BRITISH CHEMICAL ABSTRACTS

A.-PURE CHEMISTRY

OCTOBER, 1935.

General, Physical, and Inorganic Chemistry.

Mathematical representation of the energy levels of the secondary spectrum of hydrogen. II, III. I. SANDEMAN (Proc. Roy. Soc. Edin., 1934—1935, 55, 49—61, 72—84).—II. Analyses of the $1s2s^3\Sigma$ and $1s2p^1\Sigma$ states and vals. of the structural consts. calc. on Dunham's solution of the Schrödinger equation are given (cf. Physical Rev., 1932, [ii], 41, 713). There is little evidence of *l*-uncoupling for these states. Potential functions are obtained and indicate that the Morse function is not applicable to the two states.

III. On the above basis the mol. consts. of the ground state, $1s1s^{1}\Sigma$, of H_{2} are determined together with those of the ground state, $1s^{2}\Sigma$, of H_{2}^{+} for comparison. N. M. B.

Gross intensities in electronic bands, with special reference to C_2 (Swan) and N_2 (second positive) systems. N. R. TAWDE (Proc. Indian Acad. Sci., 1935, 2, A, 67—81).—A general survey is given. The Swan systems of C_2 and N_2 are considered relative to conditions of excitation. The probabilities of transition, the temp., and the "centres of intensity" are discussed. Explanations are suggested for unusual intensity features of bands excited in different sources, especially in A. N. M. B.

Theory of ${}^{3}\Sigma^{+}$ — ${}^{3}\Sigma^{-}$ transitions in band spectra. R. D. PRESENT (Physical Rev., 1935, [ii], 48, 140— 148).—Mathematical. The interpretation of certain faint absorption bands in O_{2} , showing Q but not Pand R branches, is examined. N. M. B.

Spectrum of aluminium vapour distilled by a tungsten coil in vacuum. E. GAVIOLA and J. STRONG (Physical Rev., 1935, [ii], 48, 136—137).—A W coil, charged with Al, and brought to incandescence in vac. of 10^{-5} mm. Hg, evaporates a cloud of metal which emits a violet-blue light found to be mainly a line spectrum containing Al I, II, W, and impurity lines. The excitation is produced by collisions with electrons from the filament and accelerated by the potential drop across it. λ 3443.6 behaves as an Al arc and not as an Al II line. N. M. B.

Rotational analysis of the S_2 bands. E. W. VAN DIJK and A. T. LAMERIS (Physica, 1935, 2, 785—786).—An analysis of the S_2 bands is given, which disagrees with those of Naude and Christy (A., 1931, 540) and Badger (Physical Rev., 1934, [ii], 46, 1025). The wave functions of the S_2 mol. are symmetrical in the nuclei; the nuclear distance in the final state is 1.73 Å. T. G. P. Polarisation of resonance radiation of calcium and the effect of weak magnetic fields. A. STEINHAUSER (Z. Physik, 1935, 95, 669–686).— Depolarisation of the 4227 Å. line gives a mean life of $2 \cdot 2 \times 10^{-8}$ sec. for the excited level. A. B. D. C.

Infra-red arc spectrum of chromium. C. C. KIESS (J. Res. Nat. Bur. Stand., 1935, 15, 79-85).— The arc spectrum of Cr has been photographed between 7720 and 11,610 Å., about 200 lines being recorded and classified. J. W. S.

Spectrum of molybdenum v. M. W. TRAWICK (Physical Rev., 1935, [ii], 48, 223—225).—The spectrum was excited in a vac. spark and photographed. About 90 lines in the region 2100—400 Å. are tabulated and classified. N. M. B.

Hyperfine structure in silver. H. HILL (Physical Rev., 1935, [ii], 48, 233–237).—Using a hollow cathode source and Fabry–Perot interferometers, 20 lines in the visible region were found to be simple, λ 7688 in the infra-red was very broad, and the resonance lines $\lambda\lambda$ 3383 and 3281 were each double, with the weaker component on the longer- λ side. The average separations were 0.055 in λ 3383 and 0.056 cm.⁻¹ in λ 3281. The doubling is attributed to a splitting of the 5S level because of nuclear spin, which is probably 3/2. N. M. B.

Spectrum of AgD. P. G. KOONTZ (Physical Rev., 1935, [ii], 48, 138—140).—A quantum analysis is tabulated for the 0,0 and 1,1 bands photographed at high dispersion from a Ag arc in D_2 . B_e is $3\cdot2595$ for the lower state. From the corresponding val. for AgH the ratio B_e^i/B_e for the two isotopic mols. is 0.50511, the ratio of the reduced masses being $0\cdot50497$. N. M. B.

Spectrum of ionised tellurium, Te III. S. G. KRISHNAMURTY (Proc. Roy. Soc., 1935, A, 151, 178— 188).—The 5p, 6p, 5d, and 6s terms in the structure of the Te III spectrum have been identified. The spectrum agrees in its general features with that of Se III, but exhibits marked deviations from the usual interval and intensity rules. The calc. third ionisation potential of Te is approx. 30.5 volts. L. L. B.

Spectrum of trebly-ionised cerium. R. J. LANG (Canad. J. Res., 1935, 13, A, 1-4).—The principal multiplets of the Ce IV spark spectrum are reported. The ionisation potential is 33.3 volts. Further data relating to the ultra-violet spectrum of La III are given. R. S.

4 K

Hyperfine structure of the mercury triplet $6^{3}P_{012}-7^{3}S_{1}$ in optical excitation. (MISS) E. E. Boggs and H. W. WEBB (Physical Rev., 1935, [ii], 48, 226-232).—The relative intensities of the hyperfine structure components of $\lambda\lambda$ 5461, 4358, and 4047 were calc. and checked experimentally. Since the excitation in optically excited Hg vapour is in two steps, the ratio of the intensities of the components due to the less abundant isotopes is < in the normal low-pressure arc. N. M. B.

High-frequency spectrum of mercury vapour. N. B. BHATT (Proc. Indian Acad. Sci., 1935, 1, A, 891-904).—Simple circuits are given, and the spectrum is mapped. A. B. D. C.

Hyperfine structure in bands of mercury hydride. S. MROZOWSKI (Z. Physik, 1935, 95, 524– 538). A. B. D. C.

Relation between the electron field emission and the work function of liquid mercury. L. R. QUARLES (Physical Rev., 1935, [ii], 48, 260—264).— The variation in the field necessary to initiate a vac. discharge between a Hg cathode and a Mo anode and the accompanying variation in the work function of the cathode were measured. Results show a more pronounced variation of the field with work function than is required by the Fowler-Nordheim theory. For a change of work function of 1 volt the field required to initiate the discharge varied from 375 to 575 kv. per cm. N. M. B.

Anomalous dispersion in thallium vapour. G. S. KVATER (Physikal. Z. Sovietunion, 1935, 7, 226—244).—The Tl lines 5350, 3775, 3529, and 3519 Å. have been investigated. The doublet 3519, 3529 Å. obeys Dorgelo's rule and $h/k = 4.67 \times 10^{-11}$. R. S.

Interferometer measurements of the hyperfine structure of some lines of singly ionised bismuth. S. SMITH and J. S. BEGGS (Canad. J. Res., 1935, 12, 690-698).—The hyperfine structures of the 6808, 6600, 5719, 5270, 5209, 5144, 4392, 4272, and 4259 Å. lines of Bi II and the 4561 Å. line of Bi III have been examined using quartz and glass Lummer plates. The separation factors of the $6p_15f_{31}14_4$ and $6p_16d_{31}8_3^\circ$ terms are deduced and the interaction consts. of the $5f_{21}$, $5f_{31}$, and $6d_{21}$ electrons ealc. J. W. S.

Transparency of the air between 1100 and 1300 Å. T. LYMAN (Physical Rev., 1935, [ii], 48, 149-151).—The transparency is demonstrated by means of a thermoluminescent screen, the selective sensitivity of the screen and the nature of the Entladungsstrahlen are examined, and a simple method of testing the transparency of LiF crystals is described. N. M. B.

Initiation of the high-frequency discharge [in hydrogen]. J. THOMSON (Nature, 1935, 136, 300). L. S. T.

Gas discharges with an electrolyte as cathode. A. KLEMENC (Z. Physik, 1935, 95, 799-800).— Polemical, against Braunbek (A., 1934, 1281).

A. B. D. C.

Gas discharges with an electrolyte as cathode. W. BRAUNBEK (Z. Physik, 1935, 95, 800).—A reply to the above. A. B. D. C.

Discharge processes in gases before breakdown. E. FLEGLER and H. RAETHER (Naturwiss., 1935, 23, 591).—Cloud chamber experiments show that the discharge in gases before breakdown takes place along canals whether the field be homogeneous or inhomogeneous. A. J. M.

Faraday dark space. K. G. EMELEUS (Proc. Roy. Irish Acad., 1935, 42, A, 31-36; cf. this vol., 556).— Qual. evidence is given that the Faraday dark space need not be traversed by fast electrons, and that diffusion in a combined electric field and concn. gradient can account for part of the conductivity, but that, in some cases, effects due to short- λ resonance radiation reaching the dark space from the negative glow, and propagated rectilinearly and not by diffusion, may be of importance electrically and optically. N. M. B.

Intensities of satellites of K_{α} . (MISS) A. W. PEARSALL (Physical Rev., 1935, [ii], 48, 133—135).— Intensities of K_{α_1} satellites were measured and plotted for elements of the at. no. range 16—29; they are, in general, < for $L\beta_2$ satellites. N. M. B.

K Series X-ray emission lines of manganese in several compounds. S. TANAKA and G. OKUNO (Japan. J. Physics, 1935, 10, 45–48).—The effect of chemical combination on the $K\alpha_1, \alpha_2, \beta_1, \beta'$ lines of Mn was studied with MnO₂, MnCO₃, KMnO₄, Mn(OAc)₂, and MnSO₄. Appreciable shifts were found for the $K\beta_1$ and $K\beta'$ lines, but scarcely any effect for the $K\alpha$ doublet. N. M. B.

Absorption and scattering of X-rays. D. BLOCHINZEV and F. HALPERIN (Physikal. Z. Sovietunion, 1935, 7, 175—188).—The absorption coeff. calc. for the K electron level in metals is in agreement with experimental data. The scattering coeffs. of Ca, Ni, and Al in the region of shorter $\lambda\lambda$ have been derived and increase with the at. no. R. S.

Excitation potential of the X-ray satellites in the L series. D. COSTER, H. H. KUIPERS, and W. J. HUIZINGA (Physica, 1935, 2, 870—878).— The doubly ionised state $L_{III}M_{IV,V}$ responsible for the satellites on the short- λ side of the $L\alpha_1$ line is mainly due to the radiationless transition $L_I \rightarrow L_{III}$ with the ejection of an *M*-electron. T. G. P.

Lines of the *M* series of niobium to silver. H. KIESSIG (Z. Physik, 1935, 95, 555-573).

A. B. D. C.

Double electron transitions in X-ray spectra. F. BLOCH (Physical Rev., 1935, [ii], 48, 187–192).— Elementary processes are examined in which simultaneous transitions of an inner and an outer at. electron result in the emission of one light quantum. Assuming the nuclear distance of the inner electron to be small compared with that of the outer electron, expressions are developed for the probability of double transitions by dipole radiation. The Cu $K\alpha_3$ satellite illustrates the case where the inner transition alone occurs by dipole emission. N. M. B. Calculation of X-ray terms according to Heisenberg's theory on electron holes. G. ARAKI (Sci. Rep. Tokyo Bunrika Daigaku, 1935, A, 2, 189-216).—The numerical vals. of K-terms and their screening consts., calc. for all atoms, are in good agreement with experiment. N. M. B.

Ionisation of a gas at different pressures by photon and corpuscular radiation. J. CLAY (Physica, 1935, 2, 811—816).—Quant. relationships between incident radiation, pressure, and ionisation are developed which satisfy the experimental results (this vol., 426). T. G. P.

Ionisation potentials calculated with the Thomas-Fermi equation and Dirac exchange correction. L. HULTHEN (Z. Physik, 1935, 95, 789-795). A. B. D. C.

Molecular orientation and the probability of dissociation of molecules by electron impact. N. SASAKI and T. NAKAO (Nature, 1935, 136, 260).— The probability of the dissociation of H_2 mols. increases rapidly as the mol. axis approaches from the perpendicular position that parallel to the electron beam. A diagram of the apparatus used in measuring the angular distribution of resulting ions is given. L. S. T.

Elastic scattering of electrons in krypton. A. L. HUGHES and S. BILINSKY (Physical Rev., 1935, [ii], 48, 155—160; cf. this vol., 557).—The calc. scattering coeffs. agree satisfactorily with experiment for electron energies 250, 350, and 510 volts, and less so for those of 780 and 950 volts.

N. M. B.

Collision efficiency of slow electrons and inert gas atoms. H. MAIER-LEIBNITZ (Z. Physik, 1935, 95, 499-523).—Measurements of collision efficiency, accurate to within 20%, have been obtained for He, Ne, and A. A. B. D. C.

Production and focussing of intense positiveion beams. M. A. TUVE, O. DAHL, and L. R. HAFSTAD (Physical Rev., 1935, [ii], 48, 241—256).— A high-intensity source of positive ions using a gaseous low-voltage arc constricted by a metal capillary, and the focussing of weak and intense beams by various electrostatic lens arrangements are described and quantitatively examined. N. M. B.

Platinum isotopes and their nuclear spin. B. VENKATESACHAR (Proc. Indian Acad. Sci., 1935, 1, A, 955—960).—The isotopes of Pt are 196, 195, 194, and 192. The nuclear spin of the odd isotope is 1/2. A. B. D. C.

Isotope abundance in platinum. B. VENKATE-SACHAR and L. SIBATYA (Proc. Indian Acad. Sci., 1935, 2, A, 101–103).—The relative abundance is estimated from an analysis of the microphotograms of the structure pattern of Pt I λ 3408·13. Assuming a positive isotope shift the results are : Pt^{196, 195, 194, 192}, abundances 16, 13, 10, ~2, respectively. At. wt. divergences are discussed. N. M. B.

Periodic system of the stable isotopes and the relation of the mass and charge of the nuclei. J. SELINOV (Physikal. Z. Sovietunion, 1935, 7, 82—98).—Empirical formulæ are proposed for the relation between the mass no. (A), at. no. (N), and no.

of neutrons (n) for stable isotopes, the nuclei of which are considered to consist entirely of neutrons and protons. For odd elements, $A=3N-2\alpha+\beta$ (approx.), $n=2(N-\alpha)+\beta$, where $\alpha=no.$ of single isotopes, and β is the pleiade no., and =0 or 2. For even elements $A=3N-2\alpha+1+\beta$ (approx.), and n= $2(N-\alpha)+1+\beta$, where $\beta = \pm 0, 1, 2, 3, 4, 5, 6, 7$, for A and ± 0 , 1, 3, 5, 7, for n. A system of isotopes exhibiting periodicity (perhaps due to a shell structure of the nucleus) is built up from these formulæ. In agreement, the mass defect curve, calc. according to the formula (mass of protons and neutrons - at. wt.)/at. no., is periodic. On dividing the mass defect by N+n/2 a curve is obtained on which isotopes of a single element are represented as a single point, with a step-like character the periodicity of which coincides with that of the calc. isotopic system. New isotopes, and the no. of single isotopes, may be predicted, and isotopes not included have been found to be radioactive. R. S. B.

Deuterium. I. D. MACGILLAVRY (Chem. Weekblad, 1935, 32, 490–493).—A review. D. R. D.

Radioactivity of the earth's crust and its influence on cosmic-ray electroscope observations made near ground level. R. D. EVANS and R. W. RAITT (Physical Rev., 1935, [ii], 48, 171–176).— Ra analyses of 23 rock specimens from the scene of cosmic-ray observations show a linear relation between the average Ra content and the local γ -ray ionisation in the cosmic-ray electroscope; this indicates that ionisation due to γ -rays arising from impact or reflexion of cosmic rays by the earth's crust is negligible, and the Th/U ratio is approx. const. An expression is found for the γ -ray ionisation above a radioactive surface. N. M. B.

Radioactivity of potassium. K. SITTE (Nature, 1935, 136, 334—335).—The existence of a rare isotope, $_{19}K^{43}$, which is transformed into $_{20}Ca^{43}$, is the only assumption which agrees with the available evidence. The radiation of K shows no track of positively-charged particles in a cloud chamber. L. S. T.

Half-lives of potassium, rubidium, neodymium, and samarium. A. RUARK and K. H. FUSSLER (Physical Rev., 1935, [ii], 48, 151—154).— The suggestion that the long apparent half-lives of K, Rb, and Nd are due to isotopes of small abundance having half-lives small in comparison with the apparent ones is examined. Using data on the relative abundance of the elements it is shown that the halflife of the active fraction of K is>10⁷ years, and, correspondingly for Rb, Nd, and Sm, >10⁸ years. The activities may be due to small radioactive fractions of well-known isotopes. N. M. B.

Absence of natural β -ray radioactivity from beryllium. E. FRIEDLANDER (Compt. rend., 1935, 201, 337—339).—Carefully purified Be salts show no β - or γ -ray activity. This is in agreement with Aston's measurements of the masses of light nuclei and with the results of artificial transmutation, which indicate that the energy of disintegration of the Be atom is of the order of 10⁶ e.v. J. W. S.

Ionisation currents produced by radon, Ra-A, and $\operatorname{Ra-}C'$ in cylindrical ionisation chambers. R. D. EVANS (Physical Rev., 1935, [ii], 48, 177-186).—An expression is derived for the ionisation produced in cylindrical ionisation chambers by Rn and its decay products, and is confirmed experimentally. Equations are also derived for α -ray ionisation above a plane surface due to a homogeneous radioactive substance below the plane, a radioactive substance uniformly distributed on a wire normal to the plane, and for the ionisation outside a dihedral angle onclosing the radioactive substance. N. M. B.

Radiative capture of protons by carbon. G. BREIT and F. L. YOST (Physical Rev., 1935, [ii], 48, 203–210).—Mathematical. The theoretical yield in the reaction $C^{12}+H^1 \rightarrow N^{13}+\gamma$ is > that observed by a factor approx. 1000. Modifications of the calculation are examined. The y-ray yield expected in the bombardment of Be⁹ by protons is calc. N. M. B.

Yield of a-particles from lithium films bombarded by protons. R. G. HERB, D. B. PARKINSON, and D. W. KERST (Physical Rev., 1935, [ii], 48, 118-124).-Abs. yields from a thick Li target were determined for proton energies up to 400 kv. For thin films the yield increases linearly in the voltage range 180-400 kv.; there is no indication of resonance levels. N. M. B.

Transformation of chemical elements by bombardment with hydrogen nuclei. F. KIRCHNER (Chem.-Ztg., 1935, 59, 713-716).-A review.

A. J. M.

Cloud-chamber studies of the y-radiation from lithium bombarded with protons. H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], 48, 125-133).—The spectrum, investigated by a cloud chamber operating in a magnetic field of 2000 gauss, consists of at least 11 lines, the highest of which is 16 me.v. The voltage excitation curve max. for the γ -radiation is at 650 kv. proton energy. The division of energy between the members of electron pairs arising from absorption, the ratio of positive to negative electrons, and an interpretation of results are examined. N. M. B.

Lower limit of the nuclear photo-effect in beryllium. L. ARZIMOVITSCH and P. PALIBIN (Physikal. Z. Sovietunion, 1935, 7, 245-254).--Neutrons could not be produced from Be⁹ by γ -radiation from an X-ray tube using tensions > 1350 kv. This is contrary to the results of Gentner (this vol., 141). R. S.

Secondary γ -rays excited by the passage of neutrons through matter. D. E. LEA (Proc. Roy. Soc., 1935, A, 150, 637-668).-When neutrons pass through matter, γ -rays are produced. The quantum energies of the radiation are $3-4\times10^6$ volts for H_2 , and 1.5×10^6 volts for Pb and Fe. The origin of the radiation is discussed; nuclear excitation appears to be the most plausible explanation in most cases. L. L. B.

Slowing down of neutrons in various substances containing hydrogen. T. BJERGE and C. H. WESTCOTT (Proc. Roy. Soc., 1935, A, 150, 709-728).-Measurements have been made of the effect of slowing down neutrons in various substances containing H, and of the scattering and absorption of slow neutrons by various nuclei. The results indicate that the majority of the neutrons slowed down in H_2O or paraffin oil have acquired gas-kinetic velocities. The cross-sections for scattering of such slow neutrons are 3×10^{-23} cm.² for the H nucleus, and about 3×10^{-24} cm.² for C and O₂. The cross-sections for absorption are 1.2×10^{-21} cm.² for B, $< 2 \times 10^{-24}$ cm.² for N₂, about 4×10^{-25} cm.² for O₂ and C, and about 2×10^{-25} cm.² for H₂. L. L. B.

Interaction of neutrons with matter. J. R. DUNNING, G. B. PEGRAM, G. A. FINK, and D. P. MITCHELL (Physical Rev., 1935, [ii], 48, 265-280).-The interaction of fast and slow neutrons with matter was investigated. The anomalous effects of slow neutrons were not observed with the lowest-energy neutrons detectable through projected electrons. A Cd shutter with Li ion-chamber permits separation of fast and slow neutron effects. The production of slow by collisions of fast neutrons with H nuclei was studied by using paraffin, H₂O, and D₂O. H₂O is about 5.5 times as effective as D_2O in producing slow neutrons. Investigation of the thermal equilibrium of slow neutrons showed that, in the range 95-373° abs., the change in the no. of disintegrations of Li and in the absorption of Cd was small. Neutronnucleus collision cross-sections for fast neutrons plotted against at. wt. give a smooth curve indicating increasing nuclear radii with at. wt. Neutronnucleus collision cross-sections for slow neutrons are tabulated for a large no. of elements. Investigation of elastic scattering of slow neutrons shows that the large neutron-nucleus of the lastic scattering. N. M. B. the large neutron-nucleus cross-sections are due to

Induced radioactivity of fluorine and calcium. O. R. FRISCH (Nature, 1935, 136, 220).—Bombard-ment of NaF and LiF with α -rays gives a radio-element, probably Na²², of half-period > 6 months, emitting positrons of approx. 2×10^5 e.v. mean energy. Ca gives a radio-element, probably Sc⁴³, with a halfperiod of 4.4 ± 0.4 hr., emitting positrons with an Al half-val. thickness of approx. 0.06 g. per cm.² No short-period activity, corresponding with the intermediate formation of Ti43, could be detected. L. S. T.

β-Ray spectra of artificially-produced radioactive elements. A. I. ALICHANOV, A. I. ALI-CHANIAN, and B. S. DŽELEPOV (Nature, 1935, 136, 257-258).—The half-life periods and the max. energy of the electrons emitted by 14 radioactive elements obtained by neutron bombardment are recorded. The results do not agree with Fermi's theory of β -ray decay nor do they fit Sargent's L. S. T. diagram.

Beta processes and nuclear stability. G. BECK (Nature, 1935, 136, 257).—A discussion. L. S. T.

Velocity of "slow neutrons." O. R. FRISCH and E. T. SØRENSEN (Nature, 1935, 136, 258).-Many of the neutrons from a Be+Rn source probably have velocities of the order of 2×10^5 cm. per sec. after passage through paraffin wax. The main part of those slow neutrons which are strongly absorbed in Cd have very nearly thermal velocities. L. S. T.

Coincidence method for investigating nuclear processes. H. J. VON BAEYER (Z. Physik, 1935, 95, 417-439). A. B. D. C.

Nature of cosmic rays. J. CLAY (Proc. Roy. Soc., 1935, A, 151, 202-210).—Theoretical. Evidence is adduced that one or more intermediate photon radiations exist between the primary radiation, which is wholly corpuscular, and most of the corpuscles observed in ionisation chambers, or in counters, or in the Wilson chamber. L. L. B.

Cosmic ray ions and the shower producing radiation. F. H. NEWMAN and H. J. WALKE (Phil. Mag., 1935, [vii], 20, 263—266). A. J. M.

Sommerfeld's fine structure constant. H. ERTEL (Z. Physik, 1935, 95, 775-777).—Theoretical. A. B. D. C.

Formation of electron-positron pairs by internal conversion of γ -radiation. M. E. Rose and G. E. UHLENBECK (Physical Rev., 1935, [ii], 48, 211— 223).—Mathematical. The probability of production of an electron and positron by the spherical γ -wave emitted from a nucleus is examined by approximation methods. N. M. B.

Calculation of pair creation by fast charged particles and the effect of screening. H. J. BHABHA (Proc. Camb. Phil. Soc., 1935, 31, 394— 406).—Mathematical. W. R. A.

Properties of dipole and quadripole radiation from nuclei. H. M. TAYLOR (Proc. Camb. Phil. Soc., 1935, 31, 407-415).—The types of radiation emitted by a quantum-mechanical system when a spinless radiating particle changes its azimuthal quantum no. by 2, 1, or 0 have been examined mathematically. W. R. A.

Diamagnetism of the Dirac electron. II. T. Muro (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 109-115; cf. A., 1934, 1054).-Mathematical. J. W. S.

Elements of the quantum theory. III. Problems of potential barriers. S. DUSHMAN (J. Chem. Educ., 1935, 12, 326-336; cf. this vol., 1050). L. S. T.

Difference in inner pressure of the condensed hydrogen isotopes. H. CLUSIUS and E. BAR-THOLME (Z. Elektrochem., 1935, 41, 487–488; cf. this vol., 155). T. G. P.

Hydrogen atom and non-Euclidian geometry. V. FOCK (Bull. Acad. Sci. U.R.S.S., 1935, 169—188).— Mathematical. J. W. S.

Transport phenomena and quantum mechanics. A. GANGULI and P. MITRA (Current Sci., 1935, 4, 22-23).—A wave-mechanical treatment is applied to transport phenomena in various stars. W. R. A.

Exact solutions of the Schrödinger equation. M. F. MANNING (Physical Rev., 1935, [ii], 48, 161– 164).—Mathematical. N. M. B.

Matrix elements for alkali metals. A. THOMA (Z. Physik, 1935, 95, 539—554).—Mathematical. A. B. D. C. Alkali metals. P. GOMBAS (Z. Physik, 1935, 95, 687–691).—Lattice const., lattice energy, and compressibility are determined theoretically for the K lattice. A. B. D. C.

Quantum levels of neutrons in the nucleus. T. HIKOSAKA (Sci. Rep. Tôhoku, 1935, 24, 208—221). —The energy vals. of the quantum states of neutrons, deduced from a simplified nuclear model, are in accord with observed vals. The theory explains periodicity in nuclear structure. J. W. S.

Neutrino theory of light. II. R. DE L. KRONIG (Physica, 1935, 2, 854—860).—Theoretical discussion. A. J. M.

Calculations of atomic wave functions. IV. Results for F', Al", and Rb'. D. R. HARTREE (Proc. Roy. Soc., 1935, A, 151, 96–105).—A continuation of previous work (A., 1933, 1101).

L. L. B.

Electron conductivity and lattice stability of binary crystals. T. NEUGEBAUER (Z. Physik, 1935, 95, 717-733).—Theoretical. Polarisation energies are calc. A. B. D. C.

Molecular emission spectra of some metallic salts. P. MESNAGE (Compt. rend., 1935, 201, 389—391; cf. this vol., 1051).—The majority of the bands in the spectra of CoCl₂, CrCl₃, FeCl₂, and FeCl₃ may be attributed to diat. mols. CoCl, CrCl, and FeCl, but a series of ultra-violet bands of FeCl₂ and FeCl₃ may be due to FeCl₂ mols. J. W. S.

Representation of statistical distributions by continuous spectra. T. H. HAZLEHURST, jun., and W. H. KELLEY, jun. (J. Chem. Educ., 1935, 12, 309-313).—The method elaborated has been applied to the representation of Maxwellian distribution of mol. velocities, electron density in the H atom, black-body radiation, phase space for a unidimensional gas, and particle density in the classical and quantised linear harmonic oscillator. L. S. T.

New interpretation of the structure of band spectra. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 92—100).—A suggested process of electronic excitation of mols. leads to a new interpretation of band structure. Calc. and observed oscillation frequencies are in good agreement.

N. M. B.

Band spectra of calcium hydride. III. B. GRUNDSTRÖM (Z. Physik, 1935, 95, 574-587).

A. B. D. C.

Absorption and fluorescence measurements of cadmium and zinc halides in the vapour phase. E. OESER (Z. Physik, 1935, 95, 699—716).— CdI_2 shows five, ZnI₂ three, and CdBr₂ two absorption max., and CdCl₂, ZnBr₂, and ZnCl₂ show only continuous absorption. The iodides and CdBr₂ show fluorescence, but the others do not, in agreement with all these halide mols. A. B. D. C.

Absorption spectrum of stannous sulphide. G. D. ROCHESTER (Proc. Roy. Soc., 1935, A, 150, 668-684).—The absorption spectrum of SnS has been analysed up to 1200°. The analysis is consistent with the assumption that the absorbing mol. is the chemical mol. SnS, and there is no evidence that any of the bands are due to the oxidation products of SnS or to S_2 . Evidence relating to Sn isotope effects is discussed. L. L. B.

Near ultra-violet absorption bands of SO₂. R. K. ASUNDI and R. SAMUEL (Proc. Indian Acad. Sci., 1935, 2, A, 30-45).—Additional data and classifications of bands are tabulated. Provisional analyses, with the help of Raman and infra-red data, are given. N. M. B.

Fine structure analysis of the red bands of magnesium oxide and isotope effect. P. C. MAHANTI (Indian J. Physics, 1935, 9, 455-486).— Measurements of the structure lines in the (0,1), (0,0), (1,0), and (2,0) bands and combination differences are tabulated. Each band has two strong P and R branches associated with Mg²⁴O, usually accompanied by fainter components due to Mg²⁵O and Mg²⁶O. The P and R branches are single; the system is due to a ${}^{1\Sigma}\rightarrow{}^{1\Sigma}$ transition. The principal mol. consts. evaluated from rotational term differences are given. N. M. B.

Band spectra of AgO and CuO. F. W. LOOMIS and T. F. WATSON (Physical Rev., 1935, [ii], 48, 280—282).—The spectra obtained by arcing between metal electrodes in O_2 at reduced pressure were photographed. Data and a vibrational analysis are given for the ultra-violet and blue system of AgO; a system in the far red was too faint for measurement. The red system of CuO is discussed. N. M. B.

Scandium oxide bands in the spectra of cold stars. (MLLE.) E. BODSON (Bull. Acad. roy. Belg., 1935, [v], 21, 535-541).—Interpretation of the bands by Russell's method (Astrophys. J., 1933, 77, 345) is in satisfactory agreement with the results of Swing's (cf. A., 1934, 125). N. M. B.

Pleochroism of crystals of rare-earth salts as evidence of the non-rotation of certain electronic orbits. E. E. JELLEY (Nature, 1935, 136, 335— 336).—The absorption spectra for various vibration directions in crystals of Nd, Pr, Sm, and Ce NH_4 sulphates have been determined. With Nd and Pr sulphates, light of certain $\lambda\lambda$ is not absorbed when its plane of direction is in certain sp. directions, indicating that the orbits of at least some of the N electrons are fixed in relation to the crystal structure. Probably the metal ions as a whole are incapable of free rotation. L. S. T.

Theory of co-ordinate linking. VII. Absorption spectra of some complex ions. R. SAMUEL, M. ZAMAN, and A. W. ZUBAIRY (Indian J. Physics, 1935, 9, 491—505; cf. this vol., 427).—Data and deductions from curves for absorption spectra of some complex salts in solutions containing KCl, KBr, NaCl, Na₂CO₃, HCl, and HBr are: K₄[Cr(CN)₆], deformation of mol.; K₂[Pd(CN)₄], mol. Stark effect only, due to positive ion; K[Cu(CN)₂], probably the same; H₂PtCl₆, true complex salt. Data and curves are also given for aq. solutions of [Co(NH₂), CO₃]Br,

are also given for aq. solutions of $[Co(NH_3)_4CO_3]Br$, $[Co(NH_3)_4(NO_2)_2]Cl$, $[Co(NH_3)_4(NO_2)_2](NO_3)$, $[Co(NH_3)_4CO_3](NO_3), 0.5H_2O$, $[Co(NH_3)_5Cl]SeO_4$, $K_2Pd(CN)_4$, $KCu(CN)_2$, and $K_4Cr(CN)_6$, the three last-named in solutions of NaCl, KCl, and Na₂CO₃. Deductions are discussed. N. M. B. Perturbation and predissociation in the $b^{3\Sigma}$ term of the CO band spectrum. L. GERO (Z. Physik, 1935, 95, 747—751). A. B. D. C.

Electronic structures of polyatomic molecules. VII. Ammonia and water type molecules and their derivatives. VIII. Ionisation potentials. IX. Methane, ethane, ethylene, and acetylene. R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 506— 514, 514—517, 517—528).—VII. From spectroscopic and ionisation potential data electron configurations in terms of mol. orbitals are obtained for NH₃, PH₃, H₂O, H₂S, and their derivatives. The longest- λ ultra-violet spectra and min. ionisation potential are ascribed in NH₃ derivatives to excitation of a nearly non-linking electron of the N atom, and in H₂O and H₂S derivatives to excitation of a non-linking O or S atom electron.

VIII. The differences between observed and predicted vals. for ionisation potentials of non-linking electrons are due mainly to charge-transfer effects.

IX. Observed ionisation potentials are interpreted with the aid of the electron configurations for the normal states of C_2H_6 , C_2H_4 , and C_2H_2 . Excited orbitals are discussed. R. C.

Absorption spectra of hydrogen cyanide, hydrazine, ethylene, and ammonia in the Schumann region, and of hydrazine in the quartz ultraviolet. H. J. HILGENDORFF (Z. Physik, 1935, 95, 781-788).—HCN shows bands between 2000 and 1790 Å., C_2H_4 predissociation bands near 1800 Å. with a heat of dissociation of 158.6 kg.-cal. per mol., and N₂H₄ continuous absorption. The ultra-violet measurements on N₂H₄ give heat of dissociation of 122.4 kg.-cal. per mol. A. B. D. C.

Absorption spectrum of methyl iodide. N. S. BAYLISS (Nature, 1935, 136, 264).—No bands were found in the spectrum through 6.6 m. of gaseous MeI at 220 mm. Continuous absorption extends to 3600 Å., but a band system is possible. The absorption limits in equiv. columns of gaseous and liquid MeI (6.6 m. at 220 mm. and 0.6 cm., respectively) occur at approx. the same λ . The determination of absorption limits by extrapolation from results obtained with short columns of gas may lead to erroneous vals., which have no thermochemical significance. L. S. T.

Absorption spectra of some polyatomic molecules containing methyl and ethyl radicals. H. W. THOMPSON (Proc. Roy. Soc., 1935, A, 150, 603-614; cf. A., 1934, 828).—Measurements have been made of the absorption spectra of ZnMe₂, ZnEt₂, HgEt₂, PbEt₄, GeMe₄, NMe₃, NEt₃, PEt₃, Et₂S, Me₂O, Et₂O, and EtSH. Most of the mols. examined show continuous absorption in the ultraviolet region, but ZnEt₂ and HgEt₂ have diffuse bands. An attempt is made to analyse these.

L. L. B. Electron affinity of free radicals. VIII. Diphenylanisylmethyl and the colour of its sodium addition compound. H. E. BENT and M. DORFMAN. IX. Pentaphenylethyl and triphenyldiphenylylethyl. M. DORFMAN (J. Amer. Chem. Soc., 1935, 57, 1452—1455, 1455—1459; cf. this vol., 1058).—VIII. The extinction coeff. of solutions of diphenylanisyl-

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methyl (R) and the val. of ΔF for the reaction of Rwith Na have been determined. The results are consistent with the reactions R + Na = NaR and NaR + R = $\text{Na}R_2$. The second reaction is somewhat erratic.

IX. ΔF for the addition of Na to pentaphenylethyl and triphenyldiphenylylethyl in Et₂O solution has been determined. E. S. H.

Absorption spectra of α - and β -carotenes and lycopene. E. S. MILLER, G. MACKINNEY, and F. P. ZSCHEILE, jun. (Plant Physiol., 1935, 10, 375–386).— Curves showing absorption over the range 3900— 5300 Å. are given. Carotenes from different localities separated on different adsorbents [MgO and Ca(OH)₂] yielded identical products. A. G. P.

Spectroscopy of an enzyme reaction. K. G. STERN (Nature, 1935, 136, 335).-When Et H peroxide is added to an active prep. of liver catalase at $p_{\rm H}$ 7, the enzyme spectrum immediately disappears and two new green absorption bands appear. After a few min. these bands decrease in intensity and the original spectrum simultaneously reappears. The cycle can be repeated by addition of fresh substrate. At 4°, the time required for the cycle is 4 times that at 24°. The reappearance of the enzyme spectrum is accompanied by the disappearance of titratable peroxide O from the system. No gas is evolved in this reaction. The spectrum of the intermediate compound is attributed to a combination of enzyme with substrate, 5×10^5 mols. of substituted peroxide per enzyme mol. being required to complete the transformation into the intermediate compound. With H_2O_2 as substrate, no apparent change of the enzyme spectrum is observed. L. S. T.

Significance of the isotope effect in the analysis of the vibration spectra of organic molecules. E. BARTHOLMÉ and H. SACHSSE (Z. Elektrochem., 1935, 41, 521—522).—The isotope effects resulting from the substitution of H by D in a mol. allows important conclusions to be reached concerning the particular portions of the mol. responsible for the vibrational spectrum concerned, even when the mol. is too complicated to permit a quant. interpretation. Results obtained by substituting D in MeOH and C_2H_6 are discussed. T. G. P.

Optical investigations of the constitution of glasses. Transformation point and boric acid anomaly. W. WEYL (Z. Elektrochem., 1935, 41, 472-476).—Absorption spectra show that the transformation point is not a true "transition point." Ni and Co have been used as indicators in the spectroscopic investigation of the chemical effects resulting from the addition of B_2O_3 to a Na borosilicate glass. The influence of B_2O_3 on the physical properties of glasses is discussed. T. G. P.

Investigations in the infra-red. I. Absorption spectrum and molecular structure of borates. M. K. SEN and A. K. S. GUPTA (Indian J. Physics, 1935, 9, 433-443).—Results of investigations on the borates of Li, K, Ca, Mn, Cu, and Pb in the range 5-15 μ agree with the predictions of Cassie (cf. this vol., 281). The val. of the true force const. of the radical compared with that of CO₃ and NO₃ shows that the linking is not localised as in BCl₃; the plane configuration is not due to repulsion of the O ions alone and follows the central quantisation more closely than NO_3 or CO_3 . N. M. B.

Quantitative studies of the infra-red absorption of organic compounds containing NH and OH groups. O. R. WULF and U. LIDDEL (J. Amer. Chem. Soc., 1935, 57, 1464—1473).—Results in the region 1.65— 1.35μ are given for many org. compounds, containing NH, NH₂, and OH groups, in CCl₄ solution. The origin of the spectra and the applicability to the detection of particular groups and the determination of some types of org. mols. are discussed. E. S. H.

Far ultra-violet absorption spectra and ionisation potentials of benzene and deuterobenzene. W. C. PRICE and R. W. WOOD (J. Chem. Physics, 1935, 3, 439—444).—The spectra of both substances, measured at 2000—1000 Å., are similar, strong continuous absorption at 1840—1600 Å. being followed by sharp bands down to about 1360 Å. An ionisation potential of $9\cdot190\pm0\cdot005$ volts is deduced for C_6H_6 , and that of C_6D_6 is about 3×10^{-4} volt greater. All the electronic states are split up into patterns believed to be due to true electronic multiplicity. From more diffuse bands below 1360 Å. the second ionisation potential of C_6H_6 is estimated at $11\cdot7\pm0\cdot3$ volts. R. C.

Near infra-red spectrum of deuterobenzene. R. B. BARNES and R. R. BRATTAIN (J. Chem. Physics, 1935, 3, 446—449).—The transmission spectrum has been examined from 1 to $13 \cdot 25 \mu$. The shifts of the infra-red active vibrations agree with a plane hexagon model for C₆H₆ (cf. A., 1934, 928). The transmission spectra of C₆H₆ and thiophen from 1 to 15μ have been observed. R. C.

Raman spectrum of deuterobenzene. R. W. WOOD (J. Chem. Physics, 1935, 3, 444—445).—The Raman spectrum of C_6D_6 and new lines in that of C_6H_6 have been observed. The shifts of the lines are discussed. R. C.

Linking energies from Raman frequencies and thermochemical data. K. S. G. Doss and M. P. V. IYER (Current Sci., 1935, 4, 25–26).—Discrepancies between the linking energy val. calc. from Raman and thermochemical data for SeiO and SiO are discussed. From the Raman frequencies of SeO_4'' , SeO_3'' , SO_4'' , and SO_3'' the heat of formation of $H'_{(aq)}$ is calc., but the vals. are not concordant, and it is therefore suggested that Raman data can be employed to calculate heat of formation of mols., but not of ions.

W. R. A.

Raman spectra of arsenic trichloride and of its mixtures. A. E. BRODSKII and A. M. SACK (J. Chem. Physics, 1935, 3, 449–451).—The Raman frequencies of C_6H_6 , CCl₄, MeOH, or EtOH are unchanged on admixture with AsCl₃, but those of AsCl₃ decrease in presence of MeOH or EtOH. It is suggested that for the frequencies of one component of a mixture to be shifted by the other the latter must have a considerable dipole moment, and in the former the linking between the parts of the mol. participating in active vibrations, here As-Cl, must be weak. The consts. of the $AsCl_3$ mol. have been calc. and agree with electron-diffraction data. R. C.

Raman spectra. II. Raman spectra of perchloric acid and nitrosyl perchlorate. W. R. ANGUS and A. H. LECKIE (Proc. Roy. Soc., 1935, **A**, **150**, 615—618).—Raman spectra of 60% HClO₄, solid NOClO₄, and solutions of NOClO₄ in HClO₄ of varying concn. have been obtained. The spectrum of NOClO₄ is similar to that of HClO₄, with the addition of a strong displacement at 2329 cm.⁻¹ assigned to the NO⁺ group. This confirms the val. previously found for this group in (NO)₂SO₄ (cf. this vol., 1056). L. L. B.

Raman spectrum of carbon disulphide. A. V. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 46-53).— A detailed investigation of the intensity and polarisation characters of the Raman lines is described. The Q branch of the principal vibration line 656 cm.⁻¹ cannot be separated from the PP and RR branches; in these the intensity distribution is similar to that in the wings accompanying the Rayleigh lines in liquids. When excited by λ 4358 the depolarisation of the line is 0.15, increasing to 0.2 if excited by λ 4046. The ratio of intensities of the peaks of 656 and 796 Raman lines is 9.2. N. M. B.

Carbon isotope in Raman scattering. I. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 86-91).—The principal Raman lines in C_6H_6 , cyclopropane, and C_2H_6 of frequency shifts 992, 1188, and 993 have feeble companion lines of shifts 985, 1175, and 974, respectively. These are attributed to C^{13} isotope replacements, *i.e.*, $C^{12}_5C^{13}H_6$, $C^{12}_2C^{13}H_6$, and $C^{12}H^{13}H_6$, respectively. This is deduced from positions and relative intensities. N. M. B.

Diffusion spectra (Raman effect) and infra-red absorption spectra of saturated aliphatic alcohols and ethylenic hydrocarbons. A. ANDANT, P. LAMBERT, and J. LECOMTE (Compt. rend., 1935, 201, 391-393).-The Raman spectra and infra-red absorption spectra (between 500 and 1600 cm.-1) of 8 saturated alcohols and the 8 ethylenic hydrocarbons produced by their dehydration have been measured. The very strong 1600 cm.-1 Raman line characteristic of the double linking does not appear in absorption. tert.-Alcohols are characterised by a very strong infrared band at 1140 cm.⁻¹ and a weak band at 1240 cm.⁻¹, neither of which has a direct equiv. in Raman spectra. The max. due to the C chains do not occur in the same positions in the two series. The combined data permit distinction between successive homologues and isomerides. Ethylenic hydrocarbons have spectra distinct from those of the alcohols from which they are derived, suggesting that the ethylenic linking disturbs the true vibrations of the C chains.

J. W. S.

Raman effect. XLIII. Raman effect and free rotation. II. K. W. F. KOHLRAUSCH and (GROSS-PRINZ) YPSILANTI. XLIV. Raman effect and free rotation. III. K. W. F. KOHLRAUSCH and W. STOCKMAIR (Z. physikal. Chem., 1935, B, 29, 274—291, 292—298; cf. this vol., 914).—XLIII. The Raman spectra of OMe·CH₂·CN, CH₂Cl·OMe, and substituted ethanes, CH₂X·CH₂Y, have been determined. Taking into account infra-red and polarisation data and utilising models (*ibid.*, 432), the Raman spectra of $CH_2X \cdot CH_2Y$ indicate that in the liquid state these are equilibrium mixtures of plane *cis*- and *trans*-forms, the latter predominating at room temp. The time of sojourn in either configuration is long compared with the time of vibration, but so short compared with that of chemical attack that chemical separation is impossible. Trumpy's deductions (*ibid.*, 565) are criticised.

XLV. From the Raman spectra of allyl derivatives, CH₂:CH·CH₂X, it is concluded that these are mixtures in the liquid state of plane *cis*- and *trans*-forms. CH₂:CH·CH:CH₂ is apparently wholly *trans*.

R. C. Raman effect in solutions of some amino-acids. N. WRIGHT and W. C. LEE (Nature, 1935, 136, 300).— Raman frequencies and estimated relative intensities are recorded for solutions of glycine, tyrosine, alanine, and cystine. L. S. T.

Decay time of fluorescence measured with an improved fluorometer. W. SZYMANOWSKI (Z. Physik, 1935, 95, 440—449).—Accuracy attained is $0.2-0.3 \times 10^{-9}$ sec. A. B. D. C.

Duration of luminosity and decay law for fluorescence radiation. W. SZYMANOWSKI (Z. Physik, 1935, 95, 450–459).—The exponential law holds for decay of fluorescence of fluorescein in H_2O . A. B. D. C.

Variation of fluorescence decay time with concentration of dye and viscosity of solvent. W. SZYMANOWSKI (Z. Physik, 1935, 95, 460—465).— Collisions of the second kind cannot directly explain extinction processes, as revealed by decay of fluorescence of fluorescein in H_2O , EtOH, Bu^BOH , and glycerol. A. B. D. C.

Molecular rotation and measurements of decay time of fluorescence. W. SZYMANOWSKI (Z. Physik, 1935, 95, 466—473).—The rate of decay of the radiation excited by polarised light depends on the orientation of the fluorescent radiation relative to the plane of polarisation. A. B. D. C.

Excitation spectra of the luminescence of solid solutions of rhoduline. S. I. GOLOUB (Physikal. Z. Sovietunion, 1935, 7, 49—57).—The excitation spectra of fluorescence and phosphorescence of solid solutions of rhoduline in sucrose have been examined and shown to be identical, indicating identical mechanisms of excitation in the case of passage to a temporary or prolonged excited state. R. S. B.

Distribution of intensity in the Rayleigh lines of compressed gases. I. Experiments with carbon dioxide. J. WEILER (Ann. Physik, 1935, [v], 23, 493-506).—The distribution of intensity of the Rayleigh lines of CO₂ at 10-80 atm. and in the neighbourhood of the crit. temp. was determined for Hg line 4047 Å. The variation of the intensity (I) in the middle of the line with pressure was determined. I \propto change of density, d, of the gas. In the middle part of the wings $I \propto d$. At high pressures an additional radiation is observed, which is connected with the inner mol. state of the compressed gas.

A. J. M.

Hindered rotation and oscillation of molecules in liquids and in crystals. S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 63-66).—The extended portion of rotation wings in liquids and the separate lines which take their place in the corresponding solids are explained as due to small mol. oscillations or incomplete rotations, the motion being properly quantised in solids, and imperfectly so in liquids. N. M. B.

Experiments with two thin metallic layers pressed together. A. DEUBNER (Naturwiss., 1935, 23, 557).—The conductivity and light absorption of thin metallic layers made by vaporisation do not vary directly with the amount of substance vaporised. That this behaviour is not due to some anomalous variation of the thickness of the layer with the amount of substance vaporised is shown by pressing together two equally thin layers of Ag $(1-2\times10^{-6} \text{ cm.})$. The properties of the two layers are not additive. It is shown that the light absorption should vary with the square of the thickness. A. J. M.

Contact phenomena in carborundum resistances. I. V. KURTSCHATOV, T. Z. KOSTINA, and L. I. RUSINOV (Physikal. Z. Sovietunion, 1935, 7, 129—154).—Existing theories of self-regulating carborundum resistances are rejected. It is suggested that the phenomenon is governed by the transference of electrons at the points of contact of the CSi particles through the operation of the wave-mechanical tunnel effect. Results agree with experimental data.

Photo-electric effect in a layer of silver deposited on nickel. N. FEDENEV (Physikal. Z. Sovietunion, 1935, 7, 58-65).—The photo-electric current has been studied with films of Ag sublimed on Ni. The work function rises from 3.7 to 4.2 volts as the film thickness increases from 0 to 3.5 Å., and then decreases, becoming const. at 3.9 volts (val. for pure Ag) at > approx. 12 Å. R. S. B.

Photo-electric cells with an artificially deposited insulating layer. W. C. VAN GEEL and J. H. DE BOER (Physica, 1935, 2, 892-900).--"Sperrschicht" cells with Se as semi-conductor, and CaF₂, SiO₂, MgO, and a cresol-CH₂O resin as insulating layers are described. The photo-electric effect is observed with such cells, although the insulating layer itself can give rise to no inner photoeffect. The photo-conduction of the insulating layer is not, therefore, a necessary factor in a "sperrschicht" cell. The connexion between photo-current (i) and intensity of light (L) is given by $i=AL^{\frac{3}{2}}$ (A const.). The inner photo-effect of the Se used obeyed the relationship $i=BL^{\frac{3}{2}}$ (B const.). A. J. M.

Selective photo-effect. P. I. LUKIRSKI and J. L. HURGIN (Physikal. Z. Sovietunion, 1935, 7, 99—107). —The photo-electric effect for pure metals is shown to be purely optical in origin, and is correlated with a variation in the electromagnetic field depending on λ and degree of polarisation. R. S. B.

Spectral photo-electric sensitivity of composite photo-cathodes on variation of the supporting metal and alkali metal. W. KLUGE (Z. Physik, 1935, 95, 734-746).—Cathodes of Ag, Au, Ni, and Cu supporting Na, K, Rb, and Cs all show a long-wave max. in the visible, and two short-wave max. in the ultra-violet. A. B. D. C.

Light distribution and the external photoeffect. F. HLUCKA (Z. Physik, 1935, 95, 486–498). —Available data are critically reviewed.

Temperature dependence of the photo-electric effect. K. MITCHELL (Proc. Camb. Phil. Soc., 1935, 31, 416—428).—The temp. dependence of the photoelectric effect with the image field agrees with Fowler's T^2 law near the threshold. Fowler's $T^{3/2}$ law rests on a mistake in the normalisation of the free wave functions. The methods of Fowler and Du Bridge for analysing experimental results are discussed; Du Bridge's method should give more trustworthy results. W. R. A.

Electrostatic potential of a crystal of the cuprite type. T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 1, A, 905-914).—Theoretical.

A. B. D. C. Dielectric loss in anisotropic liquids. V. FREDERIKS, G. MICHAILOV, and D. BENESCHEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 2, 469– 473).—A repetition of the work of Ornstein *et al.* (A., 1933, 338) on *p*-azoxyanisole gave results in disagreement with Kast's. W. R. A.

Molecular polarisation and association. W. HEROLD (Z. physikal. Chem., 1935, B, 29, 259-273). -The calculation from the variation of mol. polarisation with concn. of orientation polarisation and concn. of double mols. when only double mols. are present in addition to single mols. is described; the method is also applicable on certain assumptions to more complex systems. Application to Parts' data for C₆H₆ solutions of Bu halides (A., 1930, 667) shows that at the concns. examined only double mols. and single mols. are present, and that the former consist of complexes with parallel and antiparallel orientations, respectively, of the moments of the components. The heat of formation of the two types of complex has been calc.; it becomes increasingly positive with increasing steric shielding of the C-halogen groups. The association is not a simple function of the shielding. **R**. C.

Influence of nuclear substituents on side-chain reactions. IV. Reconsideration of the quantitative relationship between energies of activation and dipole moments. D. P. Evans, V. G. MORGAN, and H. B. WATSON (J.C.S., 1935, 1174-1178) .-In three cases where energies of activation have been determined for a given reaction of a series of m- or p-substituted aromatic compounds, their relationships with the dipole moments of the corresponding substituted benzenes is given generally by $E = E_0 \pm$ $C(\mu + a\mu^2)$. It represents a slight modification of Nathan and Watson's original formula. The same relationship is found in eleven other reactions, on the assumption that, throughout a series of nuclearsubstituted compounds, all factors other than the energy of activation are const. It is suggested that both the constancy of factors other than E and the relationship between E and μ may persist, with

R. S.

A. B. D. C.

reservations, throughout a large no. of side-chain processes. H. W.

Rotating polar groups in organic molecules. W. ALTAR (J. Chem. Physics, 1935, 3, 460-472).— The variation with temp. of the dipole moment of mols, with rotating polar groups may be quantitatively explained in terms of intramol. forces opposing free rotation. Application to $(\cdot CH_2Cl)_2$ of considerations derived from a discussion of the statistical wt. to be assigned to a configuration and the approximation of the periodic potential function by its first and second Fourier component indicates the presence of repulsive forces between the two Cl atoms at distances as large as 4 Å. The *cis*- and *trans*forms of (:CHCl)₂ probably both have approx. the same heat of formation. An explanation of the observed equilibrium ratio of the two forms is offered. R. C.

Dielectric constant of hydrogen at pressures up to 1425 atm., and at temperatures of 25° and 100°. A. MICHELS, P. SANDERS, and A. SCHIPPER (Physica, 1935, 2, 753—756; cf. A., 1933, 447).—The dielectric const. has been measured up to 1425 atm. The Clausius-Mosotti expression $P=(\varepsilon-1)/(\varepsilon+2)d$ is fulfilled. T. G. P.

Magnetic variation of the dielectric constant of liquids. A. PIEKARA and M. SCHÉRER (Compt. rend., 1935, 201, 335—337).—The increase of the dielectric const. (ε) of a liquid under the action of a magnetic field follows the law $\Delta \varepsilon = AH^2 + BH^4$, where A and B are consts. characteristic of the liquid. The increase for C₆H₆ and CHCl₃ under a field of 50 k. gauss is independent of λ between 500 and 1500 m. The sign of the change is the same whatever the orientation of magnetic to electric fields. For C₆H₆ the effect is about twice as great for perpendicular fields as for parallel fields. The results can be explained by mol. deformation. J. W. S.

Electric moments of alkyl borates and substituted boric acids. M. M. OTTO (J. Amer. Chem. Soc., 1935, 57, 1476—1478).—The electric moments of Bu borate, amyl borate, phenyl-, *n*-amyl-, and *n*-butyl-boric acids in C_6H_6 and dioxan solutions have been determined. The acids are not associated in C_6H_6 , and no compounds are formed with dioxan.

Dielectric properties of some vegetable oils. G. R. PARANJPE and P. Y. DESHPANDE (Proc. Indian Acad. Sci., 1935, 1, A, 880—886).—d, n, and dielectric const. at 30 m. have been determined at 26° for castor, olive, sesame, and coconut oils in C₆H₆, and give the electric moments as 3.68, 3.03, 2.91, and 2.82×10^{-18} , respectively. A. B. D. C.

Specific rotatory power and stereochemistry of the cinchona alkaloids.—See this vol., 1256.

Solvent action. X. Rotatory powers of dimethylene tartrate, methylenetartaric acid, and its dimethyl ester in the presence of added solvents and salts. H. G. RULE and J. P. CUNNING-HAM. XI. Influence of solvent, concentration, and temperature on the rotatory powers of *l*menthyl o-substituted benzoic esters. H. G. RULE and A. DUNBAR (J.C.S., 1935, 1038-1043,

1043—1049).—X. $[M]_{5461}^{20}$ has been determined for dimethylene tartrate (I), methylenetartaric acid (II), and Me, methylenetartrate (III) in various solvents. The characteristic rotatory powers of (I) and (III) in solution rise in magnitude as the dipole moment of the solvent increases. The rotatory power of the strongly-associated (II), on the other hand, varies irregularly with the solvent, and the observed changes may be interpreted on the assumption that solutesolvent and solute-solute association both raise the rotation. In agreement with the demands of the association hypothesis, the optical rotation of (III) dissolved in a non-polar solvent increases with the concn. of the ester and the rotatory powers of solutions in a highly polar and in a non-polar solvent approach one another as the temp. rises. The cationic effects produced by the addition of metallic chlorides to aq. solutions of the above esters are identical with those found for optically active acids and their salts. Such effects must therefore be transmissible through the dipoles as well as through ionised groupings contained in the active solute.

XI. $[M]^{20}$ has been observed for *l*-menthyl *o*-substituted benzoates (substituent NO2, CO2H, H, OH, Cl, OMe) in various solvents. The effect of concn. on $[M]_{b=01}^{\infty}$ for the esters in C₄H₆ and the behaviour of *l*-menthyl *o*-nitrobenzoate (IV) at various concns. in mixtures of solvents have been investigated. The influence of temp. on $[M]_{5461}$ of the esters in PhNO₂, PhBr, decahydronaphthalene, and PhCN has been observed. With the more polar NO_2 ester and H phthalate, the rotations fall as the polarity of the solvent increases or as the concn. of these esters in a non-polar solvent rises. In each case the temp.rotation curves for the ester in polar and in non-polar solvents converge as the temp. rises. These changes are explained on the theory of dipoles by assuming varying degrees of solute-solute or solute-solvent association in accordance with experimental conditions. For the remaining esters the observed changes are irregular. In general, solvents of exceptionally high refractive index tend to yield solutions of abnormally high rotatory power with each of the six esters examined, thus showing the existence of a minor effect due to the refractivity of the solvent. In $n - C_6 H_{14}$ the rotatory powers of l-menthyl salicylate exhibit an exaltation between the concns. c=35 and c=65. H. W.

Rotatory dispersion of α -iodopropionic acid and β -octyl iodide. W. KUHN and H. BILLER (Z. physikal. Chem., 1935, B, 29, 256—258).—The absorption and rotatory dispersion of β -octyl iodide and Me α -iodopropionate and the rotatory dispersion of α -iodopropiondimethylamide have been measured. The results confirm the view that (+)-iodopropionic acid corresponds with d(-)-lactic acid. Levene and Rothen's methods (A., 1934, 476) are criticised. R. C.

Electro-optical Kerr effect in ammonia, nitrogen, and oxygen. W. M. BREAZEALE (Physical Rev., 1935, [ii], 48, 237—240).—The following abs. vals. for the Kerr const. were obtained : anhyd. NH₃ at 6500 and 5750 Å., 13—30 atm., and 40—80° $62\cdot3\pm1\cdot8\times10^{-12}$; N₂ and O₂ at 6500 Å., approx.

E. S. H.

100 atm., and 20-65° 4.64 ± 0.10 and $6.94\pm0.30\times10^{-12}$, respectively. N. M. B.

Geometrical structure of the N_3H molecule. G. HERZBERG, F. PATAT, and H. VERLEGER (Z. Elektrochem., 1935, 41, 522—524).—The infra-red rotation-vibration spectrum of gaseous N_3H consists of an intense band at 1.045 μ and a weaker one at 0.808 μ . The fine structures indicate that the N atoms lie in a straight line. In most of the mols. the H is not in this line, but a linear modification probably exists. T. G. P.

Rotation and vibration of the methane molecule. H. A. JAHN (Ann. Physik, 1935, [v], 23, 529— 556).—Mathematical, employing a group theory method. A. J. M.

Character of binding in the carbon monoxide molecule. R. J. JAANUS and J. A. SHUR (Physikal. Z. Sovietunion, 1935, 7, 19–25).—The val. -118 ± 6 $\times 10^{-7}$ has been determined for the mol. magnetic susceptibility (χ) of CO by a modification of Lehrer's method (A., 1926, 1086). Since Pascal's additivity law, with a C:O linking, gives $\chi = -42.5 \times 10^{-7}$, it is inferred that the val. of χ implies a triple or even quadruple linking. R. S. B.

Dissociation of the carbon monoxide molecule. B. ROSEN (Nature, 1935, 136, 226).—A correction (cf. this vol., 925). L. S. T.

Theory of ionic recombination. W. R. HARPER (Proc. Camb. Phil. Soc., 1935, 31, 429–430).—The correction of a numerical error in a previous paper (A., 1932, 554) gives better agreement with experimental data. W. R. A.

Statistical theory of superlattices. H. A. BETHE (Proc. Roy. Soc., 1935, A, 150, 552—575).— Assuming interaction between nearest neighbouring atoms only, the order in an alloy containing two sorts of atoms in equal proportions is calc. statistically. At high temp. the state of the crystal as regards order is rather similar to a liquid, but at low temp. the crystal as a whole is ordered, and the structure is "solidlike." The long-distance order and energy as functions of temp. aro discussed qualitatively and calc. The theory of Bragg and Williams (A., 1934, 954) gives a fair approximation. L. L. B.

Molecular constants and potential energy curves for diatomic molecules. M. L. HUGGINS (J. Chem. Physics, 1935, 3, 473-479).-Using a modified Morse equation for the potential energy of a diat. mol., in which the repulsive term is the same for all electronic states of a particular mol., U= $ce^{-a(r-r_{13})} - C'e^{-a'(r-r_e)}$, and putting $a = 6.0 \times 10^8$ cm.⁻¹, r_{12} vals. calc. from the band spectrum consts. are approx. const. at 1.46 Å. for all except highly excited states of all diat. mols. containing only elements in the first period of the periodic scheme and with < 12 electrons. This indicates that the repulsive term is nearly const., and permits calculation from the vals. of two mol. consts. of those of others. The calc. vals. of $\omega_e y_e$ and $\omega_c z_e$ are small, but ± 0 . To obtain the observed dissociation energy a must be taken as 4.0×10^8 cm.⁻¹ R. C.

Surface tension and its variation with temperature. A. GANGULI and P. MITRA (Current Sci., 1935, 4, 23—24).—London's (A., 1931, 149) quantummechanical expression of van der Waals force requires modification for liquids and solids. A further modification for absorption phenomena is suggested. W. R. A.

Possibility of faulty explanations in X-ray diascopy due to neglecting the selective absorption of X-rays. F. REGLER (Physikal. Z., 1935, 36, 530-535).—Errors can easily arise in dealing with X-ray diagrams when the K-absorption edge of the substance which is being irradiated lies in the λ range of the X-rays used. Such errors occur particularly in the investigation of metals in solutions of salts which have approx. the same degree of absorption as the metal. The contrast of the X-ray photograph obtained with regard to selective absorption, and methods of increasing it, are considered. A. J. M.

Crystal and slit systems for X-ray monochromatisation and spectroscopy. G. I. HARPER (Proc. Roy. Soc., 1935, A, 151, 118—141).—A quant. theory of the use of crystal and slit systems in X-ray physics for the production of monochromatised beams and for the analysis of composite radiations is developed. L. L. B.

X-Ray source in a single crystal. G. BORR-MANN (Naturwiss., 1935, 23, 591—592).—Secondary X-rays produced by the irradiated single crystal interfere and give a Laue pattern. A. J. M.

Tabulated data for the seventeen plane groups. A. L. PATTERSON (Z. Krist., 1935, 90, 543—554).— Tables necessary for the application of the preceding paper are given. B. W. R.

Technique of structure determination. A. HETTICH (Z. Krist., 1935, 90, 473-492).—Summarised or improved ideas under the following heads are given: (a) allotting of indices to Weissenberg (moving-film) photographs; (b) adjustment of the specimen on the goniometer by X-rays, when visible faces are not available; (c) varying effective exposure time in photometric work, due to the location of poles of planes at varying angles from the equator; (d) the "Eigen" diagram, a new concept in X-ray Fourier treatment of groups of atoms; (e) optical methods of synthesis of Fourier components in the final determination of crystal structure.

B. W. R.

Detection and evaluation of residual distortion in crystals, with special reference to electric steel. G. L. CLARK and M. M. BECKWITH (Z. Krist., 1935, 90, 392-398).—4% Si steel after cold-working and heat-treatment gives an X-ray photograph intermediate between a Laue and a powder diagram; an arbitrary modulus depending on distortion and position of the spots is found to measure quantitatively the degree of residual distortion, and to correspond with the magnetic properties. B. W. R. Determination of the distortion axis of bent crystals from Laue diagrams. W. Boas and H. EKSTEIN (Z. Krist., 1935, 90, 408—414).—A mathematical treatment, applied in particular to a Zn crystal. B. W. R.

Polished layer of metals. M. MIWA (Sci. Rep. Töhoku, 1935, 24, 222—239).—The diffraction patterns of Cr. Fe, Co, Ni, Cu, Zn, and Ag become blurred as the surfaces are polished, certain lines becoming more weakened than others until finally they yield two diffuse lines, the spacing of which indicates that the surface becomes an amorphous liquid-like layer (cf. Beilby). The results with Cd, Sn, and Sb indicate that their polished surfaces consist of minute pseudocrystals, whilst polished surfaces of Si, Mn, and Bi, owing to their brittleness, are cryst. J. W. S.

Grain changes in polymorphic transformation. G. TAMMANN and W. BOEHME (Z. anorg. Chem., 1935, 223, 365-368).-When polymorphic transformation occurs in a cryst. melt, the boundaries of the original grains may, or may not, be overstopped, depending mainly on whether the original crystallisation occurred as dendrites and spherolites or as crystallites, respectively. KNO_3 , $N\dot{H}_4NO_3$, AgI, AgNO₃, and TINO₃ crystallised as dendrites, S and resorcinol as spherolites. A small, irregularly oriented grain is favourable for the strength of Fe and alloy steels; the $\delta - \gamma$ transition gives much smaller grains, the $\gamma-\beta$ smaller still, but as the orientation of β and γ grains is identical, this gives no technical improvement of Fe. The $\beta-\alpha$ transition is accompanied by no change of size or orientation of grains. The effect of certain admixtures on the Fe transitions is briefly discussed. S. J. G.

Amorphous antimony. J. A. PRINS (Nature, 1935, 136, 299).—Changes in the electron diffraction patterns of amorphous Sb obtained by distillation in vac. (A., 1933, 657) show that crystallites oriented at random are formed at $120-150^{\circ}$ according to the thinness of the film. The patterns of explosive Sb are identical with those of the amorphous films. The diamagnetic susceptibility increases markedly when explosive Sb changes to the ordinary form. This and the heat of crystallisation suggest that explosive Sb is in the supercooled liquid state. L. S. T.

Recrystallisation of pure aluminium. J. CAL-VET, J. J. TRILLAT, and M. PAIČ (Compt. rend., 1935, 201, 426-428).—The rate of recrystallisation of very pure cold-rolled Al was high, being complete in 32-48 hr. at 40°, and in < 1 min. at 100°.

J. S. A.

Transformation of magnetite at low temperature. H. SHOJI (Sci. Rep. Tôhoku, 1935, 24, 250— 253).—Comparison of the X-ray diffraction patterns of magnetite at room temp. and at -190° indicates no lattice transformation between these temp. Hence the transformation found at -162° by thermal, dilatometric, electric, and magnetic methods is probably a change either in the state of the electrons or in the orientation of the atoms. J. W. S.

Fine structure of X-ray absorption edges of alloys. II. CuBe, NiO, and $AuCu_3$ (statistic and ordered phases). R. SMOLUCHOWSKI (Z.

Physik, 1935, 95, 588—598; cf. this vol., 812).—The character of the linkings throughout the lattice affects the position of the edges, but not their fine structure. The fine structures of β -brass and CuBe, similar lattices, are totally different, due to change of at. no. from Zn to Be. A. B. D. C.

Crystal structure and composition of rhombic cobalt silicide. B. BOREN, S. STÅHL, and A. WEST-GREN (Z. physikal. Chem., 1935, B, 29, 231—235; cf. A., 1934, 482).—Co₂Si has the space-group V_{λ}^{16} . The Si atoms form zigzag chains in the direction of the c axis, the at. arrangement being similar to that in FeB, CoB, and Cr₃C₂. R. C.

Crystal structure of aluminium orthophosphate AlPO₄. H. F. HUTTENLOCHER (Z. Krist., 1935, 90, 508—516).—The prep., morphology, and X-ray examination of AlPO₄ are described; the crystal is hexagonal, $a_0 4.93$, $c_0 2 \times 5.47$ Å. The similarity to quartz and AlAsO₄ is indicated. B. W. R.

Diffraction of X-rays by a linear crystal grating of AgCN. C. D. WEST (Z. Krist., 1935, 90, 555-558).—AgCN cryst. from aq. $\dot{\rm NH}_3$ solution has a structure in which $\cdot {\rm Ag} \cdot {\rm C} \cdot {\rm N} \cdot {\rm C} \cdot {\rm Ag} \cdot$ chains are extended along the c axis in regular hexagonal packing with other similar chains. Photographs are described which correspond with diffraction from this lattice, if random translation along the length of the chain is assumed. B. W. R.

Symmetry alterations of etch figures due to optically active impurities. J. Novik (Z. Krist., 1935, 90, 385–391).—Small concess. of malic acid (active) in AcOH (inactive) produce considerable changes in the symmetry of etch-figures on the cleavage plane of CaCO₃. Various concess. of sucrose had no such effect. B. W. R.

Mineral carbonates. K. SCHOKLITSCH (Z. Krist., 1935, 90, 433—445).—Lattice consts. and various physical data for a series of mineral carbonates (dolomite, magnesite, siderite, etc.) are determined and collated with the chemical composition.

B. W. R.

X-Ray analysis of the structure of iridescent shells. S. RAMASWAMY (Proc. Indian Acad. Sci., 1935, 1, A, 871—879).—X-Ray diffraction patterns of the nacreous layer show it to consist of aragonite crystals with their c axes normal to the surface, and the ab planes variously distributed depending on the species examined. A. B. D. C.

Crystal structure of cyanuric triazide. (MISS) I. E. KNAGGS (Proc. Roy. Soc., 1935, A, 150, 576– 602).—Crystals of $(C_3N_3)(N_3)_3$ have been examined by X-rays and subjected to a Fourier analysis about the zone parallel to the hexagonal axis. The mol. is planar and has a 3-fold axis of symmetry, and the 2 mols. of the unit cell are situated on planes separated along the c axis by half its length. The configuration of the mol. has been determined, and the following interat. distances are given: C—N outside the C_3N_3 ring, 1·38 Å.; C—N in the C_3N_3 ring, 1·38 Å.; C=N in the C_3N_3 ring, 1·31 Å.; N=N, 1·26 Å.; N=N, 1·11 Å. The N₃ group is linear, and is linked to a C only of the C_3N_3 ring. The latter is a 6-membered ring having trigonal symmetry and alternate double and single linkings. There is no oscillating double linking as in C_6H_6 . The mols. are arranged in sheets 2.98 Å. apart. L. L. B.

Study of the crystal structures of s-di-iodoethane and s-di-iodoethylene. H. P. KLUG (Z. Krist., 1935, 90, 495–507).—(CH₂I)₂ and s-trans-C₂H₂I₂ are isomorphous, monoclinic, space-group C_{2h}^{5} , a_0 7.582, b_0 12.897, c_0 5.810 Å., β 90° 12′, and a_0 7.280, b_0 13.310, c_0 5.553 Å., β 90°, respectively. The pseudorhombic cell is used as the basis for discussion; the I parameters are fixed from intensity measurements. B. W. R.

Crystallography of pentaerythritol tetraphenyl ether. J. BEINTEMA, P. TERPSTRA, and W. J. VAN WEERDEN (Rec. trav. chim., 1935, 44, 627—630).— Pentaerythritol Ph₄ ether crystallises in the tetragonal bisphenoidal class, a:c=1:0.6843. The crystals are built on a body-centred lattice; space-group S_4^3 , 2 mols. in unit cell of dimensions $12.32 \times 12.32 \times 8.43$ Å. The mol. possesses fourfold alternating axis of symmetry. A structure is suggested in which the planes of the Ph are parallel to {110} and the aliphatic C show considerable departures from the ideal angle between the valencies. H. W.

Crystalline structure of the sugars. I. Simple sugars and glycosides. E. G. Cox, T. H. GOODWIN, and (MISS) A. I. WAGSTAFF (J.C.S., 1935, 978—982).— The cell dimensions and space-groups of sorbose, α -galactose, α -methylgalactoside, α -fucose, α -methylgalactoside-6-bromohydrin, β -methylarabinoside, and α -methylfucoside are recorded. The accepted configurations of the groups attached to Cl are confirmed. F. R. G.

Crystal structure of methylene-blue. W. H. TAYLOR (Chem. and Ind., 1935, 732—734).—X-Ray data are given for the chloride, bromide, iodides I and II of methylene-blue, and also for Se methylene-blue bromide. The mols. of all these compounds (excepting the iodide II) are probably lath-shaped, parallel to the *b* axis with flat faces perpendicular to the *c* axis, separated by about 3.5 Å.; in the special case of the iodide I the I can be located with more certainty. Evidence supports the *p*- rather than the *o*-quinonoid structure. B. W. R.

Crystallographic and refractometric researches on the natural and synthetic corpus luteum hormone. A. NEUHAUS (Z. Krist., 1935, 90, 415-432).—Luteosterone C and D from natural sources are examined crystallographically and optically; the etch-figures, piezoelectric behaviour, d, and mol. refractivity are also observed. No difference is found between the natural and the synthetic product. The D compound will change into the C, but the reverse transformation has not been observed.

B. W. R.

X-Ray studies of the structures of hair, wool, and related fibres. III. Configuration of the keratin molecule and its orientation in the biological cell. W. T. ASTBURY and W. A. SISSON (Proc. Roy. Soc., 1935, A, 150, 533-551).—It is shown by direct measurement that the "backbone spacing" (4.65 Å.) and the "side-chain spacing" (9.8 Å.) of the keratin "grid" are those of planes at right angles, as proposed previously from indirect evidence (A., 1934, 352). The significance of this fact in the study of proteins and the structure of the biological cell is pointed out. The method used was to destroy the axial symmetry of the keratin-fibre structure by lateral compression in the presence of steam; after such compression the keratin grids are found to be so oriented that the "side-chain spacing" stands normal to the plane of flattening, whilst the "backbone spacing" lies in this plane. The crystallites of β -keratin are broader in the direction of the backbone spacing than in that of the side-chain spacing. The biological cells in keratinous structures are in general flat, and laid down with their flat sides roughly parallel to the natural surface of the specimen.

L. L. B.

Measurements of previously unknown large interplanar spacings in natural materials. G. L. CLARK, E. A. PARKER, J. A. SCHAAD, and W. J. WARREN (J. Amer. Chem. Soc., 1935, 57, 1509).— Modifications of X-ray technique permit large interplanar spacings to be detected. Preliminary results obtained with living nerve, collagen, gelatin, keratin, gel rubber, and cellulose are reported. E. S. H.

Scattering of fast electrons by crystals. N. PISARENKO (Physikal. Z. Sovietunion, 1935, 7, 26– 42).—Theoretical. It is shown that the inelastic scattering of fast electrons by a dielectric lattice is not influenced by the crystal structure. The influence of heat oscillations of the crystal atoms corresponds with only a small part of the background intensity of electron diffraction diagrams. R. S. B.

Dilatations in Rochelle salt. I. VIGNESS (Physical Rev., 1935, [ii], 48, 198—202; cf. A., 1934, 1163). —The inverse piezoelectric effect was studied by means of mechanical dilatometers. The dilatation of a crystal in a given direction varied with the field direction, indicating a permanent electric polarisation within the crystal. Prolonged application of voltage slowly changes this polarisation, giving rise to an inverse piezoelectric fatigue effect. N. M. B.

Magnetostriction of bismuth single crystals. D. SHOENBERG (Proc. Roy. Soc., 1935, A, 150, 619– 637).—Measurements of the transverse magnetostriction of Bi single crystals confirm the general features of the phenomenon found by Kapitza in large fields (A., 1932, 565) for the region of much lower fields (~15,000 gauss) available in an electromagnet. A new magnification method for measuring the extremely small changes of length involved ($\sim 5 \times 10^{-7}$ cm.) is described. L. L. B.

Size and arrangement of bismuth microcrystals formed from vapour. C. T. LANE (Physical Rev., 1935, [ii], 48, 193—198).—The magnetoresistance R of Bi films deposited on glass and mica was measured at -180° and 20° for various angles between the film normal and the magnetic field (H=16,000). The ratio R_{-180}/R_{20} rises steeply for thicknesses $0.1-0.4 \mu$ and then gradually to 4μ ; the thermal coeff. of resistance shows no such anomaly. X-Rays show all the films composed mainly of small crystals with (111) parallel to the backing. R varies with the direction of H; the current direction in the film is const. The relation of results to film structure is discussed. N. M. B.

Ferromagnetism for small variations of field. R. GANS and H. WITTKE (Ann. Physik, 1935, [v], 23, 459-464).—The work of Jordan on ferromagnetic losses in weak alternating fields (this vol., 149) is criticised. A. J. M.

Magnetic after-effect. H. WITTKE (Ann. Physik, 1935, [v], 23, 442-458).—The magnetic after-effect is a property dependent on the material only, and not on the variation of the field strength with time.

A. J. M.

Formation and magnetic properties of some ferrites. D. P. RAYCHAUDHURI (Indian J. Physics, 1935, 9, 425-432).—The magnetic properties of ferrites depend largely on the method of their prep.; for the dry method the main factors are duration of heating and temp. Effects of time and temp. are given for the ferrites of Co and Zn, eliminating discrepancies in previous reports. Data for Curie point, susceptibility, and X-ray structure are given for 15 ferrites. N. M. B.

Propagation of the magnetic reversal wave. D. S. STEINBERG (Physikal. Z. Sovietunion, 1935, 7, 155—174).—The magnetisation wave in stretched Fe–Ni wires has been studied. The wave is initiated only when a crit. field strength is attained at any given point and continues only so long as the frontal field preceding the wave + the impressed field = the crit. field. R. S.

Change in the resistance of magnetite in a magnetic field at low temperature. P. A. CHALLLEEV (Physikal. Z. Sovietunion, 1935, 7, 108—114).—The electrical resistance (ρ) of magnetite has been studied at 80—120° abs. in fields of 3000, 7000, and 8750 gauss. ρ decreases in the field, with a max. decrease (8—10% with 8750 gauss) at 111.4° abs. It is considered that at 111° abs. magnetite undergoes a change similar to that of a ferromagnetic body at the Curie point. R. S. B.

Influence of temperature on the electrical conductivity of quartz. R. RADMANECHE (Compt. rend., 1935, 201, 448—449).—For SiO₂ plates cut perpendicular to the optic axis, at -64° to 3000° , log i=a/T+b, where i=current at const. p.d. and a and b are consts. At $< -64^{\circ}$ i is immeasurable. R. S. B.

Condition of electrons in superconductors. J. STARK (Physikal. Z., 1935, 36, 515—516).—Free electrons, in consequence of an axial structure of their electric fields, exert mutual directional forces on each other, and by arranging their axes parallel to each other an ordered arrangement is produced, which may be called an electron crystal. In superconduction it is supposed that the electron crystal moves as a whole through the metal. It is to be expected that forces which distort the electron crystal will alter the conditions under which superconduction occurs. Such forces are thermal agitation (hence the appearance of superconduction below a certain temp.), magnetic forces (variation of transition point in a magnetic field), and inter-at. forces (unique transition point for each metal). It is to be expected that the size of crystallites in a metal will affect the transition point, and that the transference of the electron crystal through a straight wire will take place more readily than through a kinked one. A. J. M.

Effect of size of crystallite on the occurrence of superconduction. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 516-519).-According to the theory of Stark (see preceding abstract) the transition temp. from the ordinary to the superconducting state should vary with crystallite size, being the lower the larger is the crystallite. In a polycryst, wire the transition should take place over a range of temp. The transition temp. was determined for Sn wires which had been subjected to various tempering processes, and of which the crystallite size had been determined. Displacements of the transition temp. were found in the direction required by Stark's theory. The effect of strains due to plastic deformation was found to be A. J. M. negligible.

Effect of kinks in wires on the occurrence of superconductivity. W. MEISSNER, K. STEINER, and P. GRASSMANN (Physikal. Z., 1935, 36, 519—520).— The curve of transition temp. between ordinary and super-conduction is displaced to lower temp. when Sn wire and foil or In and Ta wire is kinked. Control experiments show that the displacement is not due to variation of the magnetic field in the neighbourhood of the kinks (see preceding abstract). A. J. M.

Properties of rotating superconducting loops in a magnetic field. K. STEINER and P. GRASS-MANN (Physikal. Z., 1935, 36, 520-524).—The interaction between a closed, superconducting, freely rotating loop and an external magnetic field, and the effect of self-induction on the current distribution of a parallel superconductor have been investigated.

Ă. J. M.

Current distribution in parallel smooth and kinked wires at the commencement of superconduction. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 524—525).—Two Sn wires of equal length, one kinked, the other straight, were arranged parallel to, and connected with, each other. A current is started in them before the onset of superconduction. When the latter takes place, the magnetic moment of the smooth loop is > that of the kinked. Superconduction begins at a higher temp. in the smooth than in the kinked loop, as required by Stark's theory. A. J. M.

Upper limit to the ohmic resistance of superconductors. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 525—527).—The variation with time of currents in superconducting Sn, Pb, In, Sn+In, and Sn+Pb has been determined. The resistance of kinked wires in the superconducting state is immeasurably small. A. J. M.

Upper limit of the thermo-electric power between superconductors. K. STEINER and P. GRASSMANN (Physikal. Z., 1935, 36, 527–528).— The thermo-electric coeff. between superconducting Pb and Sn is $< 5 \times 10^{-14}$ volt per degree, and that between Sn and In $< 3 \times 10^{-15}$. A. J. M.

Variation with magnetic field and temperature of the thermoelectric properties of ferromagnetics. F. E. LOWANCE and F. W. CONSTANT Physical Rev., 1935, [ii], 48, 257—260).—Measurenents on Fe, Ni, Co, and permalloy from room temp. to above the Curie point indicate that the e.m.f. roduced by a magnetic field in these thermocouples is onditioned by the crystal structure, the change in irection of the resulting spins, or intrinsic magnetistion in separate crystal regions, and that this effect is related to the change in length on magnetisation. N. M. B.

Diamagnetism of the Thomas-Fermi ion. T. HIRONE (Sci. Rep. Tôhoku, 1935, 24, 264-267).--On the basis of the Thomas-Fermi model of a metallic on, a relationship is developed expressing diamagnetic usceptibility of ions as a function of at. no. and alency. The theory is in closer accord with exerimental data for alkali and alkaline-earth metal ons than Sommerfeld's (Z. Physik, 1932, 78, 283).

J. W. S.

Diamagnetism of thallium single crystals. R. RAO and K. C. SUBRAMANIAM (Nature, 1935, 36, 336-337).-At 30°, the diamagnetic susceptiility parallel to the hexagonal axis of a single Tl rystal is 0.407×10^{-6} unit and perpendicular to it, 163×10^{-6} unit, giving a magnetic anisotropy, $\cdot 50$, > the corresponding vals. for similar metals. The calc. mean val. for polycryst. Tl is 0.244×10^{-6} nit. The susceptibilities remain const. up to 35°, the transition temp. to the cubic form, when the nean val. decreases to 0.170×10^{-6} and remains the ame for all orientations of the crystal in the magnetic ield. The hexagonal structure of Tl is due to the valency electrons (6s and 6p), whilst in the cubic nly the single valency electron (6p) is active. The ingle valency electron apparently contributes a paramagnetic susceptibility of +4 per g.-atom, a val. f the same order as those for Cu, Ag, and Au.

L. S. T.

Magnetic susceptibility of ice. L. SIBAIYA Current Sci., 1935, 4, 41; cf. this vol., 689). shiwara's results (A., 1915, ii, 141) are discussed.

W. R. A.

Magneto-chemical investigations. XV. Magnetic behaviour of a number of sulphides with byrites structure. H. HARALDSEN and W. KLEMM Z. anorg. Chem., 1935, 223, 409—416).—Two lattice tructures are possible for metallic disulphides MS_2 , (a) pyrites lattice, M^{++} and S_2^{--} , and (b) layer attice, S_2 groups indistinguishable and ions M^{++++} and S^{--} . The difference in magnetic properties between M^{++} and M^{++++} enables a distinction to be made between the two lattices. Determinations of the permeabilities and susceptibilities of MnS_2 , NeS_2 , NiS_2 , and CoS_2 show they possess the "ideal" or pyrites lattice. CoS_2 is anomalous in being erromagnetic at -183° , the susceptibility falling apidly with rising temp., explained by postulating barallel spin vectors in place of the more usual antiparallelism. S. J. G.

Molecular susceptibilities of some diamagnetic compounds in different solvents. O. E. FRIVOLD and H. SOGN (Ann. Physik, 1935, [v], 23, 413–424).— The mol. susceptibilities of LiCl, LiBr, NaClO₄, CaCl₂, CaBr₂, Ca(NO₃)₂, SrBr₂, and Ba(ClO₄)₂ were determined in H₂O, EtOH, and (in some cases) in $COMe_2$. The mol. susceptibilities of the salts in aq. solution were, in general, > in non-aq. solution. Magnetic properties of substances in solution are not, therefore, strictly additive. A. J. M.

Diamagnetic properties of inorganic compounds in aqueous solution and in the solid state. M. FLORDAL and O. E. FRIVOLD (Ann. Physik, 1935, [v], 23, 425-430).—The mol. susceptibilities of LiCl, LiBr, NaCl, KF, KCl, KBr, KI, CaCl₂, CaBr₂, ZnCl₂, SrCl₂, CdBr₂, BaCl₂, and K₄Fe(CN)₆ were determined in the solid state and in aq. solution. In the case of uni-univalent salts the difference between the two vals. of the mol. susceptibility is within the experimental error, but it is > for bi-univalent salts. A. J. M.

Magnetometric measurement of susceptibility of ferromagnetic powders. D. P. RAYCHAUDHURI (Indian J. Physics, 1935, 9, 417–424).—An improved method is described. Data are given for Fe_2O_3 , Fe_3O_4 , and the ferrites of Mn, Co, Cu, Ni, and Zn. In certain cases magnetic viscosity is observed for NiO, Fe_2O_3 . N. M. B.

Velocity of sound in low-temperature liquids at ultrasonic frequencies. A. PITT and W. J. JACKSON (Canad. J. Res., 1935, 12, 686–689).— The velocity of ultrasonic waves of 427 kilocycles per sec. is 912 m. per sec. in liquid O_2 at $-182 \cdot 9^{\circ}$ and 1127 m. per sec. in H_2 at $-252 \cdot 7^{\circ}$. J. W. S.

Kinetic theory of gases. I. Absorption of sound. II. General equations of motion and heat conductivity and their application to gliding and temperature jumps. K. F. HERZFELD (Ann. Physik, 1935, [v], 23, 465-475, 476-492).—Theoretical. A. J. M.

Melting curve of oxygen. J. H. C. LISMAN and W. H. KEESOM (Physica, 1935, 2, 839).—The m.p. of O_2 has been determined at pressures between 48 and 168 kg. per sq. cm. T. G. P.

Bakerian lecture. Anomalous specific heats of crystals, with special reference to the contribution of molecular rotations. R. H. FOWLER (Proc. Roy. Soc., 1935, A, 151, 1—22).—The present state of the theory of the partition functions of solids and their success or failure in describing the observed facts are discussed. The various types of anomaly in the sp. heat curves not provided for by the simpler versions of the theory are dealt with, and an account is given of a theory of the contribution that mol. rotations may make to the sp. heats, and in general to the equilibrium properties of crystals (cf. this vol., 683). L. L. B.

Second virial coefficient and specific heats of oxygen. J. A. VAN LAMMEREN (Physica, 1935, 2, 833-839).—The second virial coeff. is recalc. by a modified method from previous data supplemented by redeterminations at liquid C_2H_4 temp. in order to obtain better fitting to the S curve in this region. Vals. of C_p and C_v at liquid O_2 temp. are recorded. T. G. P.

Heat capacity of oxygen at high temperatures from ozone explosions and the energy of the $^{1}\Delta$ level of the neutral oxygen molecule : correction for the temperature gradient in explosions. B. LEWIS and G. VON ELBE (J. Amer. Chem. Soc., 1935, 57, 1399—1401).—Previous determinations (cf. A., 1933, 343) have been corr. for the temp. gradient existing in the exploded gases at max. pressure. The new vals. agree with those calc. from band spectroscopic data. The $^{1}\Delta$ O level is determined as 0.85 volt. E. S. H.

Thermal properties of deuterium oxide and their interpretation. R. S. BROWN, W. H. BARNES, and O. MAASS (Canad. J. Res., 1935, 12, 699—701). —The heat capacities of D_2O between initial temp. of 4° to -78.5° and a final temp. of 25° have been determined. The average sp. heat of D_2O between 4° and 25° is 1.028 g.-cal. and the latent heat of fusion 74.2 ± 0.2 g.-cal. The sp. heat of solid D_2O is > that of H_2O at the same temp. and varies from 0.579 at 0° to 0.391 at -70° . The results accord with the view that liquid D_2O is more highly associated than H_2O . J. W. S.

Anomaly in the specific heat of anhydrous ferrous chloride. O. N. TRAPEZNIKOVA and L. V. SCHUBNIKOV (Physikal. Z. Sovietunion, 1935, 7, 66— 81).—The sp. heat of powdered FeCl₂ has been determined at 16—120° abs. A sharp max. (7.22 g.-cal. per mol.) occurs at 23.5° abs., and is discussed in comparison with similar magnetic phenomena.

R. S. B.

Anomaly of the specific heat of anhydrous chromium trichloride. O. N. TRAPEZNIKOVA and L. V. SCHUBNIKOV (Physikal, Z. Sovietunion, 1935, 7, 255–256).—The sp. heat-temp. curve of $CrCl_3$ has been determined up to 50° abs. There is a sharp max. at 16.8° abs. and two broad max., none of which coincides with the Curie point, in contradistinction to FeCl₂ (cf. A., 1934, 1164). R. S.

Theory of liquids. IV. T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 1-9; cf. this vol., 1058).—Mathematical. Equations are deduced for the forces on a particle vibrating in a spherical space under attractive and repulsive forces between it and uniformly distributed matter outside the space.

Properties of real gases according to the thermodynamic equation of state. VIII. The inversion line of the Joule-Thomson effect for helium. W. JACYNA (Z. Physik, 1935, 95, 692-697; cf. this vol., 1064). A. B. D. C.

Vapour pressure of hexadeuterobenzene. C. L. WILSON (Nature, 1935, 136, 301).—The v.p. of C_6D_6 is > that of C_6H_6 over the range 0—80°., The b.p. at 760 mm. is 0.8° lower (cf. this vol., 967).

L. S. T.

Entropy of manganous ammonium sulphate at temperatures close to absolute zero, in relation to the magnetic anisotropy of the salt at room temperatures. K. S. KRISHNAN and S. BANERJEE (Proc. Indian Acad. Sci., 1935, 2, A, 82–85).—The entropy-temp. curve close to 0° abs. can be predicted from magnetic anisotropy measurements at room temp. N. M. B.

Calculation of entropies from X-ray data. F. S. LEI (J. Chinese Chem. Soc., 1935, 3, 199–205). —The rotational entropy at 25° of C_6H_6 calc. from mol. dimensions by the approx. formula (A., 1933, 218) agrees with the val. calc. by the exact equation. J. G. A. G.

Influence of magnetic field on the coefficient of viscosity of liquids. P. K. RAHA and S. D. CHAT-TERJEE (Indian J. Physics, 1935, 9, 445-454).--Long-chain aliphatic liquids, COMe₂ and Pr^aOH, show diminution of viscosity in a magnetic field; aromatic liquids, PhNO₂, PhMe, and an alcohol with side chains, isoamyl alcohol, show an increase; CCl₄, H₂O, and aq. Ce(NO₃)₃ show no change. For PhNO₂, $d\eta/\eta$ increases linearly with rise of temp., with no indication of saturation. The thermal variation of $d\eta/\eta$ for PhNO₂ is given. N. M. B.

Influence of a magnetic field on the viscosity of *p*-azoxyanisole. M. MIESOWICZ (Nature, 1935, 136, 261).—The viscosity of *p*-azoxyanisole at 125°, measured by the damping effect on an oscillating plate, is increased approx. 3.5 times by a magnetic field of 2400 gauss. The effect disappears after transition to the isotropic liquid phase. L. S. T.

X-Ray study of copper-silver alloys. E. A. OWEN and J. ROGERS (J. Inst. Metals, 1935, 57, Advance copy, 173—184).—Parameter measurements, with the precision X-ray camera, on Ag-Cu alloys show that the solubilities of Cu in Ag and of Ag in Cu are 8.5 and 8.4%, respectively, at 778°, 1.8 and 1.4% at 500°, 0.2 and 0.1% at 200°, and, by extrapolation, practically zero at room temp. A. R. P.

Gold-copper alloys. M. LE BLANC and G. WEHNER (Ann. Physik, 1935, [v], 23, 570).—Variations in the results of different workers on Au-Cu alloys are due to insufficient tempering, and conscquent non-attainment of equilibrium conditions. The work of Broniewski and Wesolowski (cf. A., 1934, 248; B., 1934, 364) is criticised. A. J. M.

X-Ray investigation of certain copper-tin alloys. E. A. OWEN and J. IBALL (J. Inst. Metals, 1935, 57, Advance copy, 185—204).—The solubility of Sn in Cu increases from 14.6% at 750° to a max. of 16.2% at 550—520° and then decreases again with fall in temp. to 9.9% at 300°. The γ -phase at 480° has a 17.917 Å. in alloys with 79.6—68.1% Cu and a 17.924 Å. in alloys with 68—66% Cu. The ε -phase is a solid solution extending over a range of about 1.5% around the composition Cu₃Sn; at 380° the at. vol. of ε saturated with Cu is 14.124 Å. and of ε saturated with Sn 14.177 Å. The transformation of γ into $\alpha + \varepsilon$ occurs at slightly above 300° and the boundary of the Cu-saturated ε -phase slopes slightly towards the Sn side between 380° and 300°.

A. R. P.

Constitution and structure of the alloys of silver and calcium. C. DEGARD (Z. Krist., 1935, 90, 399–407).—Thermal measurements have suggested the existence of a number of Ag-Ca compounds. When the alloys are melted in vac. and examined by X-rays, the only compounds indicated are AgCa (face-centred cubic, a_0 9.07 Å.) and Ag₃Ca (tetragonal, c/a 0.88). There is no evidence for AgCa₂, Ag₄Ca, and Ag₂Ca. B. W. R.

Determination of certain phase boundaries in the silver-zinc thermal diagram by X-ray ana-

Ń. M. B.

lysis. E. A. OWEN and I. G. EDMUNDS (J. Inst. Metals, 1935, 57, Advance copy, 321-330).—The $\gamma-(\gamma+\delta)$ boundary lies at $48\cdot6\%$ Ag between 20° and 530° and then bends towards the Zn side, reaching $47\cdot8\%$ Ag at 608°. The $(\gamma+\delta)-\delta$ boundary lies at $44\cdot5\%$ Ag up to 530° and then bends towards $43\cdot2\%$ Ag at 608°; the $\delta-(\delta+\eta)$ boundary lies at $21\cdot3\%$ Ag up to 300° and is continued by the $\delta-(\delta+\epsilon)$ boundary which bends towards the Zn side and reaches $20\cdot5\%$ Ag at 408°. The $(\delta+\epsilon)-\epsilon$ boundary slopes from $6\cdot2\%$ Ag at 343° to $9\cdot0\%$ Ag at 408°. A. R. P.

Alloys of magnesium. III. Constitution of the magnesium-rich alloys containing aluminum and cadmium. J. L. HAUGHTON and R. J. M. PAYNE (J. Inst. Metals, 1935, 57, Advance copy, 369—380).—Addition of Cd to Mg-Al alloys depresses the liquidus slightly, 20% Cd lowering that of the 80:20 Mg-Al alloy by 50°, but has little effect on the eutectic temp. of the Al-Mg system, 20% Cd depressing this temp. by only 5°. The solubility of Al in Mg rises almost linearly from 4% at 200° to about 10% at 400°; addition of 20% Cd depresses these vals. to 1.5% and 6%, respectively. Binary alloys of Al and Mg containing 5—10% Cd if slowly cooled from within the solid solution range may be obtained with the pptd. Al₂Mg₃ in a pearlitic condition; a larger amount of Cd prevents this behaviour. A spheroidising treatment can also be given to the alloys.

A. R. P.

X-Ray investigation of iron-nickel alloys. F. MARSCHAK and D. STEPANOV (Z. Elektrochem., 1935, 41, 599-602).—Examination of Fe-Ni alloy electrodeposits shows that they consist of solid solutions, although there is evidence of slight heterogeneity at 30-50% Ni. E. S. H.

Dissolution of electrodeposits of iron-nickel alloys. D. STEPANOV, F. MARSCHAK, N. BALA-SCHOVA, and V. KABANOVA (Z. Elektrochem., 1935, 41, 597-599).—The loss of wt. of Fe-Ni alloys immersed in sea- H_2O , 2—25N- H_2SO_4 , and 0-01N-lactic acid, respectively, has been determined as a function of composition of the alloy. The anodic behaviour of the alloys in the same electrolytes has also been examined. The results support the view that Fe and Ni form an unbroken series of solid solutions.

E. S. H.

Kinetics of the breakdown of the solid solution Al-Mg. M. I. ZACHAROVA and V. K. TSCHIKIN (Z. Physik, 1935, 95, 769—774).—The limiting solubility of Al in Mg has been determined by X-rays at 150°, 218°, and 300°. The kinetics of breakdown of the solid solution vary greatly with the thermal treatment of the alloy. A. B. D. C.

Two-component system iron-tantalum. W. JELLINGHAUS (Z. anorg. Chem., 1935, 223, 362—364).—Equilibrium data for the range 0—50 at.-% Tl are recorded, together with X-ray and magnetic data. The compound FeTl is indicated. S. J. G.

Magnetic properties of some nickel alloys. D. P. RAY-CHAUDHURY and P. N. SEN GUPTA (Sci. and Cult., 1935, 1, 114).—The magnetic susceptibilities of alloys with Al, As, and Cr have been examined with reference to the influence of temp. C. W. G.

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Diagram of state and magnetic properties of platinum-iron alloys. L. GRAF and A. KUSSMANN (Physikal. Z., 1935, 36, 544-551).-The variation of magnetic properties of Pt-Fe alloys with composition and the concn. range in which intermediate phases are present have been investigated by micrographic, X-ray, and magnetic methods. The connexion between cryst. structure and magnetic properties has also been studied. The addition of Pt to Fe at first results in an increase of the saturation magnetism up to 10% > that of α -Fe; the val. then decreases with the formation of face-centred cubic y-crystals. At room temp., in the neighbourhood of 26 at.-% Pt, the alloys consist almost entirely of γ -crystals, and are not ferromagnetic. Between 30 and 70 at.-% Pt the alloys are again strongly ferromagnetic (Curie point up to 450°). The ferromagnetic carriers are facecentred cubic y-mixed crystals which are transformed below 1200° into ferromagnetic FePt (space-centred cubic, a 2.88 Å., without superstructure), with Curic point about $100^{\circ} >$ that of mixed crystals of the same composition. Between 30 and 70 at.-% Pt, the hysteresis loop is very wide, giving a coercivity of 1800 gauss with a retentivity of 3000-4000 c.g.s. The width of the hysteresis loop is, in part, due to the distortion of the lattice on transition from mixed crystal to compound. A. J. M.

Special state of matter in certain alloys in relation to the volume. W. BILTZ and F. WEIBKE (Z. anorg. Chem., 1935, 223, 321-361).-In the case of intermetallic compounds, the increment (contribution made per g.-atom by an element to the mol. vol. of the alloy) of a metal remains fairly const., independent of the nature and quantity of the partner. For a high degree of constancy the proportions should be < definite limits, and the two partners should lie far apart in the electrochemical series. The increments are somewhat < the at. vols., so that a contraction occurs when intermetallic compounds are formed; the contraction is a max. for the light and easily compressible metals. The vol. of mixedcrystal alloys is also an additive function of const. increments; the increment for a given element in a mixed crystal is usually slightly different from its val. in a compound. The connexion between the increment vals. and the lattice types of metals and alloys is discussed. In accordance with the electron theory of metals it is found that the contraction depends on the difference in nobility of the two metals and on their relative amounts. Metals in alloys behave like the free metals under pressure, and as a result the compressibility of alloys should be < for metals in the free state, since in alloys the metals are already compressed. This is found experimentally. Existing data and new results are discussed. S. J. G.

Criterion for ordered atomic distributions in series of metallic mixed crystals. H. J. SEEMANN (Z. Physik, 1935, 95, 796—798).—Mixed crystals with unordered at. distribution will give an ordered distribution if the lattice const. of the unordered mixed crystal is > that corresponding with linear variation of the const. from one pure metal to the other.

A. B. D. C.

Special type of unstable mixed crystals with anomalous lattice constants. G. NATTA (Naturwiss., 1935, 23, 527-528).-The structure of films obtained by depositing metals on plates of other metals and then treating with dil. HNO₃ has been examined by the method of electron diffraction. The composition and structure of the film depend on the ratio of the at. radius of the pptd. metal to that of the pptg. metal. Films obtained by pptn. of Pt, Pd, or Ag on a metal of smaller at. radius, e.g., Cu, are solid solutions of Pt, Pd, or Ag in the Cu lattice, with consts. between those of Cu and the pptd. metal. The val. of the lattice const. depends on the thickness of the film, the [HNO₃], and the conditions of prep. of the film. The structure of films of Cu-Pt containing 30-70% Pt attains lower symmetry on heating. If Pt is deposited on a metal of greater at. radius, e.g., Ag, the lattice const. of the freshly prepared film is that of Ag. The film is insol. in 30% HNO₃. On keeping for some days, or more rapidly on heating to 700°, the lattice const. becomes smaller. The film consists of unstable mixed crystals with the lattice const. of the foundation metal. A colour change often accompanies the contraction of the lattice.

A. J. M.

Perfect ternary solid solutions. H. SELTZ (J. Chem. Physics, 1935, 3, 503—505).—Equations for the solidus and liquidus surfaces for systems in which there is complete miscibility in the solid state and both liquid and solid solutions are perfect have been derived from fugacities (cf. A., 1934, 365). The system Au-Cu-Ni deviates markedly from ideality at low mol. fractions of Au. R. C.

Specific heats of *iso*butyric acid-water mixtures at 15°. D. G. DAVIES (J.C.S., 1935, 1166-1167).—A sudden increase of sp. heat occurs at a conen. of about 22% of acid, above which two liquid layers exist. E. S. H.

Molecular clustering in binary liquid mixtures. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1935, 1, A, 915—927).—Depolarisation of light in different states of polarisation has been determined for scattering by the binary mixtures CS_2 -MeOH, MeOH-*n*hexane, H_2O -Pr^{β}CO₂H, NH₂Ph-*cyclo*hexane, PhNO₂*n*-hexane, NH₂Ph-*n*-hexane, PhOH-H₂O, H₂O-NMe₃; the results indicate presence of clusters from the crit. solution temp. to considerably higher temp.

A. B. D. C.

Optical investigations on the constitution of solutions and glasses. W. WEYL (Angew. Chem., 1935, 48, 573—575).—The optical properties of aq. and org. solutions are compared with those of glasses. E. S. H.

Solubility of a mixture of hydrogen and nitrogen in water at 25° in the pressure range 50— 1000 atmospheres. R. WIEBE and V. L. GADDY (J. Amer. Chem. Soc., 1935, 57, 1487—1488).—Data are recorded for the mixture $3H_2: 1N_2$. The solubility of the mixture can be calc. within a few % from the vals. for the pure components. E. S. H.

Diffusion of hydrogen and deuterium in palladium. I. W. JOST and A. WIDMANN (Z. physikal. Chem., 1935, B, 29, 247-255).—At 192-302.5° the diffusion coeff. for $H=5.95\times10^{-3}e^{-5720/RT}$ (sq. cm.; sec.). At 302.5° that for D is 1/1.35 times the H val., which agrees with the ratio of the thermal velocities of H and D. R. C.

Connexion between adsorptivity and physicochemical properties of substances. S. S. URAZOV-SKI and S. S. SCHARASCHENIDZE (Ukrain. Chem. J., 1935, 10, 152—160).—In homologous series the adsorptivity by C varies linearly with the dielectric const. and with the surface tension. R. T.

Adsorption of atmospheric ions by active charcoal. W. ZIMMERSCHIED (Kolloid-Z., 1935, 72, 135—151).—Adsorption measurements in the ionised atm. provided by a Bunsen flame have been carried out, using three kinds of charcoal, each in three different states of division. The lighter ions are the more easily adsorbed; the amount of adsorption is ∞ the ion density, and increases with decreasing particle size of the adsorbent. Little difference was observed in the behaviour of the different kinds of C. Adsorption probably occurs at the outer surface of the C, not at inner surfaces such as pores. E. S. H.

Ion adsorption and exchange. E. J. W. VERWEY (Kolloid-Z., 1935, 72, 187—192).—Theoretical. Electrolyte adsorption is discussed in terms of the processes: (1) adsorption of ions which determine the potential, (2) exchange of the oppositely-charged ion, (3) pure adsorption of the electrolyte.

E. S. H.

Surface activity of silica gel treated with lime. A. MAFFEI and A. BATTAGLIA (Annali Chim. Appl., 1935, 25, 309—318).—Absorption of CaO by SiO₂ gel diminishes progressively as the temp. to which the gel has been previously heated rises. Especially with gels heated at low temp., the absorptive power is decreased by quenching the heated gel in H₂O at 20°. Velocity of dehydration curves, which express variations in the v.p., show that CaO increases the surface and adsorbent activity of the gel. T. H. P.

Influence of surface tension of the intermicellar liquid on the structure formation of silica gel. V. S. VESSELOVSKI and I. A. SELAJEV (Kolloid-Z., 1935, 72, 197—202).—The formation of xerogels of SiO₂ by drying the hydrogel in air, and in air saturated with the vapours of xylene, PrOH, *iso*amyl alcohol, Bu^gCO₂H, PhOH, and EtOH, respectively, has been studied. The sorption properties of the resulting xerogels are influenced strongly by the surface tension of the intermicellar liquid. Other factors, such as concn. of SiO₂ in the hydrogel, ageing, etc., are of less importance. Alkaline hydrogels provide xerogels which are richer in pores than those derived from acid hydrogels. E. S. H.

Capillary systems. XVII. (1) Regular logarithmic sphere-spirals and sphere-screws. E. MANEGOLD and H. LINDEMANN (Kolloid-Z., 1935, 72, 151-164; cf. this vol., 443).--Mathematical. E. S. H.

Transparency of thin metallic films in the ultra-violet. H. H. HARTZLER (J. Opt. Soc. Amer., 1934, 24, 339—341).—A method for the production of thin metallic films is described. The observations, which extend from 4300 to 1600 Å., have afforded no evidence of any well-defined regions of transparency in Cu, Ag, Au, Mg, Al, Sn, Pb, As, Sb, and Bi. J. L.

Interference colours in oil films on water. K. B. BLODGETT (J. Opt. Soc. Amer., 1934, 24, 313—315).— A high-grade motor lubricating oil, oxidised by heat (or by exposure to light), is most suitable for the production of thin films; the more the oil is oxidised, the thinner is the film obtained. Films showing any required spectral colour are obtained by progressive dilution with an unoxidised oil or by altering the thickness of the films by compressing them in a confined area with the use of movable wax-coated barriers. J. L.

Physical properties of surfaces. II. Viscous flow of liquid films. Range of action of surface forces. S. H. BASTOW and F. P. BOWDEN (Proc. Roy. Soc., 1935, A, 151, 220–233).—Films of a dil. solution of a liquid crystal shows a pronounced rigidity, but thin films of H₂O, cyclohexane, EtOH, AcOH, Et palmitate, and LiCl solution behave as perfect fluids even when cooled to within 0.1° of the f.p. The viscosity of the film is the same as that of the liquid in bulk, and there is no evidence for rigid oriented chains of mols. extending from the surface to a distance of 1500–50,000 Å. as reported. If such chains exist, their length is certainly < 1000 Å. L. L. B.

Expansion of films of myosin on potassium lactate. S. A. Moss, jun., E. K. RIDEAL, and E. C. B. SMITH (Nature, 1935, 136, 260).—At $p_{\rm H}$ 7, unimol. layers of myosin (I) expand on 0.5M-K lactate > on equiv. solutions of KCl or other neutral salts. The extension occurs to a smaller degree with tartrates, but not with acetates or propionates. With lactate it increases with a rise in $p_{\rm H}$. The effect appears to be sp. for (I). Lactate may facilitate relaxation of fibrils during muscle recovery.

L. S. T. Mechanism of flotation. IV. Oriented coagulation in non-polar and in aqueous media. Z. V. VOLKOVA (Kolloid-Z., 1935, 72, 229-233; cf. this vol., 820, 1071).—The oriented coagulation of asbestos fibres and BaSO₄ particles is described, and discussed as a condition for flotation. E. S. H.

Theory of flotation. Wo. OSTWALD (Z. physikal. Chem., 1935, 173, 393-400).—A defence of the linear theory (cf. this vol., 931). R. C.

Effect of flotation reagents on the charge of suspensions of mineral particles. M. TICHONOV (Bull. Acad. Sci. U.R.S.S., 1935, 239-254).--Alkaline solutions of peat-tar and oleic acid do not recharge an apatite suspension, probably because they affect the particles chemically. Both $Ca(OH)_2$ and oleic acid change the sign of the charge on quartz. Quartz particles adsorb oleic acid and $Ca(OH)_2$ coagulates colloidal muds. K ethylxanthate does not change the sign of oxidised pyrites which has not been treated with strong acids, but it is adsorbed by purified pyrites, changing the sign of the charge. Colloidal quartz muds, treated with $Ca(OH)_2$, change the sign of their charge and are adsorbed by pyrites grains. Electric charges are an important factor, but do not wholly explain the phenomena of flotation.

J. W. S. Osmotic theory. K. WOHL (Physikal. Z., 1935, 36, 566).—The theory of Fredenhagen (A., 1934, 252, 728) according to which the v.p. of a solution is ∞ no. of free mols. of solvent per unit vol., is shown to give results which are thermodynamically impossible. A. J. M.

[Osmotic theory.] K. FREDENHAGEN (Physikal. Z., 1935, 36, 566—567).—A reply to Wohl (preceding abstract). A. J. M.

[Osmotic theory.] K. WOHL (Physikal. Z., 1935, 36, 567).—A reply to the above. A. J. M.

Kinetic significance of osmotic pressure. M. VON STACKELBERG (Z. Elektrochem., 1935, 41, 615 617).—Theoretical. E. S. H.

Study of solvation and measurement of thickness of the solvate sheath. N. S. SCHEINKER (Kolloid-Z., 1935, 72, 192–197).—Measurements of diffusion and η have shown that malachite-green is solvated in EtOH-H₂O solutions and that desolvation occurs on adding light petroleum or C₆H₆. The thickness of the solvate sheath is 1·2–1·3 Å.

E. S. H. Density of aqueous solutions of lanthanum, cerous, praseodymium, and neodymium chlorides at 25°. C. M. MASON and H. L. LELAND (J. Amer. Chem. Soc., 1935, 57, 1507—1508).—Data are recorded with an estimated accuracy of ± 0.0002 g. per c.c. E. S. H.

Compressibility of strong electrolytes. H. FALKENHAGEN and C. BACHEM (Z. Elektrochem., 1935, 41, 570—575; cf. this vol., 820).—The adiabatic compressibilities of NaCl, KBr, BaCl₂, Na₂CO₃, MgSO₄, K₃Fe(CN)₆, and K₄Fe(CN)₆ at concns. < 1 mol. per litre have been derived from optical measurements of ultrasonic wave velocities. The apparent mol. compressibility is $\propto c^{1/2}$ for strong electrolytes, and $\propto c$ for non-electrolytes. T. G. P.

Determination of refractive index of aqueous solutions of electrolytes with free electric waves. A. DEMBER (Ann. Physik, 1935, [v], 23, 507-528).-The method involves the use of free electric waves $(\lambda 92.5 \text{ cm.})$. The positions of resonance were determined by setting up a stationary wave in the solution between a parabolic reflector and a plane mirror, thus giving the wave-length in the liquid. Solutions of HCl(0.0024M), NaCl(0.0084M), and MgSO₄(0.0112M) have the same n, and therefore the same dielectric const. The calc. conductivity ratio for high and low frequencies shows a considerable increase (11%) due to dispersion in the case of the MgSO₄ solution. The results agree with the Debye-Onsager-Falkenhagen theory. Solutions of $CO(NH_2)_2$ show a molar increase of dielectric const. of 2.85 ± 0.4 , whilst 0.22M-HgCl₂ shows a decrease of 1.25 ± 0.4 , due to the admixture of symmetrical, non-polar HgCl₂ mols. with H₂O dipoles. A. J. M.

Effect of change of temperature on the constitution of water in solutions of electrolytes. C. S. S. RAO (Proc. Roy. Soc., 1935, A, 151, 167-178; cf. this vol., 295).—The effect of a rise in temp. on the constitution of H_2O in the pure liquid and in SN solutions of LiCl, NaNO₃, and H_2SO_4 has been investigated by a study of the Raman H₂O band. With rise of temp. (1) the position of the intensity max., as well as that of the lower-frequency portion, shifts towards higher frequency; (2) the part of the intensity curve on the lower-frequency side becomes less convex, whilst that on the higher-frequency side remains more or less unaltered in position and shape; (3) the band gets sharper, except in H_2SO_4 at 95° , which shows an increased broadening at this temp. These results are explained as being due to a simplification of the more complex H₂O mols. into simpler types, and by a change in the water of hydration of the ions of the solute. The peculiar result in H_2SO_4 at 95° is interpreted as being due to a breakdown of the hydrates present in solution into free ions and single H_oO mols. L. L. B.

Hydrogen-ion concentrations in, and absorption spectra of, aqueous solutions of chromium ammines. I. T. UÉMURA and H. SUÉDA (Bull. Chem. Soc. Japan, 1935, 10, 267—289).—The spectra at a series of $p_{\rm H}$ vals. for a no. of Cr ammines are used to follow the changes in constitution of the ammines with changing $p_{\rm H}$. Cr ammines which do not contain OH within the complex react acid in aq. solution, giving $p_{\rm H}$ 3—4 at concns. 0.003—0.002*M*. On increasing to $p_{\rm H}$ 4.5 approx., OH enters the complex except with [Cr(NH₃)₆]Cl₃ and [Cr(NH₃)₅Cl]Cl₂. Both H₂O of constitution and Cl if present alongside H₂O in the complex are easily replaceable by OH. S. J. G.

Liesegang rings. E. B. HUGHES (Kolloid-Z., 1935, 72, 212—216).—The theory formerly developed (cf. this vol., 702) is amplified and supported by measurements of ring distances. E. S. H.

Periodic precipitates (Liesegang rings). L. MAX (Kolloid-Z., 1935, 72, 217—221).—The formation of periodic diffusion structures, which conform with the conditions of Wo. Ostwald's diffusion-wave theory, is described. The theory is amplified by extending the concept of reversibility to include many physical changes, and is thus applied to the formation of periodic structures involving no chemical change.

E. S. H.

Formation of platinum sols. I. W. PAULI and T. SCHILD (Kolloid-Z., 1935, 72, 165-178).—The concn. and purification by electro-decantation of Pt sols, prepared by electro-dispersion in dil. HCl, is described. The composition, properties, and reactions of the sols have been investigated. Determinations of the ratio H^{\cdot}: Cl^{\prime} support the view that the charging complex is of the type [PtCl₂(OH)₂]H₂. Analogies with Au sols are pointed out. E. S. H.

Electrical properties of colloidal solutions. V. J. N. MUKHERJEE and S. MUKHERJEE (Kolloid-Z., 1935, 72, 178—186).—A reply to criticism (cf. A., 1934, 488). E. S. H.

Effect of aggregation on the cataphoretic velocity of colloidal particles. J. N. MUKHERJEE and S. G. CHAUDHURY (Sci. and Cult., 1935, 1, 111— 112).—A summary. C. W. G.

Deformation of swollen cellulose ester. O. KRATKY, G. SAITO, and V. BIERSTEIN (Z. Elektrochem., 1935, 41, 518—519).—When a film of cellulose acctate is increased 20—30% in vol. by swelling in aq. dioxan and then stretched, the extensiondouble refraction curve indicates a net-like behaviour and saturation is reached at 100% extension. When the swelling is 45-55% the curve indicates that the micelles are carried along by the movement of the swelling agent. When the swelling is still greater the curve is linear up to an extension of 280%, and the double refraction then increases rapidly to saturation; the micelles appear to have an independent (Brownian) movement. A. G.

Diffusion of fatty acids in presence of cholate. O. FURTH and H. HERRMANN (Biochem. Z., 1935, 279, 326-337; cf. A., 1934, 961).—The rate of diffusion of iodobehenic acid into gelatin in presence of Na glycocholate (I) is scarcely affected by changes in degree of acidity, presence of sugar, proteins, or blood-serum, or age of the gelatin, and not much by changes in the concn. of (I) or in the degree of dispersion of the gelatin. Inorg. ions greatly reduce the rate of diffusion. The colloidal condition of the gelatin and the degree of dispersion of the acid have no predominating influence on this rate. Ionic effects, depending on the electric charges, may be the decisive factors. The diffusion proceeds in accordance with Stefan's law (diffusion coeff. 0.006-0.010). The diffusion of the acid, in presence of (I), through porous glass plates into H₂O also follows the law, but (I) diffuses more rapidly than does the acid and retards its diffusion. W. McC.

Humic acids. K. ZEILE (Kolloid-Z., 1935, 72, 211-212).—The diffusion coeff. of humic acid, prepared by extracting peat with $(CH_2)_6N_4$ or $CO(NH_2)_2$ solutions, is 0.1345-0.1075 sq. cm. per day. The calc. particle wt. is 1060-1650.

E. S. H.

Isoelectric point of gelatin. R. A. DULITZKAJA (Kolloid-Z., 1935, 72, 205-211).—The isoelectric points of three kinds of gelatin have been determined by electrophoretic, nephelometric, and viscosimetric experiments. The mean results are 4.87, 5.09, and 5.65-6.08 for the three gelatins. Potentiometric titrations with acid and alkali have also been carried out. A review of the results, together with published data, suggests that natural, unchanged collagen has a higher isoelectric point than gelatin, and that the variable vals. found for gelatin are due to different degrees of hydrolysis. E. S. H.

Heat capacity measurements on gelatin gels. III. W. R. HORN and J. H. MENNIE (Canad. J. Res., 1935, 12, 702-706).—The heat capacity of gelatin gels between 0° and 25° is > the sum of the heat capacities of the H₂O and gelatin. For gels containing >0.9 g. of H₂O per g. of gelatin the discrepancy is 6.7 g.-cal. per g. of dry gelatin. There is a sharp discontinuity in the heat capacity-concn. curve at 0.52 g. of H₂O per g. of gelatin, and it is inferred that this amount of H₂O is closely bound at 0°, whilst at higher temp. there is less bound H₂O or it is less firmly bound. J. W. S.

Physical chemistry of lipins. II. Protective power of lipins. M. SPIEGEL-ADOLF (J. Amer. Chem. Soc., 1935, 57, 1431-1433; cf. A., 1932, 1089).—Kephalin (I) (prep. described) protects colloidal Au against flocculation 3-4 times as efficiently as does brain-lecithin (II), whilst egg-lecithin (III) is still less effective. Unlike (III), (I) is not flocculated by serum-albumin (IV) and only aged (I) is rendered cloudy by high pseudoglobin concns. One part of (I) prevents heat-coagulation of 2 (not 3) parts of (IV) in H_2O and pptn. of 10 parts of (II) by proteins. (I) and (II) protect cholesterol sol against pptn. by salts or proteins, but (I) is 10 times the more effective. The protective power of (I) for Au is unimpaired by boiling, but that for cholesterol sols is largely destroyed by ultra-violet light. Irradiated (I), however, does not ppt. Au sol nor does it hæmolyse erythro-R. S. C. cytes.

Colloid chemistry of edestin. I. K. HOL-WERDA (Biochem. Z., 1935, 279, 353–380).—The separation of edestin (18.4% N, 0.03% ash, isoelectric point about $p_{\rm H}$ 7.0) from sols (obtained by peptisation with salt solutions) by addition of H₂O is a form of coacervation, the separation and peptisation being colloidal processes. The effect of addition of salts on the acidity and peptisation of the sols and the effect of protein concn. and acidity on the viscosity of the sols have been measured. Denaturation by salts is usually not appreciable if the $p_{\rm H}$ is >5.2. During peptisation lyotropic influences, especially those of anions, are pronounced. W. McC.

Dissociation constants of weak and moderately strong electrolytes. II. Dissociation constant and solubility of 2:4-dinitrophenol in salt solutions. H. VON HALBAN, G. KORTUM, and M. SEILER (Z. physikal. Chem., 1935, 173, 449-465; cf. this vol., 34).—The optical determination of the dissociation const., K_c , has been extended to NaClO₄ and BaCl₂ solutions and the solubility in NaCl, KCl, KCl₄, NaClO₄, and BaCl₂ solutions of concn. 0.01-1M at 25° determined. The considerable differences between the K_c -concn. curves for the various salt solutions are due principally to the activity coeff. of the undissociated acid; the variations in the mean activity coeff. of the acid ions are smaller. Theories of salting in and salting out so far proposed are inadequate; in addition to hydration, sp. properties of the ion which are influenced by the oppositely charged R. C. partner appear to be involved.

Dissociation constants of acids in light and heavy water. O. HALPERN (J. Chem. Physics, 1935, 3, 456—457).—The ratio of the consts. for an acid in H_2O and D_2O is the larger the weaker is the acid, owing to the differences in zero-point energy of the proton (deuteron) when combined with the anion and in the dissociated hydrated state. R. C.

Determination of the second dissociation constant of carbonic acid. O. WEIDER (Ber., 1935, 68, [B], 1423—1430).—The method depends on the extrapolation of the concn.-dissociation const. (K_2) of the given solutions first to vals. in pure NaCl solution with the same [Na⁺] and then to vals. in pure H₂O. If the actual dissociation const. is $K_{2,0}$, then K_2 = [H⁺][CO₃⁻⁻]/[HCO₃⁻⁻] and $K_{2,0}$ =^aH^{+a}CO₃⁻⁻/^aHCO₃⁻⁻. $K_{2,0}$ is the val. of K_2 at infinite dilution. Determinations are based on electrochemical measurements, using the chain, Pt,H₂,[x],3.5N-KCl|0.1N-KCl, HgCl| Hg, and the measured potential is expressed $E = E_0 + E_D + (RT/F \log e)\log a_{\rm H}^+$, in which E_0 is a const. and E_D the diffusion potential. The uncertainty in the val. of E_0 is overcome by an adaptation of the method of Bjerrum and Unmack. At 0° and 18° the vals. of K_2 are 2.29×10^{-11} and 4.01×10^{-11} , respectively. H. W.

Multivalent amino-acids and peptides. IV. Apparent dissociation constants of α -aminotricarballylic acid and of glycyl- α -aminotricarballylic acid. J. P. GREENSTEIN and N. R. JOSEPH (J. Biol. Chem., 1935, 110, 619-624).—Measurements at 25° show that the dissociation range of the peptide is narrower than that of the NH₂-acid. F. A. A.

Hydrogen-ion concentration of lead solutions. D. N. MEHTA and S. K. K. JATKAR (J. Indian Inst. Sci., 1935, 18, A, 75–83).— $p_{\rm H}$ vals. of solutions of PbO and Sb₂O₃ agree with those calc. from solubility data. C. W. G.

Heavy-metal compounds as neutral constituents of complex cations. E. HAYEK (Z. anorg. Chem., 1935, 223, 382-386).-The undissociated mol. of a compound in solution may become attached to a cation. This cation (best derived from its perchlorate, since perchlorates are highly dissociated) should be very small (e.g., Be) or strongly polarising (e.g., Ag', Hg'', Pb'', Tl'); the neutral mol. which is to become attached should be a sparingly sol. compound, composed of a strongly polarising cation and an easily polarisable anion, since these show small dissociation (e.g., halides of Ag, Hg, Pb, Tl). Solubility experiments along these lines gave the following results : halides of Ag and Hg dissolve in solutions of corresponding perchlorates with increasing ease as at. wt., and therefore polarisability of the halogen, increases; PbI₂ dissolves in perchlorates of Ag and Hg, but not of Pb. Among oxides, PbO being amphoteric dissolves readily in its salt solution; Ag₂O and HgO, less amphoteric, dissolve slightly in conc. AgClO₄, although HgO is insol. in Hg(ClO₄)₂. Ag₂S and Ag₂Se are sol. in AgClO₄. Certain results were confirmed by transference experiments. The following compounds were isolated by dissolving the neutral constituent in hot conc. solution of the corresponding [Hg(HgI₂)](ClO₄)₂; perchlorate and cooling : $[Hg(HgI_2)_2](ClO_4)_2; [Hg(AgBr)_2](ClO_4)_2;$ 2AgClO₄,AgI; [Hg(HgO)₂](ClO₄)₂. S. J. G.

Vapour pressures of aqueous potassium chloride solutions, and their thermodynamic utilisation. Z. SHIBATA and K. NIVA (Z. physikal. Chem., 1935, 173, 415–426).—The v.p. and v.-p. depressions have been measured at 0—10° from 0.2786M to saturation. The product of the entire heat of dissolution and concn., in mol. per litre, of the saturated solution at 0—25° is -17,811 g.-cal. From the results there have been calc. differential and last heats of dissolution, and the activity in each solution of the H_2O at 0—25° and the KCl at 25°. R. C.

Determination of thermodynamic properties of solutions of mineral salts during evaporation and crystallisation. G. I. VOINILOVITSCH, L. K. ACHRAP, and L. S. MAI (J. Appl. Chem. Russ., 1935, 8, 589-597).—Formulæ are derived which connect the v.p. with the heats of evaporation and dilution of aq. solutions, and with the heats of dissolution of various salts. R. T.

Free energy of sulphur dioxide. A. R. GORDON (J. Chem. Physics, 1935, 3, 336–337).—Vals. of $(F^{\circ}-E_{0}^{\circ})/T$ are calc. from spectroscopic data. The heat of formation of SO₂ from S₂ and O₂ is calc. from the heats of formation of SO₂ and H₂S, and from the dissociation energy of H₂S. Equilibrium consts. for the reactions $\frac{1}{2}S_{2}(g)+O_{2}=SO_{2}$ and $SO+\frac{1}{2}O_{2}=SO_{2}$ are tabulated for the range 298·1–2800° abs.

N. M. B.

Heat of formation of azoimide. P. GUNTHER and R. MEYER (Z. Elektrochem., 1935, 41, 541).— From the explosion of gaseous HN_3 at 60—100 mm., the heat of formation from its elements is found to be 70.9 ± 0.5 kg.-cal. at const. vol. T. G. P.

Heat content and lattice structure of active ferric oxide. II. Amorphous ferric oxide hydrate as initial material. R. FRICKE and L. KLENK (Z. Elektrochem., 1935, 41, 617-622; cf. A., 1934, 1083).—The heat of dissolution of amorphous Fe_2O_3,xH_2O , after dehydration at 250°, in HF has been determined and the influence of the duration of dehydration investigated. The vals. obtained decrease as the duration of heating increases; the max. difference, 13,000 g.-cal. per mol. Fe_2O_3 , is regarded as a lower limit for the heat of crystallisation in the change amorphous $Fe_2O_3 \rightarrow \alpha$ - Fe_2O_3 .

E. S. H.

Apparent molal heat capacities of amino-acids and other organic compounds. J. T. EDSALL (J. Amer. Chem. Soc., 1935, 57, 1506—1507).—Comparison of published data for the mol. heat capacities of org. compounds in dil. aq. solution and in the pure state shows that the presence of a hydrocarbon chain tends to produce a positive deviation from the ideal solution law, whilst substances which contain many polar groups behave more nearly like ideal solutes in H_2O . E. S. H.

Thermodynamic problem. R. EMDEN (Z. Elektrochem., 1935, 41, 622–623).—A discussion (cf. this vol., 301, 446). E. S. H.

System $HgCl_2$ -PbCl₂. M. VAN DRIEL (Z. anorg. Chem., 1935, 223, 318—320).—Two liquid phases coexist between 6 and 44 mol.-% PbCl₂; the threephase temp. $[L_1+L_2+S_{PbCl_3}]$ is 414°. The eutectic point lies very close to the m.p. of $HgCl_2$. S. J. G.

Oxygen pressures of liquid $FeO-Fe_2O_3$ melts. W. KRINGS and H. SCHACKMANN (Z. Elektrochem., 1935, 41, 479-487).-O₂ pressures of molten FeO-Fe₂O₃ mixtures, with or without added SiO₂ or CaO, have been measured between 1550° and 1600° and 5 and 500 mm., and the dependence on temp. and composition has been determined. T. G. P.

System calcium carbide-lime. G. FLUSIN and C. AALL (Compt. rend., 1935, 201, 451-453).—The f.-p. diagram of the system CaC₂-CaO in presence of traces of SiO₂, Fe₂O₃, Al₂O₃, MgO, C, and SO₃ has eutectics at 68% of CaC₂ (1750°) and at 35.6% of

 CaC_2 (1800°), with a max. at 52.5% of CaC_2 (1980°) corresponding with the compound CaC_2 , CaO. R. S. B.

Decomposition pressures of nitrates and sulphates. III. Anhydrous copper nitrate. B. NEUMANN and A. SONNTAG (Z. Elektrochem., 1935, 41, 611—615; cf. A., 1933, 45, 1246).—Decomp. pressures of $Cu(NO_3)_2$ at different temp. are recorded and the heats of formation calc. The thermal decomp. involves the intermediate formation of $4CuO_3N_2O_5$. E. S. H.

Critical points of transformation of difficultly fusible oxides, and of their hydrates, at high temperatures. P. N. LASCHTSCHENKO and D. I. KOMPANSKI (J. Appl. Chem. Russ., 1935, 8, 628— 653).—Cooling curves suggest the hydrates ZnO,H₂O, Al₂O₃,0.5, 1, 2, and 3H₂O, Cr₂O₃,H₂O, SnO₂,0.5 and 1H₂O, TiO₂,0.5 and 1H₂O. The transformation points recorded are : ZnO 570°, Al₂O₃ 940°, bauxite 950°, kaolin 860°, obsidian 850°, SnO₂ 400—420°, cassiterite 425—435°, TiO₂ 650°, and brookite 760— 790°. R. T.

Active oxides. XCI. Active states occurring during the chemical combination of two metallic oxides. G. F. HUTTIG (Z. Elektrochem., 1935, 41, 527—538; cf. this vol., 930).—A comprehensive survey of recorded results. New data are given for the systems MgO-Fe₂O₃, ZnO-Fe₂O₃, CaO-Fe₂O₃, CuO-Cr₂O₃, Fe₂O₃-Cr₂O₃, Fe₂O₃-Al₂O₃, Fe₂O₃-CuO, CdO-Fc₂O₃, Cr₂O₃-Al₂O₃, Cr₂O₃-CuO, SiO₂-Fe₂O₃, SiO₂-Cr₂O₃, TiO₂-Fe₂O₃, TiO₂-Cr₂O₃. T. G. P.

Stabilities of aluminates. H. ZUR STRASSEN (Z. Elektrochem., 1935, 41, 476—478).—The affinities for Al_2O_3 of the oxides of Ca, Cd, Zn, Mg, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Bi have been compared by studying the equilibria $M^{IO}+M^{IIO},Al_2O_3 \Longrightarrow M^{IIO}+M^{IO},Al_2O_3$. Three reaction types are indicated : (a) the oxides and aluminates exist in four separate phases, (b) the oxides and the aluminates form mixed crystals, and (c) the aluminates are completely, but the oxides incompletely, miscible. The stability of the aluminates generally increases with decreasing lattice energy of the bivalent oxide. Aluminates of the spinel type are divisible into two groups on the basis of their reaction with gehlenite (2CaO,Al_2O_3,SiO_2): MgO,Al_2O_3 and ZnO,Al_2O_3 are more stable, and the rest less stable, than is gehlenite. T. G. P.

System ultramarine-sulphur. E. GRUNER (Z. Elektrochem., 1935, 41, 478—479).—Chemical and X-ray examination of the thermal desulphurisation of ultramarine, and its reaction with KCN, show that a part of the S is linked to the free alkali of the fundamental lattice unit, since the sulphide-S cannot be removed without loss of alkali, although the lattice is not thereby affected. T. G. P.

Equilibrium NaCl-HCl-H₂O at 18°. R. FRICKE and F. BRUMMER (Z. anorg. Chem., 1935, 223, 397– 398).—The solubility of NaCl in 0—5*M*-HCl has been determined at 18°. S. J. G.

Matter-current-work relationships in ideal electrochemical polyphase systems. Faraday's law of electrolysis in ideal galvanic cells. E. LANGE and K. NAGEL (Z. Elektrochem., 1935, 41, 575–582).—Theoretical. T. G. P.

Electrolytic transport of carbon in solid steel. W. SEITH and O. KUBASCHEWSKI (Z. Elektrochem., 1935, 41, 551—558).—Diffusion of C along a steel wire heated to 1000° has been studied photomicrographically and by conductivity measurements. The "mobility" of C towards the cathode determined by independent methods is 1.6 and 2.2×10^{-5} (sq. cm. sec. volt), whilst an evaluation from the diffusion const. gives 0.8×10^{-5} on the assumption that univalent C is involved. Diffusion also occurs towards the anode, but much more slowly. T. G. P.

Reaction of borax-glycerol-water solutions. P. VAN DER WIELEN (Pharm. Weekblad, 1935, 72, 875-877).—The $p_{\rm H}$ varies with the composition of the solvent. Solutions containing 20% of glycerol are neutral.

E.m.f. of the quinhydrone electrode in heavy water. Acidic dissociation of deuteroquinone. V. K. LA MER and S. KORMAN (J. Amer. Chem. Soc., 1935, 57, 1511).— $E_{\rm D}$ — $E_{\rm H}$ =0.0345 volt. The ratio of the acid dissociation consts. is given by $K_{\rm H}/K_{\rm D}$ =3.84. E. S. H.

Theory of galvanic potentials. I. P. GROSS and O. HALPERN (J. Chem. Physics, 1935, 3, 458— 460).—Thermodynamic considerations show that differences in normal electrode potentials can be expressed by the difference between a group of quantities which refer only to the properties of the substances forming the electrode and are independent of the solvent, *e.g.*, heat of vaporisation of the neutral electrode atom, and another group relating to the free energy liberated when a gaseous ion of the substance forming the electrode is dissolved in the solvent. There is no general theoretical evidence of the equivalence of voltaic and galvanic potentials.

R. C.

Polarographic studies with the dropping mercury cathode. LI. Electroreduction of unsaturated acids. L. SCHWAER (Coll. Czech. Chem. Comm., 1935, 7, 326-335).-There is a sharp rise in the current-voltage curve at the potential, v, at which the unsaturated acid (I) is reduced (2F per mol.), and the saturation current \propto [(I)]. In N-HCl, only undissociated mols. of (I) are reduced, and the vals. of v with respect to the N-Hg₂Cl₂ electrode are pyruvic (-0.2 volt) < acetylenedicarboxylic < fumaric (II) and maleic (III) < aconitic < mesaconic (IV) and citraconic (V) < cinnamic acid (-0.96). The anions of these acids and the sorbate ion in neutral and alkaline solutions have sp. vals. of v between -1.2 and -2.1 which depend on the [neutral salt]. Bi- and ter-valent cations decrease the magnitude of v. The cis- and trans-forms of an acid have the same v in acid solution, but in neutral and alkaline solution, the magnitude of v for (II) is < (III) and (IV) is < (V) in 4N-Li₂SO₄; an excess of NH₄, primary, sec., and tert.-amine ions reverses the relative orders of magnitude, probably owing to buffer action. Crotonic, itaconic, and lævulic acids are not reduced. The nature of the system of double linkings which are

reducible is discussed, and the polarographic determination of unsaturated acids in mixtures is indicated. J. G. A. G.

Asymmetry of the ferrous iron-dichromate titration curve. P. K. WINTER and H. V. MOYER (J. Amer. Chem. Soc., 1935, 57, 1402—1403).—A symmetrical curve is obtained when a sufficiently long time is allowed for the potential to approach equilibrium after the end-point is passed. The abnormal asymmetry is due to the fact that the dichromate-chromic electrode potential is not strictly reversible. E. S. H.

Simultaneous cathodic and anodic directcurrent polarisation of electrodes. I. Electrodes of platinum, palladium, and gold. P. S. TUTUNDžić (Z. Elektrochem., 1935, 41, 602-611).—The influence of a superimposed d.c. on the potential of cathodes of Pt, Pd, and Au in 2N-H₂SO₄ at room temp. and on the decomp. potential has been studied, with reference to direction of current, p.d., and c.d. The depolarising effect obtained in the one direction is < that obtained by the use of oxidising agents in the solution. When the opposite polarisations are equal, the electrode attains a const. end val. of $+0.927\pm0.005$ volt, which is regarded as the true potential of formation of H₂O. E. S. H.

Processes [occurring] on the anode during the electrolysis of picrates in non-aqueous solvents. E. HERTEL and F. KRUGER (Z. Elektrochem., 1935, 41,564—569).—The dependence of the anode potential on the nature of the solvent, concn., stirring, anode surface, and temp. has been determined in an endeavour to explain the peculiar relationship which exists between anodic and applied potential during electrolysis. T. G. P.

Absolute rate of reactions in condensed phases. W. F. K. WYNNE-JONES and H. EYRING (J. Chem. Physics, 1935, 3, 492-502).-The activated complex theory (this vol., 586) shows the rate of a reaction of any order in any phase where the slow process is the surmounting of a potential energy barrier to be equal to the product of a transmission coeff., a universal frequency, an equilibrium const. between an activated complex and the reactants, and an activity coeff. factor. The theory is successfully applied to numerous unimol. and bimol. reactions, including those having velocities anomalous from the point of view of the collision theory, and to acid-base catalysis. Brönsted's, Lewis', and other earlier theories of reaction rate are special cases of the present theory. The latter reduces velocity problems to the thermodynamic calculation of an equilibrium const. for the activated complex and the calculation of a transmission coeff. which often ≈ 1 . R. C.

Entropy and the absolute rate of chemical reactions. II. Unimolecular reactions. O. K. RICE and H. GERSHINOWITZ (J. Chem. Physics, 1935, 3, 479—489).—The considerations previously advanced (this vol., 306) are further developed and correlated with Eyring's theory (*ibid.*, 586). The rates of numerous unimol. reactions may be accounted for either by examining the extent to which rotational degrees of freedom must be frozen out for the reverse bimol. or termol. association to occur or by Eyring's method. R. C.

Statistical mechanical treatment of the activated complex in chemical reactions. L. S. KASSEL (J. Chem. Physics, 1935, 3, 399-400).—A crit. discussion of Eyring's method of computing abs. reaction rates (this vol., 586). H. J. E.

Mechanism of polymerisation reactions. I. H. DOSTAL and H. MARK (Z. physikal. Chem., 1935, B, 29, 299—314).—Theoretical. Kinetic formulæ are derived assuming that polymerisation to chains consists in nucleus formation followed by growth, the relative rates of the two processes determining the course of the reaction (cf. A., 1934, 607). R. C.

Activation energy of unimolecular reactions. II. O. K. RICE and H. GERSHINOWITZ (J. Chem. Physics, 1935, 3, 490—492).—The theory previously developed (A., 1934, 846) is revised, and related to Kassel's quantum theory of unimol. reactions (A., 1928, 960). The connexion between observed activation energy and the energy required to break the linking is discussed. R. C.

Mechanism of chemical reactions. C. N. HINSHELWOOD (J.C.S., 1935, 1111-1115).-Theoretical. Two classes of activated mols. are distinguished: (i) preactivated mols. which have received so much energy that they can decompose after a certain internal redistribution of energy, and (ii) critically activated mols. which possess sufficient energy in sp. linkings to ensure decomp. within the next vibration period. These conceptions lead to a general interpretation of the wide variations in the vals. of the probability factor P found when the equation rate= $PZe^{-E/RT}$ is applied to catalysed and uncatalysed unimol. and bimol. reactions. Factors greatly affecting the magnitude of P for bimol. reactions are mol. orientation, the short time available for appropriate redistribution of energy during the life of the collision complex, and entities facilitating sp. energy transfers. The relation between P and the energy of activation, E, in series of related reactions is J. G. A. G. discussed.

Thermodynamic theory of detonation. R. L. SCORAH (J. Chem. Physics, 1935, 3, 425-430).— Theoretical. The speed at which detonation is stable is determined from considerations of available energy. Agreement with experimental vals. was obtained for a H_2-O_2 mixture. H. J. E.

Thermal decomposition of ozone. M. RITCHIE (Nature, 1935, 136, 221).—A reply to criticism (cf. this vol. 1080). L. S. T.

Thermal reactions of gaseous hydrocarbons. Paraffins, olefines, acetylenes, and cycloparaffins. G. EGLOFF and E. WILSON (Ind. Eng. Chem., 1935, 27, 917–933).—A survey is given of published work on the mechanism of the thermal reactions of gaseous hydrocarbons. The reaction products may be accounted for by (1) polymerisation, (2) hydrogenation to C_2H_6 , (3) scission of one C-H, (4) scission of the double linking, (5) dehydrogenation to C_2H_2 . For gaseous paraffins and higher olefines, the reactions occurring at < 750° must be considered in addition to the reactions of C_2H_4 . The nature of the products is dependent on temp., pressure, and contact time and the energy of activation is an important guide to possible reactions at a given temp. C. C.

Pyrolysis of propane in presence of water vapour.—See this vol., 1221.

Flash points and explosion limits of ethyl alcohol-trichloroethylene mixtures. K. R. DIE-TRICH and H. GRASSMANN (Z. Spiritusind., 1935, 58, 251–252).—The flash point of EtOH is raised by additions of > 50% C₂HCl₃, being 22° and 50° for mixtures containing 80% and 90% C₂HCl₃, respectively. The explosion region for EtOH-C₂HCl₃-air mixtures gradually narrows for vapours arising from liquid EtOH-C₂HCl₃ mixtures containing > 40% C₂HCl₃, whilst mixtures containing < 72% C₂HCl₃ give non-explosive vapours. S. J. G.

H-atom concentration and mechanism of the thermal decomposition of some organic molecules. H. SACHSSE [with F. PATAT] (Z. Elektrochem., 1935, 41, 493–494).—From measurements of the stationary concn. of H atoms during the decomp. of $COMe_2$, MeCHO, EtCHO, CH₂O, and C₂H₆, using para-H₂ as indicator, the authors assess the relative merits of Rice and Herzfeld's (A., 1934, 369) and Fletcher and Hinshelwood's (A., 1933, 910) theories of the thermal dissociation of org. mols. T. G. P.

Equilibrium and kinetics of bromine chloride (BrCl). G. BRAUER and E. VICTOR (Z. Elektrochem., 1935, 41, 508-509; cf. A., 1934, 984).— Reaction between Br and Cl₂ has been examined spectro-photometrically. The bimol. dark reaction is a chain process strongly influenced by the walls. The heat of reaction is 310 ± 30 g.-cal., and $K=0.144\pm$ 0.003. The photo-reaction is affected equally by light in the continuous or banded regions, and is a chain process of quantum yield $1-2\times10^3$.

T. G. P. Limits of inflammability of diethyl ether and ethylene in air and oxygen. G. W. JONES, W. P. YANT, W. E. MILLER, and R. E. KENNEDY (U.S. Bur. Mines Rep. Invest., 1935, No. 3278, 1—5).—The following vals. indicate the lower and upper limits, respectively. In air : Et₂O 1.85, 36.50%, C₂H₄ 2.75, 28.60%; in O₂ : Et₂O 2.10, 82.00%, C₂H₄ 2.90, 79.90%. E. S. H.

Reactions of oxides of nitrogen with atomic oxygen and nitrogen. M. L. SPEALMAN and W. H. RODEBUSH (J. Amer. Chem. Soc., 1935, 57, 1474– 1476).—The reaction $NO_2+O=NO+O_2$ is estimated to have a probability 10^{-5} per collision at 40° . The reactions $N+NO_2=2NO$ and $N+NO=N_2+O$ are fairly rapid. The reaction $NO+O=NO_2$ appears to take place by triple collision and is accompanied by the O afterglow. E. S. H.

Reactivity of atoms and groups in organic compounds. XVI. Relative effect of substituents on the rates at which aryl and alkyl chlorides react with ethyl alcohol. J. F. NORRIS, E. V. FASCE, and C. J. STAUD. XVII. Effect of change in reactant and of temperature on the relative reactivities of substitution products of benzoyl chloride. J. F. NORRIS and H. H. YOUNG, jun. XVII. Effect of the solvent on the rate of reaction between benzoyl chloride and ethyl alcohol. J. F. NORRIS and E. C. HAINES (J. Amer. Chem. Soc., 1935, 57, 1415—1420, 1420—1424, 1425—1427; cf. this vol., 487).—XVI. k for the first-order reaction of C_6H_4X -COCl with an excess of EtOH at 0°, Pr^gOH at 25°, and H₂O in COMe₂ at 0° and of C_6H_4X -CHPhCl with EtOH at 25° and H₂O in COMe₂ at 60° are determined by measurement of Λ . With EtOH the effect of substituents is > with Pr^gOH. BzCl reacts 6 times as fast with H₂O as with EtOH at 0°, but the effect of substitution, except by Me, in the EtOH is > in the H₂O series. The relative effects of substitution, except by p-Me, are opposite with BzCl and CHPh₂Cl. The relative k for C_6H_4X -COCl-EtOH at 0° are X=0.2.2, m. 20.5, and p-NO₂ 21.6, o. 3.7, m. 0.85, and p-Me 0.78, o. 29, m. 1.1, and p-OMe 0.81, o. 3.5, m. 5.6, and p-Cl 1.9, and o. 2.9, m. 4.1, and p-I 1.9.

XVII. Changes of k for the reaction of C_6H_4X -COCl with MeOH and EtOH with change of X are in the same order except for the pair, X=o-Me and m-Cl. Heat of reaction, measured by k, with EtOH at 0° and 25°, bears no relation to the abs. val. of k, but is controlled by the nature and position of X. 2:4:6-Tri-nitroand -bromo-benzoyl chloride react very slowly with MeOH; 2:4:6- $C_6H_2Me_3$ -COCl reacts very fast.

XVIII. k for the second-order reaction of BzOH with EtOH at 25° in 17 solvents is measured. R. S. C.

Oxidation of silicon hydrides. I. H. J. EME-LÉUS and K. STEWART (J.C.S., 1935, 1182—1189; cf. this vol., 451).—At the lower crit. oxidation pressure, P_i , of SiH₄-O₂ mixtures at 15°, there is a sp. approx. hyperbolic relation between p_{0} , and p_{SiH_4} depending on the diameter, D, of the tube (p_{0} , is much $< p_{\text{SiH}_4}$). P_i is depressed by adding N₂ and by increasing D. Induction periods were observed. The upper crit. oxidation pressure, P_u , at 100° is raised slightly by adding N₂ and He, but $P_{0,+}+P_{\text{SiH}_4}$ is diminished. P_u is depressed by SO₂, C_2H_4 , C_6H_6 , EtI, CHCl₃, COMe₂, and EtOH. There is very little reaction at pressures $>P_u$, and the effect of temp. on P_u has been investigated. A branched-chain mechanism is proposed which, with the data for P_u , leads to a chain length of 2 and a probability of branching of 1 in 6. J. G. A. G.

Kinetics of the reaction between carbonyl sulphide and water. H. W. THOMPSON, C. F. KEARTON, and S. A. LAMB (J.C.S., 1935, 1033-1037). —The reaction between COS and H_2O (i) in aq. solution at 15.5-47.4°, (ii) in EtOH at 60-75°, and (iii) in the gas phase at 244-382° has been investigated. The reaction between the vapours is partly heterogeneous, and the very slow reaction between EtOH and COS, probably $COS + EtOH \longrightarrow CO_2 + EtSH$, does not interfere with (ii). The velocities of the bimol. reactions in (ii) and (iii) are several powers of 10 < the vals. calc. by means of the observed energies of activation, 15,000 and 25,700 g.-cal., respectively. The velocity coeff. in (i) is $k=5\times 10^{16}\eta e^{-26,260/RT}$, corresponding with a collision frequency slightly > the calc. val., and is diminished by added AcOH and HCl. The results suggest that, in general, the reaction between COS and H_2O is "slow" and becomes "normal" only in an ionic atm. J. G. A. G.

Kinetic medium and salt effects in reactions between ions of unlike sign. Reaction between ammonium ion and cyanate ion. J. C. WARNER and E. L. WARRICK (J. Amer. Chem. Soc., 1935, 57, 1491—1495).—The rate of conversion of NH_4CNO into $CO(NH_2)_2$ has been studied at 50° in H_2O and in binary mixtures of H_2O with MeOH, EtOH, $Pr^{\beta}OH$, and 1:4-dioxan having dielectric consts. ranging from 65 to 40. The primary salt effect in each solvent mixture agrees well with that predicted by the Brönsted–Christiansen theory for a reaction between univalent ions of opposite charge. Differences in rate consts. at equal dielectric consts. are discussed. E. S. H.

Kinetics of the Friedel-Crafts ketone and hydrocarbon syntheses. H. ULICH and G. HEYNE (Z. Elektrochem., 1935, 41, 509-514).—The progress of the reactions between (I) BzCl and C6H6 and (II) $Pr^{\alpha}Cl$ and $C_{6}H_{6}$ in CS_{2} solution in presence of (a) AlCl₃ and of (b) GaCl₃ have been studied by measuring the vol. of HClevolved. (I) is unimol., and proceeds by way of MCl₃-BzCl complexes. The resulting COPh, forms more stable complexes with AlCl₃ than does BzCl, and thus deactivates the catalyst. (II) proceeds by way of MCl₃-Pr^aCl complexes which are in equilibrium with similar complexes formed by C₆H₆ and by the reaction products. The changes in equilibrium concn. of the complexes caused by the reaction result in dissolution of $AlCl_a$ in the early stages of (IIa) with an increase in reaction velocity, whereas in (IIb) the catalyst is dissolved from the start. GaCl₃ is a better catalyst than $AlCl_3$ for reaction (II). T. G. P.

Kinetics of the reaction between hydrogen peroxide and the sodium salt of p-toluenesulphonchloroamide (chloramine-T). J. COULL, H. B. HOPE, and B. GOUGUELL (J. Amer. Chem. Soc., 1935, 57, 1489—1490).—A differential equation expressing the rate of reaction at const. [H^{*}] and [Cl'] has been developed. E. S. H.

Relation between the rates of reactions and oxidation-reduction potentials. I. Oxidation of formate ion by halogens in the dark. II. Oxidation of oxalate by halogens in the dark. B. F. CHOW (J. Amer. Chem. Soc., 1935, 57, 1437— 1440, 1440—1443).—I. The empirical relation previously reported for the oxidation of oleic acid and linseed oil (A., 1934, 607) holds also for the oxidation of HCO_{9}' by I or Br.

II. The same relation is applicable to the oxidation of $C_2O_4^{\prime\prime}$ by Cl_2 , Br, or I. E. S. H.

Rates of reaction of brominated malonic and succinic acid salts with the thiosulphate ion at two temperatures. M. H. BEDFORD, R. J. AUSTIN, and W. L. WEBB (J. Amer. Chem. Soc., 1935, 57, 1408—1411).—Reaction velocities have been determined over a range of concn. and temp. The results cannot be explained by the Brönsted theory, but are explicable in terms of the orientation hypothesis of La Mer and Kamner. E. S. H.

Study of enzyme action by thermal analysis of reaction velocity. I. Action of invertase.—See this vol., 1278.

Factors determining the velocity of reactions in solution. Formation of quaternary ammonium salts in benzene solution. C. A. WINKLER and C. N. HINSHELWOOD (J.C.S., 1935, 1147-1151).-The activation energies, E, of twelve reactions between alkyl halides and C5H5N, quinoline, NMe3, and NEt3 are calc. from velocity measurements at 4-140° The probability factor P, in the equation $k=PZe^{-EIRT}$, is of the order 10^{-6} — 10^{-8} . The vals. of k, the velocity coeff., for MeI>EtI>Pr^{β}I, are related chiefly to increases of E, but P decreases in the series EtI(Br) >Pr^aI(Br). Orientation effects account for the vals. of P; $NMe_3 > NEt_3$ and $C_5H_5N > quinoline$. k and P increase in the series alkyl Br < alkyl I, possibly owing to the ability of I to facilitate crit. activation (cf. this vol., 1206). J. G. A. G.

Rate of transformation into methylcarbamide of methylammonium cyanate dissolved in ethyl alcohol. (MISS) C. C. MILLER (Proc. Roy. Soc., 1935, A, 151, 188-201).—The rate of transformation 1935, **A**, 191, 183–2017.—The fact of transformation of NH₃Me·CNO into NHMe·CO·NH₂ over the conen. range 0.04-0.0002M at 0° and 10° in EtOH con-taining 1.91 wt.-% of H₂O was determined. The rate in EtOH was 500 times that in H₂O at infinite dilution and the same temp. The rate in EtOH solutions was represented by $v=k_0C^2F$, where the conens. of the ions wave involved and the reaction kinetic factor F had were involved, and the reaction kinetic factor F had the significance attached to it by Brönsted. Assuming that $F=f^2$, the distances between the centres of reacting ions were calc. at 0° and 10°. The vals. found differed by 25% at the two temp., contrary to the almost const. vals. which have been obtained by others from e.m.f. data. The increased rate of reaction in EtOH compared with ag. solutions was associated with changes in the crit. increment of the reaction, the dielectric const. of the solvent, and the distance between the centres of the reacting ions. Kinetic activities are similar to, but not identical with, thermodynamic activities. L. L. B.

Kinetics of absorption of oxides of nitrogen by 78% sulphuric acid. A. N. TZETTLIN (Ukrain. Chem. J., 1935, 10, 242–261).—The velocity of absorption varies linearly with the concn. of N oxides in the gas, whilst the velocity coeff. attains a max. val. when the gas contains 40% of NO+NO₂. The application of these findings to factory practice is discussed. R. T.

Kinetics of formation of silver sulphide from silver and sulphur or hydrogen sulphide. H. REINHOLD and H. SEIDEL (Z. Elektrochem., 1935, 41, 499-507).—Reaction velocities have been measured for (1) $2Ag+S_{Bq}=\beta-Ag_2S$, (II) $2Ag+S_{Hq}=\alpha-Ag_2S$, (III) $2Ag+S_{gas}=\beta-Ag_2S$, (IV) $2Ag+S_{gas}=\alpha-Ag_2S$, (V) $2Ag+H_2S=\beta-Ag_2S+H_2$, (VI) $2Ag+H_2S=\alpha-Ag_2S+H_2$, (VII) $Ag+\frac{1}{4}I_2=\alpha-AgI$, (VIII) $2Ag+Te=\alpha-Ag_2Te$. The velocities are determined by the slowest of the reactions occurring in or between the phases M, M+MX, MX, MX+X, X. The velocities of (I), (II), (III), and (VII) are determined by the rate of diffusion in the reaction zone, and are α its thickness. The velocities of (V) and (VI) are determined by the velocity at the boundary MX-X, and are approx. α the partial pressure of S in the H_2S equilibrium. The velocity of (IV) is identical with that of (II) at high temp; at low temp. it is independent of the zone thickness, and ∞ the v.p. of $S_{\text{liq.}}$, and thus determined by the reaction at the boundary MX-X. (VIII) is characterised by an induction period, and its velocity is determined by the reaction at the boundary M-MX. T. G. P.

Anomalous behaviour of nickel sulphide. W. H. CONE, M. M. RENFREW, and H. W. EDELBLUTE (J. Amer. Chem. Soc., 1935, 57, 1434—1436).—The initial rate of dissolution of NiS in HCl depends on $[H_2S]$ in the system and is increased by the presence of nascent H. H₂S is more strongly adsorbed by NiS than by PbS, CdS, or FeS, the amount increasing with increasing [HCl]. The Ni sulphide has the composition NiS_x, where x is \leq 1 and increases with increasing [H₂S]. E. S. H.

Corrosion of steel.—See B., 1935, 807.

Oxidation and reduction reactions of colloidally dissolved substances. III. Reduction of colloidal manganese dioxide. V. N. Skvorzov (Kolloid-Z., 1935, 72, 203-205; cf. A., 1933, 916).—The rate of oxidation of $H_2C_2O_4$ by colloidal MnO₂ in acid solution has been investigated and an equation developed. E. S. H.

Autoxidation of *n*-hexadecane. G. ARDITTI (Compt. rend., 1935, 201, 396–398; cf. B., 1931, 661; 1932, 7).—There is an induction period in the absorption of O_2 by $n \cdot C_{16}H_{34}$ which is the shorter the higher is the temp. After this induction period the velocity of absorption increases rapidly to a max., then diminishing and tending slowly towards zero. In the absence of unsaturated compounds this absorption α the amounts of H_2O , CO_2 , CO, H_2 , and CH_4 formed. The first stages of the oxidation are accompanied by the production of a preponderance of CO, formation of CO_2 occurring later. The amount of H_2+CH_4 formed α the O_2 absorbed. The loss of O_2 is > the O evolved in gaseous products, so it is concluded that some products remain in solution. J. W. S.

Theory of the catalysis of the ortho-paratransformation by paramagnetic gases. F. KALC-KAR and E. TELLER (Proc. Roy. Soc., 1935, A, 150, 520—533).—The reaction velocity depends not only on the interaction energy between the nuclear moment and the magnetic field, but also on the nuclear spin. The reaction can be used to determine the ratio of the magnetic moments of the proton and the deuteron. L. L. B.

Catalysis of acetylene polymerisation in ultraviolet light by mercury vapour. W. KEMULA (Coll. Czech. Chem. Comm., 1935, 7, 319-320; cf. A., 1934, 168).-Polemical (cf. *ibid.*, 852). J. G. A. G.

Polarographic studies with the dropping mercury cathode. L. Secondary or catalytic effects in heavy water. O. H. MULLER (Coll. Czech. Chem. Comm., 1935, 7, 321-325).—The evolution of H_2 at the dropping Hg cathode catalysed by cysteine in buffered Co^{**} solutions (cf. A., 1933, 964) and by Mg and, to a smaller extent, by Ca deposited from aq. Cl' solutions (*ibid.*, 131) is \gg that of D_2 from D_2O . The height of the max. in the current-voltage curve decreases as $[D_2O]$ in the aq. solutions is increased. These differences are not observed with aq. Tl', Ni", Co", and Ba", and electrolytic separation of D_2O may be due to a difference between the rates at which D_2O and H_2O react at the cathode either directly or by secondary reactions, and not to a difference between the overpotentials of D' and H'. J. G. A. G.

Effect of addition agents on deposition of tin from alkaline stannate baths.—See B., 1935, 809.

Influence of nuclear substituents on side-chain reactions. II. Factors controlling the velocities of acid-catalysed prototropy of nuclear-sub-stituted acetophenones. D. P. EVANS, V. G. MOR-GAN, and H. B. WATSON. III. Base-catalysed prototropy of substituted acetophenones. V. G. MORGAN and H. B. WATSON (J.C.S., 1935, 1167-1173, 1173-1174; cf. A., 1933, 1124).-II. The velocity of bromination of eleven p- and m-derivatives of COPhMe, using 0.1M solutions in 75% AcOH in the presence of 0.5M-HCl, has been determined at $15-45^{\circ}$ and the energy of activation, E, calc. In agreement with theory (this vol., 569) the velocities for the halogen and NO_2 -derivatives are > and for $m - C_6H_4$ Me COMe is < the calc. vals. (cf. A., 1933, 505, 890). The factor causing the deviations is independent of temp., and it is not necessary to assume variations in the proportion of fruitful collisions between activated ketone mols. and catalyst, since the observed rates are not necessarily a true measure of the relative speeds of the initial reaction which determines E. Apparent changes in a probability factor may originate in a subsequent stage of the process. Similar considerations apply to other reactions.

III. The velocity of bromination of 0.1M solutions of *m*- and *p*-derivatives of COPhMe in 75% AcOH in presence of 2% wt./vol. of cryst. NaOAc at 35° is NO₂>F, I>Cl, Br>H, in general agreement with the theory. J. G. A. G.

Reactions catalysed by aluminium chloride. XI.—See this vol., 1221.

Catalytic action of monoses on the formaldehyde condensation. II.—See this vol., 1224.

Esterification of hydroxy-acids and polyhydric alcohols.—See this vol., 1223.

Acid catalysis in non-aqueous solvents. II. Rearrangement of N-bromoacetanilide in chlorobenzene catalysed by trichloroacetic acid. R. P. BELL and (SIR) R. V. H. LEVINGE (Proc. Roy. Soc., 1935, A, 151, 211-219).—The velocity of rearrangement of NBrAcPh (I) in PhCl catalysed by $CCl_3 \cdot CO_2H$ has been measured at 35°, 45°, 50°, and 65°. The eatalytic const. is independent of acid concn., and decreases with increasing concns. of (I) and p- $C_6H_4Br\cdotNHAc$. The mol. statistics of the unretarded reaction were investigated. Only about 1 in every 10⁴ of collisions possessing the necessary energy leads to reaction. This factor is interpreted as due to purely spatial effect. L. B.

Heterogeneous catalysis. II. Graphite and diamond as adsorbents and catalysts. E. STOR-

FER (Z. Elektrochem., 1935, 41, 540-541; cf. this vol., 696).—A discussion. T. G. P.

Mechanism of the catalysis of hydrogen peroxide by platinum. V. A. ROITER (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 49–53).— It is suggested that O adsorbed at the active centres is reduced electrolytically by H_2O_2 on the inactive surface. The theory is discussed in connexion with experimental data. R. S.

Influence of sorbed gas on the catalytic activity of hydrogen peroxide decomposition catalysts. II. V. A. ROITER and I. G. SCHAFRAN (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 29–33; cf. A., 1930, 1531).—The activity of Pt is increased by evacuation at 0·1 mm. The original activity is restored on exposure to the atm., and it is concluded that the whole surface is involved in the decomp. reaction. An irreversible poisoning effect due to diffusion of the P_2O_5 drying agent occurs at 10⁻⁶ mm. R. S.

Mechanism of the catalytic combustion of ammonia. M. BODENSTEIN (Z. Elektrochem., 1935, 41, 466—468).—Intermediate products from the combustion of NH_3 at 0.01 mm. on an electrically heated Pt surface were isolated at mean free path distances on a surface cooled with liquid air. NH_2OH , HNO_2 , and a little HNO_3 were found, but no N_2H_4 . The effluent gases, principally N_2 with a little N_2O , contained no NO. A mechanism is suggested. T. G. P.

(A) Activation of chromium catalysts by barium oxide. (B) Poisoning of chromium catalysts by arsenic and other catalyst poisons. I. E. ADADUROV and D. V. GERNET (J. Appl. Chem. Russ., 1935, 8, 606-611, 612-627).-(A) The activity of a catalyst containing BaO 0.1, SnO₂ 1, and Cr₂O₃ 1 mol. is little < that of Pt; the stability and cheapness of the catalyst render it eminently suitable for the H_2SO_4 industry.

(B) As_2O_3 inactivates the above catalyst at 450– 475°, but not at 550°; inactivation is due to occlusion of the active surface by adsorbed As_2O_3 , and may be reversed by heating in a stream of CO. The use of CO-H₂ mixtures for regeneration leads to inactivation, due to reduction of SnO_2 to Sn; at the same time H₂S is evolved, pointing to production of S from SO₂ as one of the stages of catalytic oxidation to SO₃. The catalyst is not inactivated by H₂O or HCl in the reaction gas, but moist HCl reversibly inactivates it. R. T.

Effect of adding oxides of different metals on the activity of tin-chromium catalysts. D. V. GERNET and A. CHITUN (J. Appl. Chem. Russ., 1935, 8, 598—605).—The activity of Cr_2O_3 -SnO₂ catalyst is reduced by admixture of oxides of Ca, Mg, Sr, Zn, Al, Bi, Mn, Ni, or Cu, but is increased by BaO or Fe_2O_3 . In general, the inactivating effect varies inversely with the at. radius of the added element, and is greater for elements of even than of odd at. no.; the effect is ascribed to deformation of the field of the original catalyst. R. T.

Activity and activation energy in heterogeneous catalysis of gas reactions. H. H. STORCH (J. Amer. Chem. Soc., 1935, 57, 1395—1398).— Theoretical. The relation $A = C_0 e^{cE}$ between the activity, A, and energy of activation, E, for contact catalytic reactions is not due entirely to a probability distribution of active centres. Other factors discussed are : (1) that the frequency of energy exchange in the adsorbed phase may be reduced markedly when multiple adsorption occurs, and hence be a function of the spacing of the catalyst atoms; (2) that in reactions involving H₂ and having a relatively low activation energy a considerable fraction of the rate is to be ascribed to a quantum-mechanical leakage through the energy barrier. E. S. H.

Influence of manganese on the corrosion of magnesium.—See B., 1935, 808.

Mechanism of the promoter action of iron ammonia catalysts.—See B., 1935, 801.

Catalysts for ammonia synthesis.—See B., 1935, 801.

Rapid oxidation of organic substances with sulphuric acid. J. MILBAUER (Z. Elektrochem., 1935, 41, 594–595).—The reaction $CO+H_2SO_4=CO_2+SO_2+H_2O$ is catalysed markedly by mixtures of Pd with Ag₂SO₄ or HgSO₄, and by SeO₂+HgSO₄. Addition of SeO₂ reduces the activity of Pd.

E. S. H.

Catalytic dehydration of ethyl alcohol by alumina. I. Effect of the water content of the catalyst. L. A. MUNRO and W. R. HORN (Canad. J. Res., 1935, 12, 707-710).—The catalytic activity of Al₂O₃ in the dehydration of EtOH vapour to yield Et₂O is a max. when the catalyst contains 5.5% H₂O. Al₂O₃ containing > 13.8% H₂O does not effect the reaction. The relative decrease in efficiency by poisoning during the course of the reaction is the greatest for the catalysts which are the most efficient initially. J. W. S.

Structure and genesis of methyl alcohol catalysts.—See B., 1935, 795.

[Catalytic] hydrogenation of naphthalene.—See B., 1935, 795.

Activity of nickel catalysts [for dehydrogenation of hydrocarbons].—See B., 1935, 802.

Catalytic dehydration of formic acid.—See B., 1935, 795.

Energetics of catalysis. V. Temperature coefficient of hydrogenation processes. E. B. MAXTED and C. H. MOON (J.C.S., 1935, 1190-1192).— The rates of hydrogenation with a Pt-black catalyst of crotonic (I) and maleic (II) acids in AcOH and in stearic acid (cf. this vol., 589) have max. vals. at 80-90° (I) and 65° (II). The mol. heats of adsorption on the Pt are : (I) 15,500 and (II) 15,000 g.-cal. The apparent activation energies of hydrogenation are, in AcOH, (I) 6800 and (II) 9000, and (I) in stearic acid 10,000, leading to the true heats of activation (cf. A., 1934, 974) 23,000, 25,000, and 26,000, respectively. J. G. A. G.

Electrolytic separation of the hydrogen isotopes. O. HALPERN and P. GROSS (J. Chem. Physics, 1935, 3, 452-456).—Assuming that the rate of production of gas on electrolysis is determined by the speed of recombination of gas atoms on the electrode, an equation is deduced giving the separation coeff., α , in terms of thermodynamic consts. of H and D and the frequencies of thermal vibration of the atoms when bound to the electrode. The calc. vals. of α agree with experiment. With rise of temp. α should fall. A relation between the normal electrode potentials of H and D has been established. R. C.

Critical voltage for formation of ozone by alternating-current discharge. M. SENKUS and A. C. GRUBB (J. Chem. Physics, 1935, 3, 529).—For each pressure and velocity of O_2 in the apparatus used there is a crit. voltage above which the discharge becomes greenish-yellow and O_3 ceases to be formed. R. C.

Oxidation of graphite in electrolytic melts. V. SIHVONEN (Suomen Kem., 1935, 8, B, 29-30).-The oxidation of a graphite anode during the electrolysis of fused NaOH+KOH at 200-550°, using a Ag cathode, and of fused Na₂CO₃+K₂CO₃+Li₂CO₃ at 400-900°, using a graphite cathode, has been studied. With the carbonates pure CO, is evolved at the anode at 400°, but at 500° there is a little CO, the % of which increases with rise of temp. No O_2 is evolved, even with a c.d. of 6 amp. per sq. cm. With rising temp. the p.d. between the graphite anode and Ag cathode increases uniformly. The p.d.-c.d. curves show no irregularities. The CO_3'' ions probably react with the C atoms (C_x) of the graphite surface giving keto-groups: $C_x+CO_3''=C_xO+CO_2+2e$; the keto-groups are then further oxidised by CO_3'' . With the alkalis, $C_x+2OH'=C_xO+H_2O+2e$, and $C_x+H_2O=C_xO+H_2$. At $400-550^{\circ}$ the p.d. and max. c.d. are > for the carbonates. No formation of O_2 , CO, formate, and oxalate occurs, and no gas is evolved at the anode, the primary product being CO₂, which dissolves in the R. S. B. melt.

Electrolytic preparation of fluorine.—See B., 1935, 802.

Action of alcoholic ammonium acetate in electroanalytical processes. H. FUCHSHUBER (Chem.-Ztg., 1935, 59, 676).—To prevent a spongy cathode deposit during the electrolysis of HNO_3 solutions of Cu, 10—15 c.c. of a saturated solution of NH_4OAc in EtOH are added to the electrolyte. Similarly, the anodic deposition of Mn-free Pb from solutions containing both elements is facilitated.

A. G. P. Chemical reactions in the lead storage battery. —See B., 1935, 773.

Anodic oxidation of aluminium by superimposing three-phase a.c. on d.c. A. MIYATA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 651— 678).—Electrolysis with superimposed three-phase a.c. on d.c. is simpler and better than the use of other polyphase a.c. for anodic oxidation of Al in $H_2C_2O_4$ solution. A stout hard film is obtained; the anode current during electrolysis reverses little, even when appreciable negative voltage is applied to the anode in each cycle; the energy efficiency of the film formation is higher than by other methods; the a.c. component introduced in the d.c. generator circuit that menaces the commutation of the machine is suppressed; and pitting of the anode during electrolysis is avoided completely. J. W. S.

Oxidation-reduction process at the surface of a diaphragm (of kaolin) interposed in a copper solution during electrolysis. Factors determining its speed of appearance. (MME.) L. GUASTALLA (Compt. rend., 1935, 201, 268—270; cf. A., 1934, 739).—The time of appearance of Cu_2O and Cu, as reduction products of Cu salts, on the anodic face of a kaolin diaphragm during electrolysis, is independent, for the same anion, of the thickness of the diaphragm, decreases with increasing $p_{\rm H}$, and increases with the dilution. R. S. B.

Electrochemical oxidation of mesitylene.—See this vol., 1229.

Electrolytic reduction of aliphatic ketones to hydrocarbons.—See this vol., 1224.

X-Ray photolysis of hydrogen peroxide. D. DEN HOED and C. W. F. SPIERS (Z. physikal. Chem., 1935, 173, 412—414; cf. A., 1928, 970).—The amount of photolysis of 0.02—0.05M aq. H_2O_2 by X-rays of $\lambda \ 0.06$ —0.5 Å., 100—200 kv., depends on the energy absorbed, not on the voltage. R. C

Occurrence of a metastable, active oxygen molecule in sensitised photo-oxidations. J.WEISS (Naturwiss., 1935, 23, 610).—The extinction of fluorescence of various dyes (eosin, uranin, trypa-flavin) by SO_3'' is considered. The dye may be dissociated photochemically into H atoms (or another radical) and then may take place either (1) the recombination of the H atoms or radicals, possibly with chemiluminescence, or (2) combination of H atoms with O_2 forming HO₂ which reacts with the acceptor. The HO₂ mol. takes the place of the metastable activated O_2 mol. in Kautsky's theory. A. J. M.

Solarisation at low intensity. A. J. REARDON and H. P. GRIGGS (J. Opt. Soc. Amer., 1934, 24, 331— 338).—By prolonged exposure the characteristic curve of a photographic emulsion has been extended beyond the known second reversal, and contains a series of max. and min. points, up to 16 reversals having been obtained with exposures up to 1759 hr. The depth of reversal gradually decreases, and the time between two successive max. or min. increases. Ageing of the emulsion decreases D_{max} and the degree of solarisation obtainable. J. L.

Photophysical changes in silver-silver chloride systems. A. E. CAMERON and A. M. TAYLOR (J. Opt. Soc. Amer., 1934, 24, 316-330).—Photo-anisotropy (emulsions red-sensitised by exposure to ultra-violet light, and then exposed to red polarised light) is shown to depend on a Ag-AgCl system alone; the same results were produced in suspensions in the absence of gelatin, and also in a single crystal of pure AgCl. The amount of free Ag does not change on production of the dichroism. Fixing the plates shifts the max. of the absorption, dichroism, and birefringence curves towards shorter $\lambda\lambda$, both for the ultra-violet-exposed plate and for the red-exposed plate. The effects are therefore due to the Ag particles. Measurements of the dichroism in the dry and wet (swollen) fixed plate, and further theoretical considerations lead to the theory that the photo-adapted image formation is due to optical resonance, and orientation of the Ag particles. Red light causes a decrease in size and an increase in no. of the Ag resonators present. It is postulated that electrons are ejected, re-forming Ag from Ag^+ at another point, only correctly dimensioned and oriented particles responding to the incident polarised light. J. L.

Photochemical formation of carbonyl chloride from chloroform, chlorine, and oxygen, and its inhibition by added substances. H. J. SCHUMACHER and D. SUNDHOFF (Z. Elektrochem., 1935, 41, 499).—The duration of inhibition of the reaction between CHCl₃, Cl₂, and O₂ \propto the quantity of MeOH, EtOH, or NH₃ added. Inhibition occurs through the removal of Cl atoms, for if the inhibitors are first chlorinated, they cease to affect the reaction. T. G. P.

Photochemical dissociation of methyl and ethyl alcohols. F. PATAT [with H. HOCH] (Z. Elektrochem., 1935, 41, 494–498).—MeOH and EtOH dissociate in light between 1800 and 2000 Å. into H_{2} , CO, and $CH_{2}O$, and H_{2} and MeCHO, respectively, with quantum yields between 1 and 2. Mechanisms are discussed. T. G. P.

Free radicals and atoms in primary photo-chemical processes. II. Photo-dissociation of aliphatic aldehydes and ketones. T. G. PEARSON and R. H. PURCELL (J.C.S., 1935, 1151-1156; cf. this vol., 48).-The identification of minute quantities of free radicals in presence of a larger amount of condensable vapour has been investigated. The radicals from the photolysis of COMe₂ and COEt₂ are proved to be free Me and Et, respectively, by identifying the products of interaction with Te, Hg, and As. The products from the photolysis of MeCHO do not remove cold metallic mirrors owing to a protective film of polymerised MeCHO, but free Me has been detected by the action on warm metallic mirrors. Approx. six times as many radicals participate in the photodissociation at 100° of COMe₂ as in that of an equiv. of MeCHO under identical conditions. These results confirm that there is a fundamental difference between the mechanisms of photolysis of aldehydes and ketones and that free radicals take some part in the photolysis of aldehydes also (cf. A., 1933, 682; 1934, 976).

Free *n*-propyl radical.—See this vol., 1221.

J. G A. G.

Photochemical oxidation of mandelic acid by methylene-blue with uranyl nitrate as photosensitiser. J. C. GHOSH, D. S. NARAYANAMURTHI, and N. K. ROY (Z. physikal. Chem., 1935, B, 29, 236— 246).—The reaction has been studied for monochromatic radiation of $\lambda\lambda$ 254—436 mµ. The mechanism $UO_2^{"}+h\nu \rightarrow UO_2^{"}*, UO_2^{"}* \rightarrow UO_2^{"}+fluorescence,$ $UO_2^{"}*+UO_2^{"} \rightarrow 2UO_2^{"}, UO_2^{"}*+OH\cdotCHPh\cdotCO_2H$ $\rightarrow UO^{"}+PhCHO+H_2O, UO"+methylene-blue+$ $H_2O \rightarrow UO_2^{"}+leuco-base leads to <math>-d$ [methyleneblue]/ $dt=I_{abs. by}$ UO," k_4 [OH·CHPh·CO_2H]/{ $Nh\nu(k_2+$ k_3 [UO_2"]+ k_4 [OH·CHPh·CO_2H])}, which, utilising Vavilov's data (cf. A., 1928, 1072), represents the course of the reaction satisfactorily. R. C.

Use of the hydrolysis of monochloroacetic acid for absolute actinometric measurements. B. J. DAIN and E. S. PUSENKIN (Ber. Ukrain, wiss. Forsch. physikal. Chem., 1935, 4, 75—81).—The photodecomp. of H_2O_2 has been studied using $CH_2Cl \cdot CO_2H$ in an actinometer arranged symmetrically with respect to the arc. The relation $\gamma \propto I^{1/2}$ (cf. A., 1930, 715) has been confirmed. R. S.

Rate of photosynthesis. W. O. JAMES (Nature, 1935, 136, 220-221).—A crit. discussion. L. S. T.

Effect of X-rays on glutathione. V. E. KINSEY (J. Biol. Chem., 1935, 110, 551—558).—A linear relation was observed between the destruction of glutathione (I) in aq. solution and the dose of X-rays. The effect increases linearly with concn. of (I) up to 0.01%and then again linearly but at a smaller rate, the energy efficiency increasing with the concn. Increase of $p_{\rm H}$ also augments destruction. H. G. R.

Attempts to produce helium 3 in quantity. F. A. PANETH and G. P. THOMSON (Nature, 1935, 136, 334).—During the bombardment of heavy H with positive rays measurable amounts of He+Ne were obtained. This gas is considered as derived from the walls of the discharge vessel and not He³ produced by at. transmutation. L. S. T.

Possibility of the ignition of electrolytic gas by fast electrons. A. E. MALINOVSKI and J. A. SKRINNIKOV (Physikal. Z. Sovietunion, 1935, 7, 43— 48).—An electron beam of 2.5×10^{-7} amp. was passed for 10—60 sec. through a mixture of 7.5% of C₂H₂ and air at 15—76 cm., and beams of 2.24×10^{-6} and $2.5 \times$ 10^{-7} amp. through electrolytic gas at 10—64 cm. No explosions occurred. R. S. B.

Action of "Erdstrahlen" on the divining rod. II. M. TRÉNEL (Angew. Chem., 1935, 48, 575-578; cf. this vol., 600).—The results previously reported are confirmed. E. S. H.

Cryogenic laboratory of the California Institute of Technology. I. A. GOETZ (Rev. Sci. Instr., 1935, [ii], 6, 217–229).—The purification and liquefaction of H_2 are described. C. W. G.

Concentration of heavy isotopes in carbohydrates. T. TITANI and M. HARADA (Bull. Chem. Soc. Japan, 1935, 10, 261–263).—Samples of H_2O were prepared by destructive distillation of cane molasses, refined cane sugar, beet sugar, grape- and milk-sugar, sol. starch, potato starch, rice flour, wheat flour, dextrin, and agar-agar. All were denser by 4–6 p.p.m. than Osaka town H_2O . Consequently the carbohydrates must contain enhanced concn. of the heavy isotope of either O or more probably H. It is considered probable that the enhanced concn. of D is located in the OH groups. S. J. G.

Quantitative isotopic exchange reactions in the carbohydrate group. W. H. HAMILL and W. FREUDENBERG (J. Amer. Chem. Soc., 1935, 57, 1427—1430).—Quant. isotopic exchange reactions have been carried out with free hexoses, their methylglycosides, and other derivatives in 11-30% and 80-96% D₂O. The exchange no. for 21 samples agrees closely with the no. of OH groups in the sample.

E. S. H.

Cupric ammonium compounds and cupric acid ammonium compounds. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 223, 393–396).— The compounds formed by the action of aq. NH_3 on solutions of Cu^{II} salts were investigated by a dialysis method with S_2O_3'' as reference ion using a membrane of Cuprophane. With $Cu(NO_3)_2$, $CuCl_2$, and $Cu(CNS)_2$, the ion present was probably $[Cu(NH_3)_4]^*$, and with $Cu(OAc)_2$, some other unknown ion; with $CuSO_4$, $CuSeO_4$, and $Cu_3(PO_4)_2$ undissociated compounds appear to be formed, viz., $[Cu(NH_3)_4SO_4]$, $[Cu(NH_3)_4SeO_4]$, and $[Cu_3(NH_3)_4(PO_4)_2]$. The earlier assumption that a $Cu(NH_4)_4$ ion is formed in all cases of dissolution of a Cu salt in aq. NH_3 , independently of the nature of the anion, appears therefore to be unjustified. S. J. G.

Precipitation of copper and of silver by the action of the latter. A. P. SERGUEEV and A. A. KOCHOUCHOVSKI (Ann. Chim. Analyt., 1935, [iii], 17, 231-232).-When Ag powder is heated in a solution of CuSO₄ containing KCl or NaCl in excess (or in an EtOH solution of anhyd. CuCl₂), Cu is deposited on the Ag and the solution or dilution yields a ppt. of AgCl. Similar treatment with NaCl solution free from Cu produces no ppt. of Ag. If Ag is enclosed in a thin paper sachet and after treatment with CuSO₄-NaCl is dipped in aq. AgNO₃, Ag is deposited on the sachet and Cu on the Ag within. By dipping a sachet containing Ag in conc. aq. KCl, washing, and then placing in aq. AgNO3, a Ag deposit is obtained on the sachet. Similar but less effective results are obtained with KNO3 solutions, and a small but distinct deposit is obtained by use of H_2O in place of the salt solution. The [Ag] of the solution remains unchanged. Conditions comparable with those of a concn. cell are attained when the wetted sachet is dipped into aq. AgNO₃. KCl intensifies the action by modifying the character of the Ag A. G. P. surface.

Action of nitrosyl chloride on some salts of silver. R. PERROT (Compt. rend., 1935, 201, 275-277).-Three types of reaction are observed between NOCl and anhyd. Ag salts at room temp. (a) Formation of nitrosyl derivatives by double decomp.; e.g., AgNO₃ rapidly forms pure NO₂, and AgClO₄ slowly forms a compact residue containing NOClO₄ (which hydrolyses to HNO_2 with H_2O). (b) Formation of NO and liberation of anion of salt. With salts of oxyacids the reaction is complicated by the transitory formation of NO_2 ; e.g., ÅgCNS gives a quant. yield of NO and a yellow polymeride of cyanogen sulphide. AgI gives I, but AgBr reacts only partly, even at 200°. AgNO₂ gives a mixture of NO and NO₂. Ag₂CO₃ reacts: $2Ag_2CO_3+3NOCI \rightarrow 3AgCl+AgNO_3+2NO+2CO_2$; a little AgNO₂ is also formed. Ag₂SO₃ gives nitrosyl pyrosulphate : $3Ag_2SO_3$ Ag_2SO_3 gives nitrosyl pyrosulphate : $3Ag_2SO_3$ + $6NOCl \rightarrow 4NO+SO_2+S_2N_2O_9+6AgCl.$ $Ag_2N_2O_2$ rapidly forms N₂ with a little NO. (c) Oxidation of the salt and reduction of NOCl to N₂ or NO; *e.g.*, $Ag_2C_2O_4$ gives CO_2 and NO, AgCNO gives N₂, Ag_2CN_2 inflames, but AgCN and Ag dicyanoimide require heating to 150° R S R heating to 150°. R. S. B.

Action of sulphur on silver. R. DUBRISAY (Compt. rend., 1935, 201, 425-426).—The direct union of Ag with S at room temp. is shown by the blackening of Ag by S vapour in vac. Substances readily adsorbed on the Ag surface retard or inhibit the action. J. S. A.

Action of carbonic acid on calcium phosphates. W. FISCHER and K. BRÜNGER (Z. anorg. Chem., 1935, 223, 422—426).—The action of H_2O+CO_2 on Ca phosphates at 15°, 120°, and 170° up to 50 atm. (as measured by the quantity of phosphate, sol. in citric acid, formed) was negligible even in presence of K and NH_4 salts. S. J. G.

Perchlorates. III. Barium ammine perchlorates. C. SMEETS (Natuurwetensch. Tijds., 1935, 17, 83—90).—Isotherms for the system $Ba(CIO_4)_2$ -NH₃ at temp. from -79° to 80° indicate the existence of compounds with 2, *five*, 6, and *nine* NH₃. Dissociation pressure curves are given.

D. R. D.

Peroxide compounds. R. SCHWARZ and F. HEINRICH (Z. anorg. Chem., 1935, 223, 387–392).— Using Liebhafsky's test (this vol., 173) the following are found to be peroxide compounds: $Ti(OH)_3O_2H$; $K_2[TiO_2(SO_4)_2]_3H_2O$; $Zr(OH)_3O_2H$; $Zr_2O_6SO_4,8H_2O$; $(NH_4)_2Cr_2O_{12},2H_2O$; and the following are additive compounds: $K_2TiO_4,4H_2O_2,2H_2O$; $ThO_2, 3H_2O_2,H_2O$; $K_2GeO_5,2H_2O_2,2H_2O$; whilst $K_4UO_6,6H_2O_2,xH_2O$ is a mixed compound. S. J. G.

Lead chlorite : double and basic salts. G. R. LEVI and G. PEYRONEL (Atti R. Accad. Lincei, 1935, [vi], 21, 381—384).—The double salts $PbCl_2, Pb(ClO_2)_2$ and $PbBr_2, Pb(ClO_2)_2$ may be crystallised from aq. solution. A basic salt, probably $Pb(ClO_2)_2, Pb(OH)_2$ or $Pb(ClO_2)_2, 2Pb(OH)_2$, may be obtained by addition of aq. NaOH to $Pb(ClO_2)_2$ suspended in H_2O . No chemical or X-ray evidence could be obtained for the existence of Schiel's $PbCl_2, 2Pb(ClO_2)_2$ and $4PbCl_2, 6Pb(ClO_2)_2, PbO.$ D. R. D.

Chemical reactions with active nitrogen. E. TIEDE [with H. KNOBLAUCH] (Z. Elektrochem., 1935, 41, 526).—N atoms react with Hg to yield Hg₃N, which decomposes quietly at 100°, and gives NH_3 with NaOH. Ga gives a substance which is not GaN. Na-rich amalgams and molten alkali metal alloys yield azides. T. G. P.

Action of hydrogen peroxide on nitrous acid. Pernitrous acid. II. K. GLEU and R. HUBOLD (Z. anorg. Chem., 1935, 223, 305-317; cf. A., 1929, 523).—The oxidising substance obtained by action of H_2O_2 or $NaNO_2$ in acid solution, previously believed to be pernitric acid, is shown to be pernitrous acid. It is identical with the product of ozonisation of NaN₃ and is prepared as follows : 1 mol. of NaNO₂ is mixed with slightly > 1 mol. of H_2O_2 , treated with much ice, and 1 mol. of M-H₂SO₄ added. Excess of NaOH is added after 2 sec., yielding an intense yellow solution containing approx. 0.1 mol. of NaNO. O. To determine H_2O_2 , NaNO₂, and NaNO₂ O when present together the H_2O_2 is titrated with 0.1N-NaOCl in alkaline solution in presence of 10 drops of 0.1N-KI until the colour of Ru-red indicator $(2RuOHCl_2,7NH_3,3H_2O; A., 1893, ii, 172)$ is discharged. Excess of 0.1N-As₂O₃ is immediately added and back-titrated with NaOCl (same indicator), to determine active O of the pernitrite. NO_2' is determined by reducing with $VOSO_4$ to NH_3 and distilling into 0.1N-HCl, nitrate being unaffected. The ratio active $O: NO_2'$ is always 1:1, proving the presence of pernitrite and absence of pernitrate.

S. J. G.

Nitrous oxide as an oxidising agent in the gaseous state. E. W. R. STEACLE and R. D. MCDONALD (Canad. J. Res., 1935, 12, 711-714).----N₂O reacts with MeOH, C_2H_4 , MeCHO, PH_3 , or CS_2 only at temp. where its decomp. becomes appreciable, and it is a much less efficient oxidising agent than mol. O_2 . It is concluded that in general N₂O does not itself act as an oxidising agent in the gaseous state, but acts merely as a reservoir of at. O when the temp. is sufficiently high. J. W. S.

Existence of a series of ammonium orthophosphates and orthoarsenates. A. DE PASSILLÉ (Compt. rend., 1935, 201, 344-345).—By progressive withdrawal of NH₃ from $(NH_4)_6P_2O_8$ and $(NH_4)_6As_2O_8$ equilibria have been obtained corresponding with the compounds $(NH_4)_5HP_2O_8$, $(NH_4)_4H_2P_2O_8$, $(NH_4)_3H_3P_2O_8$, $(NH_4)_2H_4P_2O_8$, $(NH_4)_5HAs_2O_8$, $(NH_4)_4H_2As_2O_8$, $(NH_4)_2H_4P_2O_8$, $(NH_4)_2H_4As_2O_8$, $(NH_4)_4H_5As_2O_8$. The heat changes of equilibria are recorded. J. W. S.

Salts of hexafluoroantimonic acid, HSbF₆. W. LANGE and K. ASKITOPOULOS (Z. anorg. Chem., 1935, **223**, 369–381).— $KSbF_6$ and $NaSbF_6$ were prepared by evaporating the pyroantimoniates with excess of 40% HF; the NH_4 and Rb salts by dissolving Sb_2O_5 in HF and evaporating with the calc. amount of NH_4F or RbF. The alkali salts are readily sol. in H_2O , and are stable if dry but hydrolysed in moist air or and are stable in dry but hydrolysed in moist are or solution: $[SbF_6]' \Longrightarrow [SbF_x(OH)_{6^-x}] \Longrightarrow [Sb(OH)_6]'$. A no. of intermediate products of hydrolysis have been isolated, *e.g.*, SbOF₃,NaF,H₂O. The less sol. salts were prepared by pptg. HSbF₆ with sol. salts of the base. NMe₄, strychnine, brucine, cocaine, nitron, and diphenylene-4: 4'-bisdiazonium salts were Introl, and diphenylene-4.4-bischazofhum sairs were prepared thus. They resemble the corresponding P compounds but are more sol. The aryldiazonium salts are readily sol. in H_2O , stable if dry, and not decomposed by detonation; when heated they decompose thus: $[ArN_2][SbF_6] \rightarrow ArF+SbF_5+N_2$. The salts of heavy and alkaline-earth metals are in time completely, hydrolyzed in solution owing to time completely hydrolysed in solution owing to insolubility of the fluoride formed. $[SbF_6]'$ is quickly and completely hydrolysed by not too dil. alkali, in contrast to $[PF_6]'$, which is unaffected; and in general $[SbF_6]'$ is more reactive than $[PF_6]'$. The salts of $[HSbF_6]$ are rhombohedral, those of $[HPF_6]$ regular. S. J. G.

Ammonium compounds of bismuth halides. R. SCHWARZ and H. STRIEBICH (Z. anorg. Chem., 1935, 223, 399–408).—Halides of non-metals are ammonolysed by NH₃, whereas metal halides add on NH₃. This can occur in two ways. (a) NH₃ mols. may enter the structure of the halide mol., surrounding the cation with a dielectric shell and displacing the anion into the outer sphere. The result is an "enclosure compound" (Einlagerungsverbindung), characterised by an ionic lattice, solubility in liquid NH₃, and a definite NH₃ dissociation pressure. (b) An "attachment compound" (Anlagerungsverbindung) may be formed, which is the first stage towards ammonolysis. No separation of the central atom and its halogen atoms occurs, the latter merely undergoing electric deformation, which leads to intense coloration. Such compounds are insol. in liquid NH₃, give no NH₃ pressure, and can be distilled without decomp. The action of NH₃ on BiCl₃, BiBr₃, and BiI₃ has been investigated in the light of the above classification. None of them undergoes ammonolysis even after 50-fold treatment with liquid NH₃. The following were formed : (a) BiCl₃, 12·5NH₃; BiBr₃ with 18·5, 14, and 3NH₃; BI₃ with 22, 12·5, 12, 4, 3, and 2NH₃; (b) BiCl₃,NH₃, BiCl₃,0·5NH₃, BiBr₃,1·5NH₃, BiBr₃,0·5NH₃. The physical and chemical properties of the compounds are elucidated with the aid of spatial models. S. J. G.

Yields in the preparation of protoactinium. A. VON GROSSE (Ber., 1935, 68, [B], 1511-1512; cf. this vol., 460).—A reply to Hahn (this vol., 593) H. W.

Constitution and formation of bleaching powder. C. W. BUNN, L. M. CLARK, and I. L. CLIFFORD (Proc. Roy. Soc., 1935, A, 151, 141-167).-As a result of phase-rule studies, all the pure compounds which could be isolated under equilibrium conditions from the system CaO-CaCl₂-Ca(OCl)₂-H₂O below 40° have been defined, and used as a basis for comparison with the solid phases present in bleaching powder, by means of microscopic and X-ray methods. Samples taken at intervals during the reaction of Cl₂ with Ca(OH)₂ have been examined by the same methods. The first stage in the reaction is the formation of Ca(OCl)₂,2Ca(OH)₂ (I) and CaCl₂,Ca(OH)₂,H₂O (II). On further chlorination the former is converted into a mixed crystal of which the chief constituent is Ca(OCl)₂. Ordinary bleaching powder (35% available Cl) is a mixture of this mixed crystal with (II). On further chlorination (II) is partly converted into CaCl₂,4H₂O, whilst the hypochlorite mixed crystal persists, with gradually changing properties. The non-deliquescent nature of bleaching powder and the difficulty of introducing >35% of available Cl into the solid are due to the presence of the very stable compound (II). The unit cell dimensions of (I) (hexagonal) and Ca(OCl)₂,3H₂O (tetragonal), and the refractivities of the OCl' ion parallel and perpendicular to its axis have been deduced. L. L. B.

Vanadates of some cobaltammine complex salts. E. NEUSSER (Z. anorg. Chem., 1935, 223, 417-421).—The following *compounds* have been prepared in a pure condition, and are described :

 $\begin{array}{ll} [\mathrm{Co}(\mathrm{NH}_3)_6](\mathrm{VO}_3)_3\,;\,\, [\mathrm{Co}(\mathrm{NH}_3)_5\mathrm{H}_2\mathrm{O}](\mathrm{VO}_3)_3\,;\\ &\, [\mathrm{Co}(\mathrm{NH}_3)_4,\mathrm{H}_2\mathrm{O},\mathrm{OH}](\mathrm{VO}_3)_2\,;\\ &\, [\mathrm{Co}(\mathrm{NH}_3)_5\mathrm{Cl}](\mathrm{VO}_3)_2,\mathrm{H}_2\mathrm{O}\,;\\ &\, [\mathrm{Co}(\mathrm{NH}_3)_5\mathrm{CO}_2](\mathrm{VO}_3)_2,\mathrm{H}_2\mathrm{O}\,;\\ &\, [\mathrm{Co}(\mathrm{NH}_3)_5\mathrm{CSN}](\mathrm{VO}_3)_2\,;\,\, [\mathrm{Co}(\mathrm{NH}_3)_4\mathrm{C}_2\mathrm{O}_4]\mathrm{VO}_3.\\ &\, \mathrm{S.~J.~G.} \end{array}$

Novel type of isomerism among complex metallic salts. F. G. MANN and D. PURDIE (Chem. and Ind., 1935, 814-815).—Compounds of the type $[(R_2S)_2PdCl_2]$, $[(R_3P)_2PdCl_2]$, and $[(R_3As)_2PdCl_2]$ have been prepared and derivatives are described of the type $[Bu^a_3PPdCl_2]_2$ (I), deep orange crystals, m.p. 144°. It is shown that in (I) both R_3P are coordinated to the same Pd. (I) has been converted into an isomeric form in which the R_3P are attached to different Pd. This gives pale yellow crystals, m.p. 71°, and dissociates in solution forming $[R_3PPdCl_2]$. R. S.

Quantitative spectral analysis.—See B., 1935, 788.

Application of Delaunay's theory of the basic parallelepipeds of crystal cell structure to determination of crystalline substances. V. LINITZKI (Ukrain. Chem. J., 1935, 10, 161—175).—Theoretical. R. T.

End-point of potentiometric titration of weak acids and bases. S. KILPI (Z. physikal. Chem., 1935, 173, 427-448; cf. this vol., 1091).-For a weak acid (base) to be titratable with a strong base (acid) Kc must be $> 27K_w$, where c is the concn. of the acid (base) calc. on the final vol. The titration is more exact than when the strong is titrated with the weak component. In the titration of a weak acid with a weak base, $K_{HA}K_{BOH}$ must be $\ll 28K_w$, and the endpoint and equiv. point coincide only if $K_{HA}K_{BOH} > 10^{-10}$. These theoretical deductions have been verified by study of the titration of H₂CO₃ in the second stage. KCl shifts the end-point towards the equiv. point. In the titration of HCO_3' with NaOH or of a mixed solution of NaOH and Na_2CO_3 with HCl the end-point is on the acid side of the equiv. point, and the more so the lower is the concn. R. C.

Determination of traces of bromine in presence of chlorine. S. GILDE (Ann. Chim., 1935, [xi], 4, 224—269).—Br' cannot be determined satisfactorily in presence of Cl' by pptn. methods. The method based on liberation of Br followed by distillation is also inaccurate. Colorimetric methods detect 0.1×10^{-6} g. Br, but the potentiometric method described is equally sensitive for determination of [Br'] of 0.2-2% and is independent of lighting conditions and coloursensitivity of the operator. Irregularities in a Hg₂Cl₂ electrode potential may arise through traces of KBr in the KCl. J. W. S.

Determination of hydrobromic acid in presence of hydrochloric acid. G. G. LONGINESCU and E. I. PRUNDEANU (Bull. Sci. Acad. Roumaine, 1935, 17, No. 3-4, 1-4).-H₂O₂ under certain conditions oxidises HBr but not HCl. 10 c.c. of KBr and KCl solution, 100 c.c. of light petroleum, 5-6 c.c. of conc. H₂SO₄, and 2-3 c.c. of H₂O₂ are mixed and shaken vigorously at intervals for 30 min. The petroleum layer (a) is then separated from the aq. layer (b); to (a) 40 c.c. of amyl alcohol + 2 g. Na are added little by little to reduce the Br to NaBr; this is extracted by H₂O, the reduction and extraction being repeated twice more. The combined aq. extracts are cautiously acidified with HNO₃, and the Br' is determined gravimetrically by pptn. as AgBr in the usual way. The HCl in aq. layer (b) is similarly determined after S. J. G. warming to destroy H₂O₂.

Does azoimide disturb micro-iodometric determinations by Winkler's method ? J. F. REITH and J. DE BEUS (Biochem. Z., 1935, 279, 203—204).— HN₃ does not interfere. P. W. C.,

Detection and determination of fluorine in natural waters.—See B., 1935, 832.

Determination of dissolved oxygen in deaërated water by Winkler's method.—See B., 1935, 832.

Atmospheric sulphur and arable soils. G. BERTRAND (Compt. rend., 1935, 201, 309-312).— In the determination of S in rain-H₂O an error is introduced during evaporation due to the absorption of S from the gas flame. H. D.

Potentiometric determination of S", CNS', and Cl'ions in presence of one another. A. J. BURSUK and A. M. ZANKO (Ber. Ukrain. wiss. Forsch. physikal. Chem., 1935, 4, 83—88).—The mixture is titrated potentiometrically with $AgNO_3$ in presence of $Ba(NO_3)_2$. S" is determined in presence of NH_3 , after which the solution is acidified with HNO_3 and the CNS' and Cl' equivalence points are obtained, in good agreement with the calc. vals. R. S.

Determination of oxides of nitrogen, excluding nitrous oxide.—See B., 1935, 766.

Sensitive test for phosphorus. Modification of Mitscherlich's procedure. R. GROS (J. Pharm. Chim., 1935, [viii], 22, 211–215).—Material containing white P is distilled with H_2O in the dark under a pressure of 15 mm. and the glow of P is observed. 0.002 mg. of P can be detected in 200 g. of sample. R. S.

Volumetric determination of phosphate. H. SIMMOH (Angew. Chem., 1935, 48, 566).—In the determination of $PO_4^{\prime\prime\prime}$ by the method of Sanfourche and Focet (A., 1934, 43) < 3.5 equivs. of AgNO₃ must be employed. Bromothymol-blue is the most suitable indicator. J. S. A.

Zinc pellets for generation of arsine in the Gutzeit method. P. A. MILLS (J. Assoc. Off. Agric. Chem., 1935, 18, 506).—Zn cast in a porcelain mould in the form of pellets 9×12.5 mm. gives a const. and uniform supply of H₂. E. C. S.

α-Naphthoflavone, a new indicator for bromatometry. E. SCHULEK (Z. anal. Chem., 1935, 102, 111—113).—The disadvantages of the usual indicators employed in the titration of As and Sb solutions with KBrO₃ solutions are discussed. The author's method is to add 10 c.c. of 50% H_2SO_4 to the As^{III} or Sb^{III} solution, dissolve 0·2 g. of KBr in the mixture, and add 2 drops of a 0·5% solution of naphthoflavone in 96% EtOH. The solution is titrated with 0·1N- or 0·01N-KBrO₃ solution until the greenish opalescence of the solution is replaced by a reddish-brown colour. With Sb^{III} it is advantageous to add 0·5 g. of tartaric acid to keep the Sb in solution. J. W. S.

Rapid photometric determination of silicon in light metals.—See B., 1935, 771.

Chemical analysis of volcanic rocks. A. M. DE JESUS (Rev. Chim. Pura Appl., 1932, [iii], 7, 115— 119).—In the determination of SiO₂, a second evaporation to dryness appears to be unnecessary as the amount so recovered is negligible; the rather larger ppt. so recovered in the case of basic rocks consists largely of TiO₂. In the Lawrence Smith method for the determination of alkalis, it is essential to heat to about 750°, as no decomp. occurs at about 375°. 4 M The Schlösing-Wende perchlorate method for the separation of K and Na is recommended. E. L.

Conditions of titration of silicofluorides, and their application to the determination of silica in silicates. A. BABKO (Ukrain. Chem. J., 1935, 10, 133-147).--0.1 g. of silicate is fused with 1 g. of KNaCO₃, the melt is boiled with H₂O and aq. HCl, the solution is diluted to 25 ml., approx. neutralised with NaOH (Me-orange), boiled, and 12-15 ml. of 5% aq. NaF are added. The solution is then made acid with HCl, 6-10 g. of CaCl₂ are introduced, and N-NaOH is added to an alkaline reaction (phenolphthalein). The solution is then made exactly neutral with HCl, diluted to 150 ml., and titrated at 90° with 0.1N-NaOH to a faint red coloration. The method involves a mean error of 1%, and requires 1 hr. R. T.

Helium. XI. Spectro-analytical detection of traces of hydrogen and neon in helium. P. L. GÜNTHER and F. A. PANETH (Z. physikal. Chem., 1935, 173, 401-411).—By a method similar to that previously described (A., 1928, 858) as little as 0.1% H₂ or 0.002% Ne can be detected in 10^{-7} c.c. of He. The air near the ground contains $< 2 \times 10^{-4}\%$ H₂. The determination of small amounts of He is described. R. C.

Microchemical colorimetric determination of sodium. A. ELIAS (Anal. Asoc. Quím. Argentina, 1935, 23, 1—3).—The triple acetate of U, Mg, and Na described by Kahane (A, 1933, 1024) dissolved in H_2O gives an orange-yellow solution which is used in the colorimetric determination of small amounts of Na. F. R. G.

Determination of sodium as sodium magnesium uranyl acetate. F. KöGLER (Angew. Chem., 1935, 18, 561—565).—The substance is dissolved in H₂O, and evaporated with HClO₄ to remove K. The filtrate and alcoholic washings are neutralised with NH₃ and evaporated to dryness. The residue is dissolved in 5 c.c. of H₂O, and Na is pptd. at 20° with Kahane's reagent (A., 1930, 726). Ba and Sr, but not Ca, interfere, and may be removed by pptn. with (NH₄)₂CO₃. SO₄" if present is removed as BaSO₄ before pptg. the K. PO₄"" if present may then be pptd. by making strongly alkaline with NH₃ (tropæolin O as indicator). In absence of SO₄", PO₄"" may be pptd. with CaCl₂. Na should be pptd. at the temp. at which Kahane's reagent is kept saturated. J. S. A.

Determination of cæsium as cæsium bismuth iodide. R. W. FELDMANN (Z. anal. Chem., 1935, 102, 102-108).—The method of Tananaev and Harmasch (A., 1932, 1010) does not give accurate results when Cs is pptd. from pure solutions of its salts or from solutions containing Cs and Rb. J. W. S.

Determination of small quantities of radium in minerals. J. A. BOTTEMA (Chem. Weekblad, 1935, 32, 482—486).—To determine the age of U minerals in which the proportion of U is too small for direct determination, the latter is deduced from the Ra content, which is measured by an ionisation chamber method. D. R. D.

Beryllium. I. I. IITAKA, Y. AOKI, and T. YAMANOBE (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 741-748).-Be may be determined with fair accuracy by pptg. Be(OH)₂ with aq. NH₂ and NH₄Cl, or KI and KIO₃, and igniting to BeO. The colorimetric titration method using quinalizarin indicator is also satisfactory, and is unaffected by the presence of Cu or Al. In presence of Mg the Be must be separated with aq. NH3 and NH4Cl, after which the Be(OH)₂ may be redissolved in HCl and titrated. J. W. S.

Volumetric determination of magnesium. W. DAUBNER (Angew. Chem., 1935, 48, 551) .--- To the solution of MgCl₂, free from metals other than the alkalis, is added a slightly acid solution of Na₂HAsO₄ together with NH4Cl. Aq. NH3 is added dropwise with stirring until cryst. MgNH₄AsO₄ is pptd. The solution is then kept for 4-5 hr. The As solution used must contain > 0.3% As₂O₅, and under these conditions the composition of the ppt. is const. The ppt. is collected, washed with EtOH, dissolved in HCl, reduced with SO_2 , and the As_2O_3 content determined volumetrically. Results appear to be accurate to $\pm 0.3\%$ on the Mg content. C. I.

Determination of small amounts of zinc in commercial nickel.—See B., 1935, 771.

New reagent for the gravimetric determination of certain metals. II. Macro- and microdetermination of cadmium. G. SPACU and M. KURAŠ (Z. anal. Chem., 1935, 102, 108-110; cf. this vol., 1094).-The solution containing Cd is treated with NH₃ until a clear solution is obtained and then a solution of thiolbenzthiazole (I) and NH₃ added. The Cd is pptd. as $Cd(C_7H_4NS_2)_2$, $2NH_3$, which at $110-120^\circ$ yields $Cd(C_7H_4NS_2)_2$. Cu and Cd can be determined in the action of the context of the solution of the context of the solution of the context of the co mined in the same solution by pptg. Cu only with (I) in neutral solution and then adding NH₃ in excess to ppt. Cd. J. W. S.

Iodometric determination of copper. Determination of copper in white metal. H. A. J. PIETERS (Chem. Weekblad, 1935, 32, 509-510).-Foote and Vance's method (this vol., 837) gave excellent results. D. R. D.

Use of 8-hydroxyquinoline in determinations of aluminium, beryllium, and magnesium. H. B. KNOWLES (J. Res. Nat. Bur. Stand., 1935, 15, 87-96).—The solution containing Al and Be is freed from Cu, Pb, Bi, etc. with H2S, from Mn, Mg, alkaline earths, and moderate amounts of Ni, Co, and Zn by pptn. with aq. NH₃, or from Fe, Ti, Zr, etc. by pptn. with excess of NaOH. To 200 c.c. of acid solution containing ≥ 0.1 g. Al and 10 c.c. of HCl are added 15 c.c. of NH_4OAc solution (30 g. NH_4OAc to 75 c.c. H_2O) and 8—10 drops of 0.04% solution of bromocresol-purple. Dil. aq. NH₂ is added until the solution turns purple, and an AcOH solution of 8-hydroxyquinoline (I) (15-25% excess) added slowly during stirring. The solution is heated to the b.p. for 1 min., cooled to 60°, filtered, and the ppt. washed with 100 c.c. of cool H₂O, dried, and weighed as Al(C₉H₆ON)₃ or determined volumetrically by dissolving in HCl, adding a slight excess of standard KBrO3 in KBr, and determining the excess by treatment with KI

and titration with $Na_2S_2O_3$. Be can be determined in the filtrate from the (I) pptn. by pptg. Be(OH)₂ from the cold solution with NaOH and subsequent ignition to BeO. In absence of Be, tartaric acid (5 times wt. of Al) can be added to the Al solution, followed by rapid addition of the (I). Both methods give slightly high results, the reasons for which are discussed. J. W. S.

Separation of iron and aluminium from alkaline-earth elements by means of ammonia. M. FERRICH (Bull. Soc. Chim. Yougoslav., 1935, 6, 27-50).-25 c.c. of solution, containing Fe^{III} and Al, are poured in a thin stream into 75 c.c. of a solution of 5 g. of NH4NO3, and 2-3 c.c. of aq. NH3 in 75 c.c. of H₂O at 85-90°, with const. stirring, and the ppt. is collected after 20 min., washed with 0.2% aq. NH₄NO₃, dried, ignited at 1200° for 20 min., and weighed. Should Mg, Ca, Sr, and Ba be present, freshly distilled aq. NH_3 , not containing traces of SiO_2 or CO_2 , should be used, and the ppt. should be washed with $\neq 400-500$ c.c. of solution. R. T.

Determination of chromium by the liquid amalgam method. P. G. Popov and M. A. NECHAMKINA (Ukrain. Chem. J., 1935, 10, 187–192). —The solution, containing Cr^{III} or Cr_2O_7'' , is reduced by Zn-Hg in 6N-H₂SO₄, and Cr^{II} is titrated with KMnO₄. R. T.

Infra-red photographs of chromium compounds. J. RZYMKOWSKI (Naturwiss., 1935, 23, 610).-The great majority of Cr compounds of all types reflect infra-red radiation in the range 720-880 mu. The use of this for the detection of Cr compounds A. J. M. on paintings is mentioned.

Determination of chromium in stainless steel. -See B., 1935, 807.

Electrolytic determination of titanium, zirconium, or aluminium in chromium steels and alloys.—See B., 1935, 807.

Analysis of very small amounts of monazite. F. HECHT and E. KROUPA (Z. anal. Chem., 1935, 102, 81-99).—The mineral is extracted with H_2SO_4 and then with HCl, the residue being weighed and subsequently treated with HF to determine SiO_2 . The solution is treated with $(NH_4)_2MoO_4$ to ppt. P, excess of Mo being removed as MoS_3 . Fe, Al, rare earths, Mn, U, Ca, and Mg are then determined by the usual methods. Pb is determined separately as PbSO4.

J. W. S.

Determination of small amounts of vanadium in uranium preparations. N. I. TSCHERVJAKOV and E. A. OSTROUMOV (Z. anal. Chem., 1935, 102, 181–186).—V and Fe^{•••} give with p-NMe₂·C₆H₄·NH₂ (I) in slightly acid solution a red to violet coloration stable in presence of excess of EtOH. For analysis, U preps. are converted into UO_2Cl_2 . To a solution of 0.2-0.5 g. in a colorimeter tube, HCl + 0.5 c.c. of H_3PO_4 are added, and then 4 vols. of EtOH. 3-4 c.c. of glycerol are added to bind the Fe as a glycerophosphate complex, and finally 1 c.c. of 0.5% aq. (I) hydrochloride. The colour is matched against that produced from V-free U_3O_8 in a solution of identical acidity, to which standard V_2O_5 solution is added. BVI JOOUT IS MUSICO . OPPENDE ON SE. TET J.S.A.

Determination of antimony in lead [by electrical resistance measurement].—See B., 1935, 808.

Determination of antimony in alloys by means of permanganate.—See B., 1935, 808.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXIX. Separation of tungsten from titanium, niobium, tantalum, and zirconium. A. R. Powell, W. R. SCHOELLER, and C. JAHN (Analyst, 1935, 60, 506-514; cf. A., 1934, 503).-W and Ti cannot be separated by fusion of the mixed oxides with $K_2S_2O_7$ and extraction with H₂O or dil. acid, nor by fusion with Na₂CO₃ and extraction with H₂O, but they may be quantitatively separated by extraction of the Na₂CO₃ melt with 10% aq. NaOH. The only procedure found to separate W from Ti and Nb, with or without Ta and Zr, consists in fusing the mixed oxides with K_2CO_3 , and treating the aq. extract of the melt with a slightly ammoniacal aq. Mg salt, whereby the earths are pptd. For accurate work the procedure should be repeated. ZrO_2 may be separated from WO₃ by fusion with Na₂CO₃ and extraction with H₂O. The applicability of the methods available for the separation of W from the individual or mixed earths is discussed. Ta and Nb may be approx. determined by titration of the alkali in the NaCI ppt. of the mixed earth acids. E. C. S.

Thermodynamic temperature scale below 1° abs. W. H. KEESOM (Physica, 1935, 2, 805—806).— A previous method (cf. A., 1934, 1061) of establishing the thermodynamic temp. scale is modified.

T. G. P.

Electric heater designed to prevent losses from creeping in the evaporation of concentrated salt solutions preliminary to mineral analysis. G. M. GUEST and E. LEVA (J. Biol. Chem., 1935, 110, 777—779).—The liquid to be evaporated is heated by an electrically heated coil well above the surface of the liquid and fitting closely around the brim of the vessel. J. N. A.

Hot plate. L. C. KREIDER (J. Chem. Educ., 1935, 12, 336-337).—A 100-watt lamp gives temp. from 30° to 70° in the arrangement described. L. S. T.

Thyraton control for incubators and waterbaths. J. W. MAVOR and E. W. THATCHER (Science, 1935, 82, 201-202). L. S. T.

Outfit for photomicrography. H. WRIGHTON (J. Roy. Microscop. Soc., 1935, [iii], 55, 79—82).— Crit. vertical illumination for metal specimens is provided. C. W. G.

Technique for X-ray studies of substances under high pressures. L. K. FREVEL (Rev. Sci. Instr., 1935, [ii], 6, 214-215).—The substance is sealed up in a cooled tube containing PhMe and the pressure is raised by warming the tube. C. W. G.

Preparation of photon counters for visible light. A. KOLIN (Rev. Sci. Instr., 1935, [ii], 6, 230-231).—A small piece of alkali metal attached to an Fe or Ni rider is heated on the anode wire of a Geiger-Müller counter to obtain a deposit of metal on the cathode. The rider and unused metal can be removed by means of a magnet. C. W. G. Arrangement for microscopical work at low temperatures. S. ERK (Z. Elektrochem., 1935, 41, 521).—Condensation of H_2O on the objective etc. is prevented by a stream of evaporated liquid air. Observations may be made down to -120° .

T. G. P. Colour measurement with the leukometer.— See B., 1935, 785.

Thin cell for use in determining the refractive indices of crystal grains. C. P. SAYLOR (J. Res. Nat. Bur. Stand., 1935, 15, 97–98). J. W. S.

Counting-field finder [for microscope]. T. E. WALLIS (Analyst, 1935, 60, 520-521). E. C. S.

Vacuum monochromator and spectrograph with quartz and fluorite optical systems for the regions $0.700-0.160 \mu$ (quartz) and $0.700-0.130 \mu$ (fluorite). C. LEISS (Z. Physik, 1935, 95, 778-780). A. B. D. C.

Investigations in the ultra-soft X-ray region. I. Spectrograph for relative measurements. E. A. W. Müller (Z. Physik, 1935, 95, 763-768). A. B. D. C.

Measurement of quantity of light by the photoelectric cell. D. V. GOGATE and D. S. KOTHARI (Indian J. Physics, 1935, 9, 487–489).—Relations are deduced for calculating quantity of light from the use of the cell and galvanometer and are verified experimentally. N. M. B.

Measurement of radium emanation implants. P. A. MACDONALD and E. M. CAMPBELL (Rev. Sci. Instr., 1935, [ii], 6, 212—214).—The change of current in an ionisation chamber produced by movement of the emanation container is amplified as though it were a half wave of a.c. Rn implants can be measured to 2%. C. W. G.

Ionising particle counters. J. R. DUNNING and S. M. SKINNER (Rev. Sci. Instr., 1935, [ii], 6, 243— 246).—Improvements in point and tube counters are described. C. W. G.

Amplification of photo-currents through emission of secondary electrons. F. M. PENNING and A. A. KRUITHOF (Physica, 1935, 2, 793-804).—The current from the cathode of a vac. or gas-filled photocell may be considerably amplified by secondary emission from a third electrode of the same material as the cathode. Evacuated secondary emission cells show a practically const. dynamic response to light variations up to ≤ 20 kilocycles. T. G. P.

Determination of the dielectric constants of solids by the method of mixtures. E. KLEINKE (Physikal. Z., 1935, 36, 565—566).—The application of Stark's method to substances with high dielectric consts., and to insulators containing conducting inclusions, is described. A. J. M.

Significance and principles of electrostatic e.m.f. measurements with the help of electron tubes. F. MULLER and W. DURICHEN (Z. Elektrochem., 1935, 41, 559-563; cf. this vol., 1097).— The utility of the method and recent developments in apparatus and technique are discussed.

T. G. P.

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Mechanism of action of solid electron rectifiers. V. P. JOUSÉ (Physikal. Z. Sovietunion, 1935, 7, 1– 18).—A new Cu₂O rectifier has been prepared, with an artificial "blocking layer" consisting of a wedge of SiO₂, B₂O₃, NaCl, S, glass, or bakelite, $10^{-6}-5\times10^{-4}$ cm. thick, attached to the Cu₂O plate and confined between Au electrodes. Current-p.d. curves have been measured at -100° to 50°. The rectifying coeff. is a max. with a blocking layer thickness of $2\times10^{-6}-10^{-5}$ cm., and may reach 100 at 1 volt. R. S. B.

Hydrogen electrode for $p_{\rm ff}$ determinations. H. C. LOCKWOOD (J.S.C.I., 1935, 54, 295-296T). -The electrode consists essentially of a U-shaped vessel down one limb of which slides a glass tubo carrying a sealed-in Pt wire. The end of the wire is arranged directly above a jet through which the H₂ bubbles. Each bubble impinges on the end of the Pt wire and, being pierced, travels up the whole length. The liquid is made to circulate by means of a suitable inlet and outlet in the U-tube. The electrode is very economical with H₂ and 40 ml. per min. is ample. Before using the electrode, the Pt wire is cleaned on fine emery cloth and recoated with a min. deposit of Pt-black. The electrode takes 0.5-5 min. to reach equilibrium. Two modified types have been designed whereby the containing vessels are incorporated and they work on 1 mm. or 5 mm., respectively.

Technique of glass electrode. H. A. BROMLEY (Analyst, 1935, 60, 533—536).—A modification of Harrison's circuit is described. E. C. S.

Degree of accuracy of the glass electrode in alkaline solutions. I. D. BURTON and J. BATE-SON (J. Soc. Leather Trades Chem., 1935, 19, 306— 313).—The results obtained by the glass electrode are < those given by the H electrode at $p_{\rm H} > 11.35$; for other vals. the agreement is good. D. W.

Antimony electrode. D. N. MEHTA and S. K. K. JATKAR (J. Indian Inst. Sci., 1935, **18A**, 85–100).— Best results were obtained with freshly polished cast electrodes. $E = -0.0293 + 0.0591 p_{\rm H}$ at 25°.

C. W. G.

Antimony[-air] electrode for $p_{\rm H}$ measurements. Mechanism of potential formation and the practical application of the electrode. P. WULFF, W. KORDATZKI, and W. EHRENBERG (Z. Elektrochem., 1935, 41, 542—551).—Measurements have been made which indicate that the $p_{\rm H}$ -dependent potential of the Sb electrode in presence of air is not determined by the Sb^{***} activity of the solution, but by the irreversible oxidation process and by the diffusion velocity of the reaction products on the electrode surface. For practical use the Sb electrode must be in contact with a well-stirred solution saturated with air, the deposit on its surface must be continuously removed, and it must be calibrated under the experimental conditions. A suitable arrangement is described. T. G. P.

Micro-quinhydrone electrode : its application to the determination of the $p_{\rm H}$ of glomerular urine of Necturus. J. A. PIERCE and H. MONTGOMERY (J. Biol. Chem., 1935, 110, 763-775).—The prep. of a micro-quinhydrone electrode which can be used for the trustworthy determination of the $p_{\rm H}$ of 10^{-4} c.c. of liquid is described. It can be inserted through or into tissues without contamination, and its accuracy is the same as that of the ordinary quinhydrone electrode. The $p_{\rm H}$ of glomerular urine from *Necturus* ranged from 7.07 to 7.63. The difference between these vals. and those obtained colorimetrically is a physiological one. J. N. A.

Micro-quinhydrone-silver chloride cell for precision e.m.f. studies on heavy water. V. K. La MER and M. H. ARMBRUSTER (J. Amer. Chem. Soc., 1935, 57, 1510-1511). E. S. H.

Pipette for storage of air-free reagents used in gasometric analysis. G. M. GUEST and F. E. HOLMES (J. Biol. Chem., 1935, **110**, 781-783).— A pipette having a capacity of approx. 25 c.c. is described. The reagent is not in contact with the stop-cock, and the pipette is considerably less fragile than the Hempel pipette. J. N. A.

Microburette with interchangeable jets. J. KHOURI (Bull. Soc. Chim. biol., 1935, 17, 1077). A. L.

Micropyknometer method for density determinations. G. R. CLEMO and A. MCQUILLEN (J.C.S., 1935, 1220).—The micropyknometer holds approx. 2 mg. and is made by drawing out each end of a short piece of capillary tube. $d^{17\cdot2}$ are: C_6H_6 0.879 and C_6D_6 0.954. J. G. A. G.

Casting molybdenum buttons in brass, for water-cooled targets in X-ray tubes. F. H. TRIMBLE (Rev. Sci. Instr., 1935, [ii], 6, 216).— Small pieces of brass placed on top of a Mo disc are heated in a small arc furnace. Good contact between the Mo and the brass is obtained without the use of a flux. C. W. G.

Mercury cistern. R. M. BOWIE (Rev. Sci. Instr., 1935, [ii], 6, 242).—The Hg of a McLeod gauge is released from a cistern through a ground valve operated by a hand lever, permitting large or small rates of flow. C. W. G.

Introducing oxygen into evacuated systems. J. B. TAYLOR (Rev. Sci. Instr., 1935, [ii], 6, 243).— O_2 diffuses through hot Ag. C. W. G.

Mechanical properties of stretched and unstretched sulphur threads and their changes with time. K. SAKURADA and H. ERBRING (Kolloid-Z., 1935, 72, 129—135).—Apparatus and technique for obtaining amorphous S threads of definite cross-section and length are described. The breaking strength of the threads depends on the temp. from which the S is cooled; it reaches a max. at 300°. The breaking strength also varies with ageing, passing through a max. after a few days; the position of this max. also depends on the temp. The elongation increases with rising temp. of prep. The breaking strength of permanently deformed S threads (extension 800— 900%) is very high (11 kg. per sq. mm.). E. S. H.

Middle piece of the Soxhlet extractor and the simple extraction tube. A problem of standardisation. The cold extractor. F. W. NEU-MANN (Chem. Fabr., 1935, 8, 326-327).—The Soxhlet
extractor is critically compared with simpler types. An apparatus in which the solvent vapour is condensed and allowed to pass through the material at any desired temp. below the b.p. is described. R. S.

Determination of absorption coefficients of sound for different materials. L. P. VARMA (Proc. Acad. Sci. Agra and Oudh, 1935, 4, 301-315).—A very sensitive method is described. C. W. G.

Device for aërating and circulating aquarium water. P. L. VARNEY (Science, 1935, 82, 136). L. S. T.

Glass manometer for laboratory use. T. E. PHIPPS, M. L. SPEALMAN, and T. G. COOKE (J. Chem. Educ., 1935, **12**, 321–323). L. S. T.

Measurement of the elastic constant of isotropic transparent solids. E. HIEDEMANN (Nature, 1935, 136, 337).—The elastic consts. of glass have been calc. from measurements of the velocity of ultrasonic compression waves. L. S. T.

Applications of pervaporation. L. FARBER (Science, 1935, 82, 158).—The apparatus described can be used for the concn. of aq. glycerol solutions of enzymes, of dil. protein solutions with simultaneous removal of salts, and the rapid evaporation of large vols. of H_2O at room temp. L. S. T. Sucking gases out of fume cupboards. W. F. Box (Chem. Weekblad, 1935, 32, 510).—A vac. pump is used to remove gases, in place of the usual flame or fan. D. R. D.

Highly polymerised compounds. CXIV. Comparison of the osmometrically and viscosimetrically determined mol. wts. of mixtures of polymeric homologues. W. KERN (Ber., 1935, 68, [B], 1439—1443).—It is shown mathematically that the mean mol. wt. of a given mixture of polymeric homologues is greater when determined by viscosimetric than by osmotic methods. With very carefully fractionated mixtures the two methods give not very dissimilar results. H. W.

Nomogram for the Hagenbach correction for the suspended level viscosimeter. L. UBBELOHDE (Oel u. Kohle, 1935, 11, 578-579). E. S. H.

Construction of a cartesian nomogram for the law of mass action. F. C. McLEAN (Science, 1935, 82, 104-105). L. S. T.

Ancient Chinese treatise on alchemy. J. R. PARTINGTON (Nature, 1935, 136, 287-288).

L. S. T.

Geochemistry.

Presence of inert gases in certain mineral spring gases in Japan. I. SUGANUMA and K. KITAOKA (Bull. Chem. Soc. Japan, 1935, 10, 289–296). —Gases escaping from certain springs in Japan, some radioactive and some inactive, have been examined spectroscopically. In all cases Ne, and sometimes A, were found in addition to He. This appears to disprove the view that the He is exclusively radioactive in origin; it is more likely that the inert gases arise from the primordial air originally entrapped in the earth, the O_2 and N_2 having been long ago lost by chemical action. S. J. G.

Isotope composition of rain and snow water. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 263–266).—Samples of rain collected at the beginning of a rainfall were somewhat denser (about 2 p.p.m.) and those at the end lighter (about 2 p.p.m.) than standard town H_2O . Samples of snow collected in 1934 and 1935 were all lighter (0.5–3.3 p.p.m.) than standard. Ice collected in a gully 2257 m. above sea level was also lighter (2.2 p.p.m.), whereas according to Emeléus *et al.* (A., 1934, 1062) the fractional crystallisation should make it heavier. An explanation is offered. S. J. G.

Analysis of water of the Velika thermal spring. 8. MIHOLIĆ (Bull. Soc. Chim. Yougoslav., 1935, 6, 51-60).—Analytical data are recorded. R. T.

The $p_{\rm H}$ of the mineral springs of Bagneres-de-Bigorre. F. L. YDRAC (Bull. Soc. Ramond, 1933— 1934, 68—69, 39—41).—Vals. of the $p_{\rm H}$ of 20 springs lie between 6.9 and 7.7, and the $p_{\rm H}$ of Labassere is 10. J. G. A. G. Chemical and chemico-physical analysis of the mineral water of the Valleverde Spring (Abruzzo). D. MAROTTA and E. SORRENTINO (Annali Chim. Appl., 1935, 25, 324—350).—This H_2O gives 0.27 g. of fixed residue (at 110°) per litre, and contains chiefly Ca(HCO₃)₂; SiO₂ is relatively high and traces of Ag are present. T. H. P.

Plankton production and the nitrate nitrogen and phosphate cycles in the Pacific Ocean off New South Wales. W. J. DAKIN and A. N. COLEFAX (Nature, 1935, 136, 339).—NO₃' and PO₄''' are reduced to a trace or even zero in the surface waters on certain occasions which always follow a spring max. in diatom production. In summer $[NO_3']$ is low, but the $[PO_4''']$ is quickly regenerated; in winter, $[PO_4''']$ for surface waters ranges from 20 to 30 mg. of P_2O_5 per cu. m. and $[NO_3']$ from 20 to 35 mg. per cu. m. L. S. T.

Phosphate in the western basin of the North Atlantic. H. R. SEIWELL (Nature, 1935, 136, 206– 208).—The vertical distribution, its variation and mechanism are described. There is probably a significant eddy transfer from the $PO_4^{\prime\prime\prime}$ -rich midstrata to impoverished surface layers. The bearing of this factor on biological fertility is discussed.

L. S. T.

Origin of petroleum water. N. TAGEEVA (Petroleum, 1935, 31, No. 32, 15-23).—There is a marked similarity between the analyses of oil-field waters from different fields. All are saline and contain only small amounts of sulphate and carbonate. The ratio Na : Cl is approx. const., averaging 0.79. Further similarity is shown on the Na : Cl basis with a number of sea-waters of different origin, and it is suggested that the typical oil-field waters may originate from sea-waters. This hypothesis is supported by other geochemical properties of oil-field waters. The fact that the Mg : Ca ratio for the latter (< 1) differs from that of sea-water, whilst Ca+Mg closely corresponds with the Mg combined with Cl in sea-water, can be explained by geochemical changes. A brief discussion is given of the geological features with which petroleum is usually associated and their bearing on the composition of oil-field waters. The geochemical significance of such constituents as Li, Sr, Ba, B, and Br in oil-field waters has yet to be elucidated. C. C.

Correlation of pre-Cambrian granites by means of heavy mineral analysis. J. T. STARK and F. F. BARNES (Geol. Mag., 1935, 72, 341—350).— Heavy mineral analyses for various localities of the Pikes Peak and Silver Plume granites of pre-Cambrian age in the Sawatch Range, Colorado, are recorded and discussed. Although the % of constituents vary widely in different specimens of a given batholith, there is a general tendency towards uniformity in the relative abundance of certain minerals, especially zircon and titanite, and a sufficiently large no. of analyses might lead to a successful correlation.

L. S. T.

Spessartite in the Cambrian manganese ore of Merionethshire. A. W. WOODLAND (Geol. Mag., 1935, 72, 384).—The silicate constituent of the ore is mainly, if not entirely, in the form of minute crystals of garnet conforming in colour and composition to pure spessartite. L. S. T.

Exogenous contact-zone at Ben Bullen, New South Wales. (MISS) G. A. JOPLIN (Geol. Mag., 1935, 72, 385-400).—The exogenous contact consists of a series of cordierite-hornfelses and of magnesian and non-magnesian marbles (petrography described). The marbles show an apparent increase in SiO₂ content, and the development of certain index minerals, viz., brucite (I), forsterite, and diopside, but this is actually due to a decreasing MgO content. Thermal metamorphism among the limestones has given rise to dolomite coronas about (I) and dactylitic intergrowths between calcite and dolomite. In the contact of the magnesian marbles the metasomatising solutions are usually Fe- and SiO₂-bearing and there is some migration of solutions derived from the marbles themselves. In the zone of the non-magnesian marbles, Fe-, SiO₂-, and Al₂O₃bearing solutions play a prominent part. L.S.T.

Mechanical composition of the London Tertiaries in the neighbourhood of Harrow-on-the-Hill. W. H. BARRETT (Geol. Mag., 1935, 72, 337— 341).—Mechanical analyses for sand, silt, and clay of three exposures are recorded. L. S. T.

Alkaline quartz-dolerites, from Bijawar, and their chemical relationships. M. P. BAJPAI (Current Sci., 1935, 4, 39—41).—The chemical composition of several quartz-dolerites from Bijawar was compared with that of Deccan basalt and spilite; approx. agreement in the amounts of all constituents, except Na₂O, was found. A further comparison was made with Gwalior and Singhbhum dolerites.

W. R. A. **Pre-Cambrian granites in the Canadian Shield.** R. T. CHAMBERLIN (Science, 1935, 82, 126-127).— A reply to criticism. The view that there are < 3granites of widely different age in the Canadian Shield is maintained. L. S. T.

Comparative study of the weathering of rocks under different climatic conditions. E. BLANCK and R. THEMLITZ (Chem. Erde, 1935, 9, 529—539; cf. A., 1928, 612).—Further analyses of samples of limestone and sandstone which had been exposed to the weather for 12 years at Göttingen and on the summit of the Brocken are recorded. L. J. S.

Microscopical study of copper ore from Nieder-Marsberg, Westphalia. F. SCHWAKE (Chem. Erde, 1935, 9, 486—528).—The several minerals (pyritc, marcasite, chalcosine, bornite, chalcopyrite, covelline, native Cu, etc.) are described and their origin is discussed. L. J. S.

Chemical structure of clay minerals and of corresponding silicates of tervalent and bivalent metals. J. HOLZNER (Chem. Erde, 1935, 9, 464-485).—A recalculation of old analyses to fit them in with theories of structure types as determined by X-rays. L. J. S.

Chemical and optical interrelations of the brittle mica group. G. KOCH (Chem. Erde, 1935, 9, 453-463).—Ten new analyses with optical data are given of margarite, clintonite, and chloritoid. These are tabulated and plotted with other data from the lit. to show the variation of the optical properties with the chemical composition. In margarite $(H_2CaAl_4Si_2O_{12})$ with replacement of Ca by Na₂ there is a linear decrease in *n* and optic axial angle and an increase in the birefringence. Clintonite (including xanthophyllite and brandisite) has the formula $H_2CaMg_3Al_2Si_2O_{12}$, equiv. to that of margarite with Mg replacing some Al. L. J. S.

Chemical weathering and soil formation in Siam. E. BLANCK, W. CREDNER, and E. VON OLDERSHAUSEN (Chem. Erde, 1935, 9, 419-452).-Analyses of rocks and soils are given from different districts, ranging from the moist tropical Malay peninsula to the northern uplands. The main types are the grey soils of the flood plains, and the yellow, brown, and red soils of the uplands. L. J. S.

Anemousite in essexite. F. F. OSBORNE (Canad. J. Res., 1935, 12, 668—675).—Anemousite (undersaturated felspar) has been found in some Monteregian essexites. J. W. S.

"Mercallite," a new mineral among the products of the fumarolic activity of Vesuvius during 1933. G. CAROBBI (Atti R. Accad. Lincei, 1935, [vi], 21, 385–393).—Mercallite consists of KHSO₄ identical in cryst. form and d with KHSO₄ crystallised from aq. solutions containing about 4% Na and 4% SO₄". D. R. D. Trieuite, a new cobalt mineral. L. DE LEEN-HEER (Natuurwetensch. Tijds., 1935, 17, 91–95).— The name trieuite is proposed for the mineral described by Schoep (A., 1921, ii, 649). Its composition is $2\text{Co}_2\text{O}_3$, CuO,6H₂O. D. R. D.

Chemical and physico-chemical properties of Dniepropetrovsk glauconites. A. J. MIKEI (Ukrain. Chem. J., 1935, 10, 262—265).—The dehydrated glauconite has pronounced permutitic activity. Analytical data are recorded. R. T.

Organic Chemistry.

Free *n*-propyl radical. T. G. PEARSON and R. H. PURCELL (Nature, 1935, 136, 221).—COPr^{α}₂ is decomposed in the light from a quartz-Hg vapour arc with the formation of free Pr^{α}. L. S. T.

Pyrolysis of propane in presence of water vapour. J. W. LANG and J. J. MORGAN (Ind. Eng. Chem., 1935, 27, 937-941).—The products of the pyrolysis of C_3H_8 at 600-700° and low partial pressures in presence of steam (which is practically inert under the prevailing conditions) have been analysed. Changes in pressure affect the products (e.g., the proportion of C_3H_6 to C_2H_4 in the unsaturated hydrocarbons is increased at higher pressures). A bimol. reaction must occur to some extent. Temp. has no effect on the proportion of primary products obtained from C_3H_8 over the temp. range normally used in this connexion; they may be accounted for by the reactions: $C_3H_8 \rightarrow C_3H_6+H_2$, $C_3H_8 \rightarrow$ $C_2H_4+CH_4$, $2C_3H_8 \rightarrow C_3H_6+C_2H_6+CH_4$. It is considered that the mechanism of hydrocarbon pyrolysis is best explained by Nef's dissociation hypothesis which postulates "active" and "inert" mols. C. C.

Reactions catalysed by aluminium chloride. XI. Branching of the carbon chain during the treatment of saturated hydrocarbons with acetyl chloride in presence of aluminium chloride. C. D. NENITZESCU and I. CHICOS (Ber., 1935, 68, [B], 1584—1587).—The action of AcCl on $n-C_5H_{12}$ in presence of AlCl₃ at 15—16° leads to $\gamma\delta$ -dimethylpentan- β -one with smaller amounts of $\gamma\delta$ -dimethyl- Δ^{γ} -penten- β -one according to the scheme: $n-C_5H_{12}$ = $Pr^{F}Et \rightarrow CMe_2$ CH-CH₂ $\rightarrow CMe_2$ Cl-CHMeAc \rightarrow

CMe₂:CMeAc or CHMePr^aAc. Similarly n-C₆H₁₄ yields δ -methyl- γ -ethylpentan- β -one and δ -methyl- γ -ethyl- Δ^{γ} -penten- β -one. The rate of reaction of paraffins of medium mol. wt. with AcCl is of the same order of magnitude as that of cyclopentane and cyclohexane; the separation of these classes in petroleum in this manner is impossible. H. W.

Nitrous oxide as an oxidising agent in the gaseous state.—See this vol., 1213.

Autoxidation of *n*-hexadecane.—See this vol., 1208.

Thermal reactions of gaseous hydrocarbons. —See this vol., 1206.

Application of Raman spectrography to the study of the ethylenic linking. L. PIAUX (Ann. Chim., 1935, [xi], 4, 147-223).—A summary and discussion of results reported previously (cf. A., 1933, 553; 1934, 583, 943). J. W. S.

Synthetic rubber "sovprene" [chloroprene]. A. L. KLEBANSKI, L. G. ZURICH, I. M. DOLGOPOLSKI, et al. (Bull. Acad. Sci. U.R.S.S., 1935, 189-226).--

Low-temp. continuous polymerisation of C_2H_2 in a slightly acid aq. solution of CuCl,NH₄Cl gives CH:C·CH:CH₂ (I) in 75-80% yield (on the C_2H_2) and 25-30% of trimerides and higher polymerides of C_2H_2 . About 40% of the C_2H_2 is converted in a single passage of the gas. The continuous prep. of chloroprene from (I) and from mixtures of (I) and C_2H_2 is described, and the conditions for converting the chloroprene into its α -polymerides, with a min. formation of balata-like polymerides which harden, are defined. Ozonisation of α -and ω -polymerides of chloroprene yields (·CH₂·CO₂H)₂ in almost quant. amount; HNO₃ gives (·CH₂·CO₂H)₂ and H₂C₂O₄. A new trimeride of C₂H₂, acetylenyldivinyl, CH₂:CH·CH:CH·C:CH, b.p. 30-32°/100 mm., gives CH₄ when treated with MgMeI, forms a Cu derivative, C₆H₅Cu, and combines with HCl to form the compound,

CH₂:CH·CH:CH·CCI:CH₂, b.p. 40—41°/25 mm., which polymerises rapidly in air. A *tetrameride* of C_2H_2 , b.p. 44°/20 mm., 51°/30 mm., was obtained. Polymerisation of the trimeride and higher polymerides of C_2H_2 yields, under some conditions, products useful in the prep. of artificial lacquers and varnishes.

The action of EtOH-KOH on βδ-dichloro-Δ^βbutene yields β-chloro-δ-ethoxy-Δ^β-butene, b.p. 143°, 62—64°/40 mm.; the corresponding alcohol, b.p. 92°/ 50 mm., forms a xanthate. Di-γ-chloro-Δ^β-butenyl ether has b.p. 142°/50 mm. The action of NaOCI on (I) gives α-chloro-β-vinylacetylene, which combines with HCl in presence of CuCl,NH₄Cl to give αβ-dichloro-Δ^{αγ}-butadiene, b.p. 60—65°/40 mm. In presence of KOH at 150°, (I) combines with MeOH to give β-methoxy-Δ^{αγ}-butadiene, b.p. 33°/27 mm., 97°/760 mm.; in absence of KOH, styrene is formed in large proportion. With KOH and EtOH at 150°, (I) gives β-ethoxy-Δ^{αγ}-butadiene, b.p. 113·4°, which yields H₂C₂O₄ and HCO₂H on oxidation with KMnO₄ or O₃, and Et sec.-Bu ether on hydrogenation.

In presence of HgSO₄ or of HgO+BF₃, (I) condenses with: (1) HCO₂H to give formoprene (II), CH₂:CH·C(O·CHO):CH₂, b.p. 42°/40 mm., which, like chloroprene, spontaneously polymerises in the air in 10 days, giving a rubber-like, plastic polymeride; with maleic anhydride, (II) condenses to give cyclohexan-1-one-3: 4-dicarboxylic acid (III), m.p. 161-162° [semicarbazone, m.p. 199° (decomp.)], (2) AcOH to give β -acetoxy- $\Delta^{\alpha\gamma}$ -butadiene, b.p. 50-52°/ 25 mm.; this condenses with maleic anhydride to form the unstable compound, CO_{2} H·CH·CH·CH. CH which undergoes isomerisation to (III) Hydro

which undergoes isomerisation to (III). Hydrogenation of (I) in presence of colloidal Pd on starch in EtOAc, or Ni, yields butadiene. T. H. P.

Application of Raman spectrography to the study of the acetylenic linking. (MLLE.) B. GREDY (Ann. Chim., 1935, [xi], 4, 5-82).—A detailed account of work already reviewed (cf. A., 1933, 553, 886; 1934, 239, 943; this vol., 73).

Active hydrogen in chloroform and the coordination formulæ proposed by Urbain and Tchakirian. E. V. ZAPPI and H. DEGIORGI (Anal. Asoc. Quím. Argentina, 1935, 23, 14-21).--0.001 mol. of CHCl₃ in C_5H_5N with MgMeI in diamyl ether gives 24.4 c.c. of gas indicating 105% of active H. Similarly CHBr₃ and CHI₃ contain 50% and 3%, respectively, of active H. These results support the formula [CX₃]H proposed by Tchakirian *et al.* (A., 1932, 901). F. R. G.

Refraction equivalents of the triple carbon linking. K. VON AUWERS (Ber., 1935, 68, [B], 1635—1638).—Examination of recorded data for 12 Δ^{α} -alkines gives the val. 2·325 for $|_{\overline{D}}$ in CR:CH and 2·573 in CR:CR. In acetylenic alcohols the corresponding vals. are 2·308 and 2·673. In conjugation a greater difference is observed between the Δ^{α} and Δ^{β} linkings. For H_a, H_{\beta}-H_a, and H_y-H_a the respective vals., 2·329, 0·124, 0·149, and 2·543, 0·143, 0·186 are calc. for the series CR:CH and CR:CR. H. W.

Structure of partly substituted sorbitols. F. MICHEEL and K. HASSE (Ber., 1935, 68, [B], 1582– 1584).—Treatment of the benzylidenesorbitol (I) of von Vargha (this vol., 325) with CPh₃Cl in C₅H₅N affords a compound C₅₁H₄₆O₆, m.p. 100–103°, $[\alpha]_{\rm B}^{\rm D}$ +20° in CHCl₃, which is very little affected by Pb(OAc)₄ in AcOH or C₆H₆ and hence is $\alpha\zeta$ -ditriphenylmethyl- $\beta\delta$ -benzylidenesorbitol. The diacetate has m.p. 106–108°. (I) is therefore $\beta\delta$ -benzylidenesorbitol (cf. von Vargha, this vol., 325).

H. W.

Alkyl peroxides. XI. Peroxides of formaldehyde. Hydroxymethyl hydrogen peroxide. A. RIEOHE and R. MEISTER (Ber., 1935, 68, [B], 1465-1473).-Et₂O solutions of CH₂O obtained by extraction of aq. CH₂O are shown by their absorption spectrum to contain the solute as hydrate, thus explaining their inability to react with H₂O₂. Me H peroxide is obtained as a relatively stable liquid by the action of H_2O_2 on the solution obtained by passing gaseous CH2O into well-cooled Et2O. (In this solution CH₂O rapidly polymerises to polyoxy-methylenes, whereas the "extracted" solution is stable.) The product affords 94% of active O. The possibility that it is a mixture of (OH·CH₂)₂O₂ and H2O2 is discounted by its unusual sensitiveness to heat and by its conversion by P_2O_5 into polymeric methylene peroxide, whereas $(OH \cdot CH_2)_2O_2$ gives tetrahydroxymethylene diperoxide. In contact with alkali $OH \cdot CH_2 \cdot O_2 H$ affords $HCO_2 H$ (97%) with H_2 and O_2 (2:1), reaction occurring to the extent of 73% and 27%, respectively, according to the schemes: 20H·CH₂· O_2 H \rightarrow 2HCO₂H+H₂+0·5O₂ and $OH \cdot CH_2 \cdot O_2 H \rightarrow HCO_2 H + H_2 O$. The liberated H is mol., since it does not decolorise methylene-blue. OH·CH₂·O₂H and FeSO₄ immediately yield 50% of HCO_2H and 50% of CH_2O . The change is OH·CH₂·O₂H → CH₂O+H₂O₂, OH·CH₂·O₂H+CH₂O → (OH·CH₂·O·)₂ → HCO₂H+CH₂O+H₂O; the H₂O₂ formed is partly used in the oxidation of Fe" to Fe^{•••} and partly catalytically decomposed under the influence of Fe^{••}. OH•CH₂·O₂H does not cause benzidine to become blue, but the addition of CH₂O gives an active solution when freshly made. MeO₂H behaves similarly, but reaction does not occur with Alk₂O₂. Apparently a labile additive product of peroxide and aldehyde is a particularly active H acceptor. H. W.

Sodium tri-iodomethanesulphonate. A. BINZ and B. HUGHES (Ber., 1935, 68, [B], 1513-1520).-Treatment of CHI₂·SO₃Na with pptd. HgO in boiling H₂O affords Na di-iodohydroxymercurimethanesulphonate (I), OH·Hg·CI₂·SO₃Na, converted by I in warm $MeOH-H_2O$ into $CI_3 \cdot SO_3Na, 2H_2O$ (II), also obtained without isolation of (I). Solutions of (II) in H_2O or EtOH free from air are neutral and stable for a protracted period in absence of light. In aq. solution under the influence of light (II) is hydrolysed to acid (mainly HI and H_2SO_4 or NaHSO₄). O_2 in presence or absence of light causes oxidation of (II) with liberation of I and acid, particularly rapidly and quantitatively in EtOH. Photohydrolysis occurs mainly according to $(II)+3H_2O=3HI+NaHSO_4+HCO_2H$ and to a smaller extent according to $(II)+3H_2O=$ $3HI + NaHSO_3 + H_2CO_3$. (II) is very slowly oxidised by the O of the blood. H. W.

Hypohalogenites of carboxylic acids. W. BOCKEMÜLLER and F. W. HOFFMANN (Annalen, 1935, 519, 165-192).-The equilibrium reaction R·CO₂H+ $Hal_2 \implies R \cdot CO_2 Hal + HHal$ can most readily be caused to pass to completion by use of the requisite Ag salt in an indifferent medium such as CCl₄ in which R·CO₂Ag and AgHal are insol. In PhNO₂ reaction proceeds more slowly, whereas the more rapid change in $CHCl_3$ or CH_2Cl_2 is accompanied by halogenation of the solvent. The oxidising power of the acyl hypohalogenites is equal to that of the halogen used in the prep. and the halogen content is half as great; generally by reason of their instability the oxidising action falls somewhat short of that expected. Decomp. of acyl hypohalogenites occurs mainly according to $R \cdot CO_2Hal \rightarrow R \cdot Hal + CO_2$ and frequently affords a useful method of degrading acids. Reaction is not homogeneous and is certainly not unimol. Its rate increases rapidly with rise in temp. and exposure to light. The halogenating action of acyl hypobromites $RH+R'\cdot CO_2Hal \rightarrow R\cdot Hal+R'\cdot CO_2H$ is mainly evident with solvents containing replaceable H, but autohalogenation may occur. Treatment of acyl hypohalogenites with a moderate amount of H_2O hydrolysis $R \cdot CO_2Hal + H_2O \rightarrow R \cdot CO_2H +$ causes HOHal leading ultimately to a solution of halogen and HHalO₃, but if very little H₂O is used an unstable, unexplained olive-green colour is developed. Acyl hypohalogenites add to the C.C linking, R.CO.Hal+ $>C:C < \rightarrow >C(O \cdot COR) \cdot CHal <$. The rates of decomp. of AcOCl in AcOH in the dark at 23°, of AcOBr in AcOH and CCl₄, of Pr^aCO₂Br in CCl₄, and of BzOBr in CCl₄ have been measured. Details are recorded of the degradation of AcOH, PraCO2H, stearic and adipic acids, and BzOH. By-Dichloropropyl acetate, b.p. 83–84°, a by-product of the addition of AcO_2Cl to allyl chloride, 2-bromocyclohexenyl butyrate, b.p. 145°/14 mm., from Pr^aCO₂Br

and cyclohexene, and 2-bromocyclohexenyl benzoate, m.p. 66°, from BzOBr and cyclohexene, appear new. H. W.

Mechanism of the thermal decomposition of diacyl peroxides. J. BÖESEKEN and P. H. HERMANS (Annalen, 1935, 519, 133—139).—The initial step in the thermal decomp. of diacyl peroxides in the presence of solvent is expressed COR·O₂·COR+R'H \rightarrow COR·O₂·COR' (I)+RH and \rightarrow COR·O₂·COH (II)+ RR'. (II) immediately yields CO₂ and R·CO₂II. (I) may then undergo further group exchange with R'H or may suffer thermal decomp., according to one or more of the schemes : (I) \rightarrow RR'+2CO₂; (I) \rightarrow R·CO₂R'+CO₂ (particularly in the case of mixed aliphatic-aromatic peroxides) or COPh·O₂·COR' \rightarrow C₆H₄R'·CO₂H+CO₂ (particularly with Bz alkoyl peroxides). H. W.

Unusual case of racemisation. E. BERGMANN and R. HARTROTT (J.C.S., 1935, 1218).—Me l- α methyl-n-valerate (cf. A., 1926, 1226) with warm MgPhBr gives dl- $\alpha\alpha$ -diphenyl- β -methyl-n-amyl alcohol, b.p. 195—197°/14 mm. (also formed from the dl-ester and MgPhBr), the K derivative of which with MeI in xylene gives α -methoxy- $\alpha\alpha$ -diphenyl- β -methylpentane, b.p. 174—176°/13 mm., converted by Na in Et₂O during 3 months at room temp. into $\alpha\alpha$ -diphenyl- β methylpentane, b.p. 163—164°/13 mm. The dl-alcohol is formed probably as a result of the spontaneous reversible dehydration of the optically active form.

J. L. D.

Addition of hydrogen bromide to non-terminal double linkings. *iso*Undecenoic acid. P. L. HARRIS and J. C. SMITH (J.C.S., 1935, 1108—1111).— Undecolic acid with HI in AcOH affords a mixture of I-compounds, which with Zn in boiling PrOH (cf. A., 1901, i, 115) gives *iso*undecenoic acid. Reaction with HBr in C_6H_6 or ligroin (cf. A., 1934, 631, 1200) in oxidising and anti-oxidising conditions always affords a product containing about 43% of the t-Bracid (cf. A., 1925, i, 770; 1934, 753) which indicates the non-participation of catalysts in the reaction (cf. A., 1933, 805). J. L. D.

Highly unsaturated acids of sardine oil. V. Constitution of eicosatetraenoic acid. VI. Constitution of eicosapentaenoic acid. VI. Constitution of eicosapentaenoic acid. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 296—300, 301—304).—V. Ozonolysis of the amyl ester of eicosatetraenoic acid (I) (cf. this vol., 1105) gives $Pr^{\alpha}CO_{2}H$, $Pr^{\alpha}CHO$, (·CH₂·CO₂H)₂, and amyl H succinate (II); the presence of $CO_{2}H\cdot[CH_{2}]_{2}$ ·CHO (III), (·CH₂·CHO)₂, and $CO_{2}H\cdot[CH_{2}]_{2}$ ·CO₂C₅H₁₁ (IV) is indicated. Minor amounts of CO_{2} and MeCHO are ascribed to the presence of small quantities of another acid. (I) is given the structure $\Delta^{\gamma_{\eta\lambda 0}}$ -eicosatetraenoic acid.

VI. The conc. acid fraction (cf. this vol., 1105), contains 68.44% of eicosapentaenoic acid (V). Ozonolysis of the amyl ester gives (II), (III), (IV), CO₂, AcOH, and MeCHO; a higher aldehyde is probably present. (V) is provisionally given the structure $\Delta^{\gamma\eta\lambda\xi\rho}$ -eicosapentaenoic acid. P. G. C.

Pyrolysis. III. Pyrolysis of carbonic and sulphurous esters. P. D. RITCHIE (J.C.S., 1935, 1054-1061; cf. this vol., 960).-36% of CO(OMe)₂ is

"cracked" at 600°, whereas 66% of CO(OEt), is decomposed at 500°. COCl₂ with Me lactate in C_5H_5N at 100° affords α -carbomethoxyethyl carbonate, b.p. 172°/32 mm., which at 420-430° is mostly converted into CH2:CH-CO2Me and Me lactate. Similarly, OH. CMe2. CO2Me affords Me a-chloroisobutyrate, b.p. 133–135°/760 mm., and α -carbomethoxyisopropyl carbonate, m.p. 66–67°, converted entirely at 445– 455° into Me methylacrylate and OH CMe2 CO2Me. α -Cyanoethyl, m.p. 44-44.5°, and α -cyanoisopropyl carbonate, m.p. 76-77°, which are prepared similarly, are converted at 460-480° into CH. CH. CN and at 430-450° into α -methylacrylonitrile, respectively. ClCO₂Me with Me lactate in C_5H_5N at 100° gives Me α -carbomethoxyethyl carbonate, b.p. 91·5—92°/12 mm.; Me α -cyanoethyl carbonate, b.p. 80·5°/10 mm., is similarly prepared. These substances are pyrolysed to give CH2:CH·CO2Me and CH2:CH·CN, which indicates that one of the two possible decomp. mechanisms predominates. OEt ·CO·OBuª is decomposed at 500-510° into EtOH and Bu°OH; both decomp. mechanisms are operative, but EtOH is formed principally. OEt CO. OPh at 500-520° gives PhOH (85%), whereas CO(OPh)₂ at 640-670° affords some CO2, C6H6, and PhOH, indicating that loss of CO₂ preceded pyrolysis of Ph₂O (cf. A., 1913, i, 259). $SOCl_2$ with Et lactate in C_5H_5N at 100° gives α -carbethoxyethyl sulphite, b.p. 158-160°/4 mm., which is pyrolysed at 390-420° to give Et lactate and CH,:CH·CO,Et. J. L. D.

Esterification of hydroxy-acids and polyhydric alcohols. B. CIOCCA and A. SEMPRONI (Annali Chim. Appl., 1935, 25, 319—323).—In the prep. of Et lactate, tartrate, citrate, and ricinoleate, glycol distearate, and glycerol tristearate, increased yields are obtained by using sulphonic acids as catalysts. The reaction mixture is kept anhyd. by passing it continuously over CaC₂ in a Soxhlet apparatus. T. H. P.

Determination of pyruvic acid. C. FROMAGEOT and P. DESNUELLE (Biochem. Z., 1935, 279, 174– 183).—A simple method is described for macro- and micro-determination of $AcCO_2H$ (I) depending on the reduction in acid medium of Ce^{TT} by (I) with determination of the Ce^{TT} by titration. The reaction is fairly sp. for α -keto-acids and is not given by HCO_2H , AcOH, $EtCO_2H$, CH₂O, MeCHO, EtCHO, MeOH, EtOH, PrOH, glycerol, sugars, glycine, and alanine. P. W. C.

Lactone of γ -hydroxyvinylacrylic acid, protoanemonin. F. B. KIPPING (J.C.S., 1935, 1145— 1147).—Protoanemonin from *Ranunculus hirsutus* or *R. bulbosus* with Pt-H₂ in EtOH gives *n*-valeric acid, γ -valerolactone, and tetrahydroanemonin, and with NaOH at 60° is converted into CHAc:CH·CO₂H, and thence by reduction (Pt-H₂) into lævulic acid, thereby confirming the structure assigned to it by Asahina *et al.* (cf. A., 1922, i, 946). $\gamma\delta$ -Dibromo- Δ^{α} -pentenoic acid when distilled affords, contrary to Muskat *et al.* (cf. A., 1930, 321, 451), a substance, m.p. 151—152° (re-solidifying at about 175—185°), mol. wt. 215, which is converted by HI into dilævulic acid, and is identical with anemonin. J. L. D.

Trihydroxybutyric acids. J.W.E. GLATTFELD and R. E. HOEN (J. Amer. Chem. Soc., 1935, 57, 1405—1407).—CH₂:CH·CH(OH)·CO₂H (improved prep. from CH₂:CH·CHO; Zn salt), AgClO₃, and OsO₄ in absence of light give *dl*-erythrolactone (20%) (phenylhydrazide of the acid, m.p. 147.5°) and *dl*-threonic acid (7% yield; phenylhydrazide, m.p. 167.5°). R. S. C.

Rotatory powers of dimethylene tartrate, methylenetartaric acid and its dimethyl ester. —See this vol., 1192.

Constitution of glauconic acids. III. H. SUT-TER and N. WIJKMAN (Annalen, 1935, 519, 97-110; cf. A., 1933, 1143).-It is proposed to retain the name glauconic acid (I) for the acid I C₁₈H₂₀O₇, and to designate the acid II $C_{18}H_{20}O_6$ glaucanic acid. (I) has $\left[\alpha\right]_{D}^{20}$ -42.6° in COMeEt. It is reduced by Zn dust in boiling AcOH to dihydroglauconic acid, m.p. 235° [Me ester, m.p. (indef.) 200°], which cannot be acetylated and is unchanged by boiling conc. HNO₃. Thermal fission of (1) affords α -ethyl- Δ^{α} -pentenal and glauconin (II) (Ag salt). Ozonisation of (II) at low temp. in EtOAc and fission of the ozonide by hydrogenation (Pd-C) gives AcCO₂H in such yield that two sources thereof in the mol. of (II) are indicated, H₂C₂O₄, HCO₂H, and CO₂H·CO·CH₂·CO₂H in addition to an unidentified $\alpha\beta$ -dicarbonyl compound. When heated with HCl (II) affords CO2 and a substance (III), C₉H₁₂O₄, m.p. 144°; the residue after treatment with AcCl yields two compounds $C_9H_{12}O_4$, m.p. 116° (IV) and m.p. 126° (V), respectively. All these compounds react with .2KOH and, after acidification of the solution, (III) and (V) yield an *acid* (VI), $C_{19}H_{14}O_5$, m.p. 140°, whereas (IV) affords an isomeric *acid* (VII), m.p. 127°. The behaviour of the compounds towards AcCl therefore resembles that of hydrochelidonic acid (VIII), and the relationship is further established by comparison of the absorption spectra of (VIII) and (VI) whereby also the structure $CO(CH_2 \cdot CH_2 \cdot CO_2H)$ of (VIII) is established. Further, like (VIII), (VI) gives a diphenylhydrazide, m.p. 275-280° (decomp.), and a mono-2: 4-dinitrophenylhydrazide, m.p. 230° (decomp.). Oxidation of (VI) or (VII) with HNO_3 gives $AcCO_2H$ in excellent yield. Comparison of the absorption spectra of (VI) and (VIII) in conjunction with the known effect of the substituent Me on ketones suggests that (VI) has the structure

 $CO(CH_2 \cdot CHMe \cdot CO_2H)_2$. This is confirmed by the condensation of $CO(CH_2 \cdot CO_2Et)_2$ with CHMeBr $\cdot CO_2Et$ and treatment of the product with boiling 20% HCl, whereby (III), (IV), and (V) are obtained. (VI) and (VII) are therefore the *r*- and *meso*-forms, respectively. H. W.

Acetoacetic condensation. X. Condensation of ethyl α -carbethoxy- α' -ethyladipate. E. R. MEINCKE and S. M. MCELVAIN (J. Amer. Chem. Soc., 1935, 57, 1443—1445; cf. this vol., 83).— $Et_2 \alpha$ -carbethoxy- α' -ethyladipate (I) (which has only 1 H α to CO₂Et) and NaOEt at 100°/200 mm. give EtOH (1.25 mols.) and Et₂ 2-ethylcyclopentanone-2:5-dicarboxylate (22%), thus confirming the author's views on the acetoacetic condensation.

OH·[CH₂]₂·CEt(CO₂Et)₂ and boiling 36% aq. NaOH give 88% of α -ethylbutyrolactone, b.p. 213—216°/740 mm., which with EtOH-HCl affords Et γ -hydroxy- α -ethylbutyrate, b.p. 78—80°/3 mm., converted by PBr₃

into the γ -Br-ester (78% yield), b.p. 90—93°/8 mm.; this with CH₂(CO₂Et)₂ yields (I) (47%), b.p. 170— 172°/8 mm. R. S. C.

Tautomerism of the system, thiocoumarindiol-thiochromonediol and of ascorbic acid.— See this vol., 1248.

Catalytic action of monoses on the formaldehyde condensation. II. A. KUSIN (Ber., 1935, 68, [B], 1494—1499; cf. this vol., 733).—The accelerating action of saccharates on the condensation of CH₂O to sugars is attributed to enol formation with 2 OH at the double linking. Since the main portion of the sugar is present in the cyclic form and only a part is enolised, OH·CH₂·CHO, which is incapable of cyclic formation, should be a more powerful catalyst than fructose or glucose (I); this is shown to be the case. In harmony with this view 1:2-isopropyl-ideneglucofuranose and 1:2-isopropylidene-3:5:6trimethylglucose have no accelerating action, whereas 3:5:6-trimethylglucose is somewhat more active than (I). Benzoin has about the same activity as (I), whereas benzil is inert. Acetoin is somewhat less effective than (I). OEt CH2 CHO is as active as (I), whereas CH2Ac·CO2Et and COMo2 are inactive. Apparently two hydroxyl O attached to the double linking are essential to activity. H. W.

Condensation of halogen-substituted aldehydes with nitromethane. F. D. CHATTAWAY and P. WITHERINGTON (J.C.S., 1935, 1178—1179; cf. A., 1895, i, 637).—Equimol. amounts of CCl₃·CHO,H₂O and NO₂Me in aq. Na₂SO₃ at 60° give $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropane, b.p. 119°/3 mm. (which does not react further with CCl₃·CHO) (Ac derivative, m.p. 61—62°). The Br₃-analogue has m.p. 78° (Ac derivative, m.p. 70°). Butylchloral hydrate with NO₂Me similarly affords $\gamma\gamma\delta$ -trichloro- α -nitro- β -hydroxypentane, b.p. 156°/4 mm. (Ac derivative, b.p. 168°/4 mm.).

Free radicals and atoms in primary photochemical processes. II. Photodissociation of aliphatic aldehydes and ketones.—See this vol., 1211.

J. L. D.

Electrolytic reduction of ketones in glacial acetic acid. II. Reduction of aliphatic ketones to hydrocarbons. S. SWANN, jun., L. F. DEDITIUS, and W. A. PYHRR (Trans. Electrochem. Soc., 1935, 68, 89–95; cf. A., 1933, 1127).—The yields of $n-C_5H_{12}$ obtained by the electrolytic reduction of COMePr^a in AcOH at cathodes of Cd, Sn, Pb, Hg, Al, Zn, Ni, Cu, and Fe correspond with the H₂ overvoltages of the cathodes. The best yield is obtained with a Cd cathode in aq. solution. E. S. H.

Identification of arabinose in presence of other pentoses. E. VOTOČEK and L. SGARZI (Coll. Czech. Chem. Comm., 1935, 7, 355—358).—Arabinose (in quantity > 0.1 g.) is identified by addition of HCN, hydrolysis to a mixture of glucono- and mannonolactone, reduction with Na-Hg, and conversion into glucosephenylosazone, which separates in the hot, whereas from xylose a phenylosazone is obtained sol. in the hot. Hexoses (particularly galactose) may interfere unless they are first removed by fermentation. P. G. C.

Conversion of derivatives of glucose into derivatives of altrose by simple optical inversions. G. J. ROBERTSON and C. F. GRIFFITH (J.C.S., 1935, 1193-1201).-2: 3-Di-p-toluencsulphonyl-4: 6benzylidene-a-methylglucoside (I) with boiling MeOH-NaOMe affords 4: 6-benzylidene-2: 3-anhydro-a-methylalloside (II), m.p. 199–200°, $[\alpha]_{D}^{15}$ +140.4° in CHCl₂ [this, or (V), on prolonged treatment with 5% KOH under pressure gives 4:6-benzylidene- α -methylaltroside, m.p. 169–170°, which is methylated to give (IV), and is hydrolysed (COMe2-HCl) to α -methylaltroside, a glass], and 4:6-benzylidene-2-methyl- α -methylaltroside (III), m.p. 98–99°, $[\alpha]_{\rm D}$ +102.7° in CHCl₃ (3-p-toluenesulphonyl, m.p. 166-167°, and 3-Bz derivative, m.p. 135-136°), in succession, the latter being methylated (Purdie's reagents) to 4: 6-benzylidene-2: 3-dimethyl-a-methylaltroside (IV), m.p. 83-S5°, hydrolysed (boiling COMe2-H2O-HCl) to 2-methyl-a-methylaltroside, m.p. 81-83°, and its structure determined by the non-identity of its derivatives with the corresponding compounds from glucose, and by converting it into altrosazone. When (I) is impure, 4:6-benzylidene-2:3-anhydro- α methylmannoside (V), m.p. 146-147° [converted by NaOH-NaOMe at 100° under pressure, after a Walden inversion at C3, into 4:6-benzylidene-3-methyl- α methylaltroside (VI), m.p. 131-133° (cf. ease of hydrolysis of the isomeric alloside), which is methylated (Purdie's reagents) to (IV) and hydrolysed to 3-methyl- α -methylaltroside, a glass, which affords 3-methyl-altrosazone, m.p. 168–169°], is also formed. 4:6-Benzylidene-a-methylglucoside with BzCl in C5H5N gives a mixture of Bz_1 and Bz_2 compounds, which with $p \cdot C_6 H_4 Me \cdot SO_2 Cl$ followed by hydrolysis (MeOH– NaOMe) affords 2-benzoyl-3-p-toluenesulphonyl-4:6benzylidene-a-methylglucoside, m.p. 184-186°, further hydrolysed to (II). Similarly with $p-C_6H_4Me\cdot SO_2Cl$ in C_5H_5N , it affords 2-p-toluenesulphonyl-4:6-benzyl-idene- α -methylglucoside, m.p. 153—154° [3-Bz deriv-ative (VII), m.p. 212—213°, hydrolysed (MeOH-NaOMe) to (V) because optical inversion occurs at the C bearing the $p-C_6H_4Me\cdotSO_2$ (cf J.C.S., 1923, 123, 44; A., 1925, i, 507)], and some 2:3-di-ptoluenesulphonate. (IV) with boiling COMe2-aq. HCl affords 2:3-dimethyl- α -methylaltroside, methylated to 2:3:4:6-tetramethyl- α -methylaltroside, a syrup,

which is hydrolysed (HCl) to 2:3:4:6-tetramethylaltrose, a syrup (cf. A., 1933, 1037), oxidised (cf. A., 1926, 385) to l-dimethoxysuccinic acid and d-trimethoxyaraboglutaric acid, which proves that (III), (IV), and (VI) have the altrose configuration. Hydrolysis (2N-HCl) of the methyl-a-methylaltrosides gives solutions containing anhydro-compounds (cf. A., 1923, i, 445; 1926, 601) in equilibrium with reducing sugar. J. L. D.

New reaction of the dichloroacetyl group in derivatives of glucose. D. J. BELL (J.C.S., 1935, 1180-1182).-The following are prepared by interaction of the appropriate glucoside with $CHCl_2 \cdot COCl$ in dry $C_5H_5N-C_6H_6$ below -10° : 2:3-bisdichloro-acetyl-4:6-benzylidene-, m.p. 120-122°, 4:6-bisdichloroacetyl-2: 3-dibenzoyl- (1), a glass, 6-dichloroacetyl-2:3:4-tribenzoyl- (II), a glass, and 6-dichloroacetyl-2:3-dibenzoyl-4-p-toluenesulphonyl- α -methylglucoside

(III), m.p. 140-142°. 2:3-Bisdichloroacetyl-4:6benzylidene-, m.p. 154-155°, 2:3:6-triacetyl-4-di-chloroacetyl-, m.p. 78-79.5°, and 6-dichloroacetyl-2:3:4-tri-p-toluenesulphonyl- β -methylglucoside (IV), m.p. 169-171°, which is obtained from 2:3:4-trip-toluenesulphonyl-β-methylglucoside, m.p. 188-189° [obtained by reduction (Zn-Fe-AcOH) of its 6-nitrate (cf. A., 1932, 254)]. The above substances when treated with AgOAc in $COMe_2-H_2O$ revert to the original compounds except (I) and (II), which suffer some racemisation; (IV) is converted into a Cl-free compound, m.p. 164°, and (III) remains unchanged. J. L. D.

Osazones. I. Anhydro-osazones. O. DIELS and R. MEYER (Annalen, 1935, 519, 157-164).-The conversion of d-glucosazone into 3:6-anhydro-d-CH'N-NHPh glucosazone (I), m.p. 180°, $[\alpha]_{\rm p}^{20}$

(U.N.NUDL
2	NINHPh
-	H
H.C	OH
H.	OH
L-(H. (I.)

-181° in MeOH, is effected in varying yield by HCO₂H at room temp., by NH₂Me, HCl, or MgSO₄ in boiling PraOH, but, most certainly, by boiling with MeOH or EtOH containing a little 20%

H2SO4. Anhydro-d-galactosazone, m.p. 220° (slight decomp.), $[\alpha]_{D}^{20} + 70.5^{\circ}$ in MeOH, anhydro-*d*-lactosaz-one, m.p. 230° (slight decomp.), $[\alpha]_{D}^{20} - 138^{\circ}$ in MeOH, and anhydromaltosazone, m.p. 209–210°, $[\alpha]_D^{20}$ -10° in MeOH, are similarly obtained. Treatment of quercitol with Br and of the product with NHPh·NH₂ affords an osazone, $C_{18}H_{20}O_3N_4$, m.p. 220° (decomp.). The well-defined m.p. of the anhydro-osazones render them very suitable for the identification of sugars. H. W

Transformation of hexoses into inositol. F. MICHEEL, H. RUHKOPF, and F. SUCKFÜLL (Ber., 1935, 68, [B], 1523—1527).—The main product of the action of ZnCl_2 in Ac₂O at 100° on 6-iodo-al-dgalactose 2:3:4:5-tetra-acetate (I) is dl-galactose hepta-acetate (II), m.p. 132°, $[\alpha]_{\rm D} \pm 0^{\circ}$, hydrolysed (Zemplen) to dl-galactose, m.p. 141–142°. al-d-Galactose penta-acetate is transformed similarly into al-d-galactose hepta-acetate, m.p. 103°, $[\alpha]_D^{20} + 9.8°$ in EtOH. The conversion of (I) into (II) cannot be attributed to simple racemisation and the intermediate production of a 6-C ring is postulated, thus :



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Constitution of isosucrose. (SIR) J. C. IRVINE and D. ROUTLEDGE (J. Amer. Chem. Soc., 1935, 57, 1411—1414).—isoSucrose (modified prep.; no sucrose formed) with Ag_2O —MeI or Me_2SO_4 or both successively gives a mixture of Me_7 ethers, which with K-MeI in liquid NH₃ gives the Me_8 ether, b.p. 180— 185°/3 mm., hydrolysed by hot 0.01N-HCl to tetramethyl-glucose and - γ -fructose, the separation of which is modified. R. S. C.

Cellulose. LIV. Acetolysis of cellulose. VI. Cellotriose and its derivatives. K. HESS and K. DZIENGEL (Ber., 1935, 68, [B], 1594-1605).-Short acetolysis of linters under relatively mild conditions is followed by pptn. of a product practically free from glucose and poor in cellobiose which is hydrolysed (Zemplén) and separated into a H₂O-insol. portion, mainly hydrocellulose (I) which serves for the prep. of limit dextrins, and a H₂O-sol. portion which contains almost all the cellotriose (II), which is isolated by fractional pptn. with EtOH. The latter process falls into two stages, the second of which is continued until the properties of the material remaining in solution agree in all respects with those of the main fraction. Thus obtained, (II) has m.p. about 203° after softening at about 200°, decomp. about 214°, $[\alpha]_{D}^{20} + 32.0^{\circ}$ to $+23.2^{\circ}$ in H₂O. The X-ray diagram is sp. and quite distinct from that of (I). Treatment of (II) with Ac₂O and C₅H₅N at (1). Treatment of (11) with Ac₂O and C₅H₅N at $\geq 40^{\circ}$ yields α -cellotriose hendeca-acetate, m.p. 219— 220° (corr.), $[\alpha]_{10}^{29} + 22 \cdot 4^{\circ}$ in CHCl₃, $[\alpha]_{25}^{25} - 6 \cdot 5^{\circ}$ in C₆H₆, $[\alpha]_{15}^{4} + 30 \cdot 9^{\circ}$ in COMe₂, whilst the corresponding β -compound, m.p. 219—220° (corr.), $[\alpha]_{20}^{29} - 6 \cdot 5^{\circ}$ in AcOH, -13 \cdot 7^{\circ} in MeOH, -18 · 2° in CHCl₃, -43 · 2° in C₆H₆, -6 · 6° in COMe₂, -17 · 5° in C₂H₂Cl₄, -30 · 1° in C₅H₅N, is isolated with difficulty from the mother-liquors and is best obtained by the addition of small liquors and is best obtained by the addition of small successive quantities of (II) to a mixture of Ac₂O, AcOH, and KOAc at 120°. Cellobiose hendecaacetate (mainly β -form) is transformed by Me₂SO₄ and 30% NaOH in COMe2 and then in C6H6 into β-hendecamethylcellotriose, m.p. 116·5—117°, $[\alpha]_{p}^{p}$ -15·42° in MeOH, -11·06° in CHCl₃, -14·62° in H₂O, $[\alpha]_{p}^{p}$ -13·97° in C₆H₆. Cellobiose octa-acetate β-hendecamethylcellotriose, m.p. 116.5-117°, is transformed similarly into *β*-octamethylcellobiose, m.p. 86-87°, [a]²¹ -16·16° in MeOH, -14·88° in $CHCl_3$, $[\alpha]_0^{20} - 12.73^\circ$ in C_6H_6 , -15.28° in H_2O .

H. W.

Pigment of egg-plant.—See this vol., 1290.

Digitalis glucosides. IV. Existence of two anhydrodigitoxigenins. S. SMITH (J.C.S., 1935, 1050—1051).—Fractional crystallisation of anhydrodigitoxigenin (A., 1931, 74) affords an α -, m.p. 234°, $[\alpha]_{D}^{\infty} + 39 \cdot 0^{\circ}$ in MeOH (Ac derivative, m.p. 144°), and a β -isomeride, m.p. 202°, $[\alpha]_{D}^{\infty} - 13 \cdot 3^{\circ}$ in MeOH (Ac derivative, m.p. 185°), which are oxidised (CrO₃-AcOH) to α -, m.p. 203° (and a product, m.p. 273°), and β -anhydrodigitoxigenone, m.p. 281°, respectively. J. L. D.

Polysaccharides. XX. Molecular size of amylose and the relationship between amylose and starch. D. K. BAIRD, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1935, 1201–1205).—Amylose (I), freshly prepared from potato starch, is sol. in cold H_2O , but changes in air into a product insol. in H_2O

and representing a higher state of aggregation of the mol. Repeated treatment of (I) with Ac_2O in C_5H_5N at 50° affords a product (mol. wt. 21,000) [easily de-acetylated, but methylated only with difficulty to yield a product similar to (II) (below)] which, determined viscosimetrically, has a chain of about 73 glucose units. Further acetylation with Cl₂ and SO₂ as catalysts gives a substance (mol. wt. 35,000) with a chain-length of about 120 glucose units. Products similar to (I) are obtained by hydrolysis; the P content is unchanged throughout. Acetylation of (I) using Cl₂ and SO₂ as catalysts gives an acetate (mol. wt. 12,000) which with Me₂SO₄ in 30% KOH-COMe₂ at 55° affords a methylated amylose (II), $[\alpha]_{p}^{p} + 215^{\circ}$ in CHCl₃, mol. wt. 4000-5000 (25 glucose units; confirmed by gravimetric determinations), which is the figure obtained for all other known methylated starches, and indicates that disaggregation of the mols. to yield a form which approximates to the chemical mol. of starch has occurred. J. L. D.

Polysaccharides. XXI. Constitution and chain-length of some starch dextrins. W. N. HAWORTH, E. L. HIRST, and (MISS) M. M. T. PLANT (J.C.S., 1935, 1214-1217) .- Potato starch with glycerol at 190-200° gives a dextrin, converted by Ac₂O-C₅H₅N at 70° into an acetate, which gives no colour with I, and is separated into fractions (I) and (II) by pptn. from CHCl₃. Repeated treatment of (I) with Me₂SO₄-30% NaOH in hot COMe₂ affords a methylated dextrin, hydrolysed by conc. HCl at -15° to a mixture of sugars from which tri- and tetra-methylmethylglucoside (9.4%, which corresponds with a mean chain-length of 12α -glucopyranose units; cf. A., 1932, 1022) are isolated after treatment with MeOH-dry HCl. Similarly determined, (II) has a mean chain-length of 8 units. The hexose residues of (I) and (II) are probably united exclusively by α -glucosidic linkings, as $[\alpha]$ is in agreement in each case with the calc. val. (cf. A., 1933, 211), and the chain-lengths derived by other methods agree with the vals. obtained above. The mols. of smaller mol. wt. show no tendency to undergo aggregation.

J. L. D.

polymerised compounds. CXV. Highly Transformation of cellulose into polymericanalogous cellulose triacetates. H. STAUDINGER and H. EILERS (Ber., 1935, 68, [B], 1611-1618).-Further examples are cited of the conversion of cellulose into polymeric-analogous compounds, showing that changes of these macro-mols. can be effected without altering the C skeleton, as is also the case with compounds of lower mol. wt. Contrary to Hess et al. (B., 1928, 705), the triacetates obtained from Cu- (1) or viscose-silk (II) by Ac₂O in C₅H₅N are sol. in CHCl₃, C₂H₂Cl₄, HCO₂H, and warm *m*-cresol; the mean degree of polymerisation is 150-300 and they have the same solubility relationships as the triacetates of similar mean mol. wt. obtained from cotton by cautious treatment with Ac_0O and H_0SO_4 or $ZnCl_2$. The triacetates from linters are more complex and insol. in the media named above. (I), (II), and a degraded technical cellulose are converted by Ac₂O and C₅H₅N into their triacetates, the mol. wt. of which does not depend on the duration of the action, thus showing that a change in the chain does not occur. The degree of polymerisation of the celluloses determined by measurement of the viscosity of their solutions in m-cresol is identical with that of the crude or repptd. triacetates. H. W.

Kinetics of benzoylation of cellulose. A. L. BERNOULLI, M. SCHENK, and F. ROHNER (Helv. Chim. Acta, 1935, 18, 1008; cf. A., 1934, 1314).—The authors' process (*loc. cit.*) is described in the patent lit. F. R. G.

Direct transformation of the skeleton substance of straw into an acetylated carbohydrate. R. S. HILPERT and O. PETERS (Ber., 1935, 68, [B], 1575-1578).-The high C content of straw is reconcilable with the absence of lignin if the presence of cellulose anhydrides is assumed. Attempts to verify the hypothesis by the direct acetylation of straw were unsuccessful, since complete reaction could not be secured, probably by reason of the slowness of the primary swelling. Preliminary treatment of the straw with alkali at low temp. causes reproducible dissolution of 20-30% of the material with production of a partly methylated cellulose anhydride. Acetylation of the product unexpectedly leads to a cellulose triacetate, thus establishing a primary fission of the anhydride. Pentosans do not disappear during acetylation, so that it must be assumed either that the present conception of OH in cellulose cannot be extended to them or that their determination is inaccurate. OMe present in the straw treated with alkali is present also in the acetate. The proportion of apparent lignin in the acetate is the same as in the original material, confirming the hypothesis that the materials separated by acids are solely reaction products of carbohydrates. The ready oxidisability of straw is evidence against the view that the main substance is carbohydrate. This property is lost in the acetate, which does not readily react with Cl₂ or OCl' and is indifferent towards alkaline KMnO₄. The properties of straw must be ascribed to the carbohydrates themselves and their mutual union.

H. W.

Quantitative isotopic exchange reactions in the carbohydrate group.—See this vol., 1212.

Preparation of diaminobutanes. IV. Gold diamine compounds. E.STRACK and H.SCHWANE-BERG (Ber., 1935, 68, [B], 1638—1651).—The following types of Au salts are obtained from diaminobutanes and, apparently, from all bases containing at least two NH₂ groups. Normal Au salts (I), $C_4H_{12}N_2$,2HAuCl₄, obtained by use of 10—15% HCl with an excess of HAuCl₄; their solubility in H₂O appears to increase with increasing proximity of the NH₂ and their ease of transition into non-typical salts also increases with their solubility. Monoaurichlorides (II),

 $C_4H_{12}N_2$,HCl,HAuCl₄, which are derived only from diamines which give freely sol. salts (I); they are obtained from conc. solution in 25% HCl by use of the theoretical amount of AuCl₃; they are freely sol. in H₂O and EtOH and pass readily into other nontypical products; they can be crystallised unchanged from conc. HCl. Derivatives (III), $C_4H_{12}N_2$,2AuCl₃, obtained by warming (I) with much H₂O or by diminishing the acidity of the dil. solution until it is

just acid to Congo-red; all derivatives (III) are less freely sol. in H₂O than compounds (I) and are formed with increasing ease as the difference in solubility increases. Compounds (IV), C4H11N2Au2Cl5, obtained pure when compounds (III) are warmed with much H_2O or, more completely, but with enclosed AcOH, when solutions of salts (I) are treated with NaOAc; they are very sparingly sol. in H₂O, freely in COMe₂, variously in EtOH; they can be crystallised unchanged from $COMe_2-Et_2O$; they appear to be formed with loss of H from NH_2 . Derivatives (V), $C_4H_{10}N_2Au_2Cl_4$, apparently derived by loss of 2 H from NH_2 ; (IV) and (V) pass completely into (I) when heated with conc. HCl. Compounds (VI) in which Au salts have lost more HCl than in (V), obtained from (I) by treatment with NaHCO3 and insol. in all org. media. Compounds (IV) unite with Et₂O, COMe₂, and, particularly, with dioxan, so that a method is afforded of detecting small amounts of Au salt and dioxan which is very firmly retained. *a*β-Diaminobutane gives salts (I), (II), decomp. 204° after softening at 197°, (III), (IV) also $+1C_4H_8O_2$, decomp. 174°, and (VI). $\alpha\beta$ -Diamino-\beta-methylpropane affords compounds (I), (II), m.p. 227° after softening at 217°, (III), (IV) $+2H_2O$, decomp. 190—191° after softening at 158°; $+C_4H_8O_2$, decomp. 173—175° after softening at 170°. r- $\beta\gamma$ -Diaminobutane affords salts (I), (II) +H₂O, (III), decomp. 235-237°, (IV), decomp. 217° after darkening at 200° and softening at 210°, also $+1C_4H_8O_2$, decomp. 215-217° after softening and darkening at about 190°. The optically active By-diaminobutanes give salts (I), (II) +1H₂O, decomp. 222—223° after softening at 217°, (III) decomp. 235—237°, (IV) +1H₂O, decomp. about 220° after darkening and softening at 210–215°, $+1C_4H_8O_2$, decomp. 215–217° after softening at 190°. meso- $\beta\gamma$ -Diaminobutane yields compounds (I), (III), decomp. 225–227° after softening at 217°, (IV) $+1H_2O$, decomp. 197°; $+1.5C_4H_8O_2$, slow decomp. above 130°. $\alpha\gamma$ -Diaminobutane affords salts (I), (III) +1H₂O, decomp. 180-181° after softening at 176°, (IV), decomp. 158-159° after softening at 150° , $+1C_4H_8O_2$, decomp. 148—150° after softening at 145°. $\alpha\gamma$ -Diamino- β -methylpropane gives substances (I), (III), decomp. 188-189°, and (IV), decomp. 196° after softening at 190° and, $+C_4H_8O_2$, decomp. about 185° after softening at 175°. αδ-Diaminobutane yields compounds (I), m.p. 231-232° when rapidly heated, (III) $+1H_2O$, (IV), m.p. 158° after softening at 155°, decomp. 164-165°, (V), decomp. 170—172°, and (VI), C₄H₈N₂, AuCl, AuOH, H₂O, violent decomp. 139°. Histamine affords salts (I), marked decomp. 222° after softening at 205° and, incipient decomp. 212°, (III), decomp. 200-202° after softening at about 190° and liquefying at 195°, converted by EtOH into the compound $\tilde{C}_5H_9N_3$,AuCl₃,H₂O, decomp. 175–180° after softening at 150°, (IV), and (VI). $\alpha\beta$ -Diaminoethane gives substances (I), decomp. 240° after softening at 230°, (III), rapid decomp. 235° after softening at 190° and slow decomp. 220°, and (IV) +1H₂O, rapid decomp. 217-220° after softening at 185° and slow decomp. about 205°. «β-Diaminopropane yields salts (I), decomp. 234° after softening at 228°, (III) $+1H_2O$, decomp. 220° after softening at 215°, and (IV), decomp. 220-225° after softening at about 195°. $\alpha\gamma$ -Diaminopropane gives salts (1)

+1H₂O, decomp. 235° after softening at 230°, (III), decomp. about 205° after softening at 180°, and (IV), decomp. 170° after softening at 165°. ad-Diamino- β -methylbutane gives compounds (I) and (V), decomp. 165° after softening at 145°. H. W.

ββ'β"-Trichlorotriethylamine. H. MCCOMBIE and D. PURDIE (J.C.S., 1935, 1217-1218).-The prep. from $\beta\beta'\beta''$ -trihydroxytriethylamine is described, and also that of some of its derivatives. J. L. D.

Derivatives of carbamylcholine. A. ERCOLI (Annali Chim. Appl., 1935, 25, 263-273).-The following compounds and their pharmacological actions are described : β -chloroethyl acetylcarbamate, m.p. 73-74°; acetylcarbamylcholine chloride; β -chloroethyl methylenedicarbamate, m.p. 148°; methylenedicarbamylcholine dichloride (I) (PtCl₄ compound $+2H_{2}O$, m.p. 230°); β -chloroethyl anhydroformaldehydecarbamate; anhydroformaldehydecarbamylcholine chloride; β-chloroethyl phenylmethylcarbamate, b.p. 165°/12 mm.; phenylmethylcarbamylcholine chloride [AuCla compound, m.p. 190°; PtCl₄ compound, m.p. 222° (decomp.)]; di-β-chloroethyl iminodicarboxylate, m.p. 202°; iminodicarboxylcholine dichloride [AuCl₃ compound, m.p. 240° (decomp.); PtCl4 compound, decomp. 248°]; dimethylcarbamylcholine chloride methochloride [AuCl₃ compound, m.p. 273° (decomp.)]. For (I), the ratio active dose : dose tolerated is > for T. H. P. carbamylcholine.

Configuration of norleucine and glucosamine. P. KARRER and V. ITSCHNER (Holv. Chim. Acta, 1935, 18, 782-790).-CHMe:CH·CH₂Br with Et phthalimidomalonate and NaOEt in EtOH yields Et phthalimido- Δ^{β} -butenylmalonate, m.p. 48°, which with conc. NaOH in EtOH-H₂O gives the cryst. Na₃ salt of o-carboxybenzamido- Δ^{β} -butenylmalonic acid; this with warm H₂O gives the hydrochloride, cryst., of dl- Δ^{β} -butenylglycine (I), m.p. 260-270° (decomp.) (Cu salt, cryst.), which with BzCl yields $dl_{\Delta^{\beta}}$ -butenylhippuric acid, m.p. 157°, oxidised (KMnO4) to dlbenzoylaspartic acid, m.p. 174° [Fischer (A., 1899, i, benzoylaspartic acid, in.p. 174 [Fischer (A., 1899, 1, 888) gives m.p. 162°], and with yeast gives $d \cdot \Delta^{\beta}$ -butenylglycine, decomp. 260—270°, $[\alpha]_{18}^{18} + 52 \cdot 5^{\circ}$ in H₂O, reduced (H₂, Pt) to *d*-norleucine, decomp. 270—280°, $[\alpha]_{18}^{18} - 23 \cdot 1^{\circ}$ in aq. HCl, and benzoylated to $d \cdot \Delta^{\beta}$ -butenylhippuric acid, m.p. 122°, $[\alpha]_{18}^{18} - 66 \cdot 0^{\circ}$ in C₆H₆, which by oxidation (KMnO₄) gives *d*-benzoyl-aspartic acid, $[\alpha]_{18}^{18} - 36 \cdot 4^{\circ}$ in aq. NaOH. F. R. G.

Action of erepsin and trypsin on polypeptides containing ψ -leucine. E. ABDERHALDEN and W. FAUST (Fermentforsch., 1935, 14, 407–412; cf. A., 1934, 516; this vol., 71).—The N-carbobenzyloxy-derivative of l- ψ -leucine (I) with PCl₅ yields the substance CO·NH O-CO>CHBu^y, m.p. 132°. (I) with PCl₅ and AcCl yields the hydrochloride, m.p. 180° (decomp.), of l- ψ -leucyl chloride, which with the Et ester of ltyrosine in C_5H_5N gives rise to 1-4-leucyl-1-tyrosine (II), m.p. 245-250° (decomp.) (p-toluenesulphonate, m.p. about 180°, $[\alpha]_0^{26}$ -7.81° in EtOH). Similarly from the hydrochloride, m.p. 185° (decomp.), of d-4leucyl chloride d-4-leucyl-l-tyrosine (III), m.p. about 245° (p-toluenesulphonate, $[\alpha]_{D}^{26}$ +27.3° in EtOH), is

obtained. (II) [but not (III)] is hydrolysed by erepsin: (II) and (III) are not hydrolysed by trypsin. W. McC.

Walden inversion. II. E. OTT [with R. DEMME and V. BARTH]. III. E. OTT and K. KRÄMER (Ber., 1935, 68, [B], 1651-1654, 1655-1658; cf. A., 1931, 1049).—II. Interaction of l(+)-asparagine with HNO₂ in H_2O proceeds slowly, is accompanied by little racemisation, and yields l(-)-malic acid; Walden inversion does not occur. In AcOH reaction is more rapid and is accompanied by much racemisation, whilst similar treatment of Et aspartate in EtOH is accompanied by Walden inversion. In explanation, it is pointed out that r-malic acid has a higher free energy content than either of its optical antipodes and, consequently, if reaction is sufficiently slow NH₂ is replaced by OH without inversion. With increasing rate of change the formation of the energy-richer r-compound becomes more pronounced, and ultimately becomes the general change. Inversion occurring when the reaction is still more rapid is explained in the same manner as the production of C_2H_6 compounds from C₂H₂ compounds by very rapid hydrogenation, whereby in the limiting case C_2H_4 compounds were not formed as intermediates.

III. Replacement of Cl by H in optically active CClPhMe·CO₂H by rapid catalytic treatment with H₂ affords CHPhMe·CO₂H with reversed sign of rotation, whereas the slower replacement by Zn dust and AcOH takes place without change of sign. In these changes racemisation is the main process. Catalytic hydrogenation with Pd-C occurs more rapidly in AcOH than in Et₂O. r-OH·CPhMe·CO₂H reacts much more rapidly than either of the optically active forms with SOCl₂, whereas even in dil. solution replacement of Cl by H takes place much more slowly with r-CClMePh·CO_oH than with the active forms. H. W.

Effect of X-rays on glutathione.-See this vol., 1212.

Ethylenic nitriles. R. VANDEWYER (Bull. Soc. chim. Belg., 1935, 44, 376–386).—Forms (I), b.p. 127.5–127.7°/766.5 mm. and 144.5–144.7°/756 mm., respectively, of Δ^2 -pentenonitrile, separable by distillation, are obtained from Me·[CH,], CHBr·CN and

quinoline (II) at 110°. Alternatively, $Me \cdot [CH_2]_2 \cdot CHCl \cdot CN$ and C_5H_5N or $Me \cdot [CH_2]_2 \cdot CH(OH) \cdot CN$ and P_2O_5 give a mixture of (I), which with 66% H₂SO₄ at 0° gives forms, m.p. 151·3—152° and 68·4—69°, respectively, of Δ^{a_2} pentenoamide, which with P_2O_5 give pure (I). Forms, $h = 165 \cdot 2 - 166^{\circ}/750 \cdot 2$ mm and 140.6—149.8°/745 b.p. 165.8-166°/759.2 mm. and 149.6-149.8°/745 mm., respectively, of Δ^{a} -hexenonitrile (III) are obtained from Me·[CH2]3·CHBr·CN (modified prep.), b.p. 82-82.5°/10 mm., and (II) at 130° or from the amides, m.p. 124.6-125.3° and 67.4-68°, respectively, which are best obtained from (III) and H_2SO_4 (2-3) days at room temp. and then 100 hr. at $40-50^{\circ}$). C_6H_{13} ·CHBr·CN gives similarly two forms of Δ^a octenonitrile, of which that of b.p. 78-78.2°/12.5 mm. gives an amide, m.p. 66.1-66.5°, whence it is regenerated by H₂SO₄. Physical data are given. R. S. C.

Racemisation in the preparation of the Grignard reagent. C. W. PORTER (J. Amer. Chem. Soc., 1935, 57, 1436).— β -Bromo-*n*-octane, $[\alpha]_{\rm D}$ +22·7° and -20·7° (prep. without racemisation from the alcohol by PBr₃), and optically active CHMePhBr were racemised during prep. of the Grignard reagent by Mg and a trace of I in Et₂O under dry N₂. R. S. C.

Plato- and plati-diammines containing methylamine. H. D. K. DREW and H. J. TRESS (J.C.S., 1935, 1212—1214).— K_2PtBr_4 with aq. NH_2Me at 0° affords [Pt(NH_2Me)₄]PtBr₄, β -di(methylamino)platinous bromide (I) [converted (AgNO₃) through the nitrate into (HCl) the β -chloride, which is obtained in only small yield from K_2PtCl_4 and NH_2Me], and

[Pt(NH₂Me)₄]Br₂, which with conc. HBr gives the αisomeride of (I) and thence the α-chloride. Similarly are obtained β-di(ethylamino)platinous bromide, the β-chloride, and α-bromide, the nitrate of which is converted into the α-nitrite, -thiocyanate, and -chloride by the action of NaNO₂, KCNS, and HCl, respectively. The appropriate Pt^{II} salts with H₂O₂ and HCl afford α- and β-di(methylamino)platinic chloride, the corresponding thiocyanates, and the Et analogues of these compounds. The β-series do not react with phenoxtellurine dibisulphate nor afford salts of Cossa's type with boiling HCl, which indicates a structure similar to that of Pt enCl₂ (cf. A., 1933, 1282; 1934, 284; this vol., 100). J. L. D.

Formation of alicyclic hydrocarbons from free radicals. F. O. RICE and O. L. POLLY (Ind. Eng. Chem., 1935, 27, 915–916).—Hg di-n-heptyl (I) in CO₂ at 350° gives cyclohexane (II), n-C₇H₁₆, n-C₁₄H₃₀, and a cyclic hydrocarbon, b.p. 145–155°, n_D^{20} 1.4260. The formation of (II) is attributed to polymerisation of C₂H₄ formed during the decomp. of (I). F. R. G.

Influence of nuclear substituents on sidechain reactions.—See this vol., 1191.

1:3:5-Fluorodinitrobenzene. A. C. DE DE-GIORGI (Anal. Asoc. Quím. Argentina, 1935, **23**, 4— 7).—The diazonium solution from 3:5-dinitroaniline and NaNO₂ in aq. HCl with 40% HBF₄ gives 3:5dinitrobenzenediazonium borofluoride, decomp. 203°, which when heated gives 1:3:5-fluorodinitrobenzene, m.p. 43°. F. R. G.

Halogenation. X. Iodination of xylenes and iodoxylenes. P. S. VARMA and K. S. V. RAMAN (J. Indian Chem. Soc., 1935, 12, 343-344; cf. this vol., 1114).—Addition of fuming HNO_3 -nitrosulphonic acid mixture to o-, m-, or p-xylene and I in hot AcOH and subsequent heating for 20 min. gives good yields of 4-iodo-o-, 4-iodo-m-, and 2-iodo-pxylene (I), respectively, with a little nitroxylene. Heating for 5.5 hr. yields (?4:5-)di-iodo-o-xylene, m.p. 73°, 4:6-di-iodo-m-xylenc, m.p. 72°, and (?2:5-)di-iodo-p-xylene (II), m.p. 104°, also obtained similarly from the I₁-compounds. (I) and conc. H₂SO₄ at room temp. slowly form (II). R. S. C.

Electrochemical oxidation of benzene homologues. VI. Mesitylene. F. FICHTER and O. MULLER (Helv. Chim. Acta, 1935, 18, 831-840; cf. A., 1927, 348).—Electrochemical oxidation of $1:3:5 \cdot C_6H_3Me_3$ (I) in $0 \cdot 5N \cdot H_2SO_4$ emulsified with Nekal B.X. using a Pb anode and a Zn cathode gives $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$, $1:3:5 \cdot C_6H_3Me_2 \cdot CHO$ (II) $(0 \cdot 2\%)$

 $C_6H_3Me_2$ ·CO₂H (III), and 2:1:3:5-a quantity of resin, AcOH, HCO₂H, and CO₂. 79% of (I) was recovered unchanged. Electrochemical oxidation of (I) using a PbO2 anode and a diaphragm yields 13% of (II), 0.8% of (III) and (IV), 0.33% of (V), 0.33% of (VI), 0.03% of (VII), and 75% of unchanged (I). Oxidation of (I) (Pt anode and diaphragm) gives lower yields of the same products, whilst addition of conc. HNO3 and AcOH increases the yield of (III) to 6.6%. Electrochemical oxidation of (I) in presence of $1:3:5:2-C_6H_2Me_3\cdot SO_3H$ gives smaller quantities of oxidation products; (V) and (VII) (PbO₂ anode) give in each case CO₂, AcOH, and HCO₂H. Oxidation of PhMe in aq. H₂SO₄ (PbO₂ anode without diaphragm) gives in addition to pcresol (0.9%) and toluquinone (1.8%) (cf. A., 1914, i, 946), PhCHO (0.08%) and BzOH (0.4%).

F. R. G.

CXVI. polymerised compounds. Highly Polystyrenes with limited swelling power. Н. STAUDINGER and E. HUSEMANN (Ber., 1935, 68, [B], 1618-1634; cf. A., 1934, 879).-Divinylbenzene (I) becomes polymerised much more readily than styrene (II), forming a hard, glassy mass, very brittle and insol. in all org. media. It is incompletely depoly-merised with difficulty. The properties of the polymerisate are in harmony with its structure from threedimensional mols. (I) yields sol. polymerides when heated in C_6H_6 or PhMe at 100° or with $SnCl_4$ in C_6H_6 or CCl₄. Polymerisation of mixtures of (I) and (II) gives a non-homogeneous product, (I) undergoing change more rapidly and being followed by a mixture of (I) and (II). If (II) is in large excess, polymerisation of (I) does not occur and a homogeneous mixed polymeride is obtained. The amount of (I) necessary for the union of the threads of (II) is not directly ∞ the length of the thread mols. With eucolloidal polystyrenes the quantity of (I) requisite to produce an insol. polystyrene is extraordinarily minute, and the viscosity of a sol. colloid can be very greatly modified by a small addition of a molecule-binding material. Mixed polymerisates of limited swelling powers yield sol. polystyrenes to suitable solvents; the η_{ep}/c vals. of these are < those of pure polystyrenes prepared under like conditions. Further, the proportion of sol. material is greatest when least (I) is used and the extracted portions are more viscous than those derived from a more strongly bonded material. In the polystyrenes of limited swelling power the threedimensional mols. of the mixed polymeride are greatly interwoven with the simple thread mols. of polystyrene. Experiments on the swelling of the insol. mixed polymerisates in C₆H₆ show that the ability to swell depends only on the no. of points of union by (I) bridges and is independent of the chain-length of the polystyrenes. The thread mols. must therefore be regarded as rigid, elastic structures which cannot be deformed at will. Swelling is at a max. in solvents which cause complete solvation of the polystyrene mols. and is much less marked in those of small power of solvation. H. W.

Walden inversion reactions of d- β -butyl, d- β octyl, and d- β -benzylmethylcarbinyl p-toluenesulphonates. J. KENYON, H. PHILLIPS, and (MISS) V. P. PITTMAN (J.C.S., 1935, 1072-1084).-d-(+)β-Butanol with p-C₆H₄Me·SO₂Cl (cf. J.C.S., 1910, 97, 2585) in C_5H_5N below 0° affords d-(+) β -butyl dl-p-toluenesulphinate, b.p. 98—100°/<0·1 mm., which with KMnO₄ in aq. COMe₂ at 0° containing MgSO₄ gives $d-(+)\beta$ -butyl dl-p-toluenesulphonate (I), b.p. $95^{\circ}/<0.1$ mm., $[\alpha]_{61}^{20} + 7.00^{\circ}$ in EtOH, which with boiling EtOH containing the appropriate Na or K salt gives $(-)\beta$ -butyl thiocyanate [hydrolysed (KOH-EtOH) to the (-)disulphide, b.p. 95-97°/14 mm., and converted by hot HNO₃ into $(+)\beta$ -butanesulphonic acid, b.p. 125°/<0.1 mm.; the disulphide is reduced (Sn-HCl-AcOH) to the (-)thiol, b.p. 83-85°], (-)selenocyanate, b.p. 83-84°/16 mm. [the (+)selenocyanate, prepared from $l-(-)\beta$ -butyl dl-p-toluenesulphonate, with boiling KOH-EtOH gives $(+)\beta$ -butyl diselenide, b.p. $130^{\circ}/16 \text{ mm.}$], (-)acetate [(+) β -butyl acetate is similarly obtained], (-)benzoate [the (+)benzoate is obtained similarly], (-)cyanide [hydrolysed to (-)methylethylacetic acid], and (-)iodide. Resolution of *dl*-methylethylacetic acid (cf. A., 1899, i, 477; 1896, i, 203) gives the (+)acid, which is converted successively through the chloride, b.p. 119—120°, and amide, m.p. 156°, into $(+)\beta$ -butyl cyanide, b.p. 125—126°. (I) with boiling EtOH– K_2CO_3 affords $(-)Et \beta$ -butyl ether, b.p. 82—83°. $(-)\beta$ -Butyl n-butyl, b.p. 130—131°, and $(-)Ph \beta$ -butyl (-) β -Built n-ouige, b.p. 150-151, and (-) μ μ p-ouige ether, b.p. 92-93°/20 mm., are prepared similarly. (I) with piperidine at 100° gives (-)N- β -butyl-piperidine, b.p. 75-76°/25 mm. (platinichloride, m.p. 197-198°), also formed from (-) β -butylamine and the piperidic for pentamethylene bromide in boiling Et₂O, thereby establishing its configuration. dl-N-B-Butylpiperidine, b.p. $70^{\circ}/21$ mm., and $(-)\beta$ -butyl-p-toluidine, b.p. $136-138^{\circ}/25$ mm., are prepared similarly. (I) with NH₃ ($d \ 0.88$) under pressure at 100° affords a low yield of $(-)\beta$ -butylamine [(-)Bz derivative, m.p. 88-89°]. (I) with MgPhBr in Et₂O at 0° affords (-)β-butylbenzene (cf. A., 1926, 509), C6H6, and Ph2, whereas with MgEtBr it gives $(-)\beta$ -butyl bromide, b.p. 90-91° (cf. A., 1925, i, 802); the latter is also obtained, together with $p-C_6H_4Me\cdot SO_2Br$, from d-β-butyl p-toluenesulphinate and Br in CHCl3 (cf. A., 1929, 1164). Conversion of $(-)\beta$ -butanol into β -butyl bromide is accompanied by inversion (cf. A., 1932, 251). d- β -Butanol and quinoline with COCl, in Et₂O afford d-(+) β -butyl chloroformate, b.p. 24-25°/13 mm., which when heated alone or with MgCl₂ or HgCl₂ gives $(+)\beta$ -butyl chloride, but in C₅H₅N the (-)isomeride is formed (cf. A., 1930, 61; 1932, 251). The following are prepared by methods analogous to those used in the Bu series except where stated. $(-)N-\beta$ -octyl-piperidine, b.p. 125-126°/13 mm., and -p-toluidine, b.p. 163-164°/15 mm.; $(-)\beta$ -octyl thiocyanate, b.p. 119-120°/15 mm. [(+)β-octanesulphonic acid (Ba salt, m.p. >320°)]; $(-)\beta$ -bromo-octane, b.p. 78-79°/18 mm., and $(-)Ph \beta$ -octyl ether, b.p. 144-145°/20 mm. d- $(+)\beta$ -Octyl p-toluenesulphonate (A., 1926, 159) with KSH in boiling EtOH gives -) β-octylthiol, b.p. 78-80°/22 mm. [converted by Me₂SO₄ and Et₂SO₄ into (-)Me, b.p. 90-91°/18 mm., and $(-)Et \beta$ -octyl sulphide, b.p. 99-100°/17

mm.], and probably some (-)di- β -octyl sulphide, b.p. $135^{\circ}/2$ mm. The *l*-(-)*p*-toluenesulphonate with PhSNa in EtOH gives $(+)Ph \beta$ -octyl sulphide, b.p. 178°/20 mm. The relationship between $\lceil \alpha \rceil$ of the thiol and of its Me and Et ethers and λ indicates that the optically active thio-ethers show no complex rotatory dispersion (cf. A., 1924, i, 934). The following are prepared from d-(+)benzylmethylcarbinyl p-toluenesulphonate (II) (J.C.S., 1923, 123, 44) by methods similar to those used in the Bu series, except where stated. $(-)\beta$ -Piperidino-, b.p. 142-143°/11 mm., (-)β-p-toluidino-, b.p. 183-184°/11 mm., $(+)\beta$ -amino-, b.p. 102°/16 mm., and $(-)\beta$ -thiocyano- α phenylpropane, b.p. 158°/16 mm., and (-)β-phenylisopropyl disulphide, b.p. 144°/0·1 mm. (II) with boiling MeCN-H₂O and NaCN gives $(-)\beta$ -cyano- α -phenylpropane, b.p. 117°/17 mm., hydrolysed to the (-)acid (J.C.S., 1903, 83, 1005). (II) with NaSPh in EtOH gives $(-)Ph \alpha$ -phenyl- β -propyl sulphide, b.p. 177-178°/11 mm.; (-)α-phenyl-β-propylthiol, b.p. 105-110°/16 mm., is obtained by reducing the disulphide. (II) with LiCl in boiling EtOH gives $(-)\beta$ -chloro- α phenylpropane, b.p. $94^{\circ}/17$ mm., also obtained from (II) with MgEtCl in Et₂O. The *l*-(-)*p*-toluenesulphonate with NaBr in EtOH gives $(+)\beta$ -bromo- α -phenylpropane, b.p. 121°/17 mm., and with boiling EtOH containing Na₂S affords di-(α -benzylethyl) sulphide, b.p. 209°/16 mm. The vals. of [α] for these compounds bear out the finding of Rule (A., 1930, 1095), whose views are used as criteria in establishing the configuration of substances the directions of rotation of which have altered as a result of chemical reaction. A change of rotatory sign is unaccompanied by change in configuration if the asymmetric atom takes no part in the reaction (cf. A., 1924, i, 940). J. L. D.

Structure of naphthalene. L. F. FIESER and W. C. LOTHROP (J. Amer. Chem. Soc., 1935, 57, 1459—1464).—Existing evidence in favour of a static 1:2-ethylenic linking in $C_{10}H_8$ is reviewed and supported by the facts that alkyl at 3, 6, or 7 increase the rate of methylation of β - $C_{10}H_7$ ·OH by p- C_6H_4 Me·SO₃Me, whereas groups at 1 decrease it, and that halogen at 3 or 6 decreases it < does halogen at 1. The static formula (I) is indicated by the facts

that $2:6-C_{10}H_6(OH)_2$ (II) couples in the 1 and 8 positions, whereas 2:6-di-(I.) hydroxy - 1:5 - dialkylnaphthalenes do not couple, and that 2:6-diallyloxy-

naphthalenes rearrange only if the 1 and 5 positions are not substituted. $2:6-C_{10}H_6(OAc)_2$ gives (Friedel-Crafts) 2:6-dihydroxy-1:5-diacetonaphthalene, m.p. $<math>263^{\circ}$ (Me_2 ether, m.p. 216° ; with NaOEt-EtOH at 170° gives probably 2:6-dihydroxynaphthalene MeEt ether, m.p. 155°), the diacetate, m.p. 189° , of which is reduced by H₂-Cu chromite in EtOH at 170° to a product, which with HBr-AcOH in N₂ gives 2:6-dihydroxy-1:5-diethylnaphthalene, m.p. 262° (not obtained by other methods; Me_2 ether, m.p. 186°). The diallyl ether, m.p. 112° , of (II), obtained by the K₂CO₃-COMe₂ method, rapidly rearranges at 190° in N₂ to give 2:6-dihydroxy-1:5-diallylnaphthalene, m.p. 168° (dicoumarone derivative, m.p. 172° ; Me_2 , m.p. 113° , and diallyl ether, m.p. 100°). (II) and CH₂PhCl, best (70%) with Na in hot PhMe, give 2:6-dihydroxy-1:5dibenzylnaphthalene (III), +xEtOH, m.p. 191° (Ac_2 derivative, m.p. 226°), converted by Zn dust into $C_{10}H_8$ only. 2:6- $C_{10}H_6(OMe)_2$ and AlCl₃-BzCl at room temp. give 2:6-dihydroxy-1:5-dibenzoylnaphthalene, m.p. 282° [lit. 275°; does not give a vat dye with AlCl₃ (cf. lit.)], from which a poor yield of (III) was obtained by hydrogenation (Cu chromite). Hydrogenation (Cu chromite) of 1:6-dihydroxy-12pleiadone (IV) gives probably 2:7-dihydroxy-1-o-methylbenzylnaphthalene, m.p. 235—236°, but the Me₂ ether of (IV) gives 1:6-dimethoxydihydropleiadene, m.p. 163°, demethylated by HBr-AcOH to the 1:6-(OH)₂compound, m.p. 217°, the diallyl ether, m.p. 93°, of which does not rearrange. R. S. C.

Selenium dioxide, a new oxidising agent. V. Some further oxidations. S. ASTIN, L. DE V. MOULDS, and H. L. RILEY (J.C.S., 1935, 901-904).-The varied reactivity of SeO₂ with org. compounds cannot be explained on a theory of intermediate compound formation. The property of SeO₂ of giving the same spectrum when many substances are burnt in its vapour (A., 1933, 685) suggests that it may have the capacity for providing O atoms in a very low energy state, and that this capacity may be effective in sp. oxidations at lower temp. The first stage in these may be removal of activated H atoms, which may or may not be followed by addition of O in a low energy state. Et acetonedicarboxylate is oxidised by SeO, to Et $\alpha\beta$ -diketobutyrate (probably through Et $\alpha\beta$ diketoglutarate), with $H_2C_2O_4$ and organoselenium compounds. Et dl-malate gives Et diketosuccinate and fumarate, or, with excess of SeO₂, H₂C₂O₄, malic acid, Et H malate, b.p. 240°/35 mm., and Et H mesoxalate; organoselenium compounds are again also formed. Et β -phenylpropionate yields Et cinnamate and β phenylpropionic acid. Dibenzyl gives benzil and stilbene; the last also gives benzil. Et mandelate is oxidised to BzCO₂Et, also formed, less readily, from $CH_2Ph \cdot CO_2Et$. Anthracene yields anthraquinone; phenanthrene is less readily oxidised. NH_2Ph and SeO₂ in MeOH combine to an unstable compound, $C_7H_{11}O_3NSe, m.p. 56^\circ$; *p*-toluidine yields a compound, m.p. 67°. These results suggested combination of SeO_2 with MeOH, and these give in fact Me H selenite or methylselenonic acid, $MeHSeO_3$, m.p. 42°. Since the NH_2Ph compound does not furnish MeOH when treated with aq. NaOH, it is suggested that it is the NH₂Ph salt of methylselenonic acid, and not of Me H selenite. E. W. W.

Derivatives of 3:5-dihalogen-substituted anilines. F. D. CHATTAWAY and G. D. PARKES (J.C.S., 1935, 1005—1008).—The following are prepared: 3:5-dibromo-, m.p. 142°, and 2:3:4:5:6pentabromo-diacetanilide, m.p. 198°; 2:3:4:5-tetrachloro-, m.p. 165°, and 3:4:5:6-tetrabromo-acetanilide, m.p. 264°; 3:5-dichloro-o-, m.p. 202°, -m-, m.p. 195°, and -p-, m.p. 221°, and 3:5-dibromo-o-, m.p. 228°, -m-, m.p. 220°, and -p-nitrobenzanilide, m.p. 240°. 3:5-Dichlorobenzeneazo-2'- and -4'-phenol, m.p. 142° and 138°; 3:5-dibromobenzeneazo-2'- and -4'-phenol, m.p. 161° and 162°; 3:5:3':5'-tetrachloro- and 3:5:3':5'-tetrabromo-2:4-bisbenzeneazophenol, m.p. 236° and 274°; 3:5-dichloro-, m.p. 203°, 4 N 2:3:4:5-tetrachloro-, m.p. 252° , and 3:5-dibromo benzencazo- β -naphthol, m.p. 235° .

Benzaldehyde - and nitrobenzaldehyde - 3 : 5 - dichloro- and 3: 5-dibromo-phenylhydrazones etc. are halogenated to the following : ω -chloro-o-, -m-, and -p-nitrobenzaldehydepentachlorophenylhydrazone, m.p. 137°, 198°, and 208°; ω-bromobenzaldehyde-, m.p. 190°, and w-bromo-o-, -m-, and -p-nitrobenzaldehyde-2:3:4:5-tetrabromophenylhydrazone, m.p. 161°, 242°, and 268°; w-bromobenzaldehyde-, m.p. 179°, and wbromo-o-, -m-, and -p-nitrobenzaldehyde-pentabromophenylhydrazone, m.p. 240°, 255°, and 265°; m- and p-nitrobenzaldehydepentachlorophenylhydrazidine, m.p. 210° and 217°; benzaldehyde-, m.p. 171°, and m- and p-nitrobenzaldehyde - 2:3:4:5-tetrabromophenylhydr azidine, m.p. 218° and 248°; benzaldehyde-, m.p. 106°, and m- and p-nitrobenzaldehyde-pentabromophenylhydrazidine, m.p. 227° and 248°. Nitroso- $CO - N - N - N \cdot C_6 Cl_5,$ cycloazipentachlorobenztriazone,

explodes 128°, and the *-tetrabromo-*, explodes 155°, and *-pentabromo-*, explodes 157°, analogues are prepared.

3: 5-Dichlorobenzenediazonium chloride and similar salts combine readily with Et acetoacetate. The following Et esters are prepared: 3: 5-dichloro-, m.p. 106°, 3: 5-dichloro-4-bromo-, m.p. 127°, 3: 5-dibromo-, m.p. 96°, and 3: 4: 5-tribromo-benzeneazoacetoacetate, m.p. 146°; α -bromoglyoxylate-3: 5-dichloro-4-bromo-, m.p. 176°, -3: 4: 5-tribromo-, m.p. 129°, α -chloro-glyoxylate-3: 5-dichloro-4-bromo-, m.p. 176°, -3: 4: 5-tetrachloro-, m.p. 128°; α -amino-glyoxylate-3: 5-dichloro-4-bromo-, m.p. 180°, and -2: 3: 4: 5-tetrachloro-4-bromo-, m.p. 180°, and -2: 3: 4: 5-tetrachloro-phenylhydrazone, m.p. 148°; 3: 5-dichlorobenzeneazo- γ -bromo-, m.p. 110°, and - $\gamma\gamma'$ -dibromo-, m.p. 126°, 3: 5-dichloro-4-bromobenzeneazo- γ -bromo-, m.p. 125°, and 3: 5-dibromobenzeneazo- γ -bromo-, m.p. 134°, and - $\gamma\gamma'$ -dibromo-acetoacetate, m.p. 123°.

 $\beta\beta\omega$ -Tribromo- α -ketopropaldehyde-3 : 5-dichloro-2 : 4dibromophenylhydrazone,

CHBr₂·CO·CBr.N·NH·C₆HCl₂Br₂, has m.p. 223°. 4-Hydroxy-, m.p. 154°, and 5-bromo-4-hydroxy-, m.p. 156°, -3-carbethoxy-1-(3': 5'-dichlorophenyl)pyrazole, and 4-hydroxy-3-carbethoxy-1-(3': 5'-dibromophenyl)pyrazole, m.p. 154°, are prepared; the acetates of these three compounds have m.p. 123°, 101°, and 125°, respectively. E. W. W.

N-Benzhydryl-N'-arylformamidines. L. E. HINKEL, E. E. AYLING, and J. H. BEYNON (J.C.S., 1935, 1219—1220).—When heated with ArNH₂, benzhydrylformamidine (I) gives N-benzhydryl-N'arylformamidines; the following are obtained from (I) and the appropriate base: N-benzhydryl-N'-phenylformamidine (II), m.p. 126.5°; N-benzhydryl-N'-p-tolylformamidine, m.p. 131°; N-benzhydryl-N'-p-chlorophenylformamidine, m.p. 124°; N-benzhydryl-N'-panisylformamidine, m.p. 137°; N-benzhydryl-N'-2naphthylformamidine, m.p. 115°. Boiling 4N-HCl converts (II) into (I) and NH₂Ph,HCl; the other compounds of the same class behave similarly. At 150—160° (II) with CH₂Ph·CN affords β -benzhydrylamino- α -phenylacrylonitrile, m.p. 141°. From (II) and CH₂(CO₂Et)₂ at 145—150°, Et benzhydrylaminomethylenemalonanilide, m.p. 145°, is obtained, and similarly CH₂Ac•CO₂Et gives benzhydrylaminomethyleneacetoacetanilide, m.p. 154°. P. G. C.

Effect of substituents on reactivity of functional groups. E. HERTEL and J. DRESSEL (Z. physikal. Chem., 1935, B, 29, 178–191).—This influence can be determined only by observation of the reactivity of these groups in simple addition reactions, or intramol. changes within the groups. Kinetic measurements show that the ability of the NMe₂ group in the substances C_6H_4X ·NMe₂ to take up a third Me by adding trinitroanisole increases as X is varied in the order NO₂, CN, Br, H, Me, OMe, NMe₂. From electrometric titration of the base with HClO₄ in AcOH it appears that the affinity of the NMe₂ in NPhMe₂ for H increases as X changes in the order NO₂, CN, Br, H. The additive power of the bases for pieric acid has also been examined. R. C.

Action of acetic anhydride on N-nitrosophenylglycine and some of its derivatives. J. C. EARL and A. W. MACKNEY (J.C.S., 1935, 899–900).—When N-nitrosophenylglycine (new prep. by treating a solution of phenylglycine in aq. NaNO₂ with HCl) is treated with Ac₂O, the product, $C_8H_6O_2N_2$, m.p. 134—134.5°, is best formulated NPh $<_{CH+CO}^{N-O}$. It is decomposed by HCl to NHPh·NH₃Cl and HCO₂H, and by NaOH to N-nitrosophenylglycine. N-Nitroso- α anilinopropionic acid, decomp. 80—81° (prepared from α -anilinopropionic acid), similarly gives a substance, $C_9H_8O_2N_2$, m.p. 98—99°, decomposed by HCl to

 α -anilinopropionic acid), similarly gives a substance, C₉H₈O₂N₂, m.p. 98—99°, decomposed by HCl to NHPh·NH₃Cl and AcOH, and by NaOH to its starting material. The N-NO-derivative, decomp. 117°, of α -anilinoisobutyric acid (best obtained from the nitrile by way of the amide) is unchanged by Ac₂O. E. W. W.

β-Substituted ethylamines. I. Preparation of β-phenylethylamines from ω-nitrostyrenes. O. SCHALES (Ber., 1935, 68, [B], 1579—1581).—β-Phenylethylamines are obtained in good yield by slow addition of ω-nitrostyrenes in AcOH to the Adams catalyst in AcOH-H₂SO₄ in presence of H₂. The prep. of homopiperonylamine and β-3-aminophenylethylamine is described. H. W.

Animines from cyclic diamines and metallic salts.—See this vol., 1087, 1089.

Oxidation-reduction indicators. I. Diphenylbenzidinesulphonic acid.—See this vol., 1092.

Mechanism of diazotisation. J. REILLY and P. J. DRUMM (J.C.S., 1935, 871-873).—On the Hantzsch-Schumann view of diazotisation as reaction between ArNH₃[•] and undissociated HNO₂, amines should, in absence of excess of mineral acid, diazotise faster the greater is their basicity, and the rate should not be appreciably affected by excess of acid over that required to prevent hydrolysis of the amine salt. This is confirmed by experiment. Of the amines $NH_2 \cdot C_6 H_4 \cdot NMe_3 Cl$ (I), $NH_2 \cdot C_6 H_4 \cdot CH_2 \cdot NMe_3 Cl$ (II), and $NH_2 \cdot C_6 H_4 \cdot [CH_2]_2 \cdot NMe_3 Cl$ (III), the effect of the positive ($\cdot NMe_3$) pole in attracting unshared electrons and thus reducing basicity will be least in (III), and greatest in (I), and the basicity will be in the order (III)>(II)>(I); it is found that the velocity coeffs. of diazotisation (at 1° and 0.001N solution), without excess of HCl, are less in the same order. Confirming the second deduction, the rate for any of the three is approx. the same whether 2 or 4 mols. excess of HCl are present. (II) is obtained by reducing dimethyl-p-nitrobenzylamine, b.p. 150°/20 mm. (picrate, m.p. 151°), to the p-NH2-compound (azo-\beta-naphthol derivative, m.p. 129.5°), converting the p-NHAc-compound, m.p. 103°, into trimethyl-pacetamidobenzylammonium iodide, m.p. 232°, and this (AgCl, HCl) into trimethyl-p-aminobenzylammonium chloride hydrochloride, m.p. 194-196°, decomp. 270°. (III) is obtained by converting trimethyl-β-p-nitrophenylethylammonium picrate (A., 1927, 236) into the hydrochloride and reducing to trimethyl-B-paminophenylethylammonium chloride hydrochloride, m.p. 283°. E. W. W.

Electrolytic reduction of *m*-halogenonitrobenzenes to the azo-compounds. T. Y. CHANG and D. S. WANG (J. Chinese Chem. Soc., 1935, 3, 218—222).—3:3'-Dichloro-, -dibromo-, and -di-iodoazobenzene are prepared electrolytically from the NO₂-compounds, using a rotatory Ni cathode and 75% EtOH (without NaOAc) as solvent.

E. W. W. Fat-soluble azo-dyes. II. Dyes from palmitic acid. O. ROUTALA and E. PULLINEN (Suomen Kem., 1935, 8, B, 29).—Palmitic acid and β -C₁₀H₇·NH₂ condense to form *palmit*- β -*naphthylamide*, m.p. 110— 111°, which is converted into the NO_2 -, m.p. 87—88°, and NH_2 -, m.p. 160—162°, -derivatives, and thence, by diazotisation and coupling, into α - and β -*naphthylamineazopalmit*- β -*naphthylamide*, m.p. 155—158° and 134—139°, respectively, red dyes sol. in fats and fatty acids. *Palmit*- α -*naphthylamide* has m.p. 112—113°. E. W. W.

Azo dyes [from N-sulphato-ethyl- or -propylanilines].—See B., 1935, 797.

Carvacrol. III. H. JOHN and P. BEETZ (J. pr. Chem., 1935, [ii], 143, 253-258).-Mainly a correction to previous work (A., 1933, 827). Owing to the presence of thymol in the sample of carvacrol previously used the compound there described as 5-acetocarvacrol is actually 6-acetothymol, its NO₂derivative is the 2-compound (I) (2-nitro-3-hydroxy-6-acetyl-1-methyl-4-isopropylbenzene), and the (NO₂)₂-derivative is the 2:5-compound, all other The derivatives requiring corresponding correction. compound described as 3-acetocarvacrol is actually 5-acetocarvacrol (II), and its NO2-derivative is the 3-compound (III), thus necessitating appropriate correction to all derivatives. Pure carvacrol, b.p. 237.5°, m.p. 1°, with AlCl₃-AcCl in PhNO₂ gives (II), m.p. 101°. Condensation of 6-acetothymol with p-NO2. C6H4. N2Cl affords 4'-nitro-2-hydroxy-5-acetyl-6-methyl-3-isopropylazobenzene, m.p. 206°, reduced (alkaline Na₂S₂O₄) to 2-amino-6-acetylthymol, m.p. 100°, identical with the compound (loc. cit.) obtained by reduction of (I). (II) and p-NO₂·C₆H₄·N₂Cl similarly afford 4'-nitro-2-hydroxy-5-acetyl-3-methyl-6isopropylazobenzene, m.p. 194°, reduced to 3-amino-5-acetylcarvacrol, m.p. 117°, identical with the compound previously obtained by reduction of (III). J. W. B.

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Therapeutic substances derived from unsymmetrical diphenyl compounds. III. Arylesters of hydroxydiphenyls. S. E. HARRIS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1935, 24, 553-557).—The following were prepared, but havo no val. as urinary disinfectants: benzoates of o- (I), m.p. 75-76°, m., m.p. 57-58°, and p-C₆H₄Ph·OH, m.p. 148·5-149·5°, 6- (II), m.p. 86-87°, and 4-chloro-, m.p. 88·5°, 4-bromo-, an oil, and 4-n-propyl-2-hydroxydiphenyl (III), m.p. 96°, x-chloro-3-, an oil, and 2-chloro-4-hydroxydiphenyl, m.p. 110-111°, and 5:7-dichloro-8-hydroxydiphenyl, m.p. 110-111°, and 5:7-dichloro-8-hydroxydiphenyl, m.p. 100-111°, and 5:7-dichloro-8-hydroxydiphenyl, m.p. 104°, (II), m.p. 107°; cinnamates of (I), m.p. 103-104°, (II), m.p. 185-186°, and acetylsalicylate, m.p. 71·5-72·5°, of (I); K sulphate of (II), decomp. 225-230°, and (III), decomp. 180-190°. The $p_{\rm II}$ of rabbits' urine is variable; that with $p_{\rm II} > 7\cdot5$ or $< 6\cdot5$ is very often germicidal.

Anionotropic and prototropic changes in cyclic systems. V. System derived from 1-hydroxyindene. H. BURTON and C. W. SHOPPEE (J.C.S., 1935, 1156-1161).-1-Hydroxy-1-phenyl-2-methylindene (I), b.p. 157°/0.6 mm., m.p. 59°, with Ac2O (7 hr.; reflux) affords, by anionotropic change, 1-acetoxy-3-phenyl-2-methylindene (II) (two forms, a, m.p. 75-76° to a turbid liquid clearing at 90-91°: β , m.p. 90—91°), which undergoes with EtOH-KOH prototropic change to 3-phenyl-2-methylhydrindanone. With SOCI₂ (I) affords 1-chloro-3-phenyl-2-methylindene, m.p. 47°, converted by AgOAc-AcOH into (II). 2:3-Dimethylindenone, m.p. 80° [2:4-dinitrophenylhydrazone, m.p. 273—274° (decomp.); semicarbazone, m.p. 197°], is obtained directly from Et β -hydroxy- β -phenyl- α -methylbutyrate, or by ringclosure of cis-+trans- $\alpha\beta$ -dimethylcinnamic acid (prep. methods of A., 1914, i, 281 are confirmed; cf. A., 1927, 257). With MgPhBr it gives 1-hydroxy-1-phenyl-2: 3-dimethylindene, b.p. 175°/0.4 mm., converted into resins when treated with Ac₂O or Ac₂O- H_2SO_1 ; neither resin gives CH_2O on ozonolysis. P. G. C.

4'-Hydroxy-1: 2-benzpyrene. L. F. FIESER, E. B. HERSHBERG, and M. S. NEWMAN (J. Amer. Chem. Soc., 1935, 57, 1509—1510).—4'-Keto-1':2':3':4'-tetrahydro-1:2-benzpyrene with Se (1 atom; 310—320°; 2 hr.) gives a poor and with S (220—230°; 75 min.) a 19% yield of 4'-hydroxy-1:2benzpyrene, m.p. 218—219° (acetate, m.p. 194—195°; benzoate, m.p. 191—192°; Me ether, m.p. 183—184°; $CO_{2}Mc$ -derivative, m.p. 239—240°; red colour in conc. H₂SO₄ with 1 drop of HNO₃ turns blue by way of green). M.p. are corr. R. S. C.

Dissociable organic oxides. Reversible oxidisability of the anthracene structure : dissociable oxide of 9:10-diphenylanthracene. C. DUFRAISSE and A. ÉTIENNE (Compt. rend., 1935, 201, 280— 282).—On theoretical grounds, 9:10-diphenylanthracene should be reversibly oxidisable, and it does in fact absorb O_2 when insolated in solution, forming a *photo-oxide*, which dissociates at 200°. E. W. W.

2-Amino-3:4-dimethoxytoluene. E. LEH-MANN and W. PAASCHE (Ber., 1935, 68, [B], 15201523).—2-Nitroveratraldehyde (I) is converted by PCl_5 into 2-nitro-3:4-dimethoxybenzylidene chloride, m.p. 43°, which could not be satisfactorily reduced catalytically. (I) is reduced by $FeSO_4$ -NH₃ to 2-aminoveratraldehyde, m.p. 38° (oxime, m.p. 124°), convorted by Zn-Hg and 6N-HCl into 2-amino-3:4dimethoxytoluene (III), b.p. 137°/15 mm. (hydrochloride, m.p. 233°; Bz derivative, m.p. 142°), better obtained similarly and directly from (I). (III) is diazotised and transformed by CuCN into 2-cyano-3:4-dimethoxytoluene, b.p. 154—157°/15 mm., m.p. 34°, which cannot be hydrolysed by acid or alkali, but is transformed by prolonged boiling with KOH in amyl alcohol into 2-cyano-4-hydroxy-3-methoxytoluene, m.p. 114°. H. W.

Preparation of 2- and 4-allylresorcinol and their transformation into hydroxy-1-chloromercurimethyl-1:2-dihydrobenzofurans. A. N. NESMEJANOV and T. S. SAREVITSCH (Ber., 1935, 1476-1479).-Gradual addition 68. [B], of CH,:CH.CH,Cl to a solution of resorcinol and Na in MeOH gives the allyl ether, which becomes isomerised during distillation to 4-allylresorcinol (I), b.p. 144-146°/10 mm., m.p. 67°, catalytically reduced to 4-propylresorcinol, m.p. 77°. β-Methyl-umbelliferone is converted by NaOMe and CH,:CH. CH, Cl in MeOH into the allyl ether, m.p. 102.5—103°, which is isomerised at 235° to methyl-allylumbelliferone, m.p. 195—196°, converted by boiling aq. NaOH into 2-allylresorcinol (II), m.p. 52°. (II) is hydrogenated to 2-propylresorcinol, m.p. 99–101°, and transformed by $HgCl_2$ in H_2O into 3-hydroxy-1-chloromercurimethyl-1: 2-dihydrobenzofuran, m.p. 151-152°. (I) similarly affords 5-hydroxy-1-chloromercurimethyl-1: 2-dihydrobenzofuran, m.p. 148-149°. H. W.

Bromination of resorcinol monobenzoate and nitration of 4:6-dibromoresorcinol 3-benzoate. Example of group migration. H. H. HODGSON and (in part) R. J. H. DYSON (J.C.S., 1935, 946-948).-In dry CHCl₃, resorcinol 3-benzoate (I) is brominated in three stages, in the 6, 4, and 2 positions. Its activated structure is therefore formulated as $BzO \cdot C \ll CH \cdot C(OH) > CH$. The first product (obtained only when the CHCl₃ is dry) is 6-bromoresorcinol 3-benzoate, m.p. 169°, which with Me₂SO₄ gives 6-bromoanisyl 3-benzoate, m.p. 140°, hydrolysed to 6-bromo-3-hydroxyanisole, which with NaNO2 forms 4-bromo-6-nitroresorcinol 3-Me ether, m.p. 114°, identified by prep. from 6-nitroresorcinol 3-Me ether and Br in CHCl₃; further bromination (NaOBr) gives 2:4-dibromo-6-nitroresorcinol 3-Me ether, m.p. 128°. For comparison, 4-bromoanisyl 3-benzoate, m.p. 65°, is prepared by converting 3-nitro-*p*-anisidine (Sandmeyer) into 4-bromo-3-nitroanisole, m.p. 32°, reducing to 4-bromo-m-anisidine (hydrochloride, m.p. 186°), and benzoylating the 4-bromo-3-hydroxyanisole thence obtained. Dibromination of (I) gives 4:6-dibromoresorcinol 3-benzoate, m.p. 155°, hydrolysed to 4:6-dibromoresorcinol; both these with BzCl yield the dibenzoate, m.p. 164°. 4:6-Dibromoresorcinol mixed with K2CO3 and treated with Me2SO4 gives 4:6-dibromoresorcinol Me₂ ether, m.p. 65°;

in aq. Na₂CO₃, 4:6-dibromoanisyl 3-benzoate, m.p. 95°, is formed. By nitration in AcOH, 2:4-dibromo-6-nitroresorcinol 3-benzoate, m.p. 141°, is obtained (scarlet Na salt), hydrolysed to 2:4-dibromo-6nitroresorcinol; nitration by diacetylorthonitric acid in Ac₂O gives a product, m.p. 130°, hydrolysed to a mixture of red and yellow crystals, m.p. 145°, apparently 4:6-dibromo-2-nitro- and 2:4-dibromo-6-nitroresorcinol. By tribromination, 2:4:6-tribromoresorcinol 3-benzoate, m.p. 120°, is formed. Resorcinol or its Me₁ ether dissolved in AcOH and treated first with oleum, then with HNO₃, yields respectively 2-nitroresorcinol, m.p. 85°, and 6-nitroresorcinol 3-Me ether, m.p. 95°; the former with Br in AcOH gives 4:6-dibromo-2-nitroresorcinol. E. W. W.

Oxidation of quinol solutions. III.—See this vol., 1083.

Lichen substances. LIV. Constitution of physodic acid. III. Y. ASAHINA and H. NOGAMI (Ber., 1935, 58, [B], 1500-1503; cf. this vol., 490).-Et 3:5-dimethoxybenzoylacetate is transformed by NaOEt and $Pr^{\alpha}I$ in EtOH into Et α -3:5dimethoxybenzoyl-n-valerate, m.p. 44-45°, which with 6% H₂SO₄ at 195° affords 3 : 5-dimethoxyvalerophenone (I), m.p. 42-43° (semicarbazone, m.p. 204°). Re-duction of (I) with Zn-Hg and HCl proceeds unsatisfactorily, whereas treatment with N₂H₄,H₂O and of the product with KOH at 220-245° affords 3: 5-dimethoxy-1-n-amylbenzene (olivetol Me, ether), b.p. $114^{\circ}/2$ mm. (Br_2 -derivative, m.p. $74.5-75.5^{\circ}$), in good yield, converted by HI into olivetol (II). Treatment of (II) with Br (0.5 mol.) in AcOH yields bromo- ($+2H_2O$) m.p. 61°, and dibromo-olivetol. Bromo-olivetol Me2 ether, Cu-bronze, and the K derivative of orcinol at 180-220° afford protophysodon Mc_3 ether, the Br_3 -derivative of which is identical with that derived from physodic acid. H. W.

Interaction of organomagnesium compounds with naphthalene- and phenanthrene-carboxylic esters. G. DARZENS and A. LEVY (Compt. rend., 1935, 201, 152-154).-Me 1-methyl-3-naphthoate (A., 1926, 1239) and MgMeBr in Et₂O afford 1-methyl-3-naphthyldimethylcarbinol, which loses H2O above 125° yielding 1-methyl-3-isopropenylnaphthalene, b.p. 154°/12 mm. (picrate, m.p. 81-81.5°). This readily polymerises to a high-melting compound, and is reduced by EtOH-Na to 1-methyl-3-isopropylnaphthalene (I), b.p. 150°/11 mm. (picrate, m.p. 84°; styphnate, m.p. 119°). Similarly Me 1-methyl-1:2:3:4-tetrahydronaphthalene-3-carboxylate (loc. cit.) and MgMeBr afford 1-methyl-1:2:3:4-tetrahydro-3-naphthyldimethylcarbinol, b.p. 159-161°/10 mm., dehydrated by $KHSO_4$ at 150° to a mixture of unsaturated compounds, b.p. 139-141°/15 mm. This mixture is reduced by boiling Na-EtOH to 1-methyl-3-isopropyl-1:2:3:4-tetrahydronaphthalene, b.p. 138-139°/16 mm., dehydrogenated by S and by Se to (I). Me 1-methylphenanthrene-3-carboxylate, m.p. 123° (cf. this vol., 975), and MgMeBr afford 1methyl-3-phenanthryldimethylcarbinol, m.p. 115°, de-hydrated to 1-methyl-3-isopropenylphenanthrene, b.p. $192^{\circ}/2$ mm., which readily polymerises. It is readily reduced by Na-EtOH to 1-methyl-3-isopropylphenanthrene (II), m.p. 79°, b.p. 18°/1.5 mm. (picrate, m.p.

150°; styphnate, m.p. 155°; the corresponding quinone has m.p. 167—168°). Me 1-methyl-1: 2:3:4tetrahydrophenanthrene-3-carboxylate (cf. loc. cit.) and MgMeBr afford 1-methyl-1: 2:3:4-tetrahydrophenanthryldimethylcarbinol, b.p. 189°/2 mm., dehydrated by KHSO₄ to a mixture of unsaturated compounds, b.p. 210°/2.5 mm. This is reduced to 1-methyl-3isopropyl-1: 2:3:4-tetrahydrophenanthrene, b.p. 208°/ 23 mm. (picrate, m.p. 67°; styphnate, m.p. 128°), dehydrogenated by S and by Se to (II). H. G. M.

Optically active diphenylhydroxyethylamines and isohydrobenzoins. VI. Di-o-methoxy-phenylhydroxyethylamines and related subphenyinydroxyethylamines and related sub-stances. N. A. B. WILSON and J. READ (J.C.S., 1935, 1120—1123).—The prep. of NH₂-alcohols, Ar·CH(OH)·CH(NH₂)·Ar (from Ar·CHO, NH₂·CH₂·CO₂H, and alkali; A., 1905, i, 131), fails with α - and β -C₁₀H₇·CHO, heptaldehyde, and the following heppaldohydeau m OM following benzaldehydes: m-OMe-, o- and m-NO2p-NMe₂-, o-OBz-, and 3: 4-(OMe)₂-. o-OMe·C₆H₄·CHO affords dl-isodi-o-methoxyphenylhydroxyethylamine (I), m.p. 136° (Ac derivative, m.p. 180°, does not react with HNO,; benzylidene derivative, m.p. 131°). (I) with d-tartaric or d-camphor-10-sulphonic acid gives l-isodi-o-methoxyphenylhydroxyethylamine (II), m.p. 111°, $[\alpha]_{\rm D} = 52.7^{\circ}$ in EtOH (Ac_2 derivative, m.p. 170°; salicylidene derivative, m.p. 106° , $[\alpha]_{\rm D} - 24.0^{\circ}$ in EtOH). (I) gives cis- $\alpha\beta$ -di-o-methoxyphenylethyl-EtOH). ethylene oxide, m.p. 127-128° [also obtainable from (II)], when converted into dl-isodi-o-methoxyphenylhydroxyethyltrimethylammonium iodide, m.p. 183-184°, and heated with Ag₂O-H₂O. A dil. H₂SO₄ solution of (II) affords with HNO2 an oil (optically inactive, Ac val. 7.4), probably a mixture of 30% of di-o-methoxyhydrobenzoin, 34% of di-o-methoxy-phenylacetaldehyde (III) (semicarbazone, m.p. 204°), and 36% of unidentified material. Di-o-methoxy-deoxybenzoinsemicarbazone, m.p. 196°, is prepared from the oil obtained by Zn-dust distillation of di-omethoxybenzoin; the last-named with Na-Hg affords di-o-methoxyhydrobenzoin, converted by hot 20% H₂SO₄ into di-o-methoxyhydrobenzoin anhydride, m.p. 175.5°, and (III). From di-o-methoxybenzoinoxime and Na-EtOH, 1-di-o-methoxyphenylhydroxylamine H d-tartrate, m.p. 160°, $[\alpha]_{D}$ - 66.0° in H₂O, is obtained. The mother-liquors contain dl-a-aminodi-o-methoxydibenzyl, m.p. 60° (Ac derivative, m.p. 156°; salicylidene derivative, m.p. 83.5°). dl-isoDi-o-chlorophenylhydroxyethylamine, m.p. 151.5° (Ac derivative, m.p. 160° ; Ac₂ derivative, m.p. 184° ; benzylidene derivative, m.p. 146.5°; salicylidene derivative, m.p. 130.5°), is not resolved by d-tartaric acid or l-menthoxyacetic acid, or by way of the methylenecamphor route, but a specimen of the base regenerated from the d-camphor-10-sulphonate had m.p. 152-152.5°, $[\alpha]_{\rm D}$ +3.5° in EtOH.

Electrolytic reduction of the following aldehydes is mentioned (products in parentheses): PhCHO (hydro-+iso-hydro-benzoin), anisaldehyde (hydro-+isohydro-anisoin), m-OMe·C₆H₄·CHO (m-methoxybenzyl alcohol; 3:5-dinitrobenzoate, m.p. 124°), o- and m-nitro- and p-dimethylamino-benzaldehyde (resins), $1 \cdot C_{10}H_7$ ·CHO ($1 - C_{10}H_7$ ·CO₂H), o- OMe·C₆H₄CHO (corresponding alcohol and acid). P. G. C.

Solubility of cholesterol in certain acyclic amines. M. VILLARET, L. JUSTIN-BESANÇON, and M. DRILHON (Compt. rend. Soc. Biol., 1935, 119. 1317-1319).-Dissolution of cholesterol (I) in NMe. is accompanied by a loss of some of the titratable alkalinity of the latter, which is ∞ the amount of (I). H. G. R.

Chemistry of some irradiation products of ergosterol. I. M. HEILBRON and F. S. SPRING (Chem. and Ind., 1935, 795-797).-In reply to Rosenheim et al. (this vol., 1120) it is pointed out that ring scission during the changes ergosterol-lumisterol $(I) \rightarrow tachysterol (II) \rightarrow calciferol (III) occurs during$ the transition $(I) \rightarrow (II)$. A definite allocation of the second nuclear ethenoid linking of (I) is not yet possible. It is fair to assume that (II) and (III) possess the same ring structure and differ in the position of their ethenoid linkings. Since the change $(I) \rightarrow (II)$ is accompanied by ring opening, the seat of this change is the unsaturated ring B, a point which is supported by the non-formation of C6HMe4·CO2H on

Me oxidation of (III) with HNO₃. of (II) and (III) depending on the mode of scission of the unsaturated ring B of (I) are considered, all of which are eliminated except (IV) by the formation of the aldehyde

C20H33 CHO by mild oxidation of (III) or its acetate (this vol., 1036). H. W.

(IV.)

Me

OH

Sterol group. XX. Partial reduction of fucosterol. D. H. COFFEY, I. M. HEILBRON, F. S. SPRING, and H. R. WRIGHT (J.C.S., 1935, 1205-1207).—Fucosteryl acetate is hydrogenated (Pd) to a mixture of a-dihydrofucosteryl acetate (I), m.p. 133-134°, $[\alpha]_{10}^{20}$ -43.53°, and the β-form (II), m.p. 121-122°, $[\alpha]_{10}^{20}$ -38.7°. Hydrolysis of (I) with EtOH-KOH gives a-dihydrofucosterol (III), m.p. 136-137°, $[\alpha]_{p}^{20}$ -38.43°, which contains 1 double linking (BzO₂H titration) and is converted by H₂ and Adams' PtO₂ catalyst into stigmasterol (IV), oxidised to stigmastanone (V). (II) on hydrolysis gives β -dihydro-fucosterol (VI), m.p. 132–133°, [α]⁵⁰ –30.36°, which also contains 1 double linking and gives (IV) on hydrogenation. CrO_3 oxidation of (III) affords α -fuco-stenone, m.p. 158° (2:4-dinitrophenylhydrazone, m.p. 272°), and similarly (VI) affords β -fucostenone (VII), m.p. 135—136° (2:4-dinitrophenylhydrazone, m.p. 185°). Reduction of fucosterol with Na-amyl alcohol affords epi-β-dihydrofucosterol (VIII), m.p. 159°, [a]20 $+12\cdot2^{\circ}$ (Ac derivative, m.p. 86°; dibromide, m.p. 139°), hydrogenated to epifucostanol, m.p. 173.5-174.5°. The latter is converted by CrO₃-AcOH into (V); the same reagent oxidises (VIII) to (VII). All vals. of $[\alpha]$ are in CHCl₃. P. G. C.

Interaction of thionyl chloride with m- and paminobenzoic acids. P. CARRE and D. LIBERMANN (Compt. rend., 1935, 201, 147-149).-Contrary to the conclusions of Michaelis et al. (A., 1893, i, 515), m-NH₂·C₆H₄·CO₂H (I) and SOCl₂ in C₆H₆ afford the diamide $C_6H_4 < C_{O^*NH}C_6H_4$ (II) (cf. A., 1883, 999).

Contrary to the conclusions of McMaster et al. (A., 1928, 271), (I) when heated with 6 mols. of SOCl₂ affords m-thionylaminobenzoyl chloride, m-COCl·C₆H₄·NSO (decomp. on distillation in vac.). With H₂O this yields mainly (II) (and some polymeride), HCl, and SO_2 , and with EtOH it yields (II), HCl, $SO(OEt)_2$, and a little Et *m*-thionylaminobenzoate (cf. A., 1893, i, 515). Similarly p-NH₂·C₆H₄·CO₂H (III) with excess of SOCl. affords p-thionylaminobenzoyl chloride, b.p. 147-150°/27 mm. (decomp.). With H₂O this yields HCl, SO₂, and an insol. substance, m.p. 325°, hydrolysed by alkalis to (III) and considered to be the diamide corresponding with (II). H. G. M.

Anthracene series. X. E. DE B. BARNETT, N. F. GOODWAY, and E. V. WEEKES (J.C.S., 1935, 1102—1104).—Anthracene (I), when boiled during 8 hr. in o-C₆H₄Cl₂ with CH₂Cl·CH₂·CO₂H (II), yields αβ-endo-9:10-dihydroanthraquinyl-9:10-propionic acid, m.p. 186°. The corresponding compounds prepared from (II) and 1: 4-dimethyl-, 9: 10-dichloro-, and 9:10-dibromo-anthracene have m.p. 250°, 245°, and 252°, respectively, and show no visible fluor-escence. The last two products gave no ionised halogen when boiled for 40 min. with 10% NaOH-EtOH. $\alpha\beta$ - endo - 9 : 10 - Dihydroanthraquinyl - 9 : 10 - β - phenylpropionic acid (III), m.p. 248°, is obtained when HCl is passed during 12 hr. into a solution of (I) and CHPh: $CH \cdot CO_2H$ in boiling $o \cdot C_6H_4Cl_2$. The following compounds were obtained by boiling (II) in $o-C_6H_4Cl_2$ with the appropriate anthrone during 8 hr. When the latter contains a substituent peri to the CO, an anthronylpropionic acid is formed, otherwise the product is an anthronylidenedipropionic acid : anthronylidenedipropionic acid, m.p. 248-250° (decomp.); 2:3-dimethylanthronylidenedipropionic acid, m.p. 298°; 1:5-dichloro-, m.p. 163°, 1:8-dichloro-, m.p. 204°, 4:5-dichloro-, m.p. 174°, 1:4-dimethyl-anthronyl-propionic acid, m.p. 168°. This last is reduced by boiling with Zn (activated by CuSO₄) and 2N-NaOH for 4 hr. to 1: 4-dimethylanthranylpropionic acid, m.p. 205°, neutral and alkaline solutions of which are strongly fluorescent. Reduction of the other anthronylpropionic acids gave uncrystallisable products, sol. in alkali. β-Phenyl-β-anthronylpropionic acid, m.p. 197° [obtained by passing HCl during 15 hr. through a boiling solution of anthrone (IV) and CHPh:CH·CO₂H in $o - C_6 H_4 Cl_2$], is reduced by Zn-NaOH-H₂O to β phenyl-\u03b3-anthranylpropionic acid, m.p. 225° (strongly fluorescent in neutral and alkaline solution). This and its isomeride (III) are not interconvertible. (IV)with CHCl₂·CO₂H, KOH, and boiling H₂O yields a little anthronylideneacetic acid, m.p. 205° (nonfluorescent). (IV) and (I) did not, however, condense with CH₂Cl·CO₂H. CHPh:CH·COCl with (IV) gave only resinous products, but when boiled with 1:5dichloroanthrone, KOH, and H2O yields 1: 5-dichloro-10-cinnamylanthrone, m.p. 148°, oxidised by CrO3-AcOH-H₂O at the b.p. to 1:5-dichloroanthronyl-acetic acid, m.p. 218°. An acid, m.p. 132°, is not formed by condensation of (II) with phenanthrene (cf. B.P. 303,389; B., 1929, 237), and commercial pyrene can be recovered, colourless but unattacked, after treatment with (II) (cf. A., 1932, 1131).

H. G. M.

Influence of solvent, concentration, and temperature on rotatory powers of *l*-menthyl *o*substituted benzoic esters.—See this vol., 1192.

Structure of betaine.—See this vol., 1064.

Rates of racemisation of acids of the type CHRR'·CO₂H.—See this vol., 1083.

Bile acids. XLVI. Behaviour of the nitrosocompound $C_{24}H_{33}O_8N$ (isobilianic acid series) and of the dioxime of 7:12-diketocholanic acid towards nitric acid. M. SCHENCK (Z. physiol. Chem., 1935, 235, 74-80).--Oxidation of the NO-



ric acid. M. SCHENCK (Z. physiol. 235, 74-80).-Oxidation of the NOcompound, C₂₄H₃₃O₈N, obtained from the dioxime of *iso*bilianic acid with 32.5% HNO₃ at 100° gives bilisoidanic acid. Treatment of the dioxime of 7 : 12-diketocholanio acid with HNO₃ affects the :N·OH groups less readily than in analogous cases, and N is not

immediately evolved from the N·OH at 12. The blue product which separates spontaneously is a mixture of (I) and a second NO-compound, provisionally designated "2N-substance." H. W.

Multiplanar cyclohexane rings. M. QUDRAT-I-KHUDA (Nature, 1935, 136, 301).—The four isomerides of 4-methylcyclohexane-1-carboxylic-1-acetic acid have again been isolated as a reply to criticism (this vol., 489). L. S. T.

ω-3-Amino-4-methoxy- and -ethoxy-benzoyl derivatives of propionic, butyric, and valeric acids. S. G. P. PLANT and (MISS) M. E. TOMLINSON (J.C.S., 1935, 1092-1093).-Adipic anhydride, PhOMe, CS₂, and AlCl₃ when refluxed for 3 hr. afford $\alpha\delta$ -dianisoylbutane (I) and δ -anisoylvaleric acid (II) (cf. A., 1932, 63). With Zn-Hg and conc. HCl (I) yields $\alpha \zeta$ -di-p-anisylhexane, m.p. 69—71°, b.p. 250— 260°/23 mm., and (II) yields ϵ -p-anisylhexoic acid, m.p. 47-49°, b.p. 208-210°/14 mm. (II) in H₂SO4 at -5° to 0° and KNO3 yield 8-3-nitro-4-methoxybenzoylvaleric acid, m.p. 107-109°, oxidised by boiling with HNO₃ (d 1.42) to 3-nitro-4-methoxybenzoic acid (III), and reduced by boiling with NH₈-H₂O-FeSO₄ solution to δ -3-amino-4-methoxybenzoylvaleric acid (IV), m.p. 116°. The following substances were prepared by similar methods : αδ-diphenetoylbutane, m.p. 127°; δ-phenetoylvaleric acid, m.p. 110°; aζ-di-p-phenetylhexane, m.p. 69—70°; ϵ -p-phenetylhexoic acid, m.p. 57°; δ-3-nitro-4-ethoxybenzoylvaleric acid, m.p. 110° [oxidised by HNO₃ (d 1·42) (steam-bath) to 3-nitro-4-ethoxybenzoic acid (V)]; δ -3-amino-4-ethoxybenzoyl-valeric acid (VI), m.p. 102°; β -3-amino-4-methoxy-benzoylpropionic acid, m.p. 138°, from the corresponding NO_2 -compound [oxidised by boiling HNO₃ (d 1.42)] to (III)]; β -3-amino-4-ethoxybenzoylpropionic acid, m.p. 144—146°, from β -3-nitro-4-ethoxybenzoylpropionic acid, m.p. 153° [oxidised to (V)]; γ -3-nitro-4-methoxy-benzoylbutyric acid, m.p. 145° [prepared by nitration of γ -anisoylbutyric acid (this vol., 961) and oxidised to (III)] y-amino-4-methoxybenzoylbutyric acid, m.p. 162-164°; y-3-nitro-4-ethoxybenzoylbutyric acid, m.p.

127° [prepared by nitration of γ -phenetoylbutyric acid (loc. cit.) and oxidised to (V)]; and γ -3-amino-4ethoxybenzoylbutyric acid, m.p. 176—178°. Attempts to cyclise (IV) and (VI) through the *m*-position were unsuccessful; the stereochemical considerations (A., 1934, 189) according to which such ring-closure is possible have, however, been illustrated by the recent prep. of *m*-ring compounds (A., 1934, 894; this vol., 844). H. G. M.

Picrotoxin. I. Constitution of picrotic acid and the C-skeleton of picrotoxinin and picrotin. D. MERCER, A. ROBERTSON, and (in part) R. S. CAHN (J.C.S., 1935, 997—1000).—The acid $C_{11}H_{10}O_4$, m.p. 202°, obtained by Hansen (A., 1933, 712) by oxidation of picrotoxinin and of picrotin with MnO₂ and H₂SO₄ (improved method described) and degradation of the resulting dibasic acid, $C_{12}H_{10}O_6$, is identified (comparison with synthetical specimen) as $\alpha\alpha$ -dimethylphthalide-4-carboxylic acid (cannabinolactonic acid). The intermediate NH₂-acid has m.p. 183—200°, and is apparently a mixture of two isomerides. The dibasic acid, $C_{12}H_{10}O_6$, is also obtained by oxidation of picrotic acid, and is identical with the acid obtained by Angelico (A., 1911, i, 1004; 1913, i 69); it is oxidised by HNO₃ to 1:2:3:4-C₆H₂(CO₂H)₄, and the structure A is therefore confirmed. By analogy



with santonin and its related lactones, it is suggested that picrotin and picrotoxinin are related to the sesquiterpenes and have the skeleton B, and that picrotic acid has not the structure proposed by Angelico (A., 1924, i, 183), but the structure C. This is confirmed by the identification of Angelico's acid, C12H14O4 (new m.p. 135-136°), obtained by hydrolytic fission of picrotic acid, as 3-carboxy-y-o-tolyl-n-butyric acid, since its Et ester, b.p. $158-160^{\circ}/1$ mm., is converted by Na in PhMe into Et 5-methyl-1-keto-1:2:3:4. tetrahydronaphthalene-2-carboxylate, b.p. 152-155°/l mm. (pyrazolone, m.p. 265°), and this by 20% H₂SO₄ 5-methyl-1-keto-1:2:3:4-tetrahydronaphthinto alene (semicarbazone, m.p. 245-246°; 2:4-dinitrophenylhydrazone, m.p. 229-230°; unstable phenylhydrazone, m.p. 105°). This is synthesised by a new method (cf. A., 1930, 593), condensing o-toluoyl chloride with Et sodioacetoacetate to give o-methylacetophenone (semicarbazone, new m.p. 210°), of which the ω -Br-derivative, b.p. 138—140°/16 mm. [converted into ω -acetoxy-o-methylacetophenone (semicarbazone, m.p. 174°)], reacts with Et sodiomalonate to form Et β -o-toluoylethane- $\alpha\alpha$ -dicarboxylate, b.p. 170°/1 mm. (2:4-dinitrophenylhydrazone, m.p. 136– 137°). This keto-ester (also prepared from o-toluoy) chloride and CH₂N₂, the product of which is converted by HCl into ω -chloro-o-methylacetophenone, and this treated with Et sodiomalonate) is reduced by Zn in EtOH-HCl to the acid, decomp. to γ -o-tolyl-n-butyric acid, m.p. 60-61°, from which the naphthalene is obtained (cf. loc. cit.). E. W. W.

4-Methoxycinnamylidenepyruvic acid. E. FRIEDMANN (J.C.S., 1935, 1053).—4-Methoxycinnamylidenepyruvic acid, m.p. 137—138° (decomp.) [Na salt, $+1.5H_2O$; 2:4-dinitrophenylhydrazone, m.p. 201° (decomp.)], is obtained from p-OMe·C₆H₄·CH:CH·CHO and AcCO₂H in cold aq. EtOH-NaOH. R. S. C.

Stereoisomerism due to restricted rotation of single linking. I. Optical isomerism of 4:6:4':6'-tetrabromodiphenic acid. H. C. YUAN and T. T. Hsü (J. Chinese Chom. Soc., 1935, 3,206-212).—From the 2-NH₂-acid, 3:5-dibromo-2iodobenzoic acid, m.p. 199°, is prepared, and its Et ester, m.p. $36-36\cdot5^\circ$, is heated with Cu-bronze. After hydrolysis, 4:6:4':6'-tetrabromodiphenic acid, m.p. 271° (decomp.), is obtained, and thence the brucine, $[\alpha]_D^{16} - 76\cdot6^\circ$, and $Na, [\alpha]_D^{16} + 47\cdot28^\circ$, salts of the d-acid, m.p. $181^\circ, [\alpha]_D^{16-5} + 258\cdot2^\circ$, and similar l-compounds (impure). The d-acid is racemised on heating in COMe₂ or AcOH, and the *l*-salt in aq. NaOH. E. W. W.

Fission of ketosulphidocarboxylic acids. O. BEHAGEL and E. SCHNEIDER (Ber., 1935, 68, [B], 1588-1593).-Desylthiolacetic acid,

CHPhBz·S·CH₂·CO₂H, m.p. 105° (oxime, m.p. 123°; semicarbazone, m.p. 178°), obtained by the action of HCl on a mixture of benzoin and SH·CH₂·CO₂H at 100°, or from CHPhBzCl and SH·CH₂·CO₂H at 100°, is converted by alkali into CH₂PhBz and

OH·S·CH₂·CO₂H (whence H₂S, OH·CH₂·CO₂H, and H₂C₂O₄). Similarly, anisoin is readily transformed into deoxyanisoin, m.p. 110°, by condensation with SH·CH₂·CO₂H and treatment of the product with NaOH. COPh·CH₂Br and SH·CH₂·CO₂H afford *benzoylmethylthiolacetic acid*, m.p. 101° [*semicarbazone*, m.p. 201° (decomp.)], hydrolysed by NaOH to COPhMe and OH·S·CH₂·CO₂H. Benzoin and SH·CH₂·CO₂H in presence of anhyd. ZnCl₂ at 100° yield $\alpha\beta$ -diphenylethylenedithiolacetic acid,

(:CPh·S·CH₂·CO₂H)₂, m.p. 213° (Me_2 ester, m.p. 97– 98°). Benzil and SH·CH₂·CO₂H in presence of HCl at 100° or chlorobenzil and SH·CH₂·CO₂H at 100° afford benzoylphenylmethylenedithiolacetic acid,

CPhBz(S·CH₂·CO₂H)₂, m.p. 185°, converted by alkali partly into CH₂PhBz, mainly into benzylidenedithiolacetic acid and BzOH. o-Desylthiolbenzoic acid, m.p. 189°, is transformed by alkali exclusively into o-benzylthiolbenzoic acid and BzOH. H. W.

n-Propyl and *n*-butyl gallate. R. M. HARRIS and J. Ĉ. SMITH (J.C.S., 1935, 1220).—The binary system of Pr^{α} and Bu^{α} gallates forms a continuous series of solid solutions with α max. m.p. 153.6°, corresponding with 57% of the former ester.

P. G. C.

Synthesis of α -naphthol-2: 4-dicarboxylic acid. B. K. MENON (J.C.S., 1935, 1061–1063).—Treatment of CH₂Ph·CO₂Et with OEt·CH:C(CO₂Et)₂ and NaOEt-EtOH at 0° and then, after removal of EtOH, at 150° during 2 hr. affords *Et* α -naphthol-2: 4-dicarboxylate, m.p. 98° (green coloration with FeCl₃), hydrolysed to the acid (I), m.p. 304° (decomp.) (gives blue fluorescence in EtOH and green coloration with FeCl₃). CO₂Et·CHPh·CH:C(CO₂Et)₂ is an intermediate compound in the condensation. When heated with NaOH-CaO (I) yields α -C₁₀H₇·OH. (I) dissolved in NaHCO₃-H₂O and coupled with $p \cdot NO_2 \cdot C_6 H_4 \cdot N_2 Cl$ affords $4 \cdot p \cdot nitrobenzeneazo \cdot \alpha$ naphthol-2-carboxylic acid, m.p. 242° (J.C.S., 1907, 91, 1260), and a compound, m.p. 262°, which may be 2-p-nitrobenzeneazo- α -naphthol-4-carboxylic acid. With PhN₂Cl (I) yields a compound, m.p. 212°, which may be 2-benzeneazo- α -naphthol-4-carboxylic acid. (I) with Me₂SO₄ and NaOH affords 1-methoxynaphthalene-2: 4-dicarboxylic acid, m.p. 252° (decomp.) [amide, m.p. 198° (decomp.); anilide, m.p. 262° (decomp.)]. H. G. M.

Dehydrogenation of phenols. VII. Coupling by dehydrogenation of guaiacol derivatives. H. ERDTMAN (Svensk Kem. Tidskr., 1935, 47, 223-230).—Ferulic acid (4-hydroxy-3-methoxycinnamic acid) gives with FeCl₃ dehydrodiferulic acid, m.p. 202-205°, having the properties of a lactone. Vanillic acid does not yield a cryst. compound with FeCl₃. Me vanillate gives with Na persulphate and Fe" Me2 dehydrodivanillate, m.p. 231-232°, hydrolysed to divanillic acid, which is methylated to Me₂ diveratrate (I). The structure of (I) is confirmed by synthesis. Vanillin with I and KI in alkaline solution gives 5-iodovanillin, m.p. 180-181.5° methylated to 5-iodoveratraldehyde, m.p. 180–181'5", oxidised to 5-iodoveratraldehyde, m.p. 73–74°, oxidised to 5-iodoveratric acid, m.p. 185–186° [Me ester (II), m.p. 106–107°]. Cu converts (II) into $Me_2 \ 2: 3: 2': 3'$ -tetramethoxydiphenyl-5: 5'-dicarb-orulate identical with (I) Varillian oxylate, identical with (I). Vanillinoxime is dehydro-genated by $FeCl_3+Na$ persulphate to a product converted by Ac_2O into 5:5'-dicyano-2:2'-diacet-oxy-3:3'-dimethoxydiphenyl, m.p. 220—221°, identical with the product obtained by the action of Ac2O on the dehydrogenation product of vanillonitrile and on dehydrovanillin. All these products therefore form Ph₂ derivatives by dehydrogenation of the OH to O. Gallic acid, unlike Me gallate, is not oxidised by air in alkaline solution to ellagic acid. E. P.

Transformation of dehydrocholic acid into β -3-hydroxy-7:12-diketocholanic acid in the organism of the toad. K. YAMASAKI and K. KYOGOKU (Z. physiol. Chem., 1935, 235, 43—46; cf. this vol., 749).—The *iso*reductodehydrocholic acid isolated from the urine or bile of toads to which Na dehydrocholate has been administered is transformed into the *semicarbazone*, which is converted by NaOEt in EtOH at 180° into β -lithocholic acid (I), m.p. 177— 178° after softening at 176°, $[\alpha]_{20}^{20}$ +25·29° in EtOH (Me ester, m.p. 115—116° after softening at 114°). Since (I) is oxidised by CrO₃ to dehydrolithocholic acid it is β -3-hydroxy-7: 12-diketocholanic acid.

H. W.

Synthesis of conjugated bile acids. I. Glycocholic acid. F. CORTESE and L. BAUMAN (J. Amer. Chem. Soc., 1935, 57, 1393—1395).—Cholic acid and HCO_2H (d 1·2) at 50—55° give triformylcholic acid, m.p. 206—207°, which with SOCl₂ affords the chloride, decomp. about 147°, and thence the amide, m.p. 187° (hydrolysed by very dil. NaOH-EtOH to cholamide, +3H₂O and +H₂O, decomp. about 115° after softening at about 107°), and with glycine a 40—60% yield of glycocholic acid, +1·5H₂O, m.p. about 130°, $[\alpha]_{D}^{25}$ (anhyd.) +32·5° in EtOH, converted by hot H₂O into impure paraglycocholic acid. Glycodeoxy-, tauro-, and taurodeoxy-cholic acids have been similarly obtained. R. S. C.

Lichen pigments of the pulvinic acid series. III. Reduction of pinastric acid and vulpinic acid. IV. Constitution of calycin and its synthesis. M. ASANO and Y. KAMEDA (Ber., 1935, 68, [B], 1565-1567, 1568-1571; cf. A., 1934, 1352).-III. The extraction of pinastric acid (I) and pulvinic acid (II) from Cetraria juniperina and C. pinastri is described. Reduction of (I) (Zn dust, AcOH; 100°) gives Me y-keto-a-phenyl-8-p-anisyl-n-valerate, m.p. 55-56° (semicarbazone, m.p. 144-145°), identical with that obtained from synthetic material (loc. cit.), and a dibasic acid, C₁₉H₁₆O₆, decomp. 218°, probably p-methoxydihydropulvinic acid, $CO - C(C_6H \cdot OMe) > C \cdot OH.$ Similar reduction of $O \cdot CH(CHPh \cdot CO_2H) > C \cdot OH.$ (II) yields Me^{*} hydrocornicularate, m.p. 144—145° (semicarbazone, decomp. 144—145°), converted into hydrocornicularic acid, m.p. 133—134° (semicarbazone, decomp. 177—178°), and an acid, $C_{19}H_{16}O_5$, m.p. about 90° after softening at about 50°, probably dihydrovulpinic acid CO____CPh O·CH(CHPh·CO, Me) C·OH.

IV. Extraction of the thalli of Sticta aurata, Ach., with warm Et₂O gives pulvinic anhydride, m.p. 222-224°, and calycin (III), $C_{18}H_{10}O_5$, m.p. 244—245° (*Ac* derivative, m.p. 177—179°). When warmed with 50% KOH (III) affords $H_2C_2O_4$, $CH_2Ph \cdot CO_2H$, and o-OH·C₆H₄·CH₂·CO₂H, and hence is o-hydroxy-pulvinic anhydride, The synthesis of (III) is effected by condensing $Et_2C_2O_4$ with o-OMe·C₆H₄·CH₂·CN in presence of NaOEt to *Et cyano*-o-methoxyphenylpyruvate, m.p. $104 - 105^{\circ}$, which on further treatment with CH_Ph.CN affords o-methoxydiphenylketipinodinitrile, CN•CHPh•CO•CO•CH(CN)•C₆H₄•OMe, m.p. 262° (decomp.) after becoming discoloured at 220°, transformed by $\hat{HI}(d 1.7)$ in AcOH into (III). If (I) is treated with HI in AcOH and the product with boiling Ac_2O p-hydroxyvulpinic acid diacetate, m.p. 175—177°, is obtained. Hydrolysis of (I) with Ba(OH)₂ and treat-ment of the product with Ac_2O and finally with HI leads to p-hydroxypulvinic anhydride, m.p. 298° (acetate, m.p. 213-215°), not identical with (III).

H. W. Lichen substances. LV. Endocrocin, a new hydroxyanthraquinone derivative. Y. ASAHINA and F. FUZIKAWA (Ber., 1935, 68, [B], 1558—1565).— Extraction of the air-dried thalli of Nephromopsis endocrocea with hot COMe₂ yields a fatty acid, a neutral, colourless compound, and endocrocin (I), $C_{16}H_{10}O_7$, m.p. about 318° (decomp.) (triacetate, m.p. 212°; dibromide, m.p. 285°). Decarboxylation of (I) at 320° or in quinoline containing Cu chromite at 170—190° affords 1:6:8-trihydroxy-3-methylanthraquinone (frangula emodin), m.p. 256—257° (Br-, m.p. 278—279°, and Br_2 -, m.p. 246—247°, -derivatives; triacetate, m.p. 197°; tribenzoate, m.p. 189—190°; emodic acid, decomp. about 300°, and its triacetate, m.p. 218°). Oxidation of emodin Me₃ ether (II) with CrO₃ in AcOH affords 3-methoxy-5-methyl-o-phthalic acid, m.p. 200° (Me₂ ester, m.p. 86°; anhydride, m.p. 166—167°). (I) is converted by Me_2SO_4 -10% NaOH into its Me_3 ether Me ester (III), m.p. 225—226°, whence endocrocin Me_3 ether, m.p. 240°, decarboxylated in quinoline containing Cu chromite to (II). Oxidation of (III) affords 3-methoxy-4-carbomethoxy-5-methyl-o-phthalic acid, m.p. 181° (bath preheated to 170°), converted by CH₂N₂ into Me_3 3-methoxy-5-methylbenzene-1:2:4-tricarboxylate, m.p. 88°, hydrolysed to 3-methoxy-5-methylbenzene-1:2:4-tricarboxylic acid, m.p. 205° (bath pre-heated to 190°), which yields an anhydride, m.p. 180°. (I) is therefore 1:6:8-trihydroxy-3-methylanthraquinone-2-carboxylic acid. H. W.

Elimination of the aldehydic group as formic acid from aromatic aldehydes. III. Mixed halogeno- and halogenonitro-benzaldehydes. G. Lock (Ber., 1935, 68, [B], 1505–1511; cf. A., 1934, 190).—Treatment of 2: $6-C_6H_3MeBr_2$ with Br at 180–200° slowly affords mainly 2: $6-C_6H_3Br_2$ ·CHBr₂, hydrolysed by H₂SO₄ (d 1·84) at 100° to 2: $6-C_6H_3Br_2$ ·CO₂H and 2: 6-dibromobenzaldehyde, m.p. 90·5° [oxime, m.p. 153° (corr.)], which is converted by 50° (KOH at 100° into m C H Br and HCO H 50% KOH at 100° into m-C₆H₄Br₂ and HCO₂H. 2:3:6-NH2 C6H2Cl2 CHO (I) is transformed into 3: 6-dichloro-2-iodobenzaldehyde, m.p. 108.5° (corr.) [oxime, m.p. 133° (corr.)], which is oxidised by Ag₂O to 3:6-dichloro-2-iodobenzoic acid, m.p. 147.5° (corr.), and converted by KOH into 2:5:1-C6H3Cl2I and HCO₂H. (I) appears to be partly polymerised, but otherwise little affected by KOH, whereas 2:3:6·NO₂·C₆H₂Cl₂·CHO yields 2:5:1·C₆H₃Cl₂·NO₂ and $HC_2 C_6H_2C_2 CHO$ yields 2.5.1- $C_6H_3C_2 HC_2$ and HCO_2H . 3:2:6- $NO_2 C_6H_2C_2 CHO$ is transformed by KOH into 2:4:1- $C_6H_3C_2 NO_2$. 6-Bromo-2-nitro-veratraldehyde, m.p. 117.5° (corr.), from 6-bromo-2nitrovanillin, NaHCO3, and Me2SO4, is oxidised by KMnO₄ to 6-bromo-2-nitroveratric acid, m.p. 198° (corr.), and converted by 50% KOH into HCO₂H and 5-bromo-3-nitroveratrole. H. W.

Peroxide effect in the Cannizzaro reaction. M. S. KHARASCH and (MRS.) M. FOY (J. Amer. Chem. Soc., 1935, 57, 1510).—PhCHO, C_6H_4 Me·CHO, and OMe· C_6H_4 ·CHO do not give the Cannizzaro reaction with 55% KOH with or without Fe^{•••} unless peroxides are present or the solution is aerated. Peroxides, therefore, are the primary catalyst and the catalytic function of Fe^{•••} is merely to hasten their formation. R. S. C.

Chlorinated cinnamaldoximes and cinnamonitriles. K. von Auwers and R. Hügel (J. pr. Chem., 1935, [ii], 143, 179—188; cf. A., 1932, 271).— α -Chloro-cis-cinnamaldehyde (I) (oxidised quantitatively to the trans-acid by AgNO₃-0.5N-NaOH) affords an oxime (II), m.p. 161—163° (Naar, A., 1891, 562, gives m.p. 157—159°) (Ac derivative, m.p. 74— 76°), hydrolysed by HCl (1:1) to (I), but converted by PCl₅ in Et₂O, or by heating with Ac₂O, into α -chloro-trans-cinnamonitrile, identical with a specimen prepared from the trans-amide. With 10% KOH-EtOH (II) affords the known β -ethoxycinnamonitrile, b.p. 158—160°/12 mm. With HCl-AcOH, CPhiC-CHO affords β -chloro-cis-cinnamaldehyde, b.p. 125—126°/10 mm. (semicarbazone, m.p. 208°; phenylhydrazone, m.p. 148°; p-nitrophenylhydrazone, m.p. 197—199°) (oxidised to the trans-acid), the oxime (III), m.p. 77–78°, of which is separated by dil. NaOH into the salt of the cis-anti-oxime, m.p. 107°, and (from the mother-liquor) the cis-syn-oxime, m.p. $94-96^{\circ}$ after purification through its Ac derivative, m.p. $69\cdot5-70\cdot5^{\circ}$ [(IV) is isolated from the acetylation mother-liquor]. (III) is converted by PCl₅-Et₂O into β -chloro-trans-cinnamonitrile (IV), m.p. $31-33^{\circ}$, but hot Ac₂O affords a mixture of the cis- and transnitriles. With 10% KOH-EtOH (IV) gives a β -ethoxycinnamonitrile, b.p. $170^{\circ}/22$ mm. (configuration uncertain), converted by hot conc. HCl into COPh·CH₉·CN. J. W. B.

Nitration of methyl ether of salicylaldehyde. S. N. CHAKRAVARTI (Current Sci., 1935, 4, 26–28).— Nitration of o-OMe·C₆H₄·CHO gives 5- and 3-nitro-2-methoxybenzaldehyde (20% yield); these are separated by crystallisation from C₆H₆ followed by fractional crystallisation of the mixed *p*-toluidides obtained from the mother-liquor. F. N. W.

Azoaldehydes. R. N. SEN and B. N. BANERJI (J. Indian Chem. Soc., 1935, 12, 293–299).—The following are prepared by the Reimer-Tiemann reaction, best with 23% NaOH and CHCl₃-EtOH (1:4) (yields in parentheses below), and, in many cases, by coupling the requisite amines and aldehydes : benzeneazoaldehydo-resorcinol, m.p. 231°, -o-cresol (4%), m.p. 76°, -thymol, m.p. 178° (phenylhydrazone, m.p. 180°), and -carvacrol, m.p. 135° (phenylhydrazone); benzeneazosalicylaldehyde, m.p. 127° (phenylhydr-azone, m.p. 198°); p- (7%), m.p. 192–193° (phenyl-hydrazone, m.p. 235–240°), o- (4%), m.p. 141° (phenylhydrazone, m.p. 192°), and m-nitro- (5%), m.p. 141 (phengi-hydrazone, m.p. 192°), and m-nitro- (5%), m.p. 163° (semicarbazone, m.p. 248°), p- (10%), m.p. 198° (semicarbazone, m.p. 300°), and o-chloro-benzeneazo-salicylaldehyde (10%), m.p. 184° (semicarbazone, m.p. 259°); p- (8%), m.p. 147° (semicarbazone, m.p. 250°), p- (8%), m.p. 147° (semicarbazone, m.p. 250°). and o-tolueneazosalicylaldehyde (8%), m.p. 120° (semicarbazone, m.p. 196°). Substitution depresses the yield in the Reimer-Tiemann reaction, which failed entirely with benzeneazo-m- and -o-nitro- and -o-chloro-phenol. The CHO in the products reacts only with difficulty and has little effect on the dyeing properties. Azotriphenylmethane and azopyronine dyes have been obtained from the above products. Carvacrylaldehyde, prepared by the Reimer-Tiemann reaction, has b.p. 237° (semicarbazone, m.p. 252°). R. S. C.

Bagasse. VI. Methyl and acetyl derivatives of bagasse lignin. H. HACHIHAMA and H. SAEGUSA (J. Soc. Chem. Ind. Japan, 1935, 38, 310B).—Bagasse lignin (I) on methylation (Me₂SO₄-10% NaOH) gives a compound with empirical formula $C_{60}H_{39}O_5(OMe)_{12}$, and on acetylation (Ac₂O-C₅H₅N) the compound $C_{60}H_{39}O_5(OAc)_5(OH)(OMe)_6$ is formed. The empirical formula of (I) is presumably $C_{60}H_{39}O_5(OH)_6(OMe)_6$. F N. W.

Supposed isolation of a second form of $\beta\beta$ -dimethylcyclohexanone. Ring rearrangement during Clemmensen reduction. A. N. DEY and R. P. LINSTEAD (J.C.S., 1935, 1063–1065).—The reduction of dimethyldihydroresorcinol (I) by the method of Crossley *et al.* (J.C.S., 1907, 91, 63) to 3:3-dimethylcyclohexanone (II) (semicarbazone, m.p.

195°) and the oxidation of this to $\beta\beta$ -dimethyladipic acid have been confirmed. Clemmensen reduction of (I) affords a ketone (semicarbazone, m.p. 162°) isomeric with (II). Contrary to the conclusions of Khuda (A., 1933, 952), this ketone is not a second form of (II) corresponding with the other multiplanar (Sachse) form of the cyclohexane ring. It is shown to be 2:4:4-trimethylcyclopentanone (A., 1918, i, 442) by its properties and by oxidation by $KMnO_4$ to $\alpha\alpha$ -dimethylsuccinic acid, by HNO_3 to a mixture of this and aaa'-trimethylglutaric acid, and by Beckmann's mixture to γ -acetyl- $\beta\beta$ -dimethylbutyric acid identical with material synthesised (cf. A., 1929, 295) by addition of mesityl oxide to malonic ester and subsequent hydrolysis and decarboxylation of the product. The C skeleton of a diketone has therefore undergone rearrangement during Clemmensen reduction. H. G. M.

Fused carbon rings. V. Synthesis of reduced dicyclic systems. J. W. BARRETT, A. H. COOK, and R. P. LINSTEAD. VI. Optical activity connected with the presence of multiplanar rings. J. W. BARRETT and R. P. LINSTEAD (J.C.S., 1935, 1065-1069, 1069-1071; cf. this vol., 750).--V. Three methods have been examined. (a) (cf. A., 1934, 1002) Condensation of CN·CH2·CO2Et with a cyclic ketone containing an α -aliphatic ester group, followed by reduction, hydrolysis, and cyclisation of the resulting dibasic acid. The primary condensation is inhibited by α - and α' -alkyl substituents. Me cyclohexanone-2-β-propionate, CN·CH2·CO2Me, and C5H11N after 6 weeks at room temp. afford some cyanoaceto-piperidide, m.p. 88-89°, b.p. 150-160°/1 mm., and Me, cyclohexylidene-1-cyanoacetate-2-β-propionate, b.p. 178-180°/1.5 mm., reduced by Al-Hg in moist Et.,0 to Me2 cyclohexane-1-cyanoacetate-2-\beta-propionate, b.p. 165°/1 mm., hydrolysed with conc. HCl to cis-cyclohexane-1-acetic-2-β-propionic acid (I) (A., 1925, i, 258) [dianilide, m.p. 165° (lit. 163°)] and a little cis-β-decalone [semicarbazone, m.p. 182—183° (decomp.) (lit., m.p. 182°)], also obtained by heating (I) at 280-300° with $Ba(OH)_2$. Et 2-methylcyclohexanone-2-and -6- β -propionates and Me 2-methylcyclopentanone-2- and -5-3-propionates failed to condense with $CN \cdot CH_2 \cdot CO_2Et$ in presence of $C_5H_{11}N$. By similar methods Et 2-methylcyclopentanone-2-carboxylate with $CN \cdot CH_2 \cdot CO_2 Et$ and $C_5 \dot{H}_{11}N$ affords a little of a condensation product, b.p. 150-157°/1 mm., reduced to the saturated CN-ester, b.p. 148-150°/1 mm., hydrolysed to 1-carboxy-1-methylcyclopentane-2-acetic acid (probably cis-), m.p. 125-126°.

(b) Michael additions. Contrary to the statement of Kon et al. (A., 1927, 150), decalin-1: 3-dione, m.p. 142° (cf. lit.), as prepared by them, is oxidised by NaOBr to trans-cyclohexane-1-carboxy-2-acetic acid, m.p. 156—157°. The oxidation by KMnO₄ to transhexahydrophthalic acid is confirmed. Et Δ^1 -cyclopentenecarboxylate with CH₂Ac·CO₂Et and EtOH-NaOEt (steam-bath) affords Et trans-cyclopentane-1-carboxylate-2-acetate, b.p. 148°/16 mm. (cf. A., 1934, 1002), a little Et trans-cyclopentane-1-carboxylate-2-acetoacetate, b.p. 176°/16 mm., and a small amount of a solid, m.p. 64° (probably dicyclic; sol. in alkali). Similarly acetylcyclohexene and CHNaAc-CO₂Et yield Et trans-3-methyl- Δ^2 -octal-1-one-4-carboxylate, b.p. 180°/9 mm. (unsaturated to KMnO₄; gives violet colour with FeCl₃), and trans-3methyl- Δ^2 -octal-1-one, b.p. 110—111°/10 mm. (reduces neutral KMnO₄ immediately), reduced catalytically (Adams) to trans-3-methyl- α -decalone, b.p. 120°/8 mm. [semicarbazone (II), m.p. 203—205°], and some highboiling auto-condensation products. (II), on distillation with KOH and a little Pd-BaSO₄, yields trans-2-methyldecalin, dehydrogenated by Se at 320— 350° to 2-C₁₀H₇Me.

(c) cycloPentanone-2- β -propionic acid, when refluxed (6 hr.) with cone. HCl and Zn-Hg, affords cyclopentane- β -propionic acid, b.p. 131°/6 mm. [solidifies in ice; Et ester, b.p. 90°/9 mm.; acid chloride (III), b.p. 66°/1.5 mm.; anilide, m.p. 110°], which yielded no α -dicyclooctanone when distilled over P₂O₅. (III) and AlCl₃ in light petroleum gave only a waxy solid.

VI. dl-trans-cycloHexane-1: 2-diacetic acid, m.p. 167°, has been resolved by means of its cinchonidine salt. The d-acid (IV) has m.p. 152° and $[\alpha]_{5461}^{18}$ +54.9° in EtOH, and the l-acid (V), not quite optically pure, m.p. 148–149°, $[\alpha]_{5461}^{19}$ –47.9° in EtOH. (IV) when heated at 290–300° with Ba(OH)₂ yields l-trans-\$-hydrindanone (VI), b.p. \$3°/10 mm., [α]³⁷₅₄₆₁ -337·2° in light petroleum (b.p. 40-50°) [semicarbazone, m.p. 242-243° (decomp.), [α]¹⁸₅₄₆₁ -109.4° in AcOH, which does not depress the m.p. (243°) of the *dl*-semicarbazone]. Similarly (V) yielded d-trans-β-hydrindanone (semicarbazone, m.p. $241-242^{\circ}$, $[\alpha]_{18}^{18}$ +96.3° in AcOH). The small amounts of unchanged active acids were nearly optically pure. (VI) was reduced by Zn-Hg and AcOH-HCl by the method of Linstead et al. (A., 1934, 1002) to 1-trans-hydrindane, b.p. 156°/747 mm., [a]¹⁹ -10.8° in light petroleum. *dl-trans-cyclo*Pentane-1:2-diacetic acid, m.p. 132°, has been resolved by means of its neutral brucine salt. The l-acid has m.p. 151°, [a]12 -63.5° in EtOH (neutral brucine salt, 151', $[\alpha]_{5401}^{10} \rightarrow 05.5'$ in EtoII (neutral or active state, m.p. 105—108°), and the nearly pure d-acid has m.p. 150—151°, $[\alpha]^{19} + 62.3^{\circ}$ in EtoH. The former when heated at 330—350° with Ba(OH)₂ affords d-trans- β -0:3:3-dicyclooctanone, m.p. 41°, $[\alpha]_{5401}^{18} + 437^{\circ}$ in light petroleum (semicarbazone, m.p. 249°, $[\alpha]_{1611}^{18}$ +139.6° in AcOH, which did not depress the m.p. of the dl-semicarbazone). This was reduced with Zn-Hg and AcOH-HCl to trans-0:3:3-dicyclooctane (VII), m.p. -30° to -29° (alone or admixed with that prepared from the *dl*-ketone), which showed the expected absence of rotation. The m.p. recorded (this vol., 750) for (VII), cis-dicyclooctane, cis- and trans- β -dicyclooctanone are 5° too low. These results confirm the correctness of the configurations given by Hückel to the cis- and trans-decalins and -hydrindanes and those by Cook et al. (A., 1934, 1002) for the corresponding *dicyclooctanes*, and prove independently that both 5- and 6-membered rings can exist in multi-planar forms. H. G. M.

Molecular transpositions in cyclic hydrocarbon series. Extension and contraction of rings. M. TIFFENEAU, P. WEILL, J. GUTMANN, and B. TCHOUBAR (Compt. rend., 1935, 201, 277–280).—Passage from a C_6 to a C_7 ring may be effected by the scheme: $CH_{2} \underbrace{CH_{2} \cdot CH_{2}}_{CH_{2} \cdot CH_{2}} \xrightarrow{C:CHR} \rightarrow CH_{2} \underbrace{CH_{2} \cdot CH_{2}}_{CH_{2} \cdot CH_{2}} \xrightarrow{C:CHR} \xrightarrow{CHR} O$

 $\rightarrow \begin{array}{c} CH_2 - CH_2 - CO \\ CH_2 \cdot CH_2 \cdot CH_2 - CH_2 \end{array} > CHR, when R = anisyl. Thus$ when C₆H₁₁·MgBr and OMe·C₆H₄·CHO are combined to form cyclohexyl-p-anisylcarbinol, m.p. 89°, and this is dehydrated (Al₂O₃ at 280°), the resulting p-anisylidenecyclohexane (I), b.p. $172^{\circ}/23$ mm., can be converted through its epoxide, b.p. 175°/18 mm., by heating, into p-anisylcycloheptanone, m.p. 60° (semicarbazone, m.p. 145°). The iodohydrin derived from (I) is, on the other hand, when dehalogenated by HgO, transformed into p-anisylcyclohexyl-1-aldehyde (semicarbazone, m.p. 219°), which is oxidised to the -1-carboxylic acid, m.p. 178°. Benzylidenecyclohexane (A., 1934, 649) gives, however, either through its epoxide, b.p. 135°/15 mm., or through its iodohydrin, phenylcyclohexane-1-aldehyde, b.p. 144-145°/19 mm. (semicarbazone, m.p. 219°). Diminution from C₇ to C_6 can be effected thus: $CH_2 < CH_2 \cdot CH_2 \cdot$ $\mathrm{CH}_2 {<} \overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2}_{\mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CR}_2} {>} 0 {\rightarrow} \mathrm{CH}_2 {<} \overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2}_{\mathrm{CH}_2 \cdot \mathrm{CH}_2} {>} \mathrm{CR} \cdot \mathrm{CHO}.$ Thus phenylcycloheptene, b.p. 131-132°/16 mm., obtained from cycloheptanone and MgPhBr by way of the carbinol, forms an epoxide which when heated yields phenylcyclohexyl-1-aldehyde and phenylcycloheptanone (semicarbazone, m.p. 155°); similarly p-anisylcycloheptene, b.p. 170—175°/14 mm., forms an epoxide converted into p-anisylcyclohexyl-1-alde-E. W. W. hyde and *p*-anisylcycloheptanone.

Cleavage of carbonyl compounds. I. Deoxybenzoin derivatives and phenacylsulphonic acid. T. Y. KAO and H. C. KUNG (J. Chinese Chem. Soc., 1935, 3, 213—217).— ω -Bromo- and $\omega\omega$ -dibromo- ω -phenyl- and ω -bromo- $\omega\omega$ -diphenyl-acetophenone, and Na acetophenone- ω -sulphonate are all hydrolysed by NaOH in either EtOH or H₂O, with formation of BzOH. E. W. W.

Constitution of the methylionones. H. KÖSTER (J. pr. Chem., 1935, [ii], 143, 249—252).—Fractional crystallisation of the semicarbazones of the mixture of methylionones obtained by cyclisation of methyl- ψ ionone and regeneration of the ketones affords (1) α -methylionone, R·CH:CH·COEt, b.p. 125—126°/9 mm. (semicarbazone, m.p. 146°), (2) β -methylionone, R'CH:CH·COEt, b.p. 133°/9 mm. (semicarbazone, m.p. 140°), (3) α -isomethylionone, R·CH:CMe·COMe, b.p. 121—122°/9 mm. (semicarbazone, m.p. 202°), and (4) β -isomethylionone, R'·CH:CMe·COMe, b.p. 124—125°/9 mm. (semicarbazone, m.p. 182°), where R= Δ^2 - and R'= Δ^1 -2 : 6 : 6-trimethylcyclohexenyl. The structures are assigned because (1) and (2) are sol. and (3) and (4) are insol. in hot Na₂SO₃ solution, and only (3) and (4) give CHI₃ with I-NaOH.

J. W. B. 7-Methyl-4-isopropyl-1-hydrindone. (MRS.) O. BLUM-BERGMANN (J.C.S., 1935, 1030).—3-Bromo-*p*cymene with activated Mg and CH(OEt)₃ in Et₂O gives 5-methyl-2-isopropylbenzaldehyde Et₂ acetal, b.p. 135—145°/15 mm., which is hydrolysed to the aldehyde and this condensed with CH₂(CO₂H)₂ to form 5-methyl-2-isopropylcinnamic acid, m.p. 145— 146.5°. Na-Hg (4%) converts this into β -3-*p*-cymylpropionic acid, new m.p. $66-68\cdot5^{\circ}$ (cf. this vol., 75), from which the hydrindone is prepared. E. W. W.

Imidochlorides. II. Condensation of benzanilide imidochloride with substituted dialkylanilines in presence of anhydrous aluminium Synthesis of dialkylaminobenzochloride. phenones. R. C. SHAH and M. B. ICHAPORIA (J.C.S., 1935, 894—896; cf. A., 1932, 386).—In Et₂O at room temp., this condensation gives, from m- and o-C₆H₄Me·NMe₂, respectively, 4-dimethylamino-2-methyl-, b.p. 195–198°/2 mm. [oxime, m.p. 158– 160°; methiodide, m.p. 163° (decomp.)], and -3-methyl-, m.p. 45°, b.p. 208-210°/12 mm. (oxime, m.p. 119°; methiodide, m.p. 184°), -benzophenone; the last is also prepared from 4 - amino - 3 - methylbenzophenone, $p \cdot C_6H_4$ Me·NMe₂ yields 2 - dimethylamino - 5 - methyl-benzophenone, b.p. 176—178°/6 mm. (NO₂-derivative, m.p. 173—175°); $o \cdot C_6H_4$ Me·NEt₂, 4-diethylamino-3-methylbenzophenone, b.p. 214—216°/15 mm.; α -C₁₀H₇·NMe₂, 4-benzoyldimethyl- α -naphthylamine, m.p. 102—104°, b.p. 283—285°/40 mm. (oxime, m.p. 212—215°); and benzyl-methyl- and -ethyl-aniline, 4-benzyl-methyl-, m.p. 78-80°, and -ethyl-, b.p. 320-325°/40 mm. (oxime, m.p. 140-142°) -aminobenzophenone, respectively. E. W. W.

Abnormal reaction of an α -bromoketone. (MISS) S. N. McGEOCH and T. S. STEVENS (J.C.S., 1935, 1032).—Ph α -bromo- β -phenylethyl ketone combines with NH₂Ph to form not only the expected *Ph* α -anilino- β -phenylethyl ketone, m.p. 106°, but also α -anilinodibenzyl ketone, m.p. 125° (also prepared from α -bromodibenzyl ketone). The former is reduced (Zn and H₂SO₄) to COPh·CH₂·CH₂Ph, the latter to CO(CH₂Ph)₂. E. W. W.

Sulphur [compounds]. VII. Preparation and properties of some thicketones. R. W. BEST and B. O. CROSEV (J. Amer. Chem. Soc., 1935, 57, 1404—1405).—By a modification of the procedure of Staudinger *et al.* (A., 1928, 1010) are prepared *Ph* C_6H_4Ph , m.p. 125.7°, α - $C_{10}H_7$, m.p., 110°, and p-tolyl thicketone (I), m.p. 35°, which are monomeric and stable for 2 years, give salts with HgCl₂ and HgI₂, with hot 10% KOH-EtOH give the COcompounds, and have absorption bands in EtOH at about 5900 Å. (I) alone gives a ppt. with SnCl₂ and is oxidised by 15% H₂O₂. R. S. C.

Unsaturated sulphur compounds. II. aB-Unsaturated ketosulphones. E. P. KOHLER and R. G. LARSEN (J. Amer. Chem. Soc., 1935, 57, 1448-1452; cf. this vol., 1115).—Ph β-benzoylvinyl sulphone (I) resembles (COPh·CH:)₂ in reactions and particularly in the stability of the isomerides. The stable, yellow trans-form, m.p. 114°, of (I) is changed in Et₂O in light into a colourless cis-form, m.p. 149° from which it is re-formed by a trace of HCl in AcOH or NaOMe in MeOH; an equilibrium mixture is formed at 160°. Probably the SO₂, like CO, contributes to more complete conjugation. (I) is obtained in fair yield from CHBr₂·CH₂·COPh (1 mol.), pure PhSO₂Na (II) (1 mol.), and KOAc (slightly >1 mol.) in hot EtOH, but is better prepared by elimination of HBr, best (92%) by KOAc in MeOH at 40°, from Ph B-bromo-B-benzoylethyl sulphone (III), m.p. 71°, which is formed (a) slowly in 5% yield with some (I) from CH₂Br·CHBr·COPh and (II) in hot EtOH or (b) from Ph β -benzoylethyl sulphone (IV), m.p. 98°, and Br in CHCl₃. (IV) is prepared by adding PhSO₂H to CH₂:CH-COPh or, better (68% yield), from CH₂Cl-CH₂·COPh and (II) in hot EtOH; with warm 5% aq. KOH it yields PhSO₂H and an oil (? polymeride of COPhMe) and with NaOEt PhSO2H and a polymeride, m.p. about 96°, of CH2:CH-COPh. With warm Zn dust-aq. AcOH (I) gives (IV); with Br (1 mol.) in various solvents oily or solid (m.p. of an impure product 95-100°) mixtures of dibromides are formed, but successive action of Br and KOAc in AcOH yields Ph \$-bromo-\$-benzoylvinyl sulphone, yellow form, m.p. 105°, isomerised in Et₂O by light to a colourless form, m.p. 128°. With HBr in AcOH (I) gives at once $Ph \alpha$ -bromo- β -benzoylethyl sulphone, m.p. 135°; with KOH-MeOH at room temp. it gives Ph α -hydroxy- β -benzoylethyl sulphone (V), m.p. 95–100°, which dissolves with formation of a Na salt in aq. NaHCO3, but is partly cleaved thereby to PhSO2H and CH2Bz CHO, so that a NaHCO3 solution of (V) gives the reactions of CH2Bz·CHO and allows recovery of only 30-40% of (V) on acidification. (I) reacts with MgPhBr mainly by 1: 4-addition to the CO·C.C. but some 1:2-addition also occurs; the primary product, OMgBr·CPh:CH·CHPh·SO₂Ph, however, is cleaved during reaction to CHBz:CHPh and PhSO₂·MgBr, which react further; the substances isolated are, therefore, CHPh, CH, COPh, Ph.SO. Ph γ -hydroxy- $\gamma\gamma$ -diphenyl- Δ° -propenyl sulphone (VI), m.p. 193° with decomp. later, and Ph a-hydroxy-yydiphenylallyl sulphone (VII), m.p. 164° (decomp.). (VI) is the product of 1:2-addition to (I); (VII) is formed therefrom by allylic rearrangement, which is unusually facile; thus, in solvents an equilibrium mixture is formed from either (VI) or (VII), and (VI) is obtained by crystallisation from C₆H₆ or (VII) from MeOH or EtOH. The structures are proved thus. Hydrogenation (2 atm.; PtO_2) of (VI) in EtOAc yields Ph γ -hydroxy- $\gamma\gamma$ -diphenyl propyl sulphone, m.p. 206°, also obtained from (IV) and MgPhBr (83%) yield). (VII) at 100° gives some $\gamma\gamma$ -diphenylacraldehyde, m.p. 44° (phenylhydrazone, m.p. 173°), also obtained (53% yield) from CPh₂:CH·MgBr and CH(OEt)₃. PhSO₂H and MgPhBr are shown in a separate experiment to give Ph_2SO (and a little Ph₂S), as assumed above. R. S. C.

Heteropolarity. XXVII. Deep-coloured aromatic five-ring ketones. W. DILTHEY, I. TER HORST, and W. SCHOMMER (J. pr. Chem., 1935, [ii], 143, 189—210).—Condensation of phenanthraquinone (I) with $CO(CH_2Ph)_2$ and KOH—EtOH in the cold affords colourless 3-hydroxy-2: 5-diphenyl-3: 4-(2:2'-

PhC ²CHPh ¹ CO (II.)

diphenylene)- Δ^4 -cyclopentenone (II), m.p. 226° [the compound, m.p. 102—103°, assigned this structure by Sen et al. (A., 1932, 272) could not be obtained] [Ac derivative, m.p. 250—251°, with decomp. to (III)], converted by hot KOH-EtOH into greenish-black 2:5diphenyl-3: 4-(2:2'-diphenylene).

 $\Delta^{2:4}$ -cyclopentadienone (III), m.p. 273°, which is

thus the product when the initial condensation is effected with heating. When poured on ice a solution of (III) in conc. H₂SO₄ affords 2-hydroxy-2: 5-diphenyl-3 : $4 - (2 : 2' - diphenylene) - \Delta^3 - cyclopentenone,$ m.p. 235-245° (decomp.), different from (II), since crystallisation from AcOH converts it into an Ac derivative, m.p. 255-256°. Addition of KOH-EtOH to a solution of (I) and CO(CH₂Ph)₂ in boiling EtOH gives (III) and 2:5-diphenyl-3:4-(2:2'diphenylene)-∆3-cyclopentenone (IV), m.p. 314-315° (block), also obtained by reduction of (III) with red P-HI at 165°, or reduction of either (II) or (III) with Zn-AcOH. Substitution of (IV) by Brboiling CHCl₃ or addition of Br-C₆H₆ to (III) affords a Br_2 -derivative (2:3- Δ^4 - or 2:5- Δ^3 -), m.p. 296— 297° (decomp.). By similar types of condensation using substituted phenanthraquinones are obtained 3 hydrory 2:5 dishered 2:4 (4) sites 2:3 dishered 3-hydroxy-2: 5-diphenyl-3: 4-(4'-nitro-2: 2'-diphenyl-ene)-, m.p. 275–276° (decomp.), -3: 4-(6'-nitro-2: 2'-diphenylene)-, m.p. 257–258° (decomp.), and -3: 4-(4'-amino-2: 2'-diphenylene)-, m.p. 254° (decomp.), $-\Delta^4$ -cyclopentenone [all of type (II)], and (in the hot) 2:5-diphenyl-3:4-(4'-amino-2:2'-diphenylene)-, m.p. 284-285°, -3: 4-(5'-amino-2: 2'-diphenylene)-, m.p. 275°, and -3: 4-(4'-methoxy-2: 2'-diphenylene)-, m.p. 273-274°, -\Delta^{2:4}-cyclopentadienone. All these compounds are halochromic and the constitution of the salts is discussed. All substituents in the phenanthraquinone nucleus have a very slight hypsochromic effect on the colour, but a definite hypsochromic effect on the H₂SO₄-colours. Similar condensation of $CO(CH_2Ph)_2$ with acenaphthene-quinone gives, in the cold, 3-hydroxy-2: 5-diphenyl- $3: 4-(1: 8-naphthylene)-\Delta^4$ -cyclopentenone, m.p. 230-231° (slow heating), and, with hot KOH-EtOH, 2:5diphenyl-3: $4-(1: 8-naphthylene)-\Delta^{2:4}$ -cyclopentadienone, m.p. 289°, reduced by Zn-AcOH to a (?) H2- or H₄-derivative, m.p. 229-230°. Similar condensation with aceanthrenequinone affords 2: 5-diphenyl-3: 4-(1:9-anthranylene)-Δ^{2:4}-cyclopentadienone, m.p. 284-J. W. B. 285° .

Alkylation of acetoacetic ester by toluenesulphonic esters. C. N. NAIR and D. H. PEACOCK (J. Indian Chem. Soc., 1935, 12, 318-321).-p-Toluenesulphonic esters of alcohols RO·C₂H₄·OH (R=aryl) (improved prep.) are used for alkylation of $CH_2Ac \cdot CO_2Et$. The $OPh \cdot C_2H_4$ ester and $CH_2Ac \cdot CO_2Et$. The $OPh \cdot C_2H_4$ ester and $ONa \cdot CMe \cdot CH \cdot CO_2Et$, best with NaI, in dry EtOH give a product, which (i) with KOH-EtOH leads to OPh·[CH₂]₃·CO₂H (I) and an acid, m.p. 156-157° (decomp.), or to (I), CH(OPh)2.CO2H, and Me y-phenoxypropyl ketone, m.p. 53-54° (semicarbazone, m.p. 144°; oxime, m.p. 78°), and (ii) with CH₂PhCl gives an ester, hydrolysed to y-phenoxy-a-benzylbutyric acid, m.p. 77° (amide, m.p. 125-126°). β -p-, b.p. 178°/35 mm., m.p. 79°, and -m-Chlorophen-oxy-, m.p. 57°, and β -2-naphthoxy-ethyl p-toluenesulphonate, m.p. 90°, lead similarly to y-p-, m.p. 120°, and -m-chlorophenoxy-, m.p. 51–52°, and -2-naphth-oxy-butyric acid, m.p. 122°, and Me γ -p-, b.p. 170– 195°/35 mm. (semicarbazone, m.p. 178°), and -m-chlorophenoxy-, b.p. 180–200°/35 mm. (semicarbazone, m.p. 146°), and γ -2-naphthoxy-propyl ketone, b.p. 220– 230°/25 mm. (semicarbazone, m.p. 174°). R. S. C.

Hydrolytic fission of aromatic ketones by acids. P. HILL and W. F. SHORT (J.C.S., 1935, 1123-1126) .---The fission Ph--CO·CH,Ph is effected by boiling AcOH-HBr when an o-OH or OMe is present in the Ph nucleus; it is facilitated by an o-Me in the Ph and retarded by NO2 in the CH2Ph nucleus. An oor p-Me in the CH2Ph accelerates decomp. 4-Hydroxy- and 4-methoxy-deoxybenzoin, 2'-methyldeoxy-benzoin (from o-toluamide and CH₂Ph·MgCl), b.p. 172-173°/10 mm., m.p. about 18° (2 : 4-dinitrophenylhydrazone, m.p. 146—147°), 4-hydroxy-2-methyldi-benzyl, and 4'-nitro-4-methoxy-2-methyldeoxybenzoin, m.p. 92—93° (from m-tolyl Me ether and 4-nitro-phenylacetyl chloride; 4'-nitro-4-hydroxy-2-methyl-deoxybenzoin, m.p. 128°, is obtained as a by-product), are stable to (or slightly decomposed by) AcOH-HBr, which decomposes the following (% fission in parentheses): 4-methoxy-2-methyldeoxybenzoin (semicarbazone, m.p. 165—165.5°) (100%), 4-methoxy-2:2'-dimethyldeoxybenzoin (2:4-dinitrophenylhydr-azone, m.p. 188—189°) (100%), 4-methoxy-2:4'-dimethyldeoxybenzoin (2:4-dinitrophenylhydrazone, m.p. 154·5—155·5°) (100%), and 4-methoxy-2-methyl-acetophenone (79%). By thermal analysis of the derived xylyl alcohols, it is shown that 53% and 42%, respectively, of o-xylyl chloride is obtained together with the p-isomeride in the reaction between PhMe and (CH₂Cl)₂O, or paraform and HCl. P. G. C.

(A) Preparation of dehydroandrosterone from cholesterol. (B) Oxidation and reduction of dehydroandrosterone. E. S. WALLIS and E. FERN-HOLZ (J. Amer. Chem. Soc., 1935, 57, 1504—1506, 1511—1512; cf. this vol., 1125).—(A) Cholesteryl acetate dibromide and CrO_3 -AcOH give dehydroandrosterone acetate (I), isolated as semicarbazone, m.p. 270° (decomp.), which with hot H_2SO_4 -EtOH gives dehydroandrosterone (II) (benzoate, $[\alpha]_D^{\circ} + 26\cdot1^{\circ}$ in CHCl₃), identical with the natural product. With (I) is formed 3-hydroxy- Δ^5 -cholenic acid, m.p. 236° (decomp.) [Me ester, m.p. 144° (Ac derivative, m.p. 156°, $[\alpha]_2^{\circ}$ \sim -18.7° in CHCl₃), pptd. by digitonin], which is pptd. by digitonin and at 240° loses 0.5H₂O.

(B) The testicular and corpus luteum hormones may be similarly constituted, since both are sensitive to alkali. The dibromide of (II) with CrO_3 gives Δ^4 -ætiocholene-3:17-dione, m.p. 170° (uncorr.), [α]³⁰ +199° in CHCl₃. Hydrogenation of (II) in presence of Pd-black in EtOH gives 3-hydroxyætioallocholen-17-one, m.p. 172° (uncorr.), [α]³⁰₂₆ +88.6° in MeOH, but in AcOH or in presence of Pt-black the CO is also reduced. R. S. C.

Sexual hormones and related substances. III. Constitution of cinchol; its transformation into **3-hydroxyætioallocholan-17-one**. W. DIRSCHERL (Z. physiol. Chem., 1935, 235, 1—7).—Acetylation of cinchocerotin and crystallisation of the product from EtOH affords acetylcinchol (I), m.p. 132° (corr.), $[\alpha]_{D}^{20}$ —38° in CHCl₃. Cinchol (II) can be pptd. by digitonin, showing that OH is attached to C-3 in the same steric arrangement as in cholesterol; recovered (II) has m.p. 140—141° (corr.). Titration of (I) with BzO₂H indicates the presence of one double linking and hydrogenation (Pd-sponge in EtOH or Et₂O) gives acetyldihydrocinchol (III), m.p. 135—136° (corr.), $[\alpha]_{p}^{\infty}$ +17.8° in CHCl₃. Oxidation of (III) with CrO₃ affords 3-acetoxyætioallocholan-17-one, the semicarbazone, m.p. 261—262° (corr.), of which is converted by AcOH-HCl followed by hydrolysis into 3-hydroxyætioallocholan-17-one, m.p. 176—177° (corr.), $[\alpha]_p$ +88.8° in EtOH. Dihydrocinchol is therefore trams-trans-trans-3-hydroxy-17-decylætioallocholan; the suggested structure of the sidechain is ·CHMe·[CH₂]₂·CHEtPr^β. H.W.

Benzoin reaction. II, III.-See this vol., 1084.

Manufacture of cyclic 1:2-aminoketones.— See B., 1935, 796.

Preparation of octoic acid derivatives of phenols [resorcinol].—See B., 1935, 761.

Action of diazomethane derivatives and of azides on 1:4- and 1:2-naphthaquinones. L.F. FIESER and J. L. HARTWELL (J. Amer. Chem. Soc., 1935, 57, 1479-1482).-1:2-Naphthaquinones, unlike the 1:4-isomerides, do not react with CH2N2 or its derivatives, nor with azides. 1:4-Naphthaquinone and MeN₃ in EtOH-C₆H₆ at 105° give 1-methyl-lin-naphthatriazole-1: 4-quinone and 1: 4naphthaquinol. 6-Bromo-1: 2-naphthaquinone (I) [prep. from $1:6:2-C_{10}H_5Br_2\cdot OH$ by way of the NO₂-ketone or, less well, $6:2-C_{10}H_6Br\cdot OH$, the 1-*p*-sulphobenzeneazo-dye, and $1:6:2-NH_2\cdot C_{10}H_5Br\cdot OH$ (*Ac*₂ derivative, m.p. 120—121°)] with PhN₃ at 66° gives the dinaphthyldiquinhydrone, converted by reductive acetylation into 6:6'-dibromo-1:2:1':2'tetra-acetoxy-4: 4'-dinaphthyl, m.p. 226-226.5° [also obtained directly from (I)]; it does not react with CH_2N_2 or $CHN_2 \cdot CO_2Et$ to give definite products. 1:2-Naphthaquinone behaves similarly. (I) with CPh_2N_2 in C_6H_6 at room temp. gives 6-bromo-1:2-dihydroxynaphthalene diphenylmethylene ether, m.p. 150.5—151°, and, in one experiment, a red substance, m.p. 210—210.5°. 4-Triphenylmethyl-1 : 2-benzo-4-Triphenylmethyl-1:2-benzoquinone and CPh_2N_2 , best in EtOH, afford similarly the corresponding diphenylmethylene ether, m.p. 258-259°, also obtained from 4-triphenylmethylpyrocatechol and CPh_2Cl_2 in C_6H_6 . 2-Diphenylmethyl-1:4-naphthaquinone does not exist in the *o*-quinonoid form, since with CH₂N₂ it affords the pyrazoline, $0 - C_6 H_4 < CO - C(CH_2Ph) N,$ which at the m.p., 167-168°, yields N₂ and 2-benzhydryl-3-methyl-1: 4naphthaquinone, m.p. 162-163°, reduced by Zn dust-AcOH to the quinol diacetate, m.p. 215-217°

R. S. C.

Reaction of hydrazoic acid with naphthaquinones. L. F. FIESER and J. L. HARTWELL (J. Amer. Chem. Soc., 1935, 57, 1482—1484).—HN₃ with 1:4- and 1:2-naphthaquinones gives the 2and 4-NH₂-derivatives, m.p. $204-205^{\circ}$ and $224-225^{\circ}$, respectively (cf. A., 1924, i, 1354), probably by way of the azidoquinols, which, however, cannot be isolated in this series owing to the high reducing power of naphthaquinols. Attempts to prove the mechanism failed. 2-Chloro-1:4-naphthaquinone and NaN₃ in EtOH give the 2-azide, m.p. 118° (decomp.), which is equally readily reduced at the N₃ and CO groups. *p*-Xyloquinone does not react with HN₃, but toluquinone and *ar*-tetrahydro-1:4-naphthaquinone, like benzoquinone, give azidoquinhydrones. 2-Methyll: 4- and 4-methyl-1: 2-naphthaquinone do not react, but 3-bromo-1: 2-naphthaquinone gives the 3-bromo-4-aminoquinone. R. S. C.

Tautomerism between diphenylmethyl-1:2naphthaquinone and hydroxy-a-naphthafuchsone. L. F. FIESER and J. L. HARTWELL (J. Amer. Chem. Soc., 1935, 57, 1484-1486).-1:2-C₁₀H₆(OH)₂ (prep. from the quinone by SO₂ in hot H_2O), m.p. (+ H_2O) 56—60°, (anhyd.) 101—102°, adds CPh₂Cl₂ at 100° to yield 2-hydroxy-1: 4-naphthafuchsone-1 (I), m.p. 202—202.5°, which exists partly in this form, since it is sol. in NaOH and gives an acetate, m.p. 158—159° (decomp.), Me ether (II) (by CH_2N_2), m.p. 177-178°, and azine, m.p. 263-264°, but also partly as 4-benzhydryl-1: 2-naphthaquinone, since reduction gives an electromotively active system of the type characteristic of naphthaquinones. (I) and 1: 2-dihydroxy-4-benzhydryl-Zn-AcOH afford Zn-AcOH afford 1: 2-dihydroxy-4-benzhydryl-naphthalene, m.p. $161-161\cdot5^{\circ}$ (Ac₂ derivative, +AcOH, m.p. $159-161^{\circ}$, and anhyd., m.p. $163-164^{\circ}$; diphenylmethylene ether, m.p. $174-175^{\circ}$). (II) yields similarly 2-methoxy-4-benzhydryl-1-naphthol, m.p. $136-137\cdot5^{\circ}$ (Ac derivative, m.p. $166-167^{\circ}$). $6:1:2\cdot C_{10}H_5Br(OH)_2$, $+H_2O$, m.p. $88-88\cdot5^{\circ}$ (Ac₂ derivative, m.p. $117-118^{\circ}$), yields similarly 6-bromo-2-hydroxynaphthafuchsone-1, m.p. $223-224^{\circ}$. α -Naphthafuchsone resembles a quinone only in its reduction products: additive reaction only in its reduction products; additive reaction involving the 2:3-ethylenic linking do not occur. R. S. C.

Degradation of naphthazarin and naphthazarin homologues by ozone. H. RAUDNITZ and F. BEHRENS (Ber., 1935, 68, [B], 1484—1487).—Ozonolysis of naphthazarin in AcOH and decomp. of the ozonide by H_2O leads to 3 : 6-dihydroxyphthalic acid. Similar treatment of methylnaphthazarin (I) from methylquinol and maleic anhydride or quinol and citraconic anhydride affords 2 : 5-dihydroxy-6- $\alpha\beta$ -diketopropylbenzoic acid, m.p. 84°; (I) is therefore 1 : 4dihydroxy-7-methyl-5 : 8-naphthaquinone. Dimethylnaphthazarin analogously yields 3(? 4)-methyl-6- $\alpha\beta$ diketopropylbenzoic acid, m.p. 165°. The anomalies observed in the ozonolysis of alkannin Me ether are due to the stable OMe. H. W.

Condensation of naphthalene with phthalic anhydride. E. DE B. BARNETT and N. R. CAMPBELL (J.C.S., 1935, 1031).—The product of this condensation (with AlCl₃ in C₂H₂Cl₄ at room temp.) contains o- β *naphthoylbenzoic acid*, m.p. 166°, a powerful sternutator, which with H₃BO₃ in conc. H₂SO₄ gives 1 : 2benzanthraquinone and other quinones, is reduced (Zn-Cu in alkali) to ω - β -*naphthyl*-o-toluic acid, m.p. 135°, and is readily decarboxylated by Cu chromite. E. W. W.

Derivatives of the di- and tetra-polymethylenoanthracenes. I. E. DE B. BARNETT and C. A. LAWRENCE (J.C.S., 1935, 1104—1107).—The diols obtained by pinacol condensation of cyclopentanone (I) and cyclohexanone (II) are readily dehydrated to conjugated dienes which undergo Diels reaction with the formation of polycyclic compounds. 1:1'-Dihydroxy-1:1'-dicyclopentyl [obtained in moderate yield by heating (water-bath) (I), Al, HgCl₂, and C₆H₆ for 1 hr. and then for a further hr. after the addition of H₂O and more C₆H₆ (cf. lit.)] when heated at 140—160° with dehydrated alum affords crude di- $\Delta^{1:1'}$ -cyclopentene (III), b.p. 208°. This when warmed with maleic anhydride affords 1:2:3:6-tetrahydro-3:4:5:6-dicyclopentenophthalic anhydride, m.p. 104°, and when boiled during 1 hr. with benzoquinone (IV) and MeOH affords tetrahydro-5:6:7:8-dicyclopenteno-1:4-naphthaquinone (V, n=3), m.p. 124°, converted by boiling with Ac₂O and C₅H₅N into 5:8dihydro-5:6:7:8-dicyclopentenonaphthaquinyl diacetate, m.p. 145°. (V, n=3) when heated with (III) affords octahydrotetracyclopentenoanthraquinone (VI, n=3), m.p. 152°. (III) when boiled with α -naphthaquinone (VII) and EtOH during 1 hr. affords tetrahydro-1:2:3:4-dicyclopentenoanthraquinone, m.p.

$$[H_{2}C]_{n} - CH CO \qquad [H_{2}C]_{n} - CH CO CH - [CH_{2}]_{n}$$

$$C CH CH CH C CH CH CH C$$

$$C CH CH CH C CH CH C$$

$$[H_{2}C]_{n} - CH CO [H_{2}C]_{n} - CH CO CH - [CH_{2}]_{n}$$

$$[H_{2}C]_{n} - CH CO (H_{2})_{n} - CH CO CH - [CH_{2}]_{n}$$

134°, converted by boiling with Ac₂O and C_5H_5N during 3 hr. into 1:4-dihydro-1:2:3:4-dicyclopentenoanthraquinyl diacetate, m.p. 195°, and oxidised with the loss of 4H by passing air through a suspension in EtOH (+a little NaOH) to 1:2:3:4-dicyclopentenoanthraquinone, m.p. 253°. This when boiled with Zn, NaOH, NH₃, EtOH, and H₂O during 6 hr. is reduced to 1:2:3:4-dicyclopentenoanthracene, m.p. 146°. By similar methods (II) is converted into $di \cdot \Delta^{1:1'}$ -cyclohexene (VIII), m.p. 28°, b.p. 245—251°, which when heated with maleic anhydride affords dodecahudronhenanthrene.9:10 dicarboradic anhydride dodecahydrophenanthrene-9: 10-dicarboxylic anhydride, m.p. 122°, and when boiled with (IV) and EtOH during 5 hr. yields dodecahydro-5:6:7:8-dibenz-1:4-naphthaquinone (V, n=4), m.p. 114°, converted by boiling with Ac_2O and C_5H_5N during 2 hr. into decahydro-5:6:7:8-dibenznaphthaquinyl diacetate, m.p. 161°. (VIII) when heated with (IV) alone yields eicositetrahydrotetrabenzanthraquinone (VI, n=4), m.p. 315° (decomp.). (VIII) when heated with (VII) dodecahydro-1:2:3:4-dibenzanthraquinone, affords m.p. 208° (decomp.), converted by boiling with Ac₂O and C₅H₅N during 2.5 hr. into decahydro-1:2:3:4dibenzanthraquinyl diacetate, m.p. 228°, and oxidised with the loss of only 2H by passing air through a suspension in EtOH+alkali to decahydro-1:2:3:4dibenzanthraquinone (IX), m.p. 254°. No pure product could be obtained from the interaction of (VIII) with naphthazarin, but 5:8-diacetoxydodecahydro-1:2:3:4-dibenzanthraquinone, m.p. 173°, is obtained when naphthazarin diacetate, (VIII), and PhMe are boiled during 2.5 hr.; the dye obtained by



subsequent hydrolysis and oxidation could not be purified. (V, n=3) when boiled with (VIII) yields

hexadecahydro-5:6:7:8-dicyclopenteno-1:2:3:4dibenzanthraquinone, m.p. 222°. (VIII) when boiled during 1 hr. with endo-9:10-o-phenylene-9:10dihydro-1:4-anthraquinone and xylene yields endo-9:10-o-phenylenetetradecahydro-1:2:3:4-dibenznaphthacenequinone (X), m.p. 260—267° (decomp.). Attempts to obtain purely aromatic hydrocarbons by Se dehydrogenation of some of the above derivatives of (VIII) were not successful.

By a method similar to that used for the prep. of (III), 1-ketotetrahydronaphthalene is converted into 1:1'-dihydroxy -1:2:3:4:1':2':3':4'-octahydro-1:1'-dinaphthyl, m.p. 191°, which when heated at 170—190° with dehydrated alum yields 3:4:3':4'-tetrahydro-1:1'-dinaphthyl, m.p. 140°. This, however, did not react with (IV) or with (VII), and gave no pure product with maleic anhydride. H. G. M.

General reaction of halogen-tannins. F. ALLE-GRI (Boll. Chim. Farm., 1935, 74, 555—556).—The violet-red colour given by a solution of I and tannin when poured into H_2O containing an electrolyte is not due to nascent I liberated by hydrolysis and oxidation of a labile iodotannin, as it is given also when the I is replaced by Cl or Br. T. H. P.

Chemistry of saponins. R. TSCHESCHE (Angew. Chem., 1935, 48, 569-573).—A review.

New sulphur-bacterium from thermal springs. —See this vol., 1281.

Echinenone and pentaxanthin.—See this vol., 1145.

Red dye of the Alkanna root. K. BRAND and A. LOHMANN (Ber., 1935, 68, [B], 1487—1494).—Percolation of Alkanna root with light petroleum and removal of the solvent followed by extraction of the residue with abs. Et_2O gives, after removal of Et_2O , a dark red oil which is transformed by $Cu(OAc)_2$ into the compound (I), $C_{21}H_{20}O_6Cu$ or $C_{20}H_{20}O_6Cu$. Treatment of (I) with 25% HCl and Et_2O affords a red oil (II) also obtained from alkannin "Merck" through the Ni compound (III) of Raudnitz *et al.* (this vol., 217). (I) and (III) are free from OMe (cf. this vol., 1254). Hydrolysis of (II) with KOH gives angelic acid in 27.5—27.8% yield. Alkannin therefore occurs in the root as a very unstable monoester. H. W.

Preparation of bixin. H. N. HOLMES and W. H. BROMUND (Science, 1935, 82, 202).—The prep. of cryst. bixin (I), m.p. 192°, by treatment of annatto seeds with COMe₂ is described. Traces of (I) give a blue solution with conc. H_2SO_4 . (I) is readily sol. in alkali. L. S. T.

Resinols of the latex of Holarrhaena antidysenterica. J. C. CHOUDHURY and D. H. PEACOCK (J.C.S., 1935, 1129—1131).—This latex contains lettoresinol-A (I), $C_{28}H_{50}O_5$, m.p. 227—228°, $[\alpha]_{15}^{33}$ +68·6° in CHCl₃, and -B (II), $C_{32}H_{54}(OH)_2$, m.p. 136—137°, $[\alpha]_{25}^{29}$ +61·1° in CHCl₃ (Ac_2 derivative, m.p. 170°, $[\alpha]_{25}^{20}$ +71·2° in CHCl₃), and much uncrystallisable gum. (I) is neutral, unchanged by hot KOH-EtOH, Ac₂O, or ketonic reagents, and contains no OMe. (II) is neutral and stable to hot KOH-EtOH. With CrO₃ (1—2 mols.) in AcOH (II) gives a hydroxyketone, $C_{32}H_{54}O_2$, m.p. 216°, isolated as Ac derivative, m.p. 208°, but with 3 mols. of CrO_3 a compound, $\text{CHO} \cdot \text{C}_{29}\text{H}_{49} < \stackrel{\text{CO}}{\text{CH}_2}$ or $\text{C}_{28}\text{H}_{47}\text{Ac} < \stackrel{\text{CO}}{\text{CH}_2}$, m.p. 265°, $[\alpha]_D^{30} + 90.6^\circ$ in CHCl_3 (disemicarbazone, m.p. 287°), and an acid, $\text{C}_{29}\text{H}_{49}$ or $_{47}(\text{CO}_2\text{H})_3$, m.p. 174–175°, $[\alpha]_D^{31} + 25.3^\circ$ in CHCl_3 . R. S. C.

Bitter principles of the Colombo root. II. K. FEIST, E. KUNTZ, and R. BRACHVOGEL (Annalen, 1935, 519, 124—133; cf. this vol., 864).—Distillation of columbin (I) with Zn dust yields o-cresol and 1:2:5-C₁₀H₅Me₃. Dehydrogenation of hydrochasmanthic acid (II) with Se at 280° affords small amounts of readily volatile hydrocarbons which give cryst. derivatives with Br and a substance, C₁₅H₁₆O₂, m.p. 205°, also obtained similarly from hydro-Vcolumbin; at 320°, 1:2:5-C₁₀H₅Me₃ is produced. (I) and chasmanthin do not show absorption in the region 405—238 mµ and therefore probably do not contain conjugated double linkings. (I) and KOH at 310° give 2:4-C₆H₃Me₂·CO₂H. Oxidation of (I) or (II) with MnO₂ and H₂SO₄ yields 1:2:3-C₆H₃(CO₂H)₃ and 1:2:3:4-C₆H₂(CO₂H)₄. d-Columbin, m.p. 194°, $[\alpha]_{50}^{20}$ +37.9° in COMe₂, is isolated from the residue of the prep. of (I).

H. W.

1:5-endoMethylenecycloheptane-2:4-dione. P. C. GUHA and S. K. RANGANATHAN (Current Sci., 1935, 4, 26).—The Me_1 ester of cyclopentane-1:3dicarboxylic acid, b.p. 156°/4 mm. (from cis-cyclopentane-1:3-dicarboxylic anhydride), with SOCl₂ gives the corresponding acid chloride, b.p. 109°/3 mm., converted by ZnMeI into Me 1-acetylcyclopentane-3carboxylate, b.p. 100°/2 mm. (semicarbazone, m.p. 139°), which is hydrolysed to 1-acetylcyclopentane-3carboxylic acid (I), b.p. 155°/5 mm. (lit. 175—205°/ 10 mm.) (semicarbazone, m.p. 169°), whilst reaction with NaOMe-MeOH gives a mixture of (I) and 1:5endomethylenecycloheptane-2:4-dione (?), m.p. 123·5° (semicarbazone, m.p. 224°). F. N. W.

Dehydrocineoles. I. Preparation of 5methyl-2-isopropylfuran and its condensation with maleic anhydride. L. W. BUTZ (J. Amer. Chem. Soc., 1935, 57, 1314-1315).-Oxidation (aq. KMnO₄ at about 6°) of methylheptenone gives $\beta\gamma$ dihydroxy-β-methylheptan-ζ-one, b.p. 138.5°/11 mm., converted by boiling 5% H₂SO₄ into β -methylhept-ane- $\gamma\zeta$ -dione, b.p. 90—92°/11 mm., which is dehydrated by conc. H_2SO_4 (at 50° and subsequent distillation) to 5-methyl-2-isopropylfuran, b.p. 135-137°/ 770 mm. This and maleic anhydride in cold Et₂O afford 2:3-dehydro-1:4-cineole-5:6-dicarboxylic anhydride [3: 6-oxido-3-methyl-6-isopropyl- Δ^4 -tetrahydrophthalic anhydride], m.p. 77°. H. B.

Carvone series. III. Carvomenthols, *l-iso*carvomenthone, and *l-iso*carvomenthylamine. R. G. JOHNSTON and J. READ (J.C.S., 1935, 1138— 1143; cf. A., 1934, 413).—Pure isomerides of this series are prepared for the first time. ≥ 2 isomerides are formed in each reaction, and these are separated before the next stage is undertaken. d-*Carvo*menthol (I), b.p. 101·8—102°/14 mm., $[\alpha]_{1^3}^{1^3} + 27\cdot69^{\circ}$ [3:5-dinitro-, m.p. 107°, $[\alpha]_{1^3}^{1^3} + 52\cdot8^{\circ}$, and p-nitrobenzoate, m.p. 60°, $[\alpha]_{1^7}^{1^7} + 51\cdot7^{\circ}$; l-, $[\alpha]_{1^7}^{1^5} - 18\cdot1^{\circ}$, and

d-menthoxyacetate, $[\alpha]_{15}^{15} +93.4^{\circ}$ in CHCl₃, oils; d-, a gum, $[\alpha]_{15}^{15} +59.6^{\circ}$ in CHCl₃, and 1-camphor-10-sulphonate, m.p. 57—58°, $[\alpha]_{15}^{15} +8.0^{\circ}$, decompose at 164—166° into $l-\Delta^{1}$ -menthene (III) and the active camphor-10-sulphonic acid; $[\alpha]$ for these and other camphor-10-subplotte acid; $[\alpha]$ for these and other solids in CHCl₃; *H phthalate*, m.p. 90—91°, $[\alpha]_{\rm D}$ +57.8° in EtOH], is obtained (1) from *d*-carvo-menthylamine and HNO₂ (gives also a torpene fraction, b.p. 61—101°/16 mm., $\alpha_{\rm D}$ +0.32°), (2) as sole product of hydrogenation (colloidal Pd) of d-dihydrocarveol in H₂O, (3) with 1-neoisocarvomenthol (III), $[\alpha]_{\rm b}^{17}$ -34.7° (3:5-dinitro-, m.p. 71-72°, $[\alpha]_{\rm b}$ -16°, and p-nitro-benzoate, m.p. 54-55°, $[\alpha]_{\rm b}$ -23.7°), by hydrogenation (Pd-CaCO₃) of d-cis-carveol (IV) in by hydrogeneration (1d 0.000_3) of d.colored vet (11) m MeOH, and (4) with 1-neocarvomenthol (V) from l-carvomenthone (VI) and Al(OPr^{β})₃. (V), b.p. $102^{\circ}/18$ mm., $[\alpha]_{p1}^{31} - 41 \cdot 70^{\circ}$ (p-nitro-, m.p. 95° , $[\alpha]_p - 22 \cdot 8^{\circ}$, and 3:5-dinitro-benzoate, m.p. 129° , $[\alpha]_p - 22 \cdot 6^{\circ}$; H phthalate, m.p. $123-124^{\circ}$, $[\alpha]_p - 48 \cdot 7^{\circ}$ in EtOH), is obtained also (a) with (II) and (I) from l-neocarvomenthylamine (hydrochloride, $[\alpha]_D^{16} - 31.9^\circ$ in H₂O) and HNO₂, (b) by hydrogenation (colloidal Pd) of *l*-neodihydrocarveol in H_2O , (c) with (II) by hydrogenation (colloidal Pd) of esters, best the acetate, $[\alpha]_{D}^{14}$ +177.5°, of *d*-trans-carveol (VII) in Et₂O (the free alcohol gives mainly p-menthane with this catalyst), and (d) from (VII) with H_2 -Pd-CaCO₃ in MeOH. dl-trans-Carveol with Pd-CaCO₃-H₂ (4 atm.) in aq. MeOH gives dl-neo-, an oil (p-nitro-, m.p. 91-92°, and 3: 5-dinitro-benzoate, m.p. 101°), and dl-isocarvomenthol (VIII), b.p. 110°/20 mm. (3:5-dinitrobenzoate, m.p. 94.5°), and only a little hydrocarbon. Reaction (d) gives also 1-isocarvomenthol, b.p. $106^{\circ}/$ 17 mm., $[\alpha]_{\rm b}^{\circ}$ -17.72° (p-nitro-, m.p. 64.5° , $[\alpha]_{\rm p}$ -27.3°, and 3:5-dinitro-benzoate, m.p. 111°, $[\alpha]_{\rm p}$ -26.7°), further obtained from l-isocarvomenthylamine (IX) and HNO2 with another alcohol, b.p. 98°/21 mm. (VIII) with Beckmann's reagent gives *l-isocarvonnenthone* (cf. *loc. cit.*), $[\alpha]_{\rm D}^{ab}$ -56.5° [*semi-carbazone*, m.p. 171-172°, $[\alpha]_{\rm D}$ -117°; with cold NaOEt is equilibrated to give 80% of (VI)], the oxime, an oil, $[\alpha]$ -79.5°, of which with Na-EtOH gives (IX), b.p. 90°/15 mm., $[\alpha]_{D^8}^{18} - 14.7^{\circ}$ [Bz, m.p. 153° (lit. 151–152°), $[\alpha]_{D} - 40.7^{\circ}$, and Ac derivative, m.p. 96°, $[\alpha]_{D} - 57.4^{\circ}$; hydrochloride, $[\alpha]_{D} - 14.3^{\circ}$ in H₂O; H d-tartrate, m.p. 179°, $[\alpha]_{D} + 5.3^{\circ}$ in H₂O], previously (loc. cit.) obtained impure by Na-EtOH reduction of the oxime of (VI). Oxidation (Beck-mann) of (I) and (V) gives (VI). Reduction of carvone to a mixture of cis- and trans-carveol is effected better by Al(OBu^{\$})3-Bu^{\$}OH than by Al $(OPr^{\beta})_{3}$ -Pr^{β}OH. Crude (VI), obtained by hydrogenation of d-carvone (X), is purified by treatment with NaOEt, oximation, reduction, benzoylation, hydrolysis, and finally oxidation, which gives a product having b.p. $98\cdot5^{\circ}/18$ mm. and $[\alpha]_{D}^{17}$ --7.8°. The *p*-nitrobenzoates of (IV) and (VII), m.p. 28° and 77°, $[\alpha]_{D}$ --57° and 264°, respectively, form a const.-crystallising mixture, m.p. 84°, $[\alpha]_D$ +85°. Hydrogenation of (X) with Rupe's Ni gives a mixture containing 62% of (VI). A 1:2-menthanediol, m.p. 112-114°, has been prepared. R. S. C.

Isomerisation of terpene oxides. I. Isomerisation of α -pinene oxide during Reformatsky's reaction. B. ARBUSOV (Ber., 1935, 68, [B], 1430– 1435).— α -Pinene oxide (I) is transformed by Zn and CH₂Br•CO₂Et into Et β -hydroxy- γ -2:2:3-trimethyl- Δ^3 -cyclopentenylbutyrate, b.p. 146—147°/4 mm., hydrolysed to β -hydroxy- γ -2:2:3-trimethyl- Δ^3 -cyclopentenylbutyric acid, m.p. 74—75°. The structure of the product follows from its formation from Zn, CH₂Br•CO₂Et, and campholenealdehyde (II) obtained by the action of ZnBr₂ in C₆H₆ on (I). Oxidation of (II) with Ag₂O affords α -campholenic acid, b.p. 142— 142·5°/10·5 mm., oxidised by KMnO₄ to dihydroxydihydrocampholenic acid, m.p. 143—144°. H. W.

Anomalous mutarotation of salts of Reychler's acid. II. Ketimine formation from amine salts of d-camphor-10-sulphonic acid. R. S. SCHREI-BER and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 1445-1447; cf. this vol., 1118).-The salts of d-camphor-10-sulphonic acid (I) with NHMe₂, m.p. $69-83^{\circ}$, $[\alpha] + 34 \cdot 6^{\circ}$, $+32 \cdot 1^{\circ}$ (all $[\alpha]$ are $[\alpha]_{1\nu}^{25}$ in 09-83, $[\alpha] +34.6$, +32.1 (an $[\alpha]$ are $[\alpha_{fn}$ m CHCl₃ and MeOH, respectively), NMe₃, m.p. 140– 145°, $[\alpha] +33°$, +29.2°, NBu₃, m.p. 128–138°, $[\alpha]$ +29.2°, +22.8°, piperidine, m.p. 135–138°, $[\alpha] +33.3°$, +30°, NHPhMe, m.p. 113–115°, $[\alpha] +29.6°$, +29.2°, NPhMe₃, m.p. 137–139°, $[\alpha] +37.9°$, +27.5°, and C_5H_5N , m.p. 185–192°, $[\alpha] +45.8°$, +31.6°, do not mutarotate in abs. MeOH, EtOH, or CHCl₃ and are not dehydrated when heated, thus confirming their structure and the authors' views (loc. cit.) on the mutarotation of the salts of primary bases. The NH_2Me salt of (I), m.p. 167-168°, $[\alpha] + 33.7°$, $+34.6^{\circ}$, does not mutarotate and loses H_2O only at 180° to form the ketimine, m.p. 296-297° (block), $[\alpha]_{p}^{25}$ -136° in EtOH (mutarotates slowly), but the NH2 CH2Ph salt mutarotates so rapidly that it cannot be obtained pure. 2-Benzyliminocamphane-10-sulphonic acid has m.p. $241-243^{\circ}$, $[\alpha] -107\cdot5^{\circ}$, $-112\cdot5^{\circ}$. Imine formation makes a large lævocontribution to α ; all imines, except camphoranil, m.p. 13.5°, $[\alpha] + 11.5°$, +7.2°, are lavorotatory. The phenylhydrazone of (I) has $[\alpha]_{D}^{25} - 185.3°$ in $CHCl_3$ -MeOH (1:1). R. S. C.

Terpene compounds. II. Synthesis of homoapofenchocamphoric acid. J. C. BARDHAN, S. K. BANERJI, and M. K. BOSE (J.C.S., 1935, 1127-1129; cf. this vol., 756).—Preliminary steps in the synthesis of β -fenchocamphorone are recorded. isoLaurolonic acid (modified prep.) and HNO₃ give $\alpha\alpha$ -dimethylglutaric acid, the Et₂ ester, b.p. 110-115°/9 mm., of which in Et₂O-EtOH gives a K-derivative, converted by $\text{Et}_{2}C_{2}O_{4}$ into $Et_{3} \gamma$ -methylbutane-axy-tricarboxylate, b.p. 145–148°/10 mm. This ester with Na and CH₂Br·CO₂Et gives $Et_4 \beta$ -methylpentane- $\beta\delta\delta\epsilon$ -tetracarboxylate, b.p. 175—176°/9 mm., which with hot 19% HCl affords β-methylpentane-βδε-tricarboxylic acid, m.p. 185-187°. The Et3 ester, b.p. 159°/8 mm., thereof with "mol." Na in C₆H₆ yields Et_2 2:2-dimethylcyclopentanone-4:5-dicarboxylate, b.p. 147-149°/9 mm., affording with hot 8% H₂SO₄ 2:2-dimethylcyclopentanone-4-carboxylic acid, m.p. 93°. The Et ester, b.p. 113°/9 mm., of the lastmentioned acid with Zn and a trace of I in C6H6 gives an impure OH-ester, converted by POCl₃-C₆H₆ into Et dehydrohomoapofenchocamphorate, b.p. 126-127°/4 mm., which is hydrogenated (PtO2) in Et20 to homoapofenchocamphoric acid, m.p. 246°, and a gummy acid. R. S. C.

Action of acraldehyde and crotonaldehyde on alloocimene. B. ARBUSOV (Ber., 1935, 68, [B], 1435—1439).—alloOcimene (I) and crotonaldehyde at 200° afford the additive product, $C_{14}H_{22}O$, b.p. 117.5—118.5°/3 mm., which with NaOEt and COMe₂ affords the substance, $C_{17}H_{26}O$, b.p. 148—150°/3 mm. Acraldehyde and (I) yield the aldehyde, $C_{13}H_{20}O$, b.p. 123—123.3°/10 mm. (semicarbazone, m.p. 200°), which condenses with COMe₂ to the compound, $C_{16}H_{24}O$, b.p. 144.5—146°/3.5 mm. H. W.

Hydrophthalides. VII. S. BERLINGOZZI and (SIGNA.) V. SENATORI (Gazzetta, 1935, 65, 424-440).-When benzylidenetetrahydrophthalide (I) is hydrolysed by conc. KOH, the resulting o-phenylacetyltetrahydrobenzoic acid (II) has m.p. 119° (A., 1932, 269). When, however, the hydrolysis is by dil. KOH in EtOH-H₂O, the product is an isomeride (III), m.p. 115° (Ag salt; oxime, m.p. 62°); this is a labile form, converted by conc. KOH into the stable (II). (III) is accompanied by a small quantity of 2-phenyl-1: 3-diketotetrahydrohydrindene, m.p. 104°, readily prepared by action of NaOMe on (I). Oxidation (alkaline KMnO₄) of both (II) and (III) gives BzOH, with some PhCHO, and traces of H₂C₂O₄ and CH₂Ph·CO₂H. Na-Hg in the cold, which is without action on (II), reduces (III) to o-phenylacetylhexahydrobenzoic acid (IV), m.p. 98° [phenylhydrazone, m.p. 50° (decomp.)], readily obtained from (II) or (III) by action of Zn and NaOH. Reduction of (II), (III), or (IV) by Na-Hg in dil. NaOH at the b.p. yields benzylhexahydrophthalide, m.p. 79°, and bis-(benzylhexahydrophthalide), $C_{30}H_{34}O_4$, m.p. 113°. From these reactions it is deduced that (III) is 2-phenylacetyl- Δ^2 -tetrahydrobenzoic acid, and (II) most probably 2-phenylacetyl- Δ^1 -tetrahydrobenzoic acid (or possibly the Δ^6 -compound). Benzylidenetetrahydrophthalide, obtained by condensation of Δ^2 -tetrahydro-

E. W. W.

Catalytic oxidations. I. Oxidations in the furan series. N. A. MILAS and W. L. WALSH (J. Amer. Chem. Soc., 1935, 57, 1389-1393).-An apparatus is described whereby an easily resinified substance may be brought rapidly in a stream of gas in contact with a heated catalyst. The technique is used to investigate the effect of varying the ratio, R, furfuraldehyde (I): air or oxygen, H_2O content, temp., time of contact with the catalyst, and the nature of the catalyst [V₂O₅ (prep. described), Bi vanadate, Mo₂O₃-V₂O₅]. Only maleic acid (II) is isolated, the max. yield, 25%, being obtained at 320° with V_2O_5 and R=180:1 (air or oxygen, moist or dry). With V2O5 in dry air at 320° furan (III), furoic acid (IV), (I), and furfuryl alcohol give max. yields of 65, 48.4, 25, and 22.5% of (II) with R=130, 242, 180,and 180, respectively. Oxidation probably proceeds thus: $(I) \rightarrow (IV) \rightarrow (III) \rightarrow (V) \rightarrow (:CH \cdot CHO)_2 \rightarrow$ (II).

$$\begin{array}{c} CH \\ \parallel \\ CH \\ CH \\ CH \\ CH \end{array} (V.) \\ R. S. C. \\ R. S. C. \\ \end{array}$$

Diphenylene oxide series. V. N. M. Culli-NANE and H. J. H. PADFIELD (J.C.S., 1935, 1131-1134; cf. A., 1934, 779).-The following and other substitutions agree with an extension of Robinson's electronic mechanism for substitution of diphenylene oxide derivatives. 2-Nitrodiphenylene oxide is un-changed by $SOCl_2$, but with Cl_2 in warm AcOH gives 6-chloro-2-nitrodiphenylene oxide (I). Diphenylene oxide (II) and Cl₂ (1 mol.) in AcOH give the 6-Cl-(III) and 3: 6-Cl₂-derivatives, but with 0.5 mol. of Cl_2 only (I) is formed. (III) and HNO₃ (d 1.5) in AcOH give (I). 2-Aminodiphenylene oxide (IV) gives (diazo-reaction) the 2-Br-compound, which with Br in hot AcOH gives a Br₂-derivative, m.p. 174°. Nitration of 2-chlorodiphenylene oxide gives probably 2-chloro-7-nitrodiphenylene oxide, m.p. 253°. Nitration of (IV) gives 3-nitro-2-aminodiphenylene oxide (previously considered to be the 1-NO2-compound), the structure of which is proved by conversion into 3-nitrodiphenylene oxide, m.p. 110°; this is reduced to the amine, which yields the known 3-Brand $3\text{-}CO_2\text{H}\text{-}derivatives}$. (II) with Na-cyclohexanol or H_2 -Pt-black in AcOH gives the $1:2:3:4-H_4$ derivative (70 and 97% yield, respectively), b.p. $151^{\circ}/20$ mm., $270^{\circ}/760$ mm. (*picrate*, m.p. 91°), dehydrogenated to (II) by S or Se at 260° or by hot 5% KMnO₄ with or without MgSO₄, but not by Hg(OAc)₂. The H₂-derivative of (II) could not be prepared by hydrogenation. PhSH and PbO at 160° give diphenylene disulphide and sulphide this properties of the state of the (thianthren), Ph₂S, and (PhS)₂. R. S. C.

Constitution phenylbenzoxanthenols and β benzoxanthone, W. KNAPP (J. pr. Chem., 1935, [ii], 143, 210).—In an earlier thesis (1931) the author put forward views in agreement with those of Dilthey et al. (A., 1934, 1227). J. W. B.

Manufacture of quinones of [benznaphthofuran].—See B., 1935, 796.

β-Hydroxyethyl ethers of substituted phenols and related substances. D. C. MOTWANI and T. S. WHEELER (J.C.S., 1935, 1098-1101).-Attempts to synthesise dihydrofuranoflavones from a coumaran or a flavone were unsuccessful; numerous flavone derivatives obtained are described. Resacctophenone (I) with $CH_2Cl \cdot CH_2 \cdot OH$, KOH, and H_2O (100°; 3 hr.) affords 2-hydroxy-4-(β-hydroxyethoxy)acetophenone (II), m.p. 106° [gives violet coloration with FeCl₃-EtOH; Ac₂ derivative, m.p. 70°; oxime, m.p. 144°; hydrazone, m.p. 123°; azine (III), melts at 253° to an opaque liquid becoming transparent at 263°; phenylhydrazone (IV), m.p. 148-149°; anil (V), m.p. 173°; benzidine condensation product, $OH \cdot C_2H_4 \cdot O \cdot C_6H_3(OH) \cdot CMe: N \cdot [C_6H_4]_2 \cdot NH_2, m.p. 288-$ 290° (softens at 153°; gives a red dye when diazotised and coupled with β -C₁₀H₇·OH); the corresponding 4-(β -acetoxyethoxy)-, m.p. 117°, and 4-(β -benzoyloxyethoxy)-, m.p. 100°, compounds give a violet color-ation with FcCl₂-EtOH and are sol. in alkali]. Only one OH of (I) reacts with CH₂Cl·CH₂·OH. (II) is reduced by Zn-Hg-conc. HCl to 2-hydroxy-4-(β hydroxyethoxy)ethylbenzene, m.p. 99-100°, b.p. 200-210°/5 mm. (gives blue-black coloration with FeCl3-EtOH; Bz derivative, m.p. 109-110°, sol. in alkali), also obtained, together with some 2: 4-di-(\beta-hydroxy-

ethoxy)ethylbenzene, m.p. 66°, from the condensation of 4-ethylresorcinol with CH2Cl·CH2 OH. Similarly *m*-methoxyphenol, CH₂Cl·CH₂·OH, and KOH afford m-(β-hydroxyethoxy)anisole, b.p. 160°/2 mm. [Ac derivative, b.p. 140°/7 mm.; Bz derivative, m.p. 91-92°; chloro-ether, b.p. 130°/5 mm. (obtained on treatment with PCl₅)]. (II) with PhCHO, KOH, and EtOH affords 2-hydroxy-4-(β-hydroxyethoxy)chalkone (VI), m.p. 123-124° [Ac2 derivative (VII), m.p. 68°; the corresponding 4-(β-acetoxyethoxy)chalkone has m.p. 139° (softens at 135°; violet coloration with FeCl₃-EtOH)], which when refluxed with EtOH-H2SO4 yields 7-(β-hydroxyethoxy) flavanone, m.p. 113°. (VII) and Br in CS₂ give a Br_2 -derivative, m.p. 122°, which with NaOH-EtOH-H₂O affords 7- $(\beta$ -hydroxyethoxy) flavone, m.p. 166° (Ac derivative, m.p. 130°); this when boiled with PhOH and HI (CO2 atm.) affords 7-hydroxyflavone (cf. A., 1926, 1149). (VI) with Br in CHCl₃ yields 5-bromo-2-hydroxy-4- $(\beta$ -hydroxyethoxy)chalkone dibromide, m.p. 204° (efferv.), hydrolysed by NaOH-EtOH-H₂O to 6-bromo-7-(β-hydroxyethoxy)flavone, m.p. 206.5°, which when refluxed with PBr5 in PhMe affords the corresponding 7- $(\beta$ -bromoethoxy)flavone, m.p. 199°. (II) with p-anisaldehyde and KOH affords 2-hydroxy-4'methoxy-4- $(\beta$ -hydroxyethoxy)chalkone, m.p. 134° [Ac₁ derivative, m.p. 134—135° (sol. in alkali; gives violet coloration with FeCl₃-EtOH); Ac₂ derivative (VIII), m.p. 87—88°]. (VIII) with Br in CS₂ affords a Br₂-compound, m.p. 105—107° (efferv.), hydrolysed to 4'-methoxy-7-(β-hydroxyethoxy) flavone, m.p. 155° [Ac derivative, m.p. 141° (efferv.)]. (II) when shaken with o-NO₂·C₆H₄·CHO, KOH, and EtOH in an ambercoloured bottle affords 2'-nitro-2-hydroxy-4-(\beta-hydroxyethoxy)chalkone, m.p. 183° (turns green on exposure to light), the Ac₂ derivative, m.p. 155°, of which regenerates the original substance on hydrolysis, thus proving that the original substance is not the lactyl-ketone. Condensation of (II) with o-OH·C₆H₄·CHO, KOH, and EtOH (60° ; 24 hr.) affords 2:2'-dihydroxy-4-(β -hydroxyethoxy)chalkone, m.p. 177°, which with dry HCl in AcOH affords 2'hydroxy-4'-(β-acetoxyethoxy)flavylium chloride, m.p. 212-213°. This with conc. aq. NaOAc yields the colour base, m.p. 180° (ferrichloride, m.p. 214°; mercurichloride, m.p. 215°; perchlorate, m.p. 201– 203°; picrate, m.p. 211–213°). (III), (IV), and (V) are insol. in aq. alkali, but dissolve on addition of alkali to an alcoholic suspension (cf. A., 1919, i, 160). H. G. M.

Structure of flavylium salts. D. W. HILL and R. R. MELHUISH (J.C.S., 1935, 1161-1166).— Flavones (>0.02-0.03 g.) can be isolated by treating an Et₂O solution with solid CaCl₂, which ppts. the CaCl₂-compound (also formed by a saturated solution of CaCl₂ in conc. HCl), from which the flavone is regenerated by H₂O. This technique is used to show that five flavylium salts not substituted in position 3 react with Na₂CO₃ or NaOH at room temp. to give 10% of flavones with some chalkone and (probably) a mixture of pyranols. The heteropolar atom of such flavylium salts is, therefore, C4. 3-Substituted flavylium salts, shown by H₂O₂-oxidation to have C2 heteropolar, under similar conditions give only pyranols. 4-Flavonols from salts unsubstituted in BRITISH CHEMICAL ABSTRACTS .- A.

position 3 are highly unstable; they are isolated as Et ethers by NaOH-EtOH at low temp., but these ethers give salts with even a trace of acid and, although fairly stable in abs. EtOH, give chalkones quanti-tatively with hot aq. EtOH. 3-Substituted flavylium salts, however, give 2-flavonols by NaOAc or NaOH, and these give Et ethers with boiling EtOH; both these flavonols and their ethers are stable to hot aq. EtOH. 2-Phenyl-, m.p. 76°, and 2-anisyl-benzo-pyranol, m.p. 86°, 2-phenylnaphthapyranol, m.p. 131-133°, and 6- and 7-methoxy-2-phenylbenzopyranol 4-Et ethers, oils, are prepared from the corresponding flavylium chlorides and 3% NaOH in EtOH- H_2O (2:1) at room temp.; with HCl or AcOH and $FeCl_3$ or $HClO_4$ they give flavylium ferrichlorides or perchlorates, and with hot 50% EtOH the chalkones. 2-Hydroxynaphthylideneacetophenone, thus obtained, has m.p. 143-144°. 3-Methylflavylium chloride and KOH-EtOH give 2-phenyl-3-methylbenzopyranol 2-Et ether, m.p. 44°. 3-Phenylflavylium perchlorate and aq. NaOAc give 2:3-diphenylbenzo-2-pyranol, m.p. 125-126° (lit. 121-122°), converted by hot EtOH into the Et ether, m.p. 80°. 3-Methoxyflavylium perchlorate gives similarly 3-methoxy-2phenylbenzo-2-pyranol, m.p. 122°, and its Et ether, m.p. 123°, stable to 50% aq. EtOH. Flavylium chloride, 6-, 7-, and 4'-methoxy-, and B-naphthaflavylium chloride with 10% NaOH, 5% Na2CO3, or (the 4'-OMe-compound) with H₂O give the corresponding flavones. 6'- and 4'-Methoxyflavone have m.p. 162° and 156°, respectively. R. S. C.

Sarsasapogenin. III. Deoxysarsasapogenin. Further degradations of sarsasapogenin. J. C. E. SIMPSON and W. A. JACOBS (J. Biol. Chem., 1935, 110, 565—573).—Sarsasapogenin in CHCl₃ is converted (with much by-product formation) by PCl₅ in CS₂ at 0° into sarsasapogenyl chloride, $C_{27}H_{43}O_2Cl$, m.p. 228—229°, reduced by Na and boiling C_5H_{11} OH to deoxysarsasapogenin (I), m.p. 216—217°, oxidised by CrO₃-AcOH at 75° to a lactone $C_{22}H_{34}O_2$ (II),



m.p. 127—128° (hydrolysed by 0.5*N*-NaOH; lactone re-formed on acidification), which is very resistant to oxidation, and a mixture of acid products from which a cryst. Me ester is obtained with CH_2N_2 . This affords, in small yield, a *disemicarbazone*, m.p. 239—240°, of a triketo-acid, $C_{27}H_{40}O_5$ (III), probably formed from (I) through the intermediate glycol. Pyrolysis of the dibasic lactonic acid $C_{22}H_{32}O_6$ (IV) (this vol., 864; formula revised; the position of the



EtOH (but not by aq. alkali) to give the Me H ester, the second CO_2Me being resistant. The above sidechain structures are deduced on the basis of these new data. J. W. B.

2:4-Derivatives of thiophen. R. O. CINNEIDE (Proc. Roy. Irish Acad., 1935, 42, B, 359-363).-Thiophen-2-carboxylic acid (I) condenses with $OH \cdot CH_2 \cdot NH \cdot CO \cdot CH_2 Cl$ in H_2SO_4 at $0-5^\circ$ to give 4-N-chloroacetamidomethylthiophen-2-carboxylic acid, m.p. 153-156°, hydrolysed by boiling N-HCl to the hydrochloride (II), m.p. 242-245°, of 4-aminomethylthiophen-2-carboxylic acid, m.p. 292-295°, decomp. 302-305° [platinichloride, m.p. 205° (decomp.); aurichloride, m.p. 204-205°], converted by KNO2 into the 4-hydroxymethyl acid, m.p. 115-117°. Oxidation of (II) with cold, alkaline KMnO₄ gives thiophen-2: 4-dicarboxylic acid. Similar condensation of (I) with OH·CH₂·NHBz affords 4-N-benzamidomethylthiophen-2-carboxylic acid, m.p. 177.5-179.5° (Et ester, m.p. 90-96°), which also gives (II) when hydrolysed with HCl-EtOH at 100°. J. W. B.

Tautomerism of the system thiocoumarindiolthiochromonediol and of ascorbic acid. F. ARNDT and B. EISTERT (Ber., 1935, 68, [B], 1572-1575).-Developments in the knowledge of the action of CH_2N_2 enable the chemistry of the thiochromonediols to be interpreted as follows. The solid diol as such is 3:4-dihydroxy-6-methyl-1-thiocoumarin (I), which, in solution, is in equilibrium with a small propor-tion of 2:3-dihydroxy-6-methylthiochromone (II), $C_6H_3Me < S-COH S-COH$. In (II) the 2-OH is much more acidic than OH in any other position. If sufficient time is allowed for (I) to become enolised during the action of CH₂N₂, the main product is therefore 3hydroxy-2-methoxy-6-methylthiochromone; further methylation can then give rise only to 2: 3-dimethoxy-6-methylthiochromone (III). The product obtained by partial hydrolysis of (III) or by the action of Me₂SO₄ on (I) is 4-hydroxy-3-methoxy-6-methylthiocoumarin, $C_6H_3Me < S \xrightarrow{C(OH), C \cdot OMe}_{CO}$, which in solution can become enolised to 2-hydroxy-3-methoxy-6methylthiochromone, converted by CH₂N₂ predominatingly into (III). If, however, (I) is introduced directly into excess of CH_2N_2 the formation of 3:4dimethoxy-6-methyl-1-thiocoumarin is favoured. The analogy of the system with that of ascorbic acid is pointed out. Tautomerism between γ -keto- α -hydroxy- and α -keto- γ -hydroxy-forms appears restricted to systems with β -OH or β -OAlk. Thus, naphthapyronone, $C_{10}H_6 < \begin{array}{c} CO \cdot CH_2 \\ O - CO \end{array}$, under varied conditions is transformed by CH_2N_2 into a *Me ether*, m. p. 207— 208°, also obtained by the action of MeI on the Ag salt and therefore formulated $C_{10}H_6 < \begin{array}{c} C(OMe).CH \\ O - CO \end{array}$. Similarly 6-methylpyronone and CH_2N_2 afford only the ether $O < \begin{array}{c} CMe.CH \\ CO - CH \end{array} > C \cdot OMe. H. W.$

Sulphur compounds of technical interest. Isomeric thiophthens. F. CHALLENGER and J. B. HARRISON (J. Inst. Petroleum Tech., 1935, 21, 135-154).-C₂H₂ and S at 440° in CO₂ give CS₂, thiophen, thionaphthen, thiopheno-2': 3'-3: 2-thiophen (I), $CH \ll CH \cdot C - S \gg CH$, m.p. 56° [picrate, m.p. 145°; styphnate, m.p. 112–113°; $Br_{4^{-}}$, m.p. 230–231°, and $NO_{2^{-}}$ derivative (II), m.p. 124.5–125°], and a second, difficultly purifiable thiophthen (III), thiopheno-2': 3'-2:3- (IV), $CH \ll CH \cdot C \cdot CH \to CH$, or, less probably, -2':3'-3:4-thiophen, $CH \ll_{S}^{CH-C:CH} > S$, m.p. 6.25-6.5°, b.p. 98°/13 mm. (picrate, m.p. 137–138°; styphnate, m.p. 127–128°; HgCl-, m.p. > 300°, Br_{3^-} , m.p. 123–124°, and NO_2 -derivative, m.p. 125.5– 126°). Citric acid and P_2S_3 afford (cf. A., 1886, 1032) a thiophthen (VI), m.p. 5.75-6°, b.p. 99-100°/ 12 mm. (picrate, m.p. 136—137°; styphnate, m.p. 129·5—130°; HgCl-, m.p. 2280°, Br_3 -, m.p. 123—124°, and NO_2 -derivative, m.p. 122—123°; Hg dithiophthienyl, decomp. > 220°), and a ? hydroxythio phthen, $C_0H_4OS_2$, m.p. 86—87° (no picrate formed; properties of a phenel). (1) with Ne obs. FtOH properties of a phenol). (I) with Na-abs. EtOH affords 3-thiol-2-ethylthiophen, C₆H₈S₂, b.p. 195-197° (Hg salt, m.p. $75-76^{\circ}$), and (III) and (VI) also give mercaptans. (II) and SnCl₂ give the aminothiophthen (Ac derivative, m.p. 220.5-221.5°). (III) with AcCl and SnCl4 in CS2 yields thiophthienyl Me ketone (VII), m.p. 113° (p-nitro-, m.p. 246-247°, and 2: 4-dinitrophenylhydrazone, m.p. 267-268°; oxime, m.p. 172-173°), reduced (Clemmensen) to an ethylthiophthen, b.p. 120-125°/15 mm. (picrate, m.p. 70°). (VI) gives similarly a Me ketone (VIII), m.p. 115-116° (oxime, m.p. $160-161^{\circ}$; p-nitro-, m.p. $241-242^{\circ}$, and 2:4-dinitro-phenylhydrazone, m.p. $267-268^{\circ}$), and (I) forms the Me ketone (IX), m.p. $126-127^{\circ}$ (oxime, m.p. 172-173°; p-nitro-, m.p. 246-247°, and 2:4dinitro-phenylhydrazone, m.p. 267°), reduced to (? 2-) ethylthiophthen, b.p. 120°/15 mm. (impure picrate, m.p. 65°). The Grignard reagent from 2-bromothiophen and S in Et₂O give dithienyl sulphide, b.p. 155°/ 14.5 mm., oxidised by H_2O_2 to the sulphone, m.p. 130–131°. (IX) and its derivatives depress the m.p. of (VII) and (VIII) and their derivatives, but derivatives of (I), (III), and (VI) do not give depressions of the m.p. when mixed, nor do (VII) and (VIII)

and their derivatives. The structure of (I) is proved by its possession of a centre of symmetry (X-ray) and its zero dipole moment. The identity of (III) and (VI) is uncertain; (VI) has a dipole moment 1.16 and (III) 1.03 (possibly low owing to impurity), the former val. being in good agreement with that (1.17) calc. for (IV). R. S. C.

Indigoid dyes. VIII. P. C. DUTTA (Ber., 1935, 68, [B], 1447-1454).-In indigoid dyes ring formation with the chromophore CO in direct union with >C:C< or with the auxochromes on the side remote from the ethylenic linking diminishes the chromophoric or auxochromic functions, since it somewhat diminishes the tension of the double linking of these C atoms the formation, stability, and strength of which are important factors in determining the colour. In compounds in which there scarcely exists the possibility of such ring formation from the >C:C< group which would diminish the tension of the double linking of the ethylenic C atoms, or when the tension can be increased, the intensity of the colour is correspondingly increased. a-Naphthaquinone is converted by 1:2- (I), 2:1- (II), and 2:3-naphthoxythiophen (III) in EtOH containing Na₂CO₃ into 2-[1:2-naphthathiophen]- (IV), m.p. > 295°, 2-[2:1-naphthathiophen]- (V), m.p. 257°, and 2-[2:3-naphthathiophen]- (VI), m.p. 269° (Na salt), -2'-[4'-hydroxynaphthalene]indigotin. Similarly



β-naphthaquinone with (I), (II), and (III), respectively, affords 2-[1:2-naphthathiophen]-, m.p. 251-252°, 2-[2:1-naphthathiophen]-, m.p. 261°, and 2-[2:3naphthathiophen]-, m.p. 261°, -1'-[3'-hydroxynaphthalene]indolignone (VII). Condensation of the indolignones with o-C₆H₄(NH₂)₂ gives the corresponding azines, C₂₈H₁₆ON₂S (VIII), m.p. 268°, 264°, and 253° after softening at 244°, respectively. α-Naphtholazosulphanilic acid and (I), (II), and (III), respectively, in boiling EtOH-H₂O containing Na₂CO₃ give 2-[1:2naphthathiophen]-, m.p. 261-262°, 2-[2:1-naphthathiophen]-, m.p. 235-237°, and 2-[2:3-naphthathiophen]-, m.p. > 295° after softening at 265°, -2'-[4'-aminonaphthalene]indigotin (IX). Anthraquinoneanil and (I), (II), and (III), respectively, in boiling Ac₂O give





m.p. 248° after softening at 244°, -9'-anthraceneindolignone [as (IV), (V), and (VI) with $R = :C < C_6 H_4 > CO]$. H. W.

Action of ethylene dibromide on N-methylpiperidine. R. LUKEŠ and O. GROSSMANN (Coll. Czech. Chem. Comm., 1935, 7, 344-354).-N-Methylpiperidine (I) heated with ethylene dibromide (II) for 2 hr. at 250° gave MeBr, NH₄Br, a portion (b.p. 110— 270°) removed by steam-distillation, and a residue. The last was made alkaline and steam-distilled, the distillate converted into a mixture of hydrochlorides, from which a cryst. product, softens at 230°, m.p. 240.5°, was separated; the base with PhNCO gave N-phenyl-N'-piperidylcarbamide, m.p. 168.1°. The mother-liquors from the hydrochloride gave an impure base, b.p. chiefly 230°, which gave no well-defined salts, cryst. hydrate, nor a slightly-sol. platinichloride and did not give a satisfactory analysis (cf. Laden-burg, A., 1892, 1487). (I) and (II) heated at 45° for 5 days gave 1-methyl-1-β-bromoethylpiperidinium bromide (III), m.p. 218° (decomp.), picrate, m.p. 133°, and aurobromide, m.p. 167°. (III) heated at its decomp. point gave MeBr, piperidine, and tar; C2H2 and dipiperidylethane were not found. P. G. C.

Manufacture and application of reagents for the carbonyl group : hydrazidoacetpyridinium chloride.—See B., 1935, 840.

New pyridine derivatives.—See this vol., 1156.

Syntheses in the pyridine series. U. BASU (J. Indian Chem. Soc., 1935, 12, 289—292).—Claisen condensation of NH, CMe:CH·CO, Et with

COPh-CMe:CH-OH (I), $p-C_6H_4$ Me-CO-CH:CH-OH, or COMe-CMe:CH-OH affords Et 6-phenyl-2 : 5-dimethyl-, b.p. 170—185°/8 mm., m.p. 59° (picrate, m.p. 146°), 6-p-tolyl-2-methyl-, m.p. 54° (picrate, m.p. 133°), and 2 : 5 : 6-trimethyl-pyridine-3-carboxylate, b.p. 134— 136°/11 mm., 256—257°/755 mm. (picrate, m.p. 187°; $HgCl_2$ compound, m.p. 118·5°), hydrolysed to the corresponding acids, m.p. 140° (decomp.), 207—208° (decomp.), and 217—218° (decomp.), respectively. Similarly, COPh-CH:CMe·NH₂ and (I) probably yield 3-benzoyl-6-p-tolyl-2-methylpyridine, an oil (picrate, m.p. 191°). R. S. C.

Methylation of pyridinecarboxylic acids. H. NIENBURG (Ber., 1935, 68, [B], 1474—1475).—The methylbetaine of 6-phenyl-2-methylpyridine-3-carboxylic acid, m.p. 240° (decomp.) after darkening (also $+1H_2O$) (sulphate, m.p. 223—224°; aurichloride, m.p. 160—161°), is not obtained by heating the acid with MeI and MeOH at 150° or 100°, with Me₂SO₄ at 100—130°, or by treatment of the alkaline solution of the acid with MeI or Me₂SO₄, but is readily prepared by hydrolysis of the adduct from its Et ester and Me₂SO₄ with conc. HCl at 100°. Similarly the additive compound of Et pyridine-2-carboxylate and Me₂SO₄ is transformed into pyridine-2-carboxylic acid Me betaine sulphate, m.p. 125—126°. H. W.

Ketimine enamine compounds. U. BASU (J. Indian Chem. Soc., 1935, 12, 299-308).—Compounds showing ketimine-enamine tautomerism exist mainly in the latter form when molten or in solution, unless, in the latter case, ionisation is repressed. Thus, CN·CH₂·CO₂Et (I) reacts with COR·CH:CR'·NH₂ to give COR. CH:CR'.NNa. CO. CH2. CN (II) and thence an a-pyridone. Condensation with CN·CH₂·CO·NH₂ (III) or $CH_2(CO\cdot NH_2)_2$ (IV) proceeds, however, by loss of NH_3 to yield $COR\cdot CH_2\cdot CR' \cdot CX \cdot CO \cdot NH_2$ (X=CN or $CO\cdot NH_2$) and thence the α -pyridone. The two types of reaction yield in some cases isomeric products and the reaction mechanism of Knoevenagel al. (A., 1902, i, 640) is thus disproved. et NH₂·CMe:CH·COPh with (IV) at 175-180° gives 6-phenyl-4-methyl-2-pyridone-3-carboxylamide, m.p. $286-287^{\circ}$ (hydrolysed by hot 80% H₂SO₄ to the known acid, m.p. 182°), and with (I) and NaOEt yields 3cyano-4-phenyl-6-methyl-2-pyridone, m.p. 277°, but with CN·CH₂·CO·NHMe (V) at 150° affords 3-cyano-6-phenyl-1: 4-dimethyl-2-pyridone and a little 3cyano-6-phenyl-4-methyl-2-pyridone (VI), m.p. 310° [formed by reaction of some (V) with liberated NH_3 to yield (III) before condensation]. NH₂·CMe:CH·CO₂Et and (IV), when melted or heated in aq. EtOH with a little piperidine, give 6-hydroxy-4-methyl-2-pyridone-3-carboxylamide, m.p. 198° (decomp.), hydrolysed by fuming HCl at 150° 2:6-dihydroxy-4-methylpyridine. Et cycloto hexanone-2-carboxylate (VII), (IV), and a little piperidine in aq. EtOH or, less well, Et tetrahydroanthranilate [prep. from (VII) and NH_3] and (IV) at 190° afford 1-hydroxy-3-keto-2:3:5:6:7:8-hexahydrolsoquinoline-4-carboxylamide, m.p. 183-184°, hydrolysed by HCl to 1:3-dihydroxy-Bz-tetra-hydroisoquinoline. COPh-CH:CMe-NHMe does not

react with (I) and NaOEt at 110° as a salt of type (II)

cannot be formed, but with (III) at 125° gives (VI).

R. S. C. Preparation of histamine and its derivatives.—

See B., 1935, 829.

Indole series. I. Derivatives of 2-phenylindole. N. CAMPBELL and R. C. COOPER (J.C.S., 1935, 1208-1211).-" Nitroso-2-phenylindole "(I), m.p. 280° (decomp.), is identical with 2-phenylindoloxime, is monomeric in camphor, resembles 3-methyloximino-2-phenylindolenine (II), but differs from 3-nitroso-2phenyl-1-methylindole (III) in absorption spectrum, and thus has the oximino-structure. 2-Phenylindole (IV), therefore, reacts with HNO, in the indolenine form, although it reacts in the indole form with CPh₃·OH in boiling AcOH to give 2-phenyl-3-triphenylmethylindole, m.p. 212°. The general order of utility of Fischer's, Bischler's, and Madelung's indole syntheses is that given; e.g., the yields of (IV) are 70, 16, and 4.5%, respectively, by these methods. Indoles are best characterised by the :N.OAc-, :N·OBz-, or PhN₂-compounds, or by the :N·OHcompound if specially purified (details given), but not well by the picrates or :CHPh derivatives. Reddelien's theory of Fischer's indole synthesis is untenable, since acetophenone-p- and -o-toluidine with NHPh·NH₂ give (IV) and not the 5- or 7-Me homologues. (I), NaOMe, and MeI in hot MeOH give (II), b.p. 193-194°/0.4 mm., m.p. 54°. 2-Phenyl-1methylindole is obtained from distilled

CPhMe:N·NPhMe, b.p. 186—192°/11 mm., m.p. 49—50°, and ZnCl₂ at 200° (2 min.), and with NaNO₂-AcOH gives (III), m.p. 144°. The following are prepared. Acetophenone-o-, m.p. 101°, -m-, m.p. 81°, b.p. 214—223°/12 mm., and -p-tolylhydrazone, m.p. 125°. 2-Phenyl-5- (Fischer; 175°; 1·5 min.), m.p. 216° [PhN₂-, m.p. 193°, :N·OH-, m.p. 273° (decomp.), :N·OBz-, m.p. 159—160°, and :N·OAc-derivatives, m.p. 169·5°], -6- (Fischer, 78%, 280°, 0·5 min.; Bischler, 50%; Madelung 40%), m.p. 193° [picrate, m.p. 145·5°; PhN₂-, m.p. 177°, :N·OH-, m.p.237° (decomp.), :N·OBz-, m.p. 142—143°, and :N·OAc-derivatives, m.p. 118—119°], -7- (Madelung, 40%), m.p. 117° (PhN₂-, m.p. 155°, :N·OH-, m.p. 244°, :N·OBz-, m.p. 163°, and :N·OAc-derivatives, m.p. 122·5°), and -4methylindole (Madelung, 5·5%) [:N·OH-, m.p. 251° (decomp.), :N·OBz-, m.p. 145·5°, and :N·OAc-derivatives, m.p. 137° and 165°, respectively. Phenacyl-mtoluidine, m.p. 110°. R. S. C.

Xanthurenic acid.—See this vol., 1268.

Manufacture of [bactericidal] azo-compounds [pyridines and quinolines].—See B., 1935, 829.

Attempts to find new antimalarials. XIII. Synthesis of ω -substituted derivatives of 8methylquinoline. W. O. KERMACK, W. MUIR, and T. W. WRIGHT (J.C.S., 1935, 1143—1145; cf. A., 1934, 1368).—Basic derivatives of this type are prepared. 8-Piperidinomethylquinoline, an oil (picrate, m.p. 179°), is obtained from (a) o-aminobenzylpiperidine [Skraup, o-nitrobenzylpiperidine, glycerol, B(OH)₃, H₂SO₄, FeSO₄] and (b) 8-bromomethylquinoline and piperidine in hot C₆H₆. 6-Piperidinomethylquinoline, an oil [picrate, m.p. 195—196° (decomp.)], is obtained by method (a) from p-aminobenzylpiperidine. 8-Diethylaminomethylquinoline, an oil (dihydrobromide, m.p. 238—239°), could be obtained only by method (b), which gives also 8-anilinomethylquinoline, m.p. 71—73° (dihydrobromide), but with NHEt₂ and p-NH₂·C₆H₄·NHAc yields di(quinolyl-8methyl)ethylamine, an oil (trihydrobromide, m.p. 202°), and N-di(quinolyl-8-methyl)-p-aminoacetanilide, m.p. 236—237°. R. S. C.

Quinoline derivatives. XLVI. Synthesis of 2-cyclohexylquinoline-4-carboxylic acid. LXVII. 2'- and 3'-Amino-2-phenylquinoline. H. JOHN and E. PIETSCH (J. pr. Chem., 1935, [ii], 143, 236— 242, 243—248).—XLVI. Isatin when heated with cyclohexyl Me ketone (I) and aq. KOH affords 2cyclohexylquinoline-4-carboxylic acid, m.p. 189° [Me (isolated as its picrate, m.p. 136°) and Et (picrate, m.p. 157°) esters; hydrochloride; sulphate; nitrate; mercurichloride], decarboxylated to 2-cyclohexylquinoline (picrate, m.p. 157°). Similar condensation of (I) with substituted isatins gives 6-iodo-2-cyclohexyl-, m.p. 227° (nitrate), and 2-cyclohexyl-6:8-dimethyl-, m.p. 206° (hydrochloride; nitrate; sulphate; mercurichloride; ferrocyanide), -quinoline-4-carboxylic acid. (I) and o-NH₂·C₆H₄·COMe (II) give 2-cyclohexyl-4methylquinoline (picrate, m.p. 178°).

XLVII. 2'-Amino-2-phenylquinoline, m.p. 161° (Ac, m.p. 133°, Ac₂, m.p. 120°, and carbamido-, m.p. 210°, derivatives), is obtained by decarboxylation of its 4-carboxylic acid, m.p. 226° (Me, m.p. 82°, Et, m.p. 73°, and Pr°, m.p. 87°, esters), obtained from isatin and (II). 3'-Amino-2-phenylquinoline, m.p. 122° (Ac₁, m.p. 135° , Ac_2 , m.p. 130° , and *benzylidene*, m.p. $68-70^{\circ}$, derivatives), and its 4-*carboxylic acid*, m.p. 228° (*Me*, m.p. 122° , and *Et*, m.p. $60-61^{\circ}$, esters), are similarly prepared. Many salts of each acid are briefly described. J. W. B.

Acridine. XII. ms-Acridine derivatives. III. Acridine-N-oxides and the "acridols." K. LEHMSTEDT (Ber., 1935, 68, [B], 1455-1464).---The product of the action of conc. H₂SO₄ on o-NO2 ·C6H4 ·CHO in C6H6 has been regarded as 10hydroxyacrid-5-one (I), but is now shown to more probably 5-hydroxyacridine be 10-oxide $C_6H_4 < C(OH) > C_6H_4$ (cf. Tanasescu *et al.*, A., 1934, 1010). Thus when heated above 200° it decomposes into O2 and acridone, a part of the gas causing further oxidation of the material. The possible linking of C and N by O is discounted by the behaviour of the material as a yellow acid dye towards cotton, by the brownish-red colour with FeCla, and by the production of a blue colour when it or certain of its derivatives is heated with NHPh₂ and H₂SO₄. It is remarkably stable to HCl in EtOH or HCl. whereas its Me or Bz derivative is readily transformed into 3-chloroacridone, identified by condensation with POCl₃ and NPhMe₂ to give 3-chloro-5-p-di-methylaminophenylacridine, m.p. 230° (1-chloro-5-p-dimethylaminophenylacridine has m.p. 279°). 5-Methoxyacridine (II) (+1H₂O), m.p. 103° (decomp.), anhyd. m.p. 63°, from the 5-Cl-compound and NaOMe is stable towards Zn dust and CaCl in EtOH-NaOMe, is stable towards Zn dust and CaCl, in EtOH- H_2O , so that it and its analogues cannot be intermediates in the conversion of (I) and its derivatives into acridone. (I) is oxidised by $KMnO_4$ in alkaline solution to the peroxide, C₂₆H₁₆O₄N₂, m.p. about 315° when plunged into a bath preheated to 220°, whereas the corresponding Me ether is stable. Reduction of (I) by Na-Hg at room temp. affords acridine, dihydroacridine, and a base C₁₃H₉ON (III) which gives a brown resin but no acridine when treated with Zn dust and CaCl₂; it is therefore probably

CH

 $C_6H_4 < O_6H_4$. Attempts to prepare the latter

substance or the acridine 10-oxide by oxidation of acridine with BzO_2H unexpectedly give the substance $C_{33}H_{22}O_4N_2$. On theoretical grounds it is suggested that 5-hydroxyacridine ("acridol") is incapable of existence. In this connexion it is shown that Marzin's "acridol" is discoloured acridone. Further, (II) is isomerised by heat to 10-methylacridone. NaHSO₄ is added to yield the Na 5-methoxy-5: 10-dihydroacridine-5-sulphonate, hydrolysed to acridone. HCN transforms (II) quantitatively into 5-cyano-acridine. H.W.

Syntheses in the hydroaromatic series. XXIV. Diene syntheses of nitrogenous hetero-rings. X. Adducts obtained from quinaldine and acetylenedicarboxylic esters. O. DIELS and H. KECH. XXV. Adducts obtained from acetylenedicarboxylic esters and hydrazo-compounds. II. O. DIELS and J. REESE (Annalen, 1935, 519, 140-146, 147-157).-XXIV. The "stable adduct" (I) from 2-methylquinoline and (:C·CO₂Me)₂ (A., 1934, 782) is converted by nitrous fumes in AcOH into the *nitrate* of a NO_2 -compound [(I) R= NO_2 ;



 $R'=CO_2Me]$, decomp. 162°, which passes under the action of H_2O into a *nitrotricarboxylic* ester [cf. (I) R=H; $R'=NO_2$], decomp. 224°. In contrast with the cases of C_5H_5N , quinoline, *iso*quinoline, and stilbazole, therefore, the formation of (I) is due to three-fold union of (iC·CO_2Me)₂ with the heterocyclic ring, thus explaining the differences in optical behaviour, and (I) has the structure (I) (R=H; $R'=CO_2Me$). The "oxidation product" of (I) has the constitution (I) (R=OH; $R'=CO_2Me$); it is transformed by CH_2N_2 into the *product* $C_{23}H_{23}O_9N_3$, decomp. about 167°, and an isomeric *substance*, decomp. about 157°. To the "colourless quinaldine adduct" the structure (II) is assigned. It yields a *hydrochloride*, m.p. 215° (slight decomp.), an enolic *Me ether*, m.p. 173°, and is transformed by excess of Br in CHCl₃ into the *derivative*, $C_{21}H_{16}O_7NBr$, decomp. 200°.

decomp. 200°. XXV (cf. A., 1934, 903). The ability to add acetylenedicarboxylic esters is a general property of hydrazo-compounds. The adducts, $C_{20}H_{22}O_4N_2$, m.p. 127°, from NHPh·NHPh and ($:C\cdot CO_2Et$)₂, $C_{20}H_{22}O_4N_2$, m.p. 146°, from ($:NH\cdot C_6H_4Me$)₂ and ($:C\cdot CO_2Me$)₂, and $C_{19}H_{20}O_4N_2$, m.p. 149°, from NHPh·NH·CH₂Ph and ($:C\cdot CO_2Me$)₂, are described. $CH_2Ph\cdotNPh\cdotNH_2$ and ($:C\cdot CO_2Me$)₂ in MeOH at 0° afford the adduct, $C_{19}H_{20}O_4N_2$ (III), m.p. 72°, whereas when reaction occurs without cooling Me_2 1-benzylindole-2 : 3-dicarboxylate (II), m.p. 102° [also obtained from (I) in boiling xylene], is produced. The adducts, $C_{20}H_{22}O_4N_2$, m.p. 87°, and $C_{27}H_{28}O_4N_2$, m.p. 158°, are derived from ($:C\cdot CO_2Me$)₂ and ($:NH\cdot CH_2Ph$)₂ and $CH_2Ph\cdotNH\cdotN(CH_2Ph)_2$, respectively. ($:C\cdot CO_2Me$)₂ and $CH_2Ph\cdotNH\cdotNPh\cdotCH_2Ph$ afford a yellow (V), m.p. 115°, and a colourless (VI), m.p. 157°, adduct. (V) $^-C\cdot CO_2Me$



is readily transformed into (VI) by traces of acid. The constitutions are assigned by analogy with the corresponding compounds of the pyridine bases. Both isomerides pass when boiled in xylene into (IV), the constitution of which follows from its hydrolysis to 1-benzylindole-2:3-dicarboxylic acid, m.p. 198° (decomp.), decarboxylated successively to 1-benzylindole-2-carboxylic acid, decomp. 196°, and 1benzylindole, m.p. 44°. In boiling C_5H_5N (V) or (VI) passes into Me 2-keto-3-benzylamino-1-benzyl-1:2-dihydroquinoline-4-carboxylate, m.p. 191°, which is hydrolysed to the corresponding acid, m.p. 164° (decomp.) (also +1H₂O), decarboxylated to 2-keto-3benzylamino-1-benzyl-1:2-dihydroquinoline (VII), m.p. 174°. (VII) is transformed by boiling HBr-AcOH into 2-keto-3-benzylamino-1:2-dihydroxyquinoline, m.p. 190°, and by distillation with Zn dust



into quinoline. It is considered that the first change in these reactions is the isomerisation of (V) to (VI), followed by the formation of the (non-isolated) diamine (IX), which reacts mainly in the

cis-form to give the indole and in the trans-form to yield the quinoline. H. W.

New metallic complexes of cyanogen compounds. J. V. DUBSKÝ, E. KRAMETZ, and J. TRTÍLEK (Coll. Czech. Chem. Comm., 1935, 7, 311— 315; cf. A., 1933, 722).—Stable $Fe(CNS)_3$,3antipyrine, m.p. 185° approx., is pptd. by adding aq. $FeCl_3$ dropwise to cold aq. 1 : 1 (mol.) KCNS and antipyrine. [$Fe(CN)_5NO$]Fe(OH),4antipyrine is pptd. similarly from aq. 1 : 2 (mol.) $Na_2Fe(CN)_5NO$ and antipyrine. J. G. A. G.

Redox potential of porphyrexide and porphyrindine. R. KUHN and W. FRANKE (Ber., 1935, 68, [B], 1528—1536).—Hydrogenation of porphyrexide (I) and phorphyrindine (II) to their colourless leucocompounds is instantaneously effected by o-, m-, or p-C₆H₄(OH)₂, ascorbic acid, or cysteine in H₂O at 15—20°, by CH₂O, glucose, or fructose, but not mannitol or sucrose in warm solution containing Na₂CO₃. HCO₂Na in warm solution containing Na₂CO₃ decolorises (II) but not (I), whereas OH·CHMe·CO₂Na, (CH₂·CO₂Na)₂, CHPh·CH·CO₂Na, and Na oleate are ineffective. Potentiometric titration of (I) using p-C₆H₄(OH)₂ over the investigated $p_{\rm H}$ region establishes the electron no. n=1, in accordance with the scheme :

 $\underset{C(\mathrm{NH})\cdot\mathrm{NH}}{\overset{\mathrm{CMe_2}-\mathrm{NO}}{\to}} \overset{\mathrm{CMe_2}\cdot\mathrm{N(OH)}}{\to} \overset{\mathrm{CMe_2}\cdot\mathrm{N(OH)}}{\to} \overset{\mathrm{CMH}}{\to} \overset{\mathrm{CM$

Results for (II) are less decisive, but at $p_{\rm II}$ 6.5—7.5 n is approx. 1, increasing in the acid and diminishing in the alkaline region. The formation of a monoradical appears very unlikely. The normal potential of (I) and (II) is much > that of any org. dye hitherto examined, and they partly fill the gap between O and p-benzoquinone. Unless undefined catalytic influences are involved, NO appears a less active oxidising agent than either of the org. radicals. In the prep. of (I) the conversion of CMe2:N.OH into OH·NH·CMe₂·CN, m.p. 99°, is best effected with 70% HCN. OH·NH·CMe₂·C(NH)·OEt,2HCl, m.p. 200° (de-comp.) [lit. m.p. 108° (decomp.)], is transformed into $OH \cdot NH \cdot CMe_2 \cdot \hat{C}(NH) \cdot NH_2, HCl, gradual decomp. 140-$ 240° [lit., m.p. 154° (decomp.)], by excess of NH3-EtOH; this is oxidised by Cl₂ in HCl-H₂O to NO•CMe₂•C(NH)•NH₂,HCl,H₂O(VI). For the transformation of (III) into (I) by KCN-H₂O the temp. 55-60° must be maintained. H. W.

Manufacture of alkylated 5-phenyl-3-ethylhydantoins.—See B., 1935, 830.

1:1'-Dimethyl-2:3'-dipiperidyl. R. LUKEŠ and O. GROSSMANN (Coll. Czech. Chem. Comm., 1935, 7, 336-343).—Analysis of the mixed bases, b.p. 128.5-131°/11.8 mm., liberated by alkali from the product of hydrogenation (PtO₂ and Ac₂O at 45—50°/ 1·3 atm.) of 2:3'-dipyridyl methosulphate indicated incomplete methylation. The mixture gave a picrate, m.p. 214°, in approx. 50% yield, incompletely converted into a mixture of mono- and di-benzoate, from which a base, b.p. 136°/20 mm., was obtained; analysis of its picrate, m.p. 191°, suggested that the base was N-methyldipiperidyl. Methylation of its syrupy hydrochloride with paraformaldehyde gave 1:1'-dimethyl-2:3'-dipiperidyl, b.p. 159°/20 mm. [picrate, m.p. 210°; platinichloride, m.p. 252—255°; aurichloride, m.p. 216° (decomp.), darkens 212°]. It is not identical with Ladenburg's dimethyldipiperidyl (A., 1892, 1487), or the product obtained by electrolytic reduction of glutamethylimide (cf. A., 1933, 512). P. G. C.

Synthesis of C-substituted pyridylpyrrole derivatives. E. OCHIAI, K. TSUDA, and S. IKUMA (Ber., 1935, 68, [B], 1551-1555).-Et 2-picoloylacetate (I) and p-nitrophenylhydrazine in dil. AcOH afford 1-p-nitrophenyl-3-2'-pyridylpyrazolone, m.p. 169°. Condensation of (I) with CMeAc:N·OH proceeds with difficulty, and reduction of the mixture with Zn dust and 75% AcOH gives tetramethylpyrazine (II) and Et β -hydroxy- β -2-pyridylpropionate, b.p. 115—117°/ 0.003 mm., m.p. 35—37°. Condensation of (I) with NH, CHMe COMe, HCl in 75% AcOH yields (II) and Et 5-2'-pyridyl-2: 3-dimethylpyrrole-4-carboxylate, m.p. 76-77° (picrate, m.p. 219°). The Na derivative of (I) is transformed by NaNO₂ in AcOH into Et α oximino-2-picoloylacetate (III), m.p. 142-143°, which is reduced by Zn dust and 75% AcOH in presence of CH₂Ac·CO₂Et to Et_2 4-2'-pyridyl-2-methylpyrrole-3 : 5-dicarboxylate, m.p. 129° (perchlorate, m.p. 212–213°; picrate, m.p. 165°; styphnate, decomp. 210–211°), hydrolysed and decarboxylated by conc. H₂SO₄ at hydrolysed and decarboxylated by conc. H_2SO_4 at 100° to 4-2'-pyridyl-2-methylpyrrole, m.p. 93° (per-chlorate, m.p. 191—192°). (III) and CH₂Ac₂ similarly afford Et 3-acetyl-4-2'-pyridyl-2-methylpyrrole-5-carb-oxylate (+H₂O), m.p. 117° after softening at about 113° (picrate, m.p. 201°; perchlorate, m.p. 159°; semicarbazone, decomp. 243°), hydrolysed to 3-acetyl-4-2' myridyl 2 methylmyrrole 5 carboxylia acid decomp 2'-pyridyl-2-methylpyrrole-5-carboxylic acid, decomp. , whence 3-acetyl-4-2'-pyridyl-2-methylpyrrole, m.p. 233 198° (perchlorate, m.p. 171°). H. W.

Piperazine. V. Compounds from N-phenylpiperazine and derivatives of chloroacetic acid. D. E. ADELSON and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 1430-1431; cf. this vol., 1133).-*N*-Phenylpiperazine (I), CH₂Cl·CO₂R, and Na₂CO₃ in EtOH give 65—75% yields of Me, b.p. 175—177° (dihydrochloride), Et (II), b.p. 194-195° (sulphate; dihydrochloride), Pra, b.p. 185-186° (dihydrochloride), and Bua N-phenylpiperazine-N'-acetate, b.p. 218-220° (slight decomp.), m.p. 54-54.5°. (II) and conc. aq. NH₃ yield the N'-acetamide, m.p. 169-170°, also obtained from (I) and $CH_2Cl \cdot CO \cdot \hat{N}H_2$. The N'acetonitrile, m.p. $65-65\cdot5^{\circ}$, is prepared from (I) by $CH_2(OMe)_2$ and HCN (40% yield) or $CH_2Cl\cdot CN$ and Na₂CO₃ in C₆H₁₄ (70% yield). (II) with Na-Bu^aOH gives the N'-OH CH₂·CH₂ derivative (35%), m.p. 82.5-83°, and the Na N'-acetate, cryst., also obtained quantitatively from (I), CH2Cl·CO2Na, and Na2CO3 R. S. C. in H.O.

Reaction of certain diazo-sulphonates from 2naphthol-1-sulphonic acid. XII. Preparation of phthalazine, phthalazone, and phthalamidine derivatives of 2-bromo-4-nitroaniline. F. M. Rowe, G. B. JAMBUSERWALA, and H. W. PARTRIDGE (J.C.S., 1935, 1134-1137; cf. A., 1933, 1059).--The reactions described below show only minor differences from those usual in this series. 2-Bromo-4nitroaniline (improved prep., also suitable for chloroxylenols; 90.2% yield), when diazotised and treated with Na β -naphthol-1-sulphonate, gives H Na 3-(2'bromo-4'-nitrophenyl)-3:4-dihydrophthalazine-1-sulphonate-4-acetate, decomp. 234-236°, converted by hot HCl into 1-hydroxy-3-(2'-bromo-4'-nitrophenyl)-3:4-dihydrophthalazine-4-acetic acid (I), m.p. 235° (Me, m.p. 179°, and Et ester, m.p. 178°; Ac derivative, m.p. 121°; anilide, m.p. 207°). (I) affords 2'-bromo-4'-nitro-3-phenylphthalaz-1-one, m.p. 197° (decomp.) (gives only resins when methylated), and with K₂Cr₂O₇ in conc. H₂SO₄ yields 2'-bromo-4'-nitro-3phenyl-4-methylphthalaz-1-one, m.p. 225°, which does not react with picric acid and gives oils when methylated. (I) is best reduced in acid solution (SnCl₂), giving the 4'-NH2-acid (II), m.p. 233-234° (Ac derivative, m.p. 205°), the hydrochloride of which is so insol. in conc. HCl as to be unchanged even when boiled therein, but which is readily converted by hot aq. H₂SO₄ into 2'-bromo-4'-amino-3-phenylphthalaz-1one (III), m.p. 242°. (III) with Zn dust and HCl gives according to the conditions poor yields of 2'bromo-4'-amino-N-phenylphthalimidine, +xEtOH, m.p. (anhyd.) 178° (also obtained from 2': 6'-dibromo-4'amino-3-phenylphthalaz-1-one), or 4'-amino-N-phenylphthalimidine, m.p. 198°, but in all cases fission predominates. 1-Keto-3-(2'-bromo-4'-nitrophenyl)-2methyltetrahydrophthalazine-4-acetic acid has m.p. 229° (Me ester, m.p. 212-213°). Ring-closure of o-carboxyacetophenone-2'-bromo-4'-nitrophenylhydrazone, m.p. $152-154^{\circ}$, does not occur in hot EtOH, AcOH, or PhNO₂, but is effected by hot Ac₂O-C₅H₅N and affords 2'-bromo-4'-nitro-3-phenyl-1-methyl-phthalaz-4-one, m.p. 200-202°. (II) with K₂Cr₂O₇-H₂SO₄, hot 10% KOH, or Na₂S yields 2'-bromo-4'amino-3-phenyl-4-methylphthalaz-1-one, +EtOH, m.p. 279–280°, and +xEtOAc, which with Zn dust and HCl gives probably impure 1-keto-3-(2'-bromo-4'aminophenyl)-4-methyltetrahydrophthalazine,m.p. 211-212°. R. S. C.

Heteropolar compounds : complex salts of silver and mercury with 4-hydroxy-2-thion-1:2:3:4-tetrahydroquinazoline. C. GHEORGIU and (MLLE.) L. MANOLESCU (Compt. rend., 1935, 201, 78—80; cf. this vol., 630).—4-Ethoxy-2-thion-3phenyl-1:2:3:4-tetrahydroquinazoline (I) with HgX₂ (X=Cl, Br, I) gives colourless complexes which yield yellow solutions when warmed, and at a high temp. lose EtOH to give insol. yellow compounds. (I) with AgNO₃ gives a colourless solution which is converted by HClO₄ and HCl into slightly coloured solutions, which when warmed to 100° give intensely coloured solutions. Structures are proposed for these coloured compounds. F. R. G.

Addition of $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene and diazomethane to alkannin methyl ether ; con-

stitution of alkannin. H. RAUDNITZ and W. STEIN (Ber., 1935, 68, [B], 1479-1484).-The product obtained by decomp. of the Ni salt of alkannin by HCl-MeOH (cf. this vol., 217) is now recognised as alkannin Me ether (I). Alkannin (II), m.p. 147°, is obtained if AcOH is used. Treatment of (II) with β_{γ} -dimethyl- $\Delta^{\alpha_{\gamma}}$ -butadiene in boiling EtOH yields an adduct, C₂₃H₂₈O₅, m.p. 159°, oxidised by air in alkaline solution to a product which, by reason of elementary analysis, freedom from OMe, and spectroscopic behaviour, is regarded as 6:7-dimethyl-2δ-methyl-Δay-pentadienylquinizarin, m.p. 216°. (I) and excess of CH2N2 in MeOH slowly afford 5: 8-dihydroxy- $1-N-methyl-6(7)-\alpha(\beta)-methoxy-\delta-methyl-\Delta^{\gamma}-pentenyl-lin$ naphthaindazole-4: 9-quinone (III), m.p. 139°. (II) has therefore the constitution (A) or the tautomeric formula.



Dianthraquinonylguanidines. M. BATTEGAY and E. RIESZ (Compt. rend., 1935, 200, 2019-2021).- β -Anthraquinonylguanidine with 1-chloroanthra-quinone (I) in boiling PhNO₂ containing Na₂CO₃ or NaOAc and some Cu gives a dianthraquinonylguanidine which cyclises to py-C-\beta-anthraquinonylamino-1 : 9-pyrimidineanthrone, m.p. about 340°. Similarly, py-C-amino-1: 9-pyrimidineanthrone with py-C-a-anthraquinonylamino-1: 9-pyrgives (I) imidineanthrone. 2-Aminoanthraquinone with CNBr in NO₂Ph at 170° gives $di-\beta\beta'$ -anthraquinonylguanidine, m.p. about 260° (hydrobromide; sulphate; Bz and Bz_3 derivatives) (which is converted by HNO₂ into a carbamide), and a polymerised Br-compound, m.p. about 215°. The 1-isomeride reacts similarly, J. L. D. but forms more of the polymeride.

Diacridyl and its derived radicals and luminescent salts, luzigenin salts. H. DECKER and W. Ретьсн (J. pr. Chem., 1935, [ii], 143, 211-235).-The chemiluminescent reactions of NN'-dimethyldiacridylium (now called luzigenin) salts (I) (Gleu et al., this vol., 281), of its related compounds, and of the derived free radicals are described and discussed in relation to structure, and nomenclature (used below) is suggested. NN'-Dimethyldiacridylium nitrate (II) (A., 1909, i, 433) is converted by conc. aq. KBr into the bromide (III), which with KCN affords 9:9'dicyanodiacridane (diacridane=9:10:9':10'-tetra-hydrodiacridyl). By the action of Zn on (III) or by reduction (Zn-AcOH) of N-methylacridone (A., 901) is obtained dimethyldiacridene, 1906, i, $\mathsf{NMe} \overset{\mathrm{C_6H}_4}{\underset{\mathrm{C_6H}_4}{\sim}} \mathsf{C:} \Big]$ (IV), m.p. 385°, decomp. 390° (corr.), which is stable to air or to reduction in acid or alkaline solution. (IV) is an en-onium conjugated pseudo-base converted (loss of fluorescence) by

HCl-C₆H₆ into methylacridan-acridinium methochloride
$$\label{eq:Me_c_6H_4} \begin{split} &\mathrm{NMe} < \overset{C_6H_4}{\underset{C_6H_4}{\overset{C_6H_6}{\overset{C_6H_6}{\overset{C_6H_6}{\overset{C_6H_6}{\overset{C_6H_6}}{\overset{C_6H_6}{\overset{C_6H_6}}{\overset{C_6H_$$
with C6H6 gives a rose coloration due to formation of

the dimethyldiacridanyl radical NMe(C_6H_4)₂CH·C(C_6H_4)₂NMe. Addition of NaOH does not regenerate (IV) but gives the colourless carbinol base NMe(C_6H_4)₂C(OH)·CH(C_6H_4)₂NMe; a *picrate*, m.p. 280°, decomp. 295°, was isolated from the C_6H_6 solution and the aq. NaOH is coloured violet due to the radical NMe $< C_6H_4 > C \cdot C_6H_4 > NMe X$



(destroyed by O2). Addition of Br to a C_6H_6 solution of (IV) gives (III). With Me₂SO₄ in hot PhMe diacridyl (V) (loc. cit.) gives only the monomethosulphate, darkens 290°, m.p. $> 350^{\circ}$, converted by aq. KBr into 10-N-methyldiacridylium bromide (VI), m.p. $> 350^{\circ}$ [with conversion N into (V)][picrate, m.p. 305° (decomp.); (V.) iodide (VII); ferricyanide, m.p. 250° (decomp.)]. With hot $K_3Fe(CN)_6$ (VI) gives a substance, m.p. 345° , probably an inter-

nal ether $(C_{27}H_{19}N_{2})_{2}O$ of the carbinol base. When shaken with $Zn-C_{6}H_{6}$ (VI) gives a violet coloration (stable to O₂) in the solution (picrate, m.p. 220°, isolated) due to the radical NMe $C_6^{C_6H_4} > C C_6^{C_6H_4} N$ (VIII), but in HCl-C₆H₆ (exclusion of O₂) monomethyldiacridine [as (IV)] is obtained, and is readily oxidised by air to (VIII), and is converted by I into (VII). (V) is similarly converted into *diacridine*, m.p. 392°, which reacts in a similar manner to its methylated derivatives. (V) must be heated with Me_2SO_4 without solvent to give (I). The final product of the chemiluminescent reaction of KOH-H₂O₂ on (I) J. W. B. is N-methylacridone (isolated).

y-Triazines. XXIX. Conversion of aminothiol-alkyl-, -aryl-, and -arylalkyl-triazines into the corresponding aminohydroxy-derivatives. General considerations and description of two new homologues, aminohydroxy-ethyl- and -propyl-triazine. XXX. Some aminohydroxyaryltriazines. XXXI. Aminohydroxy-benzyland -styryl-triazines. A. OSTROGOVICH and V. GALEA (Gazzetta, 1935, 65, 349-356, 357-366, 367-370).-XXIX. H₂O₂ and an aminothioltriazine in aq. KOH give the aminohydroxytriazine. The following are prepared (each m.p. in this series is with decomp.): aminohydroxy-ethyl-, m.p. 277-278° (+2 or 3H₂O) (hydrochloride, m.p. 214-216°; picrate, m.p. 191—192°; Ag salt, m.p. 265—270°), and -n-propyl-, m.p. 274—275° (picrate, m.p. 195—196°), -γ-triazines.

XXX. Aminohydroxyphenyltriazine (A., 1930, 1449) (hydrochloride, m.p. 295-296°; sulphate, m.p. 238—240°). Aminohydroxy-o-, m.p. 292—293° (picrate, m.p. 255—256°), -m-, m.p. 217—219° (picrate, m.p. 292—293°), and -p-, m.p. 333—334° (hydrochlor-ida m. 202°, 203°). ide, m.p. 294-296°; picrate, m.p. 304-305°; Ag salt), -tolyltriazines. Aminohydroxyanisyltriazine, m.p. 327-328° (hydrochloride, m.p. 290-291°; picrate, m.p. 308-309°; Ag salt).
XXXI. Aminohydroxybenzyltriazine, new m.p. 277-278° (cf. Elzanowski, Diss., Freiburg, 1898) (hydrochloride, m.p. 220-222°; picrate, m.p. 208-210°; Ag salt). Aminohydroxystyryltriazine, m.p. 308-309° (picrate, m.p. 271-273°). E. W. W.

New colour reactions of pyrrolidine and proline. II. W. GRASSMANN and K. VON ARNIM (Annalen, 1935, 519, 192—208; cf. A., 1934, 665).— The final proof of the constitution of the dyes obtained from ninhydrin (I) or isatin (I) with proline (III), hydroxyproline (IV), or pyrrolidine (V) is given by the prep. of the dye o-C₆H₄ $<_{CR}^{CR}$ >NH (R=

 $o-C_6H_4 < \stackrel{C}{\underset{NH}{\sim}} CO)$ from (II) and dihydro*iso*indole and

by the observation that 3-methyl-4-ethyl- but not 2:4-dimethyl-3-othyl-, 4:5-dimethyl-3-ethyl-, 2:4:5-trimethyl-3-ethyl-pyrrolidine, or methylpyrrolidine condenses with (II). Dyes obtained from (III) and 5-iodo-, 5:7-dibromo-, 5-nitro-, 5-sulpho-, 1-methyl-, 1-acetyl-, and 1-benzoyl-isatin and from thionaphthenquinone, acenaphthenequinone (IV), α-naphthaisatin, β-naphthaquinone, and phenanthraquinone are prepared in AcOH. Analogous condensation products are derived in poorer yield from (IV). A red dye is obtained from (I) and piperidine-3-carboxylic acid and a green dye from piperidine and (VI). Pyrroline (VII) behaves similarly to (V) and its derivatives, yielding a cryst. blue dye with (II). The absorption spectra of the dyes from (IV) and (VII) are closely similarly to one another and differ markedly from the differently constituted pyrrole-blue dyes. The condensation products from pyrrole, (I), (V), or thionaphthenquinone are similar to the known pyrrole dyes, and hence have the following constitutions:



(II) and (III) give a colourless intermediate product, too unstable to be isolated. If 1-methyl-, dibromoor iodo-isatin is substituted for (II), cryst. compounds of the type $NH < C_6H_4 > C(CH < CH_2 CH_2)_2$, are obtained which lose (V) and form the dyes when heated with Ac₂O. The golden-yellow intermediate product

from (I) and (III) (loc. cit.) has the structure (A). These monopyrrolidinyl compounds are characterised by enhanced condensing power, thus giving the possibility of

the prep. of asymmetric dyes; the products from pyrrolidinylninhydrin and (II), phthalonic acid and mesoxalic esters, and from pyrrolidinylacenaphthenequinone and (II) or thionaphthenquinone are described. The following substances do not react with (III), (V), or their intermediate products: anthraquinone, α -naphthaquinone, 1:3-diketohydrindene, COPh-COPh, phthalonic acid, phenylglyoxylanilide, COMePh, COPh₂, fluorenone, camphorquinone, phthalimide, glyoxal, COMe·CHO, Ac₂, dihydroxytartaric acid, and diketosuccinic ester. The presence of two vicinal CO groups in an aromatic ring system appears essential for the change. The colour reaction of proline peptides with (II) in AcOH is sp. to those containing terminal proline-N. The dyes obtained are identical with those derived from (III) and reaction therefore involves the separation of the proline residue from the remaining peptide. The micro-detection of (III) is effected by bringing the solution to $p_{\rm H}$ 7 by a phosphate buffer, immersing a few threads of acetate silk, adding a little (II), and boiling for a few min. In the presence of (III) the threads assume a pure blue colour. The test is less sensitivo for (IV). H. W.

Production of therapeutically active tetrazole derivatives of terpene series.—See B., 1935, 830.

Oxidation of ætioporphyrin. M. DEŽELIČ (Bull. Soc. Chim. Yougoslav., 1935, 6, 11-25).—Ætioporphyrin (I) in CHCl₃-AcOH and PbO₂ yield successively a green product (II), $C_{32}H_{38}O_6N_4$, m.p. > 250°, ætioxanthoporphyrinogen (III), and methylethylmaleimide (IV). Oxidation with CrO₃ yielded only (IV), whilst HIO₃ afforded a mixture of products containing I, yielding the substance $C_{32}H_{38}O_8N_4$, m.p. 140°, on hydrolysis with aq. Na₂CO₃, and converted into (IV) on further oxidation. (I) and HCl and HIO₃ in AcOH give tetrachloroætioporphyrin dihydrochloride (V), decomp. > 200°, oxidised to (III) by PbO₂. (II), (III), and (V) regenerate (I) when reduced with Na-Hg. (I) and conc. HNO₃ afford a mixture of nitroætioporphyrin nitrate, m.p. 150° (decomp.), whilst fuming HNO₃ gives dinitroætioporphyrin. The NO₂ of (VI) is replaced by SO₃H by the action of oleum. R. T.

Pyocyaninium perchlorate. R. KUHN and K. SCHÖN (Ber., 1935, 68, [B], 1537—1539).—Leucopyocyanine is converted by Cl_2O_4 in Et_2O into *pyocyaninium perchlorate* (I), $C_{13}H_{12}O_5N_2Cl$, which is somewhat unstable. The semi-quinonoid nature of (I) is established by titration with Na₂SnO₂ and the radical nature by the paramagnetism. According to measurements of the rate of diffusion in H_2O and C_6H_6 pyocyanine is unimol. H. W.

Manufacture of derivatives of the anthraquinone series containing nitrogen and sulphur. —See B., 1935, 762.

Alkaloids of Heliotropium lasciocarpum. IV. Degradation of heliotridane to a pyrrole base. G. MENSCHIKOV (Ber., 1935, 68, [B], 1555—1558; cf. this vol., 995).—Heliotridane methiodide is converted by Ag₂O into de-N-methylheliotridane, b.p. $162 \cdot 5 - 163^{\circ}$, $[\alpha]_{\rm b} - 36^{\circ}$ (picrate, m.p. $118 \cdot 5 - 120^{\circ}$), which appears to polymerise readily when impure. It is hydrogenated (Adams) to dihydrode-N-methylheliotridane (I), b.p. $165 - 165 \cdot 5^{\circ}$, $[\alpha]_{\rm b} - 1 \cdot 5^{\circ}$ (methiodide, m.p. 144° after becoming turbid at $137 - 138^{\circ}$; picrate, m.p. $125 - 126^{\circ}$). Dehydrogenation of (I) over Pd-asbestos at $270 - 275^{\circ}$ affords $2 H_2$ and an optically inactive pyrrole base, $C_9H_{15}N$, b.p. $189 - 191^{\circ}$. Heliotridane therefore contains a pyrrolidine ring. H. W. [Simplification of Pictet's synthesis of nicotine.] M. EHRENSTEIN (Ber., 1935, 68, [B], 1550).—A reply to Späth (this vol., 995). H. W.

Synthesis of *dl*-eserethole and bufotenine. Synthetical experiments on eserine. IV. T. HOSHINO, T. KOBAYASHI, and K. SHIMODAIRA (Proc. Imp. Acad. Tokyo, 1935, 11, 192-194; cf. this vol., 227, 499) .- Hydrolysis of the p-toluenesulphonate of β-(5-hydroxy-3-indolyl)ethylmethylamine (norbufotenine) with HCl affords a gum, but the Et ether (I) is readily obtained from its *p*-toluenesulphonate. The Grignard derivative of (I) with MeI gives iso-noreservethole, m.p. $71-72^{\circ}$ (cf. A., 1932, 952; 1933, 164) (*H oxalate*, m.p. 152-153°), the hydrochloride of which with McI at 100° gives dl-escrethole, isolated as the picrate, m.p. 150—151° (lit., 155°; cf. this vol., 636). β -(2-Methyl-3-indolyl)ethyl bromide, readily obtained from the alcohol and PBr₃, when heated with aq. NH_3 , NH_2Me , and $NHMe_2$ gives β -(2methyl-3-indolyl)ethyl-amine, -methylamine, m.p. 82-83°, and -dimethylamine, m.p. 97-98°. Similarly, β -3-indolylethyl alcohol gives β -3-indolylethyl-amine, -methylamine (deoxynorbufotenine), and -dimethylamine (deoxybufotenine), m.p. 49–50°, and β -(5-ethoxy-3-indolyl)ethyl alcohol, m.p. 74–75°, gives β -(5-ethoxy-3-indolyl)ethylamine, (I), and bufotenine Et ether (*picrate*, m.p. 144—145°); the last-named with AlCl₃ in boiling C₆H₆ gives bufotenine identical with the natural product (cf. A., 1934, 1232). J. L. D.

Specific rotatory power of salts of quinine, quinidine, cinchonine, and cinchonidine. C. LAPP (Compt. rend., 1935, 201, 80—81; cf. A., 1933, 618).—Vals. of $[\alpha]$ for different λ are given for the bases, their hydrochlorides, and dihydrochlorides, whence the spatial configurations of the bases are deduced and the differences between their pharmacological properties explained. F. R. G.

Specific rotatory power and stereochemistry of the Cinchona alkaloids. C. LAPP (Bull. Soc. chim., 1935, [v], 2, 1407-1424).-[a] of quinine, quinidine, cinchonine, and cinchonidine in aq. solution and as a function of $p_{\rm H}$ has been determined. The graphs corresponding with the different $\lambda\lambda$ in forms of a double S form a family and correspond with the saturation of the two basic junctions. The rotation due to each of the asymmetric C has been determined. It is concluded that C1 and C2 are fixed, whereas C3 and C4 are under the influence of ionisation. The $[\alpha]$ increases as the electric charges on the mol. due to dissociation increase. The results and the pharmacodynamic properties suggest that the OMe and vinyl chains are parallel in the lævorotatory alkaloids and anti-parallel in the dextrorotatory compounds. H. W.

Modified Cinchona alkaloids. III. Chlorodihydro-bases. J. A. GOODSON (J.C.S., 1935, 1094– 1097).—Addition of HCl to the vinyl groups in quinine (I), cinchonidine, cinchonine, or quinidine gives two isomerides. The Cl is, therefore, at the α -C. Names such as "hydrochloroquinine," "chlorocinchonide," etc. are replaced by the rational chlorodihydro-nomenclature, the isomeride with the higher $[\alpha]$ being given the prefix α and the other α' . CuCl₂ forms salts with

these bases and is, therefore, not a sp. reagent for the vinyl group in this series. The following are described, m.p. being corr. and $[\alpha]$ in N-HCl : α -, sinters at 203°, m.p. 210°, decomp. 215°, $[\alpha]_{p}^{20} - 251°$ [dinitrate, m.p. 209°, decomp. 212°, $[\alpha]_{p}^{20} - 196\cdot6°$ in H₂O; tartrate, +7H₂O, m.p. (anhyd.) 187°, decomp. 198°, $[\alpha]_{p}^{20} - 209\cdot4°$; cuprichloride, B,2HCl,CuCl₂, decomp. 215° after sintering at 212°], and α' -chlorodihydroquinine, $+xC_6H_6$ and $+xH_2O$, m.p. (anhyd.) 194° (decomp. 225°) after sintering at 184°, $[\alpha]_D^{\infty} - 168.1°$ [dinitrate, (decomp. 225°) after sintering at 184°, $[\alpha]_{\rm D}^{-1}$ –168·1° [dinitrate, sinters at 219°, decomp. 223°, $[\alpha]_{\rm D}^{-1}$ –132·8° in H₂O; tartrate, +2H₂O, decomp. (anhyd.) 228° after sintering at 223°, $[\alpha]_D^{21} - 132 \cdot 3^\circ$; cuprichloride, 2B,4HCl,CuCl₂, +3H,O, decomp. (anhyd.) 198° after sintering at 190°], both about as active as (I) against bird malaria in doses of 5 mg. per 20 g. body-wt. a-, sinters at 233°, decomp. 236°, $[\alpha]_{D}^{po} + 226^{\circ}$ [dihydrochloride, sinters at 279°, decomp. 283°, $[\alpha]_{D}^{p2} + 196 \cdot 7^{\circ}$ in H₂O; tartrate, $+2H_2O$, decomp. (anhyd.) 204° after sintering at 196°, $[\alpha]_{D}^{a}$ +185.4°; cuprichloride, B,2HCl,CuCl₂, +H₂O, decomp. (anhyd.) 234° after sintering at 228°], and a'-chlorodihydrocinchonine, sinters at 220°, decomp. 223°, $[\alpha]_{D}^{22} + 176^{\circ}$ [dihydrochloride, sinters at 273°, decomp. 276°, $[\alpha]_{D}^{22} + 154^{\circ}$ in H₂O; tartrate, +2H₂O, decomp. (anhyd.) 212° after sintering at 209°, $[\alpha]_{D}^{20} + 142^{\circ}$; cuprichloride, B,2HCl,CuCl₂, +H₂O, decomp. (anhyd.) 235° after sintering at 230°], both inactive against bird malaria. α -, sinters at 229°, decomp. 231°, $[\alpha]_{D}^{23}$ -135.6° (cuprichloride, B,2HCl,CuCl₂, sinters at 218°, decomp. 220°), and α' -chlorodihydrocinchonidine, sinters at 244°, decomp. 246°, $[\alpha]_{10}^{a}$ -62.5° [H sulphate, +3H₂O, decomp. (anhyd.) 176° after sintering at 162°, $[\alpha]_{D}^{22}$ -59.5° in H₂O; tartrate, sinters at 210°, decomp. 212°, [a] -52.4°; dihydrobromide, sinters at 256°, decomp. 257°, $[\alpha]_{\rm p}^{\rm a} = -50.4^{\circ}$ in H₂O; cuprichloride, 2B,4HCl,CuCl₂,+7H₂O, decomp. (anhyd.) 185° after sintering at 175°]. α , $+2H_2O$, m.p. (anhyd.) 206°, (decomp. 225°) after sintering at 198°, $[\alpha]_{D}^{24} + 276\cdot3^{\circ}$

sintering at 175 j. a, $+211_{2}$ 0, in.p. (annyal, 200, (decomp. 225°) after sintering at 198°, $[\alpha]_{P}^{24} + 276\cdot3°$ [dihydrobromide, sinters at 250°, decomp. 253°, $[\alpha]_{P}^{22} + 200°$ in H₂O; tartrate, $+2H_2O$, decomp. (anhyd.) 162° after sintering at 157°, $[\alpha]_{P}^{25} + 224\cdot7°$; cuprichloride, B,2HCl,CuCl₂, sinters at 230°, decomp. 233°], and α' -chlorodihydroquinidine, $+3H_2O$, m.p. (anhyd.) 200° (decomp. 229°) after sintering at 195°, $[\alpha]_{P}^{22} + 240\cdot7°$ [tartrate, $+11H_2O$, decomp. (anhyd.) 196° after sintering at 152°, $[\alpha]_{P}^{12} + 203°$; cuprichloride, B,2HCl,CuCl₂, sinters at 230°, decomp. 236°].

Ř. S. C.

New ergot alkaloid. H. H. DALE (Science, 1935, 82, 99—101).—Concerning nomenclature (cf. this vol., 1157). L. S. T.

New alkaloid of ergot. S. SMITH and G. M. TIMMIS (Nature, 1935, 136, 259).—Ergometrinine (I) $C_{19}H_{23}O_2N_3$, decomp. approx. 195°, $[\alpha]_{5461}^{29}$ +520° in CHCl₃ (nitrate; hydrobromide; sulphate) is isomeric with and convertible into ergometrine (II) (this vol., 655). Its aq. solutions are dextrorotatory. The relationship between (I) and (II) is apparently similar to that between ergotoxine-ergotinine and ergotamine-ergotaminine. L. S. T.

Constitution of phæanthine. H. KONDO and I. KEIMATSU (Ber., 1935, 68, [B], 1503-1505).-Elementary analyses and determination of OMe establish the formula $C_{34}H_{30}O_2N_2(OMe)_4$ for phæanthine (I). Comparison of the properties of (I) and tetrandine shows them to be optical antipodes. (I) (A) or (B).



Alkaloids of Hanfangchi. I. Hanfanchin A. C. F. Hsu [with, in part, G. H. WANG and T. W. Lu] (J. Chinese Chem. Soc., 1935, 3, 260-273).-Hanfangchi, a Chinese drug with diuretic and antipyretic properties, from the roots of plants of family Menispermaceæ, contains four alkaloids, hanfanchin A (see below), B, m.p. 241-242°, and C, amorphous, in the non-phenolic fraction, and the fourth in the phenolic fraction. The extract of Hanfangchi with boiling 90% EtOH is dissolved in dil. HCl, substances sol. in light petroleum are removed, and the base is liberated and taken up successively in CHCl₃, Et₂O, and COMe₂. Hanfanchin B is removed with C₆H₆, and hanfanchin A, C₃₆H₄₂O₆N₂ or C₃₇H₄₃O₆N₂, m.p. 218-218^{.5}°, $[\alpha]_{\rm b}^{18}$ +268^{.7°} in CHCl₃, is crystallised from COMe₂ (yield 0.6%). It forms a picrate, m.p. 247°, phosphate, m.p. 241-242.5°, dimethiodide, m.p. 259—260°, aurichloride, m.p. 185°, platinichloride, decomp. 225—228°, and an Ac₄ derivative, m.p. 100° (softening at 95°), $[\alpha]_{D}^{18} + 37.16^{\circ}$ in CHCl₃. It is probably a tert.-base, without phenolic OH, N.NO, 0₂CH₂, or C:O, containing two double linkings, 2 NMe and 4 OMe, and perhaps an O-bridge. Intraperitoneal injection of the hydrochloride into the albino rat (lethal dose, 220 mg. per kg. body-wt.) has no characteristic effect. The above properties show that hanfanchin A is different from tetrandine (cf. A., 1932, 1048). E. W. W.

Alkaloids of Anagyris fætida. II. H. R. ING (J.C.S., 1935, 1053—1054; cf. A., 1933, 727).—The mother-liquors from the prep. of anagyrine and cytisine from the seeds of A. fætida yield N-methylcytisine and d-sparteine. R. S. C.

Alkaloids of the Cactaceæ. L. RETI (Anal. Asoc. Quím. Argentina, 1935, 23, 26-40).—A lecture.

Configuration of heterocyclic compounds. II. Phenoxarsonium salts. M. S. LESSLIE and E. E. TURNER(J.C.S., 1935, 1051—1052; cf. A., 1934, 1118).— Two phenoxarsonium salts could not be resolved, thus supporting the theory previously proposed (*loc. cit.*) regarding the cause of the dissymmetry of phenox-

arsine compounds. 2-Methylphenoxarsinic acid and a trace of I in CHCl₂ and conc. HCl give with SO₂ at 50° 10-chloro-2-methylphenoxarsine (I), m.p. 100-101°, which with MgMeI affords 2:10-dimethylphenoxarsine, b.p. 195°/17 mm.; this with MeI in EtOH gives 2: 10: 10-trimethylphenoxarsonium iodide (II), m.p. 205° (decomp.); the corresponding d-camphorsulphonate, $+H_2O$, m.p. 275–276° (decomp.), $[\alpha]^{20}$ $+26.2^{\circ}$ in EtOH, and d- α -bromocamphor- π -sulphonate, +H₂O, m.p. 263-264° (decomp.), $[\alpha]_{3461}^{20}$ +67·1° in EtOH, +64·2° in CHCl₃, are unchanged by crystallisation and give inactive (II). (I) and MgPhBr give 10-phenyl-2-methylphenoxarsine, b.p. 250°/10 mm., m.p. 61-62°, which with MeI at 100° yields 10-phenyl-2: 10-dimethylphenoxarsonium iodide (III), m.p. $179-180^{\circ}$ (decomp.), the corresponding d- α -bromocamphor- π -sulphonate, $[\alpha]_{5461}^{20}$ +25.5° in EtOH, being unchanged by crystallisation and giving inactive (III). R. S. C.

Germicidal and antiseptic activity of some mercury compounds.—See this vol., 1161.

Aryl selenohalides. V. Hydrolysis of aryl selenomonohalides and selenenic acids of the benzene series. O. BEHAGEL and W. MULLER (Ber., 1935, 68, [B], 1540-1549; cf. A., 1934, 313).-The hypothesis that the hydrolysis of aryl selenohalides occurs according to SeRHal+H, $O \rightarrow R \cdot SeOH +$ HHal is strengthened by the isolation of a series of selenenic acids (cf. Foster, A., 1934, 539). The possibility of obtaining the latter compounds depends essentially on the stability of the monohalide, which increases with the negative nature of the aryl residue. o-NO2.C6H4.SeBr is converted by AgOAc in boiling MeOH into o-nitrophenyl selenoacetate, m.p. 52°, and is hydrolysed by boiling H_2O to o-nitro-phenylseleninic acid, $NO_2 \cdot C_6 H_4 \cdot SeOH$, decomp. (indef.) 165—170°, and 2:2'-dinitrodiphenyl diselenide, m.p. 211°. Se m-nitrophenyl bromide, from the Br_3 -compound at 100°/diminished pressure, is converted by alcoholic alkali or AgOAc in MeOH into (m- $NO_2 \cdot C_6 H_4 \cdot Se \cdot)_2$. Se p-nitrophenyl bromide, m.p. 92°, is transformed into p-nitrophenyl selenoacetate, m.p. 62°. [(NO₂)₂C₆H₃Se·]₂ and Br in CHCl₃ afford Se 2:4-dinitrophenyl bromide, m.p. 118°, whence 2:4-dinitrophenyl selenoacetate, m.p. 133°, and 2:4-di-nitrophenylselenenic acid, decomp. >220°. (o- $NO_2 \cdot C_6 H_4 \cdot Se)_2$ is reduced by $N_2 H_4$, H_2O in boiling EtOH to (o- $NH_2 \cdot C_6 H_4 \cdot Se)_2$, m.p. 99°, whence 2:2'dibenzamidodiphenyl diselenide, m.p. 146-147°, converted by Br in CHCl3 into Se bromo-o-benzamidophenyl tribromide, which, with AgOAc in boiling MeOH, yields bromo-o-benzamidophenylseleninic acid. m.p. 178° (decomp.). 2:2'-Dichlorodiphenyl diselenide has m.p. 74°. Naphthyl selenocyanide and Br in CHCl₃ yield Se tribromonaphthyl tribromide, m.p. 137°, converted by Zn dust in boiling PhMe into hexabromodinaphthyl diselenide, m.p. 162-164°. 2:4:6-Tribromophenyl selenocyanide m.p. 113-114°, and Br in CHCl₃ afford Se 2:4:6-tribromophenyl bromide, m.p. 99–100°, transformed by H_2O , alkali, or AgOAc into 2:4:6:2':4':6'-hexabromodiphenyl diselenide, m.p. 212°. 1-Anthraquinonyl selenocyanide, from the bromide and KCN in boiling EtOH, is converted by conc. NH₃ at 130-140° into anthraquin(A)

onylselenazole (A), m.p. 208-209°. 1-Anthraguinonyl selenoacetate and 1-anthraquinonylselenolacetic acid, m.p. 245° are described. Se 1-anthraquinonyl bromide is converted by the requisite amine into the corresponding amide, diethylamide, m.p. 107-108°, anilide, m.p. 192°, and p-diethylaminophenyl

1-anthraquinonyl selenide, m.p. > 300°. Hydrolysis of Se 1-anthraquinonyl trichloride gives 1-anthraquinonylseleninic acid, m.p. (indef.) 203°, after darkening. H. W.

Organic derivatives of silicon. XLIX. Reduction of the tetranitrotetraphenylsilicanes. F. S. KIPPING and J. C. BLACKBURN. L. Nitration of phenyltriethyl-, diphenyldiethyl-, and triphenylethyl-silicane. F. S. KIPPING and N. W. CUSA (J.C.S., 1935, 1085-1088, 1088-1091; cf. A., 1933, 1062).-XLIX. Tetra-m-aminotetraphenyl-A., 1955, 1002).—ALLA. Terra-intradictional prendge silicane (I), m.p. about 380° (decomp.), sublimes at about 350° (tetrahydrochloride; oxalate; picrate; platinichloride; sulphate; Ac_4 derivative, m.p. 300—301°), is obtained from the corresponding (NO₂)₄-compound by Zn-HCl-AcOH or PtO₂-H₂ (2-3 atm.) in EtOAc, but Sn-HCl-COMe, affords by condensation tetra-m-isopropylaminotetraphenylby condensation tetra-m-isopropyamithotetraphengi-silicane, m.p. 135° [tetrahydrochloride, m.p. 300° (decomp.)]. (I) is stable to hot KOH-EtOH or aq. KOH and to conc. H_2SO_4 at 50-60°, does not eliminate NH₂Ph with Br, and, after diazotisation, couples with β -C₁₀H₇OH. The mixture of tetranitrotetraphenylsilicanes previously described (A., 1932, 1050) probably contains compounds other than the s-m- and $-p-(NO_2)_4$ -derivatives; the presence of the p-compound is proved by liberation on reduction of 26% of NH_2Ph ; reduction led to (I), tri-m-aminotriphenylsilicol, amorphous (trihydrochloride, cryst.), and probably benzidine compounds.

L. The p-Si·C₆H₄·NH₂ linking is readily broken by acids, but the m-linking resists acids and alkalis. Both p- and m-Si·C₆H₄·NO₂ linkings are very stable to acids, but much less so to hot alkalis. The probable proportions of p- and m-nitration by HNO₃-Ac₂O are: SiPhEt₃ 83 and 17, SiPh₂Et₂ 70 and 30, SiPh₃Et 40 and 60, and SiPh₄ 24 and 76%, respectively. o-Nitration does not occur. The products are not all s-substituted. SiPhEt₃ affords a NO₂-compound, which with Br-H₂O at 110° gives (SiEt₃)₂O and C₆H₄Br·NO₂ (95%). SiPh₂Cl₂ and MgEtI (3 mols.) afford diphenyldiethylsilicane, b.p. 295–298°, giving the m- $(NO_2)_2$ -compound (III) (11%), m.p. 102–103°, and an oily mixture which on acid reduction yields much NH₂Ph and with Br-H₂O at 110° gives $C_{c}H_{4}Br\cdot NO_{2}$ (mixture; 97%). (II) with Br gives 98% of $m\cdot C_{c}H_{4}Br\cdot NO_{2}$ and with Zn-HCl-AcOH or H_2 -PtO₂ in ÉtOAc di-m-aminodiphenyldiethylsilicane, m.p. 89-90° (Ac₂ derivative, m.p. 163-164°), stable to hot HCl and slowly decomposed by hot 10% KOH. The nitration product of SiPh₃Et gives similar results with Br. Phenyldicuclohexylethylsilicane has m.p. 52-53°. R. S. C.

Correlation of the viscosities of protein solutions with their ability to crystallise.-See this vol., 1266.

Colloid chemistry of edestin.—See this vol., 1203.

Sodium hydroxide as a substitute for iodine in Robinson's sulphur dioxide method [for determining organic carbon]. C. K. LI (J. Chinese Chem. Soc., 1935, 3, 288–292).—The gases evolved during digestion with conc. H_2SO_4 are absorbed by approx. 0.7N-NaOH, an aliquot of which is then added dropwise to excess (1 vol.) of 0.1N-I acidified with 1 vol. of N-HCl and 6 vols. of H₂O. The excess of I is determined by means of Na₂S₂O₃. The org. C found in 15 soils is 89-95% (mean 92.96%) of that found by Robinson's method (conversion factor 1.116), leading to the factor 1.20 (cf. B., 1929, 487).

J. G. A. G. Microanalytical determination of chlorine and bromine in organic substances. M. JUREČEK (Coll. Czech. Chem. Comm., 1935, 7, 316-318).--The products of combustion in O₂ of 5-12 mg. of substance (cf. Pregl) are absorbed by conc. aq. Na_2CO_3 and Na_2SO_3 . After diluting to 30-40 ml., the SO_3'' is oxidised by heating with H_2O_2 and, when Br' is present, the excess of H_2O_2 is removed by heating with N_2H_4 , H_2SO_4 . After acidifying with 1 ml. of conc. HNO₃, the Cl' or Br' is titrated with 0.01N-Hg(NO₃)₂ [indicator : Na₂Fe(CN)₅NO]. In general, calc. and observed % differ by $\Rightarrow 0.15$. J. G. A. G.

Determination of organic halogens. II. Stepanov method. C. L. TSENG, M. HU, and M. C. CHIANG (J. Chinese Chem. Soc., 1935, 3, 223-237).-Modified procedures for determining Cl, Br, and I are described, and the method is extended to the determination of org. F. After reaction with Na and EtOH, the F in the resulting solution is determined as CaF₂, or volumetrically by the Ca-H₂C₂O₄-KMnO₄ method; the last is also applied to the Parr bomb method (this vol., 876). E. W. W.

Rapid Kjeldahl determination of nitrogen. H. LUNDIN, J. ELLBURG, and H. RIEHM (Z. anal. Chem., 1935, 102, 161-172).-The substance is oxidised with a mixture of 3 vols. of $H_2SO_4 + 2$ vols. of H_3PO_4 + sufficient, but not a great excess of, 30% H_2O_2 , in presence of Cu+HgSO₄ as catalyst. Details are given of standardised apparatus and procedure for routine serial analysis. The time for a complete J. S. A. analysis is about 30 min.

Determination of sulphur in organic substances. P. SAARINEN (Suomen Kem., 1935, 8, A, 57-61).—A claim of priority in the use of HClO₄ (cf. A., 1934, 910). Preliminary oxidation is effected by HNO3, and HClO4 used only in the final stage. Loss of S in volatile form is avoided by using a long E. W. W. glass-bead reflux.

Determination of sulphur in organic compounds by the semimicro-Carius method. E. P. CLARK (J. Assoc. Off. Agric. Chem., 1935, 18, 476-477).—The procedure and apparatus are described. E. C. S.

Micro-volumetric determination of sulphur in organic compounds containing halogen and nitrogen. D. T. GIBSON and T. H. CAULFIELD (Analyst, 1935, 60, 522-525).-Cowie and Gibson's method (A., 1934, 910) is improved by the incorporation of Vieböck's Hg(OH)CN method (A., 1932, 529, 631) for the halogen determination. In presence of N, a method based on the use of $BaCl_2$ and K_2CrO_4 is employed. E. C. S.

2:4:6-Trinitrobenzoyl chloride as a reagent for the identification of alcohols. M. C. CHANG and C. H. KAO (J. Chinese Chem. Soc., 1935, 3, 256—259).—This reagent has the advantage of giving esters of high m.p., and of being resistant to H_2O . The following are described : Me, m.p. 160— 161°; Et, m.p. 156—157°; Pr^a , m.p. 145—146°; Pr^{β} , m.p. 154—155°; Bu^a , m.p. 125—126°; Bu^{β} , m.p. 127—128°; n-amyl, m.p. 124—125°; isoamyl, m.p. 134—135°; n-hexyl, m.p. 129—130°; isohexyl, m.p. 139—140°; n-heptyl, m.p. 127—128°; n-octyl, m.p. 124—125°; sec.-octyl, m.p. 148—149°; n-nonyl, m.p. 124—125°; n-decyl, m.p. 123—124°; allyl, m.p. 146—147°; and benzyl, m.p. 176—177°, 2:4:6trinitrobenzoates. E. W. W.

p-Nitrobenzhydrazide as reagent for the identification of aldehydes and ketones. P. CHEN (J. Chinese Chem. Soc., 1935, 3, 251-255).— The following are described : form-, m.p. $229-230^{\circ}$; acet-, m.p. 199° ; prop-, m.p. $165-166^{\circ}$; n-but-, m.p. $145-146^{\circ}$; n-valer-, m.p. $134-135^{\circ}$; isovaler-, m.p. 150° ; n-hex-, m.p. $128-129^{\circ}$; n-hept-, m.p. $113-114^{\circ}$; n-oct-, m.p. $108-109^{\circ}$; n-non-, m.p. $103-104^{\circ}$; benz-, m.p. $252-253^{\circ}$; m-nitrobenz-, m.p. $277-278^{\circ}$; and furfur-, m.p. $249-250^{\circ}$, -aldehyde-p-nitrobenzoylhydrazones; acetone-, m.p. 162° ; Me Et ketone-, m.p. 133° ; Me hexyl ketone-, m.p. 90° ; acetophenone-, m.p. $198-199^{\circ}$; benzylideneacetone-, m.p. $193-194^{\circ}$, and -acetophenone-, m.p. $153-154^{\circ}$; p-methyl-, m.p. $218-219^{\circ}$, m-nitro-, m.p. $231-232^{\circ}$, and p-methoxy-, m.p. $199-200^{\circ}$, -acetophenone-; acetylacetone-, m.p. 124° ; and Et acetoacetate-, m.p. $105-106^{\circ}$, -p-nitrobenzoylhydrazones. E. W. W.

Semicarbazides. III. o-Tolylsemicarbazide as a reagent for the identification of aldehydes and ketones. H. H. LEI, P. P. T. SAH, and C. SHIH (J. Chinese Chem. Soc., 1935, 3, 246—250).—The following are described: acet., m.p. 143—145°; prop., m.p. 129—130°; n-but., m.p. 96—98°; isobut., m.p. 113—115°; n-valer., m.p. 131—132°; n-hex., m.p. 111—113°; n-hept., m.p. 122—123°; n-oct., m.p. 125—126°; n-non., m.p. 120—121°; n-dec., m.p. 99—100°; benz., m.p. 181—183°; m- and pnitrobenz., m.p. 213—215° and 229—230°; p-homosalicyl., m.p. 208—209°; and furfur., m.p. 172— 175°, -aldehyde-o-tolylsemicarbazones; Me Et ketone., m.p. 168—170°; Me hexyl ketone., m.p. 116—118°; m-nitro., m.p. 215—217°, p-methyl., m.p. 200—203°, and p-methoxy-acetophenone., m.p. 182—184°; benzophenone., m.p. 149—151°; benzylideneacetone., m.p. 171—172°; Et acetoacetate., m.p. 117—118°; lævulic acid., m.p. 185—188° (Et, m.p. 111—113°, and CH_2Ph , m.p. 133—135°, esters); and furylacetone., m.p. 176—178°, -o-tolylsemicarbazones. E. W. W.

Detection of citric acid. PESEZ (J. Pharm. Chim., 1935, [viii], 22, 160-163).—A mixture of aq. citric acid (2 drops), Br-H₂O (1 drop), conc. H₂SO₄ (2-3 drops), and saturated aq. KMnO₄ (1 drop) is boiled. Further addition of 2 c.c. of conc. H_2SO_4 followed by warming causes any ppt. to dissolve; 0.1 c.c. of an EtOH solution of codeine followed by heating at 100° for 1—2 min. produces a bluish violet colour. Resorcinol, thymol, β -naphthol, salicylic acid and its Me ester can replace codeine with a modification of the colour produced. The reaction depends on the formation of glyoxal and can also be applied to the detection of the opium alkaloids.

P. G. M.

Gravimetric determination of ester derivatives of p-aminobenzoic acid, with special reference to anæsthesin and novocaine in presence of other substances. E. SCHULEK and I. FLODERER (Z. anal. Chem., 1935, 102, 186-198).--The p-NH₂·C₆H₄·CO₂H (I) derivative is dissolved in HCl, and then hydrolysed to free (I) by boiling with a small excess of 10% aq. NaOH. If other hydrolysable substances are present, the substance is first boiled with 1% HCl; in presence of very H2Osol. or insol. substances (e.g., sugar or talc), the (I) derivative may first be isolated by extraction with org. solvents. After hydrolysis the solution is extracted with CHCl₃, and the aq. residue is acidified, diluted, and boiled free from CHCl₃. NaOH is added, and the solution evaporated to dryness. The residue is dissolved, acidified, and diazotised at 2-3° with 0.1N-NaNO2. Excess of HNO2 is removed with $CO(NH_2)_2$, and the solution is diluted to contain > 0.02 g. of (1) per 100 c.c. A fresh alkaline 0.5% solution of $\beta\text{-}C_{10}H_7\text{-}OH$ is added, and $\beta\text{-}$ naphtholazo-p-aminobenzoic acid is pptd. on acidifying. The ppt. is washed with H_2O and dried at 100°. J. S. A.

Colorimetric determination of salicylic acid. J. E. HEESTERMAN (Chem. Weekblad, 1935, 32, 463).—The violet colour obtained when Fe^{...} is added to a solution of salicylic acid rapidly fades, but is permanent for 48 hr. when produced in 0.04N-AcOH. S. C.

Thioglycollic acid, a reagent for lignin. P. KLASON (Svensk Kem. Tidskr., 1935, 47, 220–223).— Holmberg's method (Ing. Vet. Akad. Handl., 1934, No. 131) is not satisfactory, because the presence of lignin of the type R·CH:CH·CH₂·OH occurring in aquatic plants cannot be shown by means of thioglycollic acid (I), and the (I) compounds are not completely insol., hence lower results are obtained with pinewood. The H_2SO_4 method is less useful. In the sulphonic acid and (I) methods, but not on digestion with 66% H_2SO_4 , H_2O is evolved. E. P.

Quinidine thiocyanate. Gravimetric and volumetric determination of quinidine. R. MONNET (J. Pharm. Chim., 1935, [viii], 22, 112—119).—The solution containing > 0.2 g. of quinidine (I) is evaporated to 20 c.c., neutralised (litmus), and quinidine thiocyanate (II) pptd. with 3 g. of KCNS. The ppt. is filtered after 2 hr., washed with 2×2 c.c. of H₂O and with 8×2 c.c. of a saturated solution of (II), dried at 105—110°, and weighed. In the presence of quinine, cinchonine, and cinchonidine the ppt. is washed finally with 6×1 c.c. of 96% EtOH saturated with (II). Under neutral conditions KCNS also gives ppts. with emetine, papaverine, strychnine, veratrine, and berberine, but not with aconitine, atropine, brucine, caffeine, cocaine, codeine, conicine, eserine, hydrastine, hyoscyamine, morphine, ethylmorphine, heroin, narceine, narcotine, nicotine, pelleterine, pilocarpine, sparteine, thebaine, theobromine, yohimbine, digitalin, strophanthin, convallamarin, salicin, acetanilide, adrenaline, antipyrine, cryogenine, exalgine, novocaine, phenacetin, pyramidone, stovaine, carbamide, urethane, and veronal. In the absence of other alkaloids, (I) may be determined volumetrically by titrating excess of CNS' in the filtrate. S. C.

Determination of hydroxydimorphine. B. DREVON (J. Pharm. Chim., 1935, [viii], 22, 97–106).—5 c.c. of solution containing 0.04—0.1 mg. of hydroxydimorphine are treated with 5 drops of 5% silicotungstic acid and 0.03 g. of K_2CO_3 . The

ppt. is adsorbed on BaSO₄, centrifuged, dried, and dissolved in 2 c.c. of acetosulphuric acid (20 c.c. of H_2SO_4 , d 1.83, and 1 c.c. of Ac₂O) and the green coloration matched against a standard solution containing 1 c.c. of 15% Cu(NO₃)₂, 1 c.c. of 20% Ni(NO₃)₂, and 0.3 c.c. of 10% Co(NO₃)₂ solutions. The test is sp. and is accurate to 5%. S. C.

Specific reaction for yohimbine. PESEZ (J. Pharm. Chim., 1935, [viii], 22, 164—165).—To 3 c.c. of conc. H_2SO_4 are added 4 drops of a 20% solution of chloral, followed by 10 drops of an aq. yohimbine salt with shaking. On warming to 50—60° the rose-coloured solution rapidly turns a greenish-blue which is very stable and is not discharged by adding 3 c.c. of H_2O . 0.2 mg. of yohimbine hydrochloride can be detected. P. G. M.

Biochemistry.

Determination of oxygen capacity of blood at high altitude. F. ALMASY and A. KRUPSKI (Biochem. Z., 1935, 279, 433–435).—Errors due to the use of other methods are avoided and accurate results are obtained by means of a modification of the method of Sendroy (A., 1931, 753). W. McC.

Continuous photographic recording of volume changes of red corpuscles. Influence of temperature and importance of $p_{\rm H}$ on permeability to glycerol and urea. S. L. ØRSKOV (Biochem. Z., 1935, 279, 241—249).—Methods are described for the continuous photographic registration of the vol. of red corpuscles, and for the determination of the permeability velocity to various substances. The vol. changes on addition of urea, EtCO·NH₂, glycol, and glycerol, and the influence of temp. on the permeability velocity with glycerol and thiourea are investigated. An influence of $p_{\rm H}$ on permeability to glycerol was detected. P. W. C.

Uric acid content of human blood corpuscles. J. HELLER (Biochem. Z., 1935, 279, 149—156).— Uric acid (I) is washed out of blood corpuscles much more slowly than is glucose (II) by hypertonic tungstate solutions. (I) also diffuses from the plasma into washed-out corpuscles much more slowly than (II). The (I) content of the corpuscles of human venous blood is 55% of that of the plasma.

P. W. C.

Influence of carbonic acid and lead on the permeability of blood corpuscles to potassium and rubidium. S. L. ØRSKOV (Biochem. Z., 1935, 279, 250—261).—The increase brought about by CO₂ in the permeability of the rabbit's red blood-corpuscle membrane by amines and NH₄⁺ is also obtained for Rb⁺ and K⁺ when Pb is present in minute amounts (4×10^{-8}) , the optimum $p_{\rm H}$ for the Pb-CO₂ (I) action being 6·3—6·6. The migration of K⁺ from the cells under the action of (I) is very rapid, 6/7 of the K⁺ being separated in 10 min., the cell vol. decreased by 46%, and the resistance to hypotonic solutions greatly increased. The permeability of the membrane to glycerol is not affected by (I). Hg⁺ in rather large concns. also causes elimination of K⁺, but the effect

represents a far-reaching modification of the membrane, glucose, Na, etc. being also lost. The cells of man and rat behave like those of rabbit, but no elimination of K occurs with cells of goat, dog, or calf. The action of Pb is inhibited or abolished by the anions of certain acids, probably by pptn. of Pb.

P. W. C. Permeation of erythrocytes by cations. M. MAIZELS (Biochem. J., 1935, 29, 1970-1982).-The small changes in the K content of human erythrocytes suspended in KCl and NaCl solutions increase slightly with external concn., but are practically unaffected by temp., moderate changes in $p_{\rm H}$, and duration of exposure. With $p_{\rm H} > 9$ or < 5.6 and in solutions of high concn. (514 milliequivs.) increased permeation is due to cell damage, but at $p_{\rm H}$ 8.3-8.8 is probably due to physical causes. In glucose solutions the rate of loss of K from the cells increases with time, rise of temp., and $p_{\rm H}$. CO₂ diffusing first out of the cell renders the external solution acid, but subsequent K' and HCO3' diffusion renders it faintly alkaline. Small amounts of electrolytes in the glucose solution retard loss of E. A. H. R. cell-K.

Electric impedance of hæmolysed suspensions of mammalian erythrocytes. H. FRICKE and H. J. CURTIS (J. Gen. Physiol., 1935, 18, 821–836).— Changes in the surface capacity and resistivity of the cells indicate that hæmolysis by H_2O is accompanied by increased permeability of the cell-membranes, whilst chemical lysis may also be accompanied by destruction of the membranes. Lysis by freezing and thawing differs from both the above. F. A. A.

Carbhæmoglobin of reduced hæmoglobin. G. GROSCURTH and R. HAVEMANN (Biochem. Z., 1935, **279**, 300—313).—Using pure human hæmoglobin (I) solutions, systematically determined p_{K_1} vals. permit the calculation of the CO₂ directly bound with (I). (I) becomes saturated with CO₂ at pressures of 60—90 mm. A study of the relationship of CO₂ capacity and p_{R} leads to the view that the reaction between (I) and CO₂ may be stated as : CO₂+Hb·NH₂ == Hb·NH·CO₂H == Hb·NH·CO₂'+H'. The dissociation const. of the $NH_2 \cdot CO_2$ group is $7 \cdot 04 \pm 0 \cdot 2$, that of the $NH_2 \cdot 9 \cdot 04 \pm 0 \cdot 05$. P. W. C.

Dependence of the composition of the proteins of blood-serum and -plasma on the diet. (A) E. ABDERHALDEN. (B) E. ABDERHALDEN and H. SIEBEL (Fermentforsch., 1935, 14, 443—461, 462—482; cf. A., 1934, 1137).—(A) Seralbumin (I) from rabbits fed on bran and receiving injections of (I) from others also fed on bran gives the defence enzyme reaction, but if (I) from rabbits fed on green food is injected, the reaction is negative. Similar results are obtained when the food consists of oats and greens, but the reaction is not sufficiently sp. to decide whether or not the kind of food affects the fine structure of the proteins of plasma and serum.

(B) The variations in resistance to attack by N-alkali, trypsin, and gastric juice (dog) of albumin and globulin fractions from the blood-plasma and -serum of the horse, ox, and rabbit do not indicate any effect of the nature of the food on the composition of the proteins of the serum and plasma.

W. McC.

Effect of protein rations on the serum-protein concentration of the rat. A. L. BLOOMFIELD (J. Exp. Med., 1935, 61, 465—471).—When high-protein diets (20—100% of caseinogen) were fed to rats, the serum-protein concent was $6\cdot1-6\cdot4\%$. On reducing the protein content of the diet the level was reduced to about $5\cdot5\%$ within 2 days, and remained approx. const. whether the diet contained 1, 5, or 10% of caseinogen. On changing from a protein-free or lowprotein to a high-protein diet, the serum-protein rose to the higher level within 2 days. About one sixth of the serum-protein is labile; the remainder forms the "basic blood colloids," depletion of which seems to meet with resistance on the part of the body.

NUTR. ABS. (m)

Physico-chemical effect of some electrolytes on the myxoprotein of blood-serum. M. PIETTRE (Compt. rend., 1935, 201, 364—366).—Potentiometric and conductometric studies of serum-myxoprotein indicate that it has no buffering power. H. D.

Protein determination from acid-combining power. E. FREUDENBERG (Z. Kinderheilk., 1935, 57, 108—115).—A method for determining the total protein in 1 ml. of serum or plasma (fluoride), based on the acid-binding power of the protein, is described. Excess of 0.1N-H₂C₂O₄ is added and the diluted fluid is titrated with 0.1N-NaOH before and after ultrafiltration. The method is inapplicable to fluids containing < 0.5% of protein. NUTR. ABS. (m)

Stability of lipin-protein complexes in bloodserum. B. DELAGE (Bull. Soc. Chim. biol., 1935, 17, 927-937).—The extraction of lipins from bloodserum by mixtures of Et_2O and increasing quantities of EtOH, PrOH, BuOH, *iso*amyl alcohol, glycol, MeCHO, or COMe₂ at room temp. follows the same course, the max. amount extracted being approx. the same in all cases. There is probably therefore an equilibrium between the free lipin and that combined with the serum-protein. A. L.

Polypeptidæmia in disease. S. MARINO (Arch. Farm. sperim., 1935, 59, 274-283).—The bloodpolypeptide-N (normally 0.0016-0.0022%) increases markedly during fever, nephritis, and pulmonary diseases. F. O. H.

Extraction of serum-lipins by cold etheralcohol mixtures in health and disease. B. DELAGE (Bull. Soc. Chim. biol., 1935, 17, 938-943).— Heifers vaccinated with the Jenner virus, in contrast with healthy animals, have little or no serum-lipin extractable by Et₂O-EtOH at room temp. A. L.

Dissociation of the lipin-protein complex in serum by alcohol. Extraction of lipins, phosphoaminolipins, and cholesterol. A. GRIGAUT (Bull. Soc. Chim. biol., 1935, 17, 1031-1039).—The amount of EtOH required to be added to blood-serum to make possible the extraction of the total cholesterol by Et_2O is much < that required for the extraction of the phosphoaminolipins (lecithin) and the total lipins. A. L.

Extraction of cholesterol from blood-serum. I. J. DREKTER, A. BERNHARD, and J. S. LEOPOLD (J. Biol. Chem., 1935, 110, 541—549).—Cholesterol (I) linked to protein is extracted by boiling EtOH; this is accompanied by denaturation of the protein, although preliminary heat-denaturation does not break the (I)-protein linking. A small proportion of (I) is present in either the absorbed or emulsified state and may be extracted with Et_2O . EtOH is the most efficient solvent for determination of the (I) in dried serum. H. G. R.

Comparison of serum, heparinised plasma, and oxalated plasma in regard to cholesterol content. W. M. SPERRY and R. SCHOENHEIMER (J. Biol. Chem., 1935, **110**, 655–658).—Oxalated plasma contains about 15% less cholesterol (I) than either serum or heparinised plasma from the same blood sample. Combined (I) and free (I) are reduced in the same proportion. (I) is not carried down with the CaC_2O_4 ppt. F. A. A.

Blood-amino-acid level after resection of the colon. F. RABBONI (Riv. Patol. sper., 1935, 14, 177–201).—Following colectomy and intravenous injection of glycine there was some increase in blood- NH_2 -acid and a change from the normal type of curve. These modifications, which indicated a change in the deaminising function of the liver, tended to disappear after about 2 months. NUTR. ABS. (m)

Suppression of renal function. X. Creatine and creatinine in blood. V. SCAFFIDI and P. GILI-BERTI (Riv. Patol. sper., 1935, 14, 59—69).—A marked increase in the blood-creatine (I) and -creatinine (II) of dogs after bilateral nephrectomy indicates that formation of (II) from (I) takes place in the organism, and not exclusively in the kidney. In one dog 88 hr. after nephrectomy the blood contained 17 mg. of (I) and 8.4 mg. of (II) per 100 ml., as compared with 2.57 and 1.4 mg., respectively, before operation.

NUTR. ABS. (m)

Changes in sugar, lactic acid, and protein contents of lymph and blood. I. Effect of insulin. II. Effect of adrenaline and pituitrin. III. Lactic acid metabolism following experimental liver damage. T. KIKUTA (Tôhoku J. Exp. Med., 1935, 25, 148-168, 218-231, 232243).—I. In dogs fasted for 48 hr. and given morphine, the glucose content of the thoracic lymph was > that of arterial blood; there was usually more lactic acid (I) in lymph than in blood. In the first period after injection of insulin there was an increase in the sugar of blood and lymph; later the fall of sugar level in the lymph was > in the blood. The changes in (I) were not const., but were similar for blood and lymph. The protein content of blood and lymph changed to some extent, but the direction of the change was not const.

II. After intravenous injection of adrenaline (II), the increase in the sugar and (I) content in the lymph was > in the blood. After intravenous injection of pituitrin there was a rise in the sugar level in blood and (less marked) in lymph. The (I) content increased, reaching a max. 30 min. after the injection. The changes in protein content of blood and lymph after injection of (II) or pituitrin were insignificant.

III. Ligature of the common bile duct or establishment of a duodenal ileus caused an increase in the (I) of the thoracic lymph, but not of the blood. Poisoning with P or tolylenediamine had a similar effect, often with a rise in blood-(I).

NUTR. ABS. (m) Improvement of the apparatus for determination of blood-sugar by the Hagedorn-Jensen method. H. J. FUCHS and W. BUSS (Biochem. Z., 1935, 279, 314—317).—The method and apparatus are described. P. W. C.

Determination of blood-sugar by the method of Crecelius and Seifert. H. ROSEGGER (Klin. Woch., 1935, 14, 343-344).—The method. gives satisfactory results. Accuracy in adding NaOH is most important. Rapid cooling is unnecessary and readings remain unchanged for 24 hr.

NUTR. ABS. (m)

Copper, blood-sugar, and adrenaline. H. HANDOVSKY (Arch. internat. Pharmacodyn., 1934, 49, 230—238).—Oral administration of Cu tyrosinate produced a decrease in blood-sugar several days after the first dose. Insulin had no effect on an animal previously treated with Cu, but there was a marked rise in blood-sugar when injection of adrenaline (I) followed treatment with Cu. Cu [through (I)] probably causes a hypersecretion of insulin, and aids the action of (I) by catalysing the decomp. of glycogen. NUTR. ABS. (m)

Silica content in the blood-serum of cattle, sheep, goats, and pigs. E. PRIBYL (Klin. Spisy Skoly Zverol. Brno, 1934, 10, 1-21).—The SiO_2 content (mg. per 100 ml.) of the serum of healthy cattle was 0.948—2.172 (average 1.394); of sheep, 1.074—1.308 (average 1.219); of goats, 0.909—1.230 (average 1.044), and of pigs, 0.725—2.011(average 1.327). The SiO₂ content of the serum of cows after calving was slightly reduced.

NUTR. ABS. (m) Magnetic micro-determination of iron in blood. C. COURTY (Compt. rend., 1935, 201, 362— 364).—A drop of blood is calcined and its magnetic power used as a measure of the Fe present. A calibrated Curie-Cheneveau magnetic balance is used. H. D. Variations in the calcium level of the blood of the domestic fowl. H. R. KNOWLES, E. B. HART, and J. G. HALFIN (Poultry Sci., 1935, 14, 83— 89).—The blood-Ca level varies from one oviposition to another, being low during shell deposition and high when no formed egg is in the shell gland. Max. and min. vals. are not const. even for the same hen. A marked difference between vals. for the uterine artery and uterine vein is recorded during shell deposition. Chickens respond rapidly to subcutancous injections of parathormone. A. G. P.

Determination of chlorine in blood. W. L. DULLÈRE (Rev. belge Sci. méd., 1935, 7, 10-20).--Chlorine is determined directly in plasma by Volhard's method. Corpuscles are diluted with about 25 vols. of H_2O , the hæmoglobin is coagulated by the addition of cold HNO₃ and separated centrifugally. Cl' is then determined in the supernatant liquid by Volhard's method. NUTR. ABS. (m)

Reducing substances and chloride in the blood of Orthoptera. R. M. MAY (Bull. Soc. Chim. biol., 1935, **17**, 1045—1053).—By the method of Baudouin and Lewin (A., 1927, 476) the reducing substance content (I) of the blood of normal and fasting adult males of *Locusta viridissima* was 0.075-0.178 and $\Rightarrow 0.092\%$, respectively. (I) for normal and fasting adult females of *Dixippus morosus* was 0.094-0.275and 0.108%, respectively, and for fasting adult males of *Orphania denticauda*, 0.041-0.261%. The Cl' content of the blood of *D. morosus* varied little, however, being 0.310-0.352%. A. L.

Vacate oxygen and oxidation quotient of serum. II. Effect of diet. W. ROMAN (Biochem. Z., 1935, 279, 381—386; cf. this vol., 508).—In 100 c.c. of rabbit serum the average val. for vacate O is 403 mg. Although there are wide individual variations the val. remains const. in the individual rabbit for long periods. Fasting causes decrease in vacate O, residual N, and oxidation quotient. Oral administration of glucose causes an increase, > that corresponding with the blood-sugar increase, in the vacate O and a decrease in the residual N. Administration of peptone causes equal increase in vacate O and residual N, and that of olive oil causes slight increase in vacate O and decrease in residual N. The increase produced by peptone is > that produced by glucose. W. McC.

Physico-chemical study of blood-sera. J. ZOZAYA (J. Biol. Chem., 1935, 110, 599-617).— The relation between d, η , and other physico-chemical consts. and the blood-protein have been determined and also the standard error of determination.

H. G. R.

Hæmolytic power of the sera of different blood groups. R. D. DE LA RIVIÈRE, N. KOSSO-VITCH, and A. CYGLER (Compt. rend. Soc. Biol., 1935, 119, 1275—1276).—The hæmolytic power of the blood groups in order of decreasing activity is B, AB, A, O; that of male serum is > that of female and of Bordet-Wassermann-negative > -positive.

H. G. R.

Blood-coagulation. III. Constancy of hydrogen-ion concentration during the coagulation of fibrinogen by thrombin. H. EAGLE and J. P. BAUMBERGER. IV. Nature of the clotting deficiency in hæmophilia. H. EAGLE (J. Gen. Physiol., 1935, 18, 809—812, 813—819).—III. The coagulation of fibrinogen by thrombin does not involve a significant shift in [H^{*}] of the free fluid.

IV. In hæmophilic plasma, the prothrombin (I) content is normal, and hæmophilic platelets function normally. The delayed coagulation is due to a retarded conversion of (I) into thrombin; this may be brought to the normal rate by the addition of excess of normal, hæmophilic, or animal platelets, but not by kephalin. F. A. A.

Influence of compounds of the moranyl series on blood-coagulation. H. GOLDIE (Compt. rend. Soc. Biol., 1935, 119, 1409—1412).—The anticoagulating power *in vitro* depends on the ability of these substances to modify the protein structure, whereas *in vivo* interaction with the modified protein may act as a complication. H. G. R.

Calcium metabolism in the first phase of blood-clotting. II. Change of state of combination of calcium during production of thrombin. H. SCHEURING (Biochem. Z., 1935, 279, 436-447; cf. this vol., 881).-Thrombokinase (I) added to blood-serum causes, parallel with the production of fresh thrombin (II), a conversion of Ca" into negative Ca complex, the extent of conversion depending on the concn. of (I) and being greatest when that concn. is optimal. The optimal concn. of (I) is independent of the Ca content of the serum, but ∞ the thrombogen (III) content. When the Ca content is increased the abs. amount of Ca complex increases, but the % amount decreases in parallel with the increase in Ca content. > and < a certain optimum [Ca] (which is the physiological Ca content of the blood) production of (II), and parallel thereto conversion of Ca^{\cdot} into Ca complex, become smaller. The optimum [Ca] is independent of the (I) content, but indirectly of the (III) content of serum or plasma. Excess of (III) inhibits coagulation because it interferes with the conversion of Ca^{**} into Ca complex and the parallel production of (II). W. McC. production of (II).

Nature of the agglutinogens of red corpuscles of different groups. R. D. DE LA RIVIÈRE and N. KOSSOVITCH (Ann. Inst. Pasteur, 1935, 55, 331-339).—The agglutinogens may be conc. by successive treatment of the red cells with EtOH and Et₂O. They are not affected by heating to 100° or by ultra-violet light. They are adsorbed by kaolin and Al(OH)₃ and may be eluted with EtOH; agglutinogen-B is adsorbed by C, whereas agglutinogen-A is not. The agglutinogen is found in the phosphatide fraction of the stroma and does not contain protein or cholesterol. No differences were observed in the P content of the fractions from different blood-groups, but considerable variations were found in the I val.

H. G. R.

Effect of repeated injections of phenol on the antibodies of normal rabbit serum. W. SCHAEFER (Compt. rend. Soc. Biol., 1935, 119, 1284—1286).— An increase in hæmolysins was observed, due probably to a modification in the organ concerned with the production of the antibodies. H. G. R. Determination of abrin and anti-abrin by a specific flocculation reaction. G. RAMON and R. RICHOU (Compt. rend. Soc. Biol., 1935, 119, 1304— 1306).—The antitoxic power of anti-abrin and antigenic power of abrin can be determined by a simple flocculation reaction. H. G. R.

Histochemistry of the adrenal gland. II. Quantitative distribution of lipolytic enzymes. D. GLICK and G. R. BISKIND (J. Biol. Chem., 1935, 110, 575—582).—The distribution of esterase and lipase in the gland, the relative no. of cells in the various zones, and the lipolytic activity per cell have been determined. The presence of a tributyrinase and a less active esterase has been established.

H. G. R.

Significance of water-soluble, diffusible substances for the production of rigidity by iodoacetic acid. F. LIPPAY and H. LÖNING (Pflüger's Archiv, 1935, 235, 448—452).—Spontaneous rigidity in $CH_2I \cdot CO_2H$ -poisoned frogs' sartorii in a moist chamber is > in Ringer's solution; hence the rigidity is dependent on the presence of H_2O -sol. diffusible substances in the treated muscle. R. N. C.

Histochemical examination of the fatty granular cells of the lung. G. OUZOUNOV (Compt. rend. Soc. Biol., 1935, 119, 1342—1344).—The granules consist probably of a mixture of cholesterol and phosphatide. H. G. R.

Interaction between the alveolar epithelium of the lung and olive oil introduced by the trachea. G. OUZOUNOV and I. MINTCHEV (Compt. rend. Soc. Biol., 1935, 119, 1344—1345).—The fat penetrates certain alveoli which contain the fatty granular cells and is gradually absorbed, whilst others remain fat-free. H. G. R.

Phosphorus content and requirements of the flour beetle, *Tribolium confusum*, Duval, and its need for vitamin-D. J. W. NELSON and L. S. PALMER (J. Agric. Res., 1935, 50, 849-852).— Analyses of all stages of the insect are recorded. The time of pupation is related to the P content of the ration, the limiting val. being approx. 0.1%. The % of P in pupæ is const. irrespective of the amount of P supplied. Slow development and small nos. of *Tribolium* in certain prepared flours are probably related to their low P contents. No evidence of a need of vitamin-D was obtained. A. G. P.

Effect of parathyroid hormone and of tuberculosis on the serum- and tissue-calcium of guinea-pigs. G. C. LINDER (Biochem. J., 1935, 29, 2095—2100).—Parathyroid extract produced only a small increase of Ca in the serum of guineapigs, but with tuberculous animals there was a larger increase. No difference was found in the decalcification of bone in either series of animals. The extract probably increased the Ca content of the brain of tuberculous animals only, whilst the liver-Ca was increased by parathyroid extract and by tuberculous infection. J. N. A.

Iron store of newborn infants. K. UTHEIM-TOVERUD (Acta paediat., 1935, 17, Suppl., 136– 140).—In newborn infants, the average Fe content per 100 g. of dry wt. was: full time, liver 200 mg.,

4 P

spleen 218 mg.; premature, liver 168 mg., spleen 183 mg. Close relationship was found between the Fe content of these organs and the age of the fœtus. Premature infants of normal mothers contained 200 mg. of Fe. Fe deficiency in the mother results in a lower Fe store in the fœtus.

NUTR. ABS. (m)

Cæsium tetraiodophenolphthalein, a new salt for gall-bladder visualisation. J. JOHNSON and L. H. HITZROT (J. Pharm. Exp. Ther., 1935, 54, 358-366).—The Cs salt is rather more efficient for X-ray gall-bladder visualisation than the Na compound. H. D.

Lactic acid content of mammalian brain. B. F. AVERY, S. E. KERR, and M. GHANTUS (J. Biol. Chem., 1935, 110, 637-642).—Cat and dog brains, frozen *in situ* with liquid air to minimise *post-mortem* changes, have lactic acid (I) contents averaging $15\cdot3$ mg. and $22\cdot3$ mg. per 100 g., respectively. A technique for the determination of $0\cdot1$ --0 $\cdot5$ mg. of (I) is described. F. A. A.

Glycogen and lactic acid in cartilage. A. IKUTA (Fukuoka Acta med., 1935, 28, 25–26).— The glycogen (I) content of the epiphyseal cartilage decreased with the age of the animal. It was abnormally high in rickets. In normal rabbits the lactic acid (II) content of the cartilage was low, increasing rapidly *post mortem*, whilst in that of rachitic rabbits the initial (II) level was higher and the *post-mortem* increase slower. In rib cartilage, which is richer in (I) and (II) than epiphyseal cartilage, there was no demonstrable increase of (I) in rickets or of (II) *post mortem*. NUTR. ABS. (m)

Histochemistry of the pituitary gland. Quantitative distribution of vitamin-C. D. GLICK and G. R. BISKIND (J. Biol. Chem., 1935, 110, 583— 588).—Pars intermedia contains 1.5 times the concn. of vitamin-C of the pars distalis or of the cortex and is the most potent source recorded. The concn. and the relative no. of cells in each portion and the vitamin content per cell are given. H. G. R.

Effect of cold on the fat and carbohydrate contents of the liver. A. LANCZOS (Pflüger's Archiv, 1935, 235, 422—427).—The body-temp. of fasting mice rises on exposure to cold, and falls during recovery. Liver-carbohydrate increases during the recovery period, muscle-carbohydrate showing no corresponding decrease. Liver-fat is unaffected during either exposure or recovery. R. N. C.

Chemical constitution of the fat of the subcutaneous connective tissue in man. I. Liquid and solid fatty acids in different periods of life. II. Liquid and solid fatty acids in patients affected with benignant and malignant neoplasm, and by cancerous cachexia. III. Cholesterol. IV. Acid and saponification values. V. Iodine value of the fat in different periods of life. VI. Iodine value of the fat in patients affected with benignant and malignant neoplasm, and by cancerous cachexia. G. STOLFI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 108—110, 110—111, 112—113, 113—115, 115—117, 117—118).—I. Unsaturated fatty acids (I) rise and saturated fatty acids fall in the subcutaneous connective tissue in children during growth, both becoming steady at maturity.

II. (I) are decreased slightly in benignant neoplasm and increased slightly in malignant neoplasm; a greater increase occurs in cancerous cachexia.

III. Cholesterol shows no appreciable alteration with age. It is increased considerably in malignant neoplasm, and to a smaller extent in benignant neoplasm and cancerous cachexia.

IV. The acid val. of the tissue-fat is not altered by age, but the sap. val. falls slightly. Neither is altered by neoplasm or cachexia.

altered by neoplasm or cachexia. V, VI. The I val. of the tissuc-fat increases with age in children, but remains steady when maturity is attained; it is unaffected in benignant neoplasm, but is increased in malignant neoplasm and cancerous cachexia. R. N. C.

Absence of allocholesterol in the organism. R. SCHOENHEIMER, H. DAM, and K. VON GOTTBERG (J. Biol. Chem., 1935, 110, 659—665).—alloCholesterol (I) is comparatively stable if high temp. and acid reaction are avoided, and may be determined in presence of cholesterol by the $CCl_3 \cdot CO_2 H$ colour test. Animal sterols do not contain appreciable quantities of (I); sterols from hens' eggs appear to contain 1%. F. A. A.

Absorbability of allocholesterol. R. SCHOEN-HEIMER, H. DAM, and K. VON GOTTBERG (J. Biol. Chem., 1935, **110**, 667–671).—Experiments on mice, hens, and a dog show that allocholesterol (I) is little, if at all, absorbed in the alimentary tract, in contrast to cholesterol (II). (I) is partly changed into (II) in the stomach. F. A. A.

Gadusene, an unsaturated hydrocarbon from animal and plant oils. Z. NAKAMIYA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 720—730).—From the unsaponifiable fractions of rice-embryo, soya, and fish-liver oils (e.g., Gadus macrocephalus, Theragra chalcogramma, Stereolepis ischinagi) an unsaturated hydrocarbon, gadusene (I), $C_{18}H_{32}$ (not identical with squalene), has been isolated. Catalytic hydrogenation yielded gadusane, $C_{18}H_{38}$. (I) may be identical with Drummond's hydrocarbon $C_{18}H_{32}$ from wheat-embryo oil and Tsujimoto's compound $C_{35}H_{60}$ from ishinagi-liver oil, since they have in common five characteristic absorption bands.

E. P.

Lipochrome content of human liver. L. ZECH-MEISTER and P. TUZSON (Z. physiol. Chem., 1934, 234, 241—244).—The livers examined (all from diseased subjects) contained $\Rightarrow 2.0$ mg. of carotene and $\Rightarrow 0.5$ mg. of lycopene and of xanthophyll per kg. J. H. B.

Lipochrome metabolism of the horse. II. Selective absorption of carotenoids in the animal body. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1935, 234, 235—240; cf. A., 1934, 1251).—In the organism of the horse the only intact carotenoid found is carotene (I), which is selectively absorbed from the fodder. (I) is accompanied by unidentified degradation products, but plant polyene alcohols (II) are absent. (II) are not absorbed and subsequently destroyed by the liver, since they are not found even in the portal blood. J. H. B. Lipochromes of marine animals. VI. Carotenoids of salmon flesh. N. A. SÖRENSEN (Z. physiol. Chem., 1935, 235, 8—11).—Two salmon oils contained astacene (I) and small amounts of unidentified pigments: (I) is the main pigment in salmon. H. W.

Blue-fluorescing substance from corpus luteum. H. von EULER and K. M. BRANDT (Naturwiss., 1935, 23, 544).—Treatment of COMe₂-sol. substances of corpus luteum with Et₂O followed by EtOH and chromatographic adsorption yields preps. of a blue-fluorescing substance (I) (cf. A., 1934, 1382; this vol., 663) with max. fluorescence at approx. 420 mµ and absorption max. at 260 and 345 mµ; it differs from lumichrome (A., 1934, 1233) in fluorescence acidity max. ($p_{\rm H}$ 2—6 for the latter). In contrast to the flavins, irradiation (Hg) of aq. solutions yields no CHCl₃-extractable fluorescent product. Methylation (Me₂SO₄) yields a product with absorption bands (in CHCl₃) at 260—280 mµ and a fluorescence band (in EtOH) between 380 and 500 mµ. Acetylation affords a blue-fluorescing substance with absorption bands at 281 and 272 mµ in CHCl₃, aq. extraction yielding a purer product with bands at 255, 265, and 278 mµ. The presence of a second substance occurring with (I) is therefore indicated. F. O. H.

III. Rabbit- and fish-(I) gave similar products on exhaustive methylation. Hydrolysis of the products gave tetramethylglucopyranose, 2:3:6-trimethylglucose, and dimethylglucoses in each case, and it is concluded that the preps. are identical, being built up of unbranched chains of 12 glucose units. H. D.

Urea production in the human placenta. J. BOTELLA-LLUSIA (Arch. Gynäkol., 1935, 159, 27–34).—The surviving human placenta converts NH_3 and NH_4 salts into urea, and can also produce it at the expense of some of its NH_2 -acids.

NUTR. ABS. (m)

Physiology of the skeletal muscle of mammals at different stages of their individual development. C. KOSCHTOJANZ and A. RJABINOWSKAJA (Pflüger's Archiv, 1935, 235, 416-421).—Creatinephosphoric acid does not appear in rabbit muscle until after the 21st day of embryonal development. It rises from 4-5% to 60-70% in the first day after birth. R. N. C.

Phosphorus compounds of brain. I. Phosphocreatine. S. E. KERR (J. Biol. Chem., 1935, 110, 625-635).—Mammalian brain, frozen *in situ* with liquid air, yields a labile P compound, associated with 1 mol. equiv. of creatine. The properties of the compound and of a Ca salt, obtained cryst., agree with those of phosphocreatine from muscle. No significant differences are found between labile P contents of cerebrum and cerebellum. F. A. A.

Phosphatides. XII. Nature of the phosphatides and other lipins of the brain and liver in the Niemann-Pick disease. E. KLENK (Z. physiol. Chem., 1935, 235, 24-36; cf. this vol., 384).-The high sphingomyelin (I) content of the brain is in contrast with the almost complete absence of cerebrosides, although a material containing sugar is present which is possibly related to, although distinct from (I). The product in the liver is a mixture of lignocero-, nervo-, stearo-, and palmitosphingomyelin, whereas that in the brain is almost homogeneous stearosphingomyelin, the absence of C24 acid derivatives being particularly characteristic. In the liver-phosphatides derivatives of the highly unsaturated C20 and C22 acids are easily identified, whereas they could not be detected with certainty in the brain. H. W.

Isolation of phosphocholine from ox liver. F. INUKAI and W. NAKAHARA (Proc. Imp. Acad. Tokyo, 1935, 11, 260—261).—60% MeOH containing H_2SO_4 extracts *phosphocholine* (*picrate*, m.p. 228° after softening at 225°), which is synthesised from choline chloride, P_2O_5 , and H_3PO_4 at 70°. J. L. D.

Water-soluble choline precursor in the human placenta. D. H. SMYTH (Biochem. J., 1935, 29, 2067—2070).—The method of Booth and Milroy (cf. below) for the extraction from the kidney of the H_2O -sol. choline precursor is applied to the placenta, and a substance (I) containing choline-N, NH₂-N, and P in the ratio 1:1:1 is isolated in small amount. (I) is probably similar to the compound obtained by the above workers. A. L.

Water-soluble precursor of choline found in the kidney and other tissues. F. J. BOOTH (Biochem. J., 1935, 29, 2071—2076).—The method, involving repeated pptn. with HgCl₂ in EtOH solution, for the extraction of the H₂O-sol. choline precursor (I) from the kidney is described. The rate of hydrolysis of, and the N distribution in, (I) indicate that it is the choline ester of sphingosinephosphoric acid. (I) has no action on the eserinised rectus of the frog, but after acetylation, which causes decomp., the Ac derivative has the properties of acetylcholine. Compounds similar to (I) are present in the brain and the liver. A. L.

Transformation of dehydrocholic acid into β -3-hydroxy-7:12-diketocholanic acid.—See this vol., 1237.

Glutathione in hens' eggs. M. TALENTI (Arch. Farm. sperim., 1935, 59, 287-290).—Direct nitroprusside tests on yolk and white of sterile or fertilised eggs indicate the presence of reduced glutathione from the time of laying; aq. CCl₃·CO₂H extracts, however, give a zero titration with I (cf. A., 1933, 298). F. O. H.

Redox potential of glutathione. J. C. GHOSH and S. C. GANGULI (Biochem. Z., 1935, 279, 296— 299).—A method for determination is described, the mean val. for E_0 being ± 0.068 . P. W. C.

Physiological action of asterubin and of other sulphur-containing derivatives of guanidine. D. ACKERMANN and H. A. HEINSEN (Z. physiol. Chem., 1935, 235, 115-121; cf. this vol., 1004).—Taurine (I), guanyltaurine (II), and asterubin (III) have no effect on blood-pressure in the dog. (I) and (II) cause decrease [preceded by increase in the case of (II)] and (III) causes increase in the sugar content of the blood. Cystamine (IV) and still more diguanylcystamine (V) lower the blood-sugar level, but tetramethylguanylcystamine (VI) raises it greatly. The blood-pressure is lowered by (IV), (V), and (VI) [(VI)>(V)>(IV)]. (V) (picrate, decomp. 211-212°; .picrolonate) is obtained by the interaction of cystamine (VII) and cyanamide and (VI) (picrate, m.p. 118°) by that of (VII) and dimethylcyanamide. W. McC.

Guanidine nucleus in pseudomucin. H. FUCHS (Biochem. Z., 1935, 279, 413—416; cf. A., 1905, i, 104).—Guanidine (I), methylguanidine, creatine, creatinine, and arginine (II) resist, for short periods, hot acid oxidation by aq. NaMnO₄. The amounts of arginine and (I) obtained from hydrolysed (30%H₂SO₄ for 12 hr.) pseudomucin by oxidation with aq. NaMnO₄ indicate that, after hydrolysis, pseudomucin contains no (I) nucleus other than that separated as (II). W. McC.

Iodometric determination of muscle-guanine. A. DMOCHOWSKI, A. ZAJDENMAN, and A. RABANOWSKA (Biochem. Z., 1935, 279, 289—295).—A micromethod for determination of tissue-guanine (I) depends on purification of the tissue hydrolysate with tungstate, pptn. with Cu, repptn. with As, and final oxidation with NaOI. The (I) content of rabbits' muscle is 11—12 mg. per 100 g., or only about half of that as determined by the enzymic method. It is suggested that the muscle contains a new purine (aminohydroxypurine ?). P. W. C.

Extractives of dog and rabbit muscle. A. N. PARSCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 35-36).—Carnitine is absent. E. P.

Nucleotides, nucleosides, and free purines of rabbit liver. G. DELL' ACQUA (Biochem. Z., 1935, 279, 403-412).-Sol. purines are irregularly distributed in the fresh liver, 100 g. of which contain an average of 44 mg. of N combined as nucleotides and 22 mg. as nucleosides and free purines. After autolysis for 24 hr. in unbuffered media there is an increase of 15% in the amount of sol. purines and the ratio nucleotide-N: nucleoside-N+free purine-N is reversed. Administration of adrenaline (\hat{I}) frequently results in increase in the amount of sol. purines, nucleosides and free purines often increasing at the expense of nucleotides. Autolysis after (I) administration is more extensive, and sol. purines increase in amount by 33%. Insulin (II) produces no change in the amount of sol. purines or in the proportions of the three fractions, but autolysis is enormously increased after giving (II) and the amount of sol. purines increases by 66%. Poisoning with P causes 100% increase in the amount of sol. purines, but subsequent autolysis (24 hr.) causes no further increase. W. McC.

Localisation of nucleic acids in the cell-nucleus. T. CASPERSSON (Naturwiss., 1935, 23, 527; cf. this vol., 375).—The powerful absorption of ultra-violet light by cell nuclei and chromosomes (e.g., of salivary glands of larvæ of *Diptera*) is due to the nucleic acids present. With thymonucleic acid the absorption exhibits a max. at 260 m μ . W. McC.

Boric acid reaction and the structure of nucleic acid. P. A. LEVENE and R. S. TIPSON (Z. physiol. Chem., 1935, 234, V).—Inosine and guanosine give a positive, thymidine gives a negative, boric acid reaction (cf. Makino, this vol., 772). J. H. B.

Chemistry of chromosomes. I. H. HELL-STRÖM, D. BURSTRÖM, and H. VON EULER (Svensk Kem. Tidskr., 1935, 47, 207-211).—The salivary glands of the larvæ of *Drosophila virilis* are used as a source of chromosomes. The variation in intensity of absorption of these between 257 and 292 m μ , as revealed by photomicrographs, suggests that they are related to the nucleic acids. Selective dissolution of chromosomes by appropriate fixing agents is also studied. E. A. H. R.

Effect of heat and hot alcohol on liver-proteins. W. H. SEEGERS and H. A. MATTILL (J. Biol. Chem., 1935, 110, 531-539).—The growth rate, biological val., and digestibility of the acid hydrolysates of dried whole liver, heated liver, and EtOH-extracted (130 hr.) liver are approx. the same. Heating at 120° for 72 hr. or EtOH-extraction for 130 hr. lowers the digestibility and thus the biological val. of the protein. H. G. R.

Influence of hydrogen peroxide on the precipitability of proteins. P. RONDONI and L. POZZI (Z. physiol. Chem., 1935, 235, 81–90).—In all cases investigated pre-treatment with H_2O_2 increased the amount of proteins pptd. by $CCl_3 \cdot CO_2H$. Somewhat similar results are obtained when thermal pptn. is used, but not when sulphosalicylic acid is employed. The phenomenon is most pronounced in serum and other complex protein systems; increase is not observed with ovalbumin. The effect is not due to acidity of H_2O_2 . H. W.

X-Ray reflexions of long spacing from tendon. R. W. G. WYCKOFF, R. B. COREY, and J. BISCOE (Science, 1935, 82, 175—176).—Long spacings observed in diffraction photographs of kangaroo tendon are recorded. Their existence shows that tendon cannot consist of parallel polypeptide chains bound together by irregularly repeated cross-linkings. Other possible structures are discussed. L. S. T.

Fibre forms in animal hairs. H. J. WOODS (Nature, 1935, 136, 262).—The results described (this vol., 1144) for fibre forms of white fox guard hairs are compared with those obtained with merino wool. L. S. T.

Correlation of the viscosities of protein solutions with their ability to crystallise. D. B. HAND (J. Gen. Physiol., 1935, 18, 847-852).-Proteins having viscosities in solution \Rightarrow serum-albumin are readily crystallised; those having viscosities \neq denatured ovalbumin have not yet been crystallised. F. A. A.

Peroxidase reaction. LIII. Arakawa reaction and calcium content of human milk. Y. UGA (Tôhoku J. Exp. Med., 1935, 25, 169—185).— There is a more or less graded fall in Ca content when passing from a human milk with a strong positive to one with a negative Arakawa reaction. Arakawapositive milk is good milk. NUTR. ABS. (m)

Mechanism of the Umikoff reaction. M. POLO-NOVSKI and F. MORENO-MARTIN (Bull. Soc. Chim. biol., 1935, 17, 960—964).—The reaction of Umikoff given by human but not by cows' milk with aq. NH_3 at 60° is due to the difference in the buffering power, being given by milk above $p_{\rm II}$ 8. A. L.

Behaviour of caseinogenate sols : hysteresislike phenomenon in the rennin coagulation of milk. M. E. POWELL and L. S. PALMER (J. Dairy Sci., 1935, 18, 401—414).—Heated Ca caseinogenatecolloidal Ca phosphate mixtures show a hysteresislike effect when coagulated by rennin at different intervals after heating. Heating of either constituent alone prior to mixing does not induce this effect. A complex containing colloidal CaC₂O₄ has not this property. Heating increases the cataphoretic migration of the complex > that of a Ca caseinogenate sol. A. G. P.

Components of gastric juice. P. NOFONEN (Acta med. scand., 1933, Suppl. 59, 386—394).—In human beings receiving fractional test meals histamine injection caused secretion of a very acid fluid, and pilocarpine injection secretion of a fluid rich in neutral chloride and N compounds but poor in acid. Normal gastric juice consists of these two secretions in varying amounts. NUTR. ABS. (m)

Gastric secretion and hypochloræmia. R. S. MACH (Schweiz. mcd. Woch., 1935, 65, 11–13).— Withdrawal of gastric juice before and at intervals during 4 hr. in which injections of histamine were given caused, in subjects suffering from gastric complaints, a slight decrease in cellular blood-Cl, but no distinct effect on plasma-Cl. NUTR. ABS.

Dependence of the amylolytic power of the intestinal juice on the type of diet. S. GEORGIEVSKI and S. ANDREEV (Pflüger's Archiv, 1935, 235, 428— 437).—The amylolytic power of the intestinal juice in the dog is closely associated with the type of diet. The amylolytic index ∞ the starch content of the diet. R. N. C.

Mucins and mucoids. G. BLIX, C. O. OLDFELDT, and O. KARLBERG (Z. physiol. Chem., 1935, 234, III—IV).—Very little H_2SO_4 was eliminated from various mucins on HCl hydrolysis, hence mucoitinsulphuric acid is not the principal carbohydrate group. Submaxillary mucin (isoelectric point $p_{\rm H}$ 2·45) contains two carbohydrate complexes, one of which (5% in amount) is dimannose-glucosamine, the other (25%), a cryst. substance, $C_{14}H_{25}O_{11}N$ (?), containing glucosamine, 2 Ac groups, and probably a polyhydroxy-acid (not hexuronic acid). It gives a positive NMe₂·C₆H₄·CHO reaction. J. H. B.

Composition of glomerular urine. XII. Reaction of glomerular urine of frogs and Necturi. H. MONTGOMERY (J. Biol. Chem. 1935, 110, 749— 761).—A colorimetric method for determining the $p_{\rm H}$ of minute vols. of liquid is described. The error when applied to protein-free buffer solutions was < 0.02 $p_{\rm H}$. The $p_{\rm H}$ of the glomerular urine from frogs and Necturi is the same as that of the plasma. J. N. A. Micro-quinhydrone electrode : application to determination of the p_{π} of glomerular urine of Necturus.—See this vol., 1218.

Effect of tonsillary extract on diuresis and on elimination of sodium chloride. E. CHIAEPPE (Boll. Soc. Ital. Biol. sperim., 1935, 10, 157—159).— Injection of tonsillary extract in rabbits increases diuresis, which reaches its max. in 3 hr., and persists longer than in non-injected animals. NaCl elimination remains const. R. N. C.

Determination of neutral sulphur in urine. A. FREDERICH and F. MANDL (Z. physiol. Chem., 1935, 235, 174—180; cf. A., 1934, 1386).—The procedure is improved by boiling the urine (2 c.c.) for 30 min. with 5—6 drops of conc. HCl, removing org. matter from the diluted liquid (10 c.c.) by shaking with 0.5 g. of wood-C, and pptg. SO_4'' (from 5 c.c. of filtrate) with 20 c.c. of benzidine reagent. The vol. (< 0.6 c.c. for satisfactory results) of 0.02Nalkali used for titration is corr. by adding 0.15 c.c. If the amount of total SO_4'' is very low or if the urine has been too much diluted, 1 c.c. of $0.02N-H_2SO_4$ is added before addition of benzidine and allowance made in calculation, the titration correction being now 0.18 c.c. W. McC.

Excretion of phosphates by the kidney. P. IVERSEN and E. JACOBSEN (Skand. Arch. Physiol., 1935, 71, 260—271).—The excretion coeff. of phosphate was determined under various experimental conditions by comparing the concn. indices of phosphate and creatinine (I), the concn. index being the ratio of the concn. in urine and plasma. The vals. found for women with healthy kidneys were 0.00— 0.27, and showed no relationship with plasma-phosphate. If diuresis was increased by H₂O intake, there was a relative increase in phosphate excretion if the (I) concn. index was < 20. With increasing blood-sugar an increase in phosphate excretion was observed, and with decreasing blood-sugar a decrease. Parathyroid or theophylline intake caused an increased, and salyrgan a decreased, excretion.

NUTR. ABS. (m)

Ammonia, urea, and $p_{\rm H}$ of urine in infants, healthy and with nutritional disturbances. V. ANGELINI (Riv. Clin. pediat., 1935, **32**, 1310).—In infants, excretion of NH₃ occurs in relatively const. amounts, whilst that of urea shows variations apparently correlated with diet. In infants with nutritional disturbances, the increase in urinary NH₃ \propto the degree of acidosis; urea varies inversely. Neither in healthy nor in sick infants is there a const. inverse relationship between $p_{\rm H}$ and excretion of NH₃. NUTR. ABS. (m)

"Free" ammonia in urine. Comparison of the Ronchese method with the so-called "micro-Schloesing" method. P. BALATRE (J. Pharm. Chim., 1935, [viii], 22, 107—112).—The Ronchese method (A., 1907, ii, 651) gives high results and the micro-Schloesing method (A., 1922, ii, 453; 1934, 1385) is preferred. S. C.

Occurrence of methylglyoxal in urine during vitamin- B_1 deficiency. J. LEHMANN (Skand. Arch. Physiol., 1935, 71, 157—165).—AcCHO occurs in the urine of rats on a basal diet with or without addition

of vitamin- B_1 or $-B_2$. Hence the presence of AcCHO in the urine is not sp. for vitamin- B_1 deficiency. Most of the AcCHO disappears within 12 hr. when the urine is kept. NUTR. ABS. (m)

Micro-determination of ketones in urine. O. CANTONI (Biochem. Z., 1935, 279, 201—202).— The author's method (this vol., 104, 880) for determination of ketones in blood is adapted for use with urine. P. W. C.

Effect of diet on volatile reducing substances in urine. S. HOFLUND (Skand. Arch. Physiol., 1935, 71, 238-250).—After a meal the amount of reducing substances increases, reaching a max. after 2—3 hr. Carbohydrates and fats cause no appreciable increase, but proteins always do. Fried is more effective than boiled meat. NUTR. ABS. (m)

Excretion of glucose by the rabbit kidney. T. W. T. DILLON and R. O'DONNELL (Proc. Roy. Irish Acad., 1935, 42B, 365-405).—A method for determining the kidney threshold for glucose (I) in the rabbit is described. It is defined as the plasma-(I) level above which (I) appears in greater concn. in the urine than in the plasma. It is independent of the rate of secretion of urine and varies between 190 and 430 mg. of (I) per 100 c.c. Injections of NaCl do not raise the kidney threshold, but urea and Na₂SO₄ cause a sharp rise, whilst insulin probably lowers it slightly. The excretion of (I) is closely analogous to the excretion of Cl', and fulfils the requirements of the "diffusion-secretion" theory, but is incompatible with the Cushny theory.

J. N. A.

Acidosis-producing substance (A.H.) of normal urine. C. FUNK, P. ZEFIROW, and I. C. FUNK (Arch. internat. Pharmacodyn., 1934, 49, 189–203). —Methods of prep. and assay of this hormone are described, and its effect on the utilisation of fats and carbohydrates is studied. It is similar to, but not identical with, the "fat metabolism" hormone of the anterior pituitary. The acidosis is not produced through the thyroid. NUTR. ABS. (m)

Determination of uric acid in urine. P. BALATRE (J. Pharm. Chim., 1935, [viii], 22, 120–123).—The method of determining uric acid by adding urine to I-KI solution containing CS_2 until the I is reduced is liable to serious errors on account of the presence of other reducing substances. S. C.

Xanthurenic acid. I. L. MUSAJO (Atti R. Accad. Lincei, 1935, [vi], 21, 368—371).—The reactions of the xanthurenic acid which imparts a green colour to the urine of albino rats fed on fibrin, ovalbumin, etc. indicate that it is a dihydroxyquinolinecarboxylic acid (cf. this vol., 1007). T. H. P.

Urinary phosphatase. W. KUTSCHER and H. WOLBERGS (Naturwiss., 1935, 23, 558-559).—The phosphatase (I) content of urine is high early in the morning, falls to a min. at midday, rises after a midday meal, and decreases gradually towards the evening. A high early-morning val. is also observed during fasting. Feeding of glucose after fasting leads to a decrease in the amount of (I) excreted corresponding with the rise in blood-sugar level. E. A. H. R. Detection of defence enzymes in urine. E. ABDERHALDEN (Fermentforsch., 1935, 14, 502– 521).—Dialysis is unnecessary and procedure is much simplified if the test is applied to suspensions (in 0.9% aq. NaCl) of the material pptd. from urine by COMe₂ instead of to blood-serum. W. McC.

Presence of the protective hormone in urine. A. DE BARBIERI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 153—154).—Injection of urine extract in guineapigs protects the animals against acute NH_4Cl poisoning; the Sato protective hormone of the liver is hence present in urine. R. N. C.

Detection of bile-pigments in urine by methylene-blue. P. BALATRE (J. Pharm. Chim., 1935, [viii], 22, 166—168).—The reaction is based on purely physical phenomena and is untrustworthy. P. G. M.

Perspiration and erythema. W. H. CAREW (Nature, 1935, 136, 340).—A film of human perspiration 1 mm. thick absorbs light slightly in the region of 330, appreciably at 290, and practically completely at 270 m μ . Uric acid may be the primary absorbing agent in sweat. L. S. T.

Ætiology of pernicious and related macrocytic anæmias. W. B. CASTLE (Science, 1935, 82, 159—164).—A lecture. L. S. T.

Colloidal dye effective in treating pernicious anæmia and evoking reticulocytosis in guineapigs. C. MERMOD and W. DOCK (Science, 1935, 82, 155—156).—The observation that repeated intravenous injection of Congo-red produces in primary anæmia effects similar to those of liver-extract has been confirmed. L. S. T.

Anæmia in the chronic rheumatic diseases. D. H. COLLINS (Lancet, 1935, 229, 548-550).— Anæmia due to diminished blood-hæmoglobin with a relatively insignificant fall in the red-cell count frequently accompanies chronic rheumatic conditions. The more severe degrees of anæmia practically only occur in atrophic arthritis. Anacidity is frequently found among females with atrophic arthritis, but deficient gastric secretion is not a const. factor in the production of anæmia in such cases. L. S. T.

Development of nutritional anæmia in dairy calves. C. E. KNOOP, W. E. KRAUSS, and R. G. WASHBURN (J. Dairy Sci., 1935, 18, 337—347).— Calves receiving exclusively a whole-milk diet developed nutritional anæmia. Supplementary feeding of Cu and Fe (40 and 400 mg. daily, respectively) prevented anæmia and markedly increased the Cu and Fe contents of livers. A. G. P.

Increase in blood-carbon monoxide in anæmia. M. LOEPER, E. BIOY, J. TONNET, and A. VARAY (Compt. rend. Soc. Biol., 1935, 119, 1319—1320).— Many types of anæmia are associated with an increase in blood-CO, although no relation between the quantity of CO and the extent of the anæmia is observed. H. G. R.

New cancer-producing hydrocarbons. A. A. MORTON, D. B. CLAPP, and C. F. BRANCH (Science, 1935, 82, 134).—s-C₆H₃Ph₃ and CPh₄ produce malignant growths in mice, but more slowly than carcinogenic compounds containing a phenanthrene nucleus. L. S. T.

Resistance of sarcomatous rats to insulin. M. PEREZ (Boll. Soc. Ital. Biol. sperim., 1935, 10, 118-121).—The min. lethal dose of insulin in rats with sarcomatous tumours is > in normal rats; both vals. fall as the fasting period increases, and the difference between them also decreases. The bloodsugar is unaltered by the presence of tumours, and is hence not associated with the increased resistance. R. N. C.

Behaviour of serum in malign tumours, pregnancy, and gynæcological diseases. C. VERCESI and F. GUERCIO (Biochem. Z., 1935, 279, 229—232).— The I val. of the material extracted with Et_2O from filter-paper on which serum of cases of pregnancy, uterus carcinoma, etc. had been dried was considerably higher in cases of malignant disease than in other diseases and pregnancy. P. W. C.

Chemistry of cataract in the diabetic. H. N. CAREY and H. M. HUNT (New England J. Med., 1935, 212, 463-468).—The cryst. lenses from 10 normal subjects contained approx. 400 mg. of cholesterol per 100 g., 9.5 mg. of Ca, and 16.5 mg. of P. Cataractous lenses contained on an average 522 mg. of cholesterol and 31.6 mg. of Ca. There were no marked differences in the Ca contents of diabetic and nondiabetic cataractous lenses, but the P content of the former was 6.2 mg. per 100 g., as compared with 19.7 mg. for the latter. NUTR. ABS. (m).

Alkali reserve in induced hypoglycaemia in normal and diabetic subjects. M. TRPODI (Policlinico, 1935, 42, 111—127).—The effect of insulin on the alkali reserve was studied. Coincident with the appearance and to some extent ∞ the degree of hypoglycæmia there was a const. fall in alkali reserve in normal and slightly diabetic subjects and in rabbits. In severe diabetes there was first a transient increase and then, when the blood-sugar fell below a certain level, a fall in alkali reserve which coincided with the disappearance of hypoglycæmia. Large doses of NaHCO₃ given intravenously when hypoglycæmia appeared had a favourable effect on slight, but none on severe, hypoglycæmia. NUTR. ABS. (m)

Glucose and lactate usages of the diabetic heart and the influence of insulin thereon. C. L. EVANS, F. GRANDE, F. Y. HSU, D. H. K. LEE, and A. G. MULDER (Quart. J. Exp. Physiol., 1935, 24, 365— 376).—The glucose (I) and lactate (II) usages of the perfused diabetic dog's heart are about half the val. for the normal organ; although the (I) consumption is trebled by the addition of insulin, that of (II) is slightly decreased. It is of fundamental importance that the diabetic heart uses (II) at about the same rate as the hyperglycæmic normal heart. NUTR. ABS. (m)

Hæmatic glycolysis in vitro in diabetes mellitus. I. Action of cortin. G. VIALE and A. CROCETTA (Boll. Soc. Ital. Biol. sperim., 1935, 10, 143—145).—Cortin in any concn. inactivates hæmatic glycolysis in depancreatised dogs. In normal dogs and diabetic patients it activates glycolysis up to a given concn., above which it inhibits it completely. R. N. C. Action of parathyroid extract on glycæmia in diabetes. J. OLMER, J. E. PAILLAS, and B. SICNASI (Compt. rend. Soc. Biol., 1935, 119, 1264—1266).— Injection of parathormone causes a lowering of blood-sugar. H. G. R.

Reducing substances in the blood in eclampsia. H. DIETEL (Arch. Gynäkol., 1935, 159, 94–97).— Iodometric titration of blood, combined with separate determination of SH-compounds, indicates an excess of a non-SH reducing substance which is identified with ascorbic acid, and is much diminished in eclampsia. The redox processes of the cells are disturbed in this condition. NUTR. ABS. (m)

Porphyrin excretion in hyperemesis gravidarum and its relationship to liver function. L. HEROLD (Arch. Gynäkol., 1935, 159, 35-40).— The average daily urinary excretion of porphyrin in pregnancy was < 0.04 mg., the highest val. being 0.066 mg. NUTR. ABS. (m)

Heat exchange of the rat in exogenous hyperthermia. K. SCHUHECKER (Pflüger's Archiv, 1935, 235, 490—513). R. N. C.

Effect of tyrosine on the function of the thyroid gland. I. ABELIN (Naturwiss., 1935, 23, 528—529). —Tyrosine administered together with thyroid preps. to animals suffering from experimental hyperthyroidism has a beneficial effect on the accompanying symptoms of disease and diminishes the metabolic action of the thyrotropic hormone. W. McC.

Pathological physiology of infarct. II. Proteolytic activity of infarct tissue. G. BORGER and T. MAYR (Z. physiol. Chem., 1935, 234, 245—253; cf. A., 1933, 852).—The proteolytic activity is much < that of normal tissue. This appears to be due to destruction of enzyme in the infarct and not to the production of inhibitors. J. H. B.

Lipæmia and uræmia. S. MARINO (Arch. Farm. sperim., 1935, 59, 245—273).—Uræmia of some types of glomerular nephritis is accompanied by increased levels of blood-phosphatide (I), -cholesterol (II), and, occasionally, -fatty acids (III). (I) and (II) slowly diminish during uræmic coma, whilst (III) markedly increase. No correlation exists between the lipæmia and arterial pressure, albuminuria, or blood-N level. The increase in blood-lipins is a defensive reaction of the organism against the toxic effect of uræmia. F. O. H.

Oxalic acid metabolism in nephritis. Determination of the acid in blood, food, urine, and fæces. R. RITTMANN and P. UNTERRICHTER (Arch. Verdauungs-Kr., 1935, 57, 120—148).—The method of Bau (A., 1921, ii, 356), with slight modifications, is satisfactory for the determination of $H_2C_2O_4$ in urine, fæces, and foods, but not in blood. In kidney disease $H_2C_2O_4$ is probably retained in the blood. NUTR. ABS. (m)

Nutritional ædema in the dog. I. Development of hypoproteinæmia on a diet deficient in protein. A. A. WEECH, E. GOETTSCH, and E. B. REEVES (J. Exp. Med., 1935, 61, 299-317).—Dogs receiving a diet very low in protein showed first a rapid and then a slow decrease in serum-albumin and total protein. The globulin, which showed wide individual variations, remained approx. const. There was a mean daily loss of 1.15 g. of N, only 3--4% of which was accounted for by the decrease in bloodprotein. In one dog, a ten-day fast caused a rise of the serum-albumin to normal. When sufficient amounts of animal protein were given there was slow regeneration of blood-protein. NUTR. ABS. (m)

Acid-base balance in cows and ewes during and after pregnancy. Milk fever and acetonæmia. J. SAMPSON and C. E. HAYDEN (J. Amer. Vet. Med. Assoc., 1935, 86, 13—23).—In normal pregnant cows there was a slight lowering of CO_2 capacity and a slight rise in blood-ketones. In milk fever and acetonæmia, there was a further lowering of CO_2 capacity and raising of ketones, together with a marked lowering of serum-Ca. In other diseases the vals. were normal. In normal ewes there was little difference between the blood of pregnant and that of non-pregnant animals. In pregnancy disease there was a lowering of CO_2 capacity and rise in ketones with ketonuria. Serum-Ca was normal. In other diseases figures were normal. Acetonæmia in cows and pregnancy disease in ewes are possibly due to disturbance of carbohydrate metabolism.

NUTR. ABS. (m)Calcium metabolism in pregnancy. W. VOG-LER (Diss., Erlangen, 1933; Bied. Zentr., 1934, A, 5, 328).—The decline in total Ca of the blood in pregnancy is probably associated with an increase in % of dialysable Ca. The activity of internal secretion glands is closely related to Ca metabolism. The tendeney toward caries in pregnancy is partly although not wholly dependent on Ca deficiency. A. G. P.

Iron metabolism during pregnancy. K. UT-HEIM-TOVERUD (Acta paediat., 1935, 17, Suppl., 131-135).-In the last trimester of pregnancy, on Fe intakes varying from 7 to 28 mg. the daily retention in 8 cases out of 10 was < the foctal requirement of 4.7 mg., as calc. by Hugounenq. Including fœtal requirements, the lowest intake with a positive balance was 13 mg.; in two cases a daily intake of 15 mg. gave a negative balance. 70 out of 181 mothers in the last trimester showed a hæmoglobin level < 70%(Sahli); in only 13 of these was hydræmia a possible explanation. Blood-Fe ranged from 40 to 59 mg. per 100 ml., figures < 45 mg. occurring in 28% of 114 women examined. Of 47 pregnant women, 28 showed hypo-acidity in the last trimester. A negative Fe balance may be due to an Fe intake below the min. needs, or to defective absorption, and leads to lowering of the blood-hæmoglobin and -Fe. NUTR. ABS. (m)

Intermediary fat metabolism in pregnancy. II. Dietary fat and blood-fat. O. BOKELMANN and A. BOCK (Arch. Gynākol., 1934, 158, 505-530). —The ketone contents of the blood and urine are somewhat higher and the blood-fatty acid content is considerably greater in pregnant than in non-pregnant women. After oral administration of large amounts of fat together with a correspondingly enriched carbohydrate diet, the blood-fatty acid and -ketone and the urinary ketone were increased, the increase being much greater in pregnant than in non-pregnant women.

NUTR. ABS. (m)

Thyroid action in pregnancy. Presence of the thyroid hormone in blood in pregnancy. K. J. ANSELMINO and F. HOFFMANN (Arch. Gynäkol., 1935, 159, 84–93).—Experiments in which serum from pregnant (10 months) and non-pregnant (intermenstrual) women was fed to rats indicate that the amount of thyroid hormone in blood is increased in pregnancy. NUTR. ABS. (m)

Effect of the hen's diet on bone changes in rachitic chicks. B. E. KLINE, C. A. ELVEHJEM, and J. G. HALPIN (Poultry Sci., 1935, 14, 116–118).— Within the limits of practical feeding, the level of vitamin-D of hen's rations did not affect the % ash in the bones of chicks. A. G. P.

Blood-magnesium in Recklinghausen's disease. J. MARX (Orvosi Hetilap, 1935, 79, 351–353).—Parathyroid hormone injected into guineapigs caused a decrease in blood-Mg and an increase in blood-Ca. The decrease in the Ca in the bones was associated with an increase in Mg.

NUTR. ABS. (m)

Impregnation of the organism by dust. I. R. FABRE (J. Pharm. Chim., 1935, [viii], 22, 145— 150).—A preliminary study of the problems involved in the physiology and pathology of silicosis, anthracosis, etc. P. G. M.

Modifications in the content of inorganic phosphorus in blood and urine in experimental scurvy. A. LEONE (Riv. Clin. Pediat., 1934, 32, 1185).—In experimental scurvy the P balance became sharply negative. The inorg. P of the blood fell and the urinary excretion increased, with a relative decrease just before death. The metabolism of carbohydrates and P, which rises with the formation of lactacidogen, possibly causes this change.

NUTR. ABS. (m)

Hypomagnesæmia in equine transit tetany. H. H. GREEN, W. M. ALLCROFT, and R. F. MONT-GOMERIE (J. Comp. Pathol., 1935, 48, 74—79).— The hypocalcæmia of equine transit tetany is associated with hypomagnesæmia. There was a 50% decrease in serum-Mg as compared with vals. taken two weeks later. NUTR. ABS. (m)

Etiology of grass tetany. V. Reduction of blood-calcium and -magnesium by a plant substance and by withdrawal of blood, fasting, and tissue necrosis. L. SEEKLES and B. SJOLLEMA (Arch. Tierheilk., 1935, 68, 386—396).—In rabbits serum-Ca was lowered by blood-sampling, fasting, or pathological change. Subcutaneous and oral administration of grass extracts (from meadows on which grass tetany had previously developed) and subcutaneous injection of earthnut extracts lowered the serum-Ca level. Some extracts produced a lowering of serum-Mg. Fractionation of the extracts did not yield a more highly active fraction.

NUTR. ABS. (m)Vitamin-C and tubercular infection. G. DI BELLA (Boll. Soc. Ital. Biol. sperim., 1935, 10, 141– 142).—The resistance of guinea-pigs to tubercle bacilli is not increased by orange-juice or ascorbic acid. R. N. C. Fat-tolerance tests and blood-sugar determinations on patients with peptic ulcer. Possible factors in the etiology of peptic ulcer. M. A. SCHNITKER and E. S. EMERY, jun. (Amer. J. Digest. Dis. Nutrit., 1935, 1, 834-840).—After ingestion of 100 g. of milk-fat, the blood-fat and -sugar level in patients suffering from peptic ulcer showed no significant variation from the levels in controls.

NUTR. ABS. (m)

Cod-liver oil treatment of wounds. J. P. STEEL (Lancet, 1935, 229, 290—292).—Crude codliver oil promotes rapid healing of burns with almost complete elimination of scar tissue. It is also useful with indolent ulcers and deep abrasions. L. S. T.

Relation between basal metabolism and endogenous nitrogen metabolism with particular reference to the determination of maintenance requirement of protein. D. B. SMUTS (J. Nutrition, 1935, 9, 403-433).-In the animals examined, adjustment to the post-adsorptive condition during fasting and to the endogenous level of urinary N excretion during sp. N starvation is more rapid in those of smaller body-size. Total endogenous N output is more closely related to body-surface than to body-wt. In a variety of animals the daily endogenous N loss approximates closely to 2 mg. of N per g.-cal. basal heat. This relationship forms a basis of calculation of the maintenance requirement of protein. Creatinine excretion bears a fairly const. proportionality to basal metabolism within a species, but in different species creatinine-N forms characteristically different % of the total endogenous N (the % decreases with body-size). A. G. P.

Liver and cerebral function. A. DE BARBIERI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 155—157).— Interference with the blood outflow from the liver in dogs affects central metabolism. Neither the protective hormone nor the antipernicious principle of the liver is involved. R. N. C.

Hæmoglobin production in rats on diets containing bread. V. C. MYERS, D. G. REMP, and F. C. BING (Cereal Chem., 1935, 12, 372-376).—Some whole-wheat breads contain twice as much Fe and Cu as white bread, rye bread being intermediate. Both Cu and Fe in bread can be effectively utilised by anæmic rats for growth and hæmoglobin production. White bread forms a fair source of Cu, but a poor one of Fe. Whole-wheat bread is not an Fe-rich food, but consumed in liberal amounts it could supply a significant proportion of the daily requirements of normal adults; its Fe appears to be equiv. to inorg. Fe for hæmoglobin production, although only 50% is in this form. The utilisation of bread-Cu is \ll two thirds as effective as the utilisation of inorg. Cu. The better growth of rats receiving bread-Cu than those on CuSO₄ is probably due to the presence in bread of elements other than Cu. E. A. F.

Nutritional value of bread in diet of human subjects and experimental animals. K. EYERLY, C. OCLASSEN, and J. A. KILLIAN (Cereal Chem., 1935, 12, 377–389).—Varying the amount of white bread in the diet of rats from 50 to 70% produced no effect on their rate of growth; there were no excessive

gains in wt. with the higher levels of white bread (60 and 70%) in the diet. Under the conditions used, a large fraction of white bread in the diet does not produce any signs of inhibition of calcification in the young, nor of decalcification in the mature rats in successive generations. Studies on the effect of white bread and sugars (sucrose, glucose, and invert sugar) on human energy metabolism showed that the experimental subjects exhibited the min. tolerance for glucose and the max. tolerance for white-bread carbohydrates, White bread exhibited a higher sp. dynamic action than sugars, and effected a more uniform distribution of heat production between carbohydrate and fat. E. A. F.

Pigmentation in black-haired rats. M. H. HAYDAK (Science, 1935, 82, 107-108).—The changes in pigmentation which occur when young rats are fed solely on whole milk are described and discussed. L. S. T.

Photometric method for the determination of chromic oxide in digestibility research after the so-called quantitative indicator method. L. PALOHEIMO and I. PALOHEIMO (Suomen Kem., 1935, 8, B, 29).— Cr_2O_3 , which has been mixed with food as an insol. indicator of the extent of digestion, may be determined in the fæces by dissolution from the ash by means of Na₂O₂. The concn. of Na₂CrO₄ is determined photometrically. R. S. B.

Effect of sudden severe anoxæmia on the function of the human kidney. R. A. McCance (Lancet, 1935, 229, 370—372).—After overbreathing and accidental anoxæmia with unconciousness the process of NH_3 excretion and the ability to concentrate H[•] were unaffected, the rates of excretion of creatinine and of $SO_4^{\prime\prime}$ were somewhat, and of urea, H_2O , Na[•], K[•], Cl['], and P greatly, reduced. Recovery was apparently complete in 3 hr. L. S. T.

Determinism of the entry of the egg into maturation in some marine invertebrates. J. J. PASTEELS (Arch. Biol., 1935, 46, 229-262).-CaCl, induces maturation of oocytes in marine invertebrates, but the effect of KCl varies. The favourable effect of high $p_{\rm H}$ is due to its acceleration of the action of CaCl₂. Maturation is unaffected by aerobic or anaerobic inhibition of respiration, but is inhibited by narcotics. The effect of CaCl₂ appears clearly in cases of species where the eggs are matured in sea-water before fertilisation, particularly where fertilisation takes place in the oocyte. The entry of the spermatozoon apparently accelerates maturation by an indirect route in which CaCl₂ plays an essential R. N. C. part.

Metabolism of the frog's egg in course of development. II. Respiration of the egg during fertilisation and mitosis. III. Respiratory metabolism and "organising centre" of the gastrula. J. BRACHET (Arch. Biol., 1935, 46, 1–24, 25–46; cf. A., 1934, 1390).—II. Eggs are not fertilised in absence of O_2 or presence of KCN, but can be activated by CHCl₃ under these conditions, indicating that the unfertilised egg is a facultative anaërobe, whilst the spermatozoön is an obligatory aërobe. Fertilisation does not immediately alter O_2 consumption, which increases slowly during segmentation, without showing any parallelism with mitoses. O_2 consumption in polyspermic eggs is > in normal eggs. Eggs from the same female show equal O_2 consumptions when fertilised by spermatozoa from different males. Cyclic variations of O_2 consumption occur during mitoses. During segmentation anaërobic reactions occur, which liberate CO_2 .

III. Destruction of the dorsal lip of the blastopore (organising centre) induces a fall in O_2 consumption > that induced by an equiv. lesion of an indifferent part of the organism; CO_2 evolution is correspondingly reduced. The isolated organising centre produces CO_2 more rapidly than the isolated marginal ventral zone. Hence the organising centre is also a centre of high respiratory metabolism. R. N. C.

Utilisation of protein concentrates by the growing chick. F. E. MUSSEHI, and C. W. ACKER-SON (Poultry Sci., 1935, 14, 119–121).—A considerable variety of protein sources does not necessarily enhance the biological val. of a concentrate when the basal ration contains ≤ 4 other sources of protein. A. G. P.

Utilisation of gelatin, casein, and zein by adult rats. I. D. MASON and L. S. PALMER (J. Nutrition, 1935, 9, 489-505).—In N balance experiments the % retention (McCollum's method) averaged 74 for casein (I), 23 for gelatin (II), and 57 for zein (III). (I) and (II) were so well digested that there was no appreciable difference between % retention and biological val. (Mitchell). The digestibility of (III) was low and variable. A significant correlation exists between exogenous facal N (expressed as % of N ingested) and exogenous urinary N (as % of N resorbed). A. G. P.

Variation of the dietary protein without simultaneous variation of the urinary quotient. O. FRANKE (Biochem. Z., 1935, 279, 205—212).—With the same individual different metabolism levels are obtained with diets having the same cal. content but different % of protein; these levels are distinguished by the fact that considerable change in total foodprotein can occur without significant change in urinary C: N and vacate O: N ratios. P. W. C.

Nutritive value of ishinagi- (Stereolepis ischinagi) and ox-liver. I. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 731—740).—Proteins of ishinagi- and ox-liver have a very high nutritive val. Diet containing 15% of liver-protein produced excellent growth in rats. Ishinagi-liver oil has a very high vitamin-A potency (about 900 cod-liver oil units); it contains a toxic substance, most of which can be removed with 90% MeOH; the residual oil yields vitamin-A on extraction with MeOH. 20 mg. of oil given orally to rats much retards the growth. Ox-liver oil contains nearly 10 times as much vitamin-A as commercial cod-liver oil, and is rich in $-B_2$ but poor in $-B_1$. E. P.

Feeding experiments with decomposition products of proteins. IV. S. MAYEDA (Proc. Imp. Acad. Tokyo, 1935, 11, 258-259; cf. A., 1933, 975).—White rats fail to grow on a basal diet containing many NH_2 -acids (enumerated) in place of protein, but respond immediately to α -amino- β -hydroxy-*n*-butyric acid (A., 1934, 638). J. L. D.

Oxidation of nucleic acid in tissues. I. Effect of the sodium salt on dehydrogenations. Y. TSUGE (Fermentforsch., 1935, 14, 422-429).— Fresh tissues (rabbit) contain nucleic acid dehydrogenase (I), the amount being greatest in the lower part of the small intestine. The decolorisation of methyleneblue (II) by (I) is more rapid when the concn. of (II) is low (1:105) than when it is high and the time of decolorisation ∞ the concn. of (I). The optimum temp. for the action of (I) is 37°. W. McC.

Cystine metabolism : its rôle in nitrogen metabolism, intestinal absorption, and oxidation coefficient. E. F. TERROINE, M. MEZINCESCO, and S. VALLA (Ann. Physiol. Physicochim. biol., 1934, 10, 1059).—Addition of cystine (I) to a carbohydrate diet, on which min. N and S excretions have been established, improved N balance, although it remained negative, and gave a positive S balance. The reduction in N excretion was similar to that produced by non-essential NH_2 -acids (glycine). Excretion of creatine and creatinine was not affected. Absorption of a large dose of (I) without other source of N was almost complete. Of the excess S excreted 85%was as SO_4 ". NUTR. ABS. (m)

Value of non-essential amino-acids in covering endogenous nitrogen metabolism. M. MEZINCESCO (Ann. Physiol. Physicochim. biol., 1934, 10, 1011).—Addition of glycine, alanine, aspartic or glutamic acid to a carbohydrate diet on which min. endogenous N excretion has been attained improved the balance by about 30%, by supplying the α -NH₂ group. There is no change in excretion of creatinine or S. Synthetic formation of creatine from NH₂-acids without the guanidine grouping or the glyoxaline nucleus is unlikely. NUTR. ABS. (m)

Metabolism of amino-acids. V. Conversion of proline into glutamic acid in kidney. H. WEIL-MALHERBE and H. A. KREBS (Biochem. J., 1935, 29, 2077—2081).—Rabbit's kidney in presence of NH₄ salts oxidises proline (I) and hydroxyproline (II) to an acid amide which reacts like glutamine, and when the kidney is poisoned with As₂O₃, α -ketoglutaric acid is formed. The stages between (I) and glutamic acid are not known, but neither (II) nor pyrrolidonecarboxylic acid (III) is an intermediate in the oxidation, since (I) reacts more rapidly than (II), and (III) has no effect on the O₂ uptake.

J. N. A. Metabolism of amino-acids. IV. Synthesis of glutamine from glutamic acid and ammonia, and the enzymic hydrolysis of glutamine in animal tissues. H. A. KREBS (Biochem. J., 1935, 29, 1951—1969).—Brain-cortex and retina of vertebrates and kidneys of rabbit and guinea-pig convert NH₄ glutamate (I) into glutamine (II). The energy for this endothermic synthesis is supplied either by respiration or, in retina, by anaërobic lactic acid fermentation. Tissues which synthesise (II) contain glutaminase (III), which hydrolyses (II) to (I). Both processes are inhibited by glutamic acid (IV). Mammalian liver also contains a (II)-splitting enzyme (V) which differs from (III) in its $p_{\rm H}$ optimum and is not inhibited by (IV). Both (III) and (V) are distinct from asparaginase. E. A. H. R.

Uric acid metabolism. D. JOFFE (Arch. Verdauungskr., 1935, 57, 25-41).—The effect of fasting, and of ingestion of ordinary purine-free food, vegetable diet, and Na nucleinate on the uric acid content of the blood of persons on a basal purine-free diet was examined. On a purine-free diet the fasting level was 2-4 mg. per 100 ml. of blood. The fluctuations following a purine-free meal were variable. After feeding Na nucleinate the rise was in general greater. NUTR. ABS. (m)

Fat metabolism. VI. α -Lauro- $\beta\gamma$ -diundecoin. P. E. VERKADE, J. VAN DER LEE, and K. HOLWERDA (Proc. K. Acad. Wetensch. Amsterdam, 1935, 38, 536—540, and Z. physiol. Chem., 1935, 234, 21—26).—The two fatty acids are liberated at the same rate from α -lauro- $\beta\gamma$ -diundecoin as from the corresponding mixture of trilaurin and triundecoin. H. G. R.

Interrelations between water and fat metabolism in relation to disturbed liver function. H. SELYE, J. B. COLLIP, and D. L. THOMSON (Lancet, 1935, 229, 297—298).—After partial hepatectomy of rats the liver remnants exhibit marked fatty changes if the animals are bled or injected with large amounts of saline, or if drinking-H₂O be withdrawn. The pituitary appears to be essential for the deposition of fat in the liver. L. S. T.

Fat formation from sucrose and glucose. S. FEYDER (J. Nutrition, 1935, 9, 457–468).—Rats fattened more rapidly on sucrose than on an equiv. supply of glucose. A. G. P.

Effect of blood-sugar concentration on the rate of absorption of sugar from the intestine. E. J. McDoUGALL (Arb. ung. biol. Forsch.-Inst., 1934, 7, 217-222).—Hyperglycæmia was produced in anæsthetised rabbits by introducing 5-10% aq. glucose (I) or xylose (II) into the jugular vein at known rates and injecting aq. 11-14% sugar solution into the small intestine. Although the blood-sugar level was about doubled, the rate of absorption from the intestine was not decreased; in the case of (I) it was increased slightly. The rate of absorption of (I) was about twice that of an equimol. solution of (II).

Effects of lactose on growth and longevity. E. O. WHITTIER, C. A. CARY, and N. R. ELLIS (J. Nutrition, 1935, 9, 521—532).—Lactose (I) produced more rapid growth of young rats than did sucrose (II), but adult animals attained greater body-wt. on (II), when fed *ad lib*. Pigs stored more fat when supplied with (II). Rats receiving (I) lived longer. A. G. P.

Rates of absorption of and glycogenesis from various sugars. S. FEYDER and H. B. PIERCE (J. Nutrition, 1935, 9, 435-455).—Wide variations in the rates of absorption of glucose (I), sucrose (II), and maize-syrup, and in the total amounts absorbed, are recorded. Rates of glycogenesis from (I) and (II) were similar in the 2 hr. following administration, but that from (I) declined subsequently. Rates for maize-syrup were lower and more const. A. G. P.

Effect of carbon dioxide on blood-sugar. Effect of change in acid-base equilibrium. Influence of the nervous system. D. CORDIER (Ann. Physiol. Physicochim. biol., 1934, 10, 1135).—In dogs anæsthetised with chloralose, inhalation of CO_2 caused progressive hyperglycæmia, but injection of NaHCO₃ or HCl (except in massive doses) had no effect on blood-sugar. The effect of CO_2 is attributed to its rapid diffusion into the liver cell. Experiments with section of the splanchnic nerves, removal of the adrenals, or section of the pneumogastrics in the neck indicate that the effect of CO_2 on blood-sugar is due partly to sympathetic nervous action, direct and indirect, and partly to direct action on the liver-cells. There is no reflex action from the lung.

NUTR. ABS. (m)

Glucose and lactate consumption of the dog's heart. C. L. EVANS, F. GRANDE, and F. Y. HSU (Quart. J. Exp. Physiol., 1935, 24, 347-364).--A perfused dog's heart utilises about three times as much lactic acid (I) as glucose (II). Addition of insulin increases the utilisation of (II), but not that of (I). NUTR. ABS. (m)

Formation of carbohydrate from glycerophosphate in the liver of the rat. C. F. CORI and W. M. SHINE (Science, 1935, 82, 134–135; cf. this vol., 523).—Inorg. $PO_4^{\prime\prime\prime}$ increases and the $PO_4^{\prime\prime\prime}$ fractions difficult to hydrolyse in N-HCl decrease when liver slices of rats are shaken for 3 hr. in oxygenated HCO3'-Ringer's solution, indicating that glycerophosphate (I) may be a source of carbohydrate (II) in the liver. Addition of α - or β -(I) or of glycerol produces a larger increase in fermentable (II) than incubation of the liver without added substrate; under anaërobic conditions an increase does not occur. During incubation of liver slices with α -(I) more inorg. PO₄" is liberated than during incubation without added substrate. The results emphasise the importance of the glycerol part of the lipin mol. as a source of (II) in the body, and do not support the view that fatty acids are converted into (II) in the mammalian liver. L. S. T.

Metabolism of lactic and pyruvic acids in normal and tumour tissues. II. Rat kidney and transplantable tumours. K. A. C. ELLIOTT, M. P. BENOY, and Z. BAKER (Biochem. J., 1935, 29, 1937-1950).-The cycle established by Elliott and Schroeder (A., 1934, 1394) for lactate (I) and pyruvate (II) metabolism is demonstrated more clearly with rat kidney, but does not occur in tumour. In tumour (I) is metabolised only slightly and succinate (III), fumarate (IV), and malate (V) not at all; (II) is oxidised as far as (III) and an equilibrium between (IV) and (V) can be established. The decomp. of oxalacetate to (II) is not catalysed by kidney. In the Clift and Cook determination of (II) (cf. A., 1933, 491) the solution should be cooled or Na_2HPO_4 added in place of $NaHCO_3$. E. A. H. R.

Ketogenesis-antiketogenesis. I. Influence of ammonium chloride on ketone formation in liver. N. L. EDSON (Biochem. J., 1935, **29**, 2082–2094).—NH₄Cl increased the production of CH₂Ac•CO₂H from AcCO₂H in liver, but in the absence of AcCO₂H there was an increased production only in a well-nourished liver, and no effect in a starved liver. Fatty acids with even and odd no. of C gave rise to β -keto-acids (I) during oxidation in liver slices, the yield being about 3 times as much with the even as with the odd. NH₄Cl accelerated the formation of (I) in the well-nourished liver. The effect of NH₃ was inhibited by glycerol. Micro-methods, suitable for tissue-slice work, for the determination of (I) and β -hydroxybutyric acid are described. J. N. A.

Dehydrogenating action of the liver on some phenylaliphatic acids. F. P. MAZZA (Boll. Soc. Ital. Biol. sperim., 1935, 10, 138—140).— O_2 consumption by liver extract or perfused liver sections is increased by γ -phenyl- and γ -hydroxy- γ -phenylbutyric (I) acids; γ -phenylcrotonic acid (II) is effective in liver sections only, whilst γ -phenylisocrotonic and α -hydroxy- γ -phenylbutyric acids are without effect. The results confirm and demonstrate the Knoop theory *in vitro*, and suggest that (II) is transformed into (I) in the liver by an inextractable hydratase.

R. N. C. Alcohol injected intravenously : rate of disappearance from the blood-stream in man. H. W. NEWMAN and W. C. CUTTING (J. Pharm. Exp. Ther., 1935, 54, 371-377).—EtOH injected intravenously is metabolised at a rate independent of its blood concn. H. D.

Central disturbance of sodium chloride metabolism. I. MOLNAR and Z. GRUBER (Orvosi Hetilap, 1935, 79, 116-120).—Normal subjects and patients suffering from cerebral disease (acromegaly, tumour, etc.) were fed for a few days on a salt-poor diet, then 10 g. of NaCl were added daily. Healthy subjects retained 10-20 g. during the first two days of increased NaCl intake and were in equilibrium from the third day, but in most cases of cerebral disease more NaCl was retained and equilibrium was not reached until the fourth day. In some cases the NaCl output periodically exceeded the intake.

NUTR. ABS. (m)

Metabolism of potassium and sodium. B. SJOLLEMA (Geneeskund. Bladen, 1934, 32, 255).— A review. NUTR. ABS. (m)

Adult rats of Iow calcium content. H. L. CAMPBELL, O. A. BESSEY, and H. C. SHERMAN (J. Biol. Chem., 1935, 110, 703—706).—A diet containing only 0.094% of Ca in the air-dried mixture when fed to 28-day-old rats sufficed for growth and health in the first but not in the second generation. Animals of the latter showed a low Ca content, were only about 75% of the normal size, failed to rear young, and were senile at the age of 1 year. J. N. A.

Growth of pigs. I. Lime and phosphate metabolism in young growing pigs. L. S. SPILDO (Beretn. Forsøgslab. Kopenhagen, 1933, No. 151; Bied. Zentr., 1935, A, 5, 327).—The P: Ca ratio of the food is more important than the abs. amounts supplied. High ratio causes ostitis fibrosa and tetany [and low serum-Ca. Low ratio induces osteoporosis, and rickets with hypercalcæmia and hypophosphatæmia. Addition of vitamin-D to a high-ratio ration improves the utilisation of Ca and favours growth. Similar addition to a low-ratio diet produces unfavourable effects. A. G. P.

Influence of phosphatic substances on calcium and phosphorus balances [of animals]. S. KOCH (Diss., Freiberg, 1933; Bied. Zentr., 1935, A, 5, 329).—Subcutaneous or intraperitoneal injection of P-containing substances into rats and guinea-pigs results in increased elimination of Ca and P and marked negative balances. Loss occurs in fæces during the injection period, and subsequently, to a considerable extent, in the urine. A. G. P.

Saliva tests. III. Detecting administration of some opium derivatives to horses. J. C. MUNCH (J. Amer. Pharm. Assoc., 1935, 24, 557— 560; cf. this vol., 397).—The administration or nonadministration of opium derivatives to 37 horses was correctly diagnosed by the mouse test, but it was impossible to infer definitely what drug had been administered. R. S. C.

Pharmacological investigation of "Senso," a Chinese drug from the dried cutaneous secretion of the toad. IV. Action of ψ -bufotalin and ψ bufotalin bromide. Y. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1935, **11**, 298—300).—The pharmacology of these substances is described. ψ -Bufotalin bromide is much less toxic than g-strophanthin, which it resembles; its lethal action is not cumulative.

J. L. D.

Pharmacological properties of a new alkaloid from ergot of rye—ergobasine. E. ROTHLIN (Compt. rend. Soc. Biol., 1935, **119**, 1302—1304).— Ergobasine resembles ergotamine in its action on the uterus, but differs in that it does not produce gangrene when given to rats in toxic doses, and in its lack of sympathicolytic action. H. G. R.

Influence of the viscosity of blood on the depressor action of yohimbine. H. BUSQUET and C. V. VISCHNIAC (Compt. rend. Soc. Biol., 1935, 119, 1376—1378).—In the dog, but not in the rabbit, the depressor action of yohimbine is decreased if the blood is made more viscous by the addition of gum and gelatin. The depressor action is then lost, but the sympathicolytic is not affected. H. G. R.

Elimination of hydrastinine in the bile and urine. J. BERNARDBEIG and F. CAUJOLLE (Compt. rend. Soc. Biol., 1935, 119, 1299—1302).—Hydrastinine appears in the urine and in the bile of the dog after intravenous injection, the rate of elimination in the former depending on the rate in the latter.

H. G. R. Inhibitory action of eserine on cholinesterase *in vivo*. M. S. JONES and H. TOD (Bio-

esterase in viro. M. S. JONES and H. TOD (Biochem. J., 1935, 29, 2242—2245).—Subcutaneous injection of eserine (I), but not of pilocarpine and adrenaline, inhibits the action of choline-esterase (II) on acetylcholine (III). This corroborates the theory that (I) acts on the parasympathetic by inhibiting (II) and thus prolonging the action of (III) present. E. A. H. R. Cumulative poisoning by lanadigin, ouabain, and digitoxin in dogs. R. C. LI and H. B. VAN DYKE (J. Pharm. Exp. Ther., 1935, 54, 415–425).— The lethal doses of ouabain, lanadigin (I), and digitoxin (II) are as 10:2:1 in the frog and 4:1:1 in. the dog. (I) was the most effective cumulative poison; dogs tolerate repeated doses of (II) much better than cats. Repeated doses of tincture of digitalis were more lethal than those of (II). H. D.

Reduction of pitressin and pitocin with cysteine. R. R. SEALOCK and V. DU VIGNEAUD (J. Pharm. Exp. Ther., 1935, 54, 433-447).—Pitressin (I) and pitocin (II) are reduced by cysteine at $p_{\rm H}$ 8 with no change in activity; treatment of the reduced products with CH₂PhCl or MeI inhibits their activity, whilst similar treatment of (I) and (II) is without effect. It is concluded that the mols. of (I) and (II) contain a S·S group which is directly associated with their activities. H. D.

Influence of hydrogen and hydroxyl ions on the anæsthetic action of propyl bromide on sticklebacks. M. THFFENEAU and D. BROUN (Compt. rend. Soc. Biol., 1935, **119**, 1382—1384).— Penetration of PrBr into the brain is accelerated by acidosis (immersion in acid H_2O) and retarded by alkalosis. Little PrBr is fixed by the gills. H. G. R.

Microdetermination of ethyl, propyl, and isopropyl bromides in the tissues of animals anæsthetised by these substances. M. TIFFENEAU and D. BROUN (Compt. rend., 1935, 201, 353—355).— The problem of hyper- and hypo-sensitivity to anæsthetics in relation to their conen. in the tissues is examined. With EtBr, $Pr^{\alpha}Br$, and $Pr^{\beta}Br$ the quantity of Br in the tissues varies with the speed of induction of the anæsthesia; the quantity in the hemispheres is in general < in the remaining parts of the brain. H. D.

Theories of narcosis of H. H. Meyer, Overton, K. H. Meyer, Traube, and Warburg. I. TRAUBE (Biochem. Z., 1935, 279, 166–173).—A reply to K. H. Meyer (this vol., 779, 893). The theories are critically discussed. P. W. C.

Chemical relationships between compounds of physiological importance having the phenanthrene nucleus. H. P. LUNDGREN (Science, 1935, 82, 130-133).—A summary. L.S.T.

"Anti-embryonic" sensitiser and lack of vitamin-A. L. NATTAN-LARRIER, L. GRIMARD, and S. NOUGUÈS (Compt. rend. Soc. Biol., 1935, 119, 1348—1350).—The sensitiser is present in rat-serum only when normal growth is retarded by deprivation of vitamin-A. H. G. R.

Effect of tyrosine on gaseous metabolism. L. BARBATO (Arch. Farm. sperim., 1935, 59, 291— 304).—Injection of tyrosine into rats or pigeons has no significant effect on the O₂ consumption at normal or subnormal temp. F. O. H.

(A) Comparison of toxicity with concentration and time. (B) Quantitative relationship between the constitution and toxicity of some rotenone derivatives. W. A. GERSDORFF (J. Agric. Res., 1935, 50, 881-891, 892-898).-(A) Glaser's formula best fits the author's data for the survival times of goldfish (2-2.5 g.) at 27° in solutions of rotenone (I) and its derivatives, but is inconvenient in use. The min. val. of $c \times t$, where c=concn. of poison and t=survival time of the fish, is suggested as criterion of toxicity. Published data give the following toxicities determined by the min. ct relative to (I)= 1 : rotenone hydrochloride 1.8, dihydrorotenone (II) 1.4, acetylrotenone (III) 0.55, toxicarol 0.55, deguelin 0.39, *iso*rotenone 0.23, tephrosin 0.15, rotenolone (IV) 0.097.

(B) Relative toxicities to goldfish (2-2.5 g.) at 27°, as defined by min. ct, are determined as follows: (II) 1.4, (I) 1.0, acetyldihydrorotenone 0.812, (III) 0.552, dihydrorotenolone 0.149, (IV) 0.0965, acetyldihydrorotenolone 0.0819, acetylrotenolone 0.0546. Saturation of the ethylenic linking increases toxicity by 50%, but transformation into the OH-derivative decreases it by 90% and acetylation by 44%. The effect of > one such change is the product of the effect of each separately. R. S. C.

Photobiological sensitisation in the ultraviolet by compounds of the acridine and quinoline series. W. HAUSMANN and F. M. KUEN (Biochem. Z., 1935, 279, 387—392; cf. A., 1932, 1284; 1934, 94).—No relationship between constitution and photodynamic action in the ultra-violet of the compounds can be traced, since similarly constituted substances behave differently in many cases. Acridine hydrochloride, bistrypaflavine nitrate, yatren, flavophosphine, diamond-phosphine, sinflavine, 2-p-acetamidostyrylmethylquinoline methosulphate, and optoquin hydrochloride sensitise. Agar may be replaced by gelatin as medium without affecting the results.

W. McC.

Photobiological desensitisation in the ultraviolet. Photobiological action of sodium sulphite on erythrocytes. F. M. KUEN (Biochem. Z., 1935, 279, 393-402).—Erythrocytes sensitised with hæmatoporphyrin are desensitised in different degrees by serum, glucose, fructose, pinacryptol, and neosalvarsan. Na₂SO₃ sensitises in presence of O₂ (not in its absence) in the region 365—248 mµ, and since it acts at λ which its solutions do not absorb, the primary photochemical effect is then on the erythrocytes and not on the Na₂SO₃. W. McC.

Aryl esters of hydroxydiphenyls.—See this vol., 1233.

Influence of dinitrophenol on carbohydrate metabolism. M. WISHNOFSKY, A. P. KANE, E. L. SHLEVIN, and C. S. BYRON (Arch. Int. Med., 1935, 56, 374–381).—In normal cases, $C_6H_3(NO_2)_2$ ·OH causes glycæmia both during fasting and after ingestion of glucose (I). In diabetes mellitus, there is no change in the blood-sugar, but a reduction in glycosuria after administration of (I). H. G. R.

Metabolic response of white rats to continued administration of dinitrophenol. B. TERADA and M. L. TAINTER (J. Pharm. Exp. Ther., 1935, 54, 454-462).—Administration of 2:4- $C_6H_3(NO_2)_2$ ·OH (I) to young rats produced little or no stimulation of metabolism. Adult rats show no tolerance to (I), which is absorbed intestinally and excreted in the urine. Nephrectomy doubles the metabolic response. H. D.

Rigidity from iodoacetic acid in muscles of cold-blooded animals. F. LIPPAY and H. PATZL (Pflüger's Archiv, 1935, 235, 438–447).—The rigidity produced spontaneously in frogs' muscles treated with $CH_2I \cdot CO_2H$ is distinct from that produced by electric excitation under similar conditions. R. N. C.

Acute carbon tetrachloride poisoning. E. R. LEHNHERR (Arch. Int. Med., 1935, 56, 98—104).— Data are given for a severe case of poisoning with CCl_4 . At first there was a decrease in the amounts of lipins in the plasma, and low vals. were obtained for total cholesterol (I) and for the ratio of ester (I) to total (I), which are typical of jaundice due to damage to the liver. There was an increase of urea, uric acid, and creatinine in the blood, which gradually returned to normal, but the NH_2 -acid-N was not altered. During the first 3 days, bile was visibly present in the urine. J. N. A.

Effect of cysteine on the toxicity of antimony. L. LAUNOY (Bull. Soc. Chim. biol., 1935, 17, 1022— 1030; cf. A., 1934, 1256).—Cysteine has considerable antitoxic action towards Sb thiomalate (I) injected into mice infected with T. brucei. When injected simultaneously with moranyl and (I) into mice infected with T. congolense, however, the antitoxic action is greatly inhibited. A. L.

Inhibition of respiration by cyanide. W. E. VAN HEYNINGEN (Biochem. J., 1935, 29, 2036— 2039).—The respiration of liver, kidney, and spleen slices is inhibited to 75—85% by 0.001M-HCN and to 80—90% by 0.01M-HCN. Lower vals. of other authors are attributed to differences in method, in particular, failure to prevent absorption of HCN by the CO₂ absorbent. H. D.

Cure of hydrocyanic acid poisoning by sodium tetrathionate. G. AURISICCHIO and G. DE NITO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 150).—HCN poisoning in animals is cured by successive injections of $Na_2S_4O_6$ and I solutions. R. N. C.

Opposite effects of hydrogen and hydroxyl ions on pharmacodynamical actions in the autonomic system. Action on uterine tonus. M. TIFFENEAU and D. BROUN (Compt. rend. Soc. Biol., 1935, 119, 1380—1382).—The tonic effects of adrenaline on the rabbit's uterus and of histamine and postpituitary extract on the guinea-pig's uterus run parallel to [OH']. An increase in [OH'] suppresses or inverts the depressor effect of adrenaline on the guinea-pig's uterus. H. G. R.

Biochemistry of the heavy metals. T. BERSIN (Z. ges. Naturwiss., 1935, 1, 187—190).—A review and discussion of the role of heavy metals in biological processes. H. J. E.

Combined action of zinc and vitamins in animal nutrition. G. BERTRAND and R. C. BHAT-TACHERJEE (Ann. Inst. Pasteur, 1935, 55, 265—272).— Mice fed on a synthetic Zn-free diet supplemented with the vitamins do not survive, but good growth is obtained on the addition of 2 mg. of Zn per 100 g. of food. Animals on a Zn diet contained 0.2 mg. more Zn than those on a Zn-free diet. H. G. R.

Biological effect of ionised air. C. T. CHASE and C. H. WILLEY (Science, 1935, 82, 157-158).-Exposure to ionised air induces coloration and subsequent death in the larvæ of *Drosophila melanogaster*. L. S. T.

Influence of a continuous electric current on the branchial permeability of some fresh-water fish. E. GRADINESCO and E. PORA (Bull. Soc. Chim. biol., 1935, 17, 1054—1057).—The branchial permeability of fresh-water fish is affected by the passage of electricity through the external H_2O medium. In most cases diffusion takes place from the fish. A. L.

Influence exercised by radioactivity on the localisation in the lung of cobalt administered in combination with pulmonary proteins. P. MASCHERFA and G. CAVALLI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 146—148).—Injection of Rntreated Co-lung-protein complex in guinea-pigs produces a deposition of Co in the lungs > with untreated complex. No deposition of Co occurs with Rn-treated Co-serum-protein complex. R. N. C.

Possibility of conveying to an organ cobalt bound to the proteins of the same organ. P. MASCHERFA (Boll. Soc. Ital. Biol. sperim., 1935, 10, 148-152).—A discourse. R. N. C.

Origin of the inhibition of cell division by X-rays. K. ERDMANN (Pflüger's Archiv, 1935, 235, 470–485).—Inhibition of yeast-cells by X-rays in solutions of NaCl-CaCl₂ or alkali chlorides at varying $p_{\rm H}$ follows the same laws as the effect of X-rays and ionic media on the shrinkage of proteins, suggesting that the origin of the inhibition of growth by X-rays is the reduction of the swelling power necessary for growth of living matter. R. N. C.

Determination of the effect of ultra-violet light on the proteins of skin and serum by means of the defence enzyme reaction. E. ABDERHALDEN and E. TETZNER (Fermentforsch., 1935, 14, 522-538; cf. A., 1934, 1137).—Proteins from the skin of rabbits which have been exposed to irradiation with the light can be distinguished, by means of the reaction, from those of the skins of non-irradiated rabbits. The degree of specificity of the reaction is low, but, in some cases at least, injection of the substrates is unnecessary. W. McC.

Cryolysis, diffusion, and particle size. Experiments on sodium oleate, ovalbumin, and polyacrylic acids. F. F. NORD and F. E. M. LANGE (Z. Elektrochem., 1935, 41, 519).—Previous results (cf. this vol., 932) are applied to the chemistry of enzymes. T. G. P.

Components of dehydrogenase systems. VI. Enzymic oxidation of hexoses in presence of adenosinetriphosphoric acid. H. VON EULER and E. ADLER. VII. Lactic acid dehydrogenase of yeast. E. ADLER and M. MICHAELIS. VIII. Activators. H. VON EULER and E. ADLER (Z. physiol. Chem., 1935, 235, 122-153, 154-163, 164-173; cf. this vol., 782).-VI. The hexose monophosphate dehydrogenase (I) system oxidises nonphosphorylated hexoses (glucose, fructose) if adenosinetriphosphoric acid (II) is added. (II) cannot be replaced by adenylic acid, creatine, phosphagen, $Na_4P_2O_7$, or hexose diphosphate or mixtures of these. By adsorption on Al(OH)₃ and elution with dil. aq. NH₃ the (I) is separated into the true (I) of the system and an enzyme, "heterophosphatase" (III), which, in presence of (II) and the system, attacks hexoses. (III) probably acts by transferring the labile P of (II) to the hexose (producing hexose monophosphate), the reaction being activated by Mg. The presence of a redox system is not essential. Sp. alcohol-(I) cannot replace (III), but Warburg's co-enzyme can replace cozymase in the system.

VII. The lactic acid-(I) of yeast, which requires no complement for anaërobic reaction and acts aërobically when an appropriate acceptor is added, differs from the flavin enzyme systems which act aërobically and anaërobically only when completed by addition of co-enzyme and flavin enzyme.

VIII. Purified cozymase activates the enzymic oxidation of EtOH, but not that of hexose monophosphate. Hence impure cozymase contains a second activator (not identical with Warburg's coenzyme). This activator is dialysable and less stable to heat than is cozymase. Cozymase is indispensable for both oxidations and probably acts without the second activator in oxidation of EtOH. W. McC.

Dehydrogenase system of peas. A. FODOR and N. LICHTENSTEIN (Fermentforsch., 1935, 14, 413-421; cf. A., 1932, 651).-Macerates of pea-flour treated with kaolin contain a dehydrogenase system (optimum activity at p_{π} 6.5; after dialysis activity increases up to $p_{\rm H}$ 8) which is activated by boiled yeast juice and by purified co-enzyme. The system is damaged (but not destroyed) by boiling or ultra-filtration (removal of proteins) and its activity decreases continuously on keeping. The activity lost on boiling is partly restored by addition of HCO2K, boiled yeast juice, or purified co-enzyme. Addition of NH2-acids (glycine, alanine, tyrosine, tryptophan) increases the activity if the macerates have been boiled, but decreases it if they have not. Boiled yeast juice with aldehyde and phosphate (but not with NH2-acid and phosphate) decolorises methylene-blue and activates the system NH2-acid-aldehyde-phosphate, but neither purified co-enzyme with NH_2 -acid or aldehyde and phosphate nor HCO_2K with NH_2 -acid or NH_2Me causes decolorisation. Neither purified co-enzyme nor HCO2K nor both together activates the system aldehyde-NH2-acid-phosphate. Peas possibly contain also a non-enzymic dehydrogenating system (e.g., aldehyde-NH2-acid-phosphate). W. McC.

Action of poisons on the dehydrogenases and oxidases of muscle. R. LABES and K. KREBS (Fermentforsch., 1935, 14, 430–442).—The succinic dehydrogenase (I) (but not the *p*-phenylenediamine oxidase) of pig muscle is poisoned by low concns. (0.02%) of K₂TeO₃, K₂SeO₃, and Zn(OAc)₂ and by PhOH (0·1–0·2%). Na₂HASO₃ and Na₂B₄O₇ (even in high concns.) have no toxic effect on (I) or the oxidase. Zn(OAc)₂ also poisons the oxidase. Under certain conditions, however, the poisons have a stimulating effect. The toxicity of K₂TeO₃ and K_2 SeO₃ is due to their reduction to colloidal Te and Se. SH and alcoholic OH groups are not involved in the respiratory action of (1). W. McC.

Mechanism of the reaction of substrates with molecular oxygen. I, II. F. J. OGSTON and D. E. GREEN (Biochem. J., 1935, 29, 1983–2004, 2005–2012).—I. An investigation of the extent to which intermediary O_2 carriers determine the reaction of substrates with mol. O_2 . Cytochrome-c (I) acts as a carrier only for succinoxidase (II) and the lactate (III) dehydrogenase of yeast, yellow pigment (IV) for glucose- (V), hexose monophosphate- (VI), hexose diphosphate- (VII), and malate- (VIII) -dehydrogenases, and flavin for (VIII) only. Glutathione is reduced by the (V) and (VI) dehydrogenases and acts as a carrier for (VII). Its efficiency is limited by its rate of autoxidation. New methods are given for the prep. of (II) and the (III), (V), (VIII), and α -glycerophosphate dehydrogenases, and the use of a high-speed ball mill for extraction of enzymes from yeast is described. The identity of (VI) and (VII) dehydrogenases is doubtful.

II. The oxidation of substrates by respiring baker's yeast is almost completely inhibited by M/600-HCN, although in vitro the oxidation of (VI) and (VII) with (IV) as O_2 carrier is not CN'-sensitive. The low Q_0 , of bottom yeast is due to co-enzyme and intermediary carrier deficiency. The increase in respiration caused by pyocyanine suggests that in vivo the (IV) in bottom yeast is not concerned in the oxidations of (V), (VI), and (VII). The succinic-fumaric system cannot act as an intermediary link between (I) and dehydrogenases in vitro. Rat liver, heart, kidney, and brain have sufficient indophenol oxidase (IX) to account for most of their respiration. (IX) in heart muscle preps. is associated with fine particles from which it cannot be separated. There is no basis for ascribing enzymic properties to (IV). E. A. H. R.

Pure cytochrome-c. H. THEORELL (Biochem. Z., 1935, **279**, 463—464; cf. A., 1932, 1054; this vol., 1024).—Purification of material from horse- or oxheart (100 kg.) by extraction, dialysis, and pptn. is completed with the help of the cataphoresis apparatus (isoelectric point $p_{\rm H}$ 9·7) or by pptn. with picrolonic acid (yield 1 g.). The Fe content is the same as that of hæmo- and myo-globin and the N content is 14%. Reduced cytochrome-c is not converted into the oxidised form by H₂O₂ but is destroyed. The oxidised form, on reduction with H₂+Pt, absorbs 0·5H₂ per Fe. In the chain of enzymes involved in biological oxidation cytochrome-c is intermediate between the respiratory enzyme and the systems which supply H. W. MCC.

Quantitative irradiation experiments with the yellow enzyme, flavinphosphoric acid, and lactoflavin. H. THEORELL (Biochem. Z., 1935, 279, 186—200).—Flavinphosphoric acid (I) is inactivated by light quantitatively in the same way as lactoflavin (II), esterification with H_3PO_4 having no effect on the reaction. Inactivation of (II) or (I) proceeds more quickly in air than in pure O_2 and still more quickly in total absence of O_2 . It is quicker in alkaline and slower in acid than in neutral solution. On irradiation in an atm. of A there is first formed deuteroleucoflavin (-phosphoric acid) (III), which on prolonged irradiation is slowly broken down to 6:7-dimethylalloxazine. If O_2 is admitted during this period of irradiation, that portion of (III) not degraded is immediately converted into deuteroflavinphosphoric acid. On irradiation with light of λ 436 m μ in presence of O_2 , the catalytic activity decreases slowly in the same way as does the light absorption and at the same velocity as the decoloration of (II). P. W. C.

Measurement of phenolase activity. R. SAM-ISCH (J. Biol. Chem., 1935, 110, 643—654).—Increase of the partial pressure of O_2 increases the rate of O_2 absorption by phenolase-substrate mixtures. Peach and apricot extracts show an optimum $p_{\rm R}$ of 4.9 with pyrocatechol as substrate, whilst apple extract has no optimum between $p_{\rm R}$ 3.7 and 6.4. An optimum concn. of substrate for different enzymes is found, at which the O_2 consumption ∞ enzyme concn. Alkali halides have an inhibiting effect inversely ∞ the at. no. of the halogen ion. The crit. temp., at which the enzyme is half destroyed in 1 hr., is for apricotoxidase 38°. A proposed unit of phenolase activity is defined. F. A. A.

Constitution of the prosthetic group of catalase. K. G. STERN (Nature, 1935, 136, 302).— The pure hæmin obtained from the catalase of horse liver yields on treatment with HI and AcOH a porphyrin with a spectrum identical with that of mesoporphyrin IX; the Me₂ esters are also identical (m.p., mixed m.p., and spectrum). The hæmatin group of catalase is thus a derivative of ætioporphyrin III and possesses a porphin skeleton with the same arrangement of the side-chains as occurs in protohæmatin IX. L. S. T.

Reversible hydrolysis of liver-catalase. K. AGNER (Z. physiol. Chem., 1935, 235, II—III).— Catalase from horse liver on dialysis against 0.1N-HCl breaks down into a coloured constituent of low mol. wt. (possibly hæmin) which dialyses and a colourless non-dialysing constituent (protein) of high mol. wt., both constituents being without action on H₂O₂. Activity is restored by re-combining the constituents. W. McC.

Concentration and properties of two amylases of barley-malt. M. L. CALDWELL and S. E. DOEB-BELING (J. Biol. Chem., 1935, 110, 739-747).— Additional evidence is given for the presence of two distinct amylases in different fractions obtained from the same extract of barley-malt. Both amylases rapidly lose their activities when heated in H₂O. They are free from carbohydrate, but give a positive protein reaction. They catalyse the hydrolysis of amyloses in different manners. At 40° the saccharogenic action of both is favoured by a $p_{\rm H}$ of 4·3-4·6, and the amyloclastic action of the amylase with a preponderance of this activity is also favoured at $p_{\rm H}$ 4·3-4·7. J. N. A.

Pancreas and diastase. H. J. DOHMEN (Deut. Z. Chirurg., 1935, 244, 620-630).—The blood of the pancreatic vein in dogs has a diastase (I) content >that of the ear vein. Since ligature of the pancreatic duct causes an increase, and removal of the pancreas a decrease, in blood-(I), (I) enters the blood-stream directly from the pancreatic glands. There is no correlation between (I) concn. and sugar content of the blood. NUTR. ABS. (m)

Study of enzyme action by thermal analysis of reaction velocity. I. Action of invertase. S. HORIBA and T. KOSAKI (Proc. Imp. Acad. Tokyo, 1935, 11, 232—234).—From observations of the rate of cooling it has been found that the early and later stages of the action of invertase can each be expressed by an empirical formula. On the assumption that the reaction is heterogeneous and that it occurs by way of the contact-catalytic action of the colloidal system of invertase, equations are derived which correspond with the two empirical ones. P. G. C.

Cozymase. VIII. Action of adenylic acid deaminase on cozymase. K. MYRBĀCK and B. ÖRTENBLAD. IX. Oxidation and reduction. K. MYRBĀCK (Z. physiol. Chem., 1935, 234, 254—258, 259—266; cf. this vol., 782).—VIII. Neither active nor alkali-inactivated cozymase yields' NH_3 with adenylic acid deaminase, indicating that adenylic acid is not liberated by the inactivation.

IX. On reduction with nascent H, cozymase is inactivated and the alkali-labile reducing group becomes stable. The OI' consumption is not much changed. After reduction no acid group is formed by treatment with alkali; the acid group probably arises from the labile reducing group. J. H. B.

Activators of glycolysis. Cozymase and adenosinetriphosphoric acid. H. VON EULER and G. GUNTHER (Z. physiol. Chem., 1935, 235, 104-114).—The production, from added glycogen, of lactic acid (I) in muscle extracts (rat) inactivated by autolysis is greatly increased by addition of hexose diphosphate (II) with cozymase as activator. When adenyl pyrophosphate is the activator addition of (II) is unnecessary. In extracts freed by dialysis from substances which suppress induction the addition of (II) or of another substance [e.g., AcCO₂H, creatinephosphoric acid, but not adenosinetriphosphoric acid (III), ascorbic acid, glutathione, or flavin enzyme] having similar action is necessary if any (I) is to be produced from the glycogen. Cozymase, alone or with (III), has no effect. The action of cozymase inactivated by heat does not differ from that of fresh W. McC. cozymase.

Linking of chemical changes in muscle extract. D. M. NEEDHAM and W. E. VAN HEYNINGEN (Biochem. J., 1935, 29, 2040—2050).—The nature of the coenzyme function of the adenylic compounds is investigated. Phosphoglyceric acid (I) is broken down to inorg. P by dialysed muscle extracts in the presence of adenylic acid (II) or adenyl pyrophosphate (III); creatine (IV) does not assist the breakdown in the absence of (II) and (III); (IV) is converted into phosphocreatine (V) when present with (I) and (II) or (III). The synthesis of (V) involves the reactions: $(I)+(II) \rightarrow (III)+AcCO_2H$, and $(III)+(IV) \rightarrow (V)+$ (II). H. D.

Rôle of glutathione in muscle glycolysis. R. GADDIE and C. P. STEWART (Biochem. J., 1935, 29, 2101-2106).—In presence of Mg^{**}, adenyl pyrophosphate (I), and reduced glutathione (II), more lactic acid (III) is produced from glycogen (IV), glucose, and hexosediphosphoric acid by dialysed rabbit muscle extracts, than if (II) is absent. AcCHO tends to accumulate in absence of (II), but this can be prevented by addition of (II). Mg^{••} and (II) in absence of (I) cause production of (III) from (IV), but omission of (II) does not increase the amount of AcCHO. J. N. A.

Enzyme systems of sarcoma and muscle dealing with hexose phosphates. F. H. SCHARLES, M. D. BAKER, and W. T. SALTER (Biochem. J., 1935, 29, 1927-1936).-Tumour extract differs from skeletal muscle extract in being unaffected by F' in its ability to form lactic acid (I) or to liberate PO,"" from hexose phosphates, in being much less susceptible to CH₂I·CO₂', in producing (I) from hexose monophosphate (II) after co-enzyme depletion, and in not esterifying PO4" with (II). This indicates that the path of carbohydrate breakdown in tumour and muscle extracts is different. Possible explanations of the inability of the former to produce (I) from glycogen are the formation of a different hexose phosphate and a lack of phosphatase. E.A.H.R.

Antiglyoxalase. R. STÖHR (Biochem. Z., 1935, 279, 184—195).—A reply to the criticisms of Girsavicius *et al.* (this vol., 122). P. W. C.

Acetylcholine-destroying action of blood. R. AMMON and G. Voss (Pflüger's Archiv, 1935, 235, 393-400).—The choline-esterase (I) content of serum is < that of whole blood or hæmolysate in human, ox, or rabbit's blood, but greater in dog's or horse's. (I) in snail's blood is excessively high. Serum-(I) is not altered in labour, but is low in umbilical cord blood. (I) is the same in whole blood and hæmolysate in all types of blood examined. (I) in human serum is not appreciably altered in the course of many weeks, but oscillates considerably in rabbit's serum. The acetylcholine-destroying power of blood *in vivo* is inhibited by eserine. R. N. C.

Action of pepsin-hydrochloric acid on caseinogen and its degradation products produced by the action of hot anhydrous glycerol. A. FODOR and S. KUK (Fermentforsch., 1935, 14, 397-406; cf. A., 1933, 621).—The octapeptide D_1 is a double tetrapeptide. When first produced it exists as an association D_A , mol. wt. 3654, $[\alpha]_D^{\infty} -79.5^{\circ}$, of 4 mols. (less $2H_2O$) of D_1 and is accompanied by a substance D_{An} , $[\alpha]_D^{\infty} -86.8^{\circ}$, which is a mixture of D_A (50%) with 2 double mols. of D_1 . Pepsin-HCl hydrolyses 4 CO·NH equivs. in D_A , 2.7 in D_{An} , and 2.45 in D_1 , and attacks caseinogen, eliminating and dissolving complexes identical with D_1 , D_A , and D_{An} .

W. McC.

Intracellular proteinases. XIV. Activation and inhibition of papain by potassium ferricyanide. E. MASCHMANN and E. HELMERT. XV. Inactivation of proteinases by iodoacetic acid. E. MASCHMANN (Biochem. Z., 1935, 279, 213-224, 225-228).—XIV. The effect of $K_3Fe(CN)_6$ (I) on the action of papain (cf. this vol., 897) is further examined. In acetate buffer the enzymic action with 4 samples of gelatin was increased by (I), but with one sample was decreased. In citrate buffer the results were inconsistent. XV. The inhibition of proteinases by $CH_2I \cdot CO_2H$ (II) is due to the reaction between an SH group of the enzyme and (II). P. W. C.

Fission of clupean by various trypsin preparations. H. HOLTER, M. KUNITZ, and J. H. NORTH-ROP (Z. physiol. Chem., 1935, 235, 19—23; cf. A., 1933, 94; Waldschmidt-Leitz *et al.*, this vol., 123).— Fission of clupean sulphate proceeded similarly with proteinase purified by adsorption and with various preps. of cryst. trypsin. H. W.

Action of erepsin and trypsin on polypeptides containing ψ -leucine.—See this vol., 1228.

Action of pepsin-hydrochloric acid and trypsinkinase on *l*-, *d*-, and *dl*-leucylalbumin. Defence enzymes produced by injection of these substrates. E. ABDERHALDEN and E. KOELITZ (Fermentforsch., 1935, 14, 483–492).—The hydrolysis of *d*- (1), *l*-, and *dl*-leucylalbumin [from plasmaalbumin (horse) by treatment first with the corresponding α -bromoisohexoyl chlorides and then with aq. NH₃] by gastric juice (dog) and trypsin-kinase proceeds at a rate < that of the hydrolysis of the untreated albumin, and the rates for the different treated albumins also differ. Except with (I), which is most slowly attacked, the degree of hydrolysis eventually equals that of the untreated albumin. Sp. defence enzymes are produced when the leucylalbumins are injected into rabbits. W. McC.

Purification of the active phosphatase in dog fæces. A. R. ARMSTRONG (Biochem. J., 1935, 29, 2020—2022).—Dog fæces are treated with H_2O , AcOH, and conc. aq. NH_3 and filtered at 0°. Protein material is pptd. with $(NH_4)_2SO_4$ and $COMe_2$ and on dissolution in aq. NH_3 is decolorised by charcoal and the active material is pptd. with $COMe_2$. Activities varied from 130 to 185 (×10³) units per g. of purified material. H. D.

Urinary phosphatase. I. W. KUTSCHER (Z. physiol. Chem., 1935, 235, 62-73).—The urine of adults invariably contains a phosphatase (I) which hydrolyses phenyl- and α - (II) and β - (III) -glycero-phosphoric acids. Its max. activity occurs at $p_{\rm H}$ 4-5. At $p_{\rm H}$ 7.84 it is inactivated to the extent of 80% within 8 days, whilst at $p_{\rm H}$ 8.32 inactivation takes place within 24 hr. It hydrolyses (III) more vigorously than (II). It is not activated by 0.01*M*-or 0.005*M*-Mg^{**}. In the urine there is also present a (I) with alkaline optimum and hydrolytic power comparable with those of the plasma-(I). Urinary (I) can be dialysed during 5-6 days without loss of activity. It is relatively stable and can be conc. in vac. at moderate temp.; at higher temp. it rapidly becomes inactive. H. W.

Effect of gangliary sympathectomy on the phosphatase content of bone. U. SACCHI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 100—103).—The phosphatasic power of the bone increases in the first few days after gangliary sympathectomy, afterwards returning to normal. R. N. C.

Plasma-phosphatase in normal and rachitic children. O. ANDERSEN (Hospitalstidende, 1935, 78, 5-18).—In children 0-3 years old, without sign

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of bone abnormality, plasma-phosphatase (I) was 0.14-0.34 unit per ml. (average 0.25). In normal children of 3-13 years, the val. was 0.06-0.26 (average 0.15). In rachitic children of 3-27 months, the val. was 0.42-1.41 (average 0.86). Following treatment with ultra-violet light and cod-liver oil, (I) decreased, in all cases, to < 0.30. Serum-Ca and -P always became normal before (I). (I) vals. > 0.40 are abnormal and those between 0.30 and 0.40 questionable. NUTR. ABS. (m)

Mechanism of the activation of intestinal phosphatase by magnesium. C. G. HOLMBERG (Biochem. Z., 1935, 279, 145—148).—A simple method for the prep. of phosphatase solutions practically free from mineral salts and proteins is described. The initial velocity of hydrolysis of glycerophosphoric acid by this prep. is not affected by Mg. An enzyme-Mg complex is formed which is not sensitive to the inhibitory action of small amounts of $PO_4^{\prime\prime\prime}$.

P. W. C.

Bone-phosphatase and solar irradiation. U. SACCHI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 94— 97).—The phosphatase content of rat bones is increased by exposure to solar radiation. R. N. C.

Phosphatases. V. Restriction of phosphatase by sulphur compounds. H. ALBERS (Ber., 1935, 68, [B], 1443—1447).—The fission of β -glycerophosphate by highly purified kidney-phosphatase (I) is notably restricted by very small amounts of glutathione and cysteine and to a smaller extent by cystine. KCN slowly reacts with (I) and causes marked restriction after prolonged action, whereas CH₂Br·CO₂H has no influence. H. W.

Specificity of phosphatases. Hydrolysis of phospho-*l*-lactic acid by phosphatase. O. T. ROTINI and C. NEUBERG (Biochem. Z., 1935, 279, 453-458; cf. Wagner-Jauregg, this vol., 731).— Extract of rabbit muscle, top and bottom yeast, and the phosphatase of Aspergillus oryzæ quantitatively convert phospho-*l*-lactic acid into *l*-lactic acid and H_3PO_4 only. W. McC.

Phosphatases in fungi. M. FRANCIOLI (Fermentforsch., 1935, 14, 493–501; cf. A., 1934, 1124).— Various fungi (e.g., Amanita, Boletus) contain lipase and one or more phosphatases. Lycoperdon giganteum at 37° (optimum $p_{\rm H}$ 5.5) liberates 81% of the H₃PO₄ of Na glycerophosphate in 140 hr. W. McC.

Phosphatases. IV. Phosphatases of yeast. H. ALBERS and E. ALBERS (Z. physiol. Chem., 1935, 235, 47-61).—Top yeast contains a single phosphatase "top yeast-phosphatase" (I) which causes vigorous fission of α - (II) and β -glycerophosphate (III). In the cell it is active between $p_{\rm H}$ 3 and 4.5 and after removal from the cell it hydrolyses (II) and (III) most readily at $p_{\rm H}$ 3.8-4.2 and hexose phosphate most readily at $p_{\rm H}$ 3.5. The ratio of fission for these substrates is $4:10:5\cdot5$. (I) is also largely present in bottom yeast, which also contains two phosphatases active near the neutral point, one of which hydrolyses (III), whereas the other is sp. towards (II). The behaviour of liberated (II), which appears enzymically homogeneous, is described. During dialysis it is suddenly and irreversibly inactivated, probably by a dissociation into carrier and activating mols. Mg^{\cdot} causes restriction of (I) independently of $p_{\rm H}$. After liberation (I) is accompanied by a natural inhibitor which can be dialysed and is decomposed when the phosphate solutions are kept. Less pure cozymase solutions also contain an inhibitor. Adsorbates of (I) on Al(OH)₃-A or -C_{γ} are completely active on the ppts.; elution by the reaction mixture does not occur. For preparative chemical purposes the adsorbates are particularly useful. The rôle of phosphatases during fermentation and the mode of hydrolysis of phosphoric esters by the yeast enzyme are discussed. H. W.

System sugar-amino-acid-yeast. F. LIEBEN and B. BAUMINGER (Biochem. Z., 1935, **279**, 321— 325; cf. Neuberg *et al.*, A., 1926, 1061).—NH₂acids (glycine, *l*-histidine, *dl*-alanine) added to glucose (1) in presence of yeast accelerate the degradation of (I) if conditions are such that CO_2 production is increased or if the mixture is agitated in O_2 , the total acidity of the mixture being increased because of production of increased amounts of AcCO₂H and lactic acid. The NH₂-acids undergo no change and no NH₃ is produced. The interaction of (I) and NH₂acid involves no far-reaching change and the course of fermentation is only temporarily affected.

W. McC.

Acid production in autolysis of yeast. II. Hydrolysis of the nucleic acid. H. HAEHN and H. LEOPOLD (Fermentforsch., 1935, 14, 539–548; cf. A., 1934, 451).—The H_3PO_4 liberated during the autolysis is derived from the nucleic acid, which is attacked successively (optimum effect at $p_{\rm H}$ 8) by polynucleotidase, nucleotidase (phosphatase), purine deaminase, and nucleosidase. Sugar (ribose) and NH₃, in amounts (approx. equiv.) which increase with the extent of autolysis, are also liberated. The course of the degradation and the extent to which it proceeds are affected by the activators (e.g., H_3PO_4) and inhibitors (guanine, hypoxanthine) produced.

W. McC. Nature of the polysaccharides of yeast. M. G. SEVAG, C. CATTANEO, and L. MAIWEG (Annalen, 1935, 519, 111-124).-A thick suspension of Saccharomyces cerevisiæ is triturated with COMe₂ and the residue is washed with Et₂O, dried, and ground. It is then subjected to prolonged agitation with a mixture of PhMe, CHCl₃, and isoamyl alcohol (1) in presence of glass beads. The sediment is dried at 70°, triturated with H₂O, and treated repeatedly with liquid air. The residue is agitated with H_2O , CHCl₃, and (I). The aq. solution is conc. at 37° and treated with MeOH, thereby affording the polysaccharide as a colourless powder, freely sol. in H₂O to a somewhat opalescent, viscous solution, sol. in 5N-HCl, N-NaOH, or 15% NaHCO₃ to solution, solving from which it is immediately pptd. by EtOH. It is partly pptd. by Fehling's solution. It has $[\alpha]_{H}^{\mu}$ +148.0° in 5N-HCl and contains about 9% Ac. It is hydrolysed by boiling 3N-HCl to glucose. The extraction of acids lines and real-moderides from extraction of acids, lipins, and polysaccharides from technical yeast is described. It appears probable that the "yeast-gum," "yeast-cellulose," and "yeast-glycogen" of Salkowski are not present as such in

the yeast, but are secondary products formed by the action of the alkali. Yeast-polysaccharide can be completely extracted by H_2O if the process is sufficiently prolonged; if extraction is incomplete it passes into an insol. form when subsequently treated with acid and alkali. Partial deacetylation probably occurs during treatment with H_2O . H. W.

Synthesis of reserve carbohydrate by yeast. II. Effect of fluoride. R. A. MCANALLY and I. S. MACLEAN (Biochem. J., 1935, 29, 2236— 2241; see this vol., 1164).—Addition of NaF to yeast incubated in maltose (I) or glucose (II) solutions always strongly inhibited glycogen (III) storage. In (II)–PO₄^{'''} media (III) storage is increased by low, and decreased by higher (> 0.01%), [NaF], probably owing to the inhibitory effect of NaF on both synthesis and breakdown of (III). The rise in (III) storage was decreased when [PO₄^{'''}] was doubled. In (I)– PO₄^{'''} media, (III) storage is high; addition of 0.01% NaF may decrease it, but this effect was decreased with increased [PO₄^{'''}]. PO₄^{'''} increases the amount of (II), but not of (I), fermented. Fermentation of (I) and (II) is inhibited by NaF, but this effect is largely counteracted by PO₄^{'''}. The wet wt. of yeast appears to be connected with its total carbohydrate content. E. A. H. R.

Yeast gum. II. Gum content and its significance in yeast. F. STOCKHAUSEN and K. SILBER-EISEN (Woch. Brau., 1935, 52, 257-259; cf. B., 1935, 649).—The gum (I) content of various yeasts varies according to the condition of growth, and no definite relationship was found between (I) content and the type of the yeast. (I) is not to be regarded as a reserve carbohydrate similar to glycogen.

W. O. K.

Ecology of a salt-marsh. E. A. T. NICOL (J. Marine Biol. Assoc., 1935, 20, 203–261).—The fauna of the marsh are described. O_2 content of the H₂O varies between 40 and 200% saturation and $p_{\rm fl}$ between 6.8 and 9.6. The alkali reserve is high, varying between 0.0098 and 0.003N. H. G. R.

Organic metabolism of sea-water with special reference to the ultimate food cycle in the sea. A. KEYS, E. H. CHRISTENSEN, and A. KROGH (J. Marine Biol. Assoc., 1935, 20, 181–196).— O_2 consumption of sterile sea- H_2O remains practically const. when stored in the dark; for non-sterile H_2O it is approx. ∞ the bacterial multiplication, is max. immediately after collection, and gradually diminishes when 10-15% of the total dissolved org. matter is destroyed. These effects are decreased by filtration. H. G. R.

Plankton production and its control. H. W. HARVEY, L. H. N. COOPER, M. V. LEBOUR, and F. S. RUSSELL (J. Marine Biol. Assoc., 1935, 20, 407— 441).—A quant. survey of zooplankton has been made and a close relation between the no. of diatoms and their pigment contents found. The relation between the plant and animal population is discussed. Much of the org. P in diatoms passes undigested through the animals. H. G. R.

Manganese in marine plankton. L. H. N. COOPER (J. Marine Biol. Assoc., 1935, 20, 201-202).-- The val. $(< 2 \times 10^{-6}$ g. per litre) was < could be detected with certainty. H. G. R.

Rate of liberation of phosphate in sea-water by the breakdown of plankton organisms. L. H. N. COOPER (J. Marine Biol. Assoc., 1935, 20, 197—200).—Breakdown of zooplankton in sea- H_2O was very rapid, more $PO_4^{\prime\prime\prime}$ being produced (from org. P in the H_2O) than was added as plankton. Breakdown of phytoplankton showed a time lag and only a part of the added P was set free. H. G. R.

Czapek's synthetic medium. B. S. NIGAM (Current Sci., 1935, 4, 29-30).—A discussion of the reactions between the inorg. salts in the Dox modification of Czapek's medium for culturing fungi.____

F. N. W.

Action of arsenic compounds on the spores of black rust disease in wheat. J. BODNAR, A. TERÉNYI, and J. PASKUJ (Biochem. Z., 1935, 279, 448—452; cf. A., 1927, 600).—The spores adsorb As from H_3AsO_4 and salvarsan (I) solutions (but not from solutions of other As compounds) and are thereby prevented from germinating, but are not killed. Part of the As of the H_3AsO_4 combines with proteins in the envelopes of the spores and cannot be washed out with H_2O . None of the As adsorbed from (I) can be so removed. Conc. solutions of K_3AsO_3 (but not of K_2HAsO_4) left in contact with the spores pass into their interior and kill them. W. McC.

Action of anemonin on micro-organisms. F. Boas and R. STEUDE (Biochem. Z., 1935, 279, 417– 423).—Anemonin (I) in concess of 1:66,000 or less inhibits the growth of moulds (e.g., Aspergillus niger, Mucor stolonifer, Saccharomyces cerevisiæ, Oidium lactis) in synthetic (poor in bios) and natural (rich in bios) media. In Ranunculus (I) acts antagonistically to the auxins also present. W. McC.

Bacteria on fresh fruit. M. M. JOHNSTON and M. J. KAAKE (Amer. J. Publ. Health, 1935, 25, 945— 947).—No generally accepted pathogens of the colontyphoid-dysentery group held responsible for severe summer diarrhœa of children were found on fruit purchased in the open market. C. J.

New sulphur-bacterium from the thermal springs of Santa Rosalia, Mexico. O. BAUDISCH (Svensk Kem. Tidskr., 1935, 47, 191–204).—An unpigmented bacterium belonging to the group Sulphomonas thio-oxidans can produce N-2N-H₂SO₄ from S and can multiply in N-H₂SO₂. As (and to a small extent Sb), but not Fe and Cu, are essential for growth. The first stage in the oxidation of S appears to be the formation of H₂S or a SH-compound. A method of detecting such compounds is described depending on the reduction of Na₂[Fe(CN)₅(H₂O)] to Na₃[Fe(CN)₅(H₂O)], which then no longer gives a red coloration with reduced phenolphthalein. Cultures containing thymine glycol (I) develop a red colour in presence of mineral acid if the O₂ concn. is low and the solution kept in the dark. It is suggested that (I) first loses a mol. of H₂O to form CO $(NH \cdot CH(OH))$ C·CH₂(II). Intramol. addition of 2 mols. of (II) gives (CO $(NH \cdot CH(OH))$ C·CH:)₂,

which is oxidised by O_2 to form the red dye $(CO < N = C(OH) > C:CH)_2$. E. A. H. R.

Neutrality of flocculating staphylococcus toxinantitoxin mixture. G. RAMON, P. NÉLIS, and R. RICHOU (Compt. rend. Soc. Biol., 1935, 119, 1306— 1308).—The point of hæmolytic neutrality does not correspond with that of flocculation neutrality.

H. G. R. A "growth substance." R. J. WILLIAMS and B. E. CHRISTENSEN (Science, 1935, 82, 178).-The organism isolated from a deep skin lesion grows very rapidly in a suitable medium. Apart from the ordinary nutrients used for yeast culture, it requires various NH₂-acids and is stimulated by pantothenic acid and cryst. vitamin-B. For rapid growth a H₂Osol. substance, abundant in liver, liver extract, kale, lucerne, and, to a smaller extent, in milk, is required. The "growth substance" concerned is probably of importance in the nutrition of animals as well as of the organism described. This nutrilite tends to be associated with casein and ovalbumin; it is only partly destroyed by long autoclaving at 20 lb. pressure in $3-4N-H_2SO_4$ or in $2N-Ba(OH)_2$. L. S. T.

Identification of asparagine as the substance stimulating the production of butyl alcohol by certain bacteria. E. L. TATUM, W. H. PETERSEN, and E. B. FRED (J. Bact., 1935, 29, 563-572). *l*-Asparagine is the active material in potato extract which stimulates the bacterial conversion of starch into BuOH. *l*-Aspartic (I) and *d*-glutamic acids when supplemented with mol. equivs. of $(NH_4)_2SO_4$ produce a similar effect. NH₂-acids and $(NH_4)_2SO_4$ alone were ineffective. NH₄ malate and to a smaller extent NH₄ succinate may be substituted for (I), but NH₄ tartrate has no effect. The transformation of starch into BuOH by certain butyric bacteria necessitates the presence of a 4- or 5-C dicarboxylic NH₂acid or a substance which can be converted into such an acid. A. G. P.

Culture of anaërobic bacteria in non-regenerated media with the addition of extracts of embryonic cells. M. WEINBERG and A. GUELIN (Compt. rend. Soc. Biol., 1935, 119, 1364-1365).— Extracts of embryonic cells stimulate the growth of anaërobic bacteria under anaërobic conditions and, owing to their powerful reducing properties, allow growth in presence of air. H. G. R.

Bacterial growth with automatic $p_{\rm H}$ control (A) Apparatus. (B) Acid production by Lactobacillus acidophilus. L. G. LONGSWORTH and D. A. MACINNES (J. Bact., 1935, 29, 595-607).--(A) The $p_{\rm H}$ of the media is determined by a glass electrode, and additions of alkali are controlled by a photo-electric relay actuated by the beam of light reflected from the mirror of the electrometer.

(B) Acid production by *L. acidophilus* is increased by maintaining a low p_{π} in the media. CO₂ is essential for the growth of the organism. A. G. P.

Relationship between molecular structure, $p_{\rm H}$, and the ability of bacteria to grow in solutions of salts of organic acids. W. F. BRUCE (J. Amer. Chem. Soc., 1935, 57, 1495–1503).—The approx. relative rates of growth of 4 bacteria in solutions of the Na salts of 70 org. acids with $p_{\rm H}$ 4—9 are reported. The solutions become more alkaline when growth occurs. Growth is better on cis- than on transisomerides, on *n*-fatty acids with an even than those with an odd no. of C, on fatty acids of low than of high mol. wt., on OH- and NH2-acids with an odd than those with an even no. of C, and on acyclic than on cyclic acids. Substitution by Ph decreases greatly the rate of growth, but by Me may either increase or decrease it. Certain pairs of saturated and unsaturated acids of otherwise similar structure (e.g., succinic and fumaric acids) show great similarity, suggesting metabolic conversion of one into the other, e.g., by dehydrogenation. R. S. C.

Anaërobic production of pyruvic acid from alanine. E. AUBEL and F. EGAMI (Compt. rend. Soc. Biol., 1935, 119, 1243).—AcCO₂H is produced anaërobically from alanine using a medium containing KNO_3 inoculated with soil bacteria. H. G. R.

Mechanism of the fermentation of glucose by B. coli. J. TIKKA (Biochem. Z., 1935, 279, 264-288).-The following scheme is suggested. Glucose is first converted into hexose diphosphate, which breaks down into 2 mols. of dihydroxyacetonephosphoric acid (I) and on dismutation gives 1 mol. each of α -glycerophosphoric and phosphoglyceric acids. The former is converted into EtOH+HCO,H $(\longrightarrow H_2 + CO_2)$, whilst the latter undergoes dephosphorylation to AcCO₂H, which is in part reduced to lactic acid and in part split into 1 mol. each of AcOH and $HCO_2H (\rightarrow H_2 + CO_2)$. The formation of AcCHO from hexose diphosphate by B. coli is detected and indicates the intermediate formation of (I). With B. coli the decarboxylation of $AcCO_2H$ (which occurs in yeast fermentation) does not occur. Instead, AcCO₂H is partly reduced to lactic acid and partly degraded to AcOH+HCO₂H, the predominance of one or other reaction being largely determined by the P. W. C. $p_{\rm H}$.

Mechanism of the fermentation of dihydroxyacetone. A. I. VIRTANEN (Biochem. Z., 1935, 279, 262—263).—Attention is directed to the difference in mechanism according to the organism, $CO(CH_2 \cdot OH)_2$ being fermented by yeast by way of hexose diphosphate, but by *B. coli* directly. P. W. C.

Preparation of crystalline dihydroxyacetone by the biochemical method. C. NEUBERG and E. HOFMANN (Biochem. Z., 1935, 279, 318—320).— The details of the prep. using yeast- H_2O -glycerol and a culture of *Acetobacter suboxydans* are described, the yield of pure cryst. product representing 77% of that theoretically possible. P. W. C.

Dismutation of *p*-tolylglyoxal. C. NEUBERG and C. OSTENDORF (Biochem. Z., 1935, 279, 459– 462).—B. coli, B. ascendens, B. lactis aërogenes, Termobacterium Lindner, yeast, and pease-meal convert *p*-tolylglyoxal into *l-p*-methylmandelic acid. W. McC.

Phosphatides of acid-fast bacteria. E. HECAT (Biochem. Z., 1935, 279, 157-165).—A method for the separation of the phosphatides of various acidfast bacteria is described. Hydrolysis of the product from human and bovine types of the tubercle bacillus gave an org. N base, very probably choline. Lecithin is therefore regarded as present. P. W. C.

Fixation of methylene-blue in vivo by leprosy bacilli. R. O. PRUDHOMME (Compt. rend. Soc. Biol., 1935, **119**, 1326—1328).—There is no change in the oxidation-reduction potential of the tissue in leprosy. Methylene-blue is fixed on the bacilli by some substance sol. in cold EtOH. H. G. R.

Eosin-methylene-blue agar for rapid direct count of *E. coli.* H. W. GEHM and H. HEUKELE-KIAN (Amer. J. Publ. Health, 1935, 25, 920—923).— Satisfactory counts are obtained, comparable with those from brilliant-green bile broth, by smears of heavily polluted H_2O on eosin-methylene-blue agar prepared by the standard method, but containing 2.0 instead of 1.5% of agar in order to give a firmer surface. C. J.

Inactivation of bacteriophage by oxidation and reactivation by ascorbic acid. I. LOMINSKI (Compt. rend. Soc. Biol., 1935, **119**, 1345—1348).— Bacteriophages can be inactivated by I, H_2O_2 , and O_2 and, in some cases, can be reactivated by ascorbic acid. H. G. R.

Trypanocidal action of certain styrylselenazole compounds. C. H. BROWNING, R. GULBRAN-SEN, and W. MCCARTNEY (J. Pharm. Exp. Ther., 1935, 54, 367—370).—2-(p-Acetamidostyryl)- (I) and 2-(p-dimethylaminostyryl)-selenazole (II) are tested for their trypanocidal action on *T. brucei* in mice. (I) has a marked but not permanent action; (II) has none, and sulphonation scarcely affects their activity. H. D.

Antiseptic action of carbazole-3-diazonium chloride and certain other diazonium compounds. Preparation of carbazole-3-diazonium chloride. C. H. BROWNING, R. GULBRANSEN, and S. H. TUCKER (J. Pharm. Exp. Ther., 1935, 54, 353-357).—Of a no. of diazonium salts the antiseptic action of carbazole-3-diazonium chloride to S. aureus and B. coli was by far the greatest, and was associated with the N₂ group, whilst with C₆H₆ and C₁₀H₈ derivatives the activity was not changed by decomp. H. D.

Rate of disappearance of certain intestinal bacteria in water. M. AITOFF and H. DOBKEVITCH (Compt. rend. Soc. Biol., 1935, **119**, 1272—1274).— Filtered tap-H₂O is more bactericidal than either boiled or distilled H₂O, probably due to the presence of Pb and Ca salts, $p_{\rm H}$ having little effect. The bacteria live longer in filtered than in boiled rain-H₂O on account of the extra dissolved O₂. H. G. R.

Resistance of Stéfansky's bacillus to ultraviolet light. R. O. PRUDHOMME (Compt. rend. Soc. Biol., 1935, 119, 1328—1330).—Irradiation for 1—2 min. with Hg-vapour lamps at 20 cm. inhibits the pathogenic action. H. G. R.

Incubator for biological laboratories. E. KRAUSS (Woch. Brau., 1935, 52, 261-262).—A large electrically-heated incubator suitable for industrial purposes is described. W. O. K. Hormonal regulation of chlorine in children. G. TÖRÖK and L. NEUFELD (Monatsschr. Kinderheilk., 1934, 61, 73—87).—Parathormone and extract of spleen increased retention of NaCl. Extracts of thymus, tonsils, liver, adrenal cortex, pincal gland, and insulin had no effect, whilst extracts of pituitary, ovary, and follicular hormone had variable effects. NUTR. ABS. (m)

Site of action of acetylcholine and its significance. M. CATTELL and H. G. WOLFF (Science, 1935, 82, 106—107).—The action of acetylcholine on the iris of the cat is peripheral to the postganglionic fibres, and presumably a direct one on the radial muscles. L. S. T.

Adrenal denervation and adrenaline hyperglycæmia. R. BERNARDINI (Riv. Patol. sper., 1935, 14, 15—23).—In rabbits the initial blood-sugar val. was 0.101—0.116% and the average vals. 5, 15, 30, and 60 min. after adrenaline (I) injection were 0.190, 0.175, 0.161, and 0.143%. After denervation of the adrenals the corresponding vals. were 0.140, 0.145, 0.129, and 0.113, and the hyperglycæmia showed a retardation, the max. occurring after 15 instead of 5 min. Hence the adrenals normally intensify the direct hyperglycæmic action of injected (I) and denervation interferes with the intensification. NUTR. ABS. (m)

Interference of ascorbic acid in the determination of adrenaline in the adrenal gland. B. C. GUHA (Sci. and Cult., 1935, 1, 111).—Since the acid (I) occurs in adrenal glands and gives an intense bluish-violet colour with Folin's tungstic acid reagent (I) must be removed from adrenal extracts [e.g., bytreatment with Pb(OAc)₂] before the adrenaline content is determined with that reagent. W. McC.

Cortical hormone and vagal excitability. A. DE BARBIERI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 152—153).—Cortin (I) increases vagal excitability in the dog. Hypovagotonia in adrenalectomised animals is due to both (I) and adrenaline deficiency. R. N. C.

Adrenalotropic substance of the anterior pituitary. K. J. ANSELMINO, L. HEROLD, and F. HOFFMANN (Arch. Gynākol., 1934, 158, 531— 543).—Injections of aq. extracts of anterior pituitary reduce the chromaffin reaction and produce vacuolisation of the cells of the suprarenal medulla. The substance responsible differs from those already known. Possibly increased medullary activity of this sort is the indirect cause of the blood-sugarraising properties of the extracts. NUTR. ABS. (m)

Hormonal regulation of blood-sugar in infants. H. SCHONFELD (Monatsschr. Kinderheilk., 1934, **61**, 241-248).—Infants fasted for 15-16 hr. were very sensitive to adrenaline injections, 0.3 ml. of 0.01% solution increasing the blood-sugar. Injections of anterior pituitary extract arrested the normal decrease in 8 out of 16 children who had previously fasted for 16 hr. In children fasted for 4 hr. the extract produced a slight increase in blood-sugar. Pituitrin caused an increase in blood-sugar in children fasted for 16 or 4 hr. NUTR. ABS. (m)

Thyrotropic hormone of the anterior pituitary. J. B. Collip and E. M. ANDERSON (J. Amer. Med. Assoc., 1935, 104, 965—969).—Injection of purified thyrotropic hormone into rats causes a 28% rise in basal metabolic rate for the first week, a fall to preinjection val. by the 2nd—3rd week, and a further fall to -29% (level in the untreated hypophysectomised rat) by the 5th week. The serum of injected animals contains an antithyrotropic substance which will inhibit the action of the hormone. This substance does not inhibit the action of thyroxine, but there is a given amount which will just prevent the rise in basal metabolic rate due to thyrotropic hormone without inhibiting thyroid hyperplasia. Severe hyperthyroidism develops in goitrous rats given the hormone. A possible hormone-antihormone balance is discussed. NUTR. ABS. (m)

Determination of the thyrotropic action of anterior pituitary preparation and the unit of the hormone. J. G. HEYL and E. LAQUEUR (Arch. internat. Pharmacodyn., 1935, 49, 338—354).— There are three levels of activity in the thyroid gland of the young guinea-pig: an inner central zone, in a continual state of flux, a middle zone which reacts readily to the pure thyrotropic hormone, and a peripheral zone which is comparatively inactive. Changes which take place in the middle zone after injection into a young animal of thyrotropic hormone in known amounts, under standard conditions, may be used to standardise the prep. and serve as a basis for the definition of a unit. NUTR. ABS. (m)

Functional correlations between the anterior pituitary and the ovary. J. A. DUBOWIK (Pflüger's Archiv, 1935, 235, 412–415).—Maturation of the ovary of *Axolotl* is accelerated by stimulation of the anterior pituitary. Extirpation of the pituitary causes hypoplasia of the ovary. The anterior pituitary hormone induces maturation in hypophysectomised animals. R. N. C.

Physico-chemical state of hormones in the blood. Diffusion of the oxytocic pituitary principle in dog- and ox-serum. D. BROUN and H. SCHEINER (Compt. rend. Soc. Biol., 1935, 119, 1379–1380).—The oxytocic hormone diffuses in serum in combination with a colloidal substance and becomes ultrafilterable only after treatment with acid or excess of CaCl₂. H. G. R.

Luteinising principle of the posterior lobe of the pituitary. A. Moszkowska (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 60-61).—Alkaline extracts of posterior lobes of ox pituitaries are without effect on the ovaries of immature guinea-pigs, but will produce cystic corpora atretica from follicles which are approaching maturity. P. G. M.

Alkaline extracts of the posterior lobe of ox pituitary. A. Moszkowska (Compt. rend. Soc. Biol., 1935, 119, 1239—1240).—There is evidence of diffusion of the corticotropic and auxogenic hormones, but not of the thyrotropic or the crinogenic, from the anterior lobe. H. G. R.

Gastric and pulmonary lesions following high doses of the vasopressor fraction of the posterior pituitary hormone. G. BERGAMI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 90–93).—The hæmorrhagic lesions produced by large quantities of vasopressin in the stomach and lungs of rats and guinea-pigs occur in regions through which acid ions normally pass. Oxytocin does not produce lesions. R. N. C.

Evaluation of gonadotropic hormone preparations on the basis of the rat-mouse ratio assay. W. O. NELSON and M. D. OVERHOLSER (J. Pharm. Exp. Ther., 1935, 54, 378—392).—The quantities of gonad-stimulating preps. corresponding with rat and mouse units are determined and shown to vary from a 5:1 rat: mouse ratio for pregnancy urine, to 1:3 for pituitary extract, and 2:1 for pregnant mare serum. Thus the ratio offers a method of differentiating between anterior pituitary and anterior pituitary-like gonadotropic complexes. H. D.

Constitution of cinchol; its transformation into 3-hydroxyætioallocholan-17-one.—See this vol., 1242.

Isolation of crystalline progestin. W. M. ALLEN (Science, 1935, 82, 89-93).—A lecture. L. S. T.

Crystalline progestin and inhibition of uterine motility in vivo. W. M. ALLEN and S. R. M. REYNOLDS (Science, 1935, 82, 155).—Both cryst. forms of progestin suppress uterine motility in rabbits. Inhibition of motility and progestational proliferation of the endometrium are produced by one and the same hormone. L. S. T.

Nomenclature of the corpus luteum hormone. W. M. ALLEN, A. BUTENANDT, G. W. CORNER, and K. H. SLOTTA (Z. physiol. Chem., 1935, 235, I, and Nature, 1935, 136, 303).—The authors recommend the names α - and β -progesterone, respectively, for the highand low-melting forms of the hormone of the corpus luteum (formerly progestin or luteosterone).

W. McC.

Biological control of follicular and luteal preparations. Presence in the corpus luteum of a substance with action resembling that of insulin. Ovarian hormones and carbohydrate metabolism. B. BRUNELLI (Arch. internat. Pharmacodyn., 1934, 49, 212-221, 222-229, 243-258).-In ovariectomised rats, \Rightarrow 20 days after operation, injection of follicular hormone reduces, and of corpus luteum hormone increases, liver-glycogen (I). Treatment of fresh corpus luteum (non-pregnant cows) by methods for the extraction of insulin from pancreas gives a prep. which, injected into rabbits, reduces bloodsugar and increases (I) in rats. In adult female rats, folliculin injected daily from the beginning of pro-œstrus had a hyperglycæmic action and mobilised (I). Corpus luteum hormone injected in metæstrus decreased blood-sugar and increased glycogen synthesis. NUTR. ABS. (m)

Effect of prolactin on the cestrus cycle of nonparous mice. I. DRESEL (Science, 1935, 82, 173).--Prolactin suspends the cestrus cycle in mature, nonparous mice for approx. 3 weeks, after which, in spite of continued injections, a prolonged cestrus of 4--8 days sets in. The suspension of the cestrus cycle during lactation thus appears to be caused by the pituitary rather than by a corpus luteum hormone. L. S. T.

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Administration of the œstrogenic substances in urine. A. GROLLMAN, H. B. SHUMACKER, jun., and E. HOWARD (J. Pharm. Exp. Ther., 1935, 54, 393—397).—The œstrogenic substances in urine may be adsorbed on to charcoal and administered orally; the adsorbed anterior pituitary-like substances are ineffective when administered in this way. H. D.

Regression of the histo-pathological modifications of the pituitary from castration, obtained with the new sex hormone extracted from male urine. A. MIGLIAVACCA (Boll. Soc. Ital. Biol. sperim., 1935, **10**, 105–108).—Injection of the male hormone in castrated rats restores the histo-pathological picture of the anterior pituitary to normal in 3 weeks. The effective dose is equiv. to half the quantity of female hormone required. R. N. C.

Male sexual hormone in the female body. H. SIEBKE (Z. ges. Naturwiss., 1935, 1, 161—171).— A discussion. Curves are given showing the male and female hormone excreted in 3 months by a female subject. The former probably comes from the follicle. H. J. E.

Hormone content of the cock's comb. A. BERDNIKOFF and C. CHAMPY (Compt. rend. Soc. Biol., 1935, 119, 1314—1315).—Folliculin is present in the comb in the free state and the male hormone in an inactive form. H. G. R.

Activity of androstenedione on the sexual organs of the male rat. E. TSCHOPP (Nature, 1935, 136, 258—259).—Androstenedione (I) is more active than androsterone (II), or the diol obtained by hydrogenation of (II), in increasing the wt. of the sexual organs of young castrated male rats. Its action on the capon's comb is less, however. The results support the view (this vol., 1125) that (I) or a similar unsaturated ketone may be identical with the less stable hormone of the testis. L. S. T.

Increased effectiveness of insulin when injected in equal doses at intervals of two to four hours. I. Use of insulin in divided doses in severe uncomplicated diabetes and in complicated medical cases. B. B. CLARK, R. B. GIBSON, and W. D. PAUL (Arch. Int. Med., 1935, 56, 360—373).—Insulin is most effective when given in equal doses at intervals of 2—4 hr. day and night. Under these conditions the daily requirement is less. H. G. R.

Influence of insulin on alcoholæmia in men. E. SERIANNI (Atti R. Accad. Lincei, 1935, [vi], 21, 394-401).—The height of the blood-EtOH curve following ingestion of aq. EtOH is reduced (41-50%) by prior subcutaneous injection of insulin (20 units). F. O. H.

Effect of parathyroid extract on normal carbohydrate metabolism. A. FERRANNINI (Policlin., 1935, 42, 285—299).—Injection of 1 ml. of extract caused the blood-sugar to fall 13—56%; when injected simultaneously with 150 g. of glucose (I) given by mouth the degree of hyperglycæmia was < when (I) was given alone, and when injected simultaneously with 1 mg. of adrenaline, hyperglycæmia was in some cases reduced. NUTR. ABS. (m) Rôle of the nervous system in the action of thyroxine on cell respiration. G. MANSFELD and G. HORVATH (Pflüger's Archiv, 1935, 235, 520— 521).—The increase of O_2 consumption in rabbit's kidney by thyroxine (I) is abolished by complete denervation of the kidneys. Excitation of the gastrocnemius nervo of the frog in Ringer's solution containing (I) produces an O_2 consumption > in absence of (I); unexcitable nerve shows no difference. Hence (I) is taken up by the nervous system and reaches the cells by the peripheral nerves, where it exerts its catalytic effect on anaërobic fermentation, and indirectly on cell oxidation. R. N. C.

Thyroglobulin studies. I. Thyroxine and iodine content of normal and goitrous human thyroglobulin. J. W. CAVETT, C. O. RICE, and J. F. MCCLENDON (J. Biol. Chem., 1935, 110, 673— 683).—Thyroglobulin (I) from goitres contains less total I, and has a lower thyroxine I : total I ratio, than (I) from normal human thyroid glands. Administration of I to the patients does not restore the I content of (I) to normal. Widely different types of goitre give the same result. Vals. of the basal metabolic rates of the patients are given. F. A. A.

Effect of the thyroid on the formation of hen's egg. V. S. ASMUNDSON and P. PINSKY (Poultry Sci., 1935, 14, 99—104).—Feeding desiccated thyroid at the rate of 1 mg. of I per 1750 g. live-wt. resulted in a reduction in yolk-wt., a small increase in shell-wt., and a reduction in body-wt. and rate of growth of the ovum. A. G. P.

Relationship of the thyroid gland and the liver. H. DOETSCH (Biochem. Z., 1935, 279, 233—240).— The acceleration of metamorphosis of tadpoles by thyroxine is inhibited by the presence of the pressjuice or pulp of liver, but not of kidney or muscle. P. W. C.

Effect of the duration in the solution on the action of thyroxine on tadpoles. P. ALPHONSE and G. BAUMANN (Compt. rend. Soc. Biol., 1935, 119, 1243—1245).—30 min. in 1:50,000 or 1 hr. in 1:400,000 thyroxine solution is sufficient to give a positive result. After immersion the animals are returned to H_2O and within 2—3 days the effect on the metamorphosis is noticeable. H. G. R.

Action of the plant hormones on the development of frog-spawn. R. M. DU PAN and M. RAMSEYER (Compt. rend. Soc. Biol., 1935, 119, 1236).—The growth hormones of plants increase the rate of development and cell division of frog-spawn. H. G. R.

Function of the corpus allatum of insects. V. B. WIGGLESWORTH (Nature, 1935, 136, 338— 339).—This gland secretes two and possibly three hormones regulating the growth of *Rhodnius*.

L. S. T. Effects of a deficiency of iodine and vitamin-A on the thyroid gland of the albino rat. H. M. COPLAN and M. M. SAMPSON (J. Nutrition, 1935, 9, 468-487).—Deficiency of I causes initial hypertrophy of the thyroid in both sexes, but persisting longer in females. It is followed in both sexes by atrophy. Deficiency of vitamin-A produces hypertrophy in females and atrophy in males. Deficiency of I and -A induces initial hypertrophy in both sexes followed by atrophy in males. A. G. P.

Internal energy relationships of organic substances. VIII. Formation of vitamin-A and the double linking rule. O. SCHMIDT (Ber., 1935, 68, [B], 1658—1662; cf. this vol., 852).—In accordance with the double linking rule the transformation of β -carotene into vitamin-A occurs according to the scheme: CMeR:CH:CH:CH:CMER \longrightarrow

 $CMeR:CH\cdot CH_2 \cdot CH(OH) \cdot CH:CMeR \longrightarrow$

2CMeR:CH·CH₂·OH. The change is therefore similar to that of ergosterol into vitamin-D. With regard to the influence of Me and Cl on substitution in the C_6H_6 nucleus the dipole effect is regarded as of secondary consequence, and the valency activity of the B electrons not as an effluence of electrostatic forces, but as a quantum-mechanical resonance effect caused by the alternating direction of spin of the corresponding B electrons. It does not appear possible to explain electrostatically by dipole forces the author's double linking rule or the closely allied radical rule of Criegee. H. W.

Vitamins-A and -D of Suiyuan vegetable oils. T. Y. Lo (Nutrit. Bull. B., No. 2, March, 1935, 22— 33).—No evidence of the presence of vitamin-A or -Dwas found in linseed, mustard-seed, or hempseed oil. The oils, especially the hempseed, may contain toxic substances. NUTR. ABS. (m)

Effect of some yeast extract factors on the growth of rats on high-fat diet. C. Y. CHEN (Nutrit. Bull. B., No. 2, March, 1935, 43—51).—Rats fed on a basal diet containing peanut oil 65%, fish-protein 29%, McCollum's salt mixture 4%, and unsaponifiable matter from cod-liver oil 2% grew well only when given dried yeast, crude extract of yeast, or purified preps. of vitamin- B_1 and $-B_2$, together with the residue of the extracted yeast. When receiving only the purified preps. of $-B_1$, $-B_2$, and $-B_4$, the rats did not grow, although these supplements were sufficient to support growth on a diet containing only 5% of fat. NUTR. ABS. (m)

B-Vitamins as substitute for insulin. W. VON DRIGALSKI (Arch. Verdauungs-Kr., 1935, 57, 1—8).—Although there is a definite relation between carbohydrate metabolism and the vitamin-B complex, more particularly $-B_1$, treatment of diabetic patients with yeast instead of insulin was unsuccessful, the complex, as present in yeast, having no effect on the glycosuria, blood-sugar level, acidosis, or insulin requirement of diabetics. NUTR. ABS. (m)

Crystalline fluorescent dehydrogenation product from vitamin- B_1 . G. BARGER, F. BERGEL, and A. R. TODD (Nature, 1935, **136**, 259).—Alkaline K_3 Fe(CN)₆ converts the vitamin hydrochloride into a pale yellow, S-containing *compound*, m.p. 221°, which, in neutral or alkaline solution, has an intense blue fluorescence. It possesses all the recorded properties of the "thiochrome" (C₁₂H₁₄ON₄S) of Kuhn *et al.* (this vol., 1026), including a similar absorption spectrum. L. S. T.

Vitamin- B_1 and $-B_2$ content of wheat products. A. F. MORGAN and M. J. HUNT (Cereal Chem., 1935, 12, 411—418).—The following vals., expressed as international units per 100 g., are given for wheat products. Vitamin- B_1 , whole wheat 125; wheat germ 758; whole wheat + 10% of germ 184; whole wheat + 20% of germ 242; whole-wheat bread 167—186. Vitamin- B_2 , whole wheat 100; germ 404; whole wheat + 20% of germ 124. E. A. F.

Antineuritic vitamin from yeast. H. RUHKOPF (Diss., Gottingen, 1933; Bied. Zentr., 1935, A, 5, 331).—The prep. of cryst. vitamin- B_1 from yeast is described. The free base, $C_{12}H_{16}ON_4S$, yields on hydrolysis with HCl $C_{12}H_{15}$ (or 17) O_2N_3S . A. G. P.

Growth-promoting action of synthetic *d*-riboflavin (6:7-dimethyl-9-[d-1-ribity] isoalloxazine). P. KARRER, H. VON EULER, M. MALMBERG, K. SCHÖPF, and F. BENZ (Svensk Kem. Tidskr., 1935, 47, 99—101).—Synthetic *d*-riboflavin, m.p. 282°, has a growth-promoting power equal to that of the purest samples of natural lactoflavin, with which it appears in other respects to be identical (cf. this vol., 359, 631). W. O. K.

Excretion and storage of vitamin-C in the human and animal body. I. Vitamin-C content of the urine of inhabitants of Sweden. H. VON EULER and M. MALMBERG (Biochem. Z., 1935, 279, 338—352).—No relationship could be traced between daily urinary excretion of vitamin-C (I) and physiological or pathological condition. The amount excreted in the urine of women is not increased during pregnancy. Although individual variations are very great, the (I) excretion of persons living (in N. Sweden) on a diet poor in (I) is much < that of persons living (in S. Sweden) on a diet richer in (I). W. McC.

Vitamin-C requirement of the guinea-pig. M. DANN and G. R. COWGILL (J. Nutrition, 1935, 9, 507-519).—Guinea-pigs require approx. 1 c.c. of lemon juice per 100 g. body-wt. No evidence was obtained of a relatively larger requirement for young rapidly-growing animals. Metabolic rate has no appreciable influence on the -C requirement.

A. G. P.

Biochemical relationships between ascorbic acid and glutathione. T. BERSIN, H. KÖSTER, and H. J. JUSATZ (Z. physiol. Chem., 1935, 235, 12—18).— A relationship is shown to exist between the ascorbic acid (I) and glutathione (II) contents of the kidney. The autoxidation of (I) at $p_{\rm H}$ 6.47 or 7.38 is considerably retarded by 10% of (II), whilst a solution of molar quantities of (I) and (II) at $p_{\rm H}$ 7.38 and 36° does not absorb O₂, although separately the reactants do so. Solutions of (I) can be protected from atm. oxidation by addition of SH-compounds, the requisite amount of the latter being much less at $p_{\rm H}$ 7 than at $p_{\rm H}$ 4.5. The formation of a compound of (I) and (II) could not be established. H. W.

Vitamin-C content of brain after administration of the vitamin. M. MALMBERG and H. VON EULER (Z. physiol. Chem., 1935, 235, 97—103).— The vitamin-C (I) content of the brain of the guineapig is reduced to 20% of its normal val. by feeding (for 14—26 days) a diet free from (I). The (I) content of the rabbit brain is not decreased by feeding such diet or increased by giving enormous (I) excess. W. McC. Distribution of vitamin-C in the brain-stem ganglia. F. PLAUT and K. STERN (Naturwiss., 1935, 23, 557—558).—Vals. are given for the vitamin-C contents of the globus pallidus (I), thalamus, caudate nucleus, and substantia nigra (II). (II) has a content significantly > (I). E. A. H. R.

Rheumatic heart disease and vitamin-C. C. B. PERRY (Lancet, 1935, 229, 426-427).--Determinations by the dichlorophenol-indophenol method of the ascorbic acid (I) excreted in the urine of children suffering from rheumatic carditis show that (I) deficiency is not an important causative factor, but that some degree of deficiency often occurs in such cases. L. S. T.

Antiscorbutic vitamin in horse-radish. K. P. KEDROV (Problems of Nutrition, U.S.S.R., 1934, 3, No. 5. 20-21).—Horse-radish is a good source of vitamin-C (I), since 20 g. daily would protect from scurvy a man on a diet otherwise lacking in (I).

NUTR. ABS. (m)

(A) Antiscorbutic properties of the turnip (Brassica napus). S. N. MATZKO. (B) Canned food enriched with vitamin-C by addition of fir-needle concentrate. N. S. JARUSSOVA. (C) Antiscorbutic action of the concentrate from the sulphited black-currant, obtained in factory conditions. T. L. IZUMRUDOVA (Problems of Nutrition, U.S.S.R., 1935, 4, No. 1, 68-70, 70-72, 72-74).—(A) The turnip, yellow or white, is a comparatively poor source of vitamin-C.

tively poor source of vitamin-C.
(B) When an infusion of fir needles mixed with rice gruel was canned about half the vitamin-C activity of the infusion was lost.

(c) A juice, prepared from sulphited black-currants on a large scale and subsequently freed from sulphite by concn. at reduced pressure, showed a high vitamin-Cactivity. NUTR. ABS. (m)

Ascorbic acid content of some plant fluids. H. N. BANERJEE (Current Sci., 1935, 4, 28-29).— The ascorbic acid (I) content of juices expressed from the following is in the decreasing order : coconut tree, Palmyra palm, pineapple, date-palm tree, and coconut. The (I) content of coconut decreases as the fruit ripens. F. N. W.

Enzymic determination of true vitamin-C. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1935, 110, 559-563).—The reducing substances are titrated both before and after removal of the ascorbic acid with ascorbic acid oxidase, after preliminary Hg(OAc)₂ treatment. H. G. R.

Determination of ascorbic acid by titration. E. W. MCHENRY and M. GRAHAM (Biochem. J., 1935, 29, 2013—2019; cf. this vol., 903).—The Harris titration of ascorbic acid (I) (A., 1933, 541) is modified by making up the indicator in HPO₄" buffer at $p_{\rm II}$ 7.2, using large dilutions, and extracting 3 times with CCl₃·CO₂H. Pigmented extracts are titrated under CHCl₃; with strawberries and red peppers the CCl₃·CO₂H extracts are washed with amyl alcohol. In the lettuce, cucumber, and turnip the conen. of (I) is greatest where photosynthesis occurs. The difference in (I) content between tetraploid and diploid tomatoes is probably due to the difference in size. From the increases in (I) content of vegetables on cooking or treatment with H_2S the presence of a complex containing (I), insol. in $CCl_3 \cdot CO_2H$, is assumed. H. D.

Effect of feeding cacao shell to cows on the vitamin-D content of butter. S. K. KON and K. M. HENRY (Biochem. J., 1935, 29, 2051–2056).—The mean vitamin-D (I) content of cacao shell and cacao shell-fat determined by curative and protective methods on rats was 35 and 300 international units per g., respectively. The feeding of 2 lb. of the shell daily for 4 weeks to shorthorn cows under winter feeding conditions increased the (I) content of the butter to the summer level, *i.e.*, from 0.20—0.25 to 0.50—0.60 international units per g. A. L.

Effect of vitamin-D on production and properties of eggs. H. W. TITUS and R. B. NESTLER (Poultry Sci., 1935, 14, 90–98).—Improvements in egg production, egg wt., and hatchability due to supplementary feeding of vitamin-D are recorded. The effect is dependent on the source as well as quantity of -D supplied. Large proportions produce deleterious results. The optimum quantity of codliver oil for confined birds is 1—2% of the diet. When viosterol is used 10—20 times the amount of -D is necessary. A. G. P.

Comparative vitamin-D requirements of growing chicks, turkeys, and pheasants. F. D. BAIRD and D. J. GREENE (Poultry Sci., 1935, 14, 70-82).--Min. requirements of vitamin-D are determined. The large demand of turkeys and pheasants may be met by feeding fortified cod-liver oil. A. G. P.

Vitamin-D in edible fungi. A. SCHEUNERT, M. SCHIEBLICH, and J. RESCHKE (Z. physiol. Chem., 1935, 235, 91-96).—The vitamin-D (I) contents (international units) of 1 g. of the fresh fungi are : Boletus edulis and Cantharellus cibarius 0.83, Helvella esculenta 1.25, Agaricus s. Psalliota campestris (grown in the dark) 0.21, (grown in the open) 0.63. B. badius and many (if not all) other fungi contain (I). The (I) content of the fungi is reduced if they are grown in the dark. W. McC.

Fat-soluble growth factor required by blowfly larvæ. II. Identity of the growth factor with cholesterol. R. P. HOBSON (Biochem. J., 1935, 29, 2023—2026; cf. this vol., 889).—Cholesterol from several sources had the same growthpromoting power for blow-fly larvæ; sitosterol, ergosterol, and lanosterol had smaller effects. The fat-sol. growth factor is therefore a sterol. H. D.

Effect of calcium and phosphorus variations and source of experimental chicks on assay of vitamin-D carriers. W. B. GRIEM, M. J. KILLIAN, L. E. CLIFCORN, W. S. THOMPSON, and E. GUNDLACH (J. Assoc. Off. Agric. Chem., 1935, **18**, 471–475).— Variation of Ca from 0.83 to 0.90% and of P from 0.48 to 0.78% produces no significant effect on the accuracy of assay by the A.O.A.C. tentative method. The origin of the white Leghorn chicks used has no effect on the result. E. C. S.

Vitamin-E. III. Evidence for the presence of a hydroxyl group. Biological utilisation of esters. Absorption spectrum. H. S. OLCOTT (J. Biol. Chem., 1935, 110, 695-701).—The presence of at least one OH in vitamin-E (I) is proved by the formation of ethers with MeI(EtI)-Ag₂O, and the formation of a urethane (II) with PhNCO. These processes destroy the activity of (I) (no litters from rats), but an active sample of (I) is regenerated by hydrolysis of (II) with KOH-EtOH. The activity of the Bz and Ac derivatives of (I) (A., 1934, 462) indicates that rats can utilise these esters, but not (II). Acetylation may destroy the antioxidant, but rancidity in the acetylated concentrate does not diminish its physiological activity. Hydrogenation (H₂-Ni at $230^{\circ}/250$ -280 atm.) neither destroys (I) nor saturates the concentrate (residual I val. 26). The conclusion (this vol., 129) that the band at 294 m μ is not due to (I) is confirmed by a lack of parallelism between its intensity and the activity of J. W. B. the sample.

Summation of [plant] cell e.m.f. H. F. ROSENE (Plant Physiol., 1935, 10, 209—224).— The polarity of a region of the root tip (*Allium cepa*) is increased or decreased when an electrolyte solution (e.g., tap-H₂O) surrounds a segment of that region. Initial conditions are restored on removal of the solution. Evidence is advanced showing that the principle of algebraic summation of e.m.f. in polar cell systems applies to the polarity of roots.

A. G. P.

Material basis of the osmotic pressure in Hedera helix and Hex aquifolium. G. PITTIUS (Bot. Archiv, 1935, 37, 43-64).—The osmotically active constituents of the plant saps are sugars (glucose, fructose, sucrose), org. acids (malic), and K and Na salts (principally malate, $PO_4^{\prime\prime\prime}$, $SO_4^{\prime\prime}$, Cl'). Tannins and related compounds are unimportant as osmotic factors. Periodic fluctuations in osmotic pressure are controlled mainly by the sugars, except in the period of shoot formation, when the rapid decline in sugar content is partly counteracted by an increase in org. acid and salts. A. G. P.

Effect of frost on wheat at progressive stages of maturity. II. Composition and biochemical properties of grain and flour. A. G. McCalla and R. NEWTON (Canad. J. Res., 1935, 13, C, 1-31; cf. B., 1934, 596).-The rate of increase in dry matter of the kernels was high for approx. 14 days after flowering, decreasing subsequently to zero at a crit. stage 24 days later. During this period, the total N content increased to a max., the salt-sol. N declined steadily, and NH3-N increased at first and subsequently fell to a negligible amount. The ratio of N to non-N materials translocated to the endosperm during active development remained approx. const. Frost did not affect the ash or invert sugar contents of the grain. The salt-sol. and non-protein-N was not altered by freezing at $-2\cdot 2^{\circ}$. In samples cut prior to the crit. stage, exposure to $< -4.4^{\circ}$ caused a decline in the total N of grain and flour and an increase in reducing sugar in flour. A. G. P.

Salt concentration and reversibility of ice formation as related to the hardness of lucerne. S. T. DENTER (Plant Physiol., 1935, 10, 403-406).— Less H_2O was frozen at -6° to -90° in lucerne roots which had been hardened than in tender roots. There appears to be no loss of electrolytes during the hardening process (see also this vol., 263, 266). A. G. P.

Temperature as a predetermining factor in the development of Avena sativa. T. M. PLITT (Plant Physiol., 1935, 10, 269-289).-Oats contain no starch in the embryo when in the resting condition. On germination at 5° starch is deposited in the embryo. During germination at 25° little or no starch appears, but the seedling contains higher proportions of pectin and reducing sugars. Protein is produced more rapidly at the higher temp. Seedlings grown at 25° were tallest, irrespective of the germination temp., and contained least N. Seedlings germinated at 25°, regardless of later conditions, had a higher % of dry matter and carbohydrates, higher ratio of sol. to insol. acid-hydrolysable carbohydrates, inglier ratio of sol. to filsol, acid-hydrolysable carbohydrates, and lower % of N than had those germinated at 5°. Oats germinated and grown at 25° with R.H. 40% made less growth, had higher % of dry matter and lower % of carbohydrate than those grown with R.H. 70%. In 6-week plants SiO₂ was deposited in the same manner in erect and recumbent plants, and was localised in calls which did recumbent plants, and was localised in cells which did not form a consecutive structure. SiO_2 deposition is unrelated to "lodging." A. G. P.

Effects of exfloration on plant metabolism. S. AUSTIN (Plant Physiol., 1935, 10, 225-243).-Cessation of growth associated with fruit development in soya beans is not affected by exfloration. The reproductive phase is controlled by day-length. The behaviour of exflorated plants resembles the response of other plants to K starvation. The length of day affects vegetative growth, probably through its influence on the [K'] in plant tissues. Exfloration results in an abnormal accumulation of carbohydrates, but not of N. In control plants the N, Ca, Mg, P, and K contents were not depleted by the development of fruits. A. G. P.

Limitations of Blackman's law of limiting factors and Harder's concept of relative minimum as applied to photosynthesis. B. N. SINGH and K. N. LAL (Plant Physiol., 1935, **10**, 245—268).— Under low light intensities $[CO_2]$ -assimilation curves are smooth and the stationary phase is either absent or limited to a small range. With high light intensities curves for wheat and linseed are regular, but show a wide range of stationary assimilation. The effects of temp. and light intensity on the photosynthetic process are examined. The theory of relative min, is of limited application. It functions to some extent when $[CO_2]$ and light intensity are low.

A. G. P.

Formation of chlorophyll and the beginning of photosynthesis. O. L. INMAN (Plant Physiol., 1935, **10**, 401–403).—Evolution of O_2 occurs very soon after chlorophyll is formed in young etiolated leaves in visible amounts, and is not delayed until the leaf is almost fully green. Absorption spectra of extracts of etiolated leaves made between 2 sec. and 2 min. after exposure indicate the formation of chlorophyll long before O_2 evolution occurs. A. G. P.

Non-indispensability of oxygen for carbon dioxide assimilation by green plants. H. GAF-FRON (Naturwiss., 1935, 23, 528; cf. Kautsky, this vol., 1177).—When Chlorella ferments in the dark in N_2 until completely free from O_2 and is then exposed to light, assimilation of CO_2 at once begins without accompanying evolution of O_2 , such evolution beginning only after some time. If CO_2 replaces N_2 during fermentation, initiation of the assimilation is also retarded. These and other facts indicate that the presence of free or loosely bound O is not essential for the initiation of CO_2 assimilation in green plants. W. McC.

Deficiency experiments in water cultures. II. W. SCHROPP and H. SOUKUP (Landw. Versuchs-Stat., 1935, **122**, 263—322; cf. B., 1934, 250).—Comparison is made of various media utilised by different investigators. Results are discussed from the viewpoint of the influence of composition, initial concn., and $p_{\rm H}$ of the nutrient on the validity of deficiency experiments with different crops. A. G. P.

Nitrogenous and carbonaceous nutrition of Chlorogonium euchlorum in the dark. Acetic acid as a product of chlorophyllic assimilation. A. Lvov and H. Dusi (Compt. rend. Soc. Biol., 1935, 119, 1260—1263).—AcOH, although favouring the growth of *C. euchlorum* in the dark, is not indispensable: it is probably an intermediary stage in starch synthesis. H. G. R.

Iron absorption and chlorosis in green plants. C. OLSEN (Compt. rend. Lab. Carlsberg, 1935, 21, No. 3, 15–52).—Lemna polyrhiza grown in Knop's solution at p_{π} 6–7 becomes chlorotic, but remains normal at $p_{\rm H}$ 4-6 or 7-10. Addition of Fe citrate or humus extract corrects the chlorotic condition. Plants having a high Fe requirement (Xanthium spinosum, Zea mays) behave similarly, whereas those requiring little Fe show no chlorosis but slightly inhibited growth at $p_{\rm H}$ 7. Chlorotic maize plants may contain > normal amounts of Fe and always have > normal % of Ca^{*}, $PO_4^{*''}$, Mg, K, and N as a result of restricted production of org. matter without disturbance of the mineral intake. Fe in chlorotic plants is immobilised by pptn. as phosphate. At $p_{\rm H}$ 8.0 the PO_4''' of Knop's solution is largely pptd. as $Ca_3(PO_4)_2$, hence the intake of PO_4''' by and the subsequent pptn. of Fe within the plants is decreased. Maize grown in acid media absorbs less PO," and has a more acid tracheal sap which opposes pptn. of Fe. Chlorosis in media of $p_{\rm H}$ 6-7 is prevented by decreasing the proportion of PO4". Alkaline media may cause chlorosis if the composition is adjusted to give an excess of PO₄" over Ca". Fe tartrate is less effective than the citrate owing to the greater ease of decomp. and pptn. as $Fe(OH)_3$. Fe^{II} salts completely prevent chlorosis at p_{π} 6—7 (cf. B., 1930, 434). A. G. P.

Kinetics of penetration. XI. Entrance of potassium into Nitella. A. G. JACQUES and W. J. V. OSTERHOUT (J. Gen. Physiol., 1935, 18, 967-985).—The rate of entrance of K into N. flexilis is independent of illumination and of $p_{\rm H}$ between $p_{\rm H}$ 6 and 8, over the external concn. range 10^{-2} to $10^{-4}M$, and varies little with external [K] between 10^{-2} and $10^{-3}M$, but rather more at lower concns. The K content of the raw sap is > that of ultrafiltered sap. F. A. A. Chemical restoration in Nitella. I. Ammonia and some of its compounds. W. J. V. OSTER-HOUT (J. Gen. Physiol., 1935, 18, 987–995; cf. this vol., 1038).—The K effect and the irritability in Nitella, removed by immersion in distilled H_2O , can be restored by NH_3 or NH_4Cl solution. The K effect can also be restored by NEt_4Cl . F. A. A.

Appearance of substances functioning like the plant auxin during the development of Discoglossus pictus, Otth. M. Rose and H. BERRIER (Compt. rend., 1935, 201, 357—359).—The sperm and egg, in the early stages of segmentation, of D. pictus have no auxin-like activity as determined by the behaviour of a coleoptile; at a later stage in the development of the egg activity appears. H. D.

Pure growth effect obtained with heated pregnancy urine. E. HELD and K. PONSE (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 56–59).—By heating to 70° pregnancy urine, previously extracted with Et_2O to remove cestrin, the luteinising principle appears to be destroyed, whilst some cestrogenic principle remains. P. G. M.

Solubility of growth factors from microorganisms. W. H. SCHOPFER (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 18—19).—Vitamin- B_1 has a max. solubility in 70% EtOH. Extraction of wheat germ or a conc. extract (obtained by means of 70% EtOH) by light petroleum yields a solution containing only lipins and yellow pigment, but CHCl₃ liberates a substance which is equally active on vegetative development and zygote formation, and is distinct from vitamin- B_1 which is almost insol. in CHCl₃. P. G. M.

Spectroscopic study of different woods of Fernando Po and the Iberian Peninsula. S. PIÑA DE RUBIES and L. LEMMEL (Bull. Soc. chim., 1935, [v], 2, 1368—1370).—Spectroscopic estimates of the elements present in 26 woods have been made. Ag, Pb, and Cr are revealed for the first time. Five of the Fernando Po woods fluoresced intensely in ultra-violet light. T. G. P.

Presence in self-blanching celery of unsaturated compounds with physiological action similar to ethylene. R. C. NELSON and R. B. HARVEY (Science, 1935, 82, 133—134).—Golden self-blanching celery in the natural blanching condition produces in the tomato the characteristic curvature of the leaves which results in presence of low concns. of certain substances containing C:C. A celery which is not self-blanching produced no such reaction. C_3H_6 , C_4H_8 , C_5H_{10} , mesityl oxide, vinyl acetate, but not di-, tri-, and tetra-chloroethylene, COMe₂, MeCHO, Et₂O, and CHCl₂, also give the reaction. L. S. T.

Essential oil of black tea. I. Fermented Formosan tea leaf. II. Formosan black tea. R. YAMAMOTO and Y. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 27, 122—129, 130—135).— I. After fermentation, steam-distillation at 100°, extraction of the distillate with Et₂O, and removal of acid constituents, 400 kg. of tea leaves yielded 13 g. of oil consisting of Me salicylate, CH₂Ph·CH₂·OH, citronellol, and their esters, Δ^{β} -hexen- γ -ol, Δ^{α} -hexen- β al, Pr^aCHO, Pr^{\beta}CHO, Bu^{\beta}CHO, geraniol (trace), a sec.-alcohol, b.p. $62^{\circ}/4$ mm., $187-189^{\circ}/760$ mm., a sec.-alcohol, b.p. $85-90^{\circ}$, and traces of a substance with odour of cinnamon. The acid constituents include salicylic acid and possibly $Pr^{\circ}CO_{2}H$ and $CH_{2}Ph \cdot CO_{2}H$.

II. Fermented and dried tea leaves were subjected to steam-distillation at 112°. There is no distinct difference between oils of black tea and of fermented tea leaf before drying. An Et₂O extract of the distillate contained Me salicylate, salicylic and palmitic acid, a *phenol*, possibly $Pr^{\circ}CO_{2}H$, $CH_{2}Ph \cdot CO_{2}H$, and Bu^gCO₂H, and, except the above *sec.*-alcohol, b.p. 85—90°, all neutral compounds of the fermented tea. Geraniol was isolated. The *sec.*-alcohol of b.p. 62°/4 mm. is chiefly responsible for the flavour of black tea. Another substance, an *ester*, sap. val. 17, yielded a primary *alcohol*, probably an unsaturated terpene, and a trace of an *acid*, m.p. 128°. E. P.

Isolation and characterisation of a starch polysaccharide from the woody tissue of the apple tree (Malus malus). C. NIEMANN, R. H. ROBERTS, and K. P. LINK (J. Biol. Chem., 1935, 110, 727-737).—The polysaccharide, $[\alpha]_D^{\alpha\beta}$ +185° in HCO·NH₂, $[\alpha]_D^{24}$ +190° in H₂O (triacetate, $[\alpha]_D^{\alpha\beta}$ +168° in CHCl₃), is essentially identical in structure with the β -amylose present in cereal and tuber starches. HCl in MeOH gave a good yield of α -methyl-d-glucoside, whilst acid hydrolysis yielded only d-glucose with a trace of xylose. J. N. A.

Levosin in grain and meal. H. COLIN and H. BELVAL (Bull. Soc. Chim. biol., 1935, 17, 1040—1044). —The method of extraction of levosin (I) from wheat flour, rye, bran, and stubble is described Hydrolysis of (I) gives 1 mol. of glucose and 9 mols. of fructose. It is hydrolysed rapidly by common moulds and slowly by yeast extracts, and is probably fermented during the process of bread making. A. L.

Cultivation of Artemisia. S. KRISHNA and B. S. VARMA (Current Sci., 1935, 4, 29).—The two periods of max. santonin content of A. brevifolia coincide with the appearance of flower buds on the plant. F. N. W.

Existence of two anhydrodigitoxigenins.—See this vol., 1226.

Pigment of egg-plant. II. C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1935, **11**, 235—237; cf. A., 1933, 651).—Two new constituents of the colouring matter of the epidermis of the egg-plant (Solanum melongena, L., var. esculentum, Ners.) are described. A, $C_{27}H_{31}O_{17}Cl, 3H_2O$, m.p. 197°, gives delphinidin chloride (I) and glucose (II) when hydrolysed by boiling HCl; the carbohydrate may be a disaccharide attached to the 3 position of (I). B (isolated by way of the picrate), $C_{36}H_{37}O_{19}Cl, 10H_2O$, gives (I), (II), and p-coumaric acid on HCl hydrolysis; the group $OH \cdot C_6H_4 \cdot CH \cdot CH \cdot CO \cdot C_{12}H_{21}O_{11}$ may be attached to the 3 position of (I). P. G. C.

Pigment of "Awobana." III. C. KURODA (Proc. Imp. Acad. Tokyo, 1935, 11, 238—239; cf. A., 1933, 614).—The presence of delphin chloride in the pigment of Awobana (flowers of *Commelina communis*) is shown by analysis and hydrolysis of the substance (m.p. 207°) to delphinidin chloride and glucose, and by comparison of the absorption spectra and colour reactions. P. G. C.

Pigment of the fruit of Rosa rugosa, Thunb. H. WILLSTAEDT (Svensk Kem. Tidskr., 1935, 47, 112—114).—Chromatographic analysis of the pigments of the fruits of *R. rugosa* has yielded rubixanthin, m.p. 160° (cf. A., 1934, 404), in addition to carotene, lycopene, and phytoxanthin. W. O. K.

Development of the chlorophyll and carotenoid pigments in barley seedlings. G. MACKINNEY (Plant Physiol., 1935, 10, 365—373).—The chlorophyll : carotene ratio was approx. const. in normal and in chlorotic seedlings. The carotene : xanthophyll ratio approached a val. of 0.60 in normal seedlings, but was consistently lower in chlorosis. An increased supply of K to the seedlings raised the pigment content of plants under certain conditions. A. G. P.

Salt-extractable proteins of wheat-flour. Ultracentrifugal study. L. KREJCI and T. SVED-BERG (J. Amer. Chem. Soc., 1935, 57, 1365-1369).-0.5N-KF, -KCl, -KBr, and -KI extract mixtures of proteins of increasing average mol. wt. (in the order quoted) from wheat-flour (I). The crude extracts all contained much non-centrifugible, lightabsorbing material (II); pptn. with $(NH_4)_2SO_4$ causes an increase in sedimentation const. and a decrease in (II). Successive extraction of (I) with 0.5N-KF (3 times) and 0.5N-KCl (5 times) and dialysis of the extracts (against distilled H₂O) gives a ppt. consisting largely of gliadin and globulin (III); the material not pptd. is (probably) leucosin and proteose. (III) polymerises in conc. solution and H. B. dissociates on dilution.

Detection of gold in animal tissues. W. J. ROBERTS (Proc. K. Acad. Wetensch. Amsterdam, 1935, 38, 540-544).—A method is described for detection of Au by means of physical development in a solution of gum arabic, AgNO₃, quinol, and citric acid. H. G. R.

Determination of pyruvic acid.—See this vol., 1223.

Microchemical test for choline and its esters in tissue extracts. F. J. BOOTH (Biochem. J., 1935, 29, 2064—2066).—The Florence reagent (I in aq. KI) may be used to detect 20×10^{-6} g. of choline per 100 g. of tissue. Acetylcholine may be detected after hydrolysis. The H₂O-sol. choline precursor gives a ppt. with (I) only after hydrolysis with aq. HCl. A. L.

Colorimetric determination of serum-bilirubin. Light-extinction curves of azobilirubin. A. KRUPSKI and F. ALMASY (Biochem. Z., 1935, 279, 424—432).—In the spectrophotometric determination of bilirubin as azobilirubin (I) accuracy is increased by the use of light-filters which partly eliminate inequalities of colour in the standard [KMnO₄, $Co_2(SO_4)_3$] and (I) solutions. The changes in the light extinction curves of (I) produced by alteration of [H'] indicate that there are three forms of (I). The colour of the solution employed in the method of Thannhauser *et al.* (A., 1922, ii, 671) is little affected by changes in [H'], and hence this method is recommended. W. McC.