4(NH_2)_2$  occurs smoothly when the base is present as salt, more slowly and less completely when the free bases are used in solvents of high b.p., e.g., PhNO<sub>2</sub>. HCl may be replaced by  $H_2SO_4$ ,  $H_3PO_4$ ,  $HNO_3$ ,  $H_2C_2O_4$ , or AcOH. Anhyd. solvents are very suitable if opportunity is given for salt formation (AcOH).  $o \cdot NH_2 \cdot C_6H_4 \cdot NHMe$ and the NaHSO<sub>3</sub> compound of methylalloxan in boiling dil. HCl afford 3: 9-dimethylflavin [3: 9-dimethylisoalloxazine], m.p. 320—325° (decomp.), which does not yield a Ag salt and cannot be removed by CHCl<sub>3</sub> from its solution in dil. alkali. H. W.

Synthesis of lumilactoflavin. R. KUHN, K. REINEMUND, and F. WEYGAND (Ber., 1934, 67, [B], 1460—1462).—Condensation of 4-amino-5-methylamino-o-xylene hydrochloride with alloxan tetrahydrate leads to 6:7:9-trimethylflavin [6:7:9trimethylisoalloxazine]. Its identity with lumilactoflavin (I) is established by direct comparison of the compounds and by alkaline hydrolysis to the same ketocarboxylic acid,  $C_{12}H_{12}O_3N_2$ , and "sublimate,"  $C_{11}H_{12}ON_2$ , and further by the identity of synthetic 3:6:7:9-tetramethylflavin with the product of the action of  $Me_2SO_4$  on (I).

Quinoline derivatives. II. Pyrazolinoquinolines. K. S. NARANG, J. N. RAY, and A. SINGH (J. Indian Chem. Soc., 1934, 11, 427–431; cf. A., 1933, 1060).—1-Phenyl-3-methylpyrazolone,

o-NO2 C6H4 CHO, and NaOAc at 150° give 4-o-nitrobenzylidene-1-phenyl-3-methylpyrazolone, m.p. 162°, reduced by Zn dust and AcOH or HCl-EtOH or by Al-Hg in moist Et<sub>2</sub>O to a mixture of 1-hydroxy-2:3-4': 5'-pyrazolinotetrahydroquinoline(I), m.p. 142° (hydrochloride, m.p. 251-252°), and 4-o-hydroxylamino-1phenyl-3-methylpyrazolone, m.p. 101-102°. o-Nitropiperonal and 6-nitroveratraldehyde give similarly 4-o-nitropiperonylidene- (II), m.p. 190°, and 4-o-nitroveratrylidene-1-phenyl-3-methylpyrazolone (III), m.p. 183°. (II) with Zn dust and HCl or Al-Hg gives 4-0-aminopiperonylidene-1-phenyl-3-methylpyrazolone, m.p. 186° (trihydrochloride, m.p. 243°), cyclised at 150° in H<sub>2</sub> to 6:7-methylenedioxy-2:3-4':5'-pyrazolino-quinoline (poor yield), m.p. 185° (picrate). (III) with Zn dust and AcOH gives o-aminoveratrylidene-1phenyl-3-methylpyrazolone, m.p. indefinite (trihydro-chloride, m.p. 226°), and thence 6:7-dimethoxy-2:3-4': 5'-pyrazolinoquinoline, m.p. 215°. Absorption spectra support the constitutions given. R. S. C.

Caffeine derivatives. III. Preparation of 8methyl- and 8-ethyl-caffeine. R. C. HUSTON and W. F. ALLEN (J. Amer. Chem. Soc., 1934, 56, 1793— 1794).—8-Methylcaffeine, m.p. 207—208.5°, is obtained in 10.8—67.5% yield from 8-methoxy- (I), 8-ethoxy- (II), 8-n-propoxy-, 8-n-butoxy-, or 8-isoamyloxy- (III) -caffeine (this vol., 906) and Ac<sub>2</sub>O at 260—270° (sealed tube). 8-Ethylcaffeine, m.p. 186— 187.5°, is similarly prepared in 7.2—19% yield from (II), (III), or 8-isopropoxy- [but not (I)] or hydroxycaffeine and  $(EtCO)_2O$  at 295—360°. 8-*n*-Propyl- and -*n*-butyl-caffeines could not be prepared by the same procedure. H. B.

Phthalocyanines. I. New type of synthetic colouring matters. R. P. LINSTEAD. II. Preparation of phthalocyanine and some metallic derivatives from o-cyanobenzamide and phthalimide. G. T. BYRNE, R. P. LINSTEAD, and A. R. Lowe. III. Preparation of phthalocyanines from phthalonitrile. R. P. LINSTEAD and A. R. LOWE. IV. Copper phthalocyanines. C. E. DENT and R. P. LINSTEAD. V. Mol. wt. of magnesium phthalocyanine. R. P. LINSTEAD and A. R. LOWE. VI. Structure of the phthalocyanines. C. E. DENT, R. P. LINSTEAD, and A. R. Lowe (J.C.S., 1934, 1016-1017, 1017-1022, 1022-1027, 1027-1031, 1031-1033, 1033-1139).-I. Br passing NH<sub>3</sub> into molten o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O in Fe vessels, crude Fe phthalocyanine (I) is obtained. It is decomposed by HNO<sub>3</sub> to o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NH (II) and the Fe<sup>III</sup> salt, by H<sub>2</sub>SO<sub>4</sub> at 100° to o-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>, (II), FeSO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and with soda-lime to PhCN and NH<sub>3</sub>. With NH<sub>2</sub>Ph, it affords the aniline compound. The general properties of (I) are described. (I) is probably produced by dehydration of (II) and fixation of NH<sub>3</sub> and the metal.

II. o-Cyanobenzamide (III) reacts with many metals at 250° to yield strongly coloured substances : the metals are Mg (metal or oxide) Fe (metal, oxide, or sulphide), Co, Ni, Sb. The reactions are exothermic and the precursor of the compounds is iminophthalimidine. MgO, (III), and  $C_{10}H_8$  yield Mg phthalocyanine,  $(C_8H_4N_2)_4Mg, 2H_2O$  (IV), which with  $H_2SO_4$ forms phthalocyanine,  $C_{32}H_{18}N_8$  (V). Fe, Ni, and Co give stable metallic phthalocyanines. Sb and (III) afford a product which contains only a trace of metal. III.  $o-C_6H_4(CN)_2$  (VI) combines very readily with metals and their derivatives to yield phthalocyanines. (IV) is prepared from (VI) and is formulated as a dihydrate, containing  $2H_2O$ , or  $H_2O+C_9H_7N$ , or  $H_2O+C_5H_5N$ , depending on the solvent. Na amyloxide and other reagents containing Na react with (VI) to

yield products which lose Na, giving (V). IV. (VI) and Cu at 190—210° yield Cu phthalocyanine (VII), which is very stable, subliming at 580° without decomp., the Cu being stable to  $H_2SO_4$ . It may be obtained from Cu and (V) at high temp. and is decomposed to (II) and  $NH_3$ . (VI) and CuCl combine



to give (VII) and CuCl<sub>2</sub>, whilst (VI) and CuCl<sub>2</sub> give HCl and *Cu monochlorophthalocyanine*,  $C_{32}H_{15}N_{s}ClCu$ , the Cl being in one of the  $C_{6}H_{6}$  nuclei.

V. The mol. wt. of (IV) has been determined by the ebullioscopic method in  $C_{10}H_8$ , using a Pt-resistance thermometer. The val. (551) confirms the formula of (IV).

VI. The reagents which react with (VI) do not give similar products with m- or p-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub>, o-xylenylene dicyanide, o-cyanocinnamonitrile, and 2:2'-diphenonitrile. The evidence for the structure of the compounds is summarised and the formulæ (V) and (VI) are advanced.

Oxidation of (IV), (V), and (VI) with  $Ce(SO_4)_3$ shows that the metallic derivatives are formed from (V) by replacement of 2 H by 1 atm. of bivalent metal. The stereochemistry of the phthalocyanines and their relationship to the porphyrins are briefly discussed.

F. R. S.

Purification of chlorophylls-a and -b; their absorption spectra; evidence for the existence of a third component of chlorophyll. F. P. ZSCHEILE, jun. (Bot. Gaz., 1934, 95, 529—562).— Earlier methods do not completely separate chlorophyll-a and -b. Modified methods are described. A third component of chlorophyll possesses properties intermediate between those of a and b. A. G. P.

Unsaturation and tautomeric mobility of heterocyclic compounds. IV. Methylation and bromination of a series of 2-p-substituted anilinothiazoles. R. F. HUNTER and E. R. PARKEN. V. Benzoxazoles. R. D. DESAI, R. F. HUNTER, and A. R. K. KHALIDI (J.C.S., 1934, 1175-1177, 1186-1190).-IV. Condensation of the appropriate substituted phenylthiocarbamide with CH2AcCl yields 2p-chloro-, m.p. 147°, -bromo-, m.p. 162°, -iodo-, m.p. 168-169°, -ethoxy-, m.p. 135-136°, -hydroxy-, m.p. 220°, and -nitro-anilino-4-methylthiazole, m.p. 181-182°. Methylation (MeI) of these compounds shows that they react in the amino-aromatic form yielding 2-p-chloro-, m.p. 138-139°, -bromo-, m.p. 154°, and -iodo-anilo-3: 4-dimethyl-2: 3-dihydrothiazole picrate, m.p. 154-155°, and 2-p-ethoxy-, m.p. 114-115°, -hydroxy-, m.p. 189-190°, and -nitro-anilino-4-methylthiazole, m.p. 151°, identical with the corresponding condensation products of CH2AcCl and the s-arylmethylthiocarbamides (s-p-hydroxy-, m.p. 186°, and -nitro-phenylmethylthiocarbamide, m.p. 183-184°). Bromination of the compounds leads to substitution products: hydro-penta-, m.p. 128-129° (decomp.), and hydro-tri-bromide, m.p. 124-126° (decomp.), of 5bromo-2-p-chloroanilino-4-methylthiazole, m.p. 126-127° (decomp.); hydro-penta-, m.p. 114-115° (decomp.), and hydro-tri-bromide, m.p. 118-119°, of 5-137°: bromo-2-p-bromoanilino-4-methylthiazole, m.p. 2-op-dibromoanilino-4-methylthiazole, m.p. 136-137°; hydrotribromide, m.p. 119-120°, of 5-bromo-2-p-ethoxyanilino-4-methylthiazole, m.p. 136-137°; hydropentabromide, m.p. 113—114° (decomp.), of 5-bromo-2-p-nitroanilino-4-methylthiazole, m.p. 162° (decomp.); hydropentabromide, m.p. 121—122°, of 5-bromo-2anilino-4-methylthiazole, m.p. 131-132° (decomp.); and hydrotribromide, m.p. 127-128°, of 5-bromo-2anilo-3: 4-dimethyl-2: 3-dihydrothiazole, m.p. 123°. 2-Phenylmethylamino-4-methylthiazole picrate has m.p. 113-114°.

V. I-Aminobenzoxazole (I) (picrate, m.p. 224°) is 4 p

methylated (MeI) to 1-imino-2-methyl-1: 2-dihydrobenzoxazole, m.p. 96° (picrate, m.p. 189-190°; Ac derivative, m.p. 92°); the isomeric 1-methylaminobenzoxazole (Ac derivative, m.p. 91°), obtained from 1-thiolbenzoxazole and NH2Me, is not formed during methylation. Bromination of (I) yields the hydrobromide, m.p. 245°, and hydrodibromide, m.p. 232° (decomp.), of 5(?)-bromo-1-aminobenzoxazole, m.p. 194-195°. Methylation of 1-anilinobenzoxazole (picrate, m.p. 188°) gives a mixture of the *picrate*, m.p. 156°, of 1-anilo-2-methyl-1:2-dihydrobenzoxazole and the picrate, m.p. 176°, of 1-phenylmethylaminobenzoxazole, also obtained from 1-thiolbenzoxazole and NHPhMe. 1-Hydrobenzoxazole is methylated to 1-keto-2-methyl-1: 2-dihydrobenzoxazole, m.p. 87-88°, and brominated to a hydrobromide of 5(?)bromo-1-hydroxybenzoxazole, m.p. 190°. 1-Thiolbenzoxazole with HgO forms a mercuric salt, m.p. 204°, with Br yields a compound, m.p. 128° (decomp.), decomposed to 5(?)-bromo-1-thiolbenzoxazole, m.p. 200°, and with  $Me_2SO_4$  followed by  $HgCl_2$  affords a compound, m.p. 162°, of  $HgCl_2$  with 1-methylthiolbenzoxazole. 1-Thio-2-methyl-1: 2-dihydrobenzoxazole has m.p. 134-135°, and 1-p-toluidinobenzoxazole, m.p. 178°. o-Aminophenol, PhCHO, and AcOH yield 1-F. R. S. phenylbenzoxazole.

Oxacyanines. (MISS) N. I. FISHER and (MISS) F. M. HAMER (J.C.S., 1934, 962-965).-2:1-C10H6(NH2) OH, HCl with Ac2O-NaOAc gives 1methyl-a-naphthoxazole, m.p. 36-37°, b.p. 178-201°/ 18-20 mm., which forms a methiodide (I), m.p. 202° (decomp.), and ethiodide, m.p. 215° (decomp.). 2-Methyl-a-naphthoxazole, m.p. 25°, gives a methiodide, m.p. 212-213° (decomp.), and ethiodide, m.p. 202- $203^{\circ}$  (decomp.). (I),  $Ac_2O$ , and amyl nitrite give 2: 2'-dimethyloxacyanine iodide, m.p. > 310° [-diethylcompound, m.p. 301° (decomp.)], which with SO2 in MeOH forms 2: 2'-dimethyl-5: 6: 5': 6'-dibenzoxacyanine iodide, m.p. > 320° (-diethyl-compound, m.p.  $> 315^{\circ}$ ). The products obtained in the 2-Me series are 2: 2'-dimethyl-, m.p. 291° (decomp.), and 2: 2'-diethyl-3:4:3':4'-dibenzoxacyanine, m.p. 283° (decomp.). The yields of oxacyanines vary from 14 to 26%. The absorption lies further into the more refrangible region of the spectrum than does that of any known kind and of cyanine dye, the simplest oxacyanines giving colourless solutions. The dibenzoxacyanines act as photographic sensitisers to gelatin-AgCl emulsions. F. R. S.

Preparation and bacteriological study of thiazole-azo-dyes. W. A. LOTT and W. G. CHRIS-TIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 785–787). 2-Aminothiazole (from thiocarbamide and  $\alpha\beta$ -dichloroethyl ether), m.p. 88.5–90.5°, is diazotised (with difficulty) and coupled with resorcinol, m-cresol, and m-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> to give the dyes (I), (II), and (III) (not obtained pure), respectively. (I) and (II) have no germicidal action, but inhibit the growth of *B.* typhosus and Staphylococcus at 1: 8000 and 1: 16,000, respectively. R. S. C.

Thiomorpholine derivatives. L. A. BURROWS and E. E. REID (J. Amer. Chem. Soc., 1934, 56, 1720– 1724).— $S(CH_2 \cdot CH_2 Br)_2$  (I) and  $NH_2 \cdot CH_2 \cdot CH_2 \cdot OH$  (II) (3 mols.) in  $C_6H_6$  give 4- $\beta$ -hydroxyethylthiomorpholine.

 $S < CH_2 \cdot CH_2 > N \cdot CH_2 \cdot CH_2 \cdot OH$ , b.p. 130°/10 mm., m.p. 35.5° [hydrochloride, m.p. 162-163°; acetate, b.p. 144°/15 mm., 269°/757 mm. (hydrochloride, m.p. 149.5°); propionate, b.p. 155°/15 mm., 277.7°/757 mm., m.p. -1° (hydrochloride, m.p. 132.6°); butyrate, b.p. 166°/15 mm., 284·7°/757 mm. (hydrochloride, m.p. 129°); valerate, b.p. 176·6°/15 mm., 291°/757 mm. (hydrochloride, m.p. 128·3°); hexoate, b.p. 186·8°/15 (*ngarochabrae*, *in.p.* 1283), *neubale*, *b.p.* 1003 (15) mm., 297°/757 mm. (*hydrochloride*, *m.p.* 121.5°); *heptoate*, *b.p.* 196.6°/15 mm. (*hydrochloride*, *m.p.* 118.6°); *benzoate*, *m.p.* 66—67° (*hydrochloride*, *m.p.* 224°); *p-nitrobenzoate*, *m.p.* 63° (*hydrochloride*, *m.p.* 219°); *p-aminobenzoate*, *m.p.* 136° (*dihydrochloride*, *m.p.* 237°)]. (I) and NH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH in CHCl<sub>3</sub> initially of a 4 *a b dydrocmercull biomermeliane m.p.* similarly afford 4-y-hydroxypropylthiomorpholine, m.p. 55° [hydrochloride, m.p. 188°; acetate hydrochloride, m.p. 145°; benzoate hydrochloride, m.p. 183.5°; p-nitrobenzoate, m.p. 77° (hydrochloride, m.p. 218°); p-aminobenzoate dihydrochloride, m.p. 219°]. 4-β-Hydroxyethylthiomorpholine 1-oxide, m.p. 45° (hydrochloride, m.p. 173-174°; acetate hydrochloride, m.p. 135-136°; propionate hydrochloride, m.p. 161-162°; butyrate hydrochloride, m.p. 158.5°; valerate hydrochloride, m.p. 149-150°; hexoate hydrochloride, m.p. 140°; heptoate hydrochloride, m.p. 156-157°), and 4-β-hydroxyethylthiomorpholine 1:1-dioxide, m.p. 54° 4-β-hydroxyethylthiomorpholine 1:1-dioxide, m.p. 54° [hydrochloride, m.p. 175.5°; acetate, m.p. 22.3° (hydro-chloride, m.p. 147°); propionate, m.p. 43—44° (hydro-chloride, m.p. 183—184°); butyrate, m.p. 21.6° (hydro-chloride, m.p. 146°); valerate, m.p. 25° (hydrochloride, m.p. 144°); hexoate, m.p. 25° (hydrochloride, m.p. 141—142°); heptoate, m.p. 27° (hydrochloride, m.p. 142.5°); benzoate, m.p. 125.5° (hydrochloride, m.p. 174°); p-nitrobenzoate, m.p. 167° (hydrochloride, m.p. 222°); p-aminohenzoate m.p. 148.6° (dihudrochloride 222°); p-aminobenzoate, m.p. 148.6° (dihydrochloride, m.p. 238°)], are prepared from (II) and

SO(CH2 ·CH2Br)2 and SO2(CH2 ·CH2Br)2, respectively. All b.p. and m.p. are corr. The aromatic esters possess local anæsthetic properties similar to those of the corresponding morpholine derivatives. H. B.

Benzthiazoloquinazolines. P. K. Bose and K. B. PATHAK (J. Indian Chem. Soc., 1934, 11, 463-465).-2-Chlorobenzthiazole and o-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, when heated, give benzthiazoloquinazoline (I), m.p. 189° (NO<sub>2</sub>-derivative, m.p. 279-280°), hydrolysed by



hot 5% KOH-EtOH to N-2-benzthiazolylanthranilic acid (2-o-carboxyanilinobenzthiazole) or 2-benzthiazolinylideneanthranilic acid,

(I.)  $m.p. 187^{\circ}$  (Na salt, m.p. 273°), reconverted into (I) by Ac<sub>2</sub>O. The 5-, m.p. 226° [NO<sub>2</sub>-, m.p. 304°, and (NO<sub>2</sub>)<sub>2</sub>-derivatives, m.p. 280°], and 4-Me-derivative, m.p. 180° of (I) were similarly prepended to 180°, of (I) were similarly prepared and led to the acids, m.p. 188-189° (Na salt, m.p. 280°) and 189°, respectively. 2-Chloro-lin.- $(\alpha)$ -naphthothiazole, m.p. 75°, gives lin.- $(\alpha)$ -naphthothiazoloquinazoline, m.p. 261°. 1-Chloro-3-methylthiazole could not be obtained by Hofmann's or Hunter's method and only in poor yield from the aminothiazole (Sandmeyer).

R. S. C. Ergot alkaloids. III. Lysergic acid. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1934, 106,

393-399).-The hydrochloride, m.p. 208-210°, and H sulphate, m.p. 220°, of lysergic acid (I), obtained by the hydrolysis of ergine (this vol., 538), were prepared. Oxidation of (I) with HNO3 gave a product resembling that obtained similarly from the acid C14H9O8N. Reduction of (I) with Na in amyl alcohol, extraction with hot EtOH, and pptn. with AcOH gave dihydrolysergic acid, m.p. 336° (decomp.), [a]] -88° in C<sub>5</sub>H<sub>5</sub>N (Me ester, m.p. 182°). H. D.

Photosynthesis of nicotine. H. E. WATSON and B. K. VAIDYA (J. Indian Chem. Soc., 1934, 11, 441-442).-2% aq. CH2O, 6.2N-NH3, and CuCO3 in ultraviolet light give NH Me, but no nicotine (I) [cf. Bhargava et al. (A., 1933, 1256), whose method of working leads to total loss of (I)]. R. S. C.

Indole series. II. Alkylation of 3-formyl-1methyloxindole and synthesis of the basic ring structure of physostigmine. P. L. JULIAN, J. PIKL, and D. BOGGESS (J. Amer. Chem. Soc., 1934, 56, 1797-1801).-1-Methyloxindole and HCO2Et in EtOH-NaOEt give 3-formyl-1-methyloxindole (I), m.p. 192° (lit. 186°), which with MeI (> 2 mols.) in MeOH-NaOMe (> 2 mols.) affords 1:3:3-trimethyl-oxindole (II), b.p. 131-132°/11 mm., m.p. 50°, also prepared from a-bromoisobutyr-N-methylanilide and AlCl<sub>3</sub> at 120—125°. 1:3-Dimethyloxindole (III), b.p. 136—138°/11 mm., m.p. 27° and 55° (stable), is obtained similarly using 1 mol. of NaOMe; further methylation gives (II). (III) is also obtained from a-bromopropion-N-methylanilide and AICl<sub>a</sub>. In the above methylation of (I), 3-formyl-1: 3-dimethyloxindole is probably first produced and then cleaved to (III). The Na salt (IV) of (I) and MeI in COMe2 give a compound,  $C_{11}H_{11}O_2N, 0.5NaI$ , m.p. 213°, hydrolysed ( $H_2O$ ) to 2-methoxy-3-formyl-1-methylindole (V), m.p. 138°, converted by prolonged boiling with EtOH into 2-ethoxy-3-formyl-1-methylindole (VI), m.p. 78°. (IV) and EtI in COMe2 similarly give a compound,  $C_{12}H_{13}O_{2}N,0.5NaI$ , m.p. 167°, also prepared from (VI) and NaI in COMe<sub>2</sub>. (V) and (VI) are readily hydrolysed (3% HCl; dil. alkali) to (I); attempted prep. of the semicarbazones, phenylhydrazones, and anils gave the corresponding derivatives of (I). CH<sub>2</sub>Cl·CN and (III) in EtOH-NaOEt afford

NMe (VII.)

1:3 - dimethyloxindolyl - 3 -194-CMe CH<sub>2</sub> >CH<sub>2</sub> acetonitrile, b.p. 194-CH-NH>CH<sub>2</sub> 196°/14 mm., m.p. 58° (-3acetonitrile, b.p. acetic acid, m.p. 178°), reduced (Na, EtOH) to B-1:3-

dimethyloxindolyl-3-ethylamine (picrate, m.p. 113) and (mainly) deoxynoreseroline (VII), b.p. 154°/17 mm. (picrate, m.p. 158°; Bz derivative, m.p. 168°). (VII) and MeI in Et<sub>2</sub>O give deoxyeseroline (picrate, m.p. H. B. 177°).

Dehydrogenation of yohimbine. R. MAJIMA and S. MURAHASI (Proc. Imp. Acad. Tokyo, 1934, 10, 341-344).-The action of Pd-black on a boiling aq. solution of yohimboaic acid and maleic anhydride leads to fumaric acid, [•CH2•CO2H]2, and tetradehydroyohimboaic acid, decomp. 335° (hydrochloride, decomp. 325°), transformed by CH<sub>2</sub>N<sub>2</sub> or HCl-MeOH into tetradehydroyohimbine, C<sub>21</sub>H<sub>22</sub>O<sub>3</sub>N<sub>2</sub>, m.p. 256-2655° (decomp.),  $[\alpha]_{1}^{\infty}$  +289.9° in AcOH, transformed by KOH in amyl alcohol into harman and m-toluic acid. Et tetradehydroyohimboate has m.p.  $281-282^{\circ}$  (decomp.),  $[\alpha]_{15}^{**} + 245 \cdot 2^{\circ}$  in AcOH. Deoxy-yohimboaic acid similarly yields tetradehydrodeoxy-yohimbine, m.p.  $251-252^{\circ}$  (decomp.) (hydrochloride, decomp.  $302^{\circ}$ ). Yohimbylamine (I),  $C_{19}H_{25}ON_3$ , m.p.  $177-178^{\circ}$ , is obtained from yohimbine by the Curtius reaction. The dihydrochloride ( $+3 \cdot 5H_2O$ ), decomp.  $293^{\circ}$ , and sulphate ( $+1 \cdot 5H_2O$ ), m.p.  $314^{\circ}$ , are described. (I) affords tetradehydroyohimbylamine dihydrochloride,  $C_{19}H_{21}ON_3,2HCl_{3}OSH_2O$ , decomp.  $342^{\circ}$ . The ZnCl<sub>2</sub> double salt, decomp.  $330-332^{\circ}$ , perchlorate, decomp. about 278° after blackening at 260°, and the sulphate ( $+3H_2O$ ), decomp.  $345^{\circ}$ , are described. H. W.

Alkaloids of fumaraceous plants. X. Dicentra oregana, Eastwood. R. H. F. MANSKE (Canad. J. Res., 1934, 10, 765–770).—By the procedure used previously (A., 1933, 728) 3% of alkaloids may be isolated from the roots of *D. oregana*, viz., dicentrine, glaucine, corydine, protopine,  $\alpha$ -allocryptopine (found for the first time in a species of *Dicentra*), and two other alkaloids ( $\delta$  and  $\epsilon$ ) which have been partly characterised. The phytochemical significance of the glaucine : dicentrine ratio is discussed. Alkaloid  $\delta$  appears to be that found in *D. eximia* and *D. formosa* (A., 1933, 990). Alkaloid  $\epsilon$ , C<sub>19</sub>H<sub>21 or 23</sub>O<sub>4</sub>N, m.p. 230° (previous sintering), is phenolic and probably contains one :NMe and two •OMe. H. N. R.

Oxidation of harmaline to harmine by nitric acid. S. ELGAZIN (Khim. Farm. Prom., 1933, 270– 271).—Harmaline nitrate (I) is prepared by agitating harmaline (1 kg.) in H<sub>2</sub>O (8 litres) at  $\geq 15^{\circ}$  while 5% HNO<sub>3</sub> is added. The excess of HNO<sub>3</sub> is neutralised, the mixture heated at 75°, clarified with C, filtered, and cooled; (I), m.p. 230–232°, crystallises. (I) (1 kg.) is dissolved in 96% EtOH (10 litres) at 50°, treated with HCl (d 1·19, 1 kg.), and the temp. slowly raised to 56–60°. After 20 min. the solid mass is cooled, filtered, washed with EtOH, and dried. Harmine cryst. from 85% EtOH has m.p. 257–259°. Yield about 80%. CH. ABS.

Cinchonine solubility.—See this vol., 1066.

Water of crystallisation of quinine sulphate. H. WALES (J. Amer. Pharm. Assoc., 1934, 23, 793— 795).—V.-p. measurements show that quinine sulphate forms an octahydrate, which in air reverts to the dihydrate. No heptahydrate is formed. R. S. C.

Strychnine and brucine. BRUSTIER and P. BLANC (Bull. Soc. chim., 1934, [v], 1, 712–719).— Brueine (I) has only two absorption bands with max. at 2666-7 and  $3059\cdot 2$  Å. Since strychnine (II) has three bands, it is probably constituted differently from (I). The absorption of (II) resembles that of  $C_5H_5N$ , whilst that of (I) and quinoline are similar. (I) and (II) also give ozonisation products with different absorptions. R. S. C.

Reduction in morphine series. II. Isomeric phenolic dihydro- $\psi$ -codeines. R. E. LUTZ and L. SMALL (J. Amer. Chem. Soc., 1934, 56, 1741-1744).—Reduction (H<sub>2</sub>, Pd-CaCO<sub>3</sub>, 80% EtOH) of  $\psi$ -codeine (I) gives (mainly) the phenolic dihydro- $\psi$ codeine-B (II), m.p. (+xEtOH) 125-127°, [ $\alpha$ ]<sup>2</sup><sub>D</sub> - 14-1° in EtOH, m.p. (anhyd.) 174.5-175.5° (from EtOAc) and 196-197° (sublimation and crystallisation from and 100 (submitted that displaying the formula of the second state of the second stat 223° (corr.) (after melting partly at 131-132°), of (II) is decomposed by conc. aq. KOH to dihydro-E-methylmorphimethine-B, m.p. 188.5-189.5°; [a]24 +28° in CHCl<sub>3</sub>, which is reduced (H<sub>2</sub>, Pd-CaCO<sub>3</sub>, EtOH) to hexahydro-E-methylmorphimethine (IV). Contrary to Speyer and Krauss (A., 1923, i, 1115), electrolytic reduction of (I) gives mainly (II) and not dihydro-4codeine-C (+EtOH) (V), m.p. 100-116° (decomp.) and 167.5-168° (corr.) [hydrochloride (+0.5H<sub>2</sub>O), m.p. 253° (corr.); salicylate, m.p. 232-234° (corr.)]. (V) is formed together with a mixture of dihydrodeoxycodeine-B and -C (see following abstract) by reduction (Na, EtOH in N<sub>2</sub>) of (I). The methiodide  $(+H_2O)$ , m.p. 238-239° (corr.), of (V) is converted (aq. KOH) into dihydro-E-methylmorphimethine-C, m.p.  $150^{\circ}$ ,  $[\alpha]_{D}^{2}$ +62.5° in CHCl<sub>3</sub> [hydriodide (+H<sub>2</sub>O), m.p. 137–138° (corr.)], also obtained in small amount by reduction (Na, EtOH) of *e*-methylmorphimethine, which is reduced further to (IV). The reductions in the methine series parallel those of the parent  $\psi$ -codeine derivatives. Structures are suggested for most of the above compounds. H. B.

Deoxycodeine. V. So-called dihydrodeoxycodeine-A. L. SMALL and R. E. LUTZ (J. Amer. Chem. Soc., 1934, 56, 1738-1740).-Reduction (Na, EtOH) of  $\alpha$ -chlorocodide (I) or deoxycodeine-A (II) gives a 1:3-mixture (III), m.p. 120-125° or 157° (according to solvent), of dihydrodeoxycodeine-B(IV), m.p. 131-133°, m.p. (anhyd. ?) 173-173.5° (obtained by sublimation), and dihydrodeoxycodeine-C(V), m.p. 108—111°,  $[\alpha]_{1}^{24}$  +5.6° (lit. -61.6°) in EtOH, and not dihydrodeoxycodeine-A (A., 1931, 1077). Treatment of the methiodide from (III) with TIOH in H<sub>2</sub>O, evaporation of the resulting solution to dryness in a vac., and sublimation of the residue at 140°/0.001 mm. gives de-N-methyldihydrodeoxycodeine-B, m.p. 114.5-145.5°,  $[\alpha]_{10}^{30} + 9.5°$  in CHCl<sub>3</sub> [similarly prepared with  $[\alpha]_{10}^{30} + 7.4°$  in CHCl<sub>3</sub> from (IV)], and de-N-methyldi-hydrodeoxycodeine-C, m.p. 175–176°,  $[\alpha]_{10}^{30} - 13.8°$ in CHCl<sub>3</sub> [also prepared from (V)]. The above reduc-tion of (I) undoubtedly gives (II); subsequent 1:2-and 1:4-addition of  $H_2$  occurs. (V) is also obtained by electrolytic reduction of chlorodihydrocodide and by reduction (Na, EtOH in  $N_2$ ) of deoxycodeine-C. Structures are suggested for (IV) and (V). Contrary to previous results (loc. cit.), vigorous reduction (Na, EtOH) of dihydrodeoxycodeine-D gives only 5% of H. B. tetrahydrodeoxycodeine.

Alkaloids of Alstonia barks. II. A. macrophylla, Wall., A. somersetensis, F. M. Bailey, A. verticillosa, F. Muell., A. villosa, Blum. T. M. SHARP (J.C.S., 1934, 1227—1232).—A. verticillosa contains sterols and echitamine; A. macrophylla contains villalstonine (I),  $C_{40}H_{50}O_4N_4$ , macralstonine (II),  $C_{44}H_{54}O_5N_4$ , macralstonidine (III),  $C_{41}H_{50}O_3N_4$ , and base M in small amount; A. somersetensis contains (I) and (III); and A. villosa contains (I) and base V in small amount. (I) has m.p. 218-260°, and is isolated as the oxalate, m.p.  $235^{\circ}$  (decomp.),  $[\alpha]_{\rm p} + 31.2^{\circ}$  in COMe<sub>2</sub>; it forms a hydrochloride (+4H<sub>2</sub>O), m.p. 270° (decomp.),  $[\alpha]_{\rm p}$  +56·3° in H<sub>2</sub>O, a sulphate (+6H<sub>2</sub>O), m.p. above 310°,  $[\alpha]_{\rm p}$  +52·94° in H<sub>2</sub>O, a hydrobromide (+4H<sub>2</sub>O), m.p. 293° (decomp.), a hydriodide, m.p. 286° (decomp.), a dimethiodide, m.p. 287° (decomp.), and a N-benzyl derivative, m.p. 246° (decomp.). (I) and KOH yield a substance, C<sub>39</sub>H<sub>48</sub>O<sub>4</sub>N<sub>4</sub>, m.p. 291-293° (decomp.), which does not contain OMe. (I) has one OMe present as ester and two NMe. (II) has m.p. 293° (decomp.),  $[\alpha]_{\rm D} + 27.5^{\circ}$  in CHCl<sub>3</sub>, and forms a sulphate, m.p. about 263° (decomp.),  $[\alpha]_{\rm D} - 36.8^{\circ}$  in H<sub>2</sub>O. Base M has been obtained as the sulphate, m.p. about 257°,  $[\alpha]_{D}$  -71.9° in H<sub>2</sub>O. (III) decomposes about 270° and has  $[\alpha]_{\rm D}$  +174.5° in C<sub>6</sub>H<sub>6</sub>; it forms a hydrochloride, m.p.  $326^{\circ}$  (decomp.),  $[\alpha]_{D} + 136 \cdot 5^{\circ}$  in H<sub>2</sub>O. It contains two NMe but no OMe and appears to contain a CH<sub>2</sub>O<sub>2</sub>. Base V has m.p.  $273^{\circ}$  (decomp.),  $[\alpha] + 54 \cdot 6^{\circ}$ . All the alkaloids give colour reactions suggesting indole F. R. S. derivatives.

Ultra-violet absorption spectra of gen-alkaloids.—See this vol., 1055.

Reactivity of nuclear chlorine in 2-chloro-5nitrophenylarsinic acid. M. J. HALL and C. S. HAMILTON (J. Amer. Chem. Soc., 1934, 56, 1779-1782).—5-Nitro-2-anilino-, m.p. 182—184°, -2-iso-butylamino-, m.p. 189—190° (decomp.), -2-n-, m.p. 135— 137°, and -iso-, m.p. 186° (decomp.), -amylamino-, and -2- $\beta$ -hydroxyethylamino-, m.p. 146—147°, -phenyl-arsinic acids, prepared from 2-chloro-5-nitrophenyl-arsinic acid (I), the requisite NH<sub>2</sub>R, anhyd. K<sub>2</sub>CO<sub>3</sub>, and a little Cu in amyl alcohol, are reduced [Fe(OH)2] to the corresponding 5-NH2-derivatives, m.p. 195° (decomp.), 192° (decomp.), 178–179° (decomp.), 186° (decomp.), and 154–155° (decomp.), respectively. (I) and [·CH2·NH2]2 similarly give 5-nitro-2-β-aminoethylaminophenylarsinic acid, m.p. 250-251° (decomp.), or 4:4'dinitro- $\alpha\beta$ -dianilinoethane-2 : 2'-diarsinic acid, decomp. 228—229° (darkens at 225°) [corresponding 4:4'- $(NH_2)_2$ -derivative, m.p. 200-201° (decomp.)]. 5-Nitro-2-phenoxy-, m.p.  $231-232^{\circ}$ , -2-p-chlorophenoxy-, m.p.  $225-230^{\circ}$ , -2-o-, m.p.  $> 250^{\circ}$ , and -p-, m.p.  $245-246^{\circ}$ , -tolyloxy-, and -2-o-, m.p.  $229^{\circ}$  (decomp.), and -p-, m.p.  $> 250^{\circ}$ , -carboxyphenoxy-phenylarsinic acids are similarly prepared from (I) and the requisite ArOH [except for the CO<sub>2</sub>H-derivatives, which are formed by oxidation ( $KMnO_4$ ) of the Me compounds]; these are reduced to the corresponding  $5NH_2$ -derivatives, m.p.  $203^{\circ}, > 250^{\circ}, > 250^{\circ}, 224^{\circ}$  (decomp.),  $227^{\circ}$  (decomp.), and  $> 250^{\circ}$ , respectively.  $o-C_{6}H_{4}Cl-OH$  and (I) similarly afford 3-nitrodiphenylene oxide-1-arsinic acid, m.p.  $203-205^{\circ}$  (32% yield) [corresponding  $NH_2$ -derivative, decomp. 218° (darkens at 210°)]. The Cl atom of (I) is less reactive than that in 4-chloro-3-nitrophenylarsinic acid (cf. A., 1932, 1049). H. B.

3-Nitro-4-hydroxyphenylarsinic acid from pchloroaniline [and from 2-nitrodiphenylamine-4-arsinic acid]. V. A. IZMAILSKI and A. M. SIMONOV (Khim. Farm. Prom., 1933, 317-326).p-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub> is transformed (Bart-Schmidt) into p-C<sub>6</sub>H<sub>4</sub>Cl·AsO<sub>3</sub>H<sub>2</sub> (yield 80%).

 $4: 3-NO_2 \cdot C_6H_3Cl \cdot AsO_3H_2$  (I) is then made by nitration

with  $H_2SO_4$  and excess of  $KNO_3$  at 100°. (I) (14 g.) is stirred at 85° for 10 hr. with 40% NaOH (50 g.);  $H_2O$  (30 c.c.) and HCl (25 c.c.) are added, the solution is filtered with C at 80°, acidified with HCl (15 c.c.), and crystallised, affording  $3:4-C_6H_3(NO_2)(OH)$ ·AsO<sub>3</sub>H<sub>2</sub> in 64% yield. Alternatively,

3: 4- $NO_2 \cdot C_6 H_3(NHPh) \cdot AsO_3 H_2$  is prepared from the 4-Cl-compound by boiling for 10 hr. with N-NaOH and fresh NH<sub>2</sub>Ph. Excess of NH<sub>2</sub>Ph is removed with steam and the ppt. washed, dried, and hydrolysed for 8 hr. with 25% NaOH. CH. ABS.

Thermal decomposition of the aryltrihydroxyarsonium chlorides. J. PRAT (Compt. rend., 1934, 199, 208—210; cf. A., 1932, 1049; 1933, 962).—The thermal decomp. of [AsPh(OH)<sub>3</sub>]Cl and [CUPb . As(OH) ]Cl follows the general course

J. W. S.

Configuration of heterocyclic compounds. I. Optical resolution of 10-methylphenoxarsine-2carboxylic acid. (MISS) M. S. LESSLIE and E. E. TURNER (J.C.S., 1934, 1170-1174).-o-Aminophenyl p-tolyl ether is converted into 2-p-tolyloxyphenylarsinic acid, m.p. 192-193°, which with H<sub>2</sub>SO<sub>4</sub> yields 2-methylphenoxarsinic acid, m.p. 245-246°. Oxidation of the Me compound with KMnO<sub>4</sub> leads to 2-carboxy-phenoxarsinic acid, m.p. 280-281°, which forms 10-chloro-, m.p. 280-281°, converted by MgMeI into dl-10-methyl-phenoxarsine-2-carboxylic acid (I), m.p. 202-203° [methiodide, m.p. 250°, and its hydrate, m.p. about 250° (decomp.)]. Fractional addition of strychnine to (I) leads to strychnine d-,  $[\alpha]_{5791}^{20}$  +33.7°, dl-,  $[\alpha]_{5791}^{*0}$  -18.2°, and 1-10-methylphenoxarsine-2-carboxylate, [a]<sup>20</sup><sub>5791</sub> -51.7° in CHCl<sub>3</sub>. The acids obtained from these salts are the d-, m.p. 135-136°, [a] 551 +95.8° in EtOH, and 1-10-methylphenoxarsine-2carboxylic acid, m.p. 135-136°, [a]<sup>20</sup> 15791 -96.0°. The



acids are optically stable. The dissymmetry of the mol. is ascribed preferably to a folded structure, but an explanation based on the

presence of an asymmetric As atom is not excluded. F. R. S.

Mercury derivatives of nitro-m-cresol.—See B., 1934, 781.

Nitration of phenyl derivatives of mercury, thallium, lead, bismuth, tin, and iodine. F. CHAL-LENGERAND E. ROTHSTEIN (J.C.S., 1934, 1258—1263).— The extent of *m*-nitration of the compounds is: Hg Ph nitrate 50, Tl Ph<sub>2</sub> oxide, 74, Tl Ph<sub>2</sub> nitrate, 75, Tl Ph<sub>2</sub> hydroxynitrate, decomp. 268°, 80, Pd Ph<sub>2</sub> nitrate, 94, triphenylbismuthine dinitrate, 85, Sn Ph<sub>2</sub> oxide, 79, and diphenyliodinium nitrate, 82.5%. The nitrated product was treated with Br, and the proportion of resulting mixed bromonitrobenzenes determined by two independent methods. The results show that the effect of variation of phenylcationic charge in the compounds nitrated needs to be considered for purposes of comparison. F. R. S.

Diphenylene selenide. C. COURTOT and A. MOTAMEDI (Compt. rend., 1934, 199, 531-533).— Ph<sub>2</sub>SeO (A., 1894, i, 89) [prepared from Ph<sub>2</sub>Se (A., 1932, 762)] and NaNH<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> give diphenylene selenide (I),  ${}^{o-C_6H_4}_{o-C_6H_4}$ >Se, m.p. 74.5° (corr.) [dichloride; dibromide, m.p. 121.5° (corr.)], and phenylseleninic acid, m.p. 122-124° (corr.). Treatment of halogenated (I) with 3% aq. NaOH affords diphenyleneseleninone, m.p. 215-216°, oxidised by KMnO<sub>4</sub> to diphenyleneselenone, m.p. 282°. F. O. H.

Sensitisation of silver halide emulsions.—See B., 1934, 781, 782.

Manufacture of dyes and their intermediates. —See B., 1934, 753.

Heat-coagulation of caseinogen. I. The role of phosphorus cleavage. G. R. HOWAT and N. C. WRIGHT (Biochem. J., 1934, 28, 1336-1345).-Heating Na or Ca caseinogenate at 120° in closed tubes transforms the whole of the P from the Na salt and 80% from the Ca salt into the acid-sol. form, whilst some non-protein-N is liberated. Heat-dephosphorised (I) and alkali-dephosphorised (II) caseinogen differ from one another and from untreated caseinogen (III) in base-binding capacity; acid-binding properties are also affected, but less so. In presence of enough Ca(OH)<sub>2</sub> to give approx. neutral solutions, (I) and (II) coagulate more rapidly at 120° than (III), whilst excess of Ca<sup>\*\*</sup> accelerates coagulation of (I) and (III). Thus, Ca" liberated during dephosphorisation increases the heat-sensitivity of the products. Factors other than those indicated are probably also involved I. A. P. in heat-coagulation.

Casein. C. PORCHER, H. VOLKRINGER, and J. BRIGANDO (Compt. rend., 1934, 199, 249-252).-Examination of the absorption spectra of Na caseinate (I) and paracaseinate (II) and of the protein (III) obtained by addition of  $CaCl_2$  to a solution of Ca caseinate at  $p_{\rm H} \ge 7$  shows that the absorption of (I) and (II) begins at about  $\lambda 2950$  Å. and presents a broad band between 2900 and about 2600 A. General absorption then begins in the neighbourhood of 2500 Å. The curves for (I) and (II) appear identical, the apparently systematic differences between 2800-2920 and 2400-2450 Å. probably lying within the experimental errors. A max. of absorption is observed at 2765 Å., the band being completely analogous with that found for albumins and NH2-acids. A second max. appears at 2840 Å. The reactions of Voisenet and Millon are positive with (I) and (II), but negative H. W. with (III).

**Fractionation of caseinogen.** J. GRÓH (Z. physiol. Chem., 1934, 226, 32-44).—Caseinogen (I) was fractionally pptd. by three methods: from solution in (a) aq. carbamide by EtOH, (b) fused PhOH at 70° by EtOH, (c) dil. aq. NH<sub>3</sub> containing 70% of EtOH by dil. HCl. All methods finally gave only two

distinct fractions with 7.8 and 3.9% tyrosine content,  $[\alpha]_{\rm b}^{\circ} + 91^{\circ}$  and  $+129^{\circ}$  in 1% aq. borax, respectively. These preps. are not derivatives, but constituents of (I) and occur in approx. equal amount. J. H. B.

Reversibly oxidisable substance from irradiated protein. M. LAMPERT and P. WELS (Arch. exp. Path. Pharm., 1934, 175, 554—557).—The SHcompound formed by ultra-violet irradiation of aq. ovalbumin (I) (A., 1933, 1063) cannot be separated by ultra-filtration or by deproteinisation with colloidal  $Fe(OH)_3$ , methods by which added glutathione, cysteine,  $\alpha$ -thiolactic and thioglycollic acid are readily separated from (I). Hence the substance is probably of high mol. wt. F. O. H.

Gold sol reaction in irradiated proteins and protein derivatives. M. SPIEGEL-ADOLF (Biochem. J., 1934, 28, 1201—1208).—Irradiation with a Hg-arc lamp causes loss of protective power and production of pptg. power towards Au sols in the case of gelatin, arginine, histidine, lysine, proline, and thymonucleic acid, possibly due to decarboxylation. Glycine and cyclic NH<sub>2</sub>-acids were not altered. Irradiation of histamine does not destroy its Au-pptg. power as rapidly as its biological activity. C. G. A.

Composition of [serum-]proteins.—See this vol., 1018.

Role of lipins in the change of state of proteins. —See this vol., 1069.

Semi-micro-apparatus for the determination of carbon and hydrogen. G. KOMPPA and W. ROHRMANN (Chem. Fabr., 1934, 7, 239—240).—Improvements have been made in the apparatus previously described (A., 1933, 731) whereby the accuracy and the no. of determinations per charge are increased, explosion hazard is reduced by the use of an asbestos plug between the boat and the Cu spiral, and drying out of the soda-lime by the CaCl<sub>2</sub> is prevented by the interposition of a tap between the two absorption tubes; if the tap is closed between determinations infrequent filling only is necessary. H. F. G.

Microdetermination of bromine in organic substances. T. LEIPERT and O. WATZLAWEK (Z. anal. Chem., 1934, 98, 113—116).—The products of combustion of the substance are collected in N-NaOH. Br is determined by oxidation to bromate and titration with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (cf. van der Meulen, A., 1931, 325). The presence of 1 drop of NH<sub>4</sub> molybdate solution accelerates the iodide-bromate reaction in feebly acid solution. D. R. D.

Oxidation of organic sulphur applied to its determination. C. LEFEVRE and M. RANGIER (Compt. rend., 1934, 199, 462-464).—Org. S, if not combined with O, is determined by oxidation with boiling alkaline KMnO<sub>4</sub>. Otherwise the substance is burnt in dry O<sub>2</sub>, the vapours being passed over Pt-10% Rh heated to bright redness and collected in aq. NaOBr. The solution and washings of the tube are united, acidified with HCl, boiled, and pptd. with BaCl<sub>2</sub>. J. W. S.

p-Benzoquinone as amine reagent. M. FOUCRY (J. Pharm. Chim., 1934, [viii], 20, 116-118).-5 c.e. of a solution of 1 g. of *p*-benzoquinone in 100 g. of EtOH and 5 g. of AcOH boiled and cooled in presence of neutral or slightly acid solutions of amines give a red colour, immediately with conc. solutions and on keeping with dil. solutions. Conc.  $\rm NH_4$  salt solutions give a positive reaction, as do some  $\rm NH_2$ -acids (glycine, alanine). C. G. A.

Determination of weak organic acids (phenols). W. MUNCH (Z. anal. Chem., 1934, 98, 107—113).— Cresol is determined by adding it to a solution in equilibrium with Ca(OH)<sub>2</sub>. The increase in Ca content of the solution (conveniently determined by pptn. of CaC<sub>2</sub>O<sub>4</sub> and titration with KMnO<sub>4</sub>) is a measure of the cresol added owing to the formation of the sol. Ca compound. A correction factor of 1·1 is needed because of the hydrolysis of the compound. Other phenolic compounds may be treated similarly.

D. R. D.

Potassium mercury iodide reagents for alkaloids. J. TRAVELL (J. Amer. Pharm. Assoc., 1934, 23, 689-698).—Red  $HgI_2$  dissolved in 10% aq. KI solution is 5-15 times as sensitive as Mayer's reagent, detecting morphine sulphate at 1:7000 and quinine sulphate at 1:1,500,000. The sensitivity to proteins is similar. The alkaloid, but not the protein, mercuriiodides are sol. in 10% KI or EtOH. C. G. A.

Determination of total sulphur in keratin. J. BARRITT (J.S.C.I., 1934, 53, 291-294T).-The Mackay method (B., 1930, 626) for the determination of total S in rubber and similar materials is unsatisfactory as a standard method for determining S in keratin (I). Two simple and comparatively rapid methods described, involving (1) wet oxidation and (2) dry oxidation, give consistent results which agreed well with vals. obtained by the Carius method. In (1) the (I) sample is refluxed with HNO<sub>3</sub> (d 1.42), oxidation being completed with Benedict-Denis reagent (II). In (2) the sample is fused with  $Na_2O_2$  in the Hodsman bomb (A., 1921, ii, 345). Examination of the method in which the (I) is dissolved in HCl before treatment with (II) showed that on hydrolysis with HCl wool evolved H.S in amount > is accounted for by the slow decomp. of cystine under similar conditions. The work of Hoffman and Gortner (A., 1922, i, 427) on the decomp. of cystine on boiling with HCl was repeated and the very slow evolution of H<sub>2</sub>S confirmed.

Reactions between nitrogenous compounds and phenols. II.—See this vol., 1082.

## Biochemistry.

Spectrophotometric characteristics of hæmoglobins. I. Ox blood- and muscle-hæmoglobins. J. H. SHENK, J. L. HALL, and H. H. KING. II. Hæmoglobin of fowls. D. E. KLEIN, J. L. HALL, and H. H. KING (J. Biol. Chem., 1934, 105, 741-752, 753-760).-I. Solutions of musclehæmoglobin (I) show absorption curves similar to those of blood-hæmoglobin (II), but displaced towards the red. Equal concess. of (I) and (II) do not display equal absorption. The ratio of the densities of the max. absorption in the yellow and in the green, the ratios of both max. to the min. between them, and the ratio of the densities at 5770 and 5820 Å. are const.; a method for determining the relative % of (I) and (II) in the same solution is based on the last-named ratio. The points of max. absorption for blood-oxyhæmoglobin are at 5420 and 5770 Å. and the min. is at 5620 Å., the vals. for muscle-oxyhæmoglobin being 5430, 5820, and 5640 A., respectively. The acid-hæmatin fractions are apparently identical. Animals on pasture have a higher (I) content than dry-lot fed animals.

II. The absorption factors calc. from spectrophotometric measurements and Van Slyke determinations on 100 chicken-blood samples are variable, although most fall at 1.20 mg. of hæmoglobin per c.c. Turkey blood also gave inconsistent results, but ox blood was const. at 1.165 mg. per c.c. C. G. A.

Determination of the isoelectric and isoionic points of hæmoglobin from measurements of membrane potentials. G. S. ADAIR and M. E. ADAIR (Biochem. J., 1934, 28, 1230—1258).—The isoelectric points (I) are determined by equilibrating conc. protein solutions with dil. buffer solutions at 0°. The isoionic point (II) is determined from the distribution of salts across membranes. The (II) of cryst. hæmoglobin is at  $p_{\rm I\!I}$  7.6; in NH<sub>4</sub> phosphate buffers of ionic conen. 0.02, 0.04, and 0.07 the (I) were 7.16, 6.91, and 6.70, respectively. The min. osmotic pressure is at  $p_{\rm I\!I}$  vals. between (I) and (II). The distribution of NH<sub>4</sub> and PO<sub>4</sub>''' between protein crystals, protein solution, and dialysate is investigated. The effect of salts on (I) may be due to a reaction  ${}^+{\rm X}^-{} + {\rm Na}^+ + {\rm Cl}^- \longrightarrow [{\rm ClX}]^- + {\rm Na}^+$ , where  ${}^+{\rm X}^-$  is a zwitterion. C. G. A.

Kinetics of hæmoglobin. IV-VII.-See this vol., 1073.

Certain conditions of existence of fishes, especially as concerning their internal environment. E. B. POWERS (Ecology, 1934, 15, 69-79). —The isoelectric point of the hæmoglobin (I) of the yellow catfish is reached in an atm. containing 0.344%of CO<sub>2</sub>. The affinity of (I) for O<sub>2</sub> increases as CO<sub>2</sub> rises from 0.344 to 1.4%, but subsequently declines with higher vals. The form of the O<sub>2</sub>-affinity curve is influenced by the alkali reserve of the blood. Epidemics of fish mortality in ponds may be attributed to sufficient rise in CO<sub>2</sub> to reach the isoelectric point of the blood. A. G. P.

Mol. wt. of erythrocruorin. II. T. SVEDBERG and I. B. ERIKSSON-QUENSEL (J. Amer. Chem. Soc., 1934, 56, 1700—1706; cf. A., 1933, 965; this vol., 92).—Erythrocruorin (I) from *Planorbis corneus* has a sedimentation const. ( $s \times 10^{13}$ ) of 33.7 and is stable at  $p_{\rm H}$  3—7.8. Gradual decomp. occurs at  $p_{\rm H} > 7.8$ , whilst at < 3, three smaller components (all stable at  $p_{\rm H}$  0.7—2) are formed. The mol. wt., calc. from measurements of sedimentation equilibrium, is about 1,300,000 (a footnote states that a more accurate method has given a val. of 1,600,000). The (I) from Daphnia pulex contains 2 components; the major constituent has  $s \times 10^{13} = 16.3$  and is stable at  $p_{\rm H} 4.5$ — 10.5 (at  $p_{\rm H} 11.5$ —12.1, the original minor constituent is the sole product present). The mol. wt. and  $s \times 10^{13}$ , respectively, of the (I) from the following are given in parentheses: Arca pexata (33,600; 3.5); Notomastus latericius (36,400; 2.1); Chironomus plumosus (31,400; 2); Thyone briareus (23,600; 2.6); Myxine glutinosa (23,100; 2.3); Petromyzon fluviatilis (19,100; 1.9); all the (I) have isoelectric points between  $p_{\rm H}$  5 and 6. The relationship between the mol. wts. of different types of red blood-proteins is discussed briefly. H. B.

Chlorohæmatoprosthetin. A. HERZOG (Biochem. Z., 1934, 272, 13—20).—Criticisms (this vol., 426) are rebutted and confirmation of the formula  $C_{33}H_{32}O_4N_4$ ClFe is provided. W. McC.

Isoelectric flocculation of porphyrins. H. FINK and W. HOERBURGER (Japan. J. Med. Sci., Biochem., 1934, 2, 371).—Okahara's results (this vol., 203) confirm previously published data (A., 1929, 879, 1340; 1930, 225; 1933, 959, 1173). F. O. H.

Cataphoresis of mammalian erythrocytes. F. O. Howirr (Biochem. J., 1934, 28, 1165—1170).— The cataphoretic velocity (I) of erythrocytes (II) of the rat, rabbit, mouse, and guinea-pig, determined by a macro-method (A., 1930, 568) in M/15 PO<sub>4</sub><sup>'''</sup> at  $p_{\rm II}$  7·37 and 25° was 1·45, 0·60, 1·42, and 1·16  $\mu$  per sec. volt cm., respectively, in agreement with Abramson (A., 1929, 1094). The (I) of (II) from mice in hypoglycæmic convulsions was lower and that of (II) from blood containing As, 0·1% glucose, or 0·1% glucose + 0·02% insulin was unchanged. In hæmolysed blood the intact (II) migrated independently of the hæmoglobin, which showed no marked (I).

H. D.

Light-filtering index of blood-serum. G. L. ROHDENBURG and R. SCHLEUSSNER (J. Lab. Clin. Med., 1934, 19, 705-712).—Clinical application is discussed. CH. Abs.

Origin of blood-proteins. R. JÜRGENS and F. GEBHARDT (Arch. exp. Path. Pharm., 1934, 175, 558— 571).—Intravenous injection of a pyretic substance into geese produces an increase in fibrinogen (I) and globulin (II) even after hepatectomy, which normally causes a disappearance of (I) and a decrease in (II). Hence (I) and (II) are at least partly of extra-hepatic origin. The blood-forming tissues, especially bonemarrow, appear to be the site of plasma-protein formation. F. O. H.

Coagulation of serum-proteins by lactic acid. W. KOPACZEWSKI (Compt. rend., 1934, 198, 2282— 2285; cf. this vol., 547).—Serum-protein fractions, separated by COMe<sub>2</sub>, when dissolved in 0.8% NaCl or N/60-NaOH are pptd. by lactic acid (I), globulins (II) more easily, and albumins less easily, than myxoproteins. Dialysis gives only a small yield of (II), relatively free from inorg. constituents, which are more slowly pptd. than those obtained by the COMe<sub>2</sub> method. Serum, after dialysis, is pptd. by (I) only if a trace of CaCl<sub>2</sub> is added, although the action of Ca salts is not sp. (II) in NaOH neutralised with HCl are not pptd. by (I). Factors which influence the coagulation of serum have similar effects on the coagulation of solutions of (II) (cf. this vol., 792), which suggests that they represent the portion of the serum which is responsible for its coagulation. J. L. D.

Catalytic fission of serum-albumin by 3% sulphuric acid. V. S. SADIKOV, V. N. MENSCHI-KOVA, R. G. KRISTALLINSKAJA, E. V. LINDKVIST-DIALKOVA, E. C. CHALENSKAJA, E. V. LINDKVIST-RISAKOVA, E. G. CHALETZKAJA, A. G. PESINA, and L. N. RUBEL (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 569–572).—Hydrolysis of serum-albumin (I) for 2 hr. at 180° with 3% H<sub>2</sub>SO<sub>4</sub> yields gaseous (II), liquid (III), and solid products. (II) contains NH3, CO<sub>2</sub>, H<sub>2</sub>S, and org. substances, the total N content being 13% of that of (I). (III), before and after hydrolysis with 25% HCl, contains 4.83 and 3.72% of tyrosine, 0.74 and 0.65% of tryptophan, and 2.10 and 1.3% of cystine, respectively. (III), which contains mainly substances with no free NH<sub>2</sub> (cyclopeptides or proline derivatives), can be fractionated by extraction with Et<sub>2</sub>O, CHCl<sub>3</sub>, or EtOAc, Et<sub>2</sub>O yielding a fraction which, on crystallisation from AcOH or EtOAc, affords cyclopeptides, m.p. 273°, 223°, and 202°. Data for the N distribution and constituents of such fractions are given. F. O. H.

Pigment-binding power of various albumin fractions. E. KYLIN (Arch. exp. Path. Pharm., 1934, 175, 711—718).—Serum-albumin consists of fractions which migrate cataphoretically at different velocities and which have different binding power (I) with dyes (naphthol-yellow-S). That different sera vary in (I) was confirmed (cf. A., 1928, 127; this vol., 541). F. O. H.

Recovery of guanidine from blood-stream after injection. J. A. SAUNDERS (Biochem. J., 1934, 28, 1157—1159).—The method for guanidine (I) determination in shed blood previously described (A., 1932, 890) is used. (I) injected into dogs is recovered from their blood up to 10 min. after injection. H. D.

Volumetric micro-determination of uric acid in urine and blood. I. RUSZNYÁK and E. HATZ (Orvosi Hetilap, 1933, 77, 200–202).—Uric acid is pptd. from urine by aq. Ag lactate, centrifuged, and dissolved in aq. NaCN, the tube being washed with aq. Na<sub>2</sub>CO<sub>3</sub>. 5 c.c. of aq. phosphotungstic acid are added; an aliquot part is treated with 10% aq. NaOH and titrated with 0.01M-K<sub>3</sub>Fe(CN)<sub>6</sub> (I). Folin's method is used for blood. Li oxalate is used to prevent coagulation. The final titration is performed with 0.005M-(I). CH. ABS.

Determination of blood-urea by direct nesslerisation of a sodium tungstate-sulphosalicylic acid filtrate. D. F. EVELETH (J. Lab. Clin. Med., 1934, 19, 783-786).—The filtrate is prepared by treating 2 c.c. of oxalated blood, which has been incubated with 1 c.c. of urease solution for 15 min. at 50°, with 13 c.c. of H<sub>2</sub>O, 2 c.c. of 10% Na<sub>2</sub>WO<sub>4</sub>, and 2 c.c. of 25% sulphosalicylic acid. CH. ABS.

Gasometric micro-determination of lipins in plasma, blood-cells, and tissues. E. KIRK, I. H. PAGE, and D. D. VAN SLYKE (J. Biol. Chem., 1934, **106**, 203-234).—Total cholesterol (I) in plasma (0.15-3 c.c.) is determined  $(\pm 0.5\%)$  by extraction with EtOH-Et<sub>2</sub>O, hydrolysis, pptn. with digitonin, and manometric micro-combustion of the ppt. The total lipins in blood (0.05 c.c.) are determined by extraction (EtOH-Et<sub>2</sub>O; evaporation at 60°; dissolution in ligroin) and determination of total non-volatile C, the free (I) by digitonin pptn., the lipin NH<sub>2</sub>-N by emulsification in H<sub>2</sub>O and determination of aliphatic NH<sub>2</sub>-N by the micromanometric HNO<sub>2</sub> method, and the total phosphatides (I) by the P content. Determination of (I) by COMe<sub>2</sub>-MgCl<sub>2</sub> gives low results owing to formation of a diaminophosphatide which is insol. in moist Et<sub>2</sub>O; micro-combustion of the whole ppt. gives accurate results. R. S. C.

Comparison of the content of chlorine, fructose, etc. in the blood of wild and domestic ducks. H. OKAMURA (Japan. J. Med. Sci., Biochem., 1934, 2, 323—339).—The following vals. (g. per 100 c.c.) were obtained for wild and domestic ducks, respectively: Cl (as NaCl), 0.465, 0.452; total sugar (as glucose), 0.116, 0.114; fructose, 0.005—0.007, 0.005— 0.007; total residual N, 0.033, 0.036; urca-N, 0.0076, 0.0053; uric acid, 0.0067, 0.0056. F. O. H.

Blood of normal chickens. H. M. DYER and J. H. ROE (J. Nutrition, 1934, 7, 623-626).— Analyses are recorded. A. G. P.

Sugar in arterial and venous blood. I. BLIT-STEIN (Arch. internat. Méd. exp., 1933, 8, 25-46).— The venous blood-sugar (I) level is usually lower, sometimes by as much as 50 mg. per 100 ml. of blood, but is more uniform than arterial (I). NUTR. ABS. (b)

Presence of sugars other than glucose in blood. H. OKAMURA (Japan. J. Med. Sci., Biochem., 1934, 2, 313—321).—Dog's blood with a sugar content of 0.145% contains fructose [0.0054% by the cryogenin colour reaction (I) (A., 1933, 737) and 0.006% by the NHPh<sub>2</sub> method] which can be isolated as the phenylmethylhydrazone. Ox-blood contains 0.003—0.006%. Modifications in (I) are suggested. F. O. H.

Light-filter for micro-determination of bloodsugar. J. W. MULL (J. Lab. Clin. Med., 1934, 19, 667). CH. ABS.

Effect of changes in blood-sugar concentration on the blood-oxalic acid level. Glucose as a source of oxalic acid. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 401-411).—The blood- $H_2C_2O_4$  level in the rabbit (normally 0.0029-0.0035%) rises during the hyperglycæmia due to fright or ingestion of glucose, falls on administration of AcCO<sub>2</sub>H, and is not influenced by intravenous injection of hexose monophosphate.  $H_2C_2O_4$  appears to play a part in carbohydrate metabolism. F. O. H.

Relation of blood-oxalic acid to food. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 373-379).—Ingestion of protein- or fat-rich diets has no marked influence on the blood- $H_2C_2O_4$  (I) in man, whilst green foods produce an increase which is not due to preformed  $H_2C_2O_4$ . Fasting for 7 days in rabbits does not affect (I); longer periods produce a fall. Ox-bile contains 0.007-0.009% of  $H_2C_2O_4$ . F. O. H.

Influence of amino-acids on the production of oxalic acid by the animal organism. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 413-425).-- The blood- $H_2C_2O_4$  of rabbits is increased by intravenous injection of aspartic acid, asparagine, and, to a slight extent, by that of l(+)- (but not of d-)aminobutyric acid; glycine, alanine, and glutamic, butyric, and succinic acids have no appreciable effect. A sample of commercial gelatin contained 0.00115% of  $H_2C_2O_4$ . F. O. H.

Oxalic acid in the blood of various species of animals. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 427).—The following vals. (mg. per 100 c.c.) were obtained : ox,  $2\cdot84$ — $3\cdot96$ ; pig,  $2\cdot90$ —  $3\cdot01$ ; dog,  $1\cdot89$ — $1\cdot90$ ; carp (after fasting),  $1\cdot30$ —  $3\cdot12$ , (normal),  $3\cdot10$ — $3\cdot42$ ; sea-bass,  $2\cdot98$ — $3\cdot67$ ; salmon,  $3\cdot15$ — $3\cdot38$ . F. O. H.

Oxalic acid in blood. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 291–303).—A modification of the method of Izumi (this vol., 201) for the determination of  $H_2C_2O_4$  in blood (I) (2 ml.) is given. Human (I) contains 3—4 and the plasma 4—6 mg. per 100 c.c. On keeping (I), the level increases and then decreases owing to pptn. of insol. derivatives, *e.g.*,  $CaC_2O_4$ . F. O. H.

Thunberg's method of citric acid determination : some further results. A. LENNÉR (Skand. Arch. Physiol., 1934, 67, 221—225).—The mean error of the method is  $\pm 0.525 \times 10^{-6}$  g. After ingestion of citric acid (I) or NaHCO<sub>3</sub> the (I) content of human serum rises, after NH<sub>4</sub>Cl it falls, and after fat or glucose it remains unchanged. The serum val. remains normally fairly const., but in women there are variations corresponding with the menstrual cycle. During pregnancy there is little change, but a considerable rise occurs during parturition, followed by a fall and a gradual return to normal. The urine of new-born infants contains (I). NUTR. ABS. (m)

The first acid change in whole blood. E. P. LAUG (J. Biol. Chem., 1934, 106, 161–171).—On removal from the body the  $p_{\rm fl}$  of whole blood decreases by about 0.008 in 5 min. This is not affected by KF (up to 1–2%) and is probably due to lactic acid production. H. G. R.

Acid-base condition of the blood. III. Value of pK' in the Henderson-Hasselbalch equation for human and dog sera, determined with the Simms electrode. H. W. ROBINSON, J. W. PRICE, and G. E. CULLEN (J. Biol. Chem., 1934, 106, 7-27).--Methods for the determination, with increased accuracy, of pK' for saturation of sera (I) with known CO<sub>2</sub> tensions and of the alkali reserve are described. pK' vals. for human and dog (I) are identical (6.09± 0.008) and are not appreciably altered by abnormal pathological conditions. H. G. R.

Influence of sodium and potassium content of the diet on the sodium concentration of human centrifuged red blood-cells. A. M. BUT-LER and E. M. MACKAY (J. Biol. Chem., 1934, 106, 107—112).—With variations in the ratio Na : K in the diet, there is no change in the serum val. As the ratio is decreased, the Na concn. in the cells becomes lower. Mg in cells is in an inverse relation to the Na : K ratio in the diet. H. G. R.
Determination of iron in blood-plasma. F. S. FOWWEATHER (Biochem. J., 1934, 28, 1160—1164).— Fe in plasma, showing a negative benzidine test for hæmoglobin, is determined colorimetrically with KCNS after ashing with  $H_2SO_4$  and  $H_2O_2$ . The vals. so obtained are > those found in the determination on protein-free filtrates. H. D.

Biochemistry of copper. III. Distribution between corpuscles and plasma. U. SARATA. IV. Content of red and white blood-cells. A. SUZUKI and U. SARATA. V. Effect of hæmorrhage on the blood-copper. U. SARATA and A. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 305– 308, 309–312, 341–354; cf. this vol., 202).—III. Serum or plasma contains  $3\cdot 28-3\cdot 52$  (ox),  $3\cdot 41-4\cdot 14$ (horse),  $3\cdot 08-5\cdot 01$  (rabbit), and  $3\cdot 48-4\cdot 47$  (man)  $\times 10^{-2}$  mg. Cu per 100 c.c. Most of the blood-Cu (approx. 80% in rabbits) is in the corpuscles.

IV. The crythrocytes (I) and leucocytes (obtained as a paste by centrifuging) of horse's blood contain, respectively, 0.882 and 0.282 mg. Cu per 100 g. The stromata and cell contents of (I) have approx. the same Cu content.

V. Acute hæmorrhage in rabbits produces a rapid increase in the blood-Cu followed by a rapid fall, after which the level slowly diminishes to the normal; reticulocyte formation (II) follows a parallel course. The increase in Cu content in (I) is > in the plasma. The rôle of Cu in (II) and anæmia is discussed.

F. O. H.

Zinc content of isolated nuclei [of blood-corpuscles]. A. KOGA (Keijo J. Med., 1934, 5, 80— 96).—The Zn contents [determined by polarographic analysis of the Ca zincate ppt. (A., 1907, ii, 53)] of the cytoplasm and nuclei (the latter contaminated by cell stromata) of blood-corpuscles are, respectively, 3·0, 8·3 (goose),; 6·9, 20·5 (tortoise); 8·8, 34·9 (toad); 1·3, 4·0 (fish, Ophicephalus argus, Cantor) mg. per 100 g. of dried substance (cf. A., 1933, 965). Hæmolysis by various salts at different temp. is discussed.

F. O. H.

Inorganic phosphorus of horse serum. Effect of age and nutrition. P. B. PEARSON (J. Biol. Chem., 1934, 106, 1—6).—With increasing age of the growing animal there is a decrease in the inorg. P (I) of the serum, which tends to become const. at maturity. Grazing on dry forage gives a val. for (I) < that of animals receiving grain, green feed, and liberal hay. Recovery from dietary hypophosphoræmia occurs within 8 days on changing to a normal diet.

H. G. R.

Colorimetric determination of nitrite in blood. E. J. STIEGLITZ and A. E. PALMER (J. Pharm. Exp. Ther., 1934, 51, 398—410).—A quant. reaction for NO<sub>2</sub>' detects it at a concn. of 0·2 p.p.m. For determination of NO<sub>2</sub>' in blood, 8 c.c. are mixed with 20 c.c. of ZnSO<sub>4</sub>,7H<sub>2</sub>O (4·5%), 1 c.c. of N-NaOH is added, and to 8 c.c. of the clear protein-free filtrate are added 8 c.c. of saturated aq.  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> and 8 c.c. of a solution of 2 : 6 : 8·NH<sub>2</sub>·C<sub>10</sub>H<sub>5</sub>(SO<sub>3</sub>H)<sub>2</sub> (1 drop of a 32·6% commercial solution of the Na<sub>2</sub> salt of " amino G" acid added to 50 c.c. of H<sub>2</sub>O and acidified with 10 c.e. of glacial AcOH). The colour developed after heating to a definite temp. (< 100°) is compared with a standard solution of NaNO<sub>2</sub> similarly treated. Normal human blood contains 0.5— $1.6 \times 10^{-6}$  g. of NO<sub>2</sub>' per 100 c.c. (mean approx.  $10^{-6}$  g.). W. O. K.

Water content of normal human blood. K. KURODA (Keijo J. Med., 1934, 5, 111—121).—The H<sub>2</sub>O content [determined by a micro-method (A., 1933, 1094)] of the blood of 34 men (varying from 76 to 81%, average 78.74%) and 45 women (varying from 77 to 84%, average 80.21%) is tabulated.

F. O. H.

Water content of the blood of mice during growth. K. KURODA (Keijo J. Med., 1934, 5, 140– 150).—During the first two weeks of life the  $H_2O$ content (I) decreases from 83.5 to 81.3%, after which it rises to approx. 83% at 5 weeks and then falls to an approx. steady val. of 79—80.5% during the 7th to 35th weeks, a second and less marked max. occurring during the 18th week. Slight differences occur in the age-(I) curves of the two sexes. F. O. H.

Glutathione blood-coagulation. and Л. KUHNAU and V. MORGENSTERN (Naturwiss., 1934, 22, 509-510).-Reduced glutathione (I) in a concn.  $\neq$  0.02*M* always inhibits coagulation. Down to 0.002M it has the effect of inhibiting coagulation at  $p_{\rm H} < 7.4$  (A-effect) and of accelerating it at  $p_{\rm H} > 7.4$ (B-effect). Oxidised glutathione has little or no A-effect, but a strong B-effect. (I) thus inhibits coagulation in circulating blood and induces it in shed blood, which becomes alkaline by loss of CO<sub>2</sub>. The action is directly on thrombin, and is inhibited by substances which react with the SH group. Cu in low. concn. increases the A-effect and does not affect the B-effect.  $Fe^{\Pi}$  reduces the A-effect and increases the B-effect. Substances forming complexes with Cu or Fe<sup>II</sup> have a corresponding influence on the A- and B-effects, and the action of (I) is regarded as a Cu-anticatalysis at  $p_{\rm H} < 7.4$  and a Fe-catalysis at  $p_{\rm H} > 7.4$ . HCN and *l*-ascorbic acid influence thrombin like (I). Analogous effects recorded with proteolytic ferments are in accordance with the assumption that thrombin is one of this class.

R. K. C.

Heparin and blood-coagulation. J. MELLANBY (Proc. Roy. Soc., 1934, B, 116, 1—9).—Heparin (I) prevents the coagulation of oxalated plasma (II) by thrombase (III) in conjunction with the neutral salt content, since it has no action on dialysed (II). The antithrombase action of (I) is annulled by thrombokinase, but the conversion of prothrombase into (III) is not affected. (I) does not act as antiprothrombase. H. G. R.

Changes in [blood-]cell volume produced by varying concentrations of different anticoagulants. V. G. HELLER and H. PAUL (J. Lab. Clin. Med., 1934, 19, 777—780).—The cell-vol. is decreased by increasing the concn. of the Na, K, and Li salts used as anticoagulants, and increased by increasing the concn. of  $NH_4$  salts. A mixture of  $K_2C_2O_4$  (40%) and  $(NH_4)_2C_2O_4$  gives a min. variation in cell vol.

CH. ABS.

Hæmolytic action of silver occurring as impurity in "chemically pure" sodium chloride. E. G. BALL (Biol. Bull., 1933, 64, 277–288).—Ag (10-3 to 10-4%) from Ag-lined vessels caused rapid hæmolysis of fish erythrocytes when the NaCl was used to prepare physiological saline solutions. CH. ABS.

Complement action of blood-serum. M. DOLADILHE (Compt. rend., 1934, 199, 539—541).— The complement action of serum-globulin (I) partly depends on the presence and physico-chemical state of albumin (II) from the same or different serum. Thus heating (II) for 25 min. at 53° influences both the dispersive power of (II) (this vol., 912) and the hæmolysis of sensitised red corpuscles by (I).

F. O. H.

Changes in the protein of the antiserum during the precipitin reaction and the composition of the precipitate. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 283—294).— Samples of serum-albumin and -globulin (I) were isolated using rabbits both before and after immunisation by parenteral administration of horse serum and also from the horse serum itself. The corresponding ppt. was also isolated. The various fractions were then injected subcutaneously into rabbits, and tables summarise the biological reactions obtained. (I) of horse and of immunised rabbit serum are different in biological reaction, as are also (I) of normal and immunised rabbit. The ppt., although showing some differences, closely resembles (I) of the immune serum. P. W. C.

Keratins. I. Lead sulphide reaction. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1934, 64, 183—190).—Unbleached horn or wool is coloured brown (due to formation of PbS) when heated with aq. Pb(NO<sub>3</sub>)<sub>2</sub> or Pb(OAc)<sub>2</sub>, but no such action occurs after bleaching with  $H_2O_2$ . The formation of PbS is, however, restored and intensified by irradiation of the bleached samples. The reaction is probably due to the presence of S'' (confirmed by the greatly increased N<sub>2</sub> evolution with Feigl's I-azide reagent), produced by irradiation, but removed by oxidation to SO<sub>4</sub>'' with  $H_2O_2$ . Feathers, bristles, and light horse-hair do not give the reaction. J. W. B.

## Sulphur in keratin.—See this vol., 1120.

Use of the Hagedorn-Jensen method in determination of skin-glucose. D. M. PILLSBURY and G. V. KULCHAR (J. Biol. Chem., 1934, 106, 351-356). —All glucose is extracted in 3 min. from sliced skin by the  $\text{ZnSO}_4$ -NaOH mixture at 100°; no appreciable amount of non-glucose reducing substances is extracted in this time. Increase in reducing substances obtained on longer extraction is due to non-fermentable substances. Recovery of added glucose is satisfactory. Similar results are obtained by the Somogyi-Shaffer-Hartmann method. C. G. A.

Mineral content of elastic ligaments. E. HEISCHKEL (Biochem. Z., 1934, 272, 235–245).— Fresh ox ligamentum nuchæ contains 52% H<sub>2</sub>O and 0.5% mineral matter, the latter consisting of Na > 64; K > 69; Ca > 33; Mg 4; Cl > 72; PO<sub>4</sub> > 69; SO<sub>4</sub> > 132; SiO<sub>2</sub> 32; Fe > 5 mg. per 100 g. The high SO<sub>4</sub> and Ca contents and the excess of Na (equiv.) over K are characteristic. P. W. C.

Inorganic constituents of the crab's shell. P. E. H. JONES (Z. physiol. Chem., 1934, 226, 1-2).- The Ca, Mg, P, and org. matter contents of *Potamobius fluviatilis*, L. (thorax), are 28.7, 0.20, 1.57, and 20.1, of *Astacus gammarus*, L. (thorax), 28.0, 0.38, 2.44, and 19.3, (claws) 30.7, 0.32, 1.30, and 18.9%, respectively, calc. on dry wt. J. H. B.

Distribution of iron in tissues, particularly liver, during peptic digestion and autolysis. W. D. McFARLANE (J. Biol. Chem., 1934, 106, 245– 266).—43—60% of the Fe in perfused rat-liver tissue (I) is in non-hæmatin form (reacts with dipyridyl after reduction by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>). All the Fe in a  $CCl_3 \cdot CO_2 H$  filtrate (II) reacts with KCNS after oxidation by H<sub>2</sub>O<sub>2</sub>. Only 40% of the non-hæmatin Fe is in (II). 50% of the total Fe in (II) is pptd. by Pb(OAc)<sub>2</sub>. All the Cu in (I) is in (II). Pepsin at  $p_{II}$  2·0 increases fivefold the Fe in (II) from fœtal calf-liver, (I), and rat-muscle tissue (max. in 40 hr.). Decomp. of org. Fe compounds (? proteinates) occurs during autoproteolytic changes in liver and spleen at  $p_{II}$  4·5, is accelerated by H<sub>2</sub>S, and inhibited by Cu. During prolonged autolysis Fe recombines with org. substances. R. S. C.

Organic phosphorus compounds in octopods. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 355—357).—The org. P compounds from the tentacles of the octopus yield a small pyrophosphate fraction which contains traces of adenylic acid, but no adenyl pyrophosphate. No creatine- and only small amounts of arginine-phosphoric (?) acid are present (cf. A., 1932, 532; this vol., 96). F. O. H.

Weight and chemical composition of Euchæta norvegica, Boeck. A. P. ORR (Proc. Roy. Soc. Edinburgh, 1934, 54, 51—55).—The amounts of chitin, fat, protein, and ash of male and female animals at various stages of their life cycle are given. W. O. K.

Spontaneous formation of lysolecithin in dried animal organs. M. FRANCIOLI (Fermentforsch., 1934, 14, 241—249).—Heart, liver, spleen, muscle, brain, adrenal, pituitary, thymus, prostate, and kidney contain lecithase-A, which is not destroyed when these organs are preserved by drying and is able at room temp. to split off an unsaturated fatty acid mol. from lecithin to give lysolecithin. P. W. C.

Origin of hydrogen sulphide evolved on boiling hen's flesh. V. S. SADIKOV, A. F. SCHOSCHIN, K. M. STARUCHINA, and M. I. LIVSCHITZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 39–43).—Total S falls from 0.935 to 0.806, cystine (I)-S from 0.414 to 0.327, methionine (II)-S from 0.251 to 0.196, and glutathione-S from 0.051 to 0% of ash- and fat-free muscle after cooking for 25 hr. at 100°. The reactions  $(I)+H_2 \longrightarrow cysteine (III), (I)+H_2O_2 \longrightarrow serine+S,$  $(III)+S \longrightarrow (I)+H_2S, and (II)+H_2O_2 \longrightarrow homo$ cystine+MeOH are postulated. R. T.

Glutathione and vitamin-C in the crystalline lens. T. W. BIRCH and W. J. DANN (Nature, 1934, 134, 383).—A reply to criticism (this vol., 1020). L. S. T.

Press-fluid from heated beef muscle. A. M. CHILD and M. BALDELLI (J. Agric. Res., 1934, 48, 1127—1134).—The % of  $Et_2O$  extract and  $H_2O$  in juice obtained by pressure for 5 min. were approx. the same as, but the N content was significantly >, when pressure was applied for 20 min. A. G. P.

Internal and external secretions of glands. P. LIVRAGA (Arch. exp. Path. Pharm., 1934, 175, 572-587).—Ligature of a part of the pancreas in cats (the blood-supply being maintained) results in degenerative changes in both the acinar and islet tissue (I) of the separated part, whilst (I) of the intact portion enlarges. The histological changes in the pancreatic and other tissues are correlated with the decrease in liver-glycogen and the variations in blood-sugar, growth, etc. F. O. H.

Formation of a hæmatopoietic substance in concentrated human gastric juice. P. J. FOUTS, O. M. HELMER, and L. G. ZERFAS (Amer. J. Med. Sci., 1934, 187, 36-49).—Whereas gastric juice cone. by ultrafiltration is not potent in pernicious anæmia, that treated by vac. distillation gives rise to a reticulocytosis (I). Juice conc. first by vac. distillation and then by ultrafiltration gives a moderate (I), and that part of the juice which passes through the filter gives a more marked response after further vac. distillation. Material in the juice, which can be activated by vac. distillation, is held back by preliminary ultrafiltration. During vac. distillation, the intrinsic factor present in the juice acts on some extrinsic factor also present, thus conferring potency. NUTR. ABS. (m)

Chemical and physical relation between bloodserum and body-fluids. II. D. R. GILLIGAN, M. C. VOLK, and H. L. BLUMGART (New Engl. J. Med., 1934, 210, 896—905).—Cerebrospinal fluid does not appear to be a dialysate or simple ultrafiltrate. The distribution of Ca, Mg, Cl',  $HCO_3'$ , inorg.  $PO_4'''$ , non-protein-N, and reducing substances between serum and cerebrospinal fluid differs from that between serum and cedema fluid. CH. ABS.

Sugar and fructose contents of human amniotic fluid. M. ITIZYÔ (Japan. J. Med. Sci., Biochem., 1934, 2, 359–369).—As pregnancy progresses the % of reducing fermentable sugar decreases (from >0.09% at 2—3 months to 0.014-0.025% at full term), whilst the abs. content increases. Approx. 10% is fructose. F. O. H.

Determination of bile-pigments. E. A. PETER-MAN and T. B. COOLEY (J. Lab. Clin. Med., 1934, 19, 723—735).—The time required to complete the change of colour from yellow to deep blue in the oxidation of bilirubin (I) depends on the  $HNO_3$  used, and on the application of heat and light. The total (I) can be determined at any stage of oxidation by determining both the blue and yellow components of the colour by means of light filters and suitable dichromatic standards. CH. ABS.

Use of hydrogen peroxide in the determination of bilirubin in bile. E. A. PETERMAN and T. B. COOLEY (J. Lab. Clin. Med., 1934, 19, 743-748).- $H_2O_2$  is used instead of HNO<sub>3</sub>. Colorimetric readings are made at the stage of max. intensity of blue, using Nile-blue as standard. CH. ABS.

Relationships between the constituents of milk. A. BLACK and LE R. VORIS (J. Agric. Res., 1934, 48, 1025–1032).—Statistical examination of detailed analyses is recorded. A. G. P.

Rapid determination of total proteins and nonprotein-nitrogen in human and cow's milk. L. D. Scort (Biochem. J., 1934, 28, 1193—1197).— The protein (I) is pptd. by  $Zn(OH)_2$ , digested with syrupy  $H_3PO_4$  and  $H_2SO_4$ , and the solution nesslerised. The non-protein-N is determined by the digestion of the supernatant liquid from (I) and aëration into standard acid. C. G. A.

Human milk. XV. Non-protein-nitrogen constituents. B. N. ERICKSON, M. GULICK, H. A. HUNSCHER, and I. G. MACY (J. Biol. Chem., 1934, 106, 145—159).—The non-protein-N (I) and  $NH_2$ -N were practically the same in the first and the last halves of lactation, but varied from a max. in the evening to a min. in the morning. In the early stages and in fever, the vals. were irregular and high. Under normal conditions (I) is similar to that of the blood, and may be used clinically as an index of abnormal disturbances. H. G. R.

Phosphatides of milk. W. DIEMAIR, B. BLEVER, and M. OTT (Biochem. Z., 1934, 272, 119—132).—The phosphatide extracted from milk powder by MeOH is chiefly a monoaminophosphatide the components of which are palmitic, stearic, and oleic acids, colamine, and choline. A diaminophosphatide is also extracted. W. McC.

Fat of human milk. A. W. BOSWORTH (J. Biol. Chem., 1934, 106, 235–244).—The fat of human milk was hydrolysed and the Me esters of the acids (I) were fractionated. A relatively large fraction was obtained corresponding with dodecoic acid (cf. cow's milk). (I) include tetra- and hexa-decenoic, oleic, linoleic, and (probably) decenoic acids, unsaturated acids with > 18 C, and two highly unsaturated acids of the arachidonic type. R. S. C.

Fat percentage of milk as affected by feeding fats to dairy cows. N. N. ALLEN (J. Dairy Sci., 1934, 17, 379-395).—The increased fat content of milk from cows receiving butter-fat, lard, tallow, and various vegetable oils averaged 10-20% of the additional fat intake. Milk yields were not affected except in the case of coconut oil, which reduced yields when fed in large amounts. The effect of the fats was apparent 12-24 hr. after feeding and persisted 30-42 hr. after cessation of the additional ration. A. G. P.

Factors influencing the initial induction period in the oxidation of milk-fat. J. L. HENDERSON and C. L. ROADHOUSE (J. Dairy Sci., 1934, 17, 321— 330).—Modifications of Greenbank and Holm's photochemical method (B., 1933, 275) for determining susceptibility to oxidation (S) are described. Exposure to light and to the action of Cu increased the S of milk-fat. Ni had a slight effect, but a Cr-Ni alloy was without influence. Milk from animals utilising body-fat while supplied with sub-maintenance rations had higher proportions of unsaturated fats and greater S. A. G. P.

Dialysis of milk. II. Factors influencing the distribution of calcium and phosphorus. L. H. LAMPITT and J. H. BUSHILL (Biochem. J., 1934, 28, 1305—1312).—An increase in the dialysable Ca and inorg. P, but no effect on org. P, results from both an increase (by dilution) and a decrease (by bacterial action) in  $p_{\pi}$ . Pasteurisation decreases the amount of sol. P and Ca. The results for fresh, pasteurised, and separated milks are : dialysable Ca 25—33%, dialysable P 43—51%, dialysable inorg. P 33—41%. H. G. R.

Zinc content of human, cow's, and goat's milk at various stages of lactation. A. Koga (Keijo J. Med., 1934, 5, 106–110).—Colostrum (human) contains 3-9 and normal milk 0.6-2.1 (human), 3.4-3.6 (cow), and 2.6-4.2 (goat) mg. Zn per kg. (cf. A., 1919, i, 420). F. O. H.

Vitamins. XX. Effect of various methods of pasteurisation on the vitamin- $B_1$  and  $-B_2$  contents of cow's milk. R. A. DUTCHER, N. B. GUERRANT, and J. G. MCKELVEY (J. Dairy Sci., 1934, 17, 455—466).—Losses of vitamin- $B_1$  and  $-B_2$  occurred in all methods of pasteurisation, but were min. when the milk was boiled for 10 min. under reflux. When pasteurised under diminished pressure losses were > under normal pressure. A. G. P.

Irradiated milk : transmission and antirachitic activation of milk films by ultra-violet radiations. G. C. SUPPLEE and M. J. DORGAS (J. Dairy Sci., 1934, 17, 433–443).—The antirachitic potency imparted to milk by ultra-violet irradiation is not  $\propto$  fat content. Penetration of radiations of 2500—2850 Å. is small and synthesis of vitamin-D in treated milk occurs substantially at the surface.

A. G. P.

Relative value of irradiated yeast and irradiated ergosterol in the production of vitamin-D milk. W. C. RUSSELL, D. E. WILCOX, J. WADDELL, and L. T. WILSON (J. Dairy Sci., 1934, 17, 445-453). —When supplied at the rate of 60,000 units daily the efficiencies of irradiated yeast and ergosterol were approx. the same with respect to vitamin-D production in milk, but the former is the more effective when fed in larger amounts. In both cases < 2%of the ingested vitamin-D appeared in the milk. Additions of quinol increased the effectiveness of ergosterol, especially at the lower level of intake.

A. G. P.

Detection of milk from cows infected with mastitis. W. H. HALVERSEN, V. A. CHERRINGTON, and H. C. HANSEN (J. Dairy Sci., 1934, 17, 281—296).—In addition to characteristic bacterial and leucocyte counts, milk from cows infected with mastitis (acute) shows a high catalase content, high  $p_{\rm H}$ , low curd tension, and usually > 0.14% Cl'.

A. G. P.

A saturated solid alcohol from the urine of pregnant mares. G. A. D. HASLEWOOD, G. F. MARRIAN, and E. R. SMITH (Biochem. J., 1934, 28, 1316–1320).—The alcohol  $(C_7H_{12}O)_n$ , m.p. 303–304·5°,  $[\alpha]_{5461}$  -44° (acetate, m.p. 168°), has been isolated from the neutral, Et<sub>2</sub>O-sol. fraction of mare's urine. H. G. R.

Urinary composition in marine fish. R. F. PITTS (J. Cell. Comp. Physiol., 1934, 4, 389-395).— Urinary Cl' was low or zero in all cases examined. Artificially induced diversis is accompanied by additional excretion of Cl',  $SO_4$ ", and Mg". The sculpin can excrete a supersaturated solution of MgHPO<sub>4</sub> in its urine. A. G. P.

Fæcal "fat": its relation to fat in the diet. A. KRAKOWER (Amer. J. Physiol., 1934, 107, 49—54). —The fæcal fats of normal individuals receiving test diets containing small and large amounts of fat have similar I vals. (I), although (I) of the fats fed vary (8·2—125·8). There is little relationship between the amount of fat fed and the amount in the fæces.

NUTR. ABS. (m)

Nature of calcium, magnesium, and phosphorus compounds excreted by the gut and their proportion in the fæces. J. MAREK, O. WELL-MANN, and L. URBANYI (Biochem. Z., 1934, 272, 277–283).—Ca is excreted by the intestine as normal and acid phosphate and as carbonate, as soaps (with a fat-rich diet), and as org. and P-containing  $H_2O$ -sol. and -insol. compounds. The ratio of these compounds varies with the diet. With a P-rich diet, sol. alkali phosphate may also be excreted in considerable amounts. Mg excreted in the fæces is partly  $H_2O$ -sol. and partly insol. Administration of excess Ca does not notably decrease the  $PO_4^{\prime\prime\prime}$  supply of the body and vice versa. P. W. C.

Cholesterol saturation of blood in allergic diseases. B. PAUL (Orvosi Hetilap, 1933, 77, 444– 446).—Blood-serum in allergy during attacks is saturated or supersaturated with cholesterol. CH. ABS.

Amount of material effective in pernicious anæmia present in dog liver. M. B. STRAUSS and W. B. CASTLE (Proc. Soc. Exp. Biol. Med., 1933, 31, 360—363).—In pernicious anæmia daily intramuscular injection of extract equiv. to 20 g. of dog liver produced no response, whereas daily injections equiv. to 20 g. of hog liver produced a reticulocyte crisis. Daily injections equiv. to 100 g. of dog liver produced a satisfactory response. The content of potent material in canine liver only is about one fifth of that in hog liver, because of the low amount of intrinsic factor in dog's gastric juice. NUTR. ABS. (m)

Influence of disease, sex, and age on the content of the human liver in metals. H. LUNDE-GARDH (Naturwiss., 1934, 22, 572).—Liver (from both sexes) has an average content ( $\times 10^{-2}$  g. per kg.) of Mn 0·2, Cu 0·5, Sr 0·6, Rb 1·4, Al 3·0, Ca 3·4, Zn 3·9, Mg 14·0, Fe 20·0, Na 118·0, and K 194·0. In some cases Ag, Pb, Sn, Ba, Cd, and B were detected. Marked increases of the Mn content occur with diabetes, of Ca, Fe, and Na with pernicious anæmia, and of Zn with cancer. The average vals., excepting that of Na, are somewhat lower in women. Certain changes occur with age, and these also are to a certain extent characteristic of the sex. F. O. H.

Changes in creatine and creatinine excretion in progressive muscular atrophy following ingestion of glycine. A. G. SCHOO and J. BOER (Nederland. Tijds. Geneesk., 1934, 78, 34).—After ingestion of 1 g. of creatine, excretion of creatine and creatinine is considerably greater in children (1) suffering from the disease than in healthy children. Administration of 4 g. of glycine (II) daily for 6 weeks brings the excretion of creatine in (I) within normal limits. After discontinuing (II) excretion of ingested creatine is again > in healthy children. (II) changes the metabolic processes in the muscles.

NUTR. ABS. (m)

Blood-sugar in cancer patients after ingestion of glucose. B. LEVIE (Nederland. Tijds. Geneesk., 1934, 78, 265).—In some but not all cases (carcinoma and sarcoma) examined, high blood-sugars were found following ingestion of 50 g. of glucose, with a late max. and delayed return to normal. NUTR. ABS. (b)

Spectrographic study of the occurrence of chromium and molybdenum in carcinoma of the human breast. A. DINGWALL and H. T. BEANS (Proc. Nat. Acad. Sci., 1934, 20, 416–420).—In 60 cases of carcinoma of the breast either Mo or Cr was detected; in only one of these were both present. These elements may have a definite significance in the metabolism of the tumour cell. P. G. M.

Relationship of internal secretions to the metabolism of malignant tumour tissue. O. O. MEYER and C. MCTIERNAN (Amer. J. Cancer, 1934, 20, 96—116).—Subcutaneous injection of thyroxine into tumour-bearing animals appears to inhibit tumour growth. Insulin, theelin, prolan, thymus extract, and adrenal cortex extract have no effect.

CH. ABS.

Acceleration of respiration of normal and tumour tissue by thionine (Lauth's violet). F. DICKENS (Nature, 1934, 134, 382–383).—Addition of thionine (I) to a lactate-containing medium increases respiration of the kidney of the rat. Respiration in presence of glucose is also increased. With Jensen rat-sarcoma, (I) increases respiration in  $PO_4^{\prime\prime\prime}$  and  $HCO_3^{\prime}$ -media containing glucose; in media containing lactate (I) and pyocyanine both produce a decrease in respiration. (I) has little or no effect on aërobic glycolysis. L. S. T.

Effect of 2:6-dichlorophenol-indophenol on tumour and kidney respiration. K. A. C. ELLIOT (Nature, 1934, 134, 254).—In the absence of glucose, respiration of cancer tissue is practically completely inhibited by  $1\cdot3 \times 10^{-3}M \cdot 2$ : 6-dichlorophenol-indophenol; in presence of glucose there is little, if any, effect. No inhibition of glycolysis occurs. With kidney cortical tissue inhibition is practically complete in both cases. L. S. T.

Rôle of 1:2:5:6-dibenzanthracene in the production of fowl tumours. J. G. CHALMERS (Biochem. J., 1934, 28, 1214—1218).—As determined by spectroscopic examination the compound disappears from the breast muscle of chickens within a few days of injection, a time short compared with that required for the production of malignant symptoms. It is not transferred to the liver. C. G. A.

Comparison of the action of polycyclic aromatic hydrocarbons in producing tumours of the connective tissue. G. BARRY and J. W. COOK (Amer. J. Cancer, 1934, 20, 58-69).—Subcutaneous injection of chrysene and 5:6-cyclopenteno-1:2-benzanthracene in lard produces tumours. Application of oleic acid, mouse fat, or solutions of chrysene to the skin does not produce epithelioma. CH. ABS. Influence of pathological processes (tumours, cachexia, and X-irradiation) on the constitution of tissue-proteins. E. G. SCHENCK (Arch. exp. Path. Pharm., 1934, 175, 401-405; cf. A., 1933, 1328).—The changes in the content and constitution of the proteins of tissues (heart, muscle, liver) due to the presence of growing tumours in rats are tabulated. Similar data for the changes due to X-irradiation of normal and diseased tissue and of the tumours themselves are also given. F. O. H.

Composition of nucleic acids of malignant tumours. K. STERN and R. WILLHEIM (Biochem. Z., 1934, 272, 180—188).—The nucleic acid of human malignant tumours contains considerably less N than normal, but no difference can be detected in the distribution of N between purine and pyrimidine bases. P. W. C.

Blood-urea-, -uric acid, and -cholesterol in meningitis and cerebral diseases. L. RICCITELLI (Klin. Woch., 1932, 11, 2155—2156; Chem. Zentr., 1934, i, 72).—In cerebral diseases, blood-urea, -uric acid, and -cholesterol are often increased. These changes are also produced by stimulation of the floor of the fourth ventricle, which is assumed to contain a regulating centre for these substances. L. S. T.

Changes in carbohydrate metabolism in disease of the mid-brain. D. ADLERSBERG and R. FRIEDMANN (Z. ges. exp. Med., 1934, 93, 316-349). —The disease is characterised by two types of reaction: (1) cerebrohepatic, with disturbance of glucose (I) and occasionally galactose (II) tolerance, marked sensitivity to insulin (III) and normal H<sub>2</sub>O metabolism, (2) cerebral, with normal (I) and (II) tolerance, reduced sensitivity to (III), and marked disturbance of H<sub>2</sub>O metabolism. NUTR. ABS. (m)

Blood-sugar [in diabetes]. E. SCHILLING (Z. ges. exp. Med., 1934, 93, 257—264).—In mild cases all types of adrenaline (I) curve are observed, whilst in moderately severe cases the curves are higher, and in very severe cases much flatter, than normal. In all cases except the very mildest the curve after glucose is higher than normal. In severe cases injection of (I) is of val. in overcoming hypoglycæmia.

NUTR. ABS. (m)

Fruit as source of carbohydrate in the diet in diabetes, liver disease, and obesity. A. DEINDL (Deut. Arch. klin. Med., 1934, 176, 311-329).--After four types of test meal, namely 600 g. of apples (I), a mixture of glucose, fructose, and sucrose equiv. to the sugar content of the apples, and equiv. amounts of glucose and fructose administered to persons with diabetes, obesity, or liver disease there is marked similarity in the glycæmic curves obtained, showing the close connexion between these pathological conditions. There is a more marked and prolonged rise in blood-sugar (II) (most pronounced in the diabetics) than occurs in normal subjects after similar meals. Although after (I), (II) does not attain so high a val. as after the mixed sugars, its return to normal is much more delayed (due to slower digestion and absorption). Hence the observed unfavourable influence of fruit on sugar tolerance in NUTR. ABS. (m) diabetes.

Utilisation of various carbohydrates by the depancreatised dog. J. L. BOLLMAN and F. C. MANN (Amer. J. Physiol., 1934, 107, 183-189).--In depancreatised dogs on a daily diet (I) of 150 g. meat, 50 g. pancreas, 50 g. cracker meal, and 200 ml. milk with 6 units of insulin, the daily excretion of glucose is 2-25 g. The increased excretion of sugar which follows addition of 50 g. of glucose to (I) is about 50 g.; results are similar with galactose, and maize-starch if allowance is made for the unhydrolysed starch in the fæces. Fructose (II) appears to be partly utilised for several days under these conditions, the average daily excretion after addition of 50 g. to (I) being about 20 g. This apparent utilisation is soon lost and the total sugar added then appears in the urine. Sucrose and inulin act like (II).

NUTR. ABS. (m)

Jerusalem artichoke in the treatment of diabetes. L. K. CAMPBELL (Arch. Int. Med., 1934, 54, 82—87).—There is no difference in the utilisation of Jerusalem artichoke in diabetes from that of an equiv. amount of oatmeal. H. G. R.

Effect of pregnancy on the insulin requirement of the diabetic. G. G. DUNCAN and F. FETTER (Amer. J. Med. Sci., 1934, 187, 347—351).—During pregnancy (I) the insulin requirement increases during the first three months, remains const. during the second, again increases in the third three months, and finally decreases suddenly after parturition. (I) need not permanently impair the diabetic's tolerance, and diabetes *per se* is not a contraindication to (I).

Induced and photochemical oxidation of sodium tartrate by air and its use in diabetes and prolonged fasting.—See this vol., 1079.

Bactericidal action of diabetic serum. E. KESTERMANN and A. KNOLLE (Deut. Arch. klin. Med., 1933, 176, 64-80).-Artificial increase of bloodsugar to a high level results in reduction of bactericidal power (I) towards B. coli but not towards staphylococci (II) or streptococci (III). Serum from less severe cases of diabetes has (I) similar to that of normal serum, although it is more easily exhausted. In severe cases the activity is reduced. There is a relationship between the severity of the illness and the degree of diminution of serum activity (IV). A similar but much smaller difference shows when (II) and (III) are used. Treatment with diet and insulin is followed by an improvement in (I). Similar decrease in (IV) is noted in cachexia following other diseases. NUTR. ABS. (m)

Retention of sodium chloride during artificially-produced fever. S. LANG (Arch. exp. Path. Pharm., 1934, 175, 406-408).—During the fever produced in dogs by intramuscular injection of milk the urinary excretion of NaCl increases. F. O. H.

Goitre in New Zealand. Relation between incidence of goitre and iodine content of soil and water. R. A. SHORE and R. L. ANDREW (Bull. Office internat. d'Hyg. publ., 1934, 26, 252—254).— There is direct relationship between the I content (I) of the soil of New Zealand and the frequency (II) of goitre, the max. incidence occurring where (II) is lowest. There is no relation between (I) of drinking  $H_2O$  and (II). NUTR. ABS. (m)

Action of 3: 5-di-iodotyrosine in hyperthyroidism. E. DELCOURT-BERNARD (Rev. belge Sci. méd., 1934, 6, 1—27).—In hyperthyroidism, di-iodotyrosine (I) usually lowers, but sometimes raises, the metabolism. The effects of (I) differ from those of Lugol's I, which has a greater effect on ventilation than on  $O_2$  consumption. (I), when it lowers the metabolic level, lowers mainly  $O_2$  consumption; when it raises the metabolism, it raises both ventilation and  $O_2$  consumption. NUTR. ABS. (m)

Potassium metabolism in hyperpiesia. L. ARMENTANO (Orvosi Hetilap, 1934, 78, 96–98).– In healthy subjects or in arteriosclerosis, following intravenous injection of 5% aq. KCl, the K content of the blood rises 10–15 mg. per 100 ml. in the first 10 min. and falls within 30 min. to or below its original level. In hyperpiesia immediate fall in the K level occurs. Decerebration in dogs diminishes blood-K. NUTR. ABS. (m)

Starvation ketonuria in infants. H. BEUMER and H. PETERS (Z. Kinderheilk., 1934, 56, 61-63).-Administration of alkali accelerates appearance of hunger acetonuria (I) and increases the output of COMe<sub>2</sub>. The occurrence of (I) following an injection of adrenaline during fasting is confirmed.

NUTR. ABS. (m)

Utilisation of ingested sugar in glycogenstoring disease. H. BIEDERMANN and W. HERTZ (Deut. Arch. klin. Med., 1934, 176, 267—271).—In one case, ingestion of 100 g. of glucose (I), 30 g. of fructose (II), or 25 g. of galactose caused no glycosuria. After (I) the hyperglycæmia was more prolonged and > normal, although the fasting bloodsugar (III) was very low (46—61 mg. per 100 ml.). The glycæmic response to (II) was normal. After (I) or (II) the output of urinary inorg. P was increased. Another case, which had (III) 53—83 mg. per 100 ml., gave similar results, but showed after (II) an increased and prolonged rise in (III). Combustion of ingested sugar is delayed in this disease. NUTR. ABS. (m)

Value of salmon oil in treatment of infantile rickets. M. M. ELIOT, E. M. NELSON, S. P. SOUTHER, and M. K. CARY (J. Amer. Med. Assoc., 1932, 99, 1075—1082).—Varieties are compared as regards vitamin-A potency. CH. ABS.

Beryllium rickets. II. Prevention and cure. H. D. KAY and D. I. SKILL (Biochem. J., 1934, 28, 1222—1227).—Be rickets can be prevented if Na glycerophosphate is administered parenterally at the same time as the Be diet. Be-rachitic animals transferred to a normal diet rapidly recover, the phosphoric ester content of the liver and erythrocytes increasing. C. G. A.

Phosphoric ester content of the red cells and liver, and the phosphatase of the kidney in experimental osteoporosis in young rats. D. I. SEILL and H. D. KAY (Biochem. J., 1934, 28, 1228–1229).--In osteoporosis caused by a low-Ca, high-P diet the phosphoric ester content of the red cells and liver is lowered. As in experimental rickets the phosphatase activity of the kidney is diminished. C. G. A.

NUTR. ABS. (m)

Phosphorus partition in chicken blood as related to diet and bone maladies. V. G. HELLER, B. ZIMMERMAN, and R. B. THOMPSON (Poultry Sci., 1934, 13, 141—147).—Doubt is thrown on reported total inorg. P contents of serum and on the use made of these vals. in interpreting the mineral and vitamin status of foods. A. G. P.

Phosphatase. III. Serum-phosphatase in diseases of the bone. A. BODANSKY and H. L. JAFFE (Arch. Int. Med., 1934, 54, 88—110).—Serumphosphatase (I) is not affected by destruction of bone (II), but is high in cases of excessive formation of abnormal (II). Determinations of (I) may be used as an indication of effective therapy in rickets and in the differential diagnosis of other bone discases.

H. G. R.

Tissue respiration and certain reducing substances in chronic fluorosis and scurvy in the guinea-pig. P. H. PHILLIPS, F. J. STARE, and C. A. ELVEHJEM (J. Biol. Chem., 1934, 106, 41-61).— The rate of  $O_2$  uptake (I), the inhibiting effect of CN', and the decolorisation time of methylene-blue for the liver tissues of guinea-pigs are not affected by scurvy (II) or by fluorosis (III), whereas the indophenol-oxidase content is diminished and the glutathione increased in both (II) and (III). In the adrenals, (I) is about 50% of the normal val. in (II) and (III), whereas (I) is low in (II) and high in (III) and in general  $\infty$  the vitamin-*C* content of the tissue. The similarity between (II) and (III) has been confirmed and extended. H. G. R.

Silica content of normal and silicotic lungs. Silicosis. F. S. FOWWEATHER (Chem. and Ind., 1934, 713—716).—The degree of pulmonary fibrosis resulting from silicosis (I) is not related to the SiO<sub>2</sub> content of the lungs; the nature of the inhaled SiO<sub>2</sub> and the condition of the tissue are probably important factors. Silicates slowly decompose in the lungs to form active SiO<sub>2</sub>; hence the long interval frequently occurring between exposure to SiO<sub>2</sub> and death. A severe type of (I) is produced by inhalation of siliceous soap powder. F. O. H.

Pathogenesis and clinical features of nontropical sprue. L. DUNNER, H. HIRSCHFELD, and M. GERALDY (Klin. Woch., 1934, 13, 138—141).— The bile and pancreas function normally, but loss of fatty acids and Ca soaps occurs. The Ca content of blood and tissues becomes insufficient.

NUTR. ABS. (b) Precipitation of ox-heart antigen by cerebrospinal fluid of neurosyphilitic patients. B. S. LEVINE (Amer. J. Syphilis Neurol., 1934, 18, 239— 248).—Globulins have been conc. and freed from  $(NH_4)_2SO_4$  sufficiently to raise the sensitivity of the pptn. reaction to a level comparable with that of complement fixation. CH. ABS.

Gaseous metabolism of small animals. H. R. KANITZ and J. APITZSCH (Biochem. Z., 1934, 272, 189–196).—Apparatus is described. P. W. C.

Respiratory exchanges. M. ZAPAN (Bull. Acad. Sci. Roumaine, 1934, 16, 147–157).—Physical fatigue is manifested by an increase in expired CO<sub>2</sub>, which  $\propto$  the work done, but is  $\geq 6.9\%$ . The amount of  $CO_2$  expired does not always correspond with the  $O_2$  used and, after heavy work, about 6 hr. is necessary to reach normal equilibrium. H. G. R.

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Influence of temperature on the chemical composition of anaërobically fatigued muscle. C. LUTWAK and W. MOZOLOWSKI (Biochem. Z., 1934, 272, 157—166).—The behaviour of P compounds of muscle stimulated anaërobically at 4° to fatigue is similar to that at 18°, whereas the formation of lactic acid and NH<sub>3</sub> is much greater at the higher temp., the lactic acid max. and the rate of its formation being different. Creatine- and adenosine-phosphoric acids are almost completely decomposed in fatigued muscle. P. W. C.

Relation of cystine and cysteine to muscle overstrain. M. ITAGAKI, M. ODAGIRI, and Z. KABUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 381—399).—Muscular activity in rabbits, dogs, and men due to exercise, injection of strychnine, or faradic stimulation produces an occasional rise in the cystine content of the urine, whilst the cysteine and cystine+ cysteine levels markedly increase. The role of SHcompounds in muscle metabolism is discussed.

F. O. H. Rôle of the endocrine glands in the resynthesis of muscle-glycogen after fatigue. R. DAMBROSI (Compt. rend. Soc. Biol., 1934, 115, 344—345).— In the dog, insufficiency of thyroid, parathyroid, pituitary, or gonads does not affect the re-formation of muscle-glycogen after severe exercise. Thyroid administration inhibits resynthesis only when the dosage is very high. NUTR. ABS. (b)

Lactic acid, total carbon dioxide, and  $p_{\rm H}$  of venous blood during recovery from severe exercise. E. P. LAUG (Amer. J. Physiol., 1934, 107, 687-692).—The max. lactic acid and min.  $p_{\rm H}$  vals. were found in man 3-6 min. after exercise. In two cases, during the first 10 min. of recovery the total CO<sub>2</sub> continued to decline, despite a fall in lactic acid and rise in  $p_{\rm H}$ . NUTR. ABS. (b)

Lactic acid metabolism of muscles made nonirritable by sugar solutions. A. H. HEGNAUER (Amer. J. Physiol., 1934, 107, 667–676).—Measurement of the lactic acid (I) content of muscles at intervals after immersion in isotonic glucose solution in  $O_2$  and  $N_2$  shows that not all the observed increase in  $O_2$  consumption (II) can be accounted for by increased lactate content. Addition of NaCl or KCl causes decrease in (II) and increase in oxidative quotient. (I) is not the sole pace-maker for (II).

NUTR. ABS. (m)

Blood-sugar in the light athletic sports. F. MEYTHALER and A. DROSTE (Klin. Woch., 1934, 13, 439—443).—The blood-sugar of trained and untrained persons is raised slightly by short-distance races (100—200 m.) and considerably by mediumdistance races (400—800 m.), after which the return to normal is delayed in the untrained. Long-distance races (10,000 m.) produce in the trained a slight rise, which declines immediately after the race. In the untrained, hyperglycæmia, or in the case of exhaustion, hypoglycæmia, was observed. NUTR. ABS. (b) Carbohydrate metabolism of the kidney. A. HEMINGWAY and H. J. PHELPS (J. Physiol., 1934, 80, 369—376).—The perfused kidney uses 0.014-0.99mg. of glucose per g. per min., whilst the perfused isolated lung uses 0.014 mg. About one third of the O<sub>2</sub> used by the kidney is employed in carbohydrate metabolism. NUTR. ABS. (m)

Fate of absorbed carbohydrate in the organism. H. SCHUR, A. LÖW, and A. KRČMA (Wien. Arch. inn. Med., 1934, 24, 463—480).—Single high doses of carbohydrate (I) cause a marked increase in depôt fat of mice, to > double the original amount. The glycogen content of liver (II) increases tenfold, and the wt. of the (II) is doubled. More than two thirds of the absorbed (I) appears in the form of fat; the transformation probably occurs in the fat tissues. Part of the absorbed (I) enters directly into metabolic processes. This implies that absorbed (I) inhibits formation of (I) from fat in (II). NUTR. ABS. (b)

Intravenous administration of glucose to infants. M. ELLERMANN and K. TORNING (Rev. franç. Pédiat., 1933, 9, 632—639).—Intravenous administration of glucose (10—20 g. according to age) is, after the initial rise, followed by a steady fall in blood-sugar to < the fasting level in < 2 hr. In diabetic children the fall is interrupted after about 1 hr., after which it is much slower. NUTR. ABS. (b)

Effect of glucose derivatives on animals (rabbits) following hepatectomy. D. R. DRURY and W. T. SALTER (Amer. J. Physiol., 1934, 107, 406-413).—A no. of hexose and triose derivatives, tested for ability to prolong the life of the hepatectomised rabbit, did not approach glucose in efficiency, the best being fructose with a survival period of 11.9 hr., as against 20 hr. with glucose. The so-called carbohydrate intermediates are of doubtful importance in the normal exchange of carbohydrate between various tissues and organs. NUTR. ABS. (b)

Heat production in Ascaris lumbricoides during feeding with glucose, fructose, and galactose. R. HOFFMANN (Z. Biol., 1934, 96, 390-400).— Compared with other sugar fermentation processes, the utilisation of glucose and fructose by A. lumbricoides results in abnormally high production of heat. A. G. P.

Fructose and lactic acid metabolism. E. STERKIN and F. M. VENGEROVA (Biochem. Z., 1934, 272, 246—258).—Oral administration of glucose, maltose, or lactose has no effect on the blood-lactic acid (I) val., but that of fructose (II), sucrose (III), or invert sugar (IV) brings about a considerable hyperlactacidæmia lasting 2—3 hr. (II) and (IV) but not (III) when administered intravenously have the same effect if the initial (I) is low, but if high, the effect may be small or hypolactacidæmia may result.

## P. W. C.

Effect of large storage of glycogen on respiration of the liver. B. WALTHARD (Z. ges. exp. Med., 1934, 93, 242—245).—Storage of glycogen (I) or fat, but especially of (I), in the rat's liver reduces its respiratory activity, indicating regressive tissue changes. The reduction in  $O_2$  consumption takes place even when (I) is in solution, and cannot be interpreted as a direct effect of (I).

NUTR. ABS. (m) Glycogen storage and fructose tolerance. P. F. MEYER (J. Bhysiol., 1934, 80, 480-490).—In rats an excessive hyperglycæmia after fructose feeding is not associated with a low glycogen (I) store nor with inability of the liver to form and hold (I), but rather with little or no (I) formation in the muscles. NUTR. ABS. (b)

Storage of glycogen in the reproductive organs of invertebrates before ovulation. M. CHAIGNE (Compt. rend. Soc. Biol., 1934, 115, 174—176).— The variations in glycogen (I) reserves in Asterias rubens, Paracentrotus lividus, Maja squinado, Sepia filliouxi, and Helix pomatia indicate that (I) forms an important store available for the formation of reproductive cells. NUTR. ABS. (m)

Occurrence of citric acid in urine and bodyfluids. W. M. BOOTHBY and M. ADAMS (Amer. J. Physiol, 1934, 107, 471-479).—Citric acid (I), which is widely distributed in the body-fluids, plays an important part in the intermediary metabolism, but is not necessarily derived from ingested (I) or carbohydrates. Urinary (I) is increased by administration of a physiologically strong base and decreased by that of a strong acid. NUTR. ABS. (m)

Urinary excretion of citric acid. I. Effect of ingestion of large amounts of orange juice and grape juice. II. Effect of ingestion of citric acid, sodium citrate, and sodium hydrogen carbonate. C. SCHUCK (J. Nutrition, 1934, 7, 679-689, 691-700).—I. Addition of 1 litre of juice to a basal diet for women resulted in an increased  $p_{\pi}$  and decreased titratable acidity in the urine. The increase in citric acid (I) excretion produced by orange juice was slightly > that from grape juice (II), but the ratio of amount excreted to amount ingested was much higher in the case of (II). Indications of a metabolic source of (I) are recorded.

II. Urinary  $p_{\rm H}$  was not appreciably affected by ingestion of (I), but was raised considerably by Na citrate (III). The titratable acidity was decreased slightly by (I) and considerably by (III). Total orgacid excretion was decreased by (I) and increased by (III). The amount of (I) excreted varied irregularly after ingestion of (I), but increased considerably after ingestion of (III). Feeding of NaHCO<sub>3</sub> caused a small increase in total org. acids and a considerable increase in the (I) excreted. A. G. P.

Blood-sugar curve after administration of fat. G. PAASCH and H. SCHÖNFELD (Monatsschr. Kinderheilk., 1934, 59, 181—182).—Oral administration of 50 g. of olive oil to children suffering from various complaints, including diabetes, had no effect on bloodsugar. NUTR. ABS. (b)

Nutritive value of food fats and oils. II. Suet and sunflower oil. A. PICKAT, N. ZENIN, O. KURT-SINA, and P. ALEXIEVA (Problems of Nutrition, U.S.S.R., 1934, 3, No. 1, 107).—Compared with butter, sunflower oil (I) has high, and suet very low, nutritive val. when fed to young rats as 30% of the calorie val. of the ration. The high biological val. of (I) is attributed to its content of highly unsaturated fatty acids. When groups of rats which have received the three rations are subsequently starved, the (I)group survives longest. NUTR. ABS. (m)

Effect of the saturated fatty acid content of the diet on the composition of body-fat. A. D. BARBOUR (J. Biol. Chem., 1934, 106, 281-288).— The saturated (I) and unsaturated acid (II) content of the body-fat (III) of albino rats  $\infty$  the (I) and (II) content, respectively, of the fat fed (20% of diet), but the (I) content of (III) never exceeds 25-27%, any excess being excreted. Excretion of arachidic acid (of pea-nut oil) is nearly quant. R. S. C.

Changes of total lipin and iodine number of blood-fat in alimentary lipæmia. W. R. WILSON and J. P. HANNER (J. Biol. Chem., 1934, 106, 323— 330).—Alimentary lipæmia is induced by feeding cream (I) (I val. 30—40) or cod-liver oil (II) (I val. 165) by mouth. The I val. of the increment was 39—60 for (I) and 118—135 for (II). The blood-fat is composed of the same fatty acids as those in the fat ingested. C. G. A.

Relation of depôt-fat to egg-yolk in laying hens. H. J. ALMQUIST, F. W. LORENZ, and B. R. BURMESTER (J. Biol. Chem., 1934, 106, 365—371).—Depôt- and yolk-fats of hens fed on malvaceous plants exhibit the Halphen test. Depôt-fat is not utilised in the formation of yolk-fat. H. G. R.

Synthesis of fat in the mammary gland. D. M. MICHLIN and Z. N. ZAPRUDSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 573—576).—The negative results of previous workers on the *in-vitro* synthesis (I) of fats by mammary gland preps. (II) are due to incomplete knowledge of the activators and inhibitors involved and to unsuitable conditions (*e.g.*, dilution). With COMe<sub>2</sub>-dried (II), (I) is increased by 50— 60% by activators such as CaCl<sub>2</sub> or bile. F. O. H.

Fat and calcium metabolism. Influence of tripalmitin and triolein on the fæcal output of Ca in full-grown rats. A. WESTERLUND (Lantbr.-Högsk. Ann., 1934, 1).—With animals on low or moderate Ca diets, receiving tripalmitin (I) and triolein (II) together in inversely varying amounts totalling up to 1.2 g. daily, (I), but not (II), adversely affects Ca metabolism by raising the fæcal Ca output and may even bring the animals into negative Ca balance. NUTR. ABS. (b)

Biology of the meal-worm. III. Fat changes during metamorphosis. M. BECKER (Biochem. Z., 1934, 272, 227-234).—Analysis of the fat of *Tenebrio* larvæ shows that whereas the reserve fat gradually disappears, the organ fat is not utilised. P. W. C.

Changes in total nitrogen content during the life of the imago of the worker honey-bee. M. H. HAYDAK (J. Agric. Res., 1934, 49, 21–28).—The most rapid increase in the N content of various parts of the insect occurred during the first 5 days after emergence, changes being greatest in heads and least in thoraxes. The N in the alimentary tract corresponded closely with the amount of pollen in the rectum, reaching a max. val. after 8 days and subsequently declining. A. G. P.

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Distribution of urinary components of nitrogen metabolism. VI. Starvation. G. Boy (Bull. Soc. Chim. biol., 1934, 16, 1009-1106).-In the rabbit, rat, dog, and pig, starvation (I), succeeding a period of carbohydrate dieting, causes in the total N excretion an immediate increase, lasting almost until death, which varies inversely with the size of the animal. The increase appears rapidly in the rabbit, reaching a val. six times the original, and slowly in the pig, where the val. is at most doubled. The vals. for the rat and the dog are intermediate, but nearer those of the pig. This increase takes place mainly in urea-, NH<sub>3</sub>-, and NH<sub>2</sub>-N; purine-N is present in small amount, creatinine is absent, creatine present. The increase in the coeffs. of protein and purine oxidation, particularly the former, from the beginning of (I) is marked, but whilst the excretion of NH<sub>2</sub>-N (II) always increases, the ratio (II)/(II) + urca-+NH<sub>2</sub>-N is lowered in the case of the rabbit, and much increased in the case of the pig. A. L.

Proteolysis in regenerating tissues. Autolysis of normal and regenerating tissues. N. V. BROMLEI and V. N. ORECHOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 44–50).—After section of the tail of *Pelobates fuscus* tadpoles, the nonprotein-N contents of the regenerated tissue and of the stump are 74 and 77 mg. per 100 g. (normal 94 mg.). The corresponding vals. after 4 hr. of autolysis at  $p_{\rm H}$  6.4 are 61, 90, and 128, and after 12 hr. 170, 310, and 184. R. T.

Specific dynamic action of proteins in the rabbit. (a) Peptone. (b) Amino-acids; glycine, d-, dl-alanine. E. LE BRETON and G. SCHAEFFER (Compt. rend. Soc. Biol., 1934, 115, 854—857, 858—860).—Widely varying results were found for the sp. dynamic action (I) of proteins, the val. at times being zero. The view that (I) conforms to a thermochemical law valid for all species and all doses of protein is therefore rejected. NUTR. ABS. (b)

Oxidation of proline and alanine by certain tissues. F. BERNHEIM and M. L. C. BERNHEIM (J. Biol. Chem., 1934, 106, 79—86).—Proline (I) and alanine (II) are oxidised at different rates by broken cell suspensions of the liver and kidney of various animals. 0.05M-NaF accelerates and increases the  $O_2$  uptake, except in the case of mouse-, rat-, and pigeon-liver and -kidney. This is partly a salt effect, and in many cases may be brought about by NaCl and KCl. Oxidation of (II) is accompanied by deamination, whereas that of (I) is not, except with guinea-pig-kidney and rat-liver. (I) and (II) act as catalysts of the reduction of methylene-blue by tissues. H. G. R.

Metabolism of amino-acids. VI. Rate of abscrption of leucine, valine, and their isomerides from the gastro-intestinal tract of the white rat. B. W. CHASE and H. B. LEWIS (J. Biol. Chem., 1934, 106,315-321).—In 3-hr. periods the absorption coeffs. of the Na salts in milliequiv. per 100 g. per hr. are for valine, 0.40; leucine, 0.34; isoleucine and norleucine, 0.27; isovaline, 0.14. There is no difference between the rate of absorption of the naturally occurring isomeride and the dl-form. No glycogen was formed in the liver following absorption. C. G. A.

Non-essential nature of tyrosine [as dietary factor]. R. S. ALCOCK (Biochem. J., 1934, 28, 1174—1177).—Rats fed on a diet containing hydrolysed caseinogen, free from tyrosine (I), grew as well as controls on diet containing (I). H. D.

Diet deficient in cystine and tissue-glutathione. A. MARENZI and B. BRAIER (Compt. rend. Soc. Biol., 1934, 115, 337—338).—The total glutathione content (I) of organs in the rat falls 24—36% on a diet low in cystine. The decrease is most marked in liver and kidney. Diet high in cystine does not appreciably increase (I). NUTR. ABS. (m)

Synthesis of purines in the mammalian organism. R. KAPELLER-ADLER, E. LAUDA, and K. VON MÉGAY (Biochem. Z., 1934, 272, 153—154; cf. this vol., 684).—The results obtained by Terroine *et al.* confirm the view that purines are synthesised, probably from the proteins of food, in the mammalian organism (pig, dog, rabbit). W. McC.

Utilisation of homogenised milk in man. K. VON STEJSKAL and C. NEUBURGER (Wien. med. Woch., 1934, 84, 317—319).—Homogenised milk is very well utilised, the amount of fat in the fæces being only about a third of that found with untreated milk. Fat absorption is promoted by the nature of the curd formation. Absorption of protein is also improved, but to a smaller extent. NUTR. ABS. (m)

Nutritive properties of protein, vitamin- $B_1$ and  $-B_2$ , and the germ in rye. D. W. JOHNSON and L. S. PALMER (J. Agric. Res., 1934, 49, 169— 181).—The favourable effects on rats of additions of liver to a rye ration are not due to improved biological val. of the protein mixture. Lysine is the primary limiting NH<sub>2</sub>-acid of the rye protein. Unsatisfactory results of feeding rye to pigs are not attributable to the germ. Vitamin deficiency under customary feeding conditions is improbable.

A. G. P.

Nutritive value of green immature soya beans. C. D. MILLER and R. C. ROBBINS (J. Agric. Res., 1934, 49, 161—167).—Cooked immature soya beans contained considerably larger amounts of protein, fat, Ca, P, and Fe than do other vegetables. Vitamin-A,  $-B_1$ , and  $-B_2$  are present in adequate proportions, but -C is deficient. A. G. P.

Physiological effects of continued use of foodstuffs grown with and without artificial fertilisers. A. SCHEUNERT (Z. Pflanz. Düng., 1934, **B**, 13, 337— 338).—Foodstuffs grown with heavy applications of fertilisers prolonged the life period of rats and improved reproductivity as compared with similar foods produced on unmanured soils. A. G. P.

Protein-free diet and the state of oxidation of the body. F. GRAPENTIN (Z. ges. exp. Med., 1933, 90, 750-757; Chem. Zentr., 1934, i, 73).--"Dysoxidative carbonuria" is observed in the rat. A. A. E.

Fundamental food requirements for growth of the rat. VII. Inheritance as a factor influencing food utilisation in the rat. H. P. MORRIS, L. S. PALMER, and C. KENNEDY (Minnesota Agric. Exp. Sta. Tech. Bull., 1933, No. 92, 56 pp.).— In female rats, food consumption per unit live-wt. increase is > in males, and carcase analyses show higher dry matter, ash, and fat, and lower N and fatfree dry matter contents. The efficiency of food utilisation is probably influenced by inheritable factors. A. G. P.

Dietary depigmentation of young rats. F. J. GORTER (Nature, 1934, 134, 382). L. S. T.

Growth: statistical interpretation. H. C. SHERMAN and H. L. CAMPBELL (Proc. Nat. Acad. Sci., 1934, 20, 413—416).—The growth data obtained from both male and female rats fed on three different diets approximate to a symmetrical frequency distribution. P. G. M.

Ageing of the organism retarded by inhalation of negatively ionised air. TCHIJEVSKY and VOY-NARD (Compt. rend., 1934, 199, 496).—Systematic inhalation of negatively ionised air causes, in animals, more rapid growth, increased wt., more robust progeny, greater resistance to disease, and obviously delayed ageing. Gaseous exchange and metabolism are increased, whereas positively-charged air produces the reverse effect. H. W.

Acid-base equilibrium of inhabitants of the tropics. IV. W. RADSMA, G. M. STREEF, and J. V. KLERKS (Arch. Neerland. Physiol., 1934, 19, 372–383).—On a rice diet [H'],  $NH_3$ , and the acidity were increased, whereas the excretion of  $PO_4^{\prime\prime\prime}$  and fixed bases was less; the morning alkaliuria, which is observed with European diets, is absent. H. G. R.

Sodium chloride requirement and its relationship to mineral metabolism. II, III. H. GLAT-ZEL (Z. ges. exp. Med., 1934, 92, 653-666; 93, 179-194) .--- II. High K and low Na intake leads to excessive output of Na with retention of K. A diet of rice with a K: N ratio just > 1 does not cause undue loss of Na or Cl, so that addition of NaCl to the diet is unnecessary. Diets (such as potatoes) with a high K : Na ratio and high K content, which cause excessive excretion of Na and Cl, require the addition of NaCl to make good the loss and to facilitate excretion of the retained K. Flesh foods require NaCl only if the blood, which contains more Na than K, is removed. The effect of the diet on the reaction of the urine has no influence on the NaCl requirements. Bunge's hypothesis is therefore confirmed.

III. With rice diet (low K) the urinary output of K is the same as the intake; addition of NaU increases the output of K. With other diets (higher K) addition of NaCl increases K retention, although the urinary output may also be increased. In all cases retention of Na and Cl, originally negative, becomes markedly positive. When K intake is sufficiently great, addition of NaCl to the diet does not prevent K retention. K retention cannot be explained by renal inefficiency. Changes in the excretion of substances other than K, Na, and Cl are not const. The principal effect of NaCl is to act as a buffer by the excretion of more Na or Cl as circumstances demand. NUTR. ABS. (m) Effect of a low-calcium ration on reproduction in cattle. C. P. FITCH, W. L. BOYD, C. H. ECKLES, T. W. GULLICKSON, L. S. PALMER, and C. KENNEDY (Cornell Vet., 1932, 22, 156—172).—The ration-Ca (I) had no appreciable effect on blood-plasma-Ca; no changes in milk or fat production could be attributed to (I). CH. ABS.

Absorption of calcium. A. R. BLISS, jun., E. O. PRATHER, jun., and R. W. MORRISON (J. Amer. Pharm. Assoc., 1934, 23, 656—662).—When administered to mice by stomach-tube in aq. solution containing equiv. amounts of Ca (0.3 mg. per g. of body-wt.) the efficacy of the salts in preventing narcosis by MgSO<sub>4</sub> is in the order lactate, gluconate, CaCl<sub>2</sub>, inositol Ca<sub>6</sub> gluconate, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, glycerophosphate, indicating the relative ease of absorption.

C. G. A.

Changes in blood-calcium and -phosphorus partition during the life cycle of the chicken. V. G. HELLER, H. PAUL, and R. B. THOMPSON (J. Biol. Chem., 1934, 106, 357—364).—The total P and total Ca rise during egg production and fall on moulting, the rises being due to lipin-P (I), adsorbable nonfilterable Ca (II), and protein-Ca; inorg. and acidsol. P remain approx. const., whilst adsorbable filterable Ca (III) falls slightly during the production period. In osteoporotic chickens (III) is > in normal, plasma-(I) and -(II) being lower. C. G. A.

Influence of calcium and phosphorus intake on bovine blood. J. E. GREAVES, E. J. MAYNARD, and W. REEDER (J. Agric. Res., 1934, 48, 1033— 1041).—Use of cottonseed cake, steamed bone flour, or bran as P supplements increased the inorg. P (I) of blood (II) to varying extents, but had no appreciable effect on the (II)-Ca. A close relationship between the P intake and (I) of (II) is demonstrated. A. G. P.

Normal development of the leg bones of chickens with respect to their ash content. H. M. HARSHAW, J. C. FRITZ, and H. W. TITUS (J. Agric. Res., 1934, 48, 997—1008).—Serum-Ca of pullets increased considerably just before the laying period, but otherwise no definite changes were apparent with increasing age. Calcification of the epiphyses of bones of females began earlier than in those of males. Variations due to difference of breed were also apparent. The Ca: P ratio in the ash of tibiæ was low immediately after hatching, but subsequently increased, in all cases, to approx. 2.0:1. A. C. P.

Chemical structure of the bone salts of healthy and rachitic animals. J. MAREK, O. WELLMANN, and L. URBANYI (Z. physiol. Chem., 1934, 226, 3— 17).—The inorg. constituents of the bones of pigs on different diets vary widely with the mineral composition of the diet. The outer layers of the tubular bones contain the least ash. P increases towards the interior, whilst Ca, Mg, and CO<sub>2</sub> are highest in the middle zone. The Ca not bound by PO<sub>4</sub><sup>('')</sup> is present as CaCO<sub>3</sub>. The main inorg. constituent is Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Contrary to the views of Gassmann (A., 1930, 1609) and Klement (A., 1929, 1328), the Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and CaCO<sub>3</sub> are present solely as a mixture and not as a complex. J. H. B. Rôle of copper in carbohydrate metabolism. H. L. KELL and V. E. NELSON (J. Biol. Chem., 1934, **106**, 343—349).—Oral administration of Cu to anæmic rats lowers the max. of the glucose (I)-tolerance curves, the hæmoglobin val. remaining unaltered. Fe alone does not improve (I) utilisation. An increase in hæmoglobin (administration of Fe+Cu) produces a proportional increase in (I) tolerance together with lower fasting blood-(I) level. Fasting blood-(I) in anæmic is > in normal rats. C. G. A.

Zinc in the nutrition of the rat. W. R. TODD, C. A. ELVEHJEM, and E. B. HART (Amer. J. Physiol., 1934, 107, 146—156).—Rats fed from weaning on a synthetic ration containing only 1.6 mg. of Zn per kg., but supplied with all the essential vitamins, show a lower growth rate than rats on the same ration to which 5.0 mg. of Zn (as ZnO or ZnCl<sub>2</sub>) have been added per 100 g. of ration. Rats on low-Zn ration lose hair. NUTR. ABS. (m)

Distribution of zinc in the animal organism. A. KOGA (Keijo J. Med., 1934, 5, 97–105).—The Zn content (I) of various tissues of the ox, dog, goose, tortoise, toad, fish (*Ophicephalus argus*, Cantor), and oyster is given. For nearly all the species examined, (I) is highest in the liver and pancreas and lowest in the lungs, brain, and testes; in the muscles and blood, (I) varies considerably with different animals. Dried oyster has a high (I) of 0.041%. F. O. H.

Effect of varying levels of iodine intake on the thyroglobulin content of the thyroid gland. M. E. JONES (Amer. J. Physiol., 1934, 107, 513— 517).—I as KI fed to dogs produced an increase of 147-249% in thyroid-I, 94-99% of which was precipitable by 95% EtOH, and therefore presumed to be in the form of thyroglobulin. KI in doses of 0.02 g. per kg. of body-wt. given daily for 4 weeks produced as great a storage of I as did doses of 0.1 g. per kg. daily for 6 weeks. NUTR. ABS. (b)

Somatic and biochemical changes in chronic alcoholics. III. Protein metabolism. B. F. GOJCHER, E. G. TSCHERNYSCHEVA, and KRASNOV-SKAJA (Acta Med. Scand., 1934, 81, 1—13).—In chronic alcoholics the total N of the urine is increased, but the NH<sub>2</sub>-acid and NH<sub>3</sub> excretion is normal. Urinary excretion of these substances after administration of 20 g. of peptone is subnormal. Rctention of H<sub>2</sub>O occurs. NUTR. ABS. (m)

Fixation of toxic substances by endocrine glands. I. Chloroform. II. Barbiturates. R. FABRE (J. Pharm. Chim., 1934, [viii], 20, 97— 101, 101—103).—I. The amount of CHCl<sub>3</sub> fixed by the endocrine glands during anæsthesia of dogs runs parallel with their lipin content, being highest for the suprarenal cortex (I). The disappearance of CHCl<sub>3</sub> from (I) is much slower than from the blood, approx. 30% remaining after 24 hr.

II. Veronal is taken up by the adrenals and thyroid to a greater extent than by blood, brain, and liver. C. G. A.

Detoxicating properties of sodium thiosulphate in "avertin" intoxication. A. BOLLIGER (Med. J. Austral., 1932, 125-140).—Clinical data are recorded.  $Na_2S_2O_3$  is retained in the body longer than phenolsulphonephthalein. CH. Abs.

Local anæsthetic of the phenoxyaminoalcohol group. E. HESSE and O. SWOBODA (Arch. exp. Path. Pharm., 1934, 175, 509—517).—2-*n*-Butoxy-5-*iso*propylphenyl  $\gamma$ -diethylamino- $\beta$ -hydroxypropyl ether has a toxicity (partly or wholly inhibited by artificial respiration or pernocton narcosis) to rabbits approx. 2.5 times that of cocaine, but 25—30 times the local anæsthetic action; as a lumbar anæsthetic it equals pantocaine. F. O. H.

Analogy between histamine- and anaphylactic shock. I-IV. A. DZSINICH and M. PELY (Arch. exp. Path. Pharm., 1934, 175, 359-371).-During the reactions (I) following injection of histamine (II) into man, the coagulation time of the blood is markedly increased, being almost doubled at the height of (I). The blistering and erythema due to intradermal injection of (II) are greatly diminished by prior administration of cholesterol (III). During (I) the blood-(III) rises (in some cases to supersaturation), whilst the (III)-saturation val. of the blood falls. Oral administration of (III) for 12 days markedly reduces the (I) due to (II), whilst the characteristic changes in the blood-(III) (actual and saturation vals.) and the rate of blood-coagulation are unchanged. The above phenomena afford evidence for the analogy between (II)- and anaphylactic shock. F. O. H.

Chemistry and pharmacology of fermented foodstuffs. I. W. KEIL and H. KRITTER (Arch. exp. Path. Pharm., 1934, 175, 736—744).—From sauerkraut juice were isolated histamine (I) (up to 0.02%), acetylcholine, and putrescine, constituents which produce the stimulation (partly inhibited by atropine) of the isolated guinea-pig's uterus. Colour reactions and pharmacological tests indicate the presence of (I) in wine-vinegar, but only betaine could be isolated. Curdled milk contains choline, but neither choline esters nor (I). The regeneration of reineckates by means of AgOAc is described.

F. O. H.

Penetration of gaseous pyridine, piperidine, and nicotine into the bodies of certain insects. C. H. RICHARDSON, L. H. GLOVER, and L. O. ELLISOR (Science, 1934, 80, 76-77).—The gaseous bases pass directly through the cuticula of cockroaches, corn-ear worm larve, and grasshoppers. L. S. T.

Elimination of morphine and quinine in human milk. W. G. TERWILLIGER and R. A. HATCHER (Surg. Gynecol. Obstet., 1934, 58, 823—826).— Although a child born to a morphine (I) addict exhibited signs of (I) addiction, (I) could not be detected in the milk. Traces of quinine can be detected after administration, but the amounts are too small to affect the nursing infant. CH. ABS.

Pharmacology of narcotine. N. COOPER and R. A. HATCHER (J. Pharm. Exp. Ther., 1934, 51, 411— 420).—Narcotine (I) intravenously administered to cats disappears from the blood-stream and becomes fixed in the lungs, liver, and kidneys, whilst only traces are eliminated in the urine following intramuscular injection of large doses. There is no evidence that (I) exerts an effect on the action of equal doses of morphine. W. O. K.

(a) [Physiological action of] hydrastine, bicuculline, and adlumine. (b) Bicucine. A. D. WELCH and V. E. HENDERSON (J. Pharm. Exp. Ther., 1934, 51, 482—491, 492—494).—(a) Hydrastine (I) and bicuculline (II) (cf. A., 1933, 617) are similar in their pharmacological action except that (II) is about 100 times as active a convulsant as (I), whilst the convulsant action of adlumine (cf. A., 1933, 841) is relatively weak and differs quantitatively from that of (I) and (II).

(b) The convulsant activity of bicucine (A., 1933, S41) is < that of (II) and is comparable with that of (I). W. O. K.

Diffusible and non-diffusible calcium in blood and cerebrospinal fluid of cats intoxicated with bulbocapnine and of human beings under bromide treatment. S. KATZENELBOGEN (J. Pharm. Exp. Ther., 1934, 51, 435-439).—In normal cats and in man with low blood-Br', the Ca content of the cerebrospinal fluid (I) is approx. equal to the diffusible Ca content of the serum, but in cats, intoxicated with bulbocapnine, in which the (I)-Ca content remains approx. const., the diffusible Ca of the blood shows a marked fall. A similar result is obtained in man with high blood-Br'. W. O. K.

Comparative actions of sympathomimetic compounds. Bronchodilator actions in perfused guinea-pig lungs. M. L. TAINTER, J. R. PEDDEN, and M. JAMES (J. Pharm. Exp. Ther., 1934, 51, 371-386).—Of various derivatives of phenylethylamine, the most active bronchodilator in perfused isolated guinea-pig's lungs was adrenaline, whilst the next three in order of activity were also pyrocatechol derivatives. A single nuclear OHgroup likewise conduces to activity. There was no consistent relationship between vasopressor and bronchodilator activity, probably because of the variety of mechanisms involved. W. O. K.

Action of diuretic drugs. I. In normal persons. H. L. BLUMGART, D. R. GILLIGAN, R. C. LEVY, M. G. BROWN, and M. C. VOLK (Arch. Int. Med., 1934, 54, 40—81).—There was an increased excretion of  $H_2O$ , Na, Cl', K, and Ca, due to a loss of extracellular body fluids, but no change in  $PO_4^{\prime\prime\prime}$ ,  $SO_4^{\prime\prime}$ , NH<sub>3</sub>, or total N. On the cessation of diuresis a compensatory retention immediately set in. There was no change in sp. gr., Na, or Cl' of the blood-serum or in the rate of glomerular filtration, but the tubular reabsorption decreased in proportion to the diuretic effect. H. G. R.

New type of fever agent. H. G. BARBOUR (Science, 1934, 80, 144-146).—p-Nitrophenylethylamine rapidly raises the body temp. of guinea-pigs and rabbits. L. S. T.

Decrease in alkali reserve and movement of chlorine in the blood during hyperthermy caused by short waves. L. BINET, M. LAUDAT, and J. AUCLAIR (Compt. rend., 1934, 199, 442–444).—This hyperthermy decreases the alkali reserve and slightly increases the Cl in the blood-plasma of dogs. R. S. C.

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Toxicity of lysolecithin. M. IWATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 174-192).-The oral administration of an EtOH extract of rice polishings to pigeons or rats on polished rice diets often caused vomiting and the excretion of greenish fæces. This toxic effect, which is due to the lysolecithin (I) in the EtOH extract and is intensified by intravenous or intramuscular injection of (I), can be counteracted by the addition of 3% of brewer's yeast to the diet, *i.e.* by a sufficient quantity of vitamin- $B_1$ . P. G. M.

Physiologically active phosphatide. L. UTKIN and R. TOPSTEIN (Biochem. Z., 1934, 272, 36-41).-Hydrolysis of the phosphatide fraction of the lipins of adrenal glands or egg-yolk with HCl in MeOH results in separation of a phosphatide (I) which has a physiological action similar to that of choline. (I) is not choline, but may be the precursor of the substance obtained by Mafori et al. (this vol., 700).

W. McC.

Weight and chemical composition of the heart under normal and pathological conditions. E. Bong, P. JUNKERSDORF, and H. STEINBORN (Z. ges. exp. Med., 1934, 92, 573-597).-Injection of phloridzin into dogs causes no reduction of heart-glycogen (I) and may cause increase, whilst glycogenogenesis from fat occurs. Adrenaline (II) acts similarly, apparently having a sp. action favouring change of fat to carbohydrate (III). In the fasting dog injection of choline results in high glycogen and low fat vals. Thyroxine causes a reduction in (I) which is < that in liver-glycogen and does not occur in young dogs. Administration of insulin to dogs on high-(III) diet causes increase in (I), but if prolonged causes reduction of glycogen and increase of fat. Administration of guanidine or synthalin causes slight reduction of glycogen in well-nourished dogs, but increase in dogs with previous inanition because of increased secretion of (II). In depancreatised dogs there is a fall in the fat content and an increase in (I). NUTR. ABS. (m)

Physiological action of vicioside. H. HERISSEY and J. CHEYMOL (Bull. Soc. Chim. biol., 1934, 16, 1176-1181) .- Vicioside injected intravenously into mice and dogs has no toxic action, and is excreted A. L. unchanged.

Pharmacology of Digitalis. H. WEESE (Arch. exp. Path. Pharm., 1934, 175, 754-758).-The min. lethal dose for cats of digitoxin (I) injected intraarterially is 0.309 and, intravenously, 0.210 mg. per kg. Following injection of (I), only traces are detectable in the blood (cf. Haferkorn and Lendle, this vol., 804). The mechanism and site of (I)-F. O. H. fixation in the organism are discussed.

Accumulation and elimination of Digitalis alkaloids in poikilotherms. L. LENDLE (Arch. exp. Path. Pharm., 1934, 175, 719-726).-Frogs can daily eliminate 50-70% of the lethal dose (I) of digitoxin (II), the elimination coeff. being therefore approx. 0.083 mg. per kg. per hr. Thus detoxification is about 80 times as rapid as in warm-blooded animals. Injection of 0.003 mg. of (II) per g. is followed by excretion of 40-50% (mainly as glucoside) during the first 24 hr. and only of traces during the second 24

hr. This rapid excretion explains the low sensitivity, comparison of the (I) for the intact frog with that for the isolated heart indicating that only 3% of the administered alkaloid acts on the heart. F. O. H.

Effect of strophanthin on gaseous metabolism during cardiac insufficiency. A. RUHL and A. WIEHLER (Arch. exp. Path. Pharm., 1934, 175, 665-680).-With cardiac insufficiency (spontaneous or by histamine- or barbituric acid-damage) in heart-lung preps., strophanthin (I) increases the heart performance and decreases coronary circulation, whilst subnormal O<sub>2</sub> consumption is increased and R.Q. decreased (this vol., 214), changes probably due to increased capillary diffusion of  $O_2$  by (I). Respiration in O2 does not remove the existing lack of O2 owing to the relatively lower increase of arterial tension.

F. O. H.

Determination of benzene in toxicology. I. Colorimetric determination of m-dinitrobenzene. M. PERONNET (J. Pharm. Chim., 1934, [viii], 20, 145-149).—The optimum conditions for the colour reaction with fructose have been determined. E. H. S.

Evaluation of light-protecting materials. F. ELLINGER (Arch. exp. Path. Pharm., 1934, 175, 481-488) .--- Various physical and biological methods are discussed. An approx. evaluation is obtained by comparison of the degree of erythema produced by ultra-violet irradiation of the bare and protected human arm, the agent being used as an ointment or dissolved in EtOH or aq. glycerol media. F. O. H.

Laxative effect of a regenerated cellulose in the diet. Its influence on mineral retention. H. MORGAN (J. Amer. Med. Assoc., 1934, 102, 995-997).-In healthy persons receiving 20 g. of cellulose (free from N, P, and Ca) in the diet the fæcal dry wt. (free from N, F, and Ca) in the energy of the free from N, F, and Ca) in the energy increases 69%, whilst the  $H_2O$  content alters only slightly. The N, P, and Ca contents of the fæces increase 4.3, 6.6, and 12.9%, respectively. NUTR. ABS. (m)

Changes in the acid-base equilibrium during progressive asphyxiation. D. CORDIER (Ann. physiol. physicochim. biol., 1934, 10, 301-330).-In dogs under chloralose anæsthesia, asphyxiation due to  $O_2$  deficiency causes a progressive decrease in the blood-CO<sub>2</sub> (I), an initial rise and then a fall in  $p_{\rm H}$ , and a progressive increase in -lactic acid (II). In asphyxiation due to confinement, an initial increase in (I) is followed by a decrease,  $p_{\rm H}$  falls, and (II) decreases and then increases. CH. ABS.

Action of calcium-precipitating acids and salts on serum-calcium and its forms (calcium quotient). S. HERMANN and M. ZENTNER (Arch. exp. Path. Pharm., 1934, 175, 500-508).—Oral or subcutaneous administration of toxic but non-lethal doses of  $Na_2C_2O_4$  or  $H_2C_2O_4$  increases the free Ca (I) (i.e., Ca not pptd. with the blood-proteins), whilst lethal doses decrease both (I) and the total Ca (II). Citric, tartaric, and phosphoric acids and their salts increase (II) and, to a greater extent, (I). CaCl<sub>2</sub> increases both (I) and (II), the Ca quotient (A., 1932 81; 1933, 1182) being unchanged, whilst prior or subsequent subcutaneous or intravenous injection does not influence the effect of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. F. O. H.

Decrease of the magnesium content of bloodserum *in vivo* by intravenous injection of substances which precipitate magnesium. L. SEEKLES and B. SJOLLEMA (Biochem. Z., 1934, 272, 222—226).—By intravenous injection of an NH<sub>2</sub>-Na<sub>2</sub>HPO<sub>4</sub> mixture into young calves, the serum-Mg can be reduced by 29% of its initial val., but there is no proportionality between the amount of decrease and of reagent injected. Usually the Ca content is also decreased. Intravenous injection of 8-hydroxyquinoline decreases the Mg content only occasionally. P. W. C.

Behaviour of thiocyanate and sulphate in the organism on different diets. W. VON MORACZEW-SKI and R. ŚLIWIŃSKI (Biochem. Z., 1934, 272, 269– 276).—CNS' and SO<sub>4</sub>" injected subcutaneously or given by mouth to rabbit and man are excreted more rapidly the more alkaline is the urine, the effects being emphasised by acidification after administration of NH<sub>4</sub>Cl or alkalisation after NaHCO<sub>3</sub>. SO<sub>4</sub>" causes diuresis and is excreted more quickly than CNS', which causes H<sub>2</sub>O retention. P. W. C.

Physiological effect of trihydrol in liquid water. A. W. C. MENZIES (Science, 1934, 80, 72— 73).—A discussion (cf. this vol., 806). L. S. T.

Application of filtered ultra-violet rays in investigation of poisoning cases. F. W. MARTIN (Analyst, 1934, 59, 531—532; cf. A., 1926, 701; 1927, 1101).—The only fluorescent inorg. substance of medico-legal importance is HgCl, which gives a brilliant salmon-pink luminescence. E. C. S.

Enzymes, vitamins, and the zone of maximum colloidality. J. ALEXANDER (Science, 1934, 80, 79-80).—A discussion. L. S. T.

Isolation of crystalline yellow respiratory enzyme : reversible hydrolysis of the enzyme. H. THEORELL (Biochem. Z., 1934, 272, 155—156).— Material (20—30 g. containing 4—5 mg. of the pigment) treated with CHCl<sub>3</sub> by the method of Warburg and Christian is freed from almost all polysaccharide and part of the contaminating protein by cataphoresis at  $p_{\rm H}$  4·2—4·5. Fractional pptn. with  $(\rm NH_4)_2\rm SO_4$  at  $p_{\rm H}$  5·2 followed by dialysis against saturated aq.  $(\rm NH_4)_2\rm SO_4$  (2 vols.) + acetate buffer  $(p_{\rm H}$  5·2, 1 vol.) gives cryst. enzyme (N 15·5%, [ $\alpha$ ]  $-30^\circ$ ) in 60% yield. Hydrolysis into the two inactive components, pigment and protein, occurs when solutions of the enzyme are dialysed against dil. HCl. Activity and yellow colour are restored when cold, electrolyte-free solutions of the components are mixed. W. McC.

Activation by co-enzyme of the alcoholdehydrogenase of yeast. J. LEHMANN (Biochem. Z., 1934, 272, 95—103; cf. Müller, this vol., 448).—Purified solutions of the dehydrogenase (I) are obtained from yeast by extraction with aq. Na<sub>2</sub>HPO<sub>4</sub>. (I) is inactive until treated with co-enzyme (II) (adenosinetriphosphoric acid). The dehydrogenase of glycerophosphoric acid is activated by (II). Yeast cells contain a very active (I) which is activated by (II). O<sub>2</sub> cannot serve as H acceptor in the dehydrogenation of EtOH. W. McC. Purine metabolism enzymes of the mammary gland and of milk. D. MICHLIN and A. Rvžowa (Fermentforsch., 1934, 14, 389—394).—Xanthineoxidase (I) is much more loosely combined with glandular tissue than are other purine metabolism enzymes, and is therefore the only enzyme of this group found in milk. During incubation of minced mammary gland, considerable formation and later destruction of uric acid occur, enzymes of both nuclein and purine metabolism being present. (I) passes into solution in the cold and at the beginning of extraction, whereas guanase and adenase are set free much later at the beginning of autolysis.

P. W. C. Peroxidase reaction. XLIV. Short-timed peroxidase reaction of blood-leucocytes; prolongation of reaction in avitaminosis-B. T. SUZUKI. XLV. Arakawa's reaction of human milk from the toxicological point of view. A. TAKAMATSU. XLVI. Arakawa reaction and chlorine content of human milk. J. NOAZKI (Tôhoku J. Exp. Med., 1934, 23, 23-45, 46-59, 69-69). CH. ABS.

Irreversible inhibition of catalase. M. G. SEVAG and L. MAIWEG (Naturwiss., 1934, 22, 561– 562).—Catalase action is reversibly inhibited by the presence of diacetyl-di-, and -mon-oxime, phenylglyoxime, acetoxime, and acetaldoxime in buffered solution if the oximes are dissolved in dil. HCl and neutralised with NaOH. The oximes are ineffective if not treated in this way. H. D.

Carboxylase. F. AXMACHER and H. BERGSTER-MANN (Biochem. Z., 1934, 272, 259—268).—A method for the prep. of carboxylase in powder form is described. Extraction with 0·1*N*-HCl or -NaOH does not give more active solutions than does extraction with NaCl. The activity of the dry prep. is powerfully inhibited by I, SbCl<sub>3</sub>, NaNO<sub>2</sub>, CH<sub>2</sub>O, and to a smaller extent by CuCl<sub>2</sub>, FeCl<sub>3</sub>, Br, and BiCl<sub>3</sub>. P. W. C.

Amylase from sweet potato (*Ipomœa Batatas*). K. V. GIRI (J. Indian Chem. Soc., 1934, **11**, 339–350). —The amylase (mostly  $\beta$ -) is pptd. by EtOH from aq. extracts of sun-dried sweet potatoes (I) and can be further purified by dialysis. It is contained mostly in the inmost parts of (I). The optimum  $p_{\rm H}$  and temp. are 5.5–6.0 and 50–55°. Inactivation by heat (rapid at 55°) is unimol. and min. at  $p_{\rm H}$  5.4– 6.0. R. S. C.

Digestibility of some varieties of starch by pancreas-amylase of the dog and the pig. J. Roos and C. ROMIJN (Arch. Néerland. Physiol., 1934, 19, 392–402).—There is no digestion of raw starch. After boiling, potato starch is digested most quickly and then follow rice, wheat, sol., and commercial starch, all varieties being hydrolysed to the extent of 50–55%. H. G. R.

Pancreatic, salivary, and Aspergillus-amylase as mixtures of two enzymes. G. GIESBERGER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 336—342).—Breakdown of sol. starch by salivary amylase (I) and by taka-diastase (II) considerably exceeds the limit of 36—40% found for malt  $\alpha$ -amylase. Diffusion experiments in gelatin indicate the existence of two forms of amylase in (I), (II), and pancreatic amylase. L. D. G.

Invertase. I. Purification by precipitation. N. TAKETOMI (J. Soc. Chem. Ind. Japan, 1934, 37, 361–362B).—EtOH, MeOH, and  $COMe_2$  may be used to ppt. crude koji-invertase (I), but have an injurious effect on the activity of the purified material. Impurities may be removed by adding 1.2% Pb(OAc)<sub>2</sub>. With  $(NH_4)_2SO_4$  (I) is only partly pptd. A. L.

Invertase concentration of germinating rye with potassium or phosphate deficiency. I. G. VON DOBY and A. BODNAR. II. G. VON DOBY and J. MAKFALVI (Fermentforsch., 1934, 14, 250— 255, 256—265).—I. The  $p_{\rm H}$  optimum of the invertase (I) of rye shoots receiving either complete or K- or PO<sub>4</sub><sup>'''</sup>-deficient nutrition is always 4.6, but whereas the concn. of (I) is 1.5—3.5 times as great with K-deficient as with complete nutrition, it is little affected by PO<sub>4</sub><sup>'''</sup> deficiency. The concn. of (I) decreases with the age of the plants. The amount of (I) increases during autolysis at 38° and  $p_{\rm H}$  4.6 with shoots receiving complete, but not with shoots receiving K-deficient, nutrition.

II. The concn. of (I) is proportional or asymptotic to the amount of N of nutrition, different sources of N giving the same result; the  $p_{\rm ff}$  optimum is in all cases 4.5 and the temp. optimum 38°. The concn. of (I) decreases at night and with age. P. W. C.

Intermediate processes in the degradation of carbohydrates (lactic acid formation and alcoholic fermentation). O. MEYERHOF (Ann. Inst. Pasteur, 1934, 53, 221-242).—A lecture.

P. G. M.

Glyoxalase. II. Distribution in tissues of normal and cancerous albino rats. M. E. PLATT and E. F. SCHROEDER (J. Biol. Chem., 1934, 106, 179— 190; cf. this vol., 449).—The kinetic behaviour of glyoxalase (I) in aq. extracts of animal tissues (except the kidney and pancreas, which contain inhibitors) is identical with that in COMe<sub>2</sub>-yeast suspension. The (I) content in aq. extracts of organs of normal and cancerous rats and mice is determined; no relation exists between this and glycolytic activity. R. S. C.

Hydrolysis of hardened oil by pancreatic lipase. F. TOFTE (Biochem. Z., 1934, 272, 308— 316).—The greater is the degree of hardening of whale (I) and soya-bean (II) oil, the less is the velocity (III) of hydrolysis by pancreatic lipase. The difference in (III) for two oils of different degree of hardening decreases with rising temp. Experiments with tripalmitin, tristearin, and a mixture of triolein and tristearin show that (III) is not determined directly by the I val. and only indirectly by its effect on the m.p. Samples of (I) and (II) of the same m.p. had approx. the same (III). P. W. C.

Enzyme action in Merlangus vulgaris and Scyllium canicula. M. VAN HAUWAERT (Natuurwetensch. Tijds., 1934, 16, 227–232).—The action of aq. glycerol extracts of macerated portions of the digestive organs of *M. vulgaris* (I) and *S. canicula* (11) on fibrin at varying  $p_{\rm H}$  vals. was examined. With (I), the stomach extract is active at  $p_{\rm H} > 6.6$ , pyloric extract in alkaline and faintly acid solution, and the intestine extract, to a less degree, at  $p_{\rm H} > 6.8$ . In the case of (II), the stomach extract is extremely active at  $p_{\rm H} < 2$ , the intestine is less active, whilst the pancreas is without effect. Starch is hydrolysed by the stomach, but not by the intestine, of (I); in the case of (II), the diastatic activity falls in the order liver, intestine, pancreas, stomach. H. F. G.

Dilatometric studies in the proteoclastic degradation of proteins. II. Peptic hydrolysis. M. SREENIVASAYA and H. B. SREERANGACHAR (Biochem. J., 1934, 28, 1219—1221).—For caseinogen there is no linear relationship between dilatometric depression and liberated  $\rm NH_2$ -N (Van Slyke), but for gelatin an approx. proportionality holds. The average depression per millimol. of  $\rm NH_2$ -N in both cases is > for tryptic hydrolysis, pointing to a different mode of attack. C. G. A.

Antitrypsin of egg-white. A. K. BALLS and T. L. SWENSON (J. Biol. Chem., 1934, 106, 409— 419).—The antitrypsin (I) has been conc. from thin egg-white and is insol. in org. solvents and sol. in H<sub>2</sub>O. It is destroyed by  $H_2O_2$  and NaOH, and may possibly be an  $\cdot$ S·S·-containing peptide. The action of (I) is the same on active and inactive trypsin, but the progress of activation is retarded, and there is a disappearance of  $CO_2H$  already present in the digestion mixture. H. G. R.

Defence enzymes of the polypeptidase group. R. ABDERHALDEN (Fermentforsch., 1934, 14, 370– 388).—Polypeptidase (I) of blood does not attack polypeptides (II) in which the free NH<sub>2</sub> is substituted. Plasma-(I) and erepsin react similarly in their behaviour to (II) and to benzoyl- and 2-naphthalenesulpho-polypeptide. After parenteral administration of these substituted (II), defence enzymes of the carboxy-(I) type appear in the blood. P. W. C.

Comparative investigation of the relative and absolute specific defence enzyme reactions using substrates from smooth and striated muscle. E. BRUNER (Fermentforsch., 1934, 14, 345-356),— The defence enzyme reactions of peptone and protein preps. from skeletal, heart, intestine, and uterus musculature of rabbit, dog, and ox are recorded.

P. W. C.

Change of blood- and organ-proteins on ageing as shown by defence enzyme reactions. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 357—366).—Using protein preps. from serum, kidney, lung, liver, brain, and muscle of rabbit and of man of various ages, differences with age are detected by defence enzyme reactions in the fine structure of the protein. P. W. C.

Dependence of the composition of the proteins of blood-serum and -plasma on the diet. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 333-344).—By means of the defence enzyme reaction, individual differences in the fine structure of serum-protein and differences due to changes of nutrition can be detected. P. W. C. Influence of ultra-violet light on serum-proteins as shown by defence-enzyme reactions. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 295-310).—Irradiation of the proteins of blood-plasma or -serum leads to their more ready disintegration, both in the body by the defenceenzyme system and *in vitro* by gastric juice.

P. W. C.

Technique of the interferometric method of [carrying out] the Abderhalden reaction. J. WADEL (Fermentforsch., 1934, 14, 266—282).—The sources of error in carrying out this reaction are discussed and a description of the prep. of the organprotein substrate, of the technique of the reaction, and of taking readings is given. P. W. C.

Critique of the interferometric method. P. HIRSCH (Fermentforsch., 1934, 14, 311-317).

P. W. C.

Arginase and arcaine. E. BALDWIN (Biochem. J., 1934, 28, 1155—1156).—Arcaine is not attacked by arginase from guinea-pig liver. H. D.

**Tyrosinase in Macrolepidoptera.** C. E. M. PUGH (Biochem. J., 1934, 28, 1198—1200).—Tyrosinase (I) is present in all 29 species tested. Peroxidase was absent from all and a feeble laccase found in some species. The difference in marking of spring and summer broods of *Pieris rapæ* and *P. brassicæ* is not due to difference in (I) content. C. G. A.

Influence of vitamin-C on the action of tyrosinase. E. ABDERHALDEN (Fermentforsch., 1934, 14, 367-369).—After addition of 0.01-0.001 g. of ascorbic acid (I) to a solution containing adrenaline (0.01 g. in 20 c.c. of H<sub>2</sub>O) the latter was not oxidised to the red pigment, and the solution gave a green FeCl<sub>3</sub> colour and the usual biological tests for adrenaline. Tyrosine, 3:4-dihydroxyphenylalanine, and *dl*-adrenaline in presence of tyrosinase were all similarly stabilised by (I). P. W. C.

Phosphoglycerase in red blood-corpuscles. A. E. BRAUNSTEIN (Biochem. Z., 1934, 272, 21–23; cf. A., 1933, 1202).—Hæmolysed (but not intact) erythrocytes (rabbit, pigcon) produce  $AcCO_2H$  from added phosphoglyceric acid. W. McC.

Influence of antiseptics on the autolytic enzymes of yeast with special reference to the elimination of phosphoric acid. H. HAEHN and H. LEOPOLD (Fermentforsch., 1934, 14, 318—332).— The formation of volatile acid and  $H_3PO_4$  and the degradation of protein are followed during autolysis of yeast at 50—52° using PhMe, CHCl<sub>3</sub>, and EtOAc as antiseptics. The normal displacement of  $p_{\rm H}$  to the acid side during autolysis without antiseptic is considerably inhibited by PhMe and CHCl<sub>3</sub>, whilst the phosphatases and proteolytic enzymes are inhibited by CHCl<sub>3</sub> and EtOAc. P. W. C.

Micrometabolism of yeast cells. E. A. PRIBRAM and L. KOTLER (J. Bact., 1934, 27, 24).— Saccharomyces cerevisiæ and S. lactis absorb more glucose than galactose or lactose. The presence of CaCl<sub>2</sub> decreases and of KCl or FeCl<sub>3</sub> increases the absorption of sugars by both organisms, the effect of KCl being > that of FeCl<sub>3</sub>. A. G. P. Biochemical control of heat-resistance [of yeast]. N. A. CHLEBNIKOVA and G. V. BOLONDZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 584—588). —With two strains of Saccharomyces cerevisiæ cultivated for 10—15 years at 8° [bottom yeast (I)] and 20° [top yeast (II)], respectively, the growth in unhopped wort at various temp.  $\propto$  the increase in NH<sub>2</sub>-N content. The optimum temp. for growth was 8—22° for (I), but approx. 40° for (II). F. O. H.

Relationship between metabolic processes of micro-organisms and the oxido-reduction potential of the medium. II. A. J. KLUYVER and J. C. HOOGERHEIDE (Biochem. Z., 1934, 272, 197-214).— By using a Au electrode within the fermentation flask of a Warburg manometric apparatus, the oxido-reduction potential of media containing living cells and the type of metabolism of the cells are determined. Using the apparatus with different kinds of yeast in a buffer medium of  $p_{\rm H}$  5.4 containing sugar, the potential was always about 90 mv. independently of the strain of yeast or the kind or concn. of the sugar. If air replaces N<sub>2</sub> in the Warburg apparatus, the potential is higher. The potential val. characterises the nature of the metabolic processes of the cell.

P. W. C. Effect of oxidation-reduction character of the medium on initiation of yeast growth. J. J. REID and I. L. BALDWIN (J. Bact., 1934, 27, 29–30). —The ability of *Saccharomyces cerevisiæ* to initiate growth is influenced by the oxidation-reduction potential of the medium. A. G. P.

Increase of invertase content of bottom yeast. R. WEIDENHAGEN (Angew. Chem., 1934, 47, 581– 582).—A max. increase ( $\times 10-15$ ) in the invertase content (I) of bottom yeast is obtained by fermentation in presence of min. concns. of sucrose (cf. A., 1925, i, 1214) and with increased aeration. Optimal conditions include a fermentation period of 8—10 hr., a temp. of 41°, and  $p_{\rm H} 4\cdot 5$ —5.5. Sucrose and fructose give the highest vals. of various carbohydrates. The growth in yeast is not related to (I). The nonappearance of the increase in (I) when air is replaced by N<sub>2</sub> indicates that it is not due to agitation or to the removal of metabolic products. F. O. H.

Effect of esters of *p*-hydroxybenzoic acid on alcoholic fermentation. R. CULTRERA (Annali Chim. Appl., 1934, 24, 282–288).—The effect of salicylic acid (I), nipagin-*M* (*p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me) (II), nipasol (the Pr ester) (III), and nipakombin (Na salts of nipagin and nipasol) (IV) on the alcoholic fermentation of a solution containing glucose, KH<sub>2</sub>PO<sub>4</sub>. NH<sub>2</sub>Ac, MgSO<sub>4</sub>, and CaSO<sub>4</sub> has been studied. At  $p_{\rm H}$  7, fermentation is stopped by > 2.6, 2.5, 1.2, and 2.5 parts per 1000 of (I), (II), (III), and (IV) respectively; at  $p_{\rm H}$  3.2 : 1, 2.05, 1, and 1.45. T. H. P.

Effects of carbohydrates on growth of Euglend anabaena var. minor in darkness. R. P. HALL (Arch. Protistenk., 1934, 82, 45—50).—Multiplication of the organism is favourably influenced by glucose and fructose and, to a smaller extent, by maltose, but by no other carbohydrate examined. No change in the  $p_{\rm H}$  of the media resulted. No change Cellulose digestion by ciliates in the ruminant stomach. E. WEINECK (Arch. Protistenk., 1934, 82, 169–202).—The mechanism of the process of digestion is examined. A. G. P.

Limits of  $p_{\rm H}$  for some saprophytic flagellates. E. G. PRINGSHEIM (Naturwiss., 1934, 22, 510).— Limits of  $p_{\rm H}$  in a buffered synthetic medium for multiplication of *Polytoma uvella*, *Polytomella agilis*, *Chilomonas paramecium*, *Chlorogonium euchlorum*, and *C. elongatum* are characteristic, and some conclusions as to their natural occurrence can be reached, subject to the fact that  $p_{\rm H}$  limits alter with the composition of the medium. R. K. C.

Photogenic granules of Watasenia scintillans (Berry). Y. K. OKADA, S. TAKAGI, and H. SUGINO (Proc. Imp. Acad. Tokyo, 1934, 10, 431–434).—The size of the granules in the brachial organs is  $2 \cdot 5 5 \mu \times 1 \cdot 0 - 3 \cdot 0 \mu$ . The granules are insol. in Et<sub>2</sub>O and CHCl<sub>3</sub>; they appear to be crystalloids of protein nature and give a positive biuret reaction, whereas those from the luminous bacteria obtained from the octopus give a negative reaction. They are not lipins, since they do not oxidise pyrogallol,  $p \cdot C_6 H_4(NH_2)_2$ , etc., as do the lipin constituents of mitochondria.

P. G. M.

Chemical constituents of the mycelium of **Oospora aurantia** (Cooke), Sacc. et Vogl. H. NISHIKAWA (Proc. Imp. Acad. Tokyo, 1934, 10, 414– 416).—By extraction of the dried mycelium with  $Et_2O$ , 3% of cryst. material is obtained. *Oosporin*,  $C_{10}H_{14}O_2$ , decomp. 176°, forms an *Ac* derivative. *Aurantin*,  $C_{16}H_{22}O_3$ , decomp. 183°, is more sol. in cold  $Et_2O$  than (I). Both compounds give a purplishbrown colour with FeCl<sub>3</sub>. P. G. M.

Biochemical origin of citric and oxalic acids. I. Formation of citric from acetic acid. V. S. BUTKEVITSCH, E. V. MENZSCHINSKAJA, and E. I. TROFIMOVA (Biochem. Z., 1934, 272, 290—307).— Evidence is brought against the view that citric acid (I) is formed by moulds from sugar by way of AcOH (II). The small amounts of (I) formed by moulds when grown on (II) arise from the mycelial substance and not directly from (II), and any apparent increase of production of (I) on addition of (I1) is due to the strong inhibition which (II) exerts on the utilisation of (I). There is no direct relationship between the utilisation of (II) and the production of (I).

## P. W. C.

Salt intake of Aspergillus niger. E. RENNER-FELT (Planta, 1934, 22, 221–239).—Normal development of the mould occurs in the absence of Ca and Mn. Spores contain larger proportions of cations than does mycelium. The intake of bases was in the order K >Mg >Na; Ca and Mg exhibited antagonism especially towards K. Salt absorption is influenced by the permeability factor, by the concn. of the ions in the medium, and by the ability of the cells to accumulate and store particular ions. A. G. P.

Citric fermentation by Aspergillus niger. W. SCHWARTZ and H. LANG (Arch. Mikrobiol., 1934, 5, 387-401).—Growth of A. niger in lemons lowers the capacityfor citric acid (I) formation, but this is restored by culture on gelatin (II) media. The fermentative capacity of the organism varies with the age of the conidia used. The yield of (I) is increased by addition of  $CaCl_2$  or (II). In the latter case the growth of the mould is simultaneously accelerated. CHCl<sub>3</sub>, As compounds, and KCN restrict the formation of (I). The last-named probably acts indirectly by retarding growth and delaying the initiation of fermentation. (II) also induces rapid decomp. of the (I) formed, but this action is minimised by addition of mineral acid to the culture. A. G. P.

Biochemistry of micro-organisms. XXXIX. Metabolic products of *Penicillium crateriforme*, Gilman and Abbot. A. E. OXFORD and H. RAIS-TRICK (Biochem. J., 1934, 28, 1321—1324).—Spiculisporic acid (A., 1931, 1092), succinic acid, and an unidentified complex polysaccharide have been isolated. H. G. R.

Ability of a mould or its metabolic products to inhibit bacterial growth. R. D. REID (J. Bact., 1934, 27, 28).—The inhibitory substance (I), produced by a mould strain closely resembling *Penicillium notatum*, is similar to but not identical with the pigment formed simultaneously. Its formation is accompanied by alkaline material, but once formed its activity is not affected by  $p_{\rm H}$ . (I) is relatively thermostable, contains enzymes (notably amylase and catalase), and is adsorbed by activated C. A. G. P.

Stimulation of fungus spore germination by aqueous plant extracts. F. WILCOXON and S. E. A. MCCALLAN (Phytopath., 1934, 24, 20).—Germination of a no. of spores was stimulated by addition of small amounts of fruit juice (orange, tomato, etc.), of aq. extracts of lily or gladiolus bulbs, or of potato or dahlia tubers. Vitamin-C and inositol with "bios II" were non-effective. The stimulatory factor is heatstable and dialysable. A. G. P.

Attempted removal of staling substances of fungus cultures. J. C. CARTER (Phytopath., 1934, 24, 4).—In media staled with *Helminthosporium* sativum or with a certain bacterial culture, sterilisation did not inactivate the staling agent, which migrated to the negative pole of a Bradfield dialyser.

A. G. P.

Fermentation of citron. C. R. FELLERS and E. G. SMITH (J. Bact., 1934, 27, 63).—Organisms concerned in the preliminary brine fermentation of citron are examined and their biochemical activities described. A. G. P.

Utilisation of slime-forming micro-organisms. J. R. SANBORN (J. Bact., 1934, 27, 61).—Under suitable conditions the activities of slime-forming organisms from pulp and paper may result in desirable products, e.g., sol. gum-like substances, insol. materials resembling cellulose, mucilaginous and gelatinous products possessing adhesive and cohesive properties. A. G. P.

Acidoproteolytes in gaseous associative fermentation in milk. C. GORINI (J. Bact., 1934, 27, 69-70).—This type of fermentation may occur in milk if only two types of saccharolytic bacteria are present, provided one of these is both saccharolytic and proteolytic, e.g., the group of Acidoproteolytes, Gorini. A. G. P. Economical sugar fermentation [by bacteria]. H. J. CONN and M. A. DARROW (J. Bact., 1934, 27, 51—52).—The soil organism, *B. globiforme*, is capable of free growth with unusually small supplies of sugar. The only by-product is  $CO_2$ , and approx. 40% of the C utilised is converted into cell substance.

A. G. P.

Synthesis of carotene by bacteria. M. A. INGRAHAM and C. A. BAUMANN (J. Bact., 1934, 27, 25-26).—Bacteria of varied types produced carotene (I), but in no case was this found in anaërobic organisms. The (I) content of a given species varied with age and cultural conditions, max. being reached shortly prior to the exhaustion of supplies of available carbonaceous matter. In *Mycobacterium phlei* variations in (I) content are paralleled by those of lipins. In media having  $p_{\rm H} > 8.3$  (I) formation was minimised. A. G. P.

Production of lipins by bacteria. I. Total fat formation by *B. prodigiosus* on solid media. II. Total fat formation by *B. prodigiosus* in nutrient solutions. G. GORBACH and A. SABLAT-NÖG (Arch. Mikrobiol., 1934, 5, 311-317, 318-327).— I. Lipin (I) formation varied with the age of the culture and the reaction of the medium, max. vals. being obtained in S-day cultures at  $p_{\rm H}$  6.6. Addition of EtOH increased the production of (I), especially in alkaline media. Among C sources examined glycerol favoured (I) formation more than did glucose or sucrose.

II. Similar conditions prevailed in liquid media, but the actual amounts of (I) produced were considerably greater. An optimum concn. for (I) formation exists for each C source. In this respect  $NH_4$  salts of org. acids (malic, lactic) were more suitable sources of N than caseinogen or peptone. The amounts of (I) obtained increased with the concn. of N supplied. The (I) contained 12.8% of unsaponifiable matter.

A. G. P.

Lipolytic activities of several bacteria causing bitter cream. J. T. MCGRATH and J. A. ANDERSON (J. Bact., 1934, 27, 68-69).-Of the fatty acid glycerides occurring in butter, only those of low mol. wt. (except tripalmitin) are rapidly hydrolysed by the organisms, tributyrin being the most readily decomposed. Glycerides of solid and semi-solid fatty acids undergo little change in 25 days. Tripalmitin is hydrolysed slowly at first, but subsequently breaks down as rapidly as the simpler homologues. Taste, odour, and throat irritation associated with bitterness in cream may be produced by additions of small amounts of the simpler acids, n- and iso-hexoic acid being particularly active in this respect. A. G. P.

Decomposition of alginic acid by microorganisms. M. C. ALLEN (J. Bact., 1934, 27, 59— 60).—Decomp. of alginic acid (I) by certain bacteria is probably an incomplete hydrolysis. The total uronic acid content suffers little loss. The medium shows rapid increase in  $p_{\rm H}$ . None of the fungi examined attacked (I). A. G. P.

Methane fermentation of organic acids and carbohydrates. D. TARVIN and A. M. BUSWELL (J. Amer. Chem. Soc., 1934, 56, 1751–1755).—The amounts of  $CO_2$  and  $CH_4$  produced during anaërobic

fermentation of various fatty, α-OH-, CO-, and NH<sub>2</sub>acids, Ph[CH<sub>2</sub>]<sub>n</sub>CO<sub>2</sub>H (I), aromatic compounds, and carbohydrates were determined. (I) (n=1-2) and BzOH are completely destroyed; lower fatty acids appear to be intermediates. Lactic acid is first reduced to EtCO<sub>2</sub>H, which is also produced by reduction (and subsequent decarboxylation) of malic and tartaric AcCO<sub>2</sub>H undergoes fission to AcOH and acids. HCO<sub>2</sub>H, whilst alanine and tyrosine (II) are deaminated. PhOH is produced from (II) and then undergoes further slow decomp. Decomp. of glucose, fructose, sucrose, and starch occurs in 2 stages : (i) production of volatile acids (and possibly some non-volatile substance), much  $CO_2$  and  $H_2$ , and little  $CH_4$ ; (ii) decomp. of intermediate acids to much CH4, little CO2, and no H2. PhCHO, C6H6, PhBr, PhMe, and NH2Ph are not attacked.

Fermentation of tobacco. J. JOHNSON (J. Agric. Res., 1934, 49, 137–160).—Heat generated during fermentation of tobacco  $\infty$  the H<sub>2</sub>O present (min. 30%). Treatment with CHCl<sub>3</sub>, HgCl<sub>2</sub>, COMe<sub>2</sub>, PhMe, or  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH largely reduces thermogenesis by restricting bacterial activity (I) and inactivating, although not destroying, enzymes (II). AgNO<sub>3</sub> lowers heat production by approx. 50%, (I) being prevented but (II) remaining unaffected. Micro-organisms, notably fungi, are concerned in the processing of cigar leaf. A. G. P.

Development of micro-organisms on fermenting tobacco. G. P. VOLGUNOV (State Inst. Tobacco Invest., U.S.S.R., 1933, No. 87, 52—72).—The influence of composition of medium, reaction, and  $O_2$ tension is discussed. Small quantities of CH<sub>2</sub>O stimulate the activity of the fungi, which do not grow in 75% CO<sub>2</sub>. CH. Abs.

Strain variation of Azotobacter and the utilisation of carbon compounds. N. R. SMITH (J. Bact., 1934, 27, 54—55).—All strains examined utilised sucrose and glucose, but considerable differences were shown in ability to act on mannitol, glycerol, lactose, starch, and dextrin. A. G. P.

Growth limits of Azotobacter chroococcum in the alkaline range. H. WENZL (Arch. Mikrobiol., 1934, 5, 358–365).—For strains isolated from arable soils the growth limit was  $p_{\rm H}$  9·1—9·2; for those from saline soils of high Na content vals. were 0·3—0·4 unit higher. A. G. P.

Magnesium, calcium, and iron requirements for growth of *Azotobacter* in free and fixed nitrogen. C. K. HORNER and D. BURK (J. Agric. Res., 1934, 48, 981—995).—The concns. of nutrient elements required by the organism to produce halfmax. growth were determined. Vals. for Ca approached zero in fixed N, and  $2-5 \times 10^{-5}M$  in free N<sub>2</sub>. Vals. for Mg and Fe were independent of the nature of the N source. Mg is essential to the growth process and no other element examined can replace it. A. G. P.

Accessory factor for legume nodule bacteria. Sources and activity. F. E. ALLISON and S. R. HOOVER (J. Bact., 1934, 27, 561—581).—The growth factor (a respiratory co-enzyme) occurs in considerable proportions in yeast, cane molasses, humic acid, and commercial ovalbumin and may be obtained in moderate concn. by extraction of commercial sucrose or cane molasses with abs. EtOH. A. G. P.

Production of peroxidase by Streptococci and its possible significance. M. A. FARRELL (J. Bact., 1934, 27, 24–25).—The presence of peroxidase (I) was demonstrated in all strains examined. Colour tests for (I) are examined. The (I) of Streptococci withstands autoclaving at 120° for 15 min. The colour reactions are inhibited by respiratory poisons (KCN,  $H_2S$ ,  $CH_2I \cdot CO_2H$ , etc.). A. G. P.

Separation of some cellular constituents of the Brucella group of micro-organisms. R. C. HUSTON, I. F. HUDDLESTON, and A. D. HERSHEY (Michigan Agric. Exp. Sta. Tech. Bull., 1934, No. 137, 25 pp.).—From B.abortus, B. melitensis (I), and B. suis nucleoproteins, sol. proteins, lipins, and sol. polysaccharides, but no simple carbohydrate, have been isolated. Each species contains two biologically inactive polysaccharides and two lipins, the proportions of these being characteristic for the different species. (I) was peculiar in yielding a N-containing substance [S substance (II)] which seems to be neither a protein nor a carbohydrate. (II) reacts with Brucella antiserum in a dilution of 1 in 10<sup>5</sup>. W. O. K.

Influence of concentration of soluble calcium on the precipitation of calcium carbonate by micro-organisms. F. T. WILLIAMS and E. B. FRED (J. Bact., 1934, 27, 58—59).—Organisms from lake muds pptd. cryst. calcite from artificial media containing 0.01-0.02% of CaCl<sub>2</sub>. A. G. P.

Products of oxidation of thiosulphate by bacteria in mineral media. R. L. STARKEY (J. Bact., 1934, 27, 53-54).—The organism examined (probably *Thiobacillus thioparus*) converted 60% of  $S_2O_3''$ -S into  $SO_4''$  and 40% into free S. A second organism produced from  $Na_2S_2O_3$  equimol. proportions of  $Na_2SO_4$  and  $H_2SO_4$ . In the case of *T. trautweinii*,  $Na_2S_4O_6$  is the initial product, although this subsequently breaks down to yield varied S products. The C assimilation of these bacteria is examined.

A. G. P.

Oxygen consumption of luminous bacteria in water containing deuterium oxide. E. N. HARVEY and G. W. TAYLOR (J. Cell. Comp. Physiol., 1934, 4, 357—362).—Luminescence (I) and respiration (II) of a salt-H<sub>2</sub>O bacterium were reduced by a heavy H<sub>2</sub>O concn. of 86%. With fresh-H<sub>2</sub>O organisms (II) was reduced without effect on (I). A. G. P.

Effect of narcotics on respiration and luminescence in bacteria with special reference to the relation between the two processes. G. W. TAYLOR (J. Cell. Comp. Physiol., 1934, 4, 329—355).— Respiration (I) and luminescence (II) vary with the amount of nutrient matter in the medium, the effect on (I) being > that on (II). Low concess of narcotics stimulate and higher proportions cause a reversible narcosis of both processes, the threshold of susceptibility for (I) being > for (II). The relative effectiveness of homologous series of narcotics  $\infty$  the relative lipin solubilities and their ability to lower surface tension. (I) and (II) are probably independent processes. Et urethane inactivates luciferase in *Cypridina* extracts. A. G. P.

Light intensity of luminous bacteria as a function of oxygen pressure. H. SHAPIRO (J. Cell. Comp. Physiol., 1934, 4, 313—327).—Light intensity (I) of Vibrio phosphorescens is not affected by  $O_2$  pressures > 1.06 mm. Hg. At lower pressures (I) declines steadily and is not measurable by a photoelectric cell at 0.076 mm. A. G. P.

Lipins of tubercle bacilli. XXXIX. Tuberculostearic acid. M. A. SPEELMAN (J. Biol. Chem., 1934, 106, 87—96).—Tuberculostearic acid (Anderson, A., 1932, 1290),  $C_{19}H_{38}O_2$ , is oxidised by  $CrO_3$  in AcOH to Me *n*-octyl ketone, azelaic and octoic acids. dl*t*-Methylstearic acid was synthesised, m.p. 20—21° (amide, m.p. 76—77°; 2:4:6-tribromoanilide, m.p. 93—94°). It resembles (I) very closely, but identity is not established. H. D.

Antigenic properties of lipins of tubercle bacilli. II. Specificity. M. YATO (Manshu-igaku-zasshi, 1932, 17, No. 5).—A study of avian, bovine, and frog types of bacilli. CH. ABS.

Toxin of tubercle bacilli. I. Refining method for tuberculin and formol-tubercle bacilli. II. Specificity of toxin of tubercle bacilli. M. YATO (Manshu-igaku-zasshi, 1933, 18, No. 4).—Tuberculin free from albumin was obtained from culture filtrates by absorption with  $Al(OH)_3$ . Intracutaneous tests are described. CH. ABS.

Spectral analysis of purified tuberculin. M. SPIEGEL-ADOLF and F. B. SEIBERT (J. Biol. Chem., 1934, **106**, 373—385).—When prepared by  $CCl_3 \cdot CO_2H$ pptn. human tuberculin contained thymus-nucleic acid (I). When fractionated with  $(NH_4)_2SO_4$  (I) was absent, the P content lower, but the biological activity was not impaired. No trace of (I) could be found in preps. from non-pathogenic acid-fast bacteria, but from pathogenic acid-fast bacteria there was a definite correspondence between (I) and the potency.

H. G. R. **Purification of vaccinia virus.** M. SCHAEFFER and H. NALIBOW (Amer. J. Public Health, 1934, 24, 736—738).—Vaccinia virus is adsorbed on casein and other adsorbents, but best on a mixture of casein and Al(OH)<sub>3</sub> adjusted to  $p_{\rm H}$  4.9—5.5 by addition of KH<sub>2</sub>PO<sub>4</sub>. It is recovered in good yield by elution at  $p_{\rm H}$  8.0. W. O. K.

Re-alkalisation effect in virus species. G. PyL (Z. physiol. Chem., 1934, 226, 18–28).—The virus of stomatitis vesicularis is stable within the  $p_{\rm H}$ range 3.5—11.5. It shows neither the double max. nor the min. given by the virus of foot-and-mouth disease and there is no "re-alkalisation effect" (cf. A., 1933, 984). J. H. B.

Artificial production of a lytic agent which behaves like bacteriophage. J. D. LE MAR and J. T. MYERS (J. Bact., 1934, 27, 49).—Optimum results were obtained by autoclaving a 48-hr., culture of *E. coli*, permitting autolysis for a further 48 hr., and subsequently oxidising (48 hr.) with 3% H<sub>2</sub>O<sub>2</sub>. Oxidation of living cultures or autolysis of killed cultures without oxidation failed to produce a lytic agent.

A. G. P.

Bacteriological media. O. ACKLIN and R. G. VUILLEMIN (Mitt. Lebensm. Hyg., 1934, 25, 224-235).-Culture experiments with B. coli, fluorescens, and putrificus in various media are described. The following " universal medium " is suggested. 18 g. of agar, 5 g. of Liebig's meat extract, and 10 g. of peptone in 750 c.c. of H<sub>2</sub>O are autoclaved at 104° for 15 min., 10 g. of commercial sol. starch are treated hot with 250 c.c. of  $H_2O$  + 2 c.c. of N-NaOH, and the two filtered solutions are mixed and adjusted to  $p_{\rm H}$  7.8-8.2 with NaOH; 10 g. of "catan," 1 g. of glucose, and 10 c.c. of 0.2M-phosphate buffer  $(p_{\rm H} 7.2)$  are added, the  $p_{\rm H}$  of the final filtered medium being adjusted to 7.0-7.2 with HCl. "Eatan" contains NaCl 18.36, total N 3.71, creatinine 0.40, and total acidity (as lactic acid) 1.91%. J. C.

Metal tank for the preparation of mass cultures of anaërobic bacteria. C. WEISS and E. J. CZAR-NETZKY (Amer. J. Public Health, 1934, 24, 713—714). —A jar made from a cast Al pressure cooker suitable for the growth of anaërobic bacteria on a large scale is described. W. O. K.

Cotton-blue as a mycological stain. C. G. C. CHESTERS (Ann. Bot., 1934, 48, 820—822).—Methods for staining permanent preps. of mycelium and for the direct examination of hyphæ in woody tissue are described. A. G. P.

Mercurochrome as a bacteriological stain. M. E. CONKLIN (J. Bact., 1934, 27, 30–31).—The use of mercurochrome in observations of changes in bacterial spores is described. A. G. P.

Effect of certain triphenylmethane dyes on Staphylococcus aureus and B. coli communis. M. V. REED and E. F. GENUNG (J. Bact., 1934, 27, 29). Bacteriostatic effects of, and the "adaptability" of the organisms to, a no. of dyes are examined.

A. G. P.

Bacteriostatic azo-compounds.—See this vol., 1109.

Preparation and germicidal properties of some alkyl derivatives of hydroxydiphenyls.— See this vol., 999.

Bacterostatic effect of indole and skatole. L. A. SANDHOLZER and R. P. TITTSLER (J. Bact., 1934, 27, 28—29).—The inhibitory action of indole (I) and skatole (II) on numerous organisms is examined. (II) is more active than (I), although there is a general parallelism in their effects in relation to concn. A. G. P.

Determination of indole in bacterial cultures. F. C. HAPPOLD and L. HOYLE (Biochem. J., 1934, 28, 1171—1173).—Indole is determined in bacterial cultures by twice extracting with light petroleum or xylenc, extracting the resultant solution with Ehrlich's reagent, and comparing the solution of rosindole with a standard. H. D.

Pneumococcicidal powers of sodium oleate and sodium ricinoleate. L. A. BARNES and C. M. CLARKE (J. Bact., 1934, 27, 107–108).—Min. concns. of the soaps necessary to devitalise broth cultures of *Pneumococcus* were 0.0004% (oleate) and 0.004%(ricinoleate). A. G. P. Survivor curves exhibited by bacterial spores in chlorine disinfection. D. B. CHARLTON and M. LEVINE (J. Bact., 1934, 27, 37–38).—The nature of survivor curves indicates differences in the mechanism of disinfection by hypochlorites and by chloroamines. A. G. P.

Germicidal efficiency of hypochlorite solutions in presence of chicken manure. E. C. MCCULLOCH (J. Bact., 1934, 27, 37).—Hypochlorite solutions containing as little as 130 p.p.m. of available Cl killed Salmonella pullorum in the presence of a 5% suspension of chicken manure. The formation of a derivative of  $\rm NH_2Cl$  by interaction with  $\rm NH_3$ from the manure is indicated. A. G. P.

Oligodynamic action of metals and metallic salts. C. W. RAADSVELD (Chem. Weekblad, 1934, 31, 497-504).—A review. H. F. G.

Practical applications of oligodynamic action. C. W. RAADSVELD (Chem. Weekblad, 1934, 31, 505– 510).—A review. H. F. G.

Effect of muscle extracts on blood-sugar. GOEBEL (Compt. rend. Soc. Biol., 1934, 115, 1135– 1137).—Rabbit muscle contains a substance (I) having a sp. effect on carbohydrate metabolism. The thyroid plays an important part in the production of (I).

NUTR. ABS. (m) Hypoglycæmic action of duodenal extracts. J. LA BARRE and J. LEDRUT (Compt. rend. Soc. Biol., 1934, 115, 750—752).—Hydrolysis of secretin by pepsin or pancreatic juice activated by enterokinase yields a product having marked hypoglycæmic action, per os or intravenously, in normal and depancreatised dogs. NUTR. ABS. (m)

Insulin content of the pancreas in cattle at various ages. A. M. FISHER and D. A. SCOTT (J. Biol. Chem., 1934, 106, 305–310).—The amount of insulin, in international units per g., obtainable from the pancreas by an improved technique (described) is: fœtal calves, < 5 months old, 29·2–38·8, 5–7 months, 21·1–24·9; calves, 6–8 weeks (milk diet), 10·4–12·8; cattle, 2 years, 3·9–6·1; cows, > 9 years, 1·7–2·0, > 7 years (pregnant), 2·0–2·3. R. S. C.

Action of phenylcarbimide on insulin. S. J. HOPKINS and A. WORMALL (Nature, 1934, 134, 290).— The activity of insulin (I) is destroyed in 10 min. at 5.—8° by treatment with phenyl- or *p*-bromophenylcarbimide. The carbimide reacts with all the free NH<sub>2</sub> of (I), which appears to contain free NH<sub>2</sub> in addition to that of the lysine mols. The basic groups of insulin appear, therefore, to be of importance in the physiological activity of (I). L. S. T.

Peptic hydrolysis of insulin. A. M. FISHER and D. A. SCOTT (J. Biol. Chem., 1934, 106, 289–303).—. A method for determining the N distribution in 0.2 gof insulin (I) is described. Destruction of the potency of (I) by pepsin is accompanied by decrease in tyrosine, increase in lysine, but no change in cystine content. Slight deactivation changes the cryst. form of (I). R. S. C.

Rôle of insulin in peripheral metabolism. N. B. LAUGHTON and A. B. MACALLUM (Nature, 1934, 134, 325).—The relative effects of Et urethane, cyanides, NaF, and  $CH_2I \cdot CO_2H$  on the action of insulin on rabbits have been examined. Results indicate that the insulin mechanism is largely concerned with the reaction between  $\alpha$ -glycerophosphoric and pyruvic acids resulting in the formation of lactic acid.

L. S. T.

Dietetic factors influencing the glucose tolerance and the activity of insulin. H. P. HIMS-WORTH (J. Physiol., 1934, 81, 29—48).—Adult male rabbits on a fat-rich diet (soya bean and limited cabbage) become resistant towards insulin (I). The hyperglycæmia following intravenous injections of glucose is also more marked and, on repeated injections, slower in declining than in rabbits receiving excess of carbohydrates (oats, bran, and excess cabbage). Thus diet alters the susceptibility towards (I), rather than causes variations in the internal secretion of (I). (I) as secreted is probably inert, and becomes activated by a tissue-kinase the production of which depends on diet. NUTR. ABS. (b)

Effect of insulin on ketonic substances. A. Löw and A. KRÖMA (Wien. Arch. inn. Med., 1934, 24, 455—462).—One hr. after injection of insulin into man or animals, an increase occurs in ketones of blood and urine, subsiding or disappearing when insulin response is greatest. NUTR. ABS. (b)

Secretion of insulin during hyperaminoacidæmia. J. LA BARRE (Compt. rend. Soc. Biol., 1934, 115, 748—750).—Injection of large doses of glycine causes hypoglycæmia, which is due chiefly to increased secretion of insulin of adrenal origin.

NUTR. ABS. (m)

Mechanism of insulin secretion. IV. Dynamics. E. S. LONDON and N. P. KOTSCHNEFF (Pflüger's Arch., 1934, 234, 194—199).—The insulin (I) content of the blood of the pancreatico-duodenal vein and femoral artery of dogs was determined by its effect on the blood-sugar (II) of mice. Increase of (II) produced by injection of glucose or adrenaline led to an increase of (I) in the pancreatico-duodenal vein : the secretion of (I) was inhibited by blockage of the vagus nerve by atropine (III). When (III) was injected prior to the production of the hyperglycæmia the secretion of (I) was stimulated.

NUTR. ABS. (b)

Assay of insulin and the blood-sugar level. M. C. HRUBETZ (Amer. J. Physiol., 1934, 107, 284— 292).—The blood-sugar (I) of rats falls progressively during the first 24 hr. of a fast, after which it approaches a const. level. No correlation between (I) and age, sex, or wt. was found. With doses of < 0.5 unit of insulin per kg. the % decrease in (I) is a logarithmic function of the dosage. This fact might be used for the assay of insulin. NUTR. ABS. (b)

Effect of insulin on the glucose-chloride relationship and anhydræmia in the blood of rabbits. A. S. CHAIKELIS (J. Biol. Chem., 1934, 105, 767—778).—A reciprocal relationship is brought about by the injection of small doses (1/32—1 unit per kg. of body-wt.) of insulin into rabbits, tending to keep the acid-base balance of the blood const. A moderate anhydræmia is also caused, together with changes in the hæmoglobin content and red blood-cell count (unrelated to blood vol.), said to be the result of the intervention of the spleen. C. G. A.

Blood-lipins in completely depancreatised dogs maintained with insulin. I. L. CHAIKOV and A. KAPLAN (J. Biol. Chem., 1934, 106, 267—279).— The lipins decrease under these conditions, particularly the cholesteryl ester (usually to zero).

Effect of the central nervous system on the action of insulin and adrenaline. F. HöGLER and F. ZELL (Klin. Woch., 1933, 12, 1719—1722; Chem. Zentr., 1934, i, 72).—Removal of the cerebrum, corpus striaticus, and mid brain (I) of rabbits has little effect on the action of insulin (II) or adrenaline (III). After removal of (I) the sensitivity towards (II) is reduced and towards (III) raised. A regulating mechanism must thus exist in (I), and must have an inhibitory action on the sympathetic part of the central blood-sugar regulation. L. S. T.

Adrenals and glucose tolerance. H. BANERJI and C. REID (J. Physiol., 1934, 81, 93—101).—The fasting blood-sugar is subnormal and the rate of disappearance of intravenously injected glucose temporarily more rapid in rabbits which survive adrenalectomy (I) for only a short time. No differences in this respect are observed in rabbits surviving (I) indefinitely. NUTR. ABS. (m)

Relationship between creatinuria and rise in blood-lactic acid after adrenaline in the rabbit. F. QUEROL and A. REUTER (Z. ges. exp. Med., 1934, 92, 598—602).—In healthy animals injection of adrenaline (I) is followed by rise in blood-sugar (II) and -lactic acid (III). Conditions (inanition, injection of urethane, thyroxine, or sulfrogel) which produce creatinuria (IV) prevent the post-(I) rise of (III), but do not interfere with the increase of (II). When the (IV) is prolonged, the rise of (III) after (I) reappears even when considerable amounts of creatine are present in the urine. NUTR. ABS. (m)

Diurnal rhythm in adrenaline secretion and carbohydrate metabolism in the rabbit and hedgehog. U. S. VON EULER and A. G. HOLM-QUIST (Pflüger's Arch., 1934, 234, 210-224).—In the hedgehog the adrenaline (I) content of the blood and adrenal glands is greater in the waking (II) than in the sleeping state (III). In the rabbit there is a rise in blood-sugar, liver-glycogen, and (I) of the blood and adrenal glands at 4—10 and 16—22 hr. The temp. rises at 16—22 hr., whilst serum-P is high at 4—16 hr. No regular differences between (III) and (II) are noticed, nor does muscular activity have a const. effect. NUTR. ABS. (m)

Effect of drugs on induced cardiac standstill. Effect of adrenaline and related compounds. M. H. NATHANSON (Arch. Int. Med., 1934, 54, 111— 130).—Adrenaline is the most active drug for the treatment of cardiac standstill, but ephedrine and phenylethanolamine are effective by the mouth. Digitalis prolonged the period of standstill. H. G. R.

Formation of adrenaline in the adrenal gland. Rôle of lipins. J. E. ABELOUS and R. ARGAUD (Compt. rend., 1934, 199, 535-537).—Treatment of adrenaline (I)- and lipin-free powder preps. of adrenal

R. S. C.

cortex (horse), or of the derived nucleoprotein, with ligroin extracts (II) of the cortical lipins in presence of 0.02N-NaOH at 22—24° for 4 hr. produces (I) due to its liberation (probably enzymic) from (I)-lipin complexes in (II). F. O. H.

Function of the adrenal cortex : general, carbohydrate, and circulatory theories. S. W. BRITTON and H. SILVETTE (Amer. J. Physiol., 1934, 107, 190-206).-The following observations do not support a proposed circulatory theory of the function of the adrenal cortex, but favour the carbohydrate theory : (1) a shift in the H<sub>2</sub>O balance in adrenalectomised animals occurred with the development of insufficiency symptoms; the liver and muscle showed increased hydration, whilst the blood became dehydrated, although the organism as a whole (rat) contained more H<sub>2</sub>O than normal; (2) the blood vol. was usually reduced after adrenalectomy; (3) intraperitoneal or intracardial injections of NaCl restored the circulatory vol., but did not affect the general condition or survival period of the adrenalectomised animal; (4) liverglycogen was practically depleted, blood-glucose reduced, and muscle-glycogen decreased in adrenalectomised guinea-pigs, cats, and marmots; in rats there was a reduction of liver-glycogen; (5) emotional excitement and adrenaline injection had practically no effect on blood-glucose of adrenalectomised cats; (6) Na lactate and glucose injections resulted in insignificant glycogen storage in adrenalectomised animals compared with normal controls.

NUTR. ABS. (b)

Effect of thyrotropic hormone on mineral metabolism. F. Eccs (Deut. Z. Chirurg., 1934, 242, 321—327).—In guinea-pigs, injection of the hormone leads to a marked fall in the Na content of serum and liver accompanied by increased urinary output and deposition in the skin. Similar results are obtained with Ca, but practically no alteration in K, Cl, or urinary vol. is observed. There is no evidence of a shift of Na between cells and plasma.

NUTR. ABS. (m) Myokinin. L. KARCZOG (Orvosi Hetilap, 1933, 77, 508—509).—The uterus-active factor of bloodserum and cerebrospinal fluid is not oxytocin but myokinin, which was also separated from the radish. CH. ABS.

Pituitrin-fixing substance in serum of pregnancy. F. G. DIETEL (Klin. Woch., 1933, 12, 1683— 1686; Chem. Zentr., 1934, i, 71).—Injection into the frog of a mixture of 0.01 c.c. of pituitrin (II) with 1 c.c. of serum (especially serum of pregnancy) does not cause expansion of the melanophores. After deproteinisation with EtOH the hormone can be determined in the conc. serum. The substance concerned is inactivated by short heating at 60° or by heating for 30 min. at 55°, and is adsorbed by kaolin. Reactivation is rapidly accomplished by addition of a small quantity of the serum. Serum contains also another substance, not adsorbed by kaolin, which adsorbs the antidiuretic component of (I). A. A. E.

Diuretic action of pituitary extracts and the responsible principle or constituent. K. I. MEL-VILLE and D. V. HOLMAN (J. Pharm. Exp. Ther., 1934, 51, 459-470).—The diuretic action of oxytocic and pressor preps. on urethanised rabbits is correlated with the quantity of vasopressin present and is probably due to the latter. W. O. K.

Anti-diuretic fraction of posterior pituitary gland. R. L. STEHLE (Arch. exp. Path. Pharm., 1934, 175, 471—480).—The action of various posterior pituitary preps. on diuresis (I) in dogs does not indicate the presence of a definite anti-diuretic principle, the action being due to the pressor substance. With certain preps.,  $1 \times 10^{-5}$  mg. partly inhibits (I), indicating that the action of the hormone concerns the regulation of the H<sub>2</sub>O balance more than the vasomotor system. F. O. H.

Effect of pituitary preparations on fat metabolism. W. RAAB (Klin. Woch., 1934, 13, 281– 285).—The presence in the pituitary of lipoitrin and orophysin, their effect on blood-fat and -ketones and on liver-fat and -glycogen, and their functional importance are reviewed. NUTR. ABS. (m)

Melanophore-enlarging action of pituitary extracts. R. L. STEHLE (Arch. exp. Path. Pharm., 1934, 175, 466—470).—The oxytocic principle (I) (cf. this vol., 117) of the pituitary gland has no melanophore-enlarging action (II) in frogs. Pitressin, a pressor prep., has 25-50% of the (II) of pituitary gland powder and is 40 times as active as the purified pressor principle (III) (*ibid*.). Partial separation of the substance causing (II) from (I) and (III) occurs during treatment of gland preps. with EtOH etc. This substance, which is adsorbed by  $Fe(OH)_3$ , is therefore not identical with, but merely a contaminant of, (III). F. O. H.

Mode of action of the contra-insulin hormone of the anterior pituitary lobe. I. Anterior pituitary lobe, thyroid gland, and carbohydrate metabolism. H. LUCKE, E. R. HEYDEMANN, and F. DUENSING (Z. ges. exp. Med., 1933, 91, 106—113; Chem. Zentr., 1934, i, 71—72).—Injection of thyrotropic hormone into the dog does not raise the bloodsugar. In the animal with injured anterior pituitary lobe thyroxine hyperglycæmia is more marked than normally; on injection of thyroxine and "präphyson" it is smaller than usual. After thyroidectomy reaction to "präphyson" alone or with thyroxine is normal. Contra-insulin and thyrotropic hormones are not identical. A. A. E.

Mode of action of the pituitary growth-hormone. E. MARGITAY-BECHT and L. BINDER (Arch. exp. Path. Pharm., 1934, 175, 353—358).—The increase in body-wt. due to injection of anterior pituitary preps. (I) into rats and the decrease when administration is discontinued are the same for both normal and thyroidectomised female rats. An increase in the basal metabolism parallel with that in body-wt. confirms the importance of the thyroid gland in the action of (I). F. O. H.

Selective gametogenic effect of certain pituitary extracts. H. M. EVANS, R. I. PENCHARZ, and M. E. SIMPSON (Science, 1934, 80, 114).-EtOH extracts of desiccated anterior pituitary tissue, or trypsin-erepsin digests of such extracts, which have a relatively greater influence on the germinal than on the internally secreting mechanism of the testis, have been prepared. L. S. T.

Does the anterior pituitary substance from urine of pregnancy raise the blood-sugar level? E. DINGEMANSE and S. KOBER (Endocrinol., 1933, 17, 149—151).—The rise is not due to pituitary hormone. CH. ABS.

**Estrogenic substances from coal and associated minerals.** R. POTONIÉ (Pharm. Ztg., 1934, 79, 878—879).—The origin, nature, and separation of æstrogenic substances from coal, asphalt, bitumen, etc. are discussed. F. O. H.

Action of folliculin on plants. III. W. SCHOELLER and H. GOEBEL (Biochem. Z., 1934, 272, 215—221; cf. this vol., 934).—The hormone alone did not, but after addition of a little NaOH (which converted it into the more readily absorbed alkali salt) did, increase the rate of development of the hyacinth. The optimum amount of hormone was 250 mouse units per week. P. W. C.

Determination of small amounts of gonadotropic material. P. A. KATZMAN and E. A. DOISY (J. Biol. Chem., 1934, 106, 125—139).—Gonadotropic material (I) can be quantitatively removed by pptn. with tungstic acid and decomp. with Ba or brucine, or (better) by adsorption on BZOH. This is probably due to adsorption of the active material on a proteinlike substance. Data are given for the daily excretion of (I) by men and women at various ages. Extracts from the urine of women after the menopause and of castrates produce less follicular stimulation and enlargement of the ovaries than extracts from urine of pregnancy and anterior lobe. H. G. R.

Hormonal interruption of broodiness in hens. K. WODZICKI (Nature, 1934, 134, 383).—Administration of prolan A, pituitrin (I), and cattle thyroid gland had no effect on the interruption of broodiness in hens. (I) had no effect on health or laying.

## L. S. T.

Physico-chemical studies of complex organic molecules. III. Surface properties of concentrates of vitamin-A. F. P. BOWDEN and L. H. BASTOW (Proc. Roy. Soc., 1934, B, 116, 27-37).--Vitamin-A forms an insol. film of the liquid expanded type, resembling that of a long-chain alcohol, slowly oxidising with a decrease in surface area. It is adsorbed on solid surfaces, not as strongly as carotene (I), and more readily from a non-polar than from a polar solvent, and can be recovered unchanged. It is taken up by freshly killed liver tissue from cyclohexane solution in contrast to (I). H. G. R.

Colour reaction for vitamin-A. E. ROSENTHAL and J. ERDÉLYI (Biochem. Z., 1934, 271, 414-419).— The reaction for vitamin-A previously described (this vol., 225) using SbCl<sub>3</sub> and pyrocatechol is greatly improved by substituting guaiacol for the latter. The colour is more stable, and accurate determinations may be made by its use in the Leitz abs. colorimeter. P. W. C.

Hydrogenation of vitamin-A fraction of the liver-oil of Stereolepsis ischinagi (Hilgendorf). Z. NAKAMIYA (Bull. Inst. Phys. Res. Japan, 1934, 13, 48-49).—The oil was hydrogenated at 70° using a PtO<sub>2</sub> catalyst. Nonacosane was not obtained. Distillation in a high vac. gave five fractions; the lowest was a hydrocarbon,  $C_{18}H_{38}$ , b.p. 85—86°, whilst the highest was probably a polymerisation product of vitamin-A (mol. wt. 451). The vitamin-A of S. ischinagi is different from that of Madara or Sukeso oils. P. G. M.

Carotenoids, their relation to other natural compounds and their biological importance. L. ZECHMEISTER (Bull. Soc. Chim. biol., 1934, 16, 993-1008).—A lecture.

Vitamin content of pituitary. E. VOGT (Med. Klin., 1933, 52, 1734—1735).—In man, hormone potency is connected with the vitamin-A (I) content of the pituitary (II). (I) is found in (II) as long as a malignant tumour (III) is growing, but becomes exhausted during the development of slow-growing tumours, so that in severe cancer cachexia it is present only in the liver in min. amounts. Hence the relatively slow growth of (III) after 60 years of age, for the (I) content of (II) declines with age.

NUTR. ABS. (m)

Vitamin content of African cereals. I. Vitamin-B complex. M. CAMIS (Atti R. Accad. Lincei, 1934, [vi], 19, 462-465).—Eragrostis teff, Sorghum athiopicum, and, to a smaller extent, Pennisetum spicatum and Eleusine coracana contain the vitamin-B complex. T. H. P.

Vitamin-B growth-promoting factor for rats, found in whole wheat. N. HALLIDAY (J. Biol. Chem., 1934, 106, 29–40).—Although wheat germ is the richest source, the factor can be extracted from bran by dil. acids or dil. EtOH, but not by  $\text{Et}_2\text{O}$ . A cryst. concentrate closely resembling vitamin- $B_4$  has been prepared by the method of Peters (A., 1933, 541). H. G. R.

Vitamin content of Philippine foods. II. Vitamin-C invarious fruits and vegetables. A.J. HERMANO and G. SEPULVEDA, jun. (Philippine J. Sci., 1934, 53, 379-390).-Of 15 common fruits and vegetables, mangoes and mandarins have the highest content (determined biologically) of vitamin-C.

F. O. H.

Vitamin-C in the adrenal glands and the pituitary of the ox. B. WESTERGAARD (Biochem. J., 1934, 28, 1212—1213).—Ascorbic acid is demonstrated in the tissues by its reduction of AgNO<sub>3</sub>. The cytoplasm is stained but not the nucleus. Some Ag granules are found in the intercellular spaces and lymph vessels. C. G. A.

Prune as an oxidation-reduction indicator. Its suitability for the titration of ascorbic acid. J. MELVILLE and G. M. RICHARDSON (Biochem. J., 1934, 28, 1565—1574).—The electrode equation for the oxazine dye, prune, is given for the range  $p_{\rm fl}$  0—10. It is useful in the range between Lauth's violet and the indophenols. It is at the limit of weakness for oxidising agents for titrating ascorbic acid, but is not weak enough to eliminate other biological reducing agents from the titration. C. G. A.

Variation in reducing power with concentration of vitamin-C and other reducing substances. N. BEZSSONOFF, A. DELIRE, and H. VAN WIEN (Bull. Soc. Chim. biol., 1934, 16, 1133—1159).— Ascorbic acid (I), pyrocatechol, quinol, and tannin are characterised by the variations of their reducing powers (II) with concn., the determinations of (II) being made by solution potential measurements and by the decolorising action on dichlorophenol-indophenol. The technique for the identification of (I) in lemon juice is described. A. L.

Identification of vitamin-C. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1934, 16, 1107—1132).—A method for the identification and determination of ascorbic acid (I) in biological liquids is based on the determination of the dienol concn. by means of the colour reaction (II) with monomolybdic-phosphotungstic acid combined with a determination of the variation of the potential of solutions with the dienol concn. This differentiates between (I) and other substances such as pyrocatechol, quinol, and tannin which also give (II). A. L.

Identification and determination of vitamin-Cin biological media. N. BEZSSONOFF and H. VAN WIEN (Bull. Soc. Chim. biol., 1934, 16, 1160-1175).-The direct determination of ascorbic acid (I) in fresh antiscorbutic juices gives results in agreement with those obtained using guinea-pigs, but in the case of a preserved vegetable (sauerkraut) the vals. are high. Human, guinea-pig, and horse urine from animals fed on antiscorbutic diet give the monomolybdic-phosphotungstic colour reaction, but in some cases the reduction curves do not correspond with (I). Summer milk had 38, winter milk, from the same source, 28 mg. of (I) per litre. Whilst the dichlorophenol-indophenol titration of cryst. extracts of animal origin indicates that (I) is the dienol present, the electrometric titration results are too low. A.L.

Antirachitic activity of salts of ergosteryl sulphate on irradiation in aqueous medium.—See this vol., 1099.

Effect of the administration of calciferol on the increased calcium excretion induced by thyroxine. L. I. PUGSLEY and E. ANDERSON (Biochem. J., 1934, 28, 1313—1315).—Administration of 5000 units of calciferol daily to rats decreases the fæcal excretion of Ca and corrects the negative Ca balance. H. G. R.

Calcium and phosphorus metabolism in diseases of the thyroparathyroid apparatus. II. Mode of action of vitamin-D. F. S. HANS-MAN (Med. J. Austral., 1934, i, 81—95).—In two patients with combined hyperthyroidism and hypoparathyroidism (I) treated with large doses of vitamin-D (II), the symptoms of (I) cleared up rapidly with little or no change in the level of Ca or P in the blood and only a very slight improvement in the Ca and P balances. The beneficial effects could not be due to better absorption of Ca from the intestinal tract. (II) probably acts by making Ca available for tissue metabolism. NUTR. ABS. (m)

Relation of the parathyroid glands to the action of irradiated ergosterol. N. B. TAYLOR, C. B. WELD, and J. F. SYKES (Proc. Roy. Soc., 1934, B, 116, 10-26).—Dale's theory (A., 1932, 1176) is not supported, the gastro-intestinal features of over-dosage of parathormone and irradiated ergosterol not being the result of the hypercalcæmia. Elevation of serum-Ca by other agents is no less in a parathyroidectomised than in a normal animal. H. G. R.

Absorption spectrum of vitamin-E. A. J. P. MARTIN, T. MOORE, M. SCHMIDT, and F. P. BOWDEN (Nature, 1934, 134, 214; cf. A., 1933, 987).—A sharp absorption band with a max. at 2940 Å. has been detected in a vitamin-E (wheat-germ oil) concentrate. L. S. T.

Improved vitamin-E-deficient diet for female rats. P. SCHOORL (Arch. Neerland. Physiol., 1934, 19, 403-407).—A diet is described in which sterility is reached in the first insemination of the first generation. H. G. R.

Carbon economy of greenhouse plants during winter in daylight alone and supplemented with electric lighting. E. K. GABRIELSEN (Planta, 1934, 22, 180—189).—The light intensity–C assimilation curves of plants artificially lighted in winter resembles that of shaded plants under normal conditions, but shows a higher max. Dry-matter production agreed with that calc. from amounts of  $CO_2$ assimilated and respired. A. G. P.

Influence of temperature on the respiration and carbon dioxide assimilation of some green algæ. F. VAN DER PAAUW (Planta, 1934, 22, 396-403).—In *Stichococcus bacillaris*, respiration (I) and  $CO_2$ -assimilation (II) are similarly affected by changes in temp. In other cases (e.g., *Oocystis* sp.) (I) increases more rapidly than (II) with rising temp. > 22°. A. G. P.

Uspenski's iron hypothesis of the distribution of algæ. E. G. PRINGSHEIM (Planta, 1934, 22, 269—312).—The extent of the formation of complex Fe compounds (I) is indicated by the limiting  $p_{\rm H}$  for max. colour formation by CNS reagents. The toxic action of Fe is reduced and its nutrient action improved by formation of (I). Numerous factors other than [Fe<sup>\*\*\*</sup>] have an important influence on the distribution of algæ in waters. A. G. P.

Presence of cellulose and its distribution in the cell-walls of brown and red algæ. G. L. NAYLOR and B. RUSSELL-WELLS (Ann. Bot., 1934, 48, 635-641).—The cellulose (I) content of a no. of species varied from 2 to 15%. The distribution of (I) in the tissues is examined. A. G. P.

Alkaloids of Dicentra oregana, Eastwood.—See this vol., 1117.

Non-infectious leaf-deforming principle from mosaic tomato plants. M. H. THORNTON and H. R. KRAYBILL (Phytopath., 1934, 24, 19).—Juice from diseased plants, after autolysis and boiling, contained the non-infectious leaf-deforming principle. The activity of the juice was not diminished by pptn. of the proteins or by extraction with  $\text{Et}_2\text{O}$ . Infected plants had less reducing sugars, sucrose, starch, and hemicellulose and more total and NO<sub>3</sub>-N than did healthy plants. A. G. P.

Uric acid reagent.—See this vol., 1083.