BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1932.

General, Physical, and Inorganic Chemistry.

Stark effect for hydrogen lines. K. SJÖGREN (Z. Physik, 1932, **77**, 290—295). A. J. M.

Intensity relationships in the helium spectrum by superposition of canal-ray motion and an electric field. H. KIRSCHBAUM (Ann. Physik, 1932, [v], **14**, 448—462). A. J. M.

Can neon lines be used as secondary standards of wave-length? H. NAGAOKA (Proc. Imp. Acad. Tokyo, 1932, **8**, 231—232).—The Ne^{20} lines show broadening due to reversals; feeble Ne^{22} lines become more pronounced at low temp. N. M. B.

Second spark spectrum of neon, Ne III. T. L. DE BRUIN (Z. Physik, 1932, **77**, 505—514). A. B. D. C.

Transition probabilities for $2P - 1S$ of sodium determined from absolute intensity measurements in flames. E. F. M. VAN DER HELD and L. S. ORNSTEIN (Z. Physik, 1932, **77**, 459—477).—The transition probability is 0.62×10^8 sec.$^{-1}$ A. B. D. C.

Stark effect in the argon spectrum. N. RYDE (Z. Physik, 1932, **77**, 515—527). A. B. D. C.

Inverse Stark effect for the two members of the principal series of rubidium and cæsium. Y. T. YAO (Z. Physik, 1932, **77**, 307—316). A. J. M.

Hyperfine structure of arc and spark spectra of barium. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **18**, 304—314).—Data are recorded for 6 lines of Ba I and 13 lines of Ba II, giving the nuclear moments 3/2 and 0 for $Ba^{135, 137}$ and $Ba^{136, 138}$, respectively. No relative shift of even isotopes is found. N. M. B.

Nuclear moment of barium as determined from the hyperfine structure of the Ba II lines. P. G. KRUGER, R. C. GIBBS, and R. C. WILLIAMS (Physical Rev., 1932, [ii], **41**, 322—326).—Hyperfine structure data for λ 4934 and λ 4554 are tabulated. The nuclear moment of $Ba^{135, 137}$ was determined as 5/2. N. M. B.

Hyperfine structure of mercury spectrum. VI. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **18**, 299—303; cf. this vol., 787).—Data are recorded and interpreted for λ 3650·15, 2464·06, and 6123·27 of Hg I, and for λ 3983·96, 2847·67, and 6149·50 of Hg II. N. M. B.

Origin of the coronal lines. J. KAPLAN (Nature, 1932, **130**, 241).—A criticism of de Bruin's conclusion (this vol., 441). L. S. T.

Theory of coupling width [of spectra]. V. WEISSKOPF (Z. Physik, 1932, **77**, 398—400).—An extension of a previous paper (cf. this vol., 552). A. J. M.

Long wave-length portion of the visible spectrum of the night light of the sky. L. A. SOMMER (Z. Physik, 1932, **77**, 374—390).—The spectrum consists of lines and bands showing the spectra of O, O_2, and H_2O. The transitions giving rise to these spectra are obtained. Comparison of wave-lengths of the lines and bands with those of the aurora reveals agreement as regards structure, but quite different intensities. A. J. M.

Cosmic radiation. G. HOFFMANN (Physikal. Z., 1932, **33**, 633—662).—A summary of methods used and results obtained during the last eight years. A. J. M.

New class of absorption series as a transition from the optical to the X-ray spectra. H. BEUTLER (Naturwiss., 1932, **20**, 673).—The absorption spectra of Rb and Hg vapours have been obtained without change in quantum no. of the valency electron belonging to the fundamental state of the atom. A. J. M.

Diffuse scattering of X-rays from sodium fluoride. G. E. M. JAUNCEY and P. S. WILLIAMS (Physical Rev., 1932, [ii], **41**, 127—135; cf. A., 1931, 896, 1205). N. M. B.

Very soft X-ray spectra of heavy elements. C. DEL ROSARIO (Physical Rev., 1932, [ii], **41**, 136—140).—Measurements in the range 43·6—104·8 Å. are recorded for Th, Pb, Ta, Hg, Au, Ir, and W. N. M. B.

Existence of K-absorption edge in phosphors, and a new sensitive method for high-frequency radiation spectral analysis. E. RUPP and F. SCHMIDT (Ann. Physik, 1932, [v], **14**, 413—414). A. J. M.

Diffraction of cathode rays by single crystals. II. Mean inner potentials of some crystals. K. SHINOHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **18**, 315—322).—The vals. obtained for calcite, rock-salt, and mica were 10·5, 6·3, and 10·4 volts, respectively. N. M. B.

Grating type and fine structure of X-ray absorption edges. K. VELDKAMP (Z. Physik, 1932, **77**, 250—256).—The fine structure of X-ray absorption edges is the same for crystals of the same type. A. B. D. C.

Shielding and the intensity of X-ray diagram lines. J. A. PRINS (Z. Physik, 1932, 77, 478—488).—The effect of a non-coulombian field on the intensity of X-ray lines is determined for ultra-soft radiation.
A. B. D. C.

Critical potential of helium. A. PLÜMER (Z. Physik, 1932, 77, 356—373).—The crit. potential of He was determined and compared with earlier vals.
A. J. M.

Dependence of high velocities and emission work of photo-electric electrons from broken zinc single-crystal surfaces on the orientation of the surfaces. A. NITZSCHE (Ann. Physik, 1932, [v], 14, 463—480).
A. J. M.

Surface ionisation of potassium by tungsten. P. B. MOON and M. L. E. OLIPHANT (Proc. Roy. Soc., 1932, A, 137, 463—480).—It is shown how surface ionisation may provide the source of a beam of positive ions which has great intensity, steadiness, and length of life. This source has been used for a detailed investigation of the drop in ionisation efficiency which occurs when fast K^+ ions strike a hot target.
L. L. B.

Dependence of luminosity due to electron collision with calcium tungstate on the energy of the colliding electrons. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, 77, 528—533).—Potential falls of approx. 8200 volts are required to give the lumens per watt of the modern "Nitra" lamp.
A. B. D. C.

Elastic electron scattering in helium. A. L. HUGHES, J. H. MCMILLEN, and G. M. WEBB (Physical Rev., 1932, [ii], 41, 154—163).
N. M. B.

Reciprocal action of two electrons. H. BETHE and E. FERMI (Z. Physik, 1932, 77, 296—306).—Mathematical.
A. J. M.

Wandering velocity of electrons. M. DIDLAUKIS (Z. Physik, 1932, 77, 352—355).—Theoretical. A simple method for calculating the migration velocity of electrons is described.
A. J. M.

Electrons, protons, and the so-called electromagnetism. E. KLEIN (Z. Physik, 1932, 77, 415—419).—An experimental method is described to discriminate qualitatively between the theory of Günther-Schulze (this vol., 442) and that of others.
A. J. M.

Theory of the passage of rapid electrons through matter. C. MØLLER (Ann. Physik, 1932, [v], 14, 531—585).

Dirac electron in simple fields. M. S. PLESSET (Physical Rev., 1932, [ii], 41, 278—290).—Mathematical.
N. M. B.

Electron diffraction and inner potential of metals. R. FRISCH (Naturwiss., 1932, 20, 689).—It is contended that the inner potential of Ag given by Bühl (this vol., 893) is in error.
A. J. M.

Polarisation of a beam of electrons by crystal reflexion. J. THIBAUD, J. J. TRILLAT, and T. VON HIRSCH (J. Phys. Radium, 1932, [vii], 3, 314—319).—The diffraction rings of electrons regularly reflected from thin Au and Pt films show no irregularity in intensity, indicating no appreciable polarisation.
N. M. B.

Electron collision at crystal surfaces as a verification of optical energy levels. R. HILSCH (Z. Physik, 1932, 77, 427—436).—Study of electron reflexion at crystal surfaces of NaCl, KCl, KI, LiF, NaF, and CaF_2 showed that the reflexion intensity diminishes at energies corresponding with the frequencies of optical absorption bands. A. B. D. C.

Investigation of finely crystalline powdered substances by electron diffraction. F. TRENDELENBURG (Naturwiss., 1932, 20, 655—656).—The powder is dusted very sparingly on to a metal foil, which is treated in the usual way.
A. J. M.

Physical constants of methyl fluoride and the at. wt. of fluorine. W. CAWOOD and H. S. PATTERSON (J.C.S., 1932, 2180—2188).—The mol. wt. and compressibility of MeF obtained by heating NMe_4F have been determined by the microbalance method (A., 1931, 890). The crit. data of MeF prepared by this method and also by the action of $KMeSO_4$ on KF, as well as the compressibility of the gas obtained by the latter method, have been measured. Both crit. and compressibility data are in close agreement in each case (cf. this vol., 106), but the compressibility and mol. wt. differ from the vals. found by Moles and Batuecas (A., 1921, ii, 389). The at. wt. of F is discussed.
J. W. S.

At. wt. of selenium and tellurium. O. HÖNIGSCHMID (Naturwiss., 1932, 20, 659).—The ratio $2Ag : Ag_2Se$ was found to be 0·732081, giving for the at. wt. of Se $78·962 \pm 0·002$. This agrees with Aston's figure obtained by mass-spectrograph determinations. The ratio $TeBr_4 : 4Ag : 4AgBr$ was determined and gave for the at. wt. of Te $127·587 \pm 0·019$, in agreement with the international val., but not with Aston's. Using other mass-spectrograph data, however, good agreement is obtained.
A. J. M.

Relative abundance of the nitrogen and oxygen isotopes. G. M. MURPHY and H. C. UREY (Physical Rev., 1932, [ii], 41, 141—148).—N_2 and O_2 from various sources were converted into NO, for which absorption spectra data gave $N^{15}O^{16}/N^{14}O^{18}$ as $0·549 \pm 0·007 : 1$, from which N^{14}/N^{15} is $346 : 1$. N. M. B.

Reversibility of certain radioactive processes. H. ZANSTRA (Z. Physik, 1932, 77, 391—394).—Theoretical. The application of the law of mass action to the process of taking up an α-particle by a nucleus with the liberation of a proton or a neutron, and the reverse operation, enables the ratio of the effective collision cross-sections to be calc. in a simple manner.
A. J. M.

Atomic disintegration in aluminium and nitrogen. E. STEUDEL (Z. Physik, 1932, 77, 139—156).—The range of protons ejected from Al and N_2 was measured for disintegration of the nuclei by α-rays from Po; no resonance effect was observed on variation of the energy of the disintegrating rays.
A. B. D. C.

Collision of α-particles with atomic nuclei. H. S. W. MASSEY (Proc. Roy. Soc., 1932, A, 137, 447—463).—The collision of α-particles with at. nuclei is discussed, using a quantum theory of collisions which allows for the perturbation of the α-particle wave by the nuclear potential barrier.

The probability of α-particle exchange on impact is shown to be large when the energy of the incident α-particle coincides with that of a virtual level of the nucleus. The anomalous scattering of α-particles by light nuclei (Mg, Al, etc.) is also considered. The new theory should provide a means of determining the radii of light nuclei. L. L. B.

Search for evidence of the radioactive decomposition of barium. T. R. HOGNESS and (MISS) R. R. COMROE (Proc. Nat. Acad. Sci., 1932, **18**, 528—531).—It is assumed that Xe and He could be formed from hypothetically radioactive Ba by α-particle disintegration. Five old Ba rocks were decomposed in a NaCl–KCl melt, all gases, except inert gases, were removed over heated Ca, and any residual gas was examined spectroscopically for Xe. Each of the specimens gave a small quantity of residual gas, but no Xe could be detected. W. R. A.

Artificial disintegration by neutrons. N. FEATHER (Nature, 1932, **130**, 237).—Photographs of the tracks produced in an expansion chamber filled with O_2 (97 vol.-%) at approx. 1 atm. when a source of Po and Be is placed in the centre provide definite evidence of disintegration. The disintegration probability for neutron–O_2 encounters is smaller but of the same order of magnitude as that for similar encounters with N nuclei. Disintegration probably occurs with capture of the incident neutron, in which case the reaction may be $O^{16} + n^1 \longrightarrow C^{13} + He^4$. Energy data show that the capture disintegration takes place with an absorption of energy in different amounts on different occasions. L. S. T.

Gamma radiation. A. BRAMLEY (Proc. Nat. Acad. Sci., 1932, **18**, 543—550).—Theoretical. W. R. A.

Constitution and stability of atomic nuclei. A. SCHIDLOF (Arch. Sci. phys. nat., 1932, **14**, 125—148).—A survey is given of the theory of emission of β-rays from radioactive nuclei, isotopes and isobars, effect of nuclear mass and stability of the α-particle, and classifications of nuclei. Data on the constitution and stability of nuclei are deduced. N. M. B.

Mass defect and binding energy of neutrons. W. BRAUNBEK (Z. Physik, 1932, **77**, 534—540).—Theoretical. The calc. mass defect of the neutron gives a binding energy of $1—1.5 \times 10^6$ volts. A. B. D. C.

Recombination of hydrogen atoms at metallic and oxidised nickel. L. S. ORNSTEIN and A. A. KRUITHOF (Z. Physik, 1932, **77**, 287—289).—The mean free path of electrons in a discharge tube, determined by means of a Faraday cage, is somewhat smaller when a surface of metallic Ni is used than when oxidised Ni is employed. The superficial oxidation must diminish the recombination of H atoms at the Ni surface. A. J. M.

Evaporation of mercury particles and its influence on measurements of the ultimate quantum of electricity. R. NESTLE (Z. Physik, 1932, **77**, 174—197).—Hg particles, without an impure surface layer, evaporate so that the mass of the particle diminishes linearly with time; this evaporation limits

the accuracy of measurements of charge by the Millikan method. A. B. D. C.

Evaporation of mercury droplets. K. SCHÄFER (Z. Physik, 1932, **77**, 198—215).—A theoretical and experimental study of evaporation of Hg particles of radii near 10^{-5} cm. Stable particles do not exist in chemically passive gases. A. B. D. C.

Cathode sputtering of beryllium and aluminium in helium. P. D. KUECK and A. K. BREWER (Rec. Sci. Instr., 1932, [ii], **3**, 427—429).—The ratio of the relative nos. of Be and Al atoms sputtered in He under identical conditions is $1.5 : 1$, the film thicknesses are in the ratio $2.45 : 1$, and the light-absorbing power is $10 : 1$. The results point to the suitability of Be as a cathode material. W. R. A.

Liquid currents and space charge around wire electrodes in water. M. KATALINIÉ (Z. Physik, 1932, **47**, 257—270). A. B. D. C.

Constitution of atomic nuclei. D. IVANENKO (Compt. rend., 1932, **195**, 439—441; cf. this vol., 672).—An elaboration of previously expressed views, the neutron being regarded as an elementary particle with spin 1/2 and obeying Fermi–Dirac statistics. C. A. S.

Band spectrum of sulphur monoxide. E. V. MARTIN (Physical Rev., 1932, [ii], **41**, 167—193).—Wave nos., rotational and vibrational structure, and spin fine-structure data are recorded for the lines of 7 bands in the region 2400—4000 Å. N. M. B.

Absorption spectrum of sulphur trioxide and heat of dissociation of oxygen. A. K. DUTTA (Proc. Roy. Soc., 1932, A, **137**, 366—372).—The absorption spectrum of SO_3 has been studied between 5000 and 2000 Å. Absorption is continuous, from 3300 to 2600 Å., where it disappears, and begins again at 2300 Å. It is assumed that in the first process of absorption SO_3 decomposes into SO_2 and normal O, and in the second process the O atom set free is in the excited state. The excitation energy of the O atom is 1.65 volts (cf. Henri's val. of 1.7 from predissociation spectra of NO_2). The heat of dissociation of O_2 calc. from the beginning of continuous absorption at 3300 Å. is 128 kg.-cal. L. L. B.

Post-dissociation radiation from sulphur trioxide. A. K. DUTTA (Nature, 1932, **130**, 241).—Gaseous SO_3 at <1 mm. gives a weak line at 6364 Å. L. S. T.

Quantitative determination of absorption spectra of hydrogen bromide and hydrogen iodide. A. K. DUTTA (Z. Physik, 1932, **77**, 404—411).—The determinations were made at various pressures. The extinction coeff. for HBr disappears at 3260 Å., and for HI at 4040 Å. The energies corresponding with the long-wave absorption limits are 87.7 kg.-cal. for HBr and 70.8 for HI. These compounds are definitely ionic. A. J. M.

Absorption and fluorescence spectra of the vapours of the mercury halides. II. $HgBr_2$ and $HgCl_2$. K. WIELAND (Z. Physik, 1932, **77**, 157—165).—Absorption and fluorescence spectra to 1500 Å. were observed for $HgBr_2$ and $HgCl_2$. The longest wave-length region of continuous absorption

gives dissociation of HgX_2 into HgX and a metastable X; the three shorter wave-length continuous absorption regions give dissociation of HgX_2 into $HgX^* + X$. HgX_2 is therefore an at. mol. (cf. this vol., 896). A. B. D. C.

Absorption spectrum of anhydrous ferric chloride. F. I. G. RAWLINS and C. P. SNOW (Z. Krist., 1932, **83**, 41).—Besides general absorption from 5000 Å. there is a sharp absorption band of width 50—100 Å. at λ 6200. This discontinuous spectrum, the first case found elsewhere than among the rare earths, is attributed to the transition $^4X - ^2Y$ in the Fe''' ion. C. A. S.

Intensity change in the rotation oscillation spectrum of water vapour (ortho- and para-water). R. MECKE (Naturwiss., 1932, **20**, 657).—The rotation–oscillation spectrum of H_2O has been analysed. An intensity change of 1 : 3 is noted in the series. The fundamental term must be a $^1\Sigma_g$ term. There are thus three dihydrides now known which exist in ortho- and para-forms, viz., H_2, H_2O, and H_2O_2. A. J. M.

Vibration–rotation spectrum of acetylene. K. HEDFELD and P. LUEG (Z. Physik, 1932, **77**, 446—458).—Rotation lines were photographically measured in bands between 11,000 and 5000 Å. A. B. D. C.

Analysis of the (0,0) $^2\Pi \longrightarrow ^2\Sigma$ **CN band at 9168 Å.** A. E. PARKER (Physical Rev., 1932, [ii], **41**, 274—277).—Rotational analysis gives consts. in agreement with transitions involving higher vibrational levels of the $^2\Pi$ state (cf. Jenkins, this vol., 211). The band origin is at $10,905 \cdot 12$ cm.$^{-1}$ N. M. B.

Ultra-violet spectrum of carbon disulphide and its apparent occurrence in the absorbing atmosphere of the sun. N. R. DHAR (Z. anorg. Chem., 1932, **207**, 209—216).—Some unidentified lines in the solar spectrum appear to agree with ultra-violet absorption lines of CS_2. E. S. H.

Effect of substitution on ultra-violet absorption and chemical properties of carbonyl compounds. W. HEROLD (Z. physikal. Chem., 1932, B, **18**, 265—290; cf. this vol., 461).—With increase in the positive character of the substituents attached to the CO group in carbonyl compounds absorption is shifted towards the red. The positive character of substituents decreases in the order H, Me, Cl, NH_2, OR. Since the carboxylic acids form semi-acetal compounds in hydroxylic solvents and their dissociation consts. increase with the positive character of the substituent, it seems that the formation of these compounds is a necessary preliminary to dissociation. In aq. solution AcOH is partly converted into the ortho-acid and in EtOH solution partly into the mono-ortho-ester. R. C.

Absorption spectrum of hexuronic acid. R. W. HERBERT and E. L. HIRST (Nature, 1932, **130**, 205).—The single broad band at approx. 263 mμ reported by Bowden and Snow (this vol., 656) occurs with equal intensity in Szent-Györgyi's purified hexuronic acid. MeOH solutions do not obey Beer's law; they are unstable and, on keeping, show a gradual diminution in the intensity of the band. Aq. solutions show a single broad band at 260 mμ with a

rapid diminution in intensity. Tetramethyl-γ-fructose, glycuronic and galacturonic acids show no selective absorption. The keto-furanose structure previously suggested (this vol., 548) requires modification. L. S. T.

Ultra-violet absorption of solutions containing two chromophoric groups. A. HILLMER and E. PAERSCH (Z. physikal. Chem., 1932, **161**, 46—57).—The absorption of binary equimol. mixtures of C_6H_6 with MeI, EtI, or $Pr^\alpha I$, and of PhPr with $Pr^\alpha I$ is additively constituted of the absorptions of the constituents. The absorption of $Ph[CH_2]_nI$ is additively constituted of the absorptions of the two chromophoric groups when $n=3$, but as n decreases the bands shift towards the red and there is exaltation of the extinction. PhI, however, does not continue this series, for the principal band is in practically the same position as in $Ph[CH_2]_3I$, and there is no exaltation. All the measurements have been made in hexane solution. R. C.

Ultra-violet absorption of substances with two chromophoric groups. A. HILLMER and E. PAERSCH (Z. physikal. Chem., 1932, **161**, 58—60; cf. preceding abstract).—Existing data show that the absorption of a substance containing two chromophoric groups sufficiently far apart is additively constituted of the absorptions of the individual groups. As the groups approach there is displacement towards the red when they come very close, and independently of this there is exaltation of the extinction. The mode of variation of the extinction as the chromophores approach depends on the nature of the latter. R. C.

Muscular hæmoglobins. J. ROCHE (Compt. rend., 1932, **195**, 501—503).—The absorption spectra of muscular hæmoglobin of the ox, horse, and dog obey the same laws as those of blood hæmoglobin. F. R. S.

Infra-red photography. G. MÖNCH and H. WILLENBERG (Z. Physik, 1932, **77**, 170—173).—Technical improvements have been made in the method previously described (cf. this vol., 444). A. B. D. C.

Infra-red dispersion of carbon dioxide. H. M. SMALLWOOD (Physical Rev., 1932, [ii], **41**, 164—166). —Mathematical. N. M. B.

Infra-red absorption spectrum of carbon dioxide. P. E. MARTIN and E. F. BARKER (Physical Rev., 1932, [ii], **41**, 291—303).—The 15 μ band has been resolved into several constituent bands each consisting of a narrow, intense, zero branch with equally spaced rotation lines on each side. The 4·3 μ band shows similar line spacing, but no zero branch. The calc. moment of inertia is $70 \cdot 8 \times 10^{-40}$ g.-cm.^{2} Harmonic and combination bands and a correlation with Raman spectra are discussed. N. M. B.

Vibrational levels of linear symmetrical triatomic molecules. D. M. DENNISON (Physical Rev., 1932, [ii], **41**, 304—312).—Fermi's theory of energy levels of mols. of the CO_2 type is applied to the results of Martin (cf. preceding abstract) and to available data for CS_2. N. M. B.

Two-minima problem and the ammonia molecule. D. M. DENNISON and G. E. UHLENBECK

(Physical Rev., 1932, [ii], **41**, 313—321).—Formulæ are deduced leading to the dimensions H—H=$1·64 \times 10^{-8}$, N—H=$1·02 \times 10^{-8}$ cm. for the NH_3 mol. N. M. B.

Raman spectrum and molecular structure of ozone. G. B. B. SUTHERLAND and S. L. GERHARD (Nature, 1932, **130**, 241).—A 30% solution of O_3 in liquid O_2 gives a very weak doublet corresponding with a mean shift of 1280 cm.$^{-1}$ when excited by the Hg arc. The O_3 mol. is concluded to be triangular but not equilateral. L. S. T.

Raman effect in salt solutions. A. SILVEIRA and E. BAUER (Compt. rend., 1932, **195**, 416—418; cf. this vol., 559).—Solutions of chlorides of Ca, Sr, Cd, Li, and H, and of $Ca(NO_3)_2$ have been examined. The line at or near 1650 cm.$^{-1}$ is due to H_2O, the position being slightly modified by the electrostatic field of the cations (cf. A., 1931, 1091). New lines are reported at 1762 for LiCl, and at 1811 for LiCl, $Mg(NO_3)_2$, and $Ca(NO_3)_2$. C. A. S.

Investigation of intermediate compound formation by means of the Raman effect. J. A. HIBBEN (Proc. Nat. Acad. Sci., 1932, **18**, 532—537).—The aldol–crotonaldehyde type of transformation has been studied, but results are inconclusive. There is evidence of possible compound formation in solution between $AlCl_3$ and EtOH and between $ZnCl_2$ and MeOH; of polymerisation of $AlCl_3$ in H_2O; of no compound formation in solution between K_2SO_4 and $Al_2(SO_4)_3$; and of a stepwise ionisation of $ZnCl_2$ in H_2O. No Raman displacements were obtained with Al_2O_3 nor hydrated $AlCl_3$. W. R. A.

Thermo-luminescence and photo-luminescence of fluorites. E. IWASE (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 910—933; cf. A., 1931, 1111).—A relation is found for the variation with temp. of photo- relative to thermo-luminescence. N. M. B.

Significance of line emission and absorption spectra of chromium phosphors. O. DEUTSCHBEIN (Z. Physik, 1932, **77**, 489—504).—Lines in the spectra of Cr phosphors are identified with lines in the Cr^{+++} spectra. A. B. D. C.

Crystalloluminescence of barium bromate. E. A. ENGLE and L. SCHULTZ (J. Colo.-Wyo. Acad. Sci., 1931, **1**, No. 3, 22).—No activating impurities are required. Luminescence is max. during slow crystallisation of a saturated solution from 72° to 55°. CH. ABS.

Mass-spectrograph study of the ionisation and dissociation by electron impact of benzene and carbon disulphide. E. G. LINDER (Physical Rev., 1932, [ii], **41**, 149—153).—C_6H_6 gave ions containing C in amounts from C_1 to C_6 with various amounts of H attached; the principal ion for electrons of 120 e-volt is $C_6H_6^+$; no negative ions and no H^+ ions were found. CS_2 at low pressure and impacts of 120 e-volts gave the ions CS_2^+, CS^+, S^+, and C^+. N. M. B.

Photo-electric cells with thin layer alkali cathodes. P. SELÉNYI (Z. Physik, 1932, **77**, 420).—A claim for priority over Sewig (this vol., 669). A. J. M.

Photo-electric primary currents in non-conducting crystals. K. HECHT (Z. Physik, 1932, **77**, 235—245).—The movement of electrons in AgCl on illumination was determined. A. B. D. C.

Theory of the crystal photo-electric effect. H. T. WOLFF (Physikal. Z., 1932, **33**, 621—624).—It is proved mathematically that crystals show a slight preferential photo-electron emission in the direction of the incident light, and that, owing to the strong light absorption of cuprite, more electrons are emitted from the front of an illuminated plane than from behind it. J. W. S.

Electrical conductivity of metals at the lowest temperatures. J. C. McLENNAN (Proc. Roy. Inst., 1932, **27**, 446—470).

Change of electrical resistance in iron crystals. W. GERLACH (Ann. Physik, 1932, [v], **14**, 613—616; cf. Englert, this vol., 985).—All determinations on resistance change of Fe crystals with magnetisation agree with results obtained with polycryst. wires. A. J. M.

Conductivity mechanism in dielectric liquids under intense electric fields. A. NIKURADSE (Z. Physik, 1932, **77**, 216—234).—Saturation and breakdown potentials were measured for several dielectric liquids, e.g., PhMe, under fields of the order of 10^5 volts per cm. and increasing electrode separation. Results agree with Schumann's theory (ibid., **76**, 707). A. B. D. C.

Electrical breakdown experiments with compressed gases and liquid carbon dioxide. O. ZEIER (Ann. Physik, 1932, [v], **14**, 415—447).—Experiments were made with air, N_2, and CO_2 at pressures of 1—120 kg. per sq. cm. Deviations from Paschen's law occurred at lower pressures as the spherical electrodes were increased in size. The deviations can be explained on the assumption of the existence of a positive space charge. A. J. M.

Characteristic temperature for Rochelle salt crystals. R. D. SCHULWAS-SOROKIN (Z. Physik, 1932, **77**, 541—546).—The temp. variations of the piezo- and di-electric consts. show a sharp max. at 22·5°. A. B. D. C.

Dielectric properties of dipolar liquids. A. E. VAN ARKEL and J. L. SNOEK (Physikal. Z., 1932, **33**, 662—664).—An improved formula connecting dielectric const. and dipole moment in place of that of Debye is put forward, and shown to agree with the experimental data. A. J. M.

Polarisation measurements on basic beryllium acetate and acetylacetonate. J. W. SMITH and W. R. ANGUS (Proc. Roy. Soc., 1932, **A**, **137**, 372—379).—Mol. polarisations have been calc. from dielectric const. and density measurements of two solutions of basic Be acetate in C_6H_6 and one in CCl_4 at 25° and 45°, and for a solution of Be acetylacetonate in CCl_4 at 20°, 25°, 35°, and 45°. Mol. refractivities were determined for each solution at 25°. The mol. polarisations do not vary with temp., but are considerably higher than the mol. refractivities. This difference is attributed to at. polarisation, and since this is more pronounced when atoms are linked by

electro-valencies than by co-valencies, it is considered that a structural formula in which all the atoms are electrically neutral is inadequate.

L. L. B.

Measurement and interpretation of certain dipole moments. A. E. VAN ARKEL and J. L. SNOEK (Z. physikal. Chem., 1932, **B**, 18, 159—166).— C_3Cl_8, CBr_3F, and CCl_3Br have zero dipole moment. The moments of all the Cl derivatives of C_2H_6 have been determined, some of these varying with the temp. and solvent. It is suggested that a solvent the dielectric const. of which shows no signs of polarity but which contains double linkings, e.g., C_6H_6, may exhibit in respect of solutes some polarity, the mol. field in the immediate neighbourhood of the mol. being much greater than that near, say, a CCl_4 mol. Deviations of observed moments from the vals. calc. by vectorial addition are ascribed to valency angle distortion, a mechanism of which is suggested in the case of CH_4 derivatives.   R. C.

Determination of configuration of certain geometrically isomeric cyclic dibromides by means of dipole moment measurements. H. L. DONLE (Z. physikal. Chem., 1932, **B**, 18, 146—152).— Configurations have been assigned to certain 1 : 2-dibromides of dihydro-di*cyclo*pentadiene and -tri*cyclo*-pentadiene by comparison of measured vals. of the dipole moments with vals. calc. from group moments by vector addition. Measurements of the ultra-violet absorption of hexane solutions show that the absorption of a *trans* form is displaced towards longer waves compared with the corresponding *cis* form.   R. C.

Dipole moments of some aromatic compounds. W. BODENHEIMER and K. WEHAGE (Z. physikal. Chem., 1932, **B**, 18, 343—346).—The dipole moments of $CH_2Ph\cdot OH$, $CHPhMe\cdot OH$, and the three chloro-bromobenzenes have been determined.   R. C.

Dipole moments of benzene derivatives with freely rotatable substituents. H. L. DONLE and K. A. GEHRCKENS (Z. physikal. Chem., 1932, **B**, 18, 316—326).—The moments of various disubstituted C_6H_6 derivatives have been determined. The val. $1\cdot56 \times 10^{-18}$ e.s.u. has been obtained for the moment of PhOH, which gives $89\pm5°$ for the angle between the group moment and the diameter of the ring passing through the O. Vals. of the moments of substituted phenols calc. by means of this angle agree with the observed vals. For NH_2Ph and PhOMe the angles are $40\pm10°$ and $80\pm10°$, respectively.   R. C.

Dielectric polarisation measurements on some nitroso-compounds. R. J. W. LE FÈVRE and J. W. SMITH (J.C.S., 1932, 2239—2245).—From measurements of the dielectric consts., refractive indices, and densities of dil. solutions the dipole moments of p-$NMe_2\cdot C_6H_4\cdot NO$ and p-$NEt_2\cdot C_6H_4\cdot NO$ have been calc. as 6·89 and 7·18, respectively, in C_6H_6 and 6·33 and 6·87 in CCl_4 and that of p-$NHMe\cdot C_6H_4\cdot NO$ in C_6H_6 as 7·38, all $\times 10^{-18}$ e.s.u. The results are discussed with reference to the behaviour of the NO-group in org. compounds.   J. W. S.

Electric moment and molecular structure. IX. Oxygen and sulphur valency angles. C. P. SMYTH and W. S. WALLS (J. Amer. Chem. Soc., 1932,

54, 3230—3240; cf. this vol., 794).—The O valency angle is $121\pm5°$ in p-substituted diphenyl ethers, about 135° in anisoles and phenetoles, and 65—140° in heterocyclic compounds. The S valency angle is about 146° in the diphenyl sulphides.   M. M. (c)

Ionisation of organic acids. H. M. SMALLWOOD (J. Amer. Chem. Soc., 1932, 54, 3048—3057).—The changes in ionisation of org. acids on substitution of polar groups are largely determined by the magnitude and orientation of the electric moments of the substituents.   E. R. S. (c)

Effect of pressure on the index of refraction of paraffin oil and glycerol. T. C. POULTER, C. RITCHEY, and C. A. BENZ (Physical Rev., 1932, [ii], 41, 366—367).—Data for density, refractive index, and the Lorenz–Lorentz const. for the range 1—13.585 and 1—7212 atm., respectively, are tabulated.

N. M. B.

Double refraction of α-thymonucleic acid in view of the double refraction of chromatin. W. J. SCHMIDT (Naturwiss., 1932, 20, 658).—It is to be expected that the chromatin form of the nucleic acid of nucleoproteins will show negative double refraction. Na α-thymonucleate shows this.

A. J. M.

Photo-electric measurement of the rotatory dispersion of some sugars in the ultra-violet region. G. BRUHAT and P. CHATELAIN (Compt. rend., 1932, 195, 462—465).—Photo-electric measurement of $[\alpha]$ for ultra-violet light is as accurate as visual measurement in the visible region, and enables small differences in dispersion to be measured. It is less accurate than the photographic method, but much more rapid, so that the mutarotation of glucose can be followed. The dispersion of glucose and fructose (I) are represented by $A/(\lambda^2-0\cdot0254)$ and $B/(\lambda^2-0\cdot0210)$, respectively; that of (I) is very similar to that of sucrose. Lowry and Richards' formula (A., 1925, ii, 265) is confirmed.   R. S. C.

Constitution of compounds and radicals consisting of sulphur and oxygen. G. HÄGG (Z. physikal. Chem., 1932, **B**, 18, 199—218).—The electronic formulæ are discussed in the light of available physical and physico-chemical data.

R. C.

Possibility of forming complex molecules. E. J. M. HONIGMANN (Naturwiss., 1932, 20, 635—638).—The formation of complex mols. is discussed. Application to association of water, $(H_2O)_x$, is considered.   W. R. A.

Constitution of certain cobaltammine bases. A. B. LAMB and R. G. STEVENS (J. Amer. Chem. Soc., 1932, 54, 2643—2653; cf. A., 1922, ii, 217; 1923, ii, 226).—Conductometric titration of several nominally tervalent ammine bases prepared from aquo-ammine bromides has shown the H_2O mols. in the complex to be completely displaced by an equiv. no. of OH′ ions. The apparent ionisations of the OH groups remaining outside the complex are high and nearly identical, irrespective of the nature of the central atom, the co-ordinated groups, and the valency of the cation. The replacement of the H_2O mols. is not, however, always complete. Interaction between aquo- and OH′ ions

is comparable with that between aquo-ions and anions generally, although the replacement of H_2O by OH' is relatively extensive and the attainment of equilibrium is unusually rapid. W. C. F. (c)

Internal structure of solid inorganic compounds at high temperatures. V. Electrical conductivity, diffusion, and reactivity of magnesium orthosilicate and magnesium orthogermanate in the solid state. W. JANDER and W. STAMM (Z. anorg. Chem., 1932, 207, 289—307; cf. A., 1931, 999, 1236, 1356).—The electrical conductivity of SiO_2, GeO_2, Mg_2SiO_4, and Mg_2GeO_4, and the rate of diffusion in the solid pairs Mg_2SiO_4–Ni_2SiO_4 and Mg_2SiO_4–Mg_2GeO_4, have been measured at high temp. The reactions between $MgO+Ni_2SiO_4$, $NiO+Mg_2SiO_4$, and $NiO+Mg_2GeO_4$ in the solid state have been investigated at about 1100°. Mg_2SiO_4 has a low ionic conductivity and crystallises mainly as a double-oxide lattice; its constitution may be represented by the equilibrium $Mg''_2SiO_4'''' \rightleftharpoons 2MgO,SiO_2$. The diffusion of Ge in Mg_2SiO_4 is very rapid at 1070—1200°, whilst the diffusion of Ni is relatively slow. Mg_2GeO_4 has a transformation point at 1065°; at lower temp. it crystallises in a spinel type and at higher temp. it is isomorphous with olivine. The spinel type has a higher electrical conductivity, which is at least partly ionic, whilst the conductivity of the olivine type is electronic. The spinel type contains Mg'', Ge'''', GeO_4'''', and O'', but as the temp. is raised a part of the O is withdrawn from the GeO_4'''' to the Mg''. The spinel lattice thus becomes unstable and is transformed into the double-oxide olivine type.
E. S. H.

Connexion between ferromagnetism and structure of ferrites. S. HILPERT and A. WILLE [with A. LINDNER] (Z. physikal. Chem., 1932, B, 18, 291—315; cf. A., 1909, ii, 672).—The magnetisability is a max. for the mol. ratio $2MO : 3Fe_2O_3$. The ferromagnetism of the ferrites depends on the presence of Fe_2O_3 acting as an acid. Ferromagnetism seems to have no connexion with lattice structure and to be a purely mol. or at. property. Various ferrites have been prepared by interaction of the chloride with an alkali ferrite at a high temp. R. C.

Variability of magnetic ionic moment of some elements of the iron series. H. FAHLENBRACH (Ann. Physik, 1932, [v], 14, 521—524).—Correction to previous work (this vol., 563). A. J. M.

Ferromagnetism and electrical properties. VI. Longitudinal and transverse ferromagnetic resistance changes. E. ENGLERT (Ann. Physik, 1932, [v], 14, 589—612).—In high external longitudinal and transverse fields the resistance change is to be ascribed to increase in spontaneous magnetisation. A. J. M.

Additivity law for diamagnetism. D. P. RAY-CHAUDHURI (Z. Physik, 1932, 77, 271—274).—Deviations from the additivity law for hydrated salts are proportional to the heat of hydration; this was established for many sulphates and other salts. A. B. D. C.

Influence of crystalline fields on the susceptibilities of salts of paramagnetic ions. I. The rare earths, especially Pr and Nd. W. G. PENNEY and R. SCHLAPP (Physical Rev., 1932, [ii], 41, 194—207).—Mathematical. N. M. B.

Magnetic susceptibilities of α- and β-manganese. (MISS) M. A. WHEELER (Physical Rev., 1932, [ii], 41, 331—336).—Pure α-Mn prepared by distillation, and β-Mn prepared by melting α-Mn in a vac. and quenching in H_2O from about 1000° gave mass susceptibilities of 9.60×10^{-6} and 8.80×10^{-6}, respectively. N. M. B.

Magnetic susceptibility of nitrogen dioxide. G. G. HAVENS (Physical Rev., 1932, [ii], 41, 337—344).—A method sensitive to 3×10^{-15} is described. Vals for mol. susceptibility are: NO_2, $\chi = 0.375\chi(O_2)$; N_2O_4, $\chi = -30 \times 10^{-6} \pm 20\%$. N. M. B.

Variations in paramagnetic anisotropy among different salts of the iron group. J. H. VAN VLECK (Physical Rev., 1932, [ii], 41, 208—215).—Theoretical. N. M. B.

Magnetochemical researches. VI. Compounds of gallium and indium. VI. Magnetic behaviour of gallium and indium halides. W. KLEMM and W. TILK (Z. anorg. Chem., 1932, 207, 175—176; cf. A., 1931, 547; this vol., 988).—The following vals. have been determined for mol. magnetic susceptibility ($\times 10^6$) at room temp.: $GaCl_2$ —63, GaI_3 —149, $InCl$ —30, $InCl_2$ —56, $InBr_3$ —107, $TlCl$ —55, $AuCl$ —49, $AuBr$ —61, AuI —91, $AuCl_3$ —112, $KAuCl_4$ —152. E. S. H.

Chlorides of nickel and cobalt in solution. Magnetic varieties. Linear relations between Curie constants and Curie points. G. FOËX (J. Phys. Radium, 1932, [vii], 3, 337—344).—The results of Fahlenbrach (cf. this vol., 563) are discussed, and some deductions (particularly a linear relation between Curie const. and Curie point) are pointed out. E. S. H.

Comparison of the primary photographic process in alkali and silver salts. R. HILSCH and R. W. POHL (Z. Physik, 1932, 77, 421—426).—The primary photographic process is transition of an electron from the anion to the cation, and the measurable transfer of electricity observed in Ag salts is a secondary phenomenon. A. B. D. C.

Surface tension determinations of malonic esters, and the constitutive nature of the parachor. A. B. BECK, A. K. MACBETH, and S. W. PENNYCUICK (J.C.S., 1932, 2258—2262).—The surface tensions of a no. of esters of malonic acid have been measured by the max. bubble pressure method, and the parachors calc. The vals. obtained are generally lower than those calc. from the consts. of Sugden or Mumford and Phillips. With unsubstituted esters the non-additivity increases with the length of the alkyl chain and may be connected with the space packing of the ester group. With substituted malonic esters the discrepancies appear to depend on the deviation of the C valencies on substitution at the central C atom. This view is supported by the conductivities of the corresponding acids (cf. A., 1931, 1126). J. W. S.

Oscillating crystal and its technical aspect. E. HABANN (Physikal. Z., 1932, 33, 615—621; cf.

A., 1931, 671).—The behaviour of various types of oscillator crystals and improved methods of arrangement are discussed. J. W. S.

X-Ray diffraction with liquids. H. MENKE (Physikal. Z., 1932, **33**, 593—604).—The theory of the diffraction patterns obtained with liquids is discussed. Experimental data are given for Hg, Ga, and CCl_4, and the results obtained compared with theoretical vals. J. W. S.

Uniform distribution of impurities in crystals after tempering. B. HOCHBERG (Z. Physik, 1932, **77**, 547—552).—Tempered $NaNO_3$ crystals show a uniform space charge on passage of current, and therefore a uniform distribution of impurity.
A. B. D. C.

Kinetics of crystallisation processes. F. VON GÖLER and G. SACHS (Z. Physik, 1932, **77**, 281—286). —An expression for the kinetics of crystallisation processes including nucleus formation and growth of crystals is derived. A. J. M.

Electric strength and crystal structure. A. WALTHER (Z. Physik, 1932, **77**, 275—276).—Criticism of von Hippel's theory (cf. this vol., 565).
A. B. D. C.

Electric strength and crystal structure. A. VON HIPPEL (Z. Physik, 1932, **77**, 277—280).—A reply (cf. preceding abstract). A. B. D. C.

Equilibrium forms of homopolar crystals. I. N. STRANSKI and L. KRASTZNOV (Z. Krist., 1932, **83**, 155—156; cf. A., 1931, 1115). C. A. S.

Stereochemistry of crystal compounds. IX. Geometrical derivation of structure types A_2B_3. W. NOWACKI (Z. Krist., 1932, **83**, 97—112; cf. this vol., 796). C. A. S.

Method of notation for the constants of the lattice types A_nB_m. P. NIGGLI (Z. Krist., 1932, **83**, 111—112; cf. this vol., 564). C. A. S.

Crystal structure of mercury. C. HERMANN and M. RUHEMANN (Z. Krist., 1932, **83**, 136—140).— Unoriented rotation photographs of Hg at —50° show it to be rhombohedral, the unit cell having a 3·05, α 72° 32′ (cf. A., 1923, ii, 864; 1929, 16). C. A. S.

X-Ray investigation on the change of direction of crystal axes during an allotropic change of a substance. H. SHÔJI (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 895—900).—Results for the changes α-Fe $\longrightarrow \gamma$-Fe, Zn blende $\longrightarrow$ wurtzite, and aragonite $\longrightarrow$ calcite are discussed. N. M. B.

Crystal structure of AuCd. A. ÖLANDER (Z. Krist., 1932, **83**, 145—148).—A Au–Cd alloy containing 47·5 at.-% Cd, d 14·5, at room temp., has a 3·144, b 4·851, c 4·745 Å., with 4 atoms in the unit cell, space-group V_h^5, each atom being surrounded by 8 of the other kind at slightly varying distances (2·89 and 2·91Å.), indicating a deformed CsCl structure. At about 400° the lattice is of CsCl type, a 3·34 and distances between atoms 2·89 Å. This supports the inference from electrode potential measurements that the β-phase existing around 50 at.-% Cd has a transition point at 267° with mol. heat of transition about 240 g.-cal. C. A. S.

Crystal structure of red manganese sulphide. H. SCHNAASE (Naturwiss., 1932, **20**, 640—641).—Red MnS exists in two cryst. modifications, one having a ZnS structure with a 5·60 Å., the other having a wurtzite structure with a 3·976, c 6·432 Å., and $c : a =$ 1·617. The at. separation is 2·425 Å. Both modifications form mixed crystals with ZnS and CdS. A disulphide, MnS_2, is formed under certain conditions; it has a hauerite structure with a 6·10 Å.
W. R. A.

Molecular rotation in solid state. Variation of crystal structure of ammonium nitrate with temperature. S. B. HENDRICKS, E. POSNJAK, and F. C. KRACEK (J. Amer. Chem. Soc., 1932, **54**, 2766— 2786).—The unit cell of tetragonal NH_4NO_3 (84·2— 125·2°) has a 5·75, b 5·75, c 5·00 Å., and n, the no. of mols. in the unit cell, is 2. The orthorhombic form (32·3—84·2°) has a 7·06, b 7·66, c 5·80 Å., and n 4, and the space-group $Pbnm$ (V_h^{16}). The orthorhombic form (—18° to 32·3°) has a 5·75, b 5·45, c 4·96 Å., n 2, and the space-group $Pmmn$ (V_h^{13}). The form stable below —18° has possibly a hexagonal structure and a 5·75, c 15·9 Å., and n 6. Diffraction diagrams of specimens at —33° and —78° do not differ materially.
L. W. (c)

Crystal structure of cæsium dithionate. G. HÄGG (Z. physikal. Chem., 1932, B, **18**, 327—342).— The hexagonal unit cell has a 6·326, c 11·535 Å., and contains two $Cs_2S_2O_6$ mols. In the S_2O_6 radical the O atoms lie at the corners of two equilateral triangles with a common trigonal axis, on which, between the triangles, are the S atoms. R. C.

Crystal structure of nickel sulphate hexahydrate. C. A. BEEVERS and H. LIPSON (Z. Krist., 1932, **83**, 123—135).—Tetragonal $NiSO_4,6H_2O$ has a 9·61, c 18·3 Å., with 4 mols. in the unit cell, space-group D_4^4 or D_4^8. The structure consists of alternate tetrahedral SO_4 and octahedral $Ni(H_2O)_6$ groups (cf. this vol., 681) arranged along the dyad axes. The crystals are dextro-rotatory for red, lævo- for blue light, approx. +2° and —1°, respectively.
C. A. S.

Crystal structure of ferric chloride. N. WOOSTER (Z. Krist., 1932, **83**, 35—41).—Ferric chloride has a rhombohedral or hexagonal unit cell, the former with a 6·69 Å., α 52° 30′, and 2 mols. $FeCl_3$; the latter with a 5·92, c 17·26, and 6 mols. Space-group C_{3i}^2 ($R\bar{3}$), perhaps C_3^4 ($R3$); Cl parameter 0·077. The structure is a layer lattice isomorphous with BiI_3 (cf. A., 1931, 549); at. distances are Fe–Cl 2·38, Cl–Cl 3·31, 3·42, and 3·67; the atoms are in the ionic state. Double refraction approx. 0·34; The recorded density, 2·898 (cf. A., 1924, ii, 489), is probably too low, d_{calc} being 3·04. C. A. S.

Crystal structure of lithium orthophosphate and its relation to the olivine type. F. ZAMBONINI and F. LAVES (Z. Krist., 1932, **83**, 26—28; cf. this vol., 39).—The unit cell of Li_3PO_4 has a 4·86, b 10·26, c 6·07 Å., thus showing close similarity to chrysoberyl and olivine (cf. A., 1926, 227, 995). This similarity is attributed to the small Li cations occupying 3/4ths of the octahedral vacancies between the hexagonally close-packed O atoms which form the skeleton of the

olivine type of structure, just as in olivine itself the Mg cations occupy 2/4ths of these vacancies.

C. A. S.

Structure of covellite. I. OFTEDAL (Z. Krist., 1932, **83**, 9—25).—The hexagonal unit cell has a 3·80, c 16·4 Å., and contains $6CuS$, space-group D_{6h}^4 ($C6/mmc$). The structure is that of Roberts and Ksanda (cf. A., 1929, 870), but with U_{Cu} 0·107 and U_S 0·125. At. distances are S–S 2·05, Cu–S 2·20— 2·35, Cu–Cu 3·2 Å.

C. A. S.

X-Ray determination of crystal structure of epsomite. G. M. CARDOSO (Trab. Mus. Nac. Cienc. Nat., 1930, Geol., No. 37, 130 pp.; Chem. Zentr., 1932, i, 1626).—Epsomite, rhombic, pseudotetragonal, has a 11·91, b 12·02, c 6·87 Å.; space-group V_4. The unit cell contains 4 mols. of $MgSO_4,7H_2O$.

Å. A. E.

Space-group of bournonite. I. OFTEDAL (Z. Krist., 1932, **83**, 157—158).—Bournonite, $CuPbSbS_3$, is rhombic, a 8·10, b 8·65, c 7·75 Å., with 4 mols. in the unit cell, space-group V_h^{13} ($Pmmn$).

C. A. S.

Space lattice of natrolite. F. HALLA and E. MEHL (Z. Krist., 1932, **83**, 140).—Further consideration of the authors' results (cf. A., 1931, 550), and of those of others (cf. A., 1930, 1240; this vol., 715), and of the fact that natrolite is pyroelectric, show the space-group to be C_{2v}^{19}.

C. A. S.

Crystal structure of kaolinite. J. W. GRUNER (Z. Krist., 1932, **83**, 75—88).—Kaolinite, SiO_2 45·73, Al_2O_3 38·37, TiO_2 1·35, Fe_2O_3 0·40, CaO 0·56, SO_3 0·16, $H_2O+110°$ 13·19, $-110°$ 0·50, total 100·26, n_α 1·556, $n_\gamma-n_\alpha$ 0·008, has a 5·14, b 8·90, c 14·51 Å., β 100° 12′—101° 30′, with 4 mols. $Al_2Si_2(OH)_4O_5$ in the unit cell; space-group C_s^4. Pauling's structure (cf. A., 1930, 1396) is confirmed. Anauxite (cf. A., 1930, 569) is kaolinite in which Al replaces Si, compensation for different valency being effected by a corresponding replacement of OH by O.

C. A. S.

Structure of hemimorphite. T. ITO and J. WEST (Z. Krist., 1932, **83**, 1—8).—Hemimorphite, $Zn_4Si_2(OH)_2O_7,H_2O$, is pyramidal orthorhombic, with a 8·38, b 10·70, c 5·11 Å., and 2 mols. in the unit cell; the $(OH)_2$ form an integral part of the mol., whilst the H_2O occupies a definite position between mols., thus explaining its removability without perceptible effect on the crystals (cf. A., 1909, ii, 154). The Si and O atoms form Si_2O_7 groups; each Zn is surrounded tetrahedrally by 3 O and one OH.

C. A. S.

X-Ray diffraction with molecules containing two carbon atoms. F. EHRHARDT (Physikal. Z., 1932, **33**, 605—614).—Liquid Cl_2-derivatives of C_2H_4 and C_2H_6 have been investigated by the Debye method and the distances of separation of the Cl atoms deduced. In $C_2H_4Cl_2$ the Cl atoms show a preferential tendency to maintain a *trans*-configuration.

J. W. S.

Determination of structure of the aromatic disulphides and diselenides RS(Se)·S(Se)R (R= Ph, CH₂Ph, Bz). L. EGARTNER, F. HALLA, and R. SCHACHERL (Z. physikal. Chem., 1932, **B, 18**, 189— 198).—Determination of the lattice structure and consts. has shown that in these compounds the dis-

tance between the S or Se atoms $>$ the interat. distance in the lattices of these elements, this effect being much more pronounced with the S than with the Se compounds.

R. C.

Rotation of carbon chains. J. D. BERNAL (Z. Krist., 1932, **83**, 153—155; cf. A., 1930, 1097; this vol., 451).—Dodecylol shows both rotating and fixed forms, with transition point at 16°; octadecyl-ammonium chloride a new fixed form in which the chains in alternate double layers slope in opposite directions. The following data are given (in this order), a, b, c (in Å.), β, d, mols. in unit cell, space-group (h denotes the high- and l the low-temp. form): $C_{29}H_{60}$ (h) 8·40, 4·85, 77·2, 90°, 0·86, 2, $C6/mcm$ (cf. A., 1928, 1176); $C_{12}H_{25}·OH$ (h) 8·25, 4·76, 34·0, 90°, 0·905, 2, $C3m$; $C_{16}H_{33}·OH$ (l) 8·80, 4·90, 44·2, 56° 40′, 0·99, 4, $P2/a$; $C_{15}H_{31}·CO_2H$ (h) 9·36, 4·95, —, —, 1·28 ?, 4, $P2/a$?; $C_7H_{15}·NH_2,HCl$ (h) 4·96, 4·96, 21·1, 90°, 1·14, 2, $P4/nmm$; and $C_{18}H_{37}·NH_2,HCl$ (l) 5·45, 5·40, 69·4, 90°, 0·97, 4, $P2_12_12_1$.

C. A. S.

Crystalline structure of hexuronic acid. E. G. COX (Nature, 1932, **130**, 205—206).—Hexuronic acid (d 1·65) has a 17·71, b 6·32, c 6·38 Å., β 102·5°; space-group C_2^2 ($P2_1$) with 4 mols. of $C_6H_8O_6$ per unit cell. X-Ray and optical results indicate that the hexuronic acid mol. has a ring structure with fewer groups projecting out of the plane of the ring than a normal carbohydrate.

L. S. T.

Crystal structure of dihydrocinchonine dihydrobromide. F. SPAENHAUER (Z. Krist., 1932, **83**, 112—116).—$C_{19}H_{24}ON_2,2HBr$ (cf. this vol., 759) is rhombic sphenoidal, $a:b:c = 0·0793:1:0·8486$, n_α 1·601, n_β 1·632, $n_\gamma-n_\alpha$ 0·132. It is isomorphous with cinchonine dihydrobromide, and not pyroelectric.

C. A. S.

Retentivity and hysteresis of magnetostriction for nickel. F. LICHTENBERGER (Z. Physik, 1932, **77**, 395—397).

A. J. M.

Barkhausen effect. III. Nature of change of magnetisation in elementary domains. R. M. BOZORTH and (MISS) J. F. DILLINGER (Physical Rev., 1932, [ii], **41**, 345—355; cf. A., 1930, 673; this vol., 327).—From an examination of annealed Fe, hard-worked Fe, and perminvar the longitudinal and transverse changes in magnetic moment with magnetisation were investigated, and interpreted in terms of the domain theory.

N. M. B.

Plastic limit properties of natural rock-salt deposited under water. L. PIATTI (Z. Physik, 1932, **77**, 401—403).

A. J. M.

Thermo- and galvano-magnetic properties of a bismuth crystal. H. E. BANTA (Physical Rev., 1932, [ii], **41**, 239—250).

N. M. B.

Variation with temperature of the thermo-electric power of nickel and some copper–nickel alloys. K. E. GREW (Physical Rev., 1932, [ii], **41**, 356—363).—The thermoelectric power against Pt was measured for pure Ni, a 94% Ni–Cu, and a 79% Ni–Cu alloy. Results are discussed in relation to Stoner's theory.

N. M. B.

Determination of true specific heats of certain gases at high temperatures by the Lummer–Pringsheim method. A. EUCKEN and O. MÜCKE (Z. physikal. Chem., 1932, B, 18, 167—188).—By means of an apparatus permitting the measurement of sp. heat under pressures of several atm. sp. heats at const. pressure of O_2, N_2, H_2, and CO_2 have been determined at 100—600°. Within the limits of experimental error (about 0·3%) the results can be represented by the Planck–Einstein formula, using characteristic temp. derived from band spectroscopic data. Sp. heat vals. obtained by the velocity of sound method, particularly for O_2 and N_2, are too low because the sound frequency is so high that the oscillational degrees of freedom are unable to absorb their full share of energy. R. C.

Heat capacities of some hydrogen halides at high temperatures as calculated from Raman spectra. J. B. AUSTIN (J. Amer. Chem. Soc., 1932, 54, 3459—3460).—Vals. for HCl, HBr, and HI are compared with the vals. selected by Eastman (U.S. Bur. Mines, Tech. Paper 445). C. J. W. (c)

Heat capacity of selenium from 100° to 300° abs. T. DE VRIES and L. F. DOBRY (J. Amer. Chem. Soc., 1932, 54, 3258—3261).—C_p for metallic Se varies from 6·08 at 100° to 7·25 at 300° abs. L. P. H. (c)

Heat capacity and free energy of formation of ethylene gas. M. E. HAAS and G. STEGEMAN (J. Physical Chem., 1932, 36, 2127—2132).—The sp. heat of gaseous C_2H_4 at 2·5—66·8°, measured with an error of $\pm 1\%$, may be represented by $C_p = 4·064 + 0·02022T$. Using these and previously published data, the free energy of formation at 0—1000° has been calc. G. M. M. (c)

Active oxides. LIII. Natural constants of stable zinc oxide. G. F. HÜTTIG and K. TOISCHER (Z. anorg. Chem., 1932, 207, 273—288).—A compilation and crit. review of data recorded in recent literature for the following properties of ZnO : m.p., v.-p. curve, heat of sublimation, triple point, sp. heats, crystal lattice consts., d, infra-red spectrum, compressibility, thermal expansion, nature of lattice, atom and ion radii, existence of modifications, κ. E. S. H.

Affinity. LVIII. Compounds of gallium and indium. VIII. Ammoniates of gallium halides. W. KLEMM, W. TILK, and H. JACOBI (Z. anorg. Chem., 1932, 207, 187—203 ; cf. this vol., 998).—The following data have been determined : $GaCl_3,NH_3$, d_4^{23} 2·189, m.p. 124°, mol. heat of formation 33 kg.-cal.; $GaBr_3,NH_3$, d_4^{25} 3·112, m.p. 124°, mol. heat of formation 30 kg.-cal.; GaI_3,NH_3, d_4^{25} 3·635, m.p. 140°, mol. heat of formation 27 kg.-cal. The results are discussed in relation to the corresponding vals. for compounds of Al and In. $GaCl_2$ does not form ammoniates ; at low temp. it reacts with NH_3, forming Ga and $GaCl_3,3NH_3$; above 100° the products of interaction of Ga powder and NH_3 are GaN and H_2. Notes are given on the use of the diphenyl oxide calorimeter. E. S. H.

Compounds of gallium and indium. V. Properties of gallium trihalides. W. KLEMM and W. TILK (Z. anorg. Chem., 1932, 207, 161—174; cf. A., 1927, 812, 831).—The following data have been determined : $GaCl_3$ has m.p. 78·0$\pm$0·3°, b.p. 205$\pm$1° (759 mm.), d (solid) 2·47, d (liquid) 2·06$_3$—0·0020$_5(t-78°)$, expansion coeff. (liquid) 100×10^{-5}, equiv. conductivity at m.p. <10^{-7}; $GaBr_3$ has m.p. 124·5$\pm$0·5°, b.p. 284$\pm$1°(750 mm.), d (solid) 3·69, d (liquid) 3·13$_8$—0·0029$_5(t-125°)$, expansion coeff. (liquid) 94×10^{-5}, equiv. conductivity at m.p. 5×10^{-6}; GaI_3 has m.p. 210$\pm$1°, b.p. 337$\pm$5°, d (solid) 4·15, d (liquid) 3·60$_0$—0·0022$_4(t-211°)$, expansion coeff. (liquid) 62×10^{-5}, equiv. conductivity at m.p. 2×10^{-2}; $SnCl_4$ has d (liquid) 2·35$_5$—0·0025$_5(t+33°)$; SnI_4 has d (liquid) 3·73$_8$—0·0024$_6(t-143°)$, equiv. conductivity at m.p. 10^{-6}; TiI_4 has d (liquid) 3·42$_6$—0·0021$_9(t-150°)$, equiv. conductivity at m.p. 10^{-6}. E. S. H.

Vapour pressures, evaporation, condensation, and adsorption. I. LANGMUIR (J. Amer. Chem. Soc., 1932, 54, 2798—2832).—The v.p., p, of liquids and solids may be represented by $p = AT^\gamma e^{-b/T}$, where p is in bars, and A, b, and γ are consts. Trouton's rule is equiv. to putting $\gamma = 0$ and $A =$ a universal const. Published v.-p. data for 20 elements give the val. 10·65$\pm$1·19 for log A. Hildebrand's rule is obtained with $\gamma = 1$ and log $A = 7·83\pm0·52$. Better results are obtained with $\gamma = 1·5$ and log $A = 6·37\pm0·22$. For solids with rigid mols. the experimental data may be represented by putting $\gamma = 1·5$ and log $A = 6·9$, but if the vapour mols. have internal degrees of freedom much larger vals. of A are required. Application of the v.-p. equation to adsorption shows the rate of evaporation, r, of atoms or mols. from monat. adsorbed surface films to be given by $r = A(2\pi mk)^{-\frac{1}{2}}\theta T e^{-b/T}$, where θ is the fraction of the surface covered by the adsorbed mols., of mass m. This agrees with experimental data for Th, O, and Cs films on W. Monat. and polyat. adsorbed films are treated by applying Clausius' virial to the repulsion of mol. dipoles, and by means of Gibbs' adsorption equation r can be obtained in terms of θ, T, and M, the dipole moment. By combining these equations with those of Boltzmann and Saha, equations are obtained for the rate of evaporation of ions and electrons. With W, apparently, the surface is homogeneous except for about 0·5%, on which adsorbed Cs atoms are held more firmly than on the remainder of the surface. P. H. E. (c)

Condition of water in the region 10—500° and from saturation pressure to 300 atmospheres. M. TRAUTZ and H. STEYER (Forsch. Gebiet Ingenieurwesens, 1931, A, 2, 45—52; Chem. Zentr., 1932, i, 1501).—Vals. for sp. vol. and the compressibility factor are tabulated for 50—300 atm. from 0° to 290°. The Joule–Thomson effect decreases markedly with rising temp. and between 50 and 300 atm. the inversion curve is linear. At low temp. the second differential coeff. of the heat content with respect to pressure is negative, at 50—55° it is zero, and then increases. C_p is a max. (10·7) at 250 atm., and at approx. 375° and 260 atm. the val. is 6·0. L. S. T.

Physical properties of pure ricinoleic acid ; refractive index, specific gravity, and viscosity. E. ANDRÉ and C. VERNIER (J. Rheology, 1932, 3, 336—340).—The prep. of very pure ricinoleic acid is described. The Na salt crystallises readily from

EtOH, and it is suggested that pure soaps may not be colloidal. For the pure acid the variation of n with temp. (15—53°) is given by $n_D = 1.4732 - 0.000035(t-15)$, d (23.6—99.7°) is given by $0.2496 - 6.53 \times 10^{-4}(t-15) - 2.2 \times 10^{-4}(t-15)^2$, viscosity (23.6—100°) is given by $\log \eta = 1.044 + 1.19(1-t/100) + 1.08(1-t/100)^2$. E. S. H.

Theory of flow of very rarified gases. R. DARBORD (J. Phys. Radium, 1932, [vii], **3**, 345—354). —Theoretical. E. S. H.

Inter-diffusion of metals. E. A. OWEN and L. PICKUP (Nature, 1932, **130**, 201—202).—X-Ray diagrams showing the inter-diffusion of Zn and Cu particles heated in a vac. are reproduced and discussed. Inter-diffusion is controlled by the thermal equilibrium diagram, the rate of diffusion in the various phases being different. The rate at a given temp. is independent of particle size. The fundamental law of inter-diffusion is, apparently, $c_0 - c = \Sigma K e^{-mt}$, where c is the composition at time t, c_0 the final composition, and K and m are consts. depending on temp. of inter-diffusion and are sp. for each phase. L. S. T.

Changes in the solid phase of the system copper–gold. M. LE BLANC and G. WEHNER (Ann. Physik, 1932, [v], **14**, 481—509).—An apparatus for the determination of conductivity in the system Au–Cu is described. For Cu there is a secondary dependence of conductivity on nuclear size which is not observed for Au. The data for alloys tempered below 450° give a curve with three max. corresponding with the existence of the compounds Cu_3Au, Cu_3Au_2, and $CuAu$, all of which form mixed crystals with excess of Cu or Au. The results were confirmed by thermo-electric force, micrographic, and X-ray determinations. A. J. M.

Constitution of the copper–silver series of alloys examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1932, **28**, 705—707).— The liquid solution consists of monat. mols. of Cu and Ag; the solid solutions consist of monat. Ag dissolved in monat. Cu, and of monat. Cu dissolved in monat. Ag. E. S. H.

Solid cadmium amalgams. X-Ray proof of compound Cd_3Hg. N. W. TAYLOR (J. Amer. Chem. Soc., 1932, **54**, 2713—2720).—X-Ray examination of solid Cd amalgams, annealed in a vac. at 147° for 72 hr., shows the existence of a new crystal phase, body-centred tetragonal, with a 16.53, c 12.09 A. Its range of existence is about 70—75 at.-% Cd. It may be regarded as Cd_3Hg or as a solid solution of Hg in Cd_3Hg. H. F. J. (c)

Crystal structures of electro-deposited alloys. X-Ray diffraction study of silver–cadmium deposits. C. W. STILLWELL and L. E. STOUT (J. Amer. Chem. Soc., 1932, **54**, 2583—2592).—Electro-deposited Ag–Cd alloys from 96.0% to 31.0% Cd are either solid solutions or compounds. For any given composition the phase stable in the thermal alloy is the predominant phase in the electro-deposited alloy. Because of the presence of appreciable amounts of phases not found in a thermal alloy of the same composition, the complete composition of the electro-deposited alloy cannot be predicted. L. W. (c)

Recrystallisation and crystal recovery of pure aluminium and some hardenable aluminium alloys containing copper after cold deformation. H. BOHNER and R. VOGEL (Z. Metallk., 1932, **24**, 169—178).—The primary and secondary recrystallisation structures of Al and its light alloys depend, not only on the composition of the alloy and the temp. and time of annealing, but also on thermal and mechanical treatment the metal has undergone, i.e., on the temp., nature, rate, and degree of deformation, and on the size and orientation of the original structure. Under certain conditions the surface layers of rolled sheets present a greater resistance to recrystallisation than does the core, and the time required to obtain a coarse-grained secondary structure is much longer than that required to obtain a fine-grained recrystallisation structure. The crit. region of deformation is greater for Al than for hardenable Cu–Al alloys; in the latter case increase in Si content lowers the crit. degree of deformation and the recrystallisation temp., whereas addition of Mn increases the crit. degree of deformation. After secondary recrystallisation of Cu–Al alloys containing Si, Mg, Mn, Cr, or Ti a regular, chess-board-like structure appears in the Lüder lines which are formed in stretching specimens quenched from 500°. The period of crystal recovery of deformed Al and its alloys depends on the thermal and mechanical treatment of the metal before deformation and is generally considerably influenced by small variations in the composition. It follows, therefore, that in the construction of recrystallisation diagrams for deformed metals and alloys the composition must be kept rigidly const. during all the tests and the thermal and mechanical treatment between casting and final deformation before recrystallisation must be standardised. A. R. P.

Time–potential curves on iron and steel and their significance. T. P. HOAR and U. R. EVANS (Iron and Steel Inst., Sept. 1932. Advance copy, 12 pp.).—Time–potential curves may be obtained by touching the metal with a filter-paper strip containing the electrolyte and connected with a N-$HgCl$ electrode in the usual way; rising curves show repair and falling curves a breakdown of the oxide film. Curves for iron and steel show rapidly falling potentials in chloride and sulphate solutions, whereas in phosphate and chromate solutions there is a rise in potential indicating a tendency to self-repair of the film. Repair is more readily effected in SO_4'' than in Cl' solutions, with pure Fe than with steel, and with smooth surfaces than with rough. Pure Fe treated with CrO_4'' shows a rise in potential when first placed in SO_4'' solutions, but a sudden breakdown occurs; a similar effect occurs in Cl' solutions, but the breakdown is more rapid. Fe alloys containing Cr give rising, falling, or level potential curves in plain Cl' solutions according to the conditions. A. R. P.

System Mg–Al–Cu. A. PORTEVIN and P. BASTIEN (Compt. rend., 1932, **195**, 441—443; cf. A., 1919, ii, 414; 1931, 1224; B., 1932, 429).—Within the limits represented by Mg–Mg_4Al_3–Mg_2Cu the thermal equilibrium data afford evidence of the solid phases Mg, Mg_4Al_3, Mg_2Cu, and $Mg_2Al_3Cu_2$, and two eutectic points at 412° and 484°. The resistivity decreases

with increase in the Al content, but increases with the Cu content unless the Al $>10\%$, when the opposite effect is produced. C. A. S.

Constitution of the Fe–C–Si system. A. Křiž and F. Poboŕil (Iron and Steel Inst., Sept., 1932. Advance copy, 27 pp.).—The equilibria for sections through the 3-dimensional diagram have been plotted at 4, 6, 8, 10, and 16% Si parallel with the plane of the binary system Fe–C and at 0·1, 0·22, 0·52, and 2·54% C parallel with the plane of the binary system Fe–Si, and based on these pseudo-binary sections isothermal sections have been constructed through the space diagram at 1000°, 1160°, 1170°, and 1300°. In the metastable system the non-variant equilibrium $\alpha+\gamma+$carbide$+$liquid occurs at 1155°; the compositions represented by the edge points of the 4-phase plane are $\alpha=10\cdot2\%$ Si, 0·26% C, $\gamma=8\cdot2\%$ Si, 0·54% C, and $L=6\cdot9\%$ Si, 2·61% C. In the stable system the non-variant 4-phase equilibrium occurs at 1165°, and the edge points of the plane are $\alpha'=9\cdot7\%$ Si, 0·22% C, $\gamma'=7\cdot7\%$ Si, 0·52% C, $L'=6\cdot4\%$ Si, 2·54% C, and $C=100\%$ C. (Cf. B., 1930, 1031.) A. R. P.

X-Ray study of phase boundaries in thermal diagrams of alloy systems. Cu–Zn system. E. A. Owen and L. Pickup (Proc. Roy. Soc., 1932, A, **137**, 397—417).—An X-ray precision camera has been used to determine parameter vals. of the lattices of various phases in the Cu–Zn system with an accuracy of 1 in 4000; the data are employed to ascertain the phase boundary compositions. The increase in parameter with composition in a pure phase is independent of temp.; for mixed phases the parameter vals. of both phase lattices are independent of the composition in this region, but these values vary with temp. At a fixed temp. the const. parameters of a phase depend on the nature of the admixed phase. The X-ray method of phase boundary determination appears to give data as accurate as those given by other methods previously employed. L. L. B.

Thermal behaviour of certain solid solutions. E. L. Nichols and (Miss) M. A. Ewer (J. Opt. Soc. Amer., 1932, **22**, 456—465; cf. this vol., 793).—When ThO containing Tb, Pr, or U as activator is heated from above by a Bunsen flame to luminescence, one or more of the following effects may be observed after removal of the flame. (*a*) An evanescent glow may appear a fraction of a sec. to 2 sec. afterwards, characterised by an abrupt rise of temp. of 10—128°. (*b*) The temp. may rise steadily to a max. and then fall more slowly than normally, but with no abrupt disturbance. (*c*) A second disturbance may be observed in the cooling curve some sec. after the subsidence of effect (*b*). (*d*) With Th_2O_3 activated by Tb a succession of abrupt perturbations occur at 400—150° and at about 5-sec. intervals. (*e*) Contact with cold H_2 when at a temp. above 200° causes a rise in temp. (*a*) is explained as due to oxidation of the reduced material or of occluded H_2, (*b*) to the gradual oxidation of suboxides or occluded H_2, (*c*) to belated release and oxidation of H_2, (*d*) to crystallographic changes in the cooling substance, and (*e*) to storage and subsequent oxidation of the H_2. J. W. S.

Diffusion of sodium chloride in aqueous solutions. L. J. Burrage (J. Physical Chem., 1932, **36**, 2166—2174).—The diffusion coeff. has been measured at 0—6M, and is a min. at about 1·5M. The coeff. for 0·1M-HCl has also been measured. R. H. C. (c)

System water–phenol. I. Densities. O. R. Howell (Proc. Roy. Soc., 1932, A, **137**, 418—433). —The d–concn. curve is complex for each temp., and there is no apparent continuity between the H_2O-rich and PhOH-rich portions. The d–temp. curve for each concn. can be represented by $d_t=d_{20}+\alpha(t-20)+\beta(t-20)^2$. The curves representing the mean d and mean concn. of the conjugate solutions are parabolic and can be expressed by $d_t^{\mathrm{mean}}=d_{20}^{\mathrm{mean}}-5\cdot75\times10^{-4}(t-20)-2\cdot50\times10^{-6}(t-20)^2$ and $wtC_t^{\mathrm{mean}}=wtC_{20}^{\mathrm{mean}}-9\cdot0\times10^{-2}(t-20)-5\cdot5\times10^{-4}(t-20)^2$, respectively. Pure PhOH melts at $40\cdot85\pm0\cdot05°$ and the crit. solution temp. is 66·4°. L. L. B.

Solubility of nitrogen in water at 25° from 25 to 1000 atmospheres. R. Wiebe, V. L. Gaddy, and C. Heins, jun. (Ind. Eng. Chem., 1932, **24**, 927). —The absorption coeff. at 1 atm. is about 20% less than that of H_2, but at 1000 atm. N_2 is less than half as soluble as H_2. J. W. S.

Solubility of gold in mercury. V. J. T. Anderson (J. Physical Chem., 1932, **36**, 2145—2165).—The solubility of Au in Hg at 280—400°, and the composition of the solid and liquid phases in the system Pb–Au–Hg at 295—360° have been determined. The Au–Hg solubility curve shows a break at 310°. R. H. C. (c)

Determination of solubility in liquefied gases. I. Solubility of potassium nitrate in liquid ammonia. A. J. Schattenstein and A. Monossohn (Z. anorg. Chem., 1932, **207**, 204—208).—Apparatus is described for determining the solubility of substances in liquefied gases and the d of the solution. The solubility of KNO_3 in liquid NH_3 is 9·7 g. per 100 g. of solution at 0° and 10·6 at 25°. E. S. H.

Solubility of calcium sulphate and calcium carbonate at 182—316°. F. G. Straub (Ind. Eng. Chem., 1932, **24**, 914—917).—The solubilities of both $CaSO_4$ and $CaCO_3$ decrease with rise of temp. over the range 182—316°. The influence of Na_2SO_4 on the solubility of these compounds has also been investigated, and from the data the activities of $CaSO_4$ for ionic strengths up to 0·05 have been calc. J. W. S.

Waters containing calcium sulphate and their use in cooling [plant]. [Solubility of calcium sulphate in presence of sodium chloride.] P. Leone and S. Vinti (Annali Chim. Appl., 1932, **22**, 393—394).—The solubility of $CaSO_4$ in H_2O containing NaCl in varying amounts from 0 to 15% at 15°, 20°, 40°, and 70° is tabulated. In 10% and 15% NaCl the solubility is considerably less at 70° than at 15°, and $CaSO_4$ may therefore separate out if natural (*e.g.*, Sicilian) waters containing much NaCl and $CaSO_4$ are used in cooling plant. E. W. W.

Solubilities of the phosphates of lead. M. Jowett and H. I. Price (Trans. Faraday Soc.,

1932, **28**, 668—681).—The solubilities of PbHPO$_4$, Pb$_3$(PO$_4$)$_2$, and Pb$_5$Cl(PO$_4$)$_3$ in aq. solutions at 37·5° have been determined and the solubility products calc. PbHPO$_4$ and Pb$_3$(PO$_4$)$_2$ are in equilibrium when [PO$_4'''$] is $3 \times 10^{-6} M$; in presence of even very low [Cl'], Pb$_5$Cl(PO$_4$)$_3$ is the stable compound. A rocking electrode vessel for use with fluid Pb amalgams is described and a val. for E_0 of cells containing a Pb electrode and a liquid junction (saturated KCl) has been obtained. The first ionisation const. of H$_3$PO$_4$ at 37·5° has been determined.   E. S. H.

Solubility of uric acid and the primary urates in water and salt solutions at 37°, with special reference to the formation of sediments in the urinary passages. G. HAMMARSTEN (Compt. rend. Lab. Carlsberg, 1932, **19**, No. 7, 1—66).—Solubilities and solubility products for Li and K urates and for the stable and unstable forms of the Na and NH$_4$ salts are given, corrected for the free acid present. Li and K urates give true solutions at 37°, whilst saturated Na and NH$_4$ urates are partly colloidal. The presence of salts with a common ion causes increased solubility product. Data are also given for Na urate in presence of KCl and LiCl and for K urate with LiCl and CaCl$_2$. The solubilities of NH$_4$ and Na urates in 0·02N-KCl are less than in pure H$_2$O, but increase at higher KCl concn. Salt effects cannot account for the large solubilities of uric acid and urates in urine, which are attributed to the tendency of urates to form stable supersaturated solutions. The solubility of Na urate is slightly raised by creatinine, but unaffected by hippuric acid.   J. B. B.

Aqueous solutions of quinine hydrochloride and ethylurethane. G. MALQUORI (Annali Chim. Appl., 1932, **22**, 440—448).—The solubility of quinine hydrochloride is increased in presence of ethylurethane. The n and d vals. for solutions of varying concn. and temp. are recorded; there is no indication of complex formation.   E. W. W.

Solubility of cholesterol in mixed solvents. J. WEICHHERZ and H. MARSCHIK (Biochem. Z., 1932, **249**, 312—322).—The solubility in various binary mixtures of EtOH, H$_2$O, dioxan, C$_6$H$_6$, and C$_6$H$_{14}$ has been determined. It is in no case additive; certain mixtures exhibit a very steep max., whilst if both the solvents are polar the solubility rises or falls continuously. The solubility curves closely resemble the mol. polarisation curves of the mixed solvents and may be largely interpreted in terms of the interaction between the dipoles of the component solvent mols., but in the case of mixtures of non-polar solvents (C$_6$H$_6$–C$_6$H$_{14}$) the max. may be attributed to solvation at different parts of the cholesterol mol. The solubility of cholesterol in the various simple solvents increases regularly as the dielectric const. of the solvent decreases (C$_6$H$_{14}$ is anomalous). With Bu$^\beta$OH and n-C$_5$H$_{11}$·OH cholesterol forms compounds and the (supersaturated) solutions readily form a cryst. mass. Solutions in Pr$^\beta$OH form transparent gels which are stable for several weeks; on crystallisation they yield intermol. compounds. A similar compound is formed with furfuraldehyde.   H. F. G.

Langmuir's adsorption theory and the adsorption isotherm. A. GANGULI (Kolloid-Z., 1932, **60**, 180—184).—Theoretical. Formulæ are derived by independent methods, expressing the relation between concn. of adsorbed substance and its concn. in the gaseous phase. A modified exponential equation for polar adsorption is derived.   E. S. H.

Argon and amorphous carbon, 10—710°. M. W. TRAVERS (Proc. Roy. Soc., 1932, A, **137**, 294—297). — The val. of $d \log V_{760}/d(1/T)$ is 0·98 $\times 10^3$, from which it follows that the energy change in the adsorption process between 300° and 700° is 4500 g.-cal./mol. The initial rate of adsorption is rapid, but the establishment of equilibrium is a relatively slow process.   L. L. B.

Anomalous adsorption on active charcoal. C. OCKRENT (Nature, 1932, **130**, 206—207; cf. this vol., 568, 689).—The 25° isotherm for the adsorption of PhOH by sugar-C is represented by 3 distinct curves, each of which appears to extrapolate to the origin and conforms to Langmuir's theory.   L. S. T.

Molecular and activated adsorption of carbon monoxide on manganous oxide surfaces. A. T. WILLIAMSON (J. Amer. Chem. Soc., 1932, **54**, 3159—3164; cf. A., 1931, 902).—The adsorption on MnO and MnO–Cr$_2$O$_3$ mixtures has been measured from −190° to 444°. The adsorption is mol. at low temp., with a heat effect = 1000—2000 g.-cal., but activated adsorption becomes noticeable above 0°. The activated absorbate partly reduces the catalyst. The reaction 2CO ⟶ C+CO$_2$ possibly occurs on MnO at 444°, but is not measurable below 300°.   G. M. P. (c)

Absorption of oxygen by sheets of rubber. G. A. LINHART (J. Physical Chem., 1932, **36**, 1908—1911).—Kohman's results (B., 1929, 334) may be represented by $C = C_\infty bt^a/(1 + bt^a)$, where c is the absorption at time t and a and b are consts.   S. L. (c)

Adsorption from solutions and its relation to the nature of the solvent and the adsorbed material. N. SATA and K. KURANO (Kolloid-Z., 1932, **60**, 137—141).—The degree of adsorption of o-, m-, and p-C$_6$H$_4$(NO$_2$)$_2$, -NO$_2$·C$_6$H$_4$·NH$_2$, and -NO$_2$·C$_6$H$_4$·OH from solutions in COMe$_2$, CCl$_4$, and C$_6$H$_6$ by C varies antibatically with the solvent power of the medium, and increases with the polar character of the solvent. Adsorption and solubility of the solute do not always vary in opposite directions. The polar properties of the solvent appear to have a greater influence than those of the solute.   E. S. H.

Inner adsorption in crystalline salts. A. KOLUSCHEWA and P. SEWRUGOWA (Kolloid-Z., 1932, **60**, 141—145).—Experiments on the inclusion of K·, Na·, Ca··, Cl', NO$_3$', KMnO$_4$, NaMnO$_4$, and Ba(MnO$_4$)$_2$ by BaSO$_4$ ppts. have given results in agreement with the views of Balarev (A., 1931, 795, 1121).   E. S. H.

Adsorption of certain alkaloids on inorganic adsorbents. G. MALQUORI (Annali Chim. Appl., 1932, **22**, 448—455).—The adsorption of nicotine, caffeine, and quinine hydrochloride on gels of SiO$_2$ and of the hydroxides of Al, Cr, and Fe is consider-

able, and follows Freundlich's law. The SiO_2 gel is much more active towards nicotine than towards quinine hydrochloride; hydrolytic adsorption of the latter is not observed. E. W. W.

Absorption of organic solvents by active charcoal, silica gel, and wash-liquids. E. BERL and L. WILL (Angew. Chem., 1932, **45**, 557—559).—The v.p.-composition curves for a no. of org. liquid binary mixtures are compared with the adsorption isotherms for C and SiO_2 gel. Excepting tetralin–CCl_4 and tetralin–C_6H_6, all the mixtures examined deviate from the requirements of true solutions. Comparison of the v.-p. curves with the heat changes on mixing suggests that the degree of mol. association is reduced in mixtures of (a) tetralin with EtOH, Et_2O, $COMe_2$, EtOAc, and hexane, (b) AcOH with Et_2O, hexane, CCl_4, C_6H_6, and $COMe_2$, and (c) cyclohexanol with EtOAc, hexane, CCl_4, C_6H_6, and EtOH. In other mixtures adsorption or compound formation is indicated. It is emphasised, however, that it is not possible to differentiate strictly between dissolution, depolymerisation, and adsorption. E. S. H.

Action of charcoal on dissolved heavy-metal [salts], especially platinic chloride. E. HEYMANN (Z. anorg. Chem., 1932, **207**, 251—256; cf. A., 1928, 471; 1930, 435).—The Pt compound adsorbed from aq. $PtCl_4$ by highly-purified beechwood C at room temp. can be removed by washing with HCl; it probably consists of $Pt(OH)_4$ or other hydrolytic product, although X-ray examination failed to reveal its composition. At 100° metallic Pt is adsorbed and has been identified by X-ray analysis. E. S. H.

Hysteresis loop in the vapour pressure–concentration isotherms of the system human hair–water and its disappearance by careful removal of foreign gases. R. FRICKE and H. MARQUARDT (Kolloid-Z., 1932, **60**, 124—129).—Hysteresis is observed in presence of air, but the curves representing absorption and loss of H_2O are coincident when gases are removed by high vac. (cf. A., 1930, 1118). E. S. H.

Equilibrium-layer theory of the formation of liquid films. C. W. FOULK (Kolloid-Z., 1932, **60**, 115—124).—Mainly a summary of published work (A., 1929, 1232; this vol., 17). Further results are given for the difference between static and dynamic surface tension in solutions of H_2SO_4 and of sucrose. E. S. H.

Absorption and classical diffusion. A. T. McKAY (Trans. Faraday Soc., 1932, **28**, 721—730). —Mainly theoretical. Experimental data are given for the absorption of H_2O by fibre boards and by waxed upper leather. E. S. H.

Quantum mechanics of activated adsorption. A. SHERMAN and H. EYRING (J. Amer. Chem. Soc., 1932, **54**, 2661—2675).—The temp.-sp. reaction rate curve for bimol. surface reactions in general exhibits a max. The quantum mechanical calculation of the activation energies for the hydrogenation of C_2H_4 and C_2H_2 and the activated adsorption of H_2 on charcoal indicates a probable mechanism for the ortho-para-H_2 conversion. H. F. J. (c)

Mechanism of ionic exchange in colloidal aluminium silicates. H. JENNY (J. Physical Chem., 1932, **36**, 2217—2258; cf. A., 1927, 415).—Electrodialysed colloidal Al silicates behave like colloidal acids, the order of strength being permutite < Putnam clay < bentonite. The lyotropic series for the adsorption of cations is Li < Na < K < Rb < Cs < H for permutite, Li = Na < K < H for Putnam clay, and Na = Li < K < H for bentonite. The release of adsorbed cations takes place in the reverse order. An explanation of the specificity of the behaviour of the cations in the exchange process is based on the magnitude of the attraction between the negative O ions of the lattice and adsorbed cations. C. T. S. (c)

Adsorption at the surface of solutions. I. Surface composition of H_2O–EtOH solutions. J. A. V. BUTLER and A. WIGHTMAN. **II. Effect of lithium chloride on the surface of H_2O–EtOH solutions.** J. A. V. BUTLER and A. D. LEES (J.C.S., 1932, 2089—2097, 2097—2104).—I. The vals. of surface tension of H_2O–EtOH solutions, determined at 25° by the max. bubble pressure method, agree with those obtained by Bircumshaw (J.C.S., 1922, **121**, 887) by the drop wt. method, and also with some by the capillary rise method. Vals. for the Gibbs adsorption have been calc. and the connexion between the Gibbs adsorption and the surface composition is derived for the case in which the adsorption affects the surface layer only. The results show that in certain concns. there is a small excess of EtOH mols. in the solution under the surface layer. Estimated compositions of the surface layer are given, and also of the adsorption below it.

II. The Gibbs equation is used to determine the adsorption of two components at the surface of a ternary solution with reference to the third as zero. Vals. of the surface tension for the system H_2O–EtOH–LiCl have been determined at 25° by the capillary rise method, and the adsorption of H_2O and EtOH with respect to LiCl is calc. At small concns. of LiCl, as for salt-free H_2O–EtOH mixtures, there is an approx. complete unimol. layer of EtOH at the surface of solutions which contain more than 6 mols.-% EtOH. The ions are separated from the under surface of this layer by a layer of solution, the thickness of which decreases as the EtOH concn. increases, and disappears in pure EtOH solution. This is attributed to the hydration of the ions. At high LiCl concns. the ions penetrate the surface to an increasing extent. M. S. B.

Surface activity and orientation of polar molecules in relation to nature of interface. VII. Surface activity and adsorption of p-toluidine at liquid–liquid interfaces. VIII. Analysis by surface tension measurements. Determination of partition coefficients of surface-active substances by capillary-manometric titration. A. TAUBMANN (Z. physikal. Chem., 1932, **161**, 129—140, 141—146; cf. A., 1930, 687).—VII. Measurements of the interfacial tension between aq. solutions of p-toluidine and hexane or C_6H_6 have shown that the adsorption at the interface obeys Langmuir's adsorption isotherm. At an air–aq. toluidine interface, however, the isotherm is applicable only at the higher

concns. For all three interfaces the surface occupied by a mol. in the saturated adsorption layer is $25 \cdot 8 \times 10^{-16}$ sq. cm., and the axial length of an oriented mol. is $6 \cdot 6 \times 10^{-8}$ cm.

VIII. Since, in general, surface-active acid or basic substances lose their activity when converted into salts by strong inorg. bases or acids, the end-point in titration may be found by measurements of surface tension, γ, preferably by the max. bubble pressure method. As titration proceeds γ rises, and becomes const. at the equiv. point. This method may be used to determine the solubility of surface-active substances in H_2O and their distribution ratio between H_2O and org. solvents. R. C.

Surface activity and electrical properties of molecules. V. K. SEMENTSCHENKO (Kolloid-Z., 1932, **60**, 177—180).—Theoretical. E. S. H.

Variation of surface tension of aqueous solutions of certain complex organic substances with time. J. C. GHOSH and M. C. NOTH (J. Physical Chem., 1932, **36**, 1916—1927).—Measurements have been made with solutions of various dyes. With true solutions, e.g., fuchsin-red, the surface reaches equilibrium too rapidly for the variation of the surface tension, γ, with time, t, to be measured; with solutions containing mainly multimol. aggregates, e.g., benzopurpurin solutions, γ changes with t as equilibrium is being established, and with colloidal dispersions, e.g., fuchsin-red with KCl, γ varies with t in a rather irregular manner. These observations have been confirmed by dialysis experiments. S. L. (c)

Capillarity. XVII. Behaviour of organic liquids between parallel plates. K. SCHULTZE (Kolloid-Z., 1932, **60**, 132—136).—The anomalies reported (this vol., 112) in the capillary rise of H_2O between small, parallel glass plates have also been observed with several org. liquids. E. S. H.

Optical detection of removal of films from iron. W. J. MÜLLER and W. MACHU (Z. physikal. Chem., 1932, **161**, 147—153).—Polemical against Tronstad (cf. this vol., 343). R. C.

[**Optical detection of removal of films from iron.**] L. TRONSTAD (Z. physikal. Chem., 1932, **161**, 154—157).—A reply to criticism (cf. preceding abstract). R. C.

[**Optical detection of removal of films from iron.**] W. J. MÜLLER and W. MACHU (Z. physikal. Chem., 1932, **161**, 158).—Final comments (cf. preceding abstracts). R. C.

Viscosity of potassium chlorate in aqueous solution. G. R. HOOD (J. Rheology, 1932, **3**, 326—333).—Viscosities of $KClO_3$ solutions have been determined at 18° between 0·002 and 0·525M and at 25° between 0·01 and 0·525M. The fluidity ϕ at 18° is related to the concn. c by the expression $\phi = 1 - 0·0028\sqrt{c} + 0·049c - 0·0275c^2$. An increase of viscosity due to ionic forces tending to maintain a space lattice structure has been observed. E. S. H.

Dependence of magnetism of Cr^{+++} in aqueous violet chromium nitrate solutions on concentration. Relation between the constants C and

θ of Weiss' law. H. FAHLENBRACH (Ann. Physik, 1932, [v], **14**, 524—530).—The behaviour of Cr^{+++} is similar to that observed with Co^{++} and Ni^{++}. At high concns. a complex anion is probably formed. The magnetic ionic moment is a little different from that given by Bose's theory. With increasing dilution the val. approximates to that derived from Hund's theory. A. J. M.

Demonstration of Tyndall effect. K. SCHUWIRTH (Kolloid-Z., 1932, **60**, 217).—A lecture experiment. E. S. H.

Electrical properties of dust and mist. H. SACHSSE (Ann. Physik, 1932, [v], **14**, 396—412).—Aërosols formed by condensation of vapour (As_2O_3, NH_4Cl, SO_3, $TiCl_4$) and paraffin oil are uncharged, as are also the mists obtained by atomising liquids. The aërosols obtained by other methods are charged, half the particles being charged positively, and the rest negatively. Charges produced by friction are proportional to the square of the radius of the particle. A. J. M.

Deduction of particle shape and size from viscosity and flow double refraction. W. KUHN (Z. physikal. Chem., 1932, **161**, 1—32; cf. this vol., 571).—Particles suspended in a streaming liquid have both translatory motion and rotational motion about their centres of gravity. For spherical particles the rotation is uniform, but elongated particles tend to assume a particular orientation in relation to the direction of flow, this tendency being opposed by the Brownian motion. If v, the rate of flow, is small, the particles tend to make an angle of 45° with the direction of flow, independently of whether they are almost spherical or are much greater in length than in thickness. With increase in v this angle diminishes, and from the change the length, l, of the particles may be deduced. Unless the particles are spherical, they increase the viscosity, η. With very long particles, the ratio of l to the thickness may be obtained from η. It is suggested that variation of η with v is due to the particles aggregating loosely to form chains or networks, which break up when v is greater. Calculation of the forces holding together these aggregates gives vals. which indicate that the ordinary forces of adhesion are adequate for the purpose. R. C.

Determination of the magnitude, form, and solvation of macro-molecules. G. V. SCHULZ (Naturwiss., 1932, **20**, 592).—If the sp. solvation vol. of a lyophilic colloidal solution, as determined by osmotic pressure measurements, is introduced into the Eisenschitz formula for the relative viscosity, a val. in good agreement with experiment is obtained. W. R. A.

Optics of colourless sols. I. Theoretical derivation of absorption coefficients. T. CASPERSON (Kolloid-Z., 1932, **60** 151—159).—With the help of Mie's theory the absorption coeffs. of colourless sols are calc. for different vals. of n, wave-length, and particle size. E. S. H.

Mercury as a dispersing medium. N. M. TSCHUJKO (Ukrain. Chem. J., 1931, **6**, [Sci.], 229—240).—Sols of Fe in Hg are flocculated by addition of Zn–Hg, and are stabilised by Sn–Hg. The viscosity of amalgams of Zn or of Sn differs little from that of

Hg, whilst that of Fe sols is higher. The particles of Fe are positively charged. R. T.

Constitution of colloidal gold. W. PAULI (Naturwiss., 1932, **20**, 551—557, 573—576).—The prep., constitution, and stability of sols of Au, [$AuCl_4$]H, and [$Au(OH)_4$]K are discussed.

W. R. A.

Structure of Bredig silver sols. I. J. LÖFFLER and W. PAULI (Kolloid-Z., 1932, **60**, 146—150).—Experiments on the prep., stability, and electrical conductivity of Ag sols prepared by electro-dispersion in aq. NH_3, KCl, NH_4Cl, HCl, H_2SO_4, Na_2SO_4, and in H_2O show that these sols, like the reduced Ag sols, owe their properties to the dissociation of ionogenic Ag complexes at the surface of the particles. The sols stabilised by OH' are flocculated on electro-dialysis, whilst those stabilised by Cl' exchange their cation for H˙. E. S. H.

Hydrogen-ion concentration of ferric hydroxide sols. W. L. McCLATCHIE (J. Physical Chem., 1932, **36**, 2087—2094; cf. A., 1923, ii, 218).—With glass and quinhydrone electrodes, p_H vals. of 4·05—4·43 were obtained, depending on the kind of bridge solution and the age of the sol. The H electrode gave higher and more irregular vals. Conc. aq. KCl as bridge solution seemed to give the most nearly correct result, about p_H ·4·4. Flocculation of the sol has no effect so long as it does not occur near the electrode. C. T. S. (c)

Emulsions. IV. Systems of sodium oleate, phenol, and water. I. J. WEICHHERZ and H. SAECHTLING (Kolloid-Z.,.1932, **60**, 192—210; cf. A., 1929, 260, 1379).—The viscosity of the system Na oleate–H_2O increases at all temp. with increasing concn., at first slowly and later rapidly. Systems containing >30% Na oleate are heterogeneous. The curve connecting the viscosity of PhOH–H_2O systems with composition shows two inflexion points, indicating two systems, PhOH in H_2O, and H_2O in PhOH. The viscosity–composition curves for Na oleate–PhOH systems indicate a low degree of solvation. Systems containing >20% Na oleate are heterogeneous at 80°. Complex relations are observed in the system Na oleate–PhOH–H_2O, especially in regard to the amount of H_2O. When the Na oleate content is const., the viscosity falls with increasing PhOH content. The observed behaviour is ascribed to the lower solvation and association of Na oleate in PhOH as compared with H_2O. At high concns. of H_2O the PhOH no longer acts as a solvent. The formation of acid soaps through the action of PhOH is also considered. The regions of heterogeneity in the ternary system have been determined.

E. S. H.

Von Weimarn's precipitation theory, and formation of colloidal gold. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1932, **36**, 1950—1959).—Contrary to this theory, the particles of colloidal Au formed by reduction processes are the larger the higher is the concn., c, of Au salt reduced. This cannot be explained by supposing that the hydrolysis of the Au salt with formation of $Au(OH)_3$ nuclei is the main factor determining the degree of dispersity, for the greater the hydrolysis of a Au

solution of given concn. before the addition of a reducing agent, the fewer and hence the larger are the particles; in the absence of hydrolysis the particles are the smaller the lower is c. Because of the low solubility of Au in H_2O, the percentage of supersaturation, s, is relatively high for all vals. of c. Hence the rate of formation of nuclei is not directly proportional to s, but is relatively greater at lower concns. At these concns. the growth of nuclei is comparatively slow, so that relatively more nuclei can be formed before the supply of Au is exhausted. For both reasons the primary particle size is smaller in the sols formed from more dil. solutions.

H. B. W. (c)

Fibrillograms of the lines of force of the crystallisation process. T. HUZELLA (Z. Krist., 1932, **83**, 89—96).—A drop of collagen solution, prepared by soaking the tendon of a rat's tail in very dil. AcOH, and a dil. aq. NaCl solution are allowed to interdiffuse on a microscope slide; the resulting fibre formation assumes various regular arrangements which are said to indicate the direction of action of the forces which cause crystallisation. C. A. S.

Mechanism of coagulation of sols by electrolytes. III. Exchange adsorption during coagulation of hydrous oxide sols. H. B. WEISER and G. R. GRAY (J. Physical Chem., 1932, **36**, 2178—2193; cf. this vol., 463).—The "super-equiv." displacement of Cl from hydrous oxide sols during gradual addition of electrolyte (A., 1928, 586) is the result of a faulty procedure which produces localised coagulation below the pptn. val., and does not allow time for equilibrium to be approached. By Weiser's method SO_4'' at all concns. enters into exchange adsorption with Cl' present in the diffuse outer layer of the oxide particles. The SO_4'' adsorption curve follows a smooth course above the Cl' displacement curve over the entire concn. range. C. T. S. (c)

Static and kinetic study of Liesegang rings. (MLLE.) S. VEIL (J. Phys. Radium, 1932, [vii], **3**, 302—313).—The distribution, opacity, and successive phases of formation of the rings have been investigated.

N. M. B.

Interfacially bound and structurally bound water in inorganic jellies. S. PRAKASH (Kolloid-Z., 1932, **60**, 184—191).—By interfacial hydration is understood the H_2O which is bound when the charge on the colloid particles is neutralised. During neutralisation the viscosity of the sol varies with the time t in accordance with the expression $\eta_t = \eta_0 e^{ht}$, where h is a hydration const., depending on the thickness of the adsorbed layer of H_2O mols. For ideal hydrophobic colloids h=0 and no increase of viscosity is observed during coagulation; for hydrophobic colloids h has high vals., which can be determined from viscosity–time measurements during gelation. The exponential rise of viscosity is observed only when the hydration is of the interfacial type; in the later stages of gelation the viscosity rises more rapidly, indicating structure hydration, or the enmeshing of H_2O by the units of structure. At all stages the total hydration can be calc. from Hatschek's equation and the interfacial hydration can be found by extrapolation of the exponential curve. Experiments on

jellies of $Zr(OH)_4$, Ce borate, Fe''' arsenate and phosphate, Sn arsenate and molybdate, and Th arsenate show that about 80% of the H_2O is in the state of interfacial hydration, in agreement with observations on syneresis and thixotropy. E. S. H.

Influence of temperature on the setting of inorganic jellies. S. Prakash (J. Indian Chem. Soc., 1932, 9, 193—203).—The time of setting of gels of Zr hydroxide, molybdate, and borate, Th molybdate and phosphate, Cr tungstate, Sn'''' arsenate, phosphate, tungstate, and molybdate decreases markedly with rising temp. Gels of Th arsenate, V_2O_5, and mercurisulphosalicylic acid show the reverse behaviour, but do not set above 60°; these resemble org. jellies in melting. Rise of temp. increases the rate of coagulation of the sols which do not undergo hydrolysis and thus aids setting. Gels of polybasic salts are hydrolysed at higher temp. and the hydroxides formed also form gels; the setting time then depends on the composition of the mixed phases. E. S. H.

Structure viscosity. I. Concentration function of structure viscosity of gelatin sols. Wo. Ostwald [with R. Auerbach, J. Feldmann, W. Stauf, and V. Trakas] (Kolloid-Z., 1932, 60, 159—170).—Concordant determinations have been made with 3 types of viscosimeter over the pressure range 0·5—150 cm. H_2O. Under turbulent streaming, <1% gelatin sols behave as dil. mol. disperse systems, but at low rates of flow a very great increase of viscosity is observed, due to some attraction among the structural components of the sol; the val. then varies markedly with the concn. The general results are in good agreement with the de Waele–Ostwald equation. Gelatin sols also show structure turbulence. E. S. H.

Influence of temperature and previous history on the osmotic pressure and micellary weight of gelatin solutions. M. Frankel (Biochem. Z., 1932, 249, 476—477).—A reply to criticism (this vol., 807). H. F. G.

Structure of gelatin sols and gels. IV. Fluidity and hydrolysis. S. E. Sheppard and R. C. Houck (J. Physical Chem., 1932, 36, 2319—2324; cf. A., 1930, 1518).—From data for the change of the fluidity with temp. the heat of hydrolysis is calc. to be 19,900—26,500 g.-cal., depending on the p_H (cf. A., 1927, 213). Fluidity changes are attributed to the hydrolysis of large mols. Dilatometric experiments show that the high viscosity of gelatin sols is not due to solvation. C. T. S. (c)

Modified gelatinisation and the influence of electrolytes on the sedimentation of the particles thus produced. H. G. B. de Jong and W. A. L. Dekker (Biochem. Z., 1932, 251, 105—115; cf. von Buzágh, A., 1931, 36).—The normal gelatinisation of dil. agar sols can be modified by mechanical agitation so that a "liquid gel" which shows little tendency to change its state is produced. Observations on the sedimentation of this gel and on the vol. of sediment produced when low concn. of neutral salts [KCl, $BaCl_2$, $Co(NH_3)_6Cl_3$] are present show that the vol. of the sediment and the vol. of the gel vary in opposite directions. An explanation of this phenomenon is given. W. McC.

Lyophilic colloids. XIV. Capillary-electric charge and hydration as state-variables of hydrophilic gels; changes in volume and elastic modulus of agar and gelatin gels. H. G. B. de Jong and J. P. Hennemann (Kolloid-Beih., 1932, 36, 123—177; cf. A., 1929, 1381).—The vol. of cylindrical agar gels does not vary in pure H_2O, but low concns. of neutral salts cause a decrease, the amount of which is determined by the cation. The vol. of isoelectric gelatin gels increases slightly in H_2O and the increase is greater for positively- or negatively-charged gels. The isoelectric gel is practically unchanged by low concns. of neutral salts, but the increase of vol. of the charged gels is strongly reduced thereby, the Schulze–Hardy rule again being observed. During these changes the elastic modulus of the gel does not alter. The decrease of vol. brought about by small quantities of electrolytes is due to discharge of the particles and is consistent with the view that the gel consists of an irregular network of micelles, which are in contact at certain unprotected or hydrophobic spots. Higher concns. of neutral salts may produce a considerable increase or decrease of vol., the Schulze–Hardy rule then being replaced by the lyotropic series; in these circumstances there is a corresponding change of elastic modulus, but in the opposite direction, the lyotropic series being thus reversed. These changes are almost completely reversible, especially when a vol. decrease and an elasticity increase are involved. The incomplete reversibility attending an increase of vol. is observed particularly with gelatin, especially under peptising conditions (with KI or KCNS), and is attributed to secondary changes in the gel structure. The changes brought about by the more conc. neutral salts are interpreted in terms of solvation and desolvation, and have also been observed with EtOH. Tannin reduces both the vol. and elasticity of agar gel and appears to have a different mechanism of dehydration. E. S. H.

Structure of cellulose acetate gels from studies of diffusion. K. Klemm and L. Friedman (J. Amer. Chem. Soc., 1932, 54, 2637—2642).—The rates of diffusion of 2—20% cellulose acetate in benzyl alcohol when brought in contact with MeOH or EtOH have been measured, and the diffusion coeff., D, and effective pore radius, R, calc. by means of the equations previously developed (A., 1930, 693). The law of diffusion is valid for this system. R varies from 18 mμ for 2% to almost zero for 23% gels. The high vals. of D are inconsistent with a solid solution. The entire behaviour is what would be predicted by the liquid–solid theory of gel structure. F. E. B. (c)

Electro-rheic effect of a thixotropic gel. E. Karrer (J. Rheology, 1932, 3, 334—335).—When a p.d. is applied to two parallel Pt plates, arranged vertically and holding between them a thin film of clay suspension, the suspension immediately flows off the plates. E. S. H.

Significance of capillary width for streaming potential. H. B. Bull (Kolloid-Z., 1930, 60,

3 x

130—132).—The electro-osmosis caused in very narrow capillaries during measurements of streaming potential sets up an opposing pressure, which leads to low vals. for the ζ potential. The magnitude of the effect is calc. For aq. solutions the effect becomes appreciable in capillaries of radius <1 μ and is observable with org. liquids in wider capillaries. E. S. H.

Phase-rule studies on the proteins. VII. Non-aqueous solutions. W. D. BANCROFT and S. L. RIDGWAY (J. Physical Chem., 1932, 36, 2299—2305; cf. this vol., 694).—Gelatin dissolved in a little H_2O was poured into a large amount of EtOH containing acid or base. Titration of the excess of acid or base showed compound formation with HCl, but adsorption only with NaOH. C. T. S. (c)

Flocculation of suspensions of myxoprotein by electrolytes. C. ACHARD and HO-DAC-AN (Compt. rend., 1932, 195, 429—432).—Electrolytes containing a uni- or bi-valent cation have no flocculating action on a suspension of myxoprotein from ox serum (cf. A., 1930, 235). With increasing concn. of $AlCl_3$ or $ThCl_4$ there is at first increasing flocculation, then a steady condition, followed by further increase, indicating either the presence of two substances in myxoprotein, or a difference in the sign of the charge which it carries. C. A. S.

Colloid–colloid reactions. III. Proteins and pure gold sol. K. OGIU and W. PAULI (Biochem. Z., 1932, 250, 535—548).—With high concns. of serum- and ov-albumin (highly purified by electrodialysis) Bredig's Au sol gives a voluminous red ppt. and with low concns. only a change of colour to violet. Addition of neutral salts in the first case gives a protective and in the second a sensitising action. Glycine never shows a sensitising action and in sufficiently high concn. shows a protective action. Carbamide in high concn. in the cold protects serumbut not ov-albumin against pptn. with Au sol. P. W. C.

Combination curves, buffering powers, and equivalent of serum-albumin. E. B. R. PRIDEAUX and D. E. WOODS (Proc. Roy. Soc., 1932, B, 111, 201—209).—Results of electrometric titrations for 1.0 and 0.1% aq. solutions of serum-albumin give a curve similar to, but more regular than, that obtained for ovalbumin (this vol., 631). The equiv. as an alkali, deduced from a slight inflexion at p_H 2.2, is 1150, and as an acid it is 1430 at p_H 10—11. Serum-albumin has a higher buffering power than ovalbumin, although their behaviour is identical at p_H 6—8. Results of quick titration of serum-albumin with relatively large amounts of alkali indicate that a max. of 34.5% of arginine is present. Heat-denaturation affects both albumins in the opposite direction to alkali hydrolysis, the former causing a large loss in buffering power towards acid. A. L.

Steric hindrance and collision diameters. H. EYRING (J. Amer. Chem. Soc., 1932, 54, 3191—3203).—The method of calculating the potentials between saturated mols. or groups of atoms is outlined and applied to two colliding H_2 mols. The result agrees with experiment. The potential energy curve for the collision of two saturated H atoms is used in constructing a potential for the rotation of the two Me groups about the C–C axis. The increase in reactivity of an H atom attached to C as the neighbouring H atoms are replaced by Me is explained by calculations which show that the potential of H is 3.1 kg.-cal. higher in C_2H_6 than in CH_4. M. M. (c)

Transitions in solution of salts of tervalent metals. IV. Equilibrium between the violet and green forms in solutions of chromic sulphate and sodium chromic sulphate. C. MONTEMARTINI and E. VERNAZZA (L'Ind. Chimica, 1932, 7, 1001—1004).—At $32.5°$ a solution of $Cr_2(SO_4)_3$ contains 34.5% of the violet form between the concn. limits of 3.5% and 7%. Equilibrium is established within 28 days from either side. Practically the same result is obtained with solutions of K and Na Cr alums, and the equilibrium is thus not altered by addition of K and Na sulphates. H. F. G.

Polyhalides. I. Formation and dissociation of polyhalides of hydrogen. S. K. RAY (J. Indian Chem. Soc., 1932, 9, 259—269).—F.-p. measurements for aq. solutions lead to the following dissociation consts.: $HCII_2$ 0.544, $HClBr_2$ 0.578, HBr_3 0.049. Heats of formation derived from these and data relating to $25°$ (or $30°$) are: $HCII_2$ 762, $HClBr_2$ 1044, HBr_3 1467 g.-cal. The f.p. is raised by the addition of Br to $0.5N$- or N-HBr, and of I to HBr or HI. This is ascribed to the separation of H trihalides with the ice, and the presence of these compounds in the solid phase is confirmed by analysis. A. G.

The phase rule. P. VAN RYSSELBERGHE (J. Physical Chem., 1932, 36, 1733—1737).—De Donder's form of the phase rule $v = C - r + 2 - \phi$, where v is the variance, C the total no. of constituents of the system, r the no. of distinct chemical reactions which can occur, and ϕ the no. of phases, is deduced and illustrated. The quantity $(C - r)$ is considered to be more intelligible than Gibbs' "no. of components." J. H. R. (c)

Cryoscopic examination of liquids for purity, and purification of cyclohexanol. J. LANGE (Z. physikal. Chem., 1932, 161, 77—82).—If two samples of a liquid contained in similar vessels are partly frozen, the proportion frozen being considerably greater with one sample than with the other, and are then placed in the same thermostat, the temp. difference established between them is a criterion of purity. A suitable apparatus is described. Pure cyclohexanol has m.p. $25.46°$. R. C.

Conversion of easily-crystallising substances into the glass state. G. TAMMANN and A. ELBRÄCHTER (Z. anorg. Chem., 1932, 207, 268—272).—An apparatus is described in which a melt or crystallisable solution is resolved by means of an air current into droplets (0.001—0.3 mm. diameter), which fall on to a cooled plate. The nos. of undercooled, crystallised, and vitreous drops are then counted. Results are given for some org. melts and aq. inorg. salt solutions. E. S. H.

Dilatometric determination of the transition temperatures of hydrated salts. M. MATSUI and S. KAMBARA (J. Soc. Chem. Ind. Japan, 1932, 35,

308—312B).—The following transition temp. are recorded : $Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4$, 32·377° ; $Na_2CO_3,10H_2O \rightleftharpoons Na_2CO_3,7H_2O$, 31·97° ; $Na_2CO_3,7H_2O \rightleftharpoons Na_2CO_3,H_2O$, 36·55°. The accuracy of the last two figures quoted is less than that of the first, owing to the relatively low rate of crystallisation of the salt. H. F. G.

Dilatometric determination of the transition temperature of sodium carbonate decahydrate. M. MATSUI, S. KAMBARA, and H. YOSHINO (J. Soc. Chem. Ind. Japan, 1932, **35**, 313—316B).—The transition temp. deca- $\rightleftharpoons$ penta-hydrate is 31·91°. The pasty mixture which is obtained by heating to above 32° crystallises slowly, and the dilatometric method is not very suitable under these conditions.
H. F. G.

Sodium aluminium sulphate. ASTRUC and MOUSSERON (Compt. rend., 1932, **195**, 423—425 ; cf. A., 1890, 1059).—Dilatometric, density, viscosity, and solubility measurements indicate that $NaAl(SO_4)_2,12H_2O$ undergoes partial dissociation below 11° and above 39°. C. A. S.

Osmotic (permutoid) binding of water in oxide hydrates and similar compounds. E. HEYMANN (Z. anorg. Chem., 1932, **207**, 257—267).— A theoretical discussion (cf. this vol., 228).
E. S. H.

Compounds of carbamide with alkaline-earth bromides. F. DE CARLI (Atti R. Accad. Lincei, 1932, [vi], **15**, 747—752).—Solubility data at 11° indicate the existence of the compounds $MBr_2,4CO(NH_2)_2,2H_2O$ (M=Ca or Sr) ; no evidence of these is afforded by density or fluidity measurements.
T. H. P.

System $FeO–SiO_2$. N. L. BOWEN and J. F. SCHAIRER (Amer. J. Sci., 1932, [v], **24**, 177—213).— Equilibria have been investigated in electrolytic Fe crucibles in vac. and in pure N_2 at temp. below 1523°. All the melts in equilibrium with Fe contain some Fe_2O_3, the wt.-% of which decreases rapidly from 11·5 as SiO_2 is added. Thus, synthetic and natural fayalite (Fe_2SiO_4) and all $FeO–SiO_2$ mixtures melt incongruently with the separation of Fe. However, by regarding the system as essentially binary, the following invariant points are obtained : FeO, m.p. 1380±5°, wüstite–fayalite eutectic at 76% FeO and 1177°, Fe_2SiO_4, m.p. 1205°, fayalite–tridymite eutectic at 62% FeO and 1178°. These results differ from those of others, but are consistent with those of Greig (A., 1928, 132). The separation of crystals of $FeSiO_3$ could not be induced from either the liquid or the glass at temp. as low as 660°. The bearing of these results on petrology and the problems of slag formation and furnace linings is discussed. FeO is a strong flux for SiO_2 at temp. above 1178°, but becomes relatively weak in comparison with CaO at 1450°. J. G. A. G.

Equilibrium of certain non-metallic systems. III. Systems $MnSiO_3–Fe_2SiO_4$ and $FeS–Fe_2SiO_4$. J. H. ANDREW and W. R. MADDOCKS (Iron and Steel Inst., Sept. 1932. Advance copy, 10 pp.).—The equilibrium diagram of the system $MnSiO_3–Fe_2SiO_4$ indicates that the compounds form a simple eutectiferous series with a limited solid solution range at

both ends ; the eutectic occurs at about 40% $MnSiO_4$ and 1110°. Above 90% Fe_2SiO_4 there is evidence of the formation of knebelite. The system $FeS–Fe_2SiO_4$ is also eutectiferous, the eutectic occurring at about 48% FeS and 1000° ; about 12% FeS is soluble in Fe_2SiO_4 and about 1% Fe_2SiO_4 in FeS. The d of mixtures in the systems MnS–MnO, $MnS–MnSiO_3$, $MnS–Fe_2SiO_4$, $MnSiO_3–Fe_2SiO_4$, and $FeS–Fe_2SiO_4$ are shown graphically. A. R. P.

Ceramics of highly refractory substances. V. Ternary systems $ZrO_2–ThO_2–CaO$, $ZrO_2–ThO_2–MgO$, $ZrO_2–BeO–CaO$, $ZrO_2–BeO–CeO_2$. O. RUFF, F. EBERT, and W. LOERPABEL (Z. anorg. Chem., 1932, **207**, 308—312 ; cf. B., 1929, 474 ; A., 1929, 650, 766).—The thermal equilibrium diagrams of these systems are compared with X-ray analyses of the products. Colourless glasses formed from the first three systems at 2450—2520° are described.
E. S. H.

Recommendation of certain thermodynamical symbols by the Deutsche Bunsen-Gesellschaft. A. EUCKEN and K. FAJANS (Z. Elektrochem., 1932, **38**, 681).—The following symbols are recommended : E=energy (general), especially in at. and mol. processes, U=internal energy, S=entropy, A=work added to a system, $\bar{A}$=work taken from a system, Q=heat added to a system, $\bar{Q}$=heat taken from a system. E. S. H.

Essential properties of a system of thermodynamics. M. RANDALL (Z. Elektrochem., 1932, **38**, 676—680).—A discussion. E. S. H.

Chlorine equilibria and absolute entropy of chlorine. A. R. GORDON and C. BARNES (J. Physical Chem., 1932, **36**, 2292—2298 ; cf. this vol., 695).—The entropy of Cl at 300—1000° has been calc. from spectroscopic data. From the known entropies of HCl, O_2, and steam, the equilibrium const. for the reaction $2Cl_2+2H_2O \rightleftharpoons 4HCl+O_2$ has been calc. at 600—1000°. The calc. and observed vals. agree. General considerations indicate that the existence of isotopes does not affect the entropy of reaction except as a second order effect.
G. M. M. (c)

Calculation of partial molal quantities. T. F. YOUNG and O. G. VOGEL (J. Amer. Chem. Soc., 1932, **54**, 3025—3029).—Formulæ to facilitate change of variable in the calculation of partial mol. properties of the constituents of solutions are presented.
M. M. (c)

Ionic activity coefficient product and dissociation of water in barium chloride solutions at 25°. H. S. HARNED and C. M. MASON (J. Amer. Chem. Soc., 1932, **54**, 3112—3120).—From e.m.f. data for $H_2|Ba(OH)_2(m_1)$, $BaCl_2(m_2)|Ba_xHg|Ba(OH)_2(m_0)|H_2$ and $H_2|Ba(OH)_2(m_0)$, $BaCl_2(m)|AgCl|Ag$ the activity coeff. of $Ba(OH)_2$ in aq. $BaCl_2$ has been calc. From these and previous results the ionic activity coeff. of H_2O in aq. $BaCl_2$ has been calc. The dissociation of H_2O in $BaCl_2$ solutions is a max. at the ionic strength 1·5. E. R. S. (c)

Heats of dissociation and the periodic law. C. R. BAILEY (Nature, 1932, **130**, 239—240).— Periodicity of physical properties extends to the heats

of dissociation of simple compounds not only in the same group but also in the same period. The experimental val. for CN lies 1·6 volts below the curve for N and C compounds suggesting decomp. into normal C and N atoms, and the val. of one-half the heat of formation of N_2O lies midway between NN and ON confirming the structure NNO and not NON for this gas. L. S. T.

Heat of formation of aluminium halides. W. KLEMM and H. JACOBI (Z. anorg. Chem., 1932, 207, 186).—A correction (cf. A., 1931, 1380). The correct heats of formation are $AlCl_3$ 167, $AlBr_3$ 121, AlI_3 71 kg.-cal. E. S. H.

Compounds of gallium and indium. VII. Heats of formation of gallium trihalides. W. KLEMM and H. JACOBI (Z. anorg. Chem., 1932, 207, 177—186; cf. this vol., 988).—The following heats of formation have been determined at 27° by direct interaction of Ga and the halogen in solution : $GaCl_3$ 125±1, $GaBr_3$ 92·4±0·3, GaI_3 51 kg.-cal. These vals. are compared with those of related compounds and the relation between heat of formation and energy of ionisation is discussed. E. S. H.

Heats of formation of indium trioxide and germanium dioxide. G. BECKER and W. A. ROTH (Z. physikal. Chem., 1932, 161, 69—76).—The heats of formation of In_2O_3 and GeO_2 at 20° under const. pressure have been found to be 222·5 kg.-cal.±0·3% and 128·1 kg.-cal.±0·5%, respectively, by combustion of the metals. The heat of formation of $GeCl_4$ is calc. to be 124 kg.-cal. It has d^{24} 7·28$_2$±0·1% under H_2O. R. C.

Heats of formation of nitrides. III. Heats of dissolution of metals and metal nitrides in acids. B. NEUMANN, C. KRÖGER, and H. KUNZ. **IV. Uranium, thorium, and lanthanum nitrides.** B. NEUMANN, C. KRÖGER, and H. HAEBLER (Z. anorg. Chem., 1932, 207, 133—144, 145—149; cf. A., 1931, 432).—III. The heats of dissolution of Mn_5N_2 in dil. H_2SO_4 and of Cr, Mg, Mg_3N_2, Ce, CeN, La, and LaN in dil. HCl have been determined; heats of formation calc. from these data are : Mn_5N_2 56·82, Mg_3N_2 115·18, CeN 156·00, LaN 145·36 kg.-cal. (calc. for N_2).

IV. The heats of formation, determined by the direct method described (*loc. cit.*), are as follows : U_3N_4 68·460, Th_3N_4 77·100, LaN 71·055 kg.-cal. per g.-atom N. E. S. H.

Heat of formation and structure of the carbon–oxygen and carbon–sulphur linkings. W. LOCHTE-HOLTGREVEN and C. E. H. BAWN (Trans. Faraday Soc., 1932, 28, 698—704).—The abs. vals. of the heats of formation of C:O and C:S linkings in CO_2 and CS_2 have been calc. from the thermochemical data for the ideal dissociation process, *i.e.*, complete dissociation in one stage. The wide variation in these heats of formation in different compounds is attributed to the influence of neighbouring atoms on the normal vibrations. The C:O linking energy in CH_2O is approx. equal to the abs. val. The val. of the force const. is not a characteristic of the type of linking, except in the elements of the first period. Force consts. of corresponding linkings decrease markedly with increasing at. wt. of the constituent elements. Force consts. and heats of linking of C:O and C:S in CO_2, COS, and CS_2 show that all the linkings in these mols. are double. E. S. H.

Relative heat contents of constituents of aqueous sodium chloride solutions. T. F. YOUNG and O. G. VOGEL (J. Amer. Chem. Soc., 1932, 54, 3030—3040).—New and old data have been used to calculate the partial mol. heat contents at 25°. The activity coeffs. derived from these vals. differ but slightly from those of Lewis and Randall. M. M. (c)

Integral heats of dilution and relative partial molal heat contents of aqueous sodium bromide and potassium bromide solutions at 25°. H. HAMMERSCHMID and A. L. ROBINSON (J. Amer. Chem. Soc., 1932, 54, 3120—3125).—Heats of dilution of 0·1—0·0002M-NaBr and -KBr solutions have been measured. Up to 0·01M the integral heat of dilution of NaBr is represented by $\Delta H = -359m^{\frac{1}{2}}$, and that of KBr by $\Delta H = -350m^{\frac{1}{2}}$, where m is the molality. L. P. H. (c)

Electrical conductivity of aqueous calcium hydroxide solutions. T. NODA and A. MIYOSHI (J. Soc. Chem. Ind. Japan, 1932, 35, 317—320B). —The conductivity of 0·002—0·02M-Ca(OH)$_2$ solutions has been determined at 5 temp. between 20° and 50°. A 0·02 mol. per kg. solution, although nearly saturated at 20°, does not crystallise at 50°. A nomogram relating temp., concn., and conductivity is given. H. F. G.

Electrical conductivity of aqueous solutions of hydrogen sulphide and the state of the dissolved gas. R. H. WRIGHT and O. MAASS (Canad. J. Res., 1932, 6, 588—595; cf. this vol., 14, 457). —Measurements between 5° and 60° suggest that H_2S forms with H_2O a complex which undergoes electrolytic dissociation. Consequently the const. of the Ostwald dilution law is an apparent rather than a real dissociation const. J. W. S.

Conductivity of germanic oxide solutions. C. E. GULEZIAN and J. H. MÜLLER (J. Amer. Chem. Soc., 1932, 54, 3142—3150).—Determination of the conductivity of solutions of GeO_2 from various sources has given vals. which are invariably much lower than those hitherto published, and are practically unaffected by temp. changes either during or after dissolution (cf. A., 1926, 350). The dissociation const. of H_2GeO_3 calc. from the conductivity data is 1·0—3·0×10⁻⁹ (cf. A., 1929, 997). E. R. S. (c)

Conductivity and degree of hydrolysis of sodium hydrogen germanate, and primary dissociation constant of germanic acid. C. E. GULEZIAN and J. H. MÜLLER (J. Amer. Chem. Soc., 1932, 54, 3151—3158).—Conductometric titration of H_2GeO_3 with NaOH indicates the existence in solution of $NaHGeO_3$. The degree of hydrolysis of this salt has been determined at different concns. At 25° the dissociation const. of H_2GeO_3 is 1·5×10⁻⁹, and the mobility of the $HGeO_3'$ ion 31·3. E. R. S. (c)

Dispersion of conductivity of certain aqueous electrolytic mixtures. M. E. SPAGHT (Physikal.

Z., 1932, **33**, 534—536).—The dispersion effect (cf. Gaertner, this vol., 126) of $Ca_2Fe(CN)_6$ on solutions of KCl, HCl, and KOH is discussed in reference to the Debye–Falkenhagen theory. W. R. A.

Complex acids. VIII. Niobic acid. H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1932, 2265—2270).—Conductometric and potentiometric titrations of solutions of K niobate with KOH and HCl afford no evidence of the existence of "pyro-" or "ortho-niobates," the niobate in solution being K_2O,Nb_2O_5, which ionises to form a colloidal anion $(NbO_3')_x$ in the presence of some stabilising free KOH. On addition of HCl very little change takes place at first in the conductivity of the NbO_3'. At a certain point there is, however, a rapid diminution probably due to aggregation which appears to be the first stage in pptn. Finally pptn. at a uniform rate occurs. M. S. B.

Electromotive force measurements with the aid of electron tubes. F. MÜLLER (Trans. Electrochem. Soc., 1932, **62**, 117—124).—The use of electron tubes in measuring e.m.f. of voltaic cells, especially those which are readily polarised or have a very high internal resistance, is reviewed and discussed. H. J. T. E.

Simple oscillators for electrochemical measurements. E. DENINA and G. SELLA (L'Ind. Chimica, 1932, **7**, 986—992).—The advantages of thermionic valve oscillators are discussed, and details, including oscillograms, are given for a variety of circuits. H. F. G.

Absolute null-point of potential measurement. E. BAUR (Z. Elektrochem., 1932, **38**, 665—666).—A discussion of the relations between the Lipmann boundary-potential, ε- and ζ-potentials leads to the conclusion that there is no occasion to depart from the accepted val. for the abs. potential of the N-Hg_2Cl_2 electrode. E. S. H.

Electrode potential of iron. II. Influence of occluded hydrogen and other factors on the electrode potential. K. MURATA (J. Soc. Chem. Ind. Japan, 1932, **35**, 290—295B).—The potential of sintered Fe powder electrodes is not influenced by occluded H or by the degree of subdivision of the Fe. A film of $Fe(OH)_3$ or $Fe(OH)_2$ on the electrodes causes the initial e.m.f. to be abnormally high, but the effect diminishes within a few days; a somewhat similar effect is produced with electrodes reduced at 650°, i.e., in such a manner that a film of highly-dispersed FeO remains on the surface. Variation of the reduction temp. between 850° and 1050°, however, does not influence the e.m.f. Electrodes which have been exposed to the air and have become covered with an oxide film yield very low initial vals. of the e.m.f., but the normal val. is attained after several days; decrease of the p_H of the electrolyte produces a similar result. H. F. G.

Iron as a hydrogen electrode. E. LIEBREICH (Z. physikal. Chem., 1932, **161**, 97—112).—The potential, E, of an Fe electrode in aq. HCl becomes more and more negative as the acid concn., c, increases up to a certain crit. concn., C. In air C is $0.0008N$, but in H_2 is smaller. When c rises above C the potential becomes increasingly positive and although initially much more negative than the potential of a H electrode it approaches this val. as c rises; the cathodic overvoltage decreases at the same time. Current–voltage curves show that at C the separation of H_2 on the Fe becomes easier. These observations are explained by supposing at. H to dissolve in the Fe, saturation being attained at the crit. concn. C. R. C.

Antimony electrode. S. BODFORSS and A. HOLMQVIST (Z. physikal. Chem., 1932, **161**, 61—68).—Although Sb_2O_3 cannot exist as a solid phase in contact with a tartrate buffer or aq. HF, the potential, E, of an Sb electrode is a linear function of the p_H and much more negative than in an acetate buffer of the same p_H. It seems that E is not determined by the concn. of either $Sb^{···}$ or $SbO^·$, but for a given p_H depends on the anion and probably also on its concn., e.g., E in $0.1N$-HCl becomes more and more negative as increasing amounts of KCl are added. A cast electrode the surface of which is continually renewed by scraping or an electrode of electrolytic Sb exhibits a more negative potential than a cast or amalgamated electrode. R. C.

Chlorine-resistant silver–lead electrodes. I. M. A. RABINOVITSCH and A. S. RUBANTSCHIK. **II.** P. B. SHIVOTINSKI (Ukrain. Chem. J., 1931, **6**, [Sci.], 245—251).—I. The electrolysis of aq. KCl or NaCl, using a Pt cathode and a Pb (39%)–Ag (61%) anode, is characterised by a series of breaks in the polarisation–voltage curve, corresponding with the decomp. potentials of $PbCl_2$, PbO_2, Ag_2O, and AgCl. Passivation of electrodes is due to formation of a film of AgCl, and the breaks due to $PbCl_2$ or PbO_2 are absent when such electrodes are used.

II. Pb–Ag anodes surrounded by PbO_2 can be used for the electrolysis of conc. aq. KCl or NaCl, without the necessity of isolating the anode electrolyte. R. T.

Electromotive force of the combination Ag–AgCl|N-KCl+buffer substance+quinhydrone|Pt. A. UHL (Z. Elektrochem., 1932, **38**, 673—676).—The combination gives a reproducible e.m.f., depending only on [Cl'], [H'], and temp. For a given p_H, the e.m.f. is proportional to the temp. At 18° the e.m.f. is proportional to p_H, but not at other temp. The e.m.f. is 0 at 18° and p_H 8.02. E. S. H.

Activity coefficient of zinc sulphate from electromotive force measurements. K. MASAKI and T. IKKATAI (Bull. Chem. Soc. Japan, 1932, **7**, 238—246).—Data for Zn–Hg (saturated amalgam)| $ZnSO_4$, Hg_2SO_4(saturated)|Hg at 25° are recorded, the concn. of $ZnSO_4$ varying from 0.0004321 to $3M$. The solubility of Hg_2SO_4 leads to abnormal e.m.f. at high dilutions. The mean activity coeffs. of $ZnSO_4$ have been calc. for the more conc. solutions. When the ion activities for $ZnSO_4$ are $1M$, E_0 is 1.37475 volts at 25°. E. S. H.

Thermodynamic properties of fused salt solutions. V. Lead bromide in silver bromide. E. J. SALSTROM (J. Amer. Chem. Soc., 1932, **54**, 2653—2661).—E.m.f. measurements have been made with the cell Ag|AgBr(l), $PbBr_2$(l)|Br(g) at 425—475° for AgBr mol. fractions of 0.10—1.00. At all temp.

the activities of solvent and solute agree with the vals. calc. by Raoult's law.　　　　　P. H. E. (c)

Potential of Ag(s)|AgCl(s), KCl (aq.), AgCl(s)| Ag(s) cell, showing effect of flowing electrolyte over one electrode only. J. Y. Cann and E. La Rue (J. Amer. Chem. Soc., 1932, 54, 3456—3458).— The above cell was investigated, the electrolyte on one side being stationary and on the other side in motion. The KCl concn. was 0·025 or 0·05M. The results support Carmody's contention (this vol., 342) that there is a drop of potential when electrolyte is flowing over the Ag(s), AgCl(s) electrode.

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Dependence of p_H on temperature in buffer solutions. S. V. Brujevicz and N. P. Karpova (Biochem. Z., 1932, 251, 60—69).—Between 0° and 25° in the buffer solutions of McIlvaine (nitrate– phosphate) and in that of Sørensen (phosphate) the temp. coeff. of the changes in p_H depends on the temp., but is scarcely affected by changes in the acidity. In Palitzsch's solution (borate) the coeff. increases very considerably as the p_H increases, and the relation between p_H and temp. is linear between p_H 8·1 and 8·2. In more alkaline solutions the coeff. decreases with rise of temp., whilst in more acid solutions it increases.　　　　　W. McC.

Effect of potassium cyanide on the oxidation– reduction potential [ferricyanide–ferrocyanide]. K. Masaki and T. Ikkatai (Bull. Chem. Soc. Japan, 1932, 7, 233—238).—The effect of KCN at 30° is represented by $E = 0·4660 + 0·0601 \log K^{0·59}$, where K is the concn. of KCN.　　　　　E. S. H.

Oxido–reduction system homogentisic acid– benzoquinoneacetic acid. G. Blix (Z. physiol. Chem., 1932, 210, 87—93).—The electrode potential of the system is +0·25 to 0·26 volt (r_H 22—23) in the physiological p_H range, i.e., more positive than any of the biological oxidation–reduction systems hitherto examined. It appears probable that physiological homogentisic acid degradation does not proceed by way of quinoneacetic acid. The dissociation consts. of the acids are calc.　　　　　J. H. B.

Measurement of the electricity liberated during down-grade reactions of organic compounds. M. C. Potter (Nature, 1932, 130, 242—243).—A reply to criticism (A., 1931, 915).　　　　　L. S. T.

Phase-boundary potentials and dielectric constants. P. Farkas (Z. Elektrochem., 1932, 38, 654—665).—Dielectric consts. have been determined for the conjugate solutions of the liquid pairs : PhOH–H_2O, BuOH–H_2O, Et_2O–H_2O, guaiacol–H_2O, o-$C_6H_4Me·NH_2$–H_2O, furfuraldehyde–H_2O, EtOAc– H_2O, $CH_2Ph·OH$–H_2O, $C_5H_{11}·OH$–H_2O, cyclohexanol– H_2O, o-cresol–H_2O, PhCHO–H_2O, and for conc. solutions of dioxan in H_2O. The boundary potentials at the interfaces of these liquid pairs (excluding Et_2O and EtOAc) have been measured when in equilibrium with dissolved NH_4Cl, $NaNO_3$, KOAc, and $AgNO_3$. The conductivities of the org.-liquid phases in distribution equilibrium with aq. N-KCl and aq. 0·5N- NH_4NO_3, respectively, have also been measured. The results are discussed in relation to Debye's formula. The determination of the metal/metal-ion potential

in the org.-liquid phase from the phase-boundary potential is discussed.　　　　　E. S. H.

Theory of concentration polarisation. B. Bružs (Z. physikal. Chem., 1932, 161, 83—96).—By methods similar to those used previously (this vol., 123) equations containing only thermodynamic quantities, and no ionic concns. or similar magnitudes, have been obtained for the Hittorf coeff., χ, and the e.m.f. of cells with liquid junctions. These permit the calculation of entropies of dilution of ions and salts and heats of dilution from the vals. of χ and e.m.f. data. The theory accounts for the formation of anode mud. The existence of heats of transport is unlikely.　　　　　R. C.

Anodic behaviour of nickel. I. K. Georgi (Z. Elektrochem., 1932, 38, 681—688).—The potential of air-passive Ni varies with the acid solution in which it is immersed and becomes more negative with time, the amount of change varying with the anion. Different vals. are assumed when air is replaced by O_2, N_2, or H_2. The loss of wt. of a Ni electrode also varies with the acid solution and the nature of the atm., the loss being greater the more positive is the potential. The vals. are compared with the potentials assumed by a Ni electrode coated with Ni_2O_3. C.d.–potential curves have been constructed for the dissolution of Ni anodes in acid and salt solutions. The potential at low c.d. is higher the greater is the size of the anion in the series Cl′, Br′, SO_4'', ClO_4'. The curves are considerably affected by previously etching the Ni with 2N-HCl or by heat-treatment, but very little by polishing.

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Passivity phenomena. XV. Passifying action of oxide layers during the anodic passification of iron in neutral solutions of sodium sulphate. W. J. Müller and W. Machu (Monatsh., 1932, 60, 359—385).—Oscillographic records obtained with Fe electrodes coated with a natural or artificial oxide layer in N-Na_2SO_4 permit the separate determination of the resistance in the pores and the layer resistance. Increase in the thickness of the layer diminishes the size of the pores with consequent increase in resistance, whilst the layer resistance increases with the thickness. The free pore-surface can be calc. (1) from the amount of Fe salt deposited, the thickness of layer being deduced from the surface- covering rule, (2) from the i_0-t_p relationship which contains no assumption regarding the thickness of the layer, and (3) from the conductivity and initial current strength ; with electrodes exposed to the air it is about 10^{-3} and with immersed electrodes about 10^{-4} of the total surface. The Fe in the pores is invariably active. Passivity is never observed under these conditions, since the current passing through the pores is never sufficiently large to cause chemical passivity of the underlying Fe. In this case, passivity depends essentially on the oxide layer over the Fe.

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Reaction of chlorine with hydrogen. W. H. Rodebush and W. C. Klingelhoefer (Proc. Nat. Acad. Sci., 1932, 18, 531).—The reaction $H_2 + Cl = HCl + H$, which has been studied at low pressures, initiates chains producing 10 mols. of HCl at 1 mm.

pressure. If the reaction $Cl_2+H=HCl+Cl$ is rapid, the reaction probability of the Cl atom is of the order of 10^{-5} per collision with the H_2 mol. The heat of activation is calc. as 5500 g.-cal. O_2 and H_2O do not affect the reaction at low pressures. W. R. A.

Kinetics of gas explosions. III. Influence of hydrogen on thermal decomposition of ozone sensitised by bromine vapour, and determination of explosion temperature. W. FEITKNECHT and B. LEWIS (J. Amer. Chem. Soc., 1932, 54, 3185—3191; cf. this vol., 701).—H_2 behaves as an inert gas in the non-explosive reaction, retarding it to about the same degree as other inert gases, but the explosion limit is about twice as high as when H_2 is replaced by He. In the explosive reaction H_2 is burned to H_2O, which with Br_2 establishes the equilibrium $2H_2O+2Br_2 \rightleftharpoons 4HBr+O_2$, at a temp. which is calc. by comparing the measured equilibrium const. with known data to be $1600\pm100°$ abs. This is probably below the max. explosion temp. in the mixtures. C. W. (c)

Mechanism of flame movement. I. Uniform movement of flame in mixtures of methane and air, in relation to tube diameter. H. F. COWARD and F. J. HARTWELL (J.C.S., 1932, 1996—2004).—The relation between the speed of uniform movement of flame in CH_4–air mixtures and the diameter of the explosion tube (horizontal) has been studied. Photographs show that the results may be explained by the effect of convection currents on the area of the flame and hence on the amount of gas burnt in unit time. The definition of the term "uniform movement of flame" is revised. F. J. W.

Explosive gaseous reactions in a dynamic system. I. Reaction of oxygen and propane. S. P. BURKE, C. F. FRYLING, and T. E. W. SCHUMANN (Ind. Eng. Chem., 1932, 24, 804—811).—The reaction between O_2 and C_3H_8 has been investigated by passing the gases through a tube in a bath at known temp. and determining the O_2 in the product. Observed and calc. curves for the variation of reaction temp. with pressure, rate of flow, etc. are in close agreement. Similar results were obtained with other paraffins, but not with C_2H_4 and C_3H_6, suggesting that oxidation of paraffins by O_2 does not involve initial formation of olefines. D. R. D.

Uniform movement of flame. J. TAUSZ and J. DRAXL (Petroleum, 1932, 28, 1—13).—The rates of downward uniform propagation of flame in vertical glass tubes of diam. 0·2—3·0 cm. have been determined for mixtures of air with H_2, C_2H_2, CO, and C_6H_6 vapour, and, in the 0·8 diam. tube only, for mixtures of air with CH_4, C_2H_6, hexane, cyclo-hexane and -hexene, and isoprene. It was considered that the statical method using a vertical tube gave more consistent results than could be obtained with a horizontal tube or by the dynamical method (cf. Bunte and Litterscheidt, B., 1930, 1053). The flame velocities in a const. mixture increased with increasing tube diam., and, in a tube of const. diam., increased, passed through a max., and fell again, with increasing concn. of the combustible gas. The so-called uniform movement could be exactly measured in general only in mixtures of composition near the lower combustion limit. In the region of uniform flame movement the rate of increase of the velocity with tube diam. fell with increasing diam.; thus, when plotted, the results gave a curve convex upwards. In the other cases, e.g., when the velocity was proportional to the diam., and for high vals. of the velocity in general, a vibratory motion of the flame was observed. Chapman and Wheeler's formula relating the max. flame velocity with tube diam. ($V=CD^k$; cf. A., 1927, 211) is discussed. It is preferable to consider the velocities corresponding with the stoicheiometrical ratios of fuel to air; these velocities (V cm. per sec.) are related to the tube diam. (D cm.) by the formula $V=A(B+\log D)$, where A is an abs. const. and B is a const. which is characteristic of the combustible gas used. A. B. M.

Pressures developed in explosion waves. C. CAMPBELL, W. B. LITTLER, and C. WHITWORTH (Proc. Roy. Soc., 1932, A, 137, 380—396).—Experiments on the shearing of Cu foils of various thicknesses by explosion waves in a no. of gaseous mixtures are described. By calibration of the foils with static air pressures approx. vals. of the actual pressures developed in any one mixture are obtained. The experimental results are in fair agreement with the vals. calc. by Jonguet's method (J. Math. pur. appl., 1905, 1, 347), especially in the case of the more dil. mixtures. Photographs of the flame before and after collision with the Cu diaphragm give approx. vals. of the time required to break the diaphragm. In general, the distance over which the flame must travel before detonation is re-established increases with increasing thickness of the foil. The pressure near the point of detonation is much greater than that obtaining when the wave is fully established. L. L. B.

Combustion of hydrocarbons. W. A. BONE (Proc. Roy. Soc., 1932, A, 137, 243—274).—A historical survey of the subject is given, and the relative merits of the "hydroxylation" and "peroxidation" theories are discussed. Much evidence is adduced in support of the former theory, and it is considered that "peroxidation" can be regarded only as supplementary to "hydroxylation." L. L. B.

Propagation of explosion waves through a system of glass and rubber tubes. C. CAMPBELL, A. KING, and C. WHITWORTH (Trans. Faraday Soc., 1932, 28, 681—688).—Photographic records of explosion waves passing through a rubber section of a long explosion gallery show that in "non-striating" mixtures (e.g., $2H_2+O_2+N_2$, CH_4+2O_2, $2CO+O_2+7\%$ H_2) the waves can pass through considerable lengths of even thin rubber tubing without appreciable alteration of velocity. In "striating" mixtures (e.g., $2CO_2+O_2$, $2H_2+O_2+CO_2$, CH_4+7O_2) a marked reduction of flame velocity may occur on passing through the rubber. This change depends on the thickness and length of rubber and may be due to release of pressure behind the wave front. E. S. H.

Explosion limits. H. W. THOMPSON (Z. physikal. Chem., 1932, B, 18, 219—240).—The presence of MgO dust in binary mixtures of air with various combustible gases displaces the lower explosion limit

in the direction of richer mixtures. With C_2H_4 this effect is more marked than with H_2 and CO, with C_6H_6 and Et_2O it is barely perceptible, and with CH_4 it is absent. At the same time, the flame speed in mixtures having compositions near the limit is reduced. SiO_2 acts similarly to MgO. By means of Fe carbonyl vapour a much greater displacement of the lower limit can be effected than with MgO, and the upper limit is displaced more than the lower limit, but in the opposite direction. It is uncertain whether these effects are due to the undecomposed carbonyl mols. or to the Fe or oxide formed by their decomp. The above action of mineral dust is ascribed to its adsorbing the radicals or atoms propagating the reaction chains, such as OH and H, and converting them into stable mols. R. C.

Decomposition of ethyl bromide, alkyl halides, and acetal in the gas phase at 300—400°. E. T. LESSIG (J. Physical Chem., 1932, 36, 2325—2337).—The rate of decomp. in the gas phase of 13 org. compounds is determined at 300—400° by measuring the pressure increase in all-glass and all-quartz vessels totally immersed in a Pb thermostat. The dissociation of EtBr is a homogeneous first order reaction : EtBr——>C_2H_4+HBr. The energy of activation is approx. 50,000 g.-cal. The dissociations of n- and iso-PrBr are of the first order and homogeneous, but complications cause a decrease of velocity coeff. with pressure ; free Br is not found. The decomp. of EtI is complicated, since I is produced. The alkyl chlorides studied do not show simple first order reactions ; the data for $CHCl_3$ are very irregular. The final pressure with acetal is nearly three times the original pressure, showing decomp. into 3 mols. This decomp. and those of methylal and Bu^β chloroformate are very complicated. E. J. R. (b)

Reduction of silver ions by ferrous ions. D. ROBERTS and F. G. SOPER (J.C.S., 1932, 2004—2008).—The reaction between Fe·· and Ag ions has an induction period during which Ag nuclei are formed. The rate of the reaction was profoundly affected by [H·] and the ionic strength of the medium, effects attributed to changes in the rate of deposition of at. Ag on the Ag nuclei. The induction period could be eliminated by the addition of a colloidal solution of Ag. F. J. W.

Kinetics of reaction between potassium permanganate and oxalic acid. I. H. F. LAUNER (J. Amer. Chem. Soc., 1932, 54, 2597—2610).—In acid solution MnO_4' reacts quickly with Mn··, forming Mn···, which, with C_2O_4'', enters into equilibrium with MnC_2O_4' by a reaction which is rapidly reversible. The rate of reaction of MnO_4' with C_2O_4'' is proportional to the MnC_2O_4' concn. and inversely proportional to the C_2O_4'' concn. The influence of the ionic strength on the velocity agrees with Brönsted's hypothesis. A reaction mechanism involving the hypothetical CO_2' ion is suggested. P. H. E. (c)

Effect of non-electrolytes on the velocity of reaction of ferric and iodide ions. P. VASS (Magyar Chem. Fol., 1931, 37, 217—229 ; Chem. Zentr., 1932, i, 1478).—The mechanism of the reaction is unchanged in aq. MeOH, EtOH, PrOH,

$COMe_2$, glycerol, sucrose, and carbamide. The velocity changes depend on ε, and the Grube–Schmid law is obeyed. Aq. carbamide forms complexes. L. S. T.

Velocity of decomposition of diazo-compounds in aqueous solution. VIII. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 298—303B).—The decomp. velocities at various temp. and the temp. coeff. of the velocity are recorded for o-, m-, and p-$C_6H_4Cl\cdot N_2Cl$. H. F. G.

Rate of esterification of methyl and ethyl alcohol in acetic acid. A. KAILAN and W. HAAS (Monatsh., 1932, 60, 386—413).—The rates of esterification of MeOH and EtOH in AcOH containing various amounts of H_2O in presence and absence of HCl as catalyst at 25° have been determined by observation of the increases of depression of the m.p. and the unimol. consts. have been calc. The latter do not alter when the H_2O content is increased from 0·2 to 1·2 mols. per kg. AcOH. Addition of 0·0038 or 0·0237 mol. HCl per kg. causes an approx. proportional increase in the case of MeOH to 31 or 240 times, in the cases of EtOH to 21 or 108 times, the val. found in the absence of catalyst. The ratio of the coeffs. of MeOH to those of EtOH is 1·5, 2·2, or 3·3 in absence or presence of the smaller or larger amounts of catalyst. Almost complete esterification is invariably observed ; this is verified by experiments starting with the esters. Between a content of 0·1 and 1·3 mols. of H_2O per kg. AcOH the cryoscopic consts. for MeOH (3·57) and EtOH (3·64) are independent of the H_2O content within the limits of measurement and of the alcohol concn. between 0·15 and 0·3. For H_2O they fall from about 3·85 to 3·1 for a total H_2O content (w=1·2) and to 2·6 for a further H_2O increase of about 0·2 mol. For both esters κ=3·9. H. W.

Rate of chlorination of anilides and phenols as affected by association. R. E. ROBERTS and F. G. SOPER (J.C.S., 1932, 1979—1982).—The rate of chlorination of anilides and phenols dissolved in solvents such as CCl_4 is increased from 3 to 7 times by doubling the concn. It is suggested therefore that the associated mol. is more reactive than the unassociated, indicating that association causes one of the O or N atoms to become more negative. This is in agreement with the singly co-ordinated mode of association. F. J. W.

Thermal decomposition of dimethylamine. H. A. TAYLOR (J. Physical Chem., 1932, 36, 1960—1966).—In the thermal decomp. at 480—510° under 3·75—600 mm. the rate of pressure increase suggests that the reaction is homogeneous and unimol., with an activation energy of 44,300 g.-cal., but the reaction is so complex that this interpretation seems doubtful. S. L. (c)

Oxidation of colloidally dissolved substances. S. VOSNESSENSKI [with I. M. ZINN] (Kolloid-Z., 1932, 60, 171—176).—The rates of oxidation of colloidal solutions and suspensions of S by Cl_2, Br, and I have been measured. The presence of Na_2SO_4 or $NaHSO_3$ in concns. insufficient to cause pptn. of S stabilises the systems and reduces their rate of oxidation. The oxidation velocity is inversely proportional to the

concn. of Na_2SO_4 (at low concns.). Humus acts as a protective colloid to S and reduces the rate of oxidation, but in presence of humus Na_2SO_4 has the effect of increasing the rate of oxidation. E. S. H.

Conversion of metal ions into neutral atoms by interaction with metallic zinc. M. CENT- NERSZWER and W. HELLER (Z. physikal. Chem., 1932, **161**, 113—128).—The dissolution of a rotating Zn plate in aq. $CuSO_4$ follows the unimol. velocity law. With increasing speed of rotation, the velocity coeff., k, increases, but ultimately becomes const., which, adopting Nernst's theory of heterogeneous reaction, is assumed to correspond with equality of the rates of diffusion and chemical reaction. Between $0°$ and $50°$ k is a linear function of the temp., its temp. coeff. being equal to that of the diffusion coeff., indicating that the thickness of the diffusion layer is const. between these temp. The reaction is therefore regarded as a pure diffusion reaction. SO_4'', Cl', and CNS' increase k, their effectiveness increasing in this order; NO_3', fatty acids, and various colloids reduce k, the colloids by mechanical action. Amalgamated Zn dissolves more rapidly than ordinary Zn. In solutions of Ni salts dissolution is extremely slow, in aq. Ag_2SO_4 it is more rapid than in aq. $CuSO_4$, and in aq. $AgNO_3$ k diminishes as reaction proceeds. There seems to be no quant. relation between k and the position of the displacing metal in the electro- chemical series. R. C.

Kinetics of dissociation of solid carbonates. P. AFANASIEV and S. ROGINSKI (Z. physikal. Chem., 1932, B, **18**, 360).—The autocatalytic character of the thermal decomp. of $CdCO_3$ has been confirmed (A., 1929, 153). The oxide obtained by complete decomp. is, however, inactive. The active oxide is not an amorphous intermediate form. R. C.

Temperature increment of reaction velocity in heterogeneous reactions. III. Reactions of cadmium oxide. K. FISCHBECK and K. SCHNAIDT (Z. Elektrochem., 1932, **38**, 649—653; cf. this vol., 475, 577).—The reactions (a) $CdO+CO=Cd+CO_2$, (b) $CdO+H_2=Cd+H_2O$, and (c) $2CdO+3S=2CdS +SO_2$ have been investigated at $300—400°$. The temp. increments E of these reactions, calc. from the formula $v=Ae^{-E/RT}$, are (a) 25·5, (b) 25·7, (c) 20·5 kg.-cal. Thus, the heats of activation of different reactions of CdO are of the same magnitude. E. S. H.

Kinetics of dissolution of dilute sodium amalgam. R. LIVINGSTON (J. Physical Chem., 1932, **36**, 2099—2100).—The mechanism proposed assumes the existence of the equilibrium $NaHg_2 = Na+\ominus+Hg_2$. S. L. (c)

Chemical inertia. LEMARCHANDS and JACOB (Compt. rend., 1932, **195**, 380—382; cf. A., 1931, 1016).—The validity of previous assumptions is substantiated by showing that the temp. of com- mencement of interaction between Cl_2 and 15 elements and the products of the b.p. of the element and its resultant chloride follow approx. the same order. C. A. S.

Velocity of corrosion from the electrochemical viewpoint. II. U. R. EVANS and T. P. HOAR (Proc. Roy. Soc., 1932, A, **137**, 343—365).—The corrosion–time curves of Fe and steel in KCl, NaCl, Na_2SO_4, and other salt solutions are linear and the temp. coeff. is low. Corrosion velocity–salt concn. curves show a max. velocity at $0·5N$, and the area of the corroded region is smallest in the region of most rapid corrosion. At high concn. corrosion is pro- portional to the O_2 solubility, but at low concn. it falls below the val. calc. therefrom. The potential at the anodic and cathodic areas has been measured in KCl solution. The corrosion rate is proportional to the current which the measured e.m.f. would force through the resistance of the circuit. L. L. B.

Film reactions and the problem of the cor- rosion of metals. L. TRONSTAD (Z. Metallk., 1932, **24**, 185—188).—The use of viscous films containing gelatin or other colloid and the corrosive media in following the reactions which occur in the corrosion of metals is illustrated; the viscosity of the solution prevents diffusion of the corrosion products and the evolution of H_2 may readily be observed under the microscope. In the case of rolled Al sheet evolution of H_2 and dissolution of metal occur in spots which become sufficiently acid to attack the metal and at the same time show pits or fissures, whereas in the case of Fe with a low C content H_2 is evolved by corrosion with almost neutral media probably by the electrolytic action of local currents the origin of which cannot with certainty be traced. A. R. P.

Stability of bleaching powder and hypochlorite solutions. J. H. WALTON and C. S. R. AYYAR.— See B., 1932, 798.

Reactions between gas and solid. IV. Azot- ation of calcium carbide and the effect of tem- perature on its velocity. T. AONO (Bull. Chem. Soc. Japan, 1932, **7**, 247—255; cf. this vol., 817).—At const. temp. below $950°$ the degree of azotation, n_t, of CaC_2 (containing 1% CaF_2) after a time t is repre- sented by $n_t=n_\infty-\{n^{1/3}-\sqrt{k'_5(t-t')}\}$, where n_∞ is the final degree of azotation and k'_5 and t' are consts. At const. temp. between $1000°$ and $1060°$ the relation is $n_t=n_\infty\{1-e^{-k'_4(t+t')}\}$, where k'_4 is the velocity coeff. At each temp. there is a max. velocity, which varies with temp. according to the approx. relation $\log Y=A-B/T$, where Y is the degree of azotation at the max. velocity, T the abs. temp., and A and B are consts. From the temp. coeff. of the velocity coeff. the apparent heat of activation of powdered technical CaC_2 is calc. as 58·6 kg.-cal. per mol. at $1000—1060°$, and about 33 kg.-cal. per mol. above $1080°$. E. S. H.

Unimolecular decomposition of explosives. S. ROGINSKI (Z. physikal. Chem., 1932, B, **18**, 364— 366).—New and existing kinetic data show that spontaneous unimol. decomp. is a general characteristic of explosives. The heat of activation, A, is about 50 kg.-cal. and the val. of the const. B of Arrhenius' equation is 10^{19}—10^{24}. Usually, the val. of $\log B$ is the higher the larger is A. No evidence of reaction chains has been observed. R. C.

Autoxidation of the double linking. P. RONA, R. ASMUS, and H. STEINECK (Biochem. Z., 1932, **250**, 149—177).—The velocity of autoxidation of the Me

esters of linoleic, linolenic, and oleic acids is greatly increased by addition of pyridine and nicotine, the increase depending on the amount added and on the p_H of the medium. Of a no. of Fe compounds examined, only a few increased the rate of autoxidation. The reaction with linoleic acid is pseudo-unimol. The action of substances inhibiting the reaction has been investigated and the mechanism of the reaction is discussed. P. W. C.

Generalised theory of acid and base catalysis applied to ionic reactions. R. LIVINGSTON (J. Amer. Chem. Soc., 1932, 54, 2393—2394). P. H. (c)

Catalytic properties and the ageing of the mineral waters of Vrnjačka Banja, Aranđelovac, and Mladenovac. G. SCHILDER (Liječnički Vjesnik [Croatian Med. J.], 1932, 54, 243—261).—The catalytic properties of natural mineral water with respect to Glenard's reaction appear to be associated with the Fe'' concn. and their ageing to be due to oxidation by atm. O_2. J. W. S.

Catalytic effect of lignosulphonic acid. E. HÄGGLUND and T. JOHNSON (Biochem. Z., 1932, 250, 321—325).—Lignosulphonic acid, in spite of its insolubility, possesses the characteristics of a strong acid and over a narrow range of p_H can catalyse the inversion of sucrose. P. W. C.

Ninth report of Committee on Contact Catalysis. J. N. PEARCE (J. Physical Chem., 1932, 36, 1969—2010).—A *résumé* of the recent papers on catalysis published prior to 1931. P. H. E. (c)

Theory of activity of contact catalysis. H. G. TANNER (J. Amer. Chem. Soc., 1932, 54, 2171—2176). —Catalytic activity is assumed to depend on the rate at which active spots act. The action of an active spot depends on its temp. fluctuations. The concept of average temp. and its possible relation to the action of promoters, supports, surface roughness, porosity, and thermionic emission are discussed. P. H. E. (c)

Basic magnesium carbonate as a promoter on a copper surface. T. HAGYARD (J.C.S., 1932, 2055—2062).—The adsorption isotherms of H_2, N_2, CO, CH_4, and NH_3 on surfaces of Cu, Cu promoted with basic Mg carbonate, and the promoter itself have been determined at 20°. The adsorbing areas have been calc. using a modified Langmuir equation. The initial surface consisted of areas of different activity and the promoter increased the extent of these areas, but not necessarily in the same ratio. The solubility of H_2 in the promoted and unpromoted Cu has been measured at 20°. The rate of dissolution is approx. proportional to the extent of the adsorption of the H_2. F. J. W.

Chain mechanism of catalytic oxidation of hydrogen. S. ROGINSKI and J. ZELDOVITSCH (Z. physikal. Chem., 1932, B, 18, 361—363).—There seems no reason to believe that vol. chains play any significant part in heterogeneous catalysis at moderate temp. The effects observed by Kobosev and Anochin (A., 1931, 1017) are purely accidental, and have nothing to do with the presence of at. H. R. C.

Röntgenographic investigations on iron catalysts for ammonia synthesis. R. BRILL (Z. Elektrochem., 1932, 38, 669—673; cf. following abstract).

—X-Ray analysis shows that α- and γ-Al_2O_3 activate the Fe catalyst only when they form mixed crystals with the Fe_2O_3 present, independently of the general state of oxidation of the Fe. If the mixed crystals are very rich in Al_2O_3 the activating effect is poor; in general, activation ensues when the mixed crystals are readily reducible. In the case of reduced Fe–Al_2O_3 catalysts, the Al_2O_3 is distributed among the Fe crystallites, so preventing their destruction through recrystallisation. E. S. H.

Activation of iron by aluminium oxide in ammonia catalysis. A. MITTASCH and E. KEUNECKE (Z. Elektrochem., 1932, 38, 666—669; cf. A., 1931, 1247).—The relative efficiencies of Fe_2O_3–Al_2O_3 catalysts prepared in different ways for the catalytic NH_3 synthesis have been determined. Al_2O_3 exerts an activating effect under conditions such that it reduces the velocity of reduction of Fe_2O_3. Chemical and X-ray evidence agree in showing that both α- and γ-Al_2O_3 form mixed crystals with Fe_2O_3, to which the activating effect is due. E. S. H.

Poisoning and activation of zinc. K. JABLCZYNSKI and J. KULESZA (Z. anorg. Chem., 1932, 207, 157—160; cf. A., 1931, 692).—The reaction between chemically pure Zn and dil. HCl is strongly retarded by small quantities of HCN. HCNS (down to $0.000002N$) accelerates the reaction markedly and CS_2 accelerates it appreciably. $CS(NH_2)_2$ and SO_2 have no influence. Under the action of poisons or of activating agents the etched surface of the Zn has a more finely-grained structure than is produced by HCl alone. Poisoning and activation cannot be attributed to an effect on impurities in the metal. E. S. H.

Catalytic partial oxidation of alcohols in the vapour phase. IV. W. L. FAITH, P. E. PETERS, and D. B. KEYES (Ind. Eng. Chem., 1932, 24, 924—926; cf. this vol., 28).—Four types of catalyst chamber, designed to improve heat transfer and temp. control in the catalytic oxidation of EtOH, are described. The effects of intermittent heating, of Cu and pyrex glass as materials for the catalyst chamber, and of the wall thickness of the latter have been investigated, as well as variation of the alcohol : air ratio. The yields of intermediate oxidation products under favourable conditions are max. J. W. S.

Hydrogenation of aromatic hydrocarbons at high pressure with nickel on kieselguhr as a catalyst. G. F. SCHOOREL, A. J. TULLENERS, and H. I. WATERMAN.—See B., 1932, 791.

Catalytic effect of acids on the rate of ester hydrolysis in relation to the ester concentration and the nature of the acid. H. M. DAWSON and W. LOWSON (Proc. Leeds Phil. Soc., 1932, 2, 331—335).—It is suggested that the process of ester hydrolysis involves a series of consecutive changes, e.g. $EtOAc + H_2O \rightleftharpoons EtOAc,H_2O$; $EtOAc,H_2O + H^· \longrightarrow EtOAc,H_2O·H^· \longrightarrow AcOH + EtOH + H^·$. In such a case the rate of combination of the $EtOAc,H_2O$ complex with the $H^·$ may be the factor determining the observed rate of hydrolysis. Measurement of the rates of hydrolysis in presence of $0.01N$-HCl, $0.1N$-$CH_2Cl·CO_2H$, $0.1N$-glycollic acid, and $0.1N$-AcOH

support this view and show that the rate depends on the ester concn. J. W. S.

Catalytic action of silica gel in the reaction of camphene and oxalic acid. Synthesis of *isoborneol. T. KUWATA and S. TATEGAI.—See this vol., 1037.

[Catalytic] reactions of phenol with hydrogen at high pressure. C. M. CAWLEY.—See B., 1932, 762.

Incomplete combustion of organic compounds in presence of catalysts. I—III. S. J. GREEN.—See B., 1932, 715.

Co-deposition of lead and bismuth. C. G. FINK and O. H. GRAY (Trans. Electrochem. Soc., 1932, 62, 189—194).—Solutions prepared by dissolving various amounts of PbO and Bi_2O_3 in aq. $HClO_4$, with addition of clove oil, were electrolysed at 20° or 40° and various c.d. at a brass cathode. At low c.d. smooth, adherent deposits ranging from pure Bi to 99% Pb were obtainable, but deposits became spongy above 0·58 amp. per sq. dm. With a solution of given composition raising the c.d. increases the proportion of Pb in the deposit. Deposits containing 75—85% Pb were most resistant to corrosion by 5% HCl or H_2SO_4. H. J. T. E.

Electrochemical production of formates from carbon dioxide. M. A. RABINOVITSCH and A. P. MASCHOVETZ (Ukrain. Chem. J., 1931, 6, [Sci.], 217—228).—Up to 90% yields of HCO_2Na are obtained by reduction of CO_2 by nascent H evolved by Na–Hg, prepared by electrolysis of NaOH, using a Hg cathode. The reaction is catalysed by Ni or Cu in the amalgam, but not by Fe. The cathode becomes foamy during the process, owing to formation of an emulsion of solution in Hg. R. T.

New method for electro-organic reductions. R. H. McKEE and C. J. BROCKMAN (Trans. Electrochem. Soc., 1932, 62, 25—43).—Aromatic NO_2-compounds insol. in H_2O dissolve readily in saturated aq. solutions of Na cymenesulphonate or p-toluenesulphonate, and many are reduced to the corresponding azo-compounds by electrolysis of these solutions at 80—90°, using a phosphor-bronze gauze cathode in a diaphragm cell with aq. Na_2SO_4 solution as anolyte. Optimum c.d. usually lie between 0·6 and 2 amp. per sq. dm. and no stirring is required. With simple mononitro-compounds the current yields are excellent, but with compounds containing OMe or similar groups the yields are lower and tarry compounds are formed. The conductivity of the solutions is much higher than that of the corresponding alcoholic solutions, so that the energy consumption is lower. The products are readily pptd. by addition of H_2O, and the solvent can be used again after concn. The CO group in benzil is also reduced with high efficiency under the above conditions, but attempts to oxidise aromatic hydrocarbons to phenols were not successful. Conditions for the cathodic reduction of 10 NO_2-compounds are specified. H. J. T. E.

Electrochemical oxidation of paraffin and mineral oils. I. A. ATANASIU.—See B., 1932, 790.

Electrolytic reduction of aliphatic ketones to hydrocarbons. S. SWANN, jun. (Trans. Electrochem. Soc., 1932, 62, 153—158).—In the electrolytic reduction of COMePr, dissolved in aq.-alcoholic H_2SO_4, to n-pentane at a Cd cathode, the highest current efficiency (74·9%) was attained by using 20 g. of COMePr in 70 c.c. of 39% H_2SO_4 at 55—60° as catholyte and passing the theoretical quantity of electricity at 5 amp. per sq. dm. The cathode was previously activated by anodic oxidation. H. J. T. E.

Electrolytic reduction of nitrobenzene to azoxybenzene. C. KERNS (Trans. Electrochem. Soc., 1932, 62, 125—144).—The influence of various factors on the current efficiency and yield of azoxybenzene in the electrolysis of $PhNO_2$ suspensions in aq. NaOH in a diaphragm cell with a Ni cathode has been studied. The reduction is favoured by high temp. and, in general, by low c.d., but the vol. of catholyte has little effect except on the time required for complete reduction. Max. yields were obtained by using 2·5% NaOH as electrolyte. Rates of stirring higher than that required to keep the $PhNO_2$ uniformly distributed throughout the electrolyte did not increase the yield. Under all conditions studied the current efficiency and yield were notably higher when the electrolysis cell was closed instead of being open to the air. H. J. T. E.

Electrochemical oxidation of naphthalene using a new type electrode. E. G. WHITE and A. LOWY (Trans. Electrochem. Soc., 1932, 62, 107—115).—A heated mixture of 60% of $C_{10}H_8$ and 40% C was pressed on to both sides of a Pt gauze, 7·62 cm. sq., and the resulting electrode used as anode in 1% H_2SO_4 solution. Max. yields of α-naphthoquinone were obtained at 25° with 0·5 amp. Notably lower current efficiencies were obtained at 55° or with currents <0·2 amp. Addition of $Ce_2(SO_4)_3$ or CrO_3 had no beneficial effect. Some CO_2 was formed and phthalic acid was detected. The previously described PbO_2 electrode (B., 1929, 886) was unsuitable because direct chemical oxidation occurs. H. J. T. E.

Temperature coefficients of photochemical reactions. N. R. DHAR and W. V. BHAGWAT (J. Indian Chem. Soc., 1932, 9, 225—232).—Theoretical. The temp. coeff. of a photochemical reaction can be calc. from the temp. coeff. of the dark reaction and its photo-acceleration at a definite temp. The increase of light absorption with rise of temp. leads to a decrease of the quantum yield, which can be explained by supposing that the no. of mols. available for activation by light absorption decreases with increased absorption. E. S. H.

Formation of carbon dioxide sensitised by chlorine in light. E. WARMING (Z. physikal. Chem., 1932, B, 18, 153—154).—Schumacher and Stieger's reaction scheme (A., 1931, 1137) is thermodynamically impossible. R. C.

[Formation of carbon dioxide sensitised by chlorine in light.] H. J. SCHUMACHER (Z. physikal. Chem., 1932, B, 18, 155).—The validity of Warming's observation (cf. preceding abstract) is conceded. R. C.

Photochemical reduction of carbon dioxide in aqueous solution. M. QURESHI and S. S. MOHAMMAD (J. Physical Chem., 1932, **36**, 2205—2216).—The photochemical reduction of CO_2 in aq. solution is studied in presence of sensitisers, with Hg arcs, W-filament lamps, and the sun as light sources. No trace of CH_2O is found when CO_2 is passed through conductivity H_2O illuminated by mixed or monochromatic ultra-violet light (254 and 312 mμ). In sunlight and in presence of inorg. catalysts no CH_2O is found. With org. catalysts CH_2O is found in nearly the same amount in the solutions of CO_2 as in the CO_2-free blanks. A trace of wax or cork (from a $NaHCO_3$ container) can cause formation of CH_2O, whilst pure $NaHCO_3$ does not. Repetition of Baly's work with basic carbonates of Ni and Co, using W lamps, gave negative results. Colloidal solutions of chlorophyll *a* and solutions of malachite-green, Me-orange, or $Cu(OAc)_2$, when sealed in bulbs without CO_2 and exposed to sunlight, contain CH_2O. The results are compared with those of other workers. E. J. R. (*b*)

Photochemical formation of carbonyl chloride under low pressure. E. WARMING (Z. physikal. Chem., 1932, **B**, **18**, 156—158).—The mathematical difficulties of Bodenstein, Lenher, and Wagner's theory (A., 1929, 894) have been overcome, and the theory has been shown to agree with the experimental data. R. C.

Photochemical oxidation of aqueous solutions of ammonia. L. GION (Compt. rend., 1932, **195**, 421—423).—4% aq. NH_3 exposed to the light of a 220-volt Hg-vapour lamp in a quartz (but not pyrex or ordinary glass) vessel at 40° is oxidised to nitrite up to a max. of 34 mg. N_2O_3 per litre, the limit being due to photochemical decomp. of the nitrite. The oxidation is due to O_3 first formed, and its acceleration by ZnO or TiO_2 is due to these oxides accelerating the formation of O_3 (cf. A., 1921, ii, 670; B., 1931, 690). C. A. S.

Reduction of ferric chloride by citric acid, malic acid, and sugars. R. M. PURKAYASTHA (J. Indian Chem. Soc., 1932, **9**, 237—241).—The photochemical reduction (at 4350 and 3660 Å.) of $FeCl_3$ by citric acid, malic acid, glycerol, and sugars (except fructose) in presence of HCl gives a zero-mol. reaction coeff. The dark reaction is very small, except with fructose. With sugars, glycerol, lactic, tartaric, and malic acids as reductants about 2 quanta are required per mol. of $FeCl_3$; with mandelic and citric acids 1 quantum per $FeCl_3$ mol. is required for reduction. E. S. H.

Autoxidation. VI. Action of light on sulphite solutions in absence and presence of oxygen. F. HABER and O. H. WANSBROUGH-JONES (Z. physikal. Chem., 1932, **B**, **18**, 103—123; cf. this vol., 703).—In solutions free from O_2 the H and HSO_3 formed by the light reaction largely disappear by the reactions $H + HSO_3 = H^{·} + HSO_3'$ and $H + HOH + HSO_3 = H_2 + H_2SO_4$. The former of these is the more important and the relative frequency of the latter diminishes as the p_H increases. The reaction $2SO_3' = S_2O_6''$ occurs very rarely. If the solution contains O_2 the autoxidation in light is affected in the same way by

variation of p_H as the H_2 evolution from O_2-free solutions. The conditions for proportionality between autoxidation and O_2 pressure have been determined. R. C.

Photochemical decomposition of some organic anions and free acids in ultra-violet light. L. FARKAS and O. H. WANSBROUGH-JONES (Z. physikal. Chem., 1932, **B**, **18**, 124—145; cf. this vol., 480).—The decomp. in their electron affinity spectrum of the anions of HCO_2Na, NaOAc, and Na succinate in aq. solution follows the equation $A',H_2O + h\nu = A + OH' + H$ (A=anion), but owing to the subsequent reaction $A + H = A' + H^{·}$ the yield of decomp. products is small. The reaction $R·CO_2'(H_2O) + h\nu \longrightarrow RH + HCO_3'$ occurs simultaneously. Addition of alkali favours the formation of acids of higher basicity and evolution of H_2. HCO_2Na yields some CO. The undissociated acids in aq. solution undergo several photochemical reactions simultaneously, one of which is always $R·CO_2H + h\nu \longrightarrow CO_2 + RH$. With AcOH and $EtCO_2H$ the reaction $R·CO_2H(H_2O) + h\nu \longrightarrow ROH + HCO_2H$ occurs, the yield being about 0·6 times that of the latter reaction. Other reactions are $PrCO_2H + h\nu \longrightarrow C_2H_4 + AcOH$ and $CO_2H·[CH_2]_2·CO_2H + h\nu \longrightarrow 2CO_2 + C_2H_6$, and all the acids form some condensation products. The quantum yield of the decomp. sometimes approaches 1. Investigation of the decomp. of AcOH vapour has shown the primary reaction of the single mol. to be the spontaneous transformation of the excited mol. into $CH_4 + CO_2$ without collision. In solution the solvent mols. compete with this reaction for the excited mols. The double acid mols. undergo a more complex reaction. When AcOH decomposes in hexane solution the solvent is also attacked. R. C.

New equation for rate of formation of photographic latent image. J. M. BLAIR and P. A. LEIGHTON (J. Physical Chem., 1932, **36**, 1649—1654). —An equation has been derived and checked experimentally by development of coated emulsions containing very small amounts of Ag halide in order to eliminate effects of buried grains. The processes of latent image formation are postulated. The ideal max. *d* has been determined by analysis of developed Ag. R. H. L. (*c*)

Photochemical oxidation of alcohols by potassium dichromate. IV. E. J. BOWEN and J. E. CHATWIN (J.C.S., 1932, 2081—2085).—The effect of changes in $[H^{·}]$ and $K_2Cr_2O_7$ concn. on the photooxidation of the lower aliphatic alcohols up to Bu has been studied. Measurements of the quantum efficiencies of a no. of acceptors have been made. The earlier work is summarised and possible reaction mechanisms are discussed. F. J. W.

Photolysis of aliphatic aldehydes. I. Propaldehyde. P. A. LEIGHTON and F. E. BLACET (J. Amer. Chem. Soc., 1932, **54**, 3165—3178).—The photolysis of EtCHO is studied using monochromatic light (range 2537—3130 Å.). The polymerisation products could not be determined; the calc. quantum efficiency of apparent polymerisation increases steadily in the pressure range 13—200 mm. from 0·03 to 0·78. The quantum efficiency of decomp. does not vary with pressure; it increases with decreasing wave-

length from 0·51 at 3130 to 1·02 at 2537 Å. Decomp. seems to be a unimol. reaction, whilst polymerisation appears to be bimol. H_2 is found in the decomp. products, showing that two decomps. occur; in one case CO and C_2H_6, whilst in the other CO, a higher hydrocarbon, and H_2 are formed. EtCHO shows fluorescence at wave-lengths longer than 2654 Å. Mechanisms for both photochemical reactions are discussed. E. J. R. (b)

Quantum yield in the photo-decomposition of the alkyl halides in non-polar solvents. W. WEST and (Miss) B. PAUL (Trans. Faraday Soc., 1932, 28, 688—697).—Quantum efficiencies for the photo-decomp. of the lower alkyl iodides in hexane solution in absence of O_2 vary with the org. radical, being 0·05 for MeI and 1·15 for $Pr^\beta I$. The yield increases with diminishing wave-length (3130—2610 Å.), is uninfluenced by concn. of the iodide (0·005—1·0M), and within these limits is independent of temp. Oxidisability and readiness of photo-decomp. in absence of O_2 are not parallel. The yield is not markedly reduced in C_6H_6 as solvent. If the deviations of the quantum yield from vals. between 1 and 2 are ascribed mainly to recombination of free alkyl groups and I atoms, the efficacy of collisions in initiating chemical reaction between free radicals and I atoms is in the order $Me > allyl > vinyl > Et > Pr^\alpha > Pr^\beta$. E. S. H.

Photochemistry of aromatic nitroaldehydes. C. JANSSEN (Z. physikal. Chem., 1932, B, 18, 241—264).—In the photochemical conversion of nitro-terephthalaldehyde (I) into nitrosoterephthalaldehyde acid in $COMe_2$ solution in light of wave-length 3740—3251 and 3740—3345 Å. at various temp. the max. yield is 1 mol. for 10 quanta. With light of const. intensity, the rate of reaction, k, diminishes as exposure continues. k increases with the rate of supply of energy, but approaches a limit. This behaviour may be explained by assuming that before exposure the normal mols. of (I) are in equilibrium in solution with an intermediate substance, and that it is this substance, and not the normal mols., which undergoes photochemical reaction (cf. A., 1926, 1247). The absorption spectra of the vapours of (I) and o-nitrobenzaldehyde (II) are continuous, indicating primary photochemical dissociation. The absorption of (II) in solution diminishes with rise in temp., which is ascribed to the presence of an intermediate substance with a relatively small absorption coeff. R. C.

Photochemistry of aromatic nitroaldehydes. F. WEIGERT (Z. physikal. Chem., 1932, B, 18, 367—368).—The theory that the photochemical decomp. of o-nitrobenzaldehyde occurs through a photosensitive |intermediate substance (cf. preceding abstract) is rejected. R. C.

Chemical action of penetrating radium radiation. XIX. Action on isobutyl and benzyl alcohols. A. KAILAN (Monatsh., 1932, 60, 270—283; cf. A., 1929, 1406).—After the prolonged action of penetrating radiation from radium on $Bu^\beta OH$ and $CH_2Ph\cdot OH$, pure and in C_6H_6 solution, it is found that the no. of mols. of monobasic acid formed (m) is of the same order as the no. of ion pairs formed

(n), the ratios m/n being 0·7 and 1·73, respectively, for the pure liquids, but less for C_6H_6 solutions. The no. (m') of PrCHO mols. formed from $Bu^\beta OH$ is also of the same order, the ratio m'/n being 0·26 for the pure liquid and 0·11 for a C_6H_6 solution. J. W. S.

Coloration of salts by radium radiation, and its application to research. K. PRZIBRAM (Arh. Hemiju, 1932, 6, 138—140).—A lecture. R. T.

Halogen compounds of the rare gases. A. VON ANTROPOFF, K. WEIL, and H. FRAUENHOF (Naturwiss., 1932, 20, 688—689).—The prep. of compounds of Kr with Cl_2 and Br is reported. The former is a dark red solid at the temp. of liquid air, and appears to be quite stable. A. J. M.

Hydrogen from iron and water at room temperature. L. T. ALEXANDER and H. G. BYERS (J. Chem. Educ., 1932, 9, 916—918).—When 100 g. of sand or orthoclase were ground in a steel ball mill for 60 hr. at 20—28° with H_2O free from CO_2, 816 c.c. of H_2 were liberated owing to chemical interaction following the removal of protective films. Contamination of materials in steel colloid mills probably results from the same action. CH. ABS.

Preparation and purification of salts by the method of base-exchange. G. AUSTERWEIL (Bull. Soc. chim., 1932, [iv], 51, 729—747).—The conditions for base-exchange in zeolites are examined. A method is devised for preparing almost quant. yields of salts by double decomp., by leading the requisite solutions successively over zeolites. This process may be carried out even when the ordinary reaction between the solutions is incomplete. In this way, KCN has been obtained in almost quant. yield from KCl and NaCN, KOAc and NaOAc have been formed from KCl and NaCl with $Ca(OAc)_2$, and $BaCl_2$ and $Ca(NO_3)_2$ yield $Ba(NO_3)_2$. The method may be employed further for the purification of commercial salts; e.g., for removing traces of $Fe^{\cdots}$ in $Al_2(SO_4)_3$, or $Ni^{\cdot\cdot}$ in $Co^{\cdot\cdot}$ salts. E. S. H.

Optical investigation of the reaction of polyhydroxides with Schweitzer's reagent. F. ROSENBLATT (Z. anorg. Chem., 1932, 207, 217—224).—Absorption measurements in the visible region show that the reaction of mannitol or glycerol with $[Cu\ en_2(H_2O)_2](OH)_2$ or Schweitzer's reagent is of the type $[Cu\ en_2(H_2O)_2](OH)_2 + 2OH\cdot CH(CH_2\cdot OH)_2 \longrightarrow [Cu\ en_2(H_2O)_2][O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH]_2 + 2H_2O$. Neither reagent gives anionic Cu with biuret. E. S. H.

Silver thiosulphates of ammonium, potassium, and sodium. II. Potassium silver thiosulphate. G. SPACU and J. G. MURGULESCU (Z. anorg. Chem., 1932, 207, 150—156; cf. A., 1931, 1252).—By potentiometric titration of $K_2S_2O_3$ and $AgNO_3$ solutions at different concns. the following compounds have been recognised: $K_2[Ag_4(S_2O_3)_3]$, $K[Ag(S_2O_3)]$, $K_4[Ag_2(S_2O_3)_3]$, $K_3[Ag(S_2O_3)_2],H_2O$. The last compound does not correspond with that obtained when $(NH_4)_2S_2O_3$ is used. E. S. H.

Hydrothermal synthesis of calcium aluminate hydrates. S. NAGAI (Z. anorg. Chem., 1932, 207, 313—318; cf. this vol., 822).—By heating CaO and Al_2O_3 (or Al_2O_3,xH_2O) with steam at high temp. and

pressures the following compounds are formed : $3CaO,Al_2O_3,6H_2O$, $2CaO,Al_2O_3,7H_2O$, $2CaO,Al_2O_3,6H_2O$, and $2CaO,Al_2O_3,3H_2O$. E. S. H.

Hydrothermal synthesis of calcium silicates at ordinary pressure. IV, V. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 320—326B, 380—384B). —IV. Na_2CO_3 solution (10%) does not dissolve CaO,SiO_2 at 100°, and may therefore be employed to separate this silicate from those of higher SiO_2 content. The method has been employed, in conjunction with determinations of free and combined CaO and SiO_2, for the examination of the products obtained by heating 1 : 1, 1·25 : 1, and 1·75 : 1 mixtures of CaO and SiO_2 (cf. this vol., 583) at temp. between 900° and 1200°. In the 1 : 1 mixtures, $3CaO,2SiO_2$ is formed during heating at 900—1100°. When a 1·25 : 1 mixture is heated for 6 hr., the CaO,SiO_2 content increases with rise of temp. from 900° to 1200° and the $2CaO,SiO_2$ content decreases, whereas with the 1·75 : 1 mixtures the reverse is the case. Even after 6 hr. three silicates are present in the product. The experiments show also that the silicate sol. in 10% Na_2CO_3 solution is a mixture of $2CaO,SiO_2$ and $3CaO,2SiO_2$.

V. In mixtures of CaO and SiO_2 (3 : 2) heated in H_2O vapour at temp. between 900° and 1200° the amount of $3CaO,2SiO_2$ and $2CaO,SiO_2$ formed increases abruptly at the highest temps., whilst that of CaO,SiO_2 diminishes; at still higher temp. (1250—1300°) about 90% of $3CaO,2SiO_2$ is present in the product. Part of the CaO remains uncombined after heating for 6 hr. at 900°. In absence of H_2O, $2CaO,SiO_2$ and $3CaO,2SiO_2$ are formed in nearly equal quantities at 1420—1450°. H. F. G.

Preparation of pure zinc chloride. R. T. HAMILTON and J. A. V. BUTLER (J.C.S., 1932, 2283—2284).—Pure $ZnCl_2$ is prepared in quantity by passing dry HCl over pure Zn in anhyd. Et_2O and evaporating the solution in vac. E. E. J. M.

Active oxides. LI. Hydrates, methyl alcoholates, and pyridinates of zinc oxalate. G. F. HÜTTIG and B. KLAPHOLZ. **LII. Characterisation of the thermal decomposition of zinc oxalate dihydrate by dispersoid-analytical investigations.** G. F. HÜTTIG and T. MEYER (Z. anorg. Chem., 1932, 207, 225—233, 234—241).—LI. $ZnC_2O_4,2H_2O$ is pptd. from aq. solutions. Previous analyses showing higher H_2O contents are due to sorbed H_2O. The crystals lose H_2O when heated, but when the composition $ZnC_2O_4,0·03H_2O$ is reached, marked decomp. occurs with evolution of CO and CO_2. There is no point of arrest corresponding with a monohydrate. The prep. of $ZnC_2O_4,2MeOH$ from $ZnCl_2$, MeOH, and $H_2C_2O_4$ in absence of H_2O is described; MeOH is given up slowly at room temp. and rapidly at 60°; H_2O converts it into the dihydrate. An attempt to prepare a similar compound with EtOH was unsuccessful. The prep. of $ZnC_2O_4,2C_5H_5N$ by adding C_5H_5N to ZnC_2O_4 in absence of H_2O is described; heat converts it into ZnC_2O_4, and H_2O into $ZnC_2O_4,2H_2O$. $C_5H_5N,H_2C_2O_4$, m.p. 149°, has been prepared by addition of the reagents in EtOH solution. The absence of compounds in other mol. ratios has been confirmed by X-ray analysis.

LII. The thermal decomp. of $ZnC_2O_4,2H_2O$ has been followed by determining d, sedimentation velocity, and resistance to stirring, and by means of photomicrographs. In the first stage ($ZnC_2O_4,2H_2O \longrightarrow ZnC_2O_4$) the particle size gradually increases and the mass becomes more homogeneous; in the second stage ($ZnC_2O_4 \longrightarrow ZnO$) these changes are reversed. E. S. H.

Appearance of intermediate stages, highly magnetic and catalytically very active, in the thermal formation of zinc–chromium spinels. G. F. HÜTTIG, H. KITTEL, and H. RADLER (Naturwiss., 1932, 20, 640; cf. this vol., 1009).—In the formation of $ZnCr_2O_4$ by heating equimol. proportions of ZnO and Cr_2O_3 an unstable intermediate product possessing ferromagnetic properties, high catalytic power, and a characteristic X-ray spectrum is formed. W. R. A.

Non-metal halogen compounds. III. Saturation pressures of boron trifluoride. E. POHLAND and W. HARLOS (Z. anorg. Chem., 1932, 207, 242—245; cf. this vol., 132).—The relation between v.p. and temp. for solid BF_3 is expressed by log $p = -1176·6/T + 1·75$ log $T - 0·0032084T + 6·6293$; for liquid BF_3, log $p = -1174·4/T + 1·75$ log $T - 0·013350T + 8·0536$. BF_3 has m.p. $-128°$ (obs.) and b.p. $-99·9°$ (by extrapolation). BF_3,HCN, prepared by direct addition, has m. p. $-40°$ (under pressure; at room temp. the gas is completely dissociated). E. S. H.

Oxonium salt from titanium tetrachloride and ethyl ether. A. DIMITRIOS and E. LADIKOS (Praktika, 1930, 5, 449—454; Chem. Zentr., 1932, i, 1648). —$TiCl_4,2Et_2O$, from $TiCl_4$ and anhyd. Et_2O, is very hygroscopic and is rapidly decomposed by H_2O. A. A. E.

Preparation of optically identical solutions of impure dyes by means of the step photometer. C. URBACH (Biochem. Z., 1932, 251, 447—451).—A photometric method is described which makes possible the repeated prep. of optically identical solutions of impure dyes, Ti-yellow being taken as an example. P. W. C.

Behaviour of germanium tetrachloride and related chlorides, especially arsenious chloride, with concentrated hydrochloric acid. E. R. ALLISON and J. H. MÜLLER (J. Amer. Chem. Soc., 1932, 54, 2833—2840).—Complete removal of $AsCl_3$, $SbCl_3$, $SnCl_4$, and $TiCl_4$ from $GeCl_4$ can be effected by extraction with conc. HCl. The distribution of $AsCl_3$ between conc. HCl and $GeCl_4$ was studied at 0°. H. F. J. (c)

Synthesis of homoplex poly-compounds of antimony bromide. A. C. VOURNASOS (Praktika, 1930, 5, 324—331; Chem. Zentr., 1932, i, 1642—1643).—The following *compounds* $X_2Sb_3Br_{11}$ are described : X=K, Na, Li, NH_4 ($2H_2O$); X_2=Ba ($2H_2O$), Cd. A. A. E.

Rhenium trioxide. II. W. BILTZ and G. A. LEHRER [with K. MEISEL] (Z. anorg. Chem., 1932, 207, 113—120).—When heated, mixtures of oxides of Re yield ReO_3 and Re. The proportion of metal present is proportional to the intensity of the Re X-ray lines. J. W. S.

Blue anhydrous iron phosphate. G. TAMMANN and H. O. VON SAMSON-HIMMELSTJERNA (Z. anorg. Chem., 1932, **207**, 319—320).—The blue colour produced by heating at 700° $FePO_4$ which has been pptd. by $(NH_4)_2HPO_4$ is due to the reducing action of H_2 formed by decomp. of $(NH_4)_2HPO_4$. The compound is probably $2FeO,P_2O_5$. E. S. H.

Roasting and reduction relations of spathic iron ore. J. KLÄRDING (Z. anorg. Chem., 1932, **207**, 246—250; cf. A., 1931, 1096).—The decomp. of siderite at 900° involves the reactions (a) $FeCO_3 = FeO + CO_2$ and (b) $3FeO + CO_2 = Fe_3O_4 + CO$. E. S. H.

Complex cyanides of iron and hexamethylene-tetramine. A. PERRET and A. GISLON (Bull. Soc. chim., 1932, [iv], **51**, 751—757).—The following *compounds* are described :
$Na_2[Fe(CN)_5NO],2C_6H_{12}N_4,5—6H_2O$;
$K_2[Fe(CN)_5NO],2C_6H_{12}N_4,3H_2O$;
$Li_2[Fe(CN)_5NO],2C_6H_{12}N_4,5H_2O$, and
$Na_4[Fe(CN)_5NO_2],2C_6H_{12}N_4,5H_2O$: all are dissociated in aq. solution. $(NH_4)_4Fe(CN)_6$ forms a series of mixed crystals with hexamethylenetetramine. No evidence could be found for the existence of the compounds $K_3Fe(CN)_6,C_6H_{12}N_4,9H_2O$ and $Na_2[Fe(CN)_5NO],C_6H_{12}N_4,11H_2O$ of Ray and Sarkar.
H. A. P.

Thiocyanates of bi- and ter-valent iron. A. ROSENHEIM, E. ROEHRICH, and L. TREWENDT (Z. anorg. Chem., 1932, **207**, 97—110).—By the interaction of EtOH solutions of RCNS (R=alkali metal) and $FeCl_3$, there are formed the *compounds* $R_4[Fe(CNS)_6],xH_2O$ containing Fe^{II}. The corresponding derivatives of Fe^{III} are formed only in aq. solution. With $R_3Fe(CNS)_6$ pyridine gives the *compound* $C_5H_6N[Fe(C_5H_5N)_2(CNS)_4]$ (cf. Reinicke's salt and corresponding Mo^{III} and V^{III} compounds; A., 1931, 697; this vol., 31). The acid of the above salt yields characteristic Tl and Cd salts. The compounds of this series are stable in org. solvents but hydrolysed by H_2O. Boiling C_5H_5N reduces them to $[Fe(C_5H_5N)_4(CNS)_2]$, which in boiling $CHCl_3$ loses part of its C_5H_5N to give $[Fe(C_5H_5N)_2(CNS)_2]$. Atm. oxidation of a $CHCl_3$ solution of $[Fe(C_5H_5N)_4(CNS)_2]$ gives $[Fe_3(C_5H_5N)_{10}(CNS)_8]$ corresponding with Fe_3O_4 and probably $[Fe(C_5H_5N)_6][Fe(C_5H_5N)_2(CNS)_4]_2$. This is most probably the same compound as obtained by Spacu (A., 1914, i, 1089) by the action of C_5H_5N on $Fe(CNS)_3$ at room temp., and previously regarded as a β-isomeride of $[Fe(C_5H_5N)_4(CNS)_2]$. Quinoline yields a *compound* $C_9H_8N[Fe(C_9H_8N)_2(CNS)_4]$ on reaction with $R_4[Fe(CNS)_6],xH_2O$. The action of C_5H_5N on $Fe(CNS)_3$ yields a *compound* of approx. composition $[Fe(C_5H_5N)_2(H_2O)_2(CNS)_2]CNS$. J. W. S.

Reduction of ilmenite in the gaseous phase. V. S. SUIROKOMSKI, E. V. SNOPOVA, and N. I. ROTKOV (Min. Suir, 1931, 6, 522—527).—Fe_2O_3 in oxidised ilmenite or titanomagnetite is reduced with H_2 to Fe at high temp. CH. ABS.

Appearance of highly magnetic intermediate stages in the thermal decomposition of non-tronite. W. GEILMANN, W. KLEMM, and K. MEISEL (Naturwiss., 1932, **20**, 639—640; cf. this vol., 1008).—The nontronite was heated up to 1200°, and samples were

taken at different high temps. Between 300° and 500° κ decreases slightly due to the loss of H_2O of constitution. At 800° κ increases and is dependent on the applied field. This indicates the formation of an unstable ferromagnetic intermediate compound in the decomp. W. R. A.

"Chloramine" as reagent in volumetric analysis. O. TOMÍČEK and B. SUCHARDA (Coll. Czech. Chem. Comm., 1932, 4, 285—299).—A detailed account of work already noted (this vol., 825).

Precision with which concentrations of solutions of hydrochloric acid and sodium hydroxide may be determined with the immersion refractometer. E. R. WASHBURN and A. L. OLSEN (J. Amer. Chem. Soc., 1932, **54**, 3212—3218).—Equations are given for computing the concn. of HCl or NaOH from the reading of the instrument and the precautions necessary are stated. A difference of 0·1 in the scale reading corresponds with a difference in normality of 0·0048 for HCl and 0·0036 for NaOH. All the results obtained at 20°, 25°, and 30° agreed within these limits. W. T. H. (c)

Use of adsorption indicators in titrations of halides of limited or reversible ionisation. A. J. BERRY (Analyst, 1932, **57**, 511—514).—Phenosafranine, tartrazine, and " pyrazolone jaune " are the only adsorption indicators which have been found satisfactory. With weak electrolytes, such as Hg or Tl halides, determinations are difficult, if not impossible. With complex compounds of the type $[ClCo(NH_3)_5]Cl_2$ adsorption indicators may be used to trace the rate of ionisation in solutions. T. McL.

Potentiometric determination of small quantities of iodide in presence of large quantities of chloride and bromide. R. FLATT and A. BONAME (Bull. Soc. chim., 1932, [iv], **51**, 761—769).—The mixture is titrated potentiometrically with $0·1N-KMnO_4$. I is liberated and later forms ICl. Br is not liberated until this second phase of the reaction is complete. By working in fairly conc. HCl solution and observing the potential rise corresponding with the formation of ICl, it is possible to determine I' in presence of 1000 times the amount of Br' and any amount of Cl'. E. S. H.

Specific reaction of iodides. C. I. KRUISHEER (Z. anal. Chem., 1932, **89**, 196—197).—The solution is mixed with an equal vol. of conc. HCl and saturated with SO_2; if I' is present a yellow colour appears which may be extracted with $C_5H_{11}·OH$. A. R. P.

Determination of the sulphate ion by precipitation as barium sulphate. J. N. FRIEND and W. N. WHEAT (Analyst, 1932, **57**, 559—562).—Precautions to be observed for the prevention of adsorption of alkali salt in the $BaSO_4$ ppt. are described. E. B. H.

Use of ultra-violet light for the detection of traces of sulphites. J. GRANT and J. H. W. BOOTH (Analyst, 1932, **57**, 514—515).—0·25 mg. of SO_2 may be detected by oxidation and the formation of quinine sulphate. HCl is used to liberate SO_2 as quinine phosphate is fluorescent, and oxidising agents must be free from S compounds. T. McL.

Sensitive reaction for the detection of thiosulphate and its separation from sulphide, sulphite, sulphate, tetrathionate, and thiocyanate. G. Spacu and P. Spacu (Z. anal. Chem., 1932, 89, 192—196).—S_2O_3'' in neutral or feebly alkaline solutions yields a cryst. violet ppt. of the *compound* [Ni en$_3$]S$_2$O$_3$ with solutions of [Ni en$_3$](NO$_3$)$_2$, whereas S'', SO$_3$'', SO$_4$'', S$_2$O$_6$'', and CNS' yield no reaction. (NH$_4$)$_2$S decomposes the ppt., but Na$_2$S is without action.   A. R. P.

Determination of tellurium as crystalline tellurium and as tellurium dioxide. O. E. Clauder (Z. anal. Chem., 1932, 89, 270—282).—Cryst. Te is pptd. quantitatively from solutions containing 15—20% HCl, and only small amounts of org. acids or H$_2$SO$_4$ by adding a 5—10% solution of H$_3$PO$_2$, N$_2$H$_4$,H$_2$SO$_4$, semicarbazide+HCl, NH$_2$OH +HCl, H$_2$SO$_3$, or TiCl$_3$, and warming gradually. The ppt. is readily washed and dried, and does not oxidise in the air. With special precautions the determination may be made in presence of moderate amounts of Sb, Bi, Cu, or Pb. TeO$_2$ is pptd. quantitatively from a hot solution containing HCl and NH$_4$Cl by adding 20% aq. hexamethylenetetramine. The TeO$_2$ is washed, dried, and weighed. This determination may be made in presence of excess of H$_2$SeO$_3$. A micro-determination by the same method is also described.   H. J. E.

Optical determination of sodium nitrite. K. Weber (Chem.-Ztg., 1932, 56, 642—643).—Unlike all other colourless inorg. salts, NaNO$_2$ absorbs radiation between 3000 and 4000 Å. For λ 3660 Å., the % absorption $A=100(1-10^{-3\cdot02cp})$, where c is the concn. of the solution (g. per 100 c.c.) and p the thickness of the layer in cm. NaNO$_2$ in brine, preserving salt, etc. may be determined by fluorometric observation of the absorption to within 0·0015%, calc. for a 10% salt solution; a 0·1% solution of quinine sulphate in N-H$_2$SO$_4$ is recommended as the fluorescent solution.   H. F. G.

Direct titration of nitrates with titanous chloride using alizarin as an adsorption indicator. A. W. Wellings (Trans. Faraday Soc., 1932, 28, 665—667).—0·01N- and 0·1N-solutions of NO$_3$' can be determined by titrating with TiCl$_3$, using alizarin as an adsorption indicator. When sufficient H$_2$O is present, the TiCl$_4$ is hydrolysed on boiling, and the colour change occurs at the surface of the colloidal TiO$_2$ particles.   E. S. H.

Determination of phosphate and glycerophosphate ions by the mercurimetric method. I. Ionesco-Matiu and (Mme.) A. Popesco (Bull. Soc. chim., 1932, [iv], 51, 769—774).—The method (cf. B., 1928, 690) has been applied successfully to the determination of PO$_4$''' and C$_3$H$_5$(OH)$_2$PO$_4$''.   E. S. H.

Titration of arsenic precipitated by hypophosphorous acid. B. S. Evans (Analyst, 1932, 57, 492—494; cf. B., 1929, 1046).—Certain filterpapers give a blue colour with I which is stable to As$_2$O$_3$, but preliminary treatment of the pulp with Br in dil. HCl prevents the formation of the colour. C$_6$H$_6$ is added as an indicator in the initial titration, starch being added for the end-point.   T. McL.

Colorimetric determination of silica. E. J. King (Contr. Canad. Biol. Fish., 1931, 7, No. 8—11, D, No. 1—4, 121—125).—An apparatus compensating for the natural colour of the H$_2$O is employed. 10% NH$_4$ molybdate (2 c.c.) and 50 vol.-% H$_2$SO$_4$ (4 drops) are added to H$_2$O (100 c.c.), the resulting colour being matched against an artificial standard of picric acid (25·6 mg. in 1 litre of H$_2$O $\equiv$ 50 mg. of SiO$_2$ in 1 litre).   Ch. Abs.

Microdetermination of carbon in the organic state in water. M. Picon.—See B., 1932, 818.

Analysis of gaseous elements in metals. N. A. Ziegler (Trans. Electrochem. Soc., 1932, 62, 175—187; cf. B., 1928, 573).—The sample is melted in a graphite crucible in vac. by means of a high-frequency induction furnace, and the gases evolved (CO, H$_2$, and N$_2$) are measured by a deflexion manometer after expansion into a known vol. Manometer readings after oxidation and selective freezing out of H$_2$O and CO$_2$ are obtained, and separate re-vaporisation of H$_2$O and CO$_2$ gives a check on the proportions of H$_2$ and O$_2$ determined by difference. The method has an accuracy of about 0·002% and is especially advantageous for small samples of low gas content.   H. J. T. E.

Determination of cæsium in presence of rubidium and other alkali metals. N. A. Tananaev and E. P. Harmasch (Z. anal. Chem., 1932, 89, 256—262).—Cs is pptd. as cryst. Cs$_3$Bi$_2$I$_9$ by adding a hot solution of BiI$_3$ in HI to the conc. solution containing Cs alone, or with other alkali metals. The ppt. is washed with aq. Cs$_3$Bi$_2$I$_9$, then with cold H$_2$O, dried 1½—1¾ hr. at 140—150°, and weighed. An accuracy >99% is obtained.   H. J. E.

Determination of traces of silver in presence of both copper and chloride. N. Kameyama and S. Makishima (J. Soc. Chem. Ind. Japan, 1932, 35, 372—373b).—The Cu is removed by adding NaOH to the solution, heating, and filtering; if sufficient Cl' is present no Ag is lost. The Ag may then be determined colorimetrically with rhodanine; 0·05 mg. of Ag in 100 c.c. of 4N-NaCl containing a little NaOH may be detected, and the intensity of the coloration is proportional to the quantity of Ag present. If the solution is nearly neutral the trace of Cu·· remaining interferes. The method is suitable for the determination of 0·1—0·001% of Ag in refined Cu.   H. F. G.

Determination of calcium by the filtration method. H. T. Bucherer and F. W. Meier (Z. anal. Chem., 1932, 89, 171—173).—Titration of the ammoniacal Ca solution containing a little EtOH with 0·1N-Na$_2$C$_2$O$_4$ at 80° is recommended.   A. R. P.

Determination of the insoluble matter in calcium hypochlorite. A. Vassiliev and H. Stutzer.—See B., 1932, 770.

Rapid gravimetric analysis without ignition of precipitates (washing with alcohol and ether). A. A. Vassiliev and A. K. Sinkovskaja (Z. anal. Chem., 1932, 89, 262—268).—Dick's method of washing the ppt. with EtOH and Et$_2$O and drying in a vac. desiccator instead of igniting (cf. A., 1929, 901; 1931, 453) gave trustworthy results for Ca, Ba, Ni, SO$_4$, and Mg.   H. J. E.

Precipitation of barium sulphate in presence of salts of thorium and uranium. L. A. VASILEVA (Uchen. Zapiski Kazan. Gos. Univ., 1930, 90, 15—26).—The ppt. contains Th and U from Th$^{····}$ and $UO_2^{··}$; $UO_2^{··}$ probably forms a solid solution in $BaSO_4$ and complex Ba, Th, and UO_2 sulphates are probably formed. CH. ABS.

Gravimetric micro-analysis of beryllium silicate rocks. H. THURNWALD and A. A. BENEDETTI-PICHLER (Mikrochem., 1932, 11, 200—220).—Full details are given of the determination of SiO_2, PO_4''', Al, Be, Mg, and Ca in a few mg. of the mineral, together with the results of applying the methods described to a 27-mg. sample of kolbeckite. H. F. G.

Use of a sulphate–hydrogen sulphate buffered solution for precipitation of zinc sulphide. C. E. P. JEFFREYS and E. H. SWIFT (J. Amer. Chem. Soc., 1932, 54, 3219—3228).—The pptn. of ZnS from such a solution is complete even at [H$^·$] as high as $2·5 \times 10^{-2}$. Ni, Fe, Mn, Cr, and Al, but not Co, may be quantitatively separated from Zn by this pptn. High [Cl'] increases the solubility of ZnS. A procedure is outlined for quant. pptn. of Zn and its separation from the other metals. The temp. should be maintained at 500° when igniting $ZnSO_4$ and at 900° when igniting to ZnO. C. E. P. J. (c)

Liquid amalgams in volumetric analysis. S. KANEKO and C. NEMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 343B).—Practical notes are given as to the reduction of solutions with Zn etc. amalgam prior to titration with $KMnO_4$ solution. H. F. G.

Luminescence analysis. IV. Fluorescence of zinc oxide. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1932, 61, 69—86).—The following fluorescence colours are shown by various samples of ZnO : yellowish-brown, golden-orange (preps. obtained at relatively low temp.), dark brown (prepared by decomp. of the basic carbonate at 300°), olive, greenish-yellow, bright green (preps. obtained by ignition of ZnO in a reducing atm.). A definite relationship between fluorescence colour and physical properties does not appear to exist. The degree of fluorescence is diminished by pulverisation. The action of moist CO_2 on ZnO (giving the salt $5ZnO,2CO_2,4H_2O$) is accompanied by changes in fluorescence which can be followed with a step photometer (A., 1931, 453). H. B.

Testing of tap water for small quantities of lead and copper. N. SCHOORL.—See B., 1932, 818.

Mechanism of precipitation processes. X. Reaction between lead acetate and iodide ions. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1932, 207, 129—132; cf. A., 1931, 182, 582, 1021).—The formation of PbI_2 is favoured by high [H$^·$] and a low mol. ratio $Pb(OAc)_2$: KI. Opposite conditions favour the pptn. of Pb(OH)I. Mixtures are often produced in this reaction. Pb(OH)I is pptd. when $Pb(NO_3)_2$ reacts with KI in presence of NH_4OAc. PbI_2 is converted into Pb(OH)I by boiling with aq. NaOAc. The solubility of Pb(OH)I is 0·074 g.-mol. per litre at 16°. E. S. H.

Electrolytic deposition of copper from nitric acid solution and a simple electrolytic separation of copper and lead. H. BJØRN-ANDERSEN (Z. anal. Chem., 1932, 89, 178—187).—Deposition of Cu from HNO_3 solutions is retarded and the pptn. of the last traces of Cu prevented by the formation of HNO_2 at the cathode, and these effects are greater the higher is the acid concentration. Quant. deposition of Cu is obtained by neutralising the solution or by addition of $CO(NH_2)_2$, which, besides destroying the HNO_2 in solution, retards formation of this acid at the cathode. For the electrolytic separation of Cu and Pb the solution is made 1·5N with HNO_3 and electrolysed with 2 amp. at 70°, using a Pt dish anode and a Pt gauze cathode; after 30 min. two thirds of the acid is neutralised with aq. NH_3 and electrolysis continued for another 30 min. to complete deposition of PbO_2 and start that of Cu at the cathode. $CO(NH_2)_2$ is added and electrolysis continued at 55° until no further Cu remains in the electrolyte. Both anode and cathode are washed with H_2O, then with EtOH, and dried, the former at 200° and the latter at 50°. A. R. P.

Determination of minute amounts of copper in presence of iron and certain other metals. L. A. HADDOCK and N. EVERS (Analyst, 1932, 57, 495—499).—Cu is adsorbed on $Fe(OH)_3$. Fe$^{···}$, or Cr$^{···}$, may be kept in solution by citric acid and NH_3 at $p_H > 9$; Al, Zn, and Sn are dissolved in NaOH and aq. NH_3 before the addition of Na diethyldithiocarbamate. Cu diethyldithiocarbamate is formed and extracted with CCl_4; the colour is proportional to the amount of Cu present. T. McL.

Rapid determination of mercury. G. SPACU and P. SPACU (Z. anal. Chem., 1932, 89, 187—191).—The neutral or feebly ammoniacal Hg$^{··}$ solution is treated at 100° with an excess of KI and boiling conc. aq. $[Cu pn_2]SO_4$ (pn=propylenediamine), whereby the Hg is pptd. completely on cooling as the dark bluish-violet cryst. compound $[Cu pn_2]HgI_4$ (21·81% Hg). The ppt. is washed with 0·1% aq. KI containing 0·1% $[Cu pn_2]SO_4$, then with 96% EtOH, and finally with Et_2O, dried in a vac. desiccator, and weighed. A. R. P.

Separation of aluminium from iron by the thiosulphate method. A. K. KUTARKINA (Uchen. Zapiski Kazan. Gos. Univ., 1930, 90, 156—161).—The separation by addition of $Na_2S_2O_3$ in slightly acid solution is more complete if the solution is boiled for nearly 1 hr.; double filtration is advisable. Excess of $NH_4^·$ should be avoided. CH. ABS.

Potentiometric analysis in the steelworks laboratory. P. DICKENS and G. THANHEISER.—See B., 1932, 801.

Electrometric determination of iron in felspar. A. K. LYLE, jun.—See B., 1932, 723.

Volumetric analysis utilising titanous sulphate solution. S. KANEKO and C. NEMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 348—349B).—A solution of $Ti_2(SO_4)_3$ prepared by reducing a solution of $Ti(SO_4)_2$ (8 g. of TiO_2 and 60 g. of K_2SO_4 per litre) with Zn–Hg may be employed for the direct titration of Fe$^{···}$ salt solutions, NH_4CNS being used as indicator. The $Ti_2(SO_4)_3$ solution is standardised by adding an excess of Fe alum and titrating the $FeSO_4$ formed with $KMnO_4$. $KClO_3$ and $KBrO_3$ may be determined by

adding a solution to an acidified solution of $FeSO_4$, and titrating the $Fe^{...}$ formed.   H. F. G.

Determination of iron in aluminium. L. Szegö.—See B., 1932, 802.

Ferrocyanides and some of their [analytical] applications. C. T. Gaspar y Arnal (Ann. Chim. Analyt., 1932, [ii], 14, 342—351).—A summary.   J. W. S.

Separation of nickel and cobalt and their determination by the filtration method. H. T. Bucherer and F. W. Meier (Z. anal. Chem., 1932, 89, 161—171).—In one portion of the solution Ni and Co together are determined by titration with 8-hydroxyquinoline at 70° in very dil. AcOH containing NaOAc, and in another portion the Ni alone is determined by titration with 0·3% dimethylglyoxime in 1 : 1 $COMe_2$-H_2O in a solution containing 2% AcOH and some NaOAc. If Co is in excess of the Ni, sufficient standard Ni solution should be added in the second titration to make the Ni : Co ratio at least 1 : 1. The end-point in each case is determined by filtration of a small portion of the solution and addition of more reagent to the filtrate.   A. R. P.

Alkaline persulphate as an analytical reagent. W. M. Dehn and D. A. Ballard (J. Amer. Chem. Soc., 1932, 54, 3264).—Heating with $K_2S_2O_8$ in presence of KOH is recommended for the pptn. of $Co(OH)_3$ and $Ni(OH)_3$, and for the oxidation of simple and complex CN compounds and S_2O_3''.   W. T. H. (c)

Titration of bivalent tin with potassium chlorate. R. M. Kulvarskaja (Z. anal. Chem., 1932, 89, 199—201).—The conc. HCl solution of Sn'' is titrated with N- or $0·1N$-$KClO_3$, using 1 drop of $0·1N$-$FeCl_2$ as indicator, a yellow colour ($FeCl_3$) appearing at the end-point. $As^{...}$ and $Sb^{...}$ do not interfere.   A. R. P.

Determination of small quantities of antimony in copper and its alloys. W. Boehm and W. Raetsch.—See B., 1932, 801.

Determination of bismuth as phosphate in presence of organic compounds. P. P. Solodov-nikov (Uchen. Zapiski Kazan. Gos. Univ., 1929, 39, 873—875).—Moser's method can be employed if a little HNO_3 is added and the solution is filtered as soon as it clears after addition of Na_2HPO_4. The ppt. may be washed with 90% EtOH when sparingly sol. org. substances are present. If EtOH is present in the solution less HNO_3 need be added.   Ch. Abs.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXIII. Quantitative separation of tantalum, niobium, titanium, and zirconium. W. R. Schoeller and A. R. Powell (Analyst, 1932, 57, 550—554).—Tannin separates quantitatively Ta, Nb, and Ti from Zr, Th, and Al, the former group being pptd. from slightly acid oxalate solution and the latter from slightly alkaline oxalate solution.   E. B. H.

Micro-m.p. apparatus. P. Muller (Ann. Chim. Analyt., 1932, [ii], 14, 340—341; cf. this vol., 36).—A m.-p. apparatus which permits the microscopic

observation of the substance during the determination is described.   J. W. S.

Hortvet cryoscope. D. Henville (Analyst, 1932, 57, 569—570).—Improvements to prevent leakage of Et_2O, to stir efficiently, to avoid parallax in reading the thermometer, and to obtain ice when required are suggested.   E. B. H.

Continuously operating laboratory furnaces. F. Seidenschnur (Chem. Fabr., 1932, 317—318).—The electrically-heated furnace described is suitable for use in research on the carbonisation of coal, the degassing of solid fuels, tar distillation, catalytic gas reactions, vapour-phase oil refining, etc. Its capacity permits a daily throughput of 5—15 kg. of coal.   H. F. G.

Photo-electric colorimetry. V. Applications of the "Sperrschicht" type of photo-electric cell. R. H. Müller (Mikrochem., 1932, 11, 353—368).—The short-circuit current of the "Sperrschicht" cell (Cu-Cu_2O-Cu etc.) is proportional to the intensity of the incident light, and such cells are therefore very suitable for colorimetric work. Typical measurements are described. The light filter and the thickness and concn. of solution used must be chosen with care ; small variations of voltage across the light source may introduce large errors.   H. F. G.

Photo-electric cell in micro-acidimetry. H. M. Partridge and R. A. Smith (Mikrochem., 1932, 11, 311—325).—In the method described a photo-electric cell, in conjunction with a suitable light filter, is employed to observe the colour change of the indicator used (bromothymol-blue) ; 5 c.c. of $0·007N$-acid may be titrated with an error of 1 part in 750 parts.   H. F. G.

Photo-electric polarimeter. G. Bruhat and P. Chatelain (Compt. rend., 1932, 195, 370—372).—The polarimeter is on the half-shadow principle, the pencils of light being separated after traversing the polarimeter tube ; a double monochromator and K cell are used, the photo-electric current, of the order of 10^{-9} amp., being amplified about 10^6 times. The method avoids the necessity of determining or compensating absorption (cf. A., 1931, 1026), and is accurate to 0·1%.   C. A. S.

Constant-temperature cells for microscopic observations. J. B. M. Coppock, J. Colvin, and J. Hume (Chem. and Ind., 1932, 700—701).—A cell for use below 40° consists of a cemented glass cell held inside a larger one, with H_2O at a const. temp. flowing between. For temp. between 150° and 400° a metal box suitably insulated and heated electrically is employed. Light is admitted by a glass window, and the sample is placed in a SiO_2 bowl.   T. McL.

Demountable cell for the X-ray investigation of liquids. S. Zeidenfeld (J. Sci. Instr., 1932, 9, 260—261).—A cell adaptable to the photographic recording of liquid haloes is described.   N. M. B.

Lindemann glass for protecting air-sensitive substances when examined by long X-rays. A. Schleede and M. Wellmann (Z. Krist., 1932, 83, 148—149).—Ordinary Lindemann glass (Li Be borate) is readily devitrified when heated. A glass suitable for long X-ray work is prepared by fusing in a Pt

crucible a mixture of Li_2CO_3 (4·4), Be carbonate (1·4), and H_3BO_3 (18·5) until a homogeneous melt is obtained. C. A. S.

Apparatus for quantum yields of gas reactions by actinometry. G. S. FORBES, G. B. KISTIAKOWSKY, and L. J. HEIDT (J. Amer. Chem. Soc., 1932, 54, 3246—3249).—An apparatus for quant. study of photochemical gas reactions attended by pressure changes is described. Two quartz cells may be exposed alternately, one for the reaction being studied and the other for determination of the quantum yield of $UO_2C_2O_4$, using monochromatic light of the same wave-length. Brief variations of light energy are followed by measurement of the energy flux through a monochromator with a thermopile. L. P. H. (c)

Heterochrome determinations with the Pulfrich photometer. E. MAYER (Physikal. Z., 1932, 33, 665—670).—The Pulfrich photometer can be used for heterochrome determinations, giving results in agreement with those obtained by other methods. A. J. M.

Intensity of illumination in spectrographs. O. OLDENBERG (J. Opt. Soc. Amer., 1932, 22, 441—455).—The intensity of the spectrum from a concave grating is calc. A cylindrical lens in front of the plate appears to be the only device capable of increasing intensity without reducing dispersion and resolving power. J. W. S.

Quartz double monochromator and vario-illuminator with mirrors (instead of lenses) for the range 0·2—3 mμ. C. LEISS (Z. Physik, 1932, 77, 412—414).—The apparatus is described. A. J. M.

Light filters for the mercury lamp. E. J. BOWEN (J.C.S., 1932, 2236—2239).—Light filters and their arrangement for obtaining monochromatic light from the Hg lamp are described. Data are presented for their transmission and their stability under illumination under different energy conditions. J. W. S.

Zero-current thermionic valve galvanometer. H. M. PARTRIDGE [with S. J. BRODERICK] (Mikrochem., 1932, 11, 337—352).—A simple triode circuit is described which is particularly useful when high-resistance (e.g., glass) or easily polarised electrodes are used. The device operates at the no-current point. H. F. G.

Automatic electrometric titrations using a valve. W. KORDATZKI and P. WULFF (Z. anal. Chem., 1932, 89, 241—256).—Details of an apparatus for recording the whole titration curve automatically are given. The apparatus may be modified for conductometric titrations. H. J. E.

Compensated thermionic electrometer. K. G. COMPTON and H. E. HARING (Trans. Electrochem. Soc., 1932, 62, 195—206).

Recent progress in electro-organic chemistry. C. J. BROCKMAN (Trans. Electrochem. Soc., 1932, 62, 265—270).

Electrolysis stand. E. REICHEL (Z. anal. Chem., 1932, 89, 173—177).—The stand contains a support for the beaker, an adjustable micro-burner below,

and a support with two parallel arms which carry the electrodes one on each side of the top of the beaker. Connexions are made between the electrodes and the arms of the support through narrow slits in the top of the beaker. In this way corrosion of the supports and contamination of the beaker contents are avoided. A. R. P.

Hydrogen electrode vessel. A. J. LINDSEY (Analyst, 1932, 57, 573).—A description of a small vessel, capacity 5—7 c.c., which can be easily cleaned, about 3 min. being required for saturation of the solution with H_2. E. B. H.

Automatic suction and drop apparatus. E. LÖWENSTEIN (Chem.-Ztg., 1932, 56, 683—684).—An apparatus for the automatic suction of liquid into a pipette and the adjustment of its vol. is described. M. S. B.

Vacuum micro-distillation. R. A. SMITH (Mikrochem., 1932, 11, 221—226).—The Pregl apparatus has been modified in such a manner that the temp. of the vapour above the boiling liquid can be measured (by a thermocouple) and fractional distillation may be carried out. H. F. G.

Micro-determination of vapour density. I. Determination of mol. wt. J. B. NIEDERL and W. J. SASCHEK. **II. Determination of b.p.** J. B. NIEDERL and I. B. ROUTH (Mikrochem., 1932, 11, 237—250, 251—273).—I. Niederl's original apparatus has been improved, and the necessary corrections for the expansion of the vessel with temp. and for the v.p. of Hg and capillary effects have been determined. Tests with various pure liquids show the method to be at least as accurate as the usual macro-methods. The v.p. and b.p. may be determined simultaneously and repeatedly on one sample (about 10 mg.), and during both heating and cooling.

II. The b.p. of a pure liquid may be determined sharply in the modified apparatus, whilst for mixtures the entire b.-p. range may be determined graphically. Results are given for EtOH, NH_2Ph, thymol, CCl_4, and C_6H_6. Various methods of calculating the b.p. to 760 mm. are compared. H. F. G.

Torsion method for measuring very small vapour pressures. K. NEUMANN and E. VÖLKER (Z. physikal. Chem., 1932, 161, 33—45).—The vessel containing the substance under examination is suspended by a torsion fibre in a space which is then evacuated. Vapour escapes from the vessel through two holes, in such a position as to establish a torque; from the resulting deflexion the v.p. can be calc. The method may be used to measure v.p. of 10^{-2} to 10^{-4} mm. with an error of 0·5—1·5%. From the v.p. of Hg and K the chemical consts. are calc. as $1·91 \pm 0·06$ and $1·105 \pm 0·05$, respectively. R. C.

Applicability of the shaking flask. H. BARSCH (Chem.-Ztg., 1932, 56, 622).—A dimensional drawing is given of a flask provided with a ground-glass stopper (with spring clip) traversed by a sealed-in glass tube which outside the flask is closed by a glass tap and inside the flask reaches nearly to the bottom, where its constricted end is bent through 180°. The flask can be used alone for ordinary purposes and after attachment of the stopper can serve in place of a separating funnel in the determination of fats etc. D. F. T.

Vacuum filtration apparatus. R. RIPAN (Z. anal. Chem., 1932, **89**, 198).—The apparatus comprises a glass head which fits into the usual conical filtration flask and is provided with two side-bulbs and a movable head for holding the filtering crucible. The lower part of the upper head is bent sideways so that by rotating it the main filtrate can be collected in the flask and the various wash-waters separately in the two side-bulbs. A. R. P.

Pressure stopcock. R. N. EVANS (Ind. Eng. Chem., 1932, **24**, 856).—The plug of a stopcock is prevented from being dislodged by a wire passing through a hole in the protruding end and holding a glass collar firmly against the shell. The collar may have one concave surface which together with the degree of stiffness of the wire allows the tension to be modified. C. A. K.

Burette with means for automatic filling and adjustment to zero. J. LEWIN (Bull. Soc. Chim. biol., 1932, **14**, 1101—1103).

Two types of laboratory pumps for pumping mercury. P. B. SHIVOTINSKI (Ukrain. Chem. J., 1931, **6**, [Sci.], 241—244).—Apparatus is described. R. T.

Apparatus for the continuous extraction of liquids by low-boiling solvents. R. T. LESLIE.—See B., 1932, 710.

Apparatus for determining oxygen in gases. K. W. HETZEL.—See B., 1932, 770.

Constant-level regulator for water-baths. T. B. VINYCOMB and A. I. VOGEL (J.C.S., 1932, 2088).—An all-metal swivel joint const.-level regulator is described. F. J. W.

Gas-heated water drying oven with recovery of distillate. E. RUPP (Chem.-Ztg., 1932, **56**, 611).——The bottom of the oven which suffers wear from the effect of the gas burners is a separate unit into which the remainder of the oven fits. C. I.

Twin-bomb method for the accurate determination of pressure–volume–temperature data and a simple method for the accurate measurement of high pressures. E. W. WASHBURN (Bur. Stand. J. Res., 1932, **9**, 271—278).—Constructional and experimental procedure is outlined. W. R. A.

Simple manometer utilising a non-volatile liquid of low density. C. G. MALMBERG and W. W. NICHOLAS (Rev. Sci. Instr., 1932, [ii], **3**, 440—443).—A closed-end manometer, in which Bu phthalate is used instead of Hg, is described. The accumulation of gas in the closed end and its removal therefrom are discussed. W. R. A.

Diamond windows for withstanding very high pressures. T. C. POULTER and F. BUCKLEY (Physical Rev., 1932, [ii], **41**, 364—365; cf. this vol., 827).—Diamond windows are superior to glass or fused quartz, permitting pressures up to 21,500 atm. even with H_2O and alcoholic solutions. N. M. B.

Geochemistry.

Occurrence of silica in the waters of the Passamaquoddy Bay Region. H. M. KING (Contr. Canad. Biol. Fish., 1931, **7**, No. 8—11, D, Nos. 1—4, 129—137).—Only where H_2O movement was not marked the SiO_2 content varied with depth. Vals. decreased during summer. Tributary fresh H_2O contained more SiO_2 than bay H_2O. CH. ABS.

Salts in river waters near Damascus. V. FROLOW (Compt. rend., 1932, **195**, 426—428; cf. this vol., 829).—The max. salt content in all the rivers occurs in Nov., at the beginning of the rains, 3 months earlier than at Palmyra; the min. is in the spring. C. A. S.

Problem of desert crusts. B. V. PIASKOVSKI (Pedology, Russia, 1931, **26**, 96—107).—Many of the crusts formed on rocks in the R. Dnieper contain Mn; such crusts are pptd. from H_2O and the discovery of crusts in any region does not indicate a desert type of climate. CH. ABS.

Determination of minerals in platinum concentrates from the Transvaal by X-ray methods. F. A. BANNISTER [with M. H. HEY] (Min. Mag., 1932, **23**, 188—206).—Previous bulk analyses of the concentrates from the platiniferous norites of the Bushveld have led to uncertain results. For the present analyses each minute grain was first submitted to a detailed X-ray examination and the grains were sorted into different lots, but not more than a few mg. of each

kind of material could be so collected. The following minerals were determined. Cooperite, PtS, has the tetragonal space-group D_{4h}^9 and the unit cell (a 4·91, c 6·10 Å.) contains 4 mols. Laurite, RuS_2, has the pyrite structure with a 5·59 Å. Braggite, $(Pt,Pd,Ni)S$, a new mineral, containing Pd 18·1, Ni 4·7%, has the tetragonal space-group D_{4h}^9 and the unit cell (a 6·37, c 6·58 Å.) contains 8 mols. Sperrylite, $PtAs_2$, has the pyrite structure with a 5·926—5·934 Å. Platinum, as minute bright cubes (a 3·91 Å.), and as magnetic dull prisms and plates (a 3·87 Å.). Two other minerals remained undetermined. These results were confirmed by the X-ray examination and analysis of synthesised material. PtS (a 4·92, c 6·12 Å., d 9·0, $d_{calc.}$ 10·1), PtS_2 (a 3·54, c 5·02, d 7·2, $d_{calc.}$ 7·86), and PdS (a 6·37, c 6·58, $d_{calc.}$ 6·87, corresponding with braggite) were the only sulphides formed. The stable existence of PdS_2 is doubtful. L. J. S.

Distinction of pyrite from marcasite in nodular growths. F. A. BANNISTER (Min. Mag., 1932, **23**, 179—187).—The nodules of FeS_2 of common occurrence in the English Chalk (and often popularly supposed to be "thunderbolts") have often been referred to marcasite. X-Ray photographs and examination of polished surfaces in reflected polarised light show, however, that this material consists wholly of pyrite. Nodular growths of marcasite appear to be rare, but stalactites from Mineral Point, Wisconsin, were determined as marcasite. L. J. S.

Legrandite, a new zinc arsenate. J. DRUGMAN and M. H. HEY [with F. A. BANNISTER] (Min. Mag., 1932, 23, 175—178).—A small specimen of blende from an old collection from Flor de Peña mine, Lampazos, Mexico, shows bright yellow radiating needles with the composition As_2O_5 42·02, ZnO 46·68, Fe_2O_3 2·14, MnO 0·05, H_2O 9·36=100·25. This agrees only approx. with a formula $Zn_3As_2O_8,3H_2O$, and the monoclinic unit cell (a 12·70, b 7·90, c 10·18 Å., β=75° 35') would contain 4·54 such mols. The formula is therefore written $Zn_{14}(AsO_4)_9OH,12H_2O$, with 1 mol. in the unit cell. d 4·01, n_α 1·675, n_β 1·690, n_γ 1·735.
L. J. S.

Changed composition of an anorthoclase-bearing rock-glass. L. HAWKES and H. F. HARWOOD (Min. Mag., 1932, 23, 163—174).—Analyses of the glass and of the separated crystals of anorthoclase from the glassy selvage of a felsite dike in Iceland indicate that the crystals cannot have grown from a liquid having the composition of the glass. The suggestion is therefore made that the glass has since suffered a change in composition by the loss of K_2O and SiO_2 and the addition of Na_2O. Glasses are more liable to metasomatic change than cryst. rocks.
L. J. S.

Bultfonteinite, a new fluorine-bearing hydrous calcium silicate from South Africa. J. PARRY, A. F. WILLIAMS, and F. E. WRIGHT (Min. Mag., 1932, 23, 145—162).—This new mineral was found in the Bultfontein and Dutoitspan diamond mines at Kimberley and in the Jagersfontein mine in Orange River Colony. It forms pale pink globular aggregates of radiating needles and has much the appearance of natrolite. Analysis gives the formula $2Ca(OH,F)_2,SiO_2$. From the manner in which the mineral is decomposed by H_2O and by dil. acids the formula is written as $2Ca(OH)_2,SiO_2+CaF_2,Ca(OH)_2$. The minute crystals are triclinic, but much complicated by polysynthetic twinning; d 2·73, n_α 1·587, n_β 1·590, n_γ 1·597. The mineral is related to afwillite (A., 1925, ii, 429) with the addition of $Ca(OH)_2$ and CaF_2, and its nearest ally is custerite.
L. J. S.

X-Ray spectra of Borschtschovotschny (Transbaikalia) monazites. K. K. MATVEEV (Bull. Acad. Sci. U.R.S.S., 1932, 1329—1346).—A description of the spectra given by granite magma and pegmatite monazites from Transbaikalia.
R. T.

Bakal (S. Ural) magnesite. L. M. MIROPOLSKI (Bull. Acad. Sci. U.R.S.S., 1932, 829—832).—The rocks consist of dolomite, with zones of transition to magnesite, which, again, in various horizons passes into siderite.
R. T.

Genesis of the Perunnal–La Zarza pyritic ore body, Spain. G. WILLIAMS (Bull. Inst. Min. Met., 1932, No. 336, 33 pp.).

Volcanic rocks from Ruwenzori, Uganda. A. HOLMES and H. F. HARWOOD (Quart. J. Geol. Soc., 1932, 88, 370—439).—Petrographical descriptions are given of volcanic rocks of Pleistocene age and their parentage is discussed. Analyses are given of turjaite, leucitite lapilli, olivine-leucitite, and potash-ankaratrite. The rocks contain small but appreciable amounts of Ba and Sr.
L. J. S.

Obsidianites in the Philippine Islands. T. HODGE-SMITH (Philippine J. Sci., 1932, 48, 581—585).—Small spheroidal or cylindrical bodies with pitted and grooved surfaces are found in alluvium. They consist of black glass (olive-brown and optically isotropic in thin chips), d 2·441—2·448, and contain SiO_2 70·88, TiO_2 0·86, Al_2O_3 12·33, Fe_2O_3 1·20, FeO 4·32, MnO trace, MgO 2·62, CaO 3·97, Na_2O 1·61, K_2O 2·39, ign. 0·18=100·36. They are compared with australites and billitonites, and are believed to be of meteoric origin.
L. J. S.

Uranothorites from the Arendal district, Norway. E. GLEDITSCH and B. QVILLER (Phil. Mag., 1932, [vii], 14, 233—243).—Chemical analysis and determination of Ra content indicate a deficiency of Pb, probably due to ground-waters, and that Th-Pb has been lost in greater proportion than U-Pb. Age estimates are much lower than the expected vals.
N. M. B.

Letovicite and accompanying [minerals]. J. SEKANINA (Z. Krist., 1932, 83, 117—122).—Both S-I and S-II and S-I paramorphs of S-II occur in the dumps of abandoned coal mines at Letovice (Lettowitz) and Boskovice (Boskowitz) in Czechoslovakia. With them are found slightly turbid colourless crystals of the new mineral letovicite, $(NH_4)_3H(SO_4)_2$, d 1·81, n_α 1·501, n_γ—n_α 0·025. This is best prepared artificially by heating at 200° 3 parts of $(NH_4)_2SO_4$ and 1 part of H_2SO_4, and crystallising the cold cryst. mass from a little H_2O; the product has d 1·831, n_α 1·499, n_γ—n_α 0·027 (cf. J.C.S., 1923, 123, 476).
C. A. S.

Actual state of Mont Pelée. ROMER (Compt. rend., 1932, 195, 393—396).—The material erupted during 1929 consists of vitreous or quartziferous dacitoids. Various fumaroles produce alunogen (temp. 90°), gypsum (temp. 86°), or NH_4Cl. A sample of gas emitted (temp. 180°) contained CO_2 3·6, SO_2 5·5, N_2 74, O_2 16·5%, with a trace of HCl.
C. A. S.

X-Ray diffractions by volcanic glasses and ashes. M. HIRATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 237—244).—The X-ray diffraction figures of glassy rocks and volcanic ashes from various parts of Japan are of two types; either there is only one diffraction ring which contracts a little when heated, or there are two diffraction rings of nearly equal intensity, and on heating the outer ring is diminished in intensity, whilst the inner contracts a little to approach the form of the first type, the diffraction diagram as a whole resembling that of fused SiO_2. It is concluded that the H_2O contained in such rocks is not in its ordinary liquid state, but is intimately connected within the mol. arrangement.
J. W. S.

Occurrence of feebly radioactive lateritic soil in Japan. S. IIMORI, J. YOSHIMURA, and S. HATA (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 901—909).—Analyses for soil previously described (cf. A., 1931, 459) are given. A new chemical criterion for determining the lateritisation of soils and clays is described.
N. M. B.

"Mummified" lignin. G. L. STADNIKOV (Brennstoff-Chem., 1932, 13, 247).—A sample of shale of

unknown origin was found to contain fibres of lignin sufficiently well preserved to exhibit all the characteristic lignin reactions. The material contained no cellulose. A. B. M.

Rôle of micro-organisms in peat formation. S. A. WAKSMAN (Brennstoff-Chem., 1932, 13, 241—247; cf. B., 1929, 965; 1930, 933, 960).—The author's experimental results bearing on the problem are collected and discussed. It is concluded that peat formation is essentially a micro-biological process; even if chemical reactions, e.g., oxidation, reduction, and hydrolysis, play a part therein the explanation of the greater part of the changes which occur in the transformation of plant material into peat must be sought for in the activity of the soil bacteria, fungi, and other micro-organisms. A. B. M.

Is petroleum formed from algæ? A. F. VON STAHL (Petroleum, 1932, 28, No. 27, 9—10).—A discussion. E. D.

Formation of mineral oil, asphalt, and coal. E. BERL, A. SCHMIDT, H. BIEBESHEIMER, and W. DIENST (Naturwiss., 1932, 20, 652—655).—All mineral oil has not been formed in exactly the same way.

The carbonisation of cellulose in alkaline media give rise to a substance which will give mineral oil on hydrogenation, and asphalt on cracking. In nature this could be brought about by CaO or dolomite deposits. It is possible to give chemical explanations. A. J. M.

Origin of coal. E. BERL, A. SCHMIDT, and H. KOCH (Angew. Chem., 1932, 45, 517—519).—A crit. review of published theories and experimental work. The lignin theory alone does not explain all the facts. Hard coals are produced from material poor in resins, waxes, and lignins, whilst lignite originates in more highly organised plant material. Lignite does not subsequently become converted into coal. H. F. G.

Origin of coal. O. HORN (Naturwiss., 1932, 20, 647—652).—A summary. A. J. M.

Properties of coals as determined by their mode of origin. H. G. A. HICKLING.—See B., 1932, 757.

Occurrence of quartz in bituminous coals. D. J. W. KREULEN (Brennstoff-Chem., 1932, 13, 312).—Bands of quartz have been found in a Russian anthracite. A. B. M.

Organic Chemistry.

Free radicals and unsaturated compounds. P. WALDEN (Inst. Internat. Chim. Solvay, 1928, 431—523; Chem. Zentr., 1932, i, 1511).—A review. L. S. T.

Common basis of intramolecular rearrangements. F. C. WHITMORE (J. Amer. Chem. Soc., 1932, 54, 3274—3283).—Many of the "abnormal" reactions of org. chemistry, including most intramol. rearrangements, are correlated by the following simple assumptions. A non-ionic linking between an atom such as C or N and an electronegative atom or group is broken during the reaction; the electronegative group takes with it a completed octet of electrons, and the atom is thus left with a sextet. This deficiency of two electrons may induce a migration of an electron pair from an adjacent atom, thus giving rise to "abnormal" or rearranged products. In the case of CO compounds a C with an open sextet may be formed by the addition of a positive ion to the O. In this case, also, the presence of the open sextet induces rearrangement. C. J. W. (b)

Absence of rearrangement of the isobutyl group during the formation of magnesium isobutyl bromide and its relation to the theory of rearrangements. F. C. WHITMORE and A. R. LUX (J Amer. Chem. Soc., 1932, 54, 3448—3454).—No rearrangement (to tert.-Bu compounds) occurs when $Bu^\beta Br$ is converted into the Grignard reagent and then into $Bu^\beta OH$ by the action of O_2. The possible relation of these facts to the theoretical consideration of rearrangements and of the Grignard reaction is indicated. C. J. W. (b)

Chlorination of neopentane. G. H. FLEMING and F. C. WHITMORE (J. Amer. Chem. Soc., 1932, 54, 3460—3461).—Chlorination of neopentane is complete in 15 min. at room temp.; a chloride (I), b. p. 24°/80 mm., f.p. —20°, and a small quantity of a dichloride, b.p. 35°/8 mm., are obtained. (I) contains 6% of tert.-halide, the amount of which is increased only slightly when (I) is heated at 140° for 1·5 hr. A Grignard reagent could not be prepared from (I). C. J. W. (b)

Production of butenes by pyrolysis of the normal monochlorobutanes. P. E. WESTON and H. B. HASS (J. Amer. Chem. Soc., 1932, 54, 3337—3343).—The thermal decomp. of α- (I) and β- (II) -chlorobutanes in absence and presence of anhyd. $CaCl_2$ (as catalyst) is studied. In absence of $CaCl_2$, decomp. of (I) at 550° and of (II) at 500° is homogeneous; (I) gives Δ^α-butene (III), but (II) affords (III) and cis- and trans-Δ^β-butenes, the composition of the product from (II) being the same at 450°, 500°, and 550°. In presence of $CaCl_2$ at 450°, (I) and (II) give the three butenes [relatively little (III) is formed]. It is not known whether the butenes rearrange in contact with the catalyst or whether the catalyst causes the reaction to proceed so that the Δ^β-butenes are formed directly from the chlorobutanes. C. J. W. (b)

Behaviour of amylene under dark electric discharge. D. MENEGHINI and I. SORGATO (Gazzetta, 1932, 62, 621—632).—Amylene vapour mixed with H_2 and subjected at atm. pressure to an electrical discharge in an ozoniser yields 85% of liquid products (C_5H_{12} isomerides, isopropylacetylene, etc.); in the gas formed, C_2H_2 derivatives predominate. Amylene alone, or mixed with N_2, does not give the saturated liquid products which are obtained with H_2. Under a corona discharge, with H_2, the amount of amylene transformed is much less, but the changes are more profound, and free C is formed. E. W. W.

Catalytic partial oxidation of alcohols in the vapour phase. IV. W. L. FAITH, P. E. PETERS, and D. B. KEYES.—See this vol., 1004.

Dehydration of diethylcarbinol. F. A. KARNATZ and F. C. WHITMORE (J. Amer. Chem. Soc., 1932, 54, 3461).—Dehydration of $CHEt_2 \cdot OH$ in a flow reactor at 40 lb. pressure and at 365—410° with a H_3PO_4 catalyst on SiO_2 gel gives a mixture of olefines, b.p. 65—70°. Ozonolysis of the mixture gives CH_2O, MeCHO, EtCHO, and PrCHO, showing the formation of normal and rearranged products. C. J. W. (b)

Neopentyl alcohol and its rearrangement products. F. C. WHITMORE and H. S. ROTHROCK (J. Amer. Chem. Soc., 1932, 54, 3431—3435).—Neopentyl alcohol (I) is stable to heat and to reagents such as I, K_2CO_3, and traces of HCl; cold conc. H_2SO_4 gives some neopentyl H sulphate. The chloride could not be obtained by saturation of (I) with HCl at —10° and then heating at 62—65°/206 hr., or with $SOCl_2$. (I) and PBr_3 give 14% of bromide, which is not formed using 48% HBr. With HBr at 40° no bromide results, but at 65° (I) is slowly converted into a mixture of approx. 72% tert.-amyl bromide, 8% of (probably) sec.-isoamyl bromide, and 20% of one or more primary bromides. The composition of the mixture is not changed by heating to 105°. C. J. W. (b)

Preparation of alcohols by high-pressure reduction of fats. R. ODA (J. Soc. Chem. Ind. Japan, 1932, 35, 349—352B).—80—90% reduction to the corresponding alcohol occurs when stearic acid, Et stearate, soya, castor, and olive oils are reduced with H_2 at 320°/120—140 atm. for 20—30 min. in the presence of a 20% Cu-kieselguhr catalyst. With coconut oil, even after a second reduction with fresh catalyst, the crude product has sap. val. 80—90, but with excess H_2 this val. is reduced to 29·0, and from the product a mixture of alcohols is obtained (cf. B., 1931, 12). No reduction occurs in Et_2O, C_6H_6, or EtOH as solvent. No ethers of the alcohols from coconut oil with cellulose or $C_5H_{11} \cdot OH$ could be obtained, but the alkoxides with $(\cdot CH_2Br)_2$ give a glycol ether, m.p. about 15°. J. W. B.

Reaction of acid iodides with ethers. E. L. GUSTUS and P. G. STEVENS (J. Amer. Chem. Soc., 1932, 54, 3461—3462).—The (cleavage) reaction between AcI (and its Cl substituted derivatives) and aliphatic ethers (and sulphides and oxides) is unimol. sec.-Ethers are more readily cleaved into alkyl iodides and esters than are primary ethers; with chloroacetyl iodides, the tendency for fission is diminished by increase of Cl atoms. $CCl_3 \cdot COI$ does not cleave primary or sec.-ethers at room temp. even with ZnI_2 as catalyst. C. J. W. (b)

Autoxidation of ethyl ether. I. R. NEU (Angew. Chem., 1932, 45, 519—520).—On the average 0·07 g. of I per 10 c.c. was liberated from mixtures of commercial Et_2O (10 c.c.) and 10% KI solution (1 c.c.) after storage in the dark for 10 hr. All the samples contained Fe, and after removal of the Fe the average amount of I liberated after storage in daylight in ordinary glass vessels, with free access of air, for 3 months, was only 0·0009 g. per 10 c.c. H. F. G.

Analytical reactions of alkyl mercaptans in benzene solution. J. R. SAMPEY and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 3404—3409).—The iodometric method (A., 1921, ii, 464) for the determination of mercaptans is applied to C_6H_6 solutions. Two acidimetric methods are given : in one the HI formed by I oxidation is titrated, whilst in the other the HCl liberated by the action of $HgCl_2$ on the mercaptan is determined. Details are given. C. J. W. (b)

Analytical reactions of alkyl sulphides in benzene and purified naphtha solutions. J. R. SAMPEY, K. H. SLAGLE, and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 3401—3404).—Alkyl sulphides (in C_6H_6 or in naphtha free from unsaturated hydrocarbons) may be determined by treatment with saturated Br-H_2O, removal of the slight excess of Br with KI, and removal of the liberated I with $Na_2S_2O_3$; the HBr is extracted with H_2O and titrated with 0·05N-NaOH. Details and precautions are given. C. J. W. (b)

tert.-Butylmercaptan. H. RHEINBOLDT, F. MOTT, and E. MOTZKUS (J. pr. Chem., 1932, [ii], 134, 257—281).—$Bu^\gamma SH$, b.p. 63·7—64·2° [Hg, m.p. 159—160°, Ag, m.p. 268—270° (decomp.), Pb, decomp. 260°, and Na salts; Me, b.p. 101—102°, and Et thioether, b.p. 56—57°/109 mm. (Me_2SO_4 etc. in alkaline solution); CH_2Ph thioether, b.p. 115—116°/15 mm. (CH₂PhI and $AgSBu^\gamma$); di-tert.-butyl sulphide, b.p. 72°/71 mm. ($Bu^\gamma I$ and $Bu^\gamma SAg$); Ac, b.p. 31—32°/11 mm., and Bz, b.p. 127°/11 mm., -derivatives ($Bu^\gamma SHg$ and the acid chloride); 3 : 5-dinitrobenzoate, m.p. 146—147° ($Bu^\gamma SH$, acid chloride, and pyridine); thionitrite, m.p. —54°, b.p. 38—39°/55 mm. ($Bu^\gamma SHg$ and NOCl; poor yield)], is prepared by interaction of $MgBu^\gamma Cl$ with S (0·8 equiv.) in Et_2O; it cannot be separated from its Et_2O solution by distillation, and is therefore converted into its Hg salt, and this decomposed by H_2S. The Hg salt also gives HgS and some $Bu^\gamma SH$ on thermal decomp. The mercaptan is oxidised to the disulphide, b.p. 84—85°/20 mm. by I or SO_2Cl_2 and alkali, and is regenerated from it by Na and abs. EtOH. It is oxidised by $KMnO_4$ to tert.-butylsulphonic acid, m.p. 115—116° (decomp.) (K and Ag salts; Me, m.p. 116°, and Et, m.p. 114·5°, esters). tert.-Butylsulphinic acid is obtained as its Mg salt by action of SO_2 on $MgBu^\gamma Cl$; its Ag salt with MeI gives Me tert.-Bu sulphone, m.p. 78—79° (decomp.). H. A. P.

Complex compounds of iridium. I. Compounds with organic sulphides. P. C. RÂY and N. ADHIKARI (J. Indian Chem. Soc., 1932, 9, 251—257).—$IrCl_4$ is slowly reduced by alkyl sulphides, especially in the presence of EtOH, and the following complex compounds were isolated : $IrCl_3,3Me_2S$, $IrCl_3,2Me_2S$, $Ir_2Cl_5,4Me_2S$, $IrCl_3,3Et_2S$, $Ir_2Cl_5,4Et_2S$, $2IrCl_2,3Et_2S$. The compounds $IrCl_3,3Alk_2S$ are non-electrolytes and the formula $[(Alk_2S)_3IrCl_3]$ is suggested. A. G.

Action of chloramine-T on disulphides containing the S·S linking. J. R. ALEXANDER and H. McCOMBIE (J.C.S., 1932, 2087).—With cold aq. chloramine-T ββ-dichlorodiethyl disulphide gives β-chloroethyl-p-toluenesulphonimidosulphine-p-toluene-

sulphonylimine, m.p. 154°. Et_2S_2 and Ph_2S_2 give the corresponding Et and Ph compounds, m.p. 187—188° and 149—151° (Na salt, m.p. 225°), respectively.
R. S. C.

Reduction of aliphatic sulphonic acid salts with phosphorus pentabromide and phosphorus tribromide. W. H. HUNTER and B. E. SORENSON (J. Amer. Chem. Soc., 1932, **54**, 3364—3367).—$MeSO_3K$ and $PBr_5 + PBr_3$ give 26% of Me_2S_2; $EtSO_3K$ similarly gives 54% of Et_2S_2, whilst with PBr_5 41% of $EtSO_2Br$ results. $BuSO_3K$ and 1 mol. of PBr_5 give 66% of *butanesulphonyl bromide*, b.p. 101—102°/11 mm.; 3·5 mols. of PBr_5 give 49% of Bu_2S_2, b.p. 227—229°/735 mm., whilst a mixture of PBr_5 and PBr_3 affords 52% of Bu_2S_2 (also formed in 63% yield with PBr_3 alone). *Na* iso*pentanesulphonate*, PBr_5, and PBr_3 give 55% of di*iso*amyl disulphide; $CH_2Ph \cdot SO_2Na$ similarly affords 87% of $(CH_2Ph)_2S_2$, whilst PBr_5 alone gives 70% of CH_2PhBr; $CHPh(SO_3K) \cdot CH_2 \cdot CO_2H$ and $PBr_5 + PBr_3$ give 80% of $CHBrPh \cdot CH_2 \cdot CO_2H$, whilst PBr_5 affords 62% of $CHBrPh \cdot CHBr \cdot CO_2H$. *Ethanesulphonamide*, m.p. 57—58°, and *dibutyl trisulphide*, b.p. 119—121°/6 mm., are described. The SO_2Br group is more easily replaced by Br (PBr_5) when attached to an aliphatic radical than when attached to an aromatic nucleus. The presence of Ph on the C attached to SO_2Br facilitates the replacement of the latter by Br.
C. J. W. (*b*)

Thiolmethionic acid. H. J. BACKER (Rec. trav. chim., 1932, **51**, 775—782).—Interaction of K thiosulphomethionate with aq. $AgNO_3$ gives a colloidal suspension of *K* Ag_2 *thiolmethionate* ($+1H_2O$) : $CH(S_2O_3K)(SO_3K)_2 + 2AgNO_3 + H_2O =$ $CH(SK)(SO_3Ag)_2 + 2KNO_3 + H_2SO_4$ (cf. hydrolysis of $Ag_2S_2O_3$ to Ag_2S). The free *acid* ($+2H_2O$), m.p. 94—95°, is prepared from the *Ba*$\frac{3}{2}$ salt ($+8H_2O$), and is characterised by a transient blue coloration with $FeCl_3$ (sensitive test for Fe‴); it titrates as a dibasic acid to Me-orange, and tribasic to phenolphthalein. The K_2 H, *Ba* H ($+3H_2O$), K_3, Tl_3, Ag_3 ($+2H_2O$), NH_4 Ag_2 ($+1H_2O$), $Pb_{\frac{3}{2}}$ ($+8H_2O$), and *strychnine* ($+6H_2O$) salts are described. The structure assigned is confirmed by the oxidation of the acid or its salts to $CH(SO_3H)_3$ by Cl_2 or Br; H_2O_2, HNO_3, or $KMnO_4$ give H_2SO_4. H. A. P.

Alcoholysis of esters by mixed magnesium alcoxides and phenoxides. D. IVANOV and T. ROUSTCHEV (Compt. rend., 1932, **195**, 467—469).—If, in the reversible reaction $RCO_2R' + R''O \cdot MgX \rightleftharpoons RCO_2R'' + R'O \cdot MgX$, both R' and R'' are alkyl radicals, the heavier R'' partly replaces R'. If R' is aryl and R'' alkyl, R'' partly replaces R', the reverse reaction occurring only very slightly. With esters of dicarboxylic acids symmetrical and mixed esters result. The following mixed *Et* iso*amyl* esters were thus obtained in the yields stated in parentheses : *oxalate*, b.p. 112—114°/20 mm. (26·1%) ; *carbonate*, b.p. 175—176°/18 mm. (23·6%) ; *malonate*, b.p. 120—122°/17 mm. (20%). R. S. C.

Acid salts of fatty acids. T. G. LEVI (Gazzetta, 1932, **62**, 709—716).—By treating fatty acids, HX, with less than the calc. amount of KOH, and washing out the excess of acid with EtOH or Et_2O, the follow-

ing salts, KX,HX, are prepared : *formate*, m.p. 105—110°, *propionate*, m.p. 85—140°, *butyrate*, m.p. 85—140°, *valerate*, m.p. 55—120°, *hexoate*, *octoate*, m.p. 80—130°, and *erucate*, m.p. 55—120°, all decomposing in Et_2O to KX and HX; *undecoate*, m.p. 90—160°, *laurate*, m.p. 80—150°, *myristate*, m.p. 95—160°, and *stearate*, m.p. 100—160°, all stable to Et_2O. All the above are stable to cold C_6H_6, but decompose in hot C_6H_6. The non-existence (cf. A., 1930, 1162) of salts of the types 2KX,HX, and KX.2HX (A., 1929, 677) is confirmed. E. W. W.

Electrochemical production of formates from carbon dioxide. M. A. RABINOVITSCH and A. P. MASCHOVETZ.—See this vol., 1005.

Use of keten in the preparation of simple and mixed acid anhydrides. C. D. HURD and M. F. DULL (J. Amer. Chem. Soc., 1932, **54**, 3427—3431).—Mixed anhydrides, RCO_2Ac, are prepared readily from keten and acids (RCO_2H). AcOH gives Ac_2O (nearly quant.) ; $PrCO_2H$ affords $PrCO \cdot OAc$ containing some of the simple anhydrides ; BzOH in Et_2O yields AcOBz (quant. yield) which on distillation at 18 mm. gives Ac_2O and Bz_2O. AcOBz and NH_2Ph afford BzOH, NHAcPh, and a little NHBzPh. Furoic acetic anhydride is also obtained in quant. yield ; with NH_2Ph it gives furoic acid and NHAcPh, whilst vac. distillation affords some furoic anhydride. Distillation at atm. pressure causes rapid and complete pyrolysis to the *s*-anhydrides. C. J. W. (*b*)

Effect of varying conditions of catalytic hydrogenation of fatty oils on nature of reaction product. H. A. WATERMAN, J. A. VAN DIJK, and C. VAN VLODROP (Rec. trav. chim., 1932, **51**, 653—666 ; cf. this vol., 601).—Hydrogenation of arachis oil at 180°/1 atm. or more with Ni–kieselguhr catalysts (Wilbuschewitsch's and Normann's methods) leads to preferential reduction of linoleic to oleic glycerides ("homogeneous hardening"), whilst at room temp./1 kg. per sq. cm. with a Pt-active C catalyst saturated acids are formed from oleic acid ("heterogeneous hardening"). Similar results are obtained with Et oleate (containing 16% linoleate and 1·5% saturated esters) and Et linoleate. H. A. P.

Phenacyl esters of oleic acid series. W. KIMURA.—See this vol., 946.

Autoxidation of the double linking. P. RONA, R. ASMUS, and H. STEINECK.—See this vol., 1003

Preparation of triglycerides of fatty acids. P. E. VERKADE, J. VAN DER LEE, and (FRL.) W. MEERBURG (Rec. trav. chim., 1932, **51**, 850—852).—*Glycerol tristridecoate*, m.p. 42·7°, *triundecoate*, m.p. 29·9°, and *trinonoate*, m.p. 8·7°, are prepared by heating an excess of the acid with glycerol and a little Zn dust in CO_2 at 130°$\rightarrow$240°/150—120 mm. In the case of trinonoin the excess of acid was removed by distillation, and in the other cases by neutralisation with KOH in 96% EtOH or in Et_2O, and crystallisation. H. A. P.

Doubly conjugated system in α- and β-elæostearic acids. R. S. MORRELL and H. SAMUELS (J.C.S., 1932, 2251—2254).—Maleic anhydride and α-clæostearic acid give an *adduct*

Me·[CH$_2$]$_3$·R·CH:CH·[CH$_2$]$_7$·CO$_2$H (R = annexed formula), m.p. 62·5°, oxidised by KMnO$_4$ in boiling COMe$_2$ to azelaic acid (36% of calc.) and much tarry material (oxidised by acid KMnO$_4$ to small amounts of valeric and azelaic acids). β-Elæostearic acid similarly gives the *adduct* Me·[CH$_2$]$_3$·CH:CH·R·[CH$_2$]$_7$·CO$_2$H, m.p. 77°, oxidised to valeric acid (63% of calc.), an unidentified *substance*, C$_{14}$H$_{24}$O$_8$, m.p. 91°, and much tar (oxidised to a little azelaic acid). Me β-elæostearate affords an *adduct*, m.p. 61°. The maleic anhydride adduct of the β-acid glyceride has a marked power of association; the adduct of the α-acid glyceride has not. Maleic anhydride could not be combined with coumarin, vinyl acetate, anthraquinone, acrylic acid, or citraconic anhydride.   H. B.

Reactions of tung oil and elæostearic acid. J. MARCUSSON.—See B., 1932, 850.

Odour and constitution. II. Alkoxy-acids and their esters. B. ROTHSTEIN (Bull. Soc. chim., 1932, [iv], 51, 838—845).—In the series OR·CH$_2$·COR′ the odour rapidly diminishes in intensity and persistence in the order R=Me>Et>Pr^β>Bu^β. The influence of olfactive radicals is greater when present as alkoxy than as ester groups. Methoxy- (*chloride*, b.p. 99°/1 atm.), ethoxy-, iso*propoxy*-, b.p. 113°/21 mm. (*chloride*, b.p. 127°), and iso*butoxy*-, b.p. 118°/18 mm. (*chloride*, b.p. 59°/22 mm.) -acetic acids are prepared by interaction of CH$_2$Cl·CO$_2$H with the appropriate Na alkoxide. The following esters are prepared in almost theoretical yield by interaction of the appropriate acid chloride and alcohol in presence of pyridine in CHCl$_3$: *CH$_2$Ph*, b.p. 136°/16 mm., *phenylethyl*, b.p. 148·5—149°/18 mm., *geranyl*, b.p. 151—152°/16 mm., and *citronellyl methoxyacetate*, b.p. 149—150°/16·5 mm.; *CH$_2$Ph*, b.p. 143°/16 mm., *β-phenylethyl*, b.p. 156°/17 mm., *γ-phenylpropyl*, b.p. 167°/16 mm., *cinnamyl*, b.p. 179°/15 mm., *terpenyl*, b.p. 157°/20 mm., *citronellyl*, b.p. 157—158°/16·5 mm., and *geranyl ethoxyacetate*, b.p. 163°/17 mm.; *CH$_2$Ph*, b.p. 149°/17 mm., *β-phenylethyl*, b.p. 158°/16 mm., *γ-phenylpropyl*, b.p. 169°/16 mm., *geranyl*, b.p. 164—165°/15 mm., and *citronellyl*, b.p. 161—162°/15 mm., iso*propoxyacetates*; *CH$_2$Ph*, b.p. 154°/17 mm., *β-phenylethyl*, b.p. 166°/15 mm., *cinnamyl*, b.p. 191°/15 mm., *geranyl*, b.p. 175°/17 mm., and *citronellyl* iso*butoxyacetate*, b.p. 170°/16 mm.   H. A. P.

Identification of α-ethoxypropionic acid. A. DEMOLIS and G. A. R. KON (J.C.S., 1932, 2283).—The acid is converted by SOCl$_2$ into the chloride, b.p. 32°/13 mm., and thence into the amide, m.p. 64°, and *anilide*, m.p. 66—67°.   H. B.

Allyl lævulate and its derivatives. P. P. T. SAH and T. MA (J. Amer. Chem. Soc., 1932, 54, 3271—3273).—*Allyl lævulate*, b.p. 133—136°/40 mm. (*semicarbazone*, m.p. 126—127°; *phenylhydrazone*, m.p. 79—80°), obtained in 60% yield by direct esterification (HCl) of the acid, and Cl$_2$ in CCl$_4$ give 40% of *βγ-dichloropropyl lævulate*, b.p. 199—202°/40 mm. (*semicarbazone*, m.p. 104—106°; *phenylhydrazone*, m.p. 73—75°). *βγ-Dibromopropyl lævulate* (*semicarbazone*, m.p. 101—102°; *phenylhydrazone*, m.p. 98—99°) has b.p. 208—210°/40 mm. The Cl- and Br-

esters are also obtained from the corresponding alcohols.   C. J. W. (b)

d-**Tartaric acid hydrates.** M. ORLOVA and A. MOROSOV (Z. Krist., 1932, 83, 150—152).—By exposing aq. solutions of *d*-tartaric acid of varying concn. to temp. down to —40°, hydrates nC$_4$H$_4$O$_6$,mH$_2$O, where n : m is 1 : 20, 1 : 10, 1 : 7, 2 : 3, and 3 : 1, have been prepared ; the first three melt below room temp., the two last are moderately permanent.   C. A. S.

δ-Lactones formed by oxidation of aldoses with bromine water. H. S. ISBELL (Bur. Stand. J. Res., 1932, 8, 615—624).—Oxidation of α- and β-*d*-mannose and α- and β-*l*-rhamnose with Br in H$_2$O saturated with CO$_2$ at 20° in presence of BaCO$_3$ (which reacts with free sugar acids, but not with their lactones) confirms the conclusion (this vol., 834) that the oxidation products are δ-lactones, since only 1—2% of the product is neutralised by the BaCO$_3$. After removal of excess of Br and BaCO$_3$, the presence of the δ-lactone was confirmed by plotting the time–p_H and time–[α] curves for the initially neutral solution so obtained. Determination of unchanged reducing sugar (Scales, A., 1919, ii, 435) and of total lactone permits the calculation of the amount of product neutralised by BaCO$_3$ during the oxidation. The larger proportion of neutralisation found with α- (24%) and β- (10·6%) -lactose, β-cellobiose (25·4%), and β-maltose (3·4%) is ascribed to the greater ease of hydrolysis of the lactones of these sugars. The β-forms of the sugars are more easily oxidised than the α, and the formation of a δ-lactone from both α- and β-*d*-mannose confirms the pyranose structure of both forms.   J. W. B.

Properties of *d*-mannuronolactone. W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1932, 54, 3409—3412).—*d*-Mannuronolactone is isolated from the hydrolysis products of the alginic acids from *Laminaria saccharina* and *Fucus serratus*. Data on the mutarotation of the lactone are given and the approx. val. for the rotation of the equilibrated mixture of the α- and β-forms of the free acid is calc. to be [α]$_D$ +12°. *Cinchonine*, m.p. 154° (decomp.), [α]$_D^{24}$ +113·3° in H$_2$O, *cinchonidine*, m.p. 154° (decomp.), [α]$_D^{14}$ —78·3° in H$_2$O, and *brucine*, m.p. 147° (decomp.), [α]$_D^{24}$ —23·1° in H$_2$O, *mannuronates* are prepared.   C. J. W. (b)

Photochemical reduction of carbon dioxide in aqueous solution. M. QURESHI and S. S. MOHAMMAD.—See this vol., 1006.

Photolysis of aliphatic aldehydes. I. Propaldehyde. P. A. LEIGHTON and F. E. BLACET.—See this vol., 1006.

Preparation of keten from acetone. J. AL (Angew. Chem., 1932, 45, 545—546).—Yields of keten of the order of 90% are obtained by passing COMe$_2$ vapour through a quartz tube containing (in order of decreasing activity) pumice and V$_2$O$_5$, quartz, or pumice, at 675—690°.   H. F. G.

Electrolytic reduction of aliphatic ketones to hydrocarbons. S. SWANN, jun.—See this vol., 1005.

Preparation of acetone from acetic acid. H. BERGSTRÖM and K. N. CEDERQUIST (Iva, 1931,

22—23, 47—48).—AcOH passed over a mixture of CaO and ThO$_2$ at 423° gives a 90·8% yield of COMe$_2$; CaCO$_3$, MgO, and ZnO are much less active.

<div align="right">Ch. Abs.</div>

Alcoholysis and hydrolysis of αγ-diketones and β-keto-esters. R. Connor and H. Adkins (J. Amer. Chem. Soc., 1932, 54, 3420—3427).—The alcoholysis and hydrolysis of various αγ-diketones and β-keto-esters at 150—250°/about 100 atm. are investigated. EtOH dried over Al(OEt)$_3$ is inactive for the alcoholysis of αγ-diketones, but EtOH containing the trace of H$_2$O not removed by CaO is rather active; Al(OEt)$_3$ is a very active catalyst for the alcoholysis. CH$_2$Bz$_2$, which is resistant to alcoholysis in presence of HCl at 60° and atm. pressure, is readily cleaved at 200° either by dry EtOH or EtOH containing Al(OEt)$_3$. Branching of the chain adjacent to one CO group decreases the rate of alcoholysis with dry EtOH (as with EtOH–HCl). The ratio of the products formed in the cleavage of an as-αγ-diketone is a function of the conditions under which alcoholysis occurs. The keto-esters are much more resistant to alcoholysis than the diketones; the latter are alcoholysed at 150° at about the same rate as are the keto-esters at 250°. EtOH dried over Al(OEt)$_3$ is not an active reagent for the cleavage of the esters; Al(OEt)$_3$ is an active catalyst. CH$_2$Ac·CO$_2$Et does not undergo alcoholysis at all readily at 200° even with moist EtOH, but does so at 250°. Et α-methyl- and α-benzyl-acetoacetate are alcoholysed as rapidly as CH$_2$Ac·CO$_2$Et, but the Me$_2$ and Et$_2$ derivatives are very resistant to cleavage. Excellent yields of ketones were obtained by hydrolysis of several β-keto-esters with H$_2$O at 200°. αα-Dialkylated β-keto-esters are stable towards H$_2$O at 200°; they can be freed from mono-alkylated β-keto-esters by such treatment. Hydrolysis of these dialkylated esters is effected by alkali at 250°. CH$_2$Ac·CO$_2$Et is hydrolysed to COMe$_2$ (97% yield); Et α-benzylacetoacetate gives 97% of δ-phenylbutan-β-one; CAcMe$_2$·CO$_2$Et affords 50% of COMePr$^\beta$ (with alkali there results 70% of COMePr$^\beta$ and 5% of AcOH and Pr$^\beta$CO$_2$H); CAcEt$_2$·CO$_2$Et and dil. EtOH give 49% of γ-ethylpentan-β-one and 45% of unchanged ester at 200°, and 84% of the ketone at 250°; CMe$_3$·CO$_2$Et at 200° undergoes 36% hydrolysis; CH$_2$BzAc and H$_2$O at 200° give 76% of AcOH and 24% of BzOH.

<div align="right">C. J. W. (b)</div>

Reducing sugars. W. Gabryelski and L. Marchlevski (Biochem. Z., 1932, 250, 385—391).—The presence of OH ions alters the spectrum of glucose and galactose very considerably, due to the formation of products containing aldehydic complexes. The change in spectrum occurs on mixing the sugar solution and the NaOH before any pigment formation has occurred. Immediate neutralisation regenerates the original spectrum but such regeneration does not occur in the later stages.

<div align="right">P. W. C.</div>

Optical rotatory dispersion in the carbohydrate group. I. T. L. Harris, E. L. Hirst, and C. E. Wood (J.C.S., 1932, 2108—2120).—The rotatory dispersions of various sugar derivatives have been measured over the range λ 6708—2380. Sucrose (cf. Lowry and Richards, A., 1925, ii, 265), α-methylmannofur-

anoside and its tetra-acetate, and β-methylmanno-pyranoside tetra-acetate exhibit simple dispersion, whilst the following show complex dispersion : α-methylgluco-pyranoside and -furanoside, α-methyl-mannopyranoside (I) and its tetra-acetate, α- and β-methylglucopyranoside tetra-acetates, "γ"-methyl-mannopyranoside tetra-acetate [3 : 4 : 6-triacetyl-β-mannopyranose 1 : 2-orthomethylacetate], α-cellobiose octa-acetate, and 4-β-glucosido-α-mannose octa-acetate. In these cases deviation from simple dispersion throughout the visual region is small and is always of the same sign; the character of the dispersion does not account for the failure of many of the substances [especially (I)] to conform with Hudson's isorotation rules (A., 1926, 714; 1930, 747). The difference between the mol. rotations of α-methylgluco-, $[\alpha]_D$ +118°, and α-methylmanno-, $[\alpha]_D$ +108° in H$_2$O, -furanoside varies from Hudson's calc. vals.

<div align="right">H. B.</div>

Hydroxymethylfurfuraldehyde as an impurity in hexoses. G. van Kleet (Rec. trav. chim., 1932, 51, 692—694).—Hydroxymethylfurfuraldehyde is present in crude glucose and is removable by recrystallisation. It is oxidised with difficulty by OI', and may cause a positive Selivanov or Ihl–Pechmann reaction after oxidation of an impure hexose with I and NaOH.

<div align="right">H. A. P.</div>

Precipitation of sugars and polyhydric alcohols by metallic hydroxides in an alkaline medium. II. Mechanism of precipitation and practical conclusions. P. Fleury and J. Courtois (J. Pharm. Chim., 1932, [viii], 16, 145—161).—When alkali is added to various metal salts in presence of glucose or mannitol the latter is removed from solution in the ppt., the results previously found in the case of Cu (cf., A., 1930, 196; this vol., 368) holding for other metals. The hydroxides probably combine with the sugar or alcohol to form a compound of similar constitution to K Sb tartrate, which then exists in the form of its alkali salt stabilised by the presence of excess of the alkali. The dissolution of the ppt. which may occur in presence of an excess of alkali is due to peptisation with the resultant formation of a colloidal solution. Fe is most effective in removing the sugar or alcohol from solution. The metals are best employed in the form of acetates. NaOH is not suitable. Aq. NH$_3$ and especially Ba(OH)$_2$ are satisfactory. It is best to add alternately small quantities of the salt solution and of the alkali to the cooled solution of the sugar or alcohol and finally to shake the mixture for 15—30 min.

<div align="right">W. O. K.</div>

Crystalline α-methylglucofuranoside (γ-methylglucoside) and its derivatives. W. N. Haworth, C. R. Porter, and A. C. Waine (J.C.S., 1932, 2254—2258).—α-*Methylglucofuranoside* 5 : 6-*monocarbonate* (I), m.p. 130°, $[\alpha]_D^{23}$ +130° in MeOH, separates from the residues from the prep. of its β-isomeride (II) (A., 1930, 196). A mixture, m.p. 106—107°, of (I) and (II) is occasionally obtained during the action of MeOH–HCl on isopropylidene-glucose carbonate; acetylation gives α-, m.p. 110—111°, $[\alpha]_D^{18}$ +148° in COMe$_2$, and β-, m.p. 164°, $[\alpha]_D^{18}$ —41° in COMe$_2$, -2 : 3-*diacetylmethylglucofuranoside*

5 : 6-*monocarbonates*, separable through their differing solubilities in aq. pyridine. The α-diacetate and (I) are hydrolysed by aq. $Ba(OH)_2$ to α-*methylglucofuranoside* (III), m.p. 62—63°, $[\alpha]_D^{20}$ +118° in H_2O, which is not hydrolysed by zymin or emulsin, but is so by 0·01N-HCl at 95—100° ($k_{bass\ 10} \times 10^5$=4500) (yielding glucose). β-Methylglucofuranoside, $[\alpha]_D$ about —77° in H_2O, has not been obtained cryst. (III) is methylated to 2 : 3 : 5 : 6 - *tetramethyl - α - methylglucofuranoside*, b.p. 94°/0·04 mm., m.p. 11°, $[\alpha]_D^{18}$ +106·5° in MeOH, hydrolysed by 0·01N-HCl at 95—100° ($k \times 10^5$=1500) to 2 : 3 : 5 : 6-*tetramethylglucofuranose*, distils at 130° (bath temp.)/0·01 mm., $[\alpha]_D^{20}$ —7·6° in H_2O (oxidised by Br to tetramethyl-γ-gluconolactone), also formed by similar hydrolysis ($k \times 10^5$=approx. 1900) of 2 : 3 : 5 : 6-*tetramethyl-β-ethylglucofuranoside*, distils at 118—120° (bath temp.)/0·1 mm., which is prepared by methylation (Me_2SO_4, alkali) of β-ethylglucofuranoside 5 : 6-monocarbonate in 50% aq. $COMe_2$ followed by Purdie's reagents. α-*Ethylglucofuranoside* 5 : 6-carbonate, m.p. 138—140°, $[\alpha]_D^{17}$ +117° in EtOH, is isolated from the mother-liquors from the prep. of the β-isomeride (*loc. cit.*); its 2 : 3-Ac_2 derivative has $[\alpha]_D$ +143° in $COMe_2$. α- and β-Ethylglucofuranosides have $[\alpha]_D^{18}$ +101° and —86° in H_2O, respectively. H. B.

Hemiacetals of aldehydogalactose penta-acetate and their optical properties. M. L. WOLFROM and W. M. MORGAN (J. Amer. Chem. Soc., 1932, 54, 3390—3393).—Crystallisation of aldehydogalactose penta-acetate from the appropriate alcohol gives the following *hemiacetals*: *Me*, m.p. 123°, $[\alpha]_D^{25}$ +3·0° ⟶ —7·7° ⟶ +15° (initial, min., and final vals. in $CHCl_3$; this order is followed below); *Et*, m.p. 133°, +1·5° ⟶ —7·5° ⟶ +6°; *Pr*, m.p. 130°, +4·2° ⟶ —8·2° ⟶ +4·5°; *Prβ*, m.p. 144°, —1° ⟶ —12° ⟶ —7°; *Buβ*, m.p. 123°, +6° ⟶ —7° ⟶ +1°; cyclo*hexyl*, m.p. 136°, 0° ⟶ —12° ⟶ —3°. The optical behaviour supports the open-chain intermediate theory of sugar mutarotation. C. J. W. (b)

Synthesis of cellobiose. K. FREUDENBERG and W. NAGAI (Naturwiss., 1932, 20, 578).—Acetobromoglucose in dioxan reacts with β-glucosan and Ag_2CO_3 to give a mixture of tetra-acetylglucosido-derivatives of β-glucosan, which, after treatment with 50% H_2SO_4, was acetylated to cryst. cellobiose octa-acetate. W. R. A.

Constitution of *allo*lactose. M. POLONOVSKI and A. LESPAGNOL (Compt. rend., 1932, 195, 465—467).—Human milk contains, besides gynolactose and *allo*lactose (I), glucosides and glucoproteins. (I), $[\alpha]$+25°, gives, when hydrolysed, a mixture of sugars, $[\alpha]$ +65°. It is hydrolysed by emulsin and, when kept for 14 days at 37° with aq. KCN and then hydrolysed by 1% H_2SO_4, gives galactose (II). The *osazone*, m.p. 176°, of (I) with boiling 5% HCl gives (II). (I) is, therefore, 3- or impure 6-β-galactosidyl-*d*-glucose. R. S. C.

Nitrogenous glucosides. I. Utilisation of glucosecarbimides for glucoside syntheses. T. B. JOHNSON and W. BERGMAN (J. Amer. Chem. Soc., 1932, 54, 3360—3363).—Bromoglucose tetra-acetate and AgCNO in xylene give two isomeric tetra-acetyl-

d-glucose-*l*-carbimides, m.p. 92° (I) and 120° (II) (cf. Fischer, A., 1914, i, 662), and s-*octa-acetyl*-d-*diglucosylcarbamide*, m.p. 164°, $[\alpha]_D^{26}$ —3·7° in $CHCl_3$ (hydrolysed to s-*d*-diglucosylcarbamide). (I) rearranges into (II) when heated. (II) and amyl alcohol boiled for 30 min. give *tetra-acetyl*-d-*glucose amylurethane*, m.p. 88°, $[\alpha]_D$ —6·61° in Et_2O; the β-*chloroethylurethane*, m.p. 114°, $[\alpha]_D^{26}$ —11·6° in Et_2O, is similarly prepared. C. J. W. (b)

Osmometric investigation in dilute solutions of polysaccharides. I. Molecular size of the α-dextrin of Schardinger (α-di- and α-tetra-amylose). M. ULMANN (Biochem. Z., 1932, 251, 458—477).—The doubtful existence of Pringsheim's α-diamylose and its identity with α-tetra-amylose as indicated chemically by Mickeley (A., 1930, 1414; this vol., 255) are confirmed by osmotic measurements. Boiling an aq. solution of α-tetra-amylose for 2 hr. does not effect any change. If small amounts of alkali are added to an α-amylose solution, the osmotic pressure at first slowly and then rapidly increases until the final vals. almost reach those required by α-diamylose. If the p_H is then readjusted to neutrality, the osmotic pressure does not change, the reaction being irreversible. If, however, the amylose is recovered by careful evaporation at room temp. the product on redissolving in H_2O gives again a val. for a tetra-amylose. If the p_H of a tetra-amylose solution be adjusted to the acid side, the osmotic pressure gives vals. corresponding with an octa- to hexadeca-saccharide. P. W. C.

Natural polylævans. IV. Carbohydrates of the Jerusalem artichoke. H. H. SCHLUBACH and H. KNOOP (Annalen, 1932, 497, 208—234; cf. Tanret, A., 1893, i, 385, 617).—Inulin (I), $[\alpha]_D^{18}$ —39·9° in H_2O (10—15%), dilævan (II), $[\alpha]_D^{18}$ —22·3° in H_2O (20—30%), impure diaraban, $[\alpha]_D^{18}$ —62·9° in H_2O (1%), and a series of products, $[\alpha]_D$ +40° to +120° (5—10%), are isolated from the tubers by extraction with H_2O in presence of $CaCO_3$ [whereby a fermentation occurs (in the cold) and mannitol (not originally present as such) is produced]; the extract is freed from aldoses (1·9%) and sucrose (6·4%) by fermentation, protein is removed with $Pb(OAc)_2$, and the crude products are separated by fractional pptn. with EtOH. (I) is purified by freezing its aq. solution. Compounds intermediate between (I) and (II) could not be isolated. Hydrolysis of (I) with 0·05N-H_2SO_4 gives fructose and a little glucose (determined by Willstätter and Schudel's or Auerbach and Bodländer's method); under the same conditions sucrose gives a slight excess of glucose. The aldose val. of (I) is undoubtedly due to the presence of small amounts of difficultly separable impurities; (I) is built up solely of fructose units. Methylation of (I), $[\alpha]_D^{20}$ —37°, gives trimethylinulin, m.p. 146·5—147°, $[\alpha]_D^{18}$ —49° in $CHCl_3$ (cf. Haworth and Learner, A., 1928, 510), which is depolymerised (EtOH–$H_2C_2O_4$) and then hydrolysed (0·25% HCl) to 3 : 4 : 6-trimethylfructose, b.p. 110—114°/0·05 mm., $[\alpha]_D^{18}$ +26·3° in $CHCl_3$ [osazones, m.p. 77—79° and 127—128° (cf. Haworth and Learner, *loc. cit.*)], also formed by methylation and subsequent degradation of (II). Hydrolysis of (II) with dil. H_2SO_4 gives fructose and

a considerable amount of a substance oxidised by hypoiodite.   H. B.

Thermal degradation of inulin to a fructose anhydride. H. H. SCHLUBACH and H. ELSNER (Annalen, 1932, **497**, 201—207).—Inulin heated with $(CH_2\cdot OH)_2$ at 140°/15 mm. for 72 hr. gives a product, M 230, $[\alpha]_D^{18}$ +29·6°, which is not identical with lævan, since on methylation (Ag_2O, MeI, MeOH) it affords pentamethyl-γ-fructose (impure) [hydrolysed by 1% HCl to (mainly) 1 : 3 : 4 : 6-tetramethylfructose (I)] and a hexamethyldihexose anhydride, b.p. 152°/0·01 mm. [converted by successive treatment with EtOH–$H_2C_2O_4$ and dil. HCl into a trimethylhexose (II), b.p. 90—93°/0·01 mm., $[\alpha]_D^{15}$ +25° in $CHCl_3$, similar to 3 : 4 : 6-trimethylfructose (III)]. (II) and $NHPh\cdot NH_2$ in 20% AcOH give a small amount of an oily osazone containing 2 OMe groups, whilst (III) affords an osazone, m.p. 126°, containing 3OMe ; (I) similarly furnishes an oily osazone containing 2OMe only. Depolymerisation of inulin with NH_2Bz at 140° gives a complex mixture of degradation products.   H. B.

Polysaccharides. X. Molecular structure of cellulose. W. N. HAWORTH and H. MACHEMER. **XI. Molecular structure of glycogen.** W. N. HAWORTH and E. G. V. PERCIVAL (J.C.S., 1932, 2270—2277, 2277—2282).—X. Cellulose acetate "C" ($COMe_2$-sol.) is prepared by a modification of Barnett's method ; this is free from degradation products and is completely deacetylated and methylated by one treatment with Me_2SO_4 and alkali under the conditions previously described (A., 1931, 941). Hydrolysis of the methylated cellulose [as (I)] with cold saturated aq. HCl, separation of the methylglucoses, conversion of these into the methylglucosides, and subsequent fractionation gives tetramethylmethylglucoside = 0·6% of tetramethylglucose [derived from A in (I)]. This indicates that the cellulose prep. consists of not less than 100 and not more than 200 β-glucose units, and has, therefore, a mol. wt. of 20,000—40,000. Cellulose is a straight chain of β-glucopyranose units linked through positions 1 : 4.

(I.)
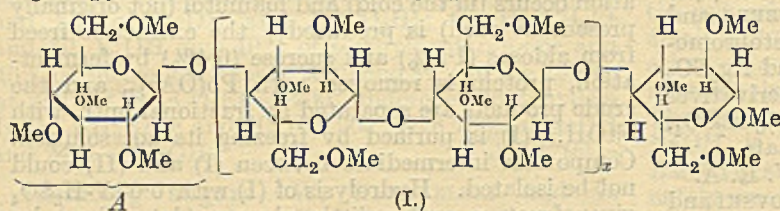
XI. *Glycogen triacetate*, $[\alpha]_D^{20}$ +170° in $CHCl_3$, prepared by acetylation with Ac_2O–pyridine, is methylated by Me_2SO_4 and alkali in $COMe_2$. The

(II).
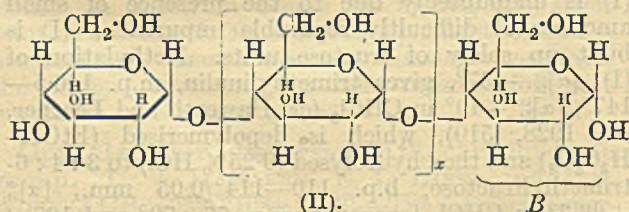
methylated glycogen (free from degraded material) is hydrolysed (as above); 9% of tetramethylgluco-

pyranose is isolated, indicating that glycogen is represented as (II), (where x has a min. val. of 10). The terminal "aldose" unit (B) in glycogen, starch, and cellulose may be modified by oxidation to the acid (or lactone) group. The originals must be consulted for details.   H. B.

Determination of the composition of additive compounds of cellulose. G. CHAMPETIER (Compt. rend., 1932, **195**, 499—501).—A comparison of the method (A., 1931, 941) with that of Schwarzkopf (this vol., 836).   F. R. S.

Acetolysis of cellulose. V. Water-soluble dextrins from cellulose. K. HESS and F. KLAGES (Annalen, 1932, **497**, 234—247).—Crude cryst. H_2O-sol. dextrins (A), obtained essentially by the method previously described (A., 1931, 827), are separated by pptn. from aq. solution with MeOH into three groups of products : (a) $[\alpha]_D^{20}$ +13° to +14° in H_2O, I val. ~ 20 (corresponds with cellohexaose), (b) $[\alpha]_D^{20}$ +15° to +16°, I val. 23 (cello-pentaose), (c) $[\alpha]_D^{20}$ +15° to +19°, I val. ~ 28 (cello-pentaose and -tetraose); the non-cryst. residue (B) from the combined mother-liquors from (A) has $[\alpha]_D^{20}$ +22·6°, I val. 38·2 (it is stated in a footnote that cryst. cellotriose has probably been isolated from B). Methylation (Me_2SO_4, alkali) of these products shows that they are not homogeneous ; hendecamethylcellotriose is obtained from (c) whilst tetradecamethylcellotetraose and higher products are obtained from (a), (b), and (c). The same interferences (Röntgen diagram) are shown by (a)—(c) as by hydrocellulose.   H. B.

Action of fluorosulphonic acid on cellulose. C. H. MÖLLERING (J. pr. Chem., 1932, [ii], **134**, 209—214).—Cellulose dissolves in 3—4 times its wt. of cold FSO_3H eventually to a clear brown, viscous liquid, which mixes in H_2O to a clear solution; titration with alkali suggests that a mixture of tetra- with a little tri-fluorosulphonyl ester has been formed.

Attempts to isolate the ester or its Ac derivative, or to dissolve cellulose in an equiv. amount of FSO_3H, failed, but removal of excess of FSO_3H from the aq. solution with Pb carbonate and evaporation of the filtrate under reduced pressure gave a solid which on analysis appeared to be a mixture of FSO_3K and a K cellulose fluorosulphonate.   H. A. P.

Rearrangements involved in the action of nitrous acid with n-butylamine. F. C. WHITMORE and D. P. LANGLOIS (J. Amer. Chem. Soc., 1932, **54**, 3441—3447).—$NaNO_2$ and NH_2Bu in dil. HCl give BuOH 25%, *sec.*-BuOH 13·2%, BuCl 5·2%, *sec.*-BuCl 2·8%, butenes 36·5%, high-boiling material 7·6%, and traces of Bu nitrites. Branched-chain Bu derivatives are not formed. The relation of these facts to the mechanism of rearrangements is discussed.   C. J. W. (*b*)

Sulphonation of amino-acids, polypeptides, and diketopiperazines. II. P. BAUMGARTEN, I. MARGGRAFF, and E. DAMMANN (Z. physiol. Chem., 1932, **209**, 145—165; cf. A., 1928, 534).—The following derivatives were obtained by sulphonation of the corresponding NH_2-acids etc. with N-pyridinium-

sulphonic acid : *glycine*-N-*sulphonic acid* [K_2 ($+H_2O$), Na_2 ($+H_2O$), Cu K_2 ($+H_2O$), $3Ag_2$ K_2 ($+H_2O$) salts], *alanine*-N-*sulphonic acid* [$4K_2$ salt ($+EtOH$)], *leucine*-N-*sulphonic acid* (K_2, $2Cu$ ($+3KOAc$), $5Ag_2$ K_2 ($+24H_2O$) salts]; *aspartic*-N-*sulphonic acid* [K_3 ($+K$ H aspartate), $2K_3$ ($+AcOH$) salts]; *glutamic*-N-*sulphonic acid* [K_3 ($+K$ H glutamate$+H_2O$), $2K_3$ ($+AcOH$) salts]; *serine*-N-*sulphonic acid* [$5K_2$ ($+2$ serine mols.), K_2 salts); *oxyproline*-N-*sulphonic acid* (K_2 salt); *tyrosine*-ON-*disulphonic acid* (K_3+K_2 H salt); *cystine*-NN'-*disulphonic acid* [$4K_4$ salt ($+3AcOH$)]; *arginine*-N-*sulphonic acid* [$4K$ salt ($+KOAc$)]; *ornithine*-NN'-*sulphonic acid* [$4K_3$ salt ($+3AcOH$)]; *histidine*-NN'-*disulphonic acid* (K_3+K_2 H salt ($+\frac{1}{2}AcOH$)]; *proline*-N-*sulphonic acid* (K_2 salt); *tryptophan*-N-*sulphonic acid* (K_2 salt); *glycyl-glycine*-N-*sulphonic acid* [K_2 salt ($+H_2O$)]; *diglycyl-glycine*-N-*sulphonic acid* [K_2 salt ($+H_2O$)]; *leucyl-glycine*-N-*sulphonic acid* [K_2 salt ($+2H_2O$)]; *glycyl-serine*-N-*sulphonic acid* [K_2 salt ($+\frac{1}{2}EtOH$)]; *glycyl-tyrosine*-ON-*disulphonic acid* [K_3 salt ($+EtOH$)]; *histidylhistidine*-NN'N''-*trisulphonic acid* [K_4 salt ($+H_2O$)]; *diketopiperazine*-NN'-*disulphonic acid* [*pyridinium* ($+\frac{1}{2}EtOH$), K_2 (also $+EtOH$), Ba ($+2H_2O$) salts]. The free sulphonic acids are readily hydrolysed in aq. solution, the peptide acids even in alkaline solution at the peptide linking. Hydrolysis of diketopiperazinedisulphonic acid first yields the diglycyl derivative and finally glycinesulphonic acid. J. H. B.

Deamination of ethyl β-methylaminopropionate. W. B. THOMAS and S. M. McELVAIN (J. Amer. Chem. Soc., 1932, 54, 3295—3298).—Et β-methylaminopropionate (I) reacts with Et β-bromo-α-methylpropionate or Et α-methylacrylate giving Et β-methyliminodipropionate, formed by elimination of NH_2Me (or its salt) from 2 mols. of (I). C. J. W. (b)

Isolation of norleucine and evidence of its identity. Thermodynamic data based on the dissociation pressures of the compounds which the isomeric leucines form with ammonia and hydrogen chloride. E. J. CZARNETZKY and C. L. A. SCHMIDT (J. Biol. Chem., 1932, 97, 333—343).—Hydrolysis of ox spinal cord by H_2SO_4 and purification by the Cu and Zn salts, dissolution in AcOH, and 10 crystallisations from H_2O gives *d*-norleucine, $[\alpha]_D^{25}$ $+22.5°$ in 20% HCl, in 0.22% yield. Identity with the synthetic compound is shown by its crystal structure and that of the Ag and Cu salts. Measurement of the pressure resulting when NH_3 or gaseous HCl is gradually admitted with shaking to a solid NH_2-acid in presence of a little H_2O vapour gives the dissociation pressure of the resulting compound, which is characteristic of the NH_2-acid used. Breaks in the straight lines obtained indicate mixtures and the position of the break allows the relative quantity of the components of the mixture to be estimated. The identity of natural and synthetic norleucine is confirmed by this method. Dissociation pressures are also recorded for the compounds of *dl*-leucine, -*iso*leucine, and -norleucine with HCl and NH_3, whence are calc. the changes in free energy, heat content, and entropy due to the dissociations. The vals. obtained differ from those for unsubstituted fatty

acids, which supports the theory that NH_2-acids exist in the solid state as "Zwitterions," since combination will then take place only when a sufficiently high energy level has been reached to cause a H atom to migrate and an electron to shift. R. S. C.

Oxidation of thiol compounds with hydrogen peroxide. I. Oxidation of cysteine with hydrogen peroxide. A. SCHÖBERL (Z. physiol. Chem., 1932, 209, 231—238).—Free cysteine and its Na salt are rapidly oxidised to cystine by H_2O_2. The reaction velocity is depressed in HCl and oxidation proceeds only in presence of catalysts such as $Cu^{..}$ and $Fe^{..}$. The latter catalyst is the more active, but is more sensitive to acid. J. H. B.

Action of nitrous acid with trimethylacetamide. F. C. WHITMORE and D. P. LANGLOIS (J. Amer. Chem. Soc., 1932, 54, 3438—3441).—NH_2Ac and HNO_2 give a quant. yield of AcOH, whilst $CMe_3 \cdot CO \cdot NH_2$ affords more than 90% of the calc. amounts of N_2 and $CMe_3 \cdot CO_2H$. Rearrangements do not occur in reactions involving the $CMe_3 \cdot CO$ group; this is in marked contrast with the analogous neopentyl derivatives. C. J. W. (b)

Hofmann rearrangement of tert.-butylacetamide and its significance in the theory of rearrangements. F. C. WHITMORE and A. H. HOMEYER (J. Amer. Chem. Soc., 1932, 54, 3435—3437).—Hofmann rearrangement of $CMe_3 \cdot CH_2 \cdot CO \cdot NH_2$ gives a quant. yield of neopentylamine; the failure of the migrating neopentyl group to rearrange to tert.-amyl is discussed in its bearing on the mechanism of rearrangement. A "negative" neopentyl group is apparently stable, whereas a "positive" neopentyl group undergoes rearrangement to tert.-amyl and related compounds. $CMe_2Et \cdot CO \cdot NH_2$ is rearranged to tert.-amylamine. C. J. W. (b)

Electro-organic reductions. R. H. McKEE and C. J. BROCKMAN.—See this vol., 1005.

Electrolytic reduction of nitrobenzene to azoxybenzene. C. KERNS.—See this vol., 1005.

Mechanism of the reduction of sulphonyl bromides with phosphorus tribromide. W. H. HUNTER and B. E. SORENSON (J. Amer. Chem. Soc., 1932, 54, 3368—3374).—The following steps are postulated in the reduction of RSO_2Br to R_2S_2 : $RSO_2Br + PBr_3 \longrightarrow RSOBr + POBr_3$; $RSOBr + PBr_3 \longrightarrow RSBr + POBr_3$; $2RSBr \rightleftharpoons R_2S_2 + Br_2$; $Br_2 + PBr_3 \rightleftharpoons PBr_5$; $RSBr + PBr_3$ (Et_2O)$\rightleftharpoons RSPBr_4$; $RSPBr_4 + 4H_2O \longrightarrow RSH + H_3PO_4 + 4HBr$. p-$C_6H_4Me \cdot SOCl$ and PBr_3 give 54% of di-p-tolyl disulphide, also obtained similarly from p-$C_6H_4Me \cdot SO_2Br$. o-$NO_2 \cdot C_6H_4 \cdot SBr$ and PBr_3 in Et_2O give 15% of di-o-nitrophenyl disulphide, which with PBr_5 in Et_2O affords 40% of o-$NO_2 \cdot C_6H_4 \cdot SBr$. *o*-*Nitrobenzenesulphonyl bromide*, m.p. 63—64°, from the disulphide and Br in AcOH, with PBr_3 gives o-$NO_2 \cdot C_6H_4 \cdot SBr$ and some disulphide; hydrolysis of the reaction product with H_2O affords o-$NO_2 \cdot C_6H_4 \cdot SH$. PBr_3 does not react with di-o-nitrophenyl disulphide in Et_2O. o-$NO_2 \cdot C_6H_4 \cdot SBr$ and PBr_3 in Et_2O (followed by hydrolysis) give o-$NO_2 \cdot C_6H_4 \cdot SH$; in C_6H_6 the disulphide results. C. J. W. (b)

Syntheses with magnesium triarylvinyl bromides. Penta-arylallyl alcohols. C. F. KOELSCH (J. Amer. Chem. Soc., 1932, 54, 3384—3389).— Benzylidenefluorene dibromide and KOH in dil. EtOH give 85—89% of α-*phenyl*-β-*diphenylenevinyl bromide*, m.p. 127°, the Grignard reagent (I) of which with BzCl affords α-*phenyl*-β-*diphenyleneacrylophenone*, m.p. 300—303°, and with CO₂ gives α-*phenyl*-β-*diphenyleneacrylic acid*, m.p. 182—183° (*amide*, m.p. 128—129°). Mg triphenylvinyl bromide (II) and COPh₂ in PhMe give *pentaphenylallyl alcohol* (III), m.p. 108—109°, and a little αα β γ δ δ-*hexaphenylbutadiene*, m.p. 213—214°. (I) and COPh₂ give αα β-*triphenyl*-γ-*diphenyleneallyl alcohol* (IV), m.p. 217—219°, whilst (II) and fluorenone give β γ γ-*triphenyl*-α-*diphenyleneallyl alcohol* (V), m.p. 150—151°. Dehydration of (III) with H₂SO₄, HCl, or AcCl in AcOH gives 1 : 1 : 2 : 3-*tetraphenylindene* (VI), m.p. 149—150°, whilst (IV) or (V) gives 2 : 3-*diphenyl*-1-*diphenyleneindene* (VII), m.p. 174—175°. Oxidation of (VI) with CrO₃ in AcOH gives *o*-benzoyltriphenylcarbinol or diphenylphthalide, whilst (VII) gives BzOH and *o*-benzoylbenzophenone-*o′*-carboxylic acid and a neutral *compound*, C₂₈H₁₈O₃ (?), m.p. 204—206°. 9-*Hydroxy*-9-*o*-*tolylfluorene* has m.p. 118—119°.   C. J. W. (*b*)

Substitution in compounds containing two or more phenyl groups. II. Nitration of 3-methyldiphenyl. W. S. M. GRIEVE and D. H. HEY (J.C.S., 1932, 2245—2247; cf. this vol., 838).— Nitration of 3-methyldiphenyl gives the 4-NO₂-derivative; homonuclear substitution predominates (cf. *loc. cit.*). The product of nitration is oxidised (CrO₃, AcOH) to 6-nitro-*m*-toluic acid (obtained similarly from 4-nitro-*m*-xylene), converted by HNO₃ (*d* 1·37) at 100° into 4 : 4′-*dinitro*-3-*methyldiphenyl*, m.p. 197° (reduced to 3-methylbenzidine), and on reduction (SnCl₂, EtOH-conc. HCl) and subsequent acetylation affords 4-*acetamido*-3-*methyldiphenyl*, m.p. 166° [synthesised from 6-nitro-*m*-toluidine and C₆H₆ by Gomberg and Bachmann's method (A., 1924, i, 1295) and oxidised by neutral KMnO₄ to 4-*acetamidodiphenyl*-3-*carboxylic acid*, m.p. 205—206°]. Nitration of 3- and 4-methyldiphenyl shows a certain parallelism to the substitution reactions of 3- and 4-methylazobenzene (Burns *et al.*, A., 1929, 58).   H. B.

Electrochemical oxidation of naphthalene using a new type electrode. E. G. WHITE and A. LOWY. —See this vol., 1005.

Synthesis of alkylphenanthrenes. III. 1 : 2 : 7-, 1 : 3 : 7-, and 1 : 6 : 7-Trimethylphenanthrenes. R. D. HAWORTH and (in part) F. M. BOLAM (J.C.S., 1932, 2248—2251; cf. this vol., 839).— 2-C₁₀H₇Me, EtCOCl, and AlCl₃ in cold PhNO₂ give 6-*methyl*-2-*naphthyl Et ketone*, b.p. 198—200°/15 mm., m.p. 61—62°, converted by KOH at 250° into 6-methyl-2-naphthoic acid and by Br in CCl₄ into 6-*methyl*-2-*naphthyl* α-*bromoethyl ketone*, m.p. 92—93°. This and CHNa(CO₂Et)₂ in C₆H₆ afford (after hydrolysis and subsequent decarboxylation) β-6-*methyl*-2-*naphthoylbutyric acid*, m.p. 118—120°, the Me ester, b.p. 195—198°/0·2 mm., of which with MgMeI gives γ-6-methyl-2-naphthyl-β-methyl-Δᵝ-pentenoic acid. Reduction of this with red P and HI and subsequent

treatment with H₂SO₄ yields 4-keto-1 : 2 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, b.p. 195—198°/ 0·5 mm. [*semicarbazone*, m.p. 217—218° (decomp.)], which when reduced (Clemmensen) and then dehydrogenated (Se) gives 1 : 2 : 7-*trimethylphenanthrene*, m.p. 120—121° (*picrate*, m.p. 148—149°, *styphnate*, m.p. 169—170°; *quinone*, m.p. 209—210°; *quinoxaline*, m.p. 184—185°).

Methylsuccinic anhydride and 2-C₁₀H₇Me give (cf. *loc. cit.*) β-6-*methyl*-2-*naphthoylisobutyric acid*, m.p. 182—183° (*Me* ester, b.p. 230—240°/15 mm., m.p. 88—89°), converted by way of γ-6-*methyl*-2-*naphthyl*-α-*methyl*-Δᵝ-*pentenoic acid*, m.p. 150—151°, and 4-*keto*-1 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 190—195°/0·4 mm., into 1 : 3 : 7-*trimethylphenanthrene*, m.p. 68—69° (*picrate*, m.p. 163—164°; *styphnate*, m.p. 160—161°; *quinone*, m.p. 174—175°; *quinoxaline*, m.p. 201—202°). Succinic anhydride and 2 : 3-C₁₀H₆Me₂ give β-6 : 7-*dimethyl*-2-*naphthoylpropionic acid*, m.p. 179—180° (*Me* ester, b.p. 235—240°/12 mm., m.p. 95—96°), converted by KOH at 250° into 6 : 7-*dimethyl*-2-*naphthoic acid*, m.p. 254—255° (*Me* ester, m.p. 147—148°) [also obtained by hydrolysis of 2-cyano-6 : 7-dimethylnaphthalene (prepared by distillation of Na 6 : 7-dimethylnaphthalene-2-sulphonate and KCN)], and by way of γ-6 : 7-*dimethyl*-2-*naphthyl*-Δᵝ-*pentenoic acid*, m.p. 155—156°, and 4-keto-1 : 6 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, b.p. 190—192°/ 0·4 mm. (*semicarbazone*, m.p. 200—202°), into 1 : 6 : 7-*trimethylphenanthrene*, m.p. 123—124° (*picrate*, m.p. 165—166°; *styphnate*, m.p. 111—112°; *quinone*, m.p. 221—222°; *quinoxaline*, m.p. 189—190°). The above trimethylphenanthrenes differ from the methylpimanthrenes obtained from *d*-pimaric and *iso*-agathicdicarboxylic acids (cf. *loc. cit.*).   H. B.

Polynuclear aromatic hydrocarbons. XIII. Condensation with 1- and 2-chloromethylnaphthalenes. E. CLAR and L. LOMBARDI (Gazzetta, 1932, 62, 539—544).—When 1-C₁₀H₇·CH₂Cl is condensed (AlCl₃ in CS₂) with 2-C₁₀H₇Me, and the product is distilled from Cu, the resulting hydrocarbon mixture is shown spectroscopically to contain naphtha-2′ : 3′-2 : 3-phenanthrene (A., 1929, 922). This is removed by addition of maleic anhydride to a solution of the mixture in boiling C₆H₄Me₂, when 1′ : 4′-*endonaphtha*-2′ : 3′ : 2 : 3-*phenanthrene*-α β-*succinic anhydride* is formed, dissolved in dil. NaOH, isolated, and decomposed by heat. The residue contains 1 : 2 : 5 : 6-and probably 1 : 2 : 7 : 8-dibenzanthracenes (cf. this vol., 747). Condensation of 1- with 2-C₁₀H₇·CH₂Cl gives the same products, together with a complex polymeride. The compounds described (A., 1931, 1283) as 2′ : 3′-naphtho- and 7 : 7′-dimethyl-2′ : 3′-naphtho-3 : 4-phenanthrene are re-examined and found to be 1 : 2 : 5 : 6-dibenzanthracene and 2′ : 2″-dimethyl-1 : 2 : 5 : 6-dibenzanthracene, respectively; the names of the former are therefore to be eliminated from the literature, together with those of their quinones and of 3 : 4-phthalyl- and dimethyl-3 : 4-phthalyl-phenanthrene (*loc. cit.*).   E. W. W.

Orthoformanilides and their transformation into the corresponding leuco-bases. A. GIACALONE (Gazzetta, 1932, 62, 577—582).—CH(OEt)₃

heated with NH_2Ph, or o- or m-toluidine gives a compound of the type $CH(NHR)_3$, which when heated at 165—170° with the hydrochloride of the amine is converted into a $CHPh_3$ derivative. Attempted acylation of the first product leads only to the acyl derivative of the amine. Amine hydrochlorides with $CH(OEt)_3$ yield hydrochlorides of the type $CH(NHR)_3,HCl$. The following are obtained. *Tri-anilinomethane*, m.p. 138° [*hydrochloride*, m.p. 240° (decomp.)], and *p*-leucaniline; *tri-o-toluidinomethane*, m.p. 150—151° (*hydrochloride*, m.p. 212—213°), and 4 : 4′ : 4″ - triamino - 3 : 3′ : 3″ - trimethyltriphenyl-methane; *tri-m-toluidinomethane*, m.p. 123° [*hydrochloride*, m.p. 221—222° (decomp.)], and 4 : 4′ : 4″ - triamino-2 : 2′ : 2″ - trimethyltriphenylmethane, m.p. 260°.   E. W. W.

Syntheses by means of magnesylurethanes. R. BINAGHI (Gazzetta, 1932, **62**, 469—477).—Phenylurethane (I) undergoes the quant. reaction: $NHPh·CO_2Et + EtMgBr = MgBr·NPh·CO_2Et + C_2H_6$, the Mg derivative (II) decomposing with H_2O to (I), and forming compounds with Et_2O and with $2C_5H_5N$. From (II) are derived : with BzCl, N-*benzoylphenyl-urethane*, m.p. 160—161° (strongly doubly refracting, hydrolysed to benzanilide) which is different from the "benzoylphenylurethane" of Wheeler and Johnson (A., 1903, i, 693); with PhCHO, N-*phenylurethano-phenylcarbinol*, m.p. 225—227°; with COPh₂, N-*phenylurethanodiphenylcarbinol*, m.p. 75—76°; with $CH_2Ph·OAc$, bis - N - (*phenylurethano)methylcarbinol*, m.p. 112—114°.   E. W. W.

Oxidation of s-tribromoaniline by chromic anhydride in acid solution. II. Mechanism. W. H. HUNTER and C. SLY (J. Amer. Chem. Soc., 1932, **54**, 3348—3353; cf. A., 1926, 839).—The properties of *s*-hexabromohydrazobenzene (I) show that it cannot be an intermediate in the production of a pentabromoquinoneimine obtained by oxidation of $s\text{-}C_6H_2Br_3·NH_2$ with CrO_3 in acid solution. It is probable that N analogues of the type postulated (*loc. cit.*) in the oxidation of *s*-halogenophenols are involved. (I) and 2 : 4 : 2′ : 4′-*tetrabromohydrazo-benzene* (II), m.p. 123—124° (*Ac₂* derivative, m.p. 178—179°) (obtained in 80% yield from the corresponding *azo*-compound, m.p. 211°, which results in 40% yield from $2:4\text{-}C_6H_3Br_2·NH_2$ and $KMnO_4$ in aq. pyridine and in 50—60% yield by reduction of *s*-hexabromoazobenzene with Zn and NH_4Cl and then oxidising with CrO_3 in AcOH), do not undergo the semidine rearrangement. In presence of a mineral acid, oxidation and reduction to the corresponding azobenzene and aniline occur; in presence of a reducing agent also, fission to the anilines occurs.   C. J. W. (*b*).

Nitration of o-chlorodimethylaniline. C. F. VAN DUIN (Rec. trav. chim., 1932, **51**, 878—886).—*o*-Chlorodimethylaniline (*picrate*, m.p. 132°) is conveniently prepared from o-chloroaniline and Me_2SO_4. Nitration in H_2SO_4 at room temp. is slow and gives the 5-NO_2-derivative, m.p. 64—65°, only; the constitution of this is proved by synthesis from 2-chloro-5-nitroaniline and Me_2SO_4. Nitration in 10% aq. HNO_3 in presence of HNO_2 gives the 4-, m.p. 78° (I), and 6-NO_2-derivative, b.p. 92—93°/6 mm. (II),

and 2-*chloro-4-nitro(mono)methylaniline*, m.p. 116—117° (III) (*nitrosoamine*, m.p. 95—96°; decomposed by boiling EtOH). (I) is also obtained by methylation of 2-chloro-4-nitroaniline, and by interaction of 1 : 2-dichloro-4-nitrobenzene and $NHMe_2$ in EtOH at 160°. The structure of (II) follows from its synthesis from 1 : 2-dichloro-3-nitrobenzene and $NHMe_2$, its stability to $NHMe_2$ at 160°, and its conversion by further nitration (HNO_3, *d* 1·51) into 2-*chloro*- 4 : 6-*dinitrophenylmethylnitroamine*, m.p. 91—92°, also obtained by nitration of 2-*chloro*-4 : 6-*dinitromethylaniline*, m.p. 133° (*nitrosoamine*). The last-named is prepared from 1 : 2-dichloro-4 : 6-dinitrobenzene and NH_2Me at room temp.; $NHMe_2$, similarly, gives 2-*chloro*-4 : 6-*dinitrodimethylaniline*, m.p. 90—91°. The structure of (III) is similarly proved by its synthesis from 1 : 2-dichloro-4-nitro-benzene and 20% NH_2Me in EtOH at 120—130°. 2-*Chloro*-6-*nitromethylaniline*, m.p. 49—50°, is obtained from 1 : 2-dichloro-3-nitrobenzene and NH_2Me. Improvements are effected in the prep. of o-chloro-acetanilide and its mononitration mixture. All m.p. are corr.   H. A. P.

Action of o-toluidine on pyruvylhydroxamic acid. E. PRINCIVALLE and F. COSSU (Gazzetta, 1932, **62**, 575—577).—Pyruvylhydroxamic acid $NaHSO_3$ compound (A., 1923, i, 1236) heated in AcOH with o-toluidine does not yield a quinoline, but *N*-acetyl-*N*′-o-tolylcarbamide.   E. W. W.

Nitration of α- and β-naphthylamine derivatives. II. Nitration of methyl and ethyl β-naphthylcarbamates and N-β-naphthyl-N′-ethyl-carbamide. C. GROENEVELD (Rec. trav. chim., 1932, **51**, 783—811).—Nitration of *Me* β-*naphthyl-carbamate* (I), m.p. 112—113° (from $C_{10}H_7·NH_2$, $ClCO_2Me$, and Na_2CO_3 in C_6H_6 at the b.p.), with HNO_3 (*d* 1·45°) gives 1 : 8-, m.p. 226—227° (decomp. ?), and 1 : 6-, m.p. 212°, -($NO_2)_2$-derivatives, identified by hydrolysis by NH_3 in MeOH at 100° to the known dinitronaphthylamines. Nitration of (I) or further nitration of its ($NO_2)_2$-derivatives with HNO_3 (*d* 1·52) gives the 1 : 6 : 8-($NO_3)_3$-derivative (II), m.p. 228—230° (decomp.) (similarly identified). The *Et* 1 : 8-, m.p. 178°, and 1 : 6-($NO_2)_2$-, m.p. 185—186°, and 1 : 6 : 8-($NO_2)_3$-, m.p. 215—216° (decomp.) (III), -derivatives are similarly prepared and identified; unlike the Me compounds, they may be prepared from the nitronaphthylamine and $ClCO_2Et$. N-β-*Naphthyl*-N′-*ethylcarbamide*, m.p. 183—184°, is prepared by interaction of $C_{10}H_7·NH_2$ with EtNCO. Nitration (HNO_3, *d* 1·52) at —10° to —5° gives N′-*nitro*-N-1 : 6 : 8-*trinitro*-2-*naphthyl*-N′-*ethylcarb-amide*, $C_{10}H_4(NO_2)_3·NH·CO·NEt·NO_2$, m.p. 101° (decomp.), which is decomposed by H_2O into 1 : 6 : 8-trinitro-β-naphthylamine, and by MeOH and EtOH into the corresponding urethanes, (II) and (III). A literature survey of the nitration of β-naphthylamine derivatives is given.   H. A. P.

Diphenyl series. II. C. FINZI and A. MANGINI (Gazzetta, 1932, **62**, 664—677).—2 : 4′-Diamino-diphenyl (A., 1931, 613) is nitrated by $EtNO_3$ in H_2SO_4 to 4-*nitro*-2 : 4′-*diaminodiphenyl* (I), m.p. 177—178°, the constitution of which is proved by

conversion into 4'-nitro-4-aminodiphenyl and into 4-nitrodiphenyl. Diazotisation of (I) under suitable conditions also yields 4-*nitro*-4'-*amino*-2-*hydroxy*-, m.p. 145—146°, 4-*nitro*-2-*hydroxy*-, m.p. 200—201°, and 4-*nitro*-2 : 4'-*dihydroxy*-*diphenyl*, m.p. 187°. 2'-Amino-4-acetamidodiphenyl (*loc. cit.*) is nitrated to 4'-*nitro*-2'-*amino*-4-*acetamidodiphenyl* (II), m.p. 225° (whence 4'-nitro-4-acetamido- and 4'-nitro-4-aminodiphenyl), and to 3 : 4'-*dinitro*-2'-*amino*-4-*acetamidodiphenyl* (III), m.p. 240—241° [whence 3 : 4'-dinitro-4-acetamido-, new m.p. 239° (cf. A., 1927, 656), and 3 : 4'-dinitro-diphenyl]. 2 : 4'-Diacetamido-diphenyl is nitrated to 4-*nitro*- (IV), m.p. 236—237°, and to 4 : 3'-*dinitro*-2 : 4'-*diacetamidodiphenyl* (V), m.p. 225—226°, also obtainable from (I) or (II), and (III) or (IV), respectively. Hydrolysis of (V) gives 4 : 3'-*dinitro*-2 : 4'-*diaminodiphenyl*, m.p. 199—200°, whence 3 : 4'-dinitro-, new m.p. 187° (cf. A., 1928, 166), 3'-*nitro*-4-*amino*-, m.p. 127°, and 3-nitro-diphenyl are successively prepared, and prove the constitutions of the new compounds, which agree with the general readiness of diphenyls to nitrate in the 4-position. E. W. W.

Behaviour of phenylhydrazones with condensing agents. II. A. GIACALONE (Gazzetta, 1932, 62, 582—587; cf. A., 1931, 1416).—Phenylhydrazones of aldehydes are condensed in presence of ZnCl₂ or of slightly diluted H₂SO₄ and CH(OEt)₃ to the following products. From *p*-tolualdehyde, pp'-4 : 4'-*dimethylbenzylidenedihydrazino*-p''-*methyltriphenyl*-*methane*, m.p. 200° (blackening); from *m*- and *p*-nitrobenzaldehydes, m-*nitro*-p'p''-3 : 3'- and p-*nitro*-p'p''-4 : 4'-*dinitrobenzylidenedihydrazinotriphenyl*-*methane*, m.p. 175° and 195°, respectively; from *o*- and *m*-chlorobenzaldehydes, o-*chloro*-p'p''-2 : 2'- and m-*chloro*-p'p''-3 : 3'-*dichlorobenzylidenedihydrazinotriphenylmethane*, m.p. about 75° and about 90°, respectively. E. W. W.

Some azoxyamide derivatives. Z. E. JOLLES (with O. ORSATTI and W. CAMIGLIERI) (Gazzetta, 1932, 62, 588—597; cf. A., 1922, i, 1072).—Benzene-azocarbonanilide [Br_3-derivative, m.p. 195° (decomp.)] is oxidised by H₂O₂–AcOH to *benzeneazoxycarbonanilide*, O:NPh:N·CO·NHPh, m.p. 136° (decomp. 155°) [*Br*-derivative, m.p. 157° (decomp.), forming *p*-bromoaniline on hydrolysis; NO_2-derivative, m.p. 182° (decomp.)]. *p*-Chlorobenzeneazocarbonamide, now prepared from *p*-chlorophenylsemicarbazide and FeCl₃, is oxidised by H₂O₂–AcOH to p-*chlorobenzeneazoxycarbonamide*, m.p. 192—192·5° (*azo*-β-*naphthol* derivative, m.p. 162·5°), and *pp'*-dichloroazoxybenzene. E. W. W.

Reactions in liquid hydrogen sulphide. IX. Reactions between persulphides of hydrogen and organic compounds. W. B. KING and J. A. WILKINSON (J. Amer. Chem. Soc., 1932, 54, 3070—3073).—H persulphides react with styrene and amylene, adding the ·S·S· group at the double linking (an oxidation reaction); they reduce (NPh)₂ to (NHPh)₂. Reaction between diazonium chlorides and persulphides occurs with explosive violence unless it is regulated by a solvent such as CS₂. F. S. (*b*)

Manufacture of aromatic monoacyldiamines. A. CARPMAEL. From I.G. FARBENIND. A.-G.—See B., 1932, 763.

Manufacture of diacylated diamines. Soc. CHEM. IND. IN BASLE.—See B., 1932, 763.

Acyl derivatives of o-aminophenol. I. C. B. POLLARD, C. E. SPARKS, and M. L. MOORE (J. Amer. Chem. Soc., 1932, 54, 3283—3286).—A study of the *ON*-diacyl derivatives of o-NH₂·C₆H₄·OH, where one of the acyl groups was always β-phenylpropionyl, has been made. In five of the six cases studied, isomerides were obtained depending on the order of introduction of the acyl groups. Complete rearrangement occurred (in five cases) during hydrolysis; in four cases the heavier and more acidic group, whilst in the other case the heavier and less acidic group, was attached to N. o-β-Phenylpropionamidophenol (I) has m.p. 131·5—132°. The following o-β-phenylpropionamidophenyl esters are prepared : *acetate*, m.p. 79·5—81°; *propionate* (II), m.p. 113·5—115·5°; *valerate*, m.p. 74—75·5°; *isovalerate*, m.p. 92—93°; *phenylacetate* (III), m.p. 90—92°; *benzoate*, m.p. 116·5—118·5°. The following derivatives of o-aminophenyl β-phenylpropionate are also described : *Ac*, m.p. 124·5—126°; *propionyl* (IV), m.p. 102·5—104·5°; *valeryl*, m.p. 72·5—74°; *isovaleryl*, m.p. 73·5—74°; *phenylacetyl* (V), m.p. 81—83°; *Bz*, m.p. 122·5—124·5°. (II) and (IV) give a mixed m.p. of 110—115°, indicating that each might be an equilibrium mixture; each substance is, however, hydrolysed to (I). Hydrolysis of (III) and (V) gives approx. 60% of (I) and 40% of o-phenylacetamidophenol. Hydrolysis of the other derivatives affords (I). C. J. W. (*b*)

Tautomerism of p-benzoquinoneoxime and p-nitrosophenol. L. C. ANDERSON and M. B. GEIGER (J. Amer. Chem. Soc., 1932, 54, 3064—3070). —Absorption curves of several derivatives of *p*-benzoquinoneoxime are given. Conclusions are reached regarding structure and ratio of isomeric forms. F. S. (*b*)

Halogen derivatives of monohydroxydiphenylmethane and their antibacterial action. E. KLARMANN, L. W. GATES, and V. A. SHTERNOV (J. Amer. Chem. Soc., 1932, 54, 3315—3328).—The following are prepared by *C*-benzylation of halogenophenols or by halogenation of hydroxydiphenylmethanes : 3-*chloro*-4-, b.p. 155—160°/5 mm.; 3-*bromo*-4-, b.p. 152—154°/3 mm.; 3-*chloro*-2-, b.p. 144°/4 mm.; 4'-*chloro*-4-, b.p. 175—177°/4 mm., m.p. 85·5°; 5-*chloro*-2-, b.p. 160—162°/3·5 mm., m.p. 48·5°; 5-*bromo*-2-, b.p. 189—192°/3·5 mm.; 4'-*chloro*-2-, b.p. 168—171°/4 mm., m.p. 61·5°; 3 : 4'-*dichloro*-4-, b.p. 160—164°/3 mm., m.p. 64°; 3-*chloro*-4'-*bromo*-4-, b.p. 182°/3 mm., m.p. 65°; 5-*chloro*-3-*methyl*-2-, b.p. 147—149°/4·5 mm., m.p. 55°; 4'-*chloro*-3-*methyl*-2-, b.p. 167—172°/4 mm., m.p. 48°; 5-*chloro*-4(6)-*methyl*-2-, b.p. 176—178°/4·5 mm.; 5-*chloro*-4 : 6-*dimethyl*-2-, b.p. 182—185°/4 mm., m.p. 68·5°; 4'-*bromo*-4 : 6-*dimethyl*-2-, b.p. 194—196°/4 mm., m.p. 101·5°, and 5-*chloro*-3-iso*propyl*-6-*methyl*-2-, b.p. 175°/3 mm., -*hydroxydiphenylmethanes*. All the above compounds are potent bactericides; some of them are extremely active towards *Staphylococcus aureus* and *Streptococcus hæmoliticus*. Certain regularities in the relation be-

tween the antibacterial action and composition are found. Thus, halogen in the *p*-position to OH causes a greater antibacterial efficiency than when in the *o*-position. The 4′-chloro-2-hydroxy- is more effective than the 4′-chloro-4-hydroxy-derivative towards the above bacteria, but less effective against *E. typhi* and *E. paradysenteriæ*. The monobromo-derivatives of both the 2- and 4-OH derivatives are less effective than the corresponding Cl analogues towards *E. typhi* and *E. paradysenteriæ*, but more so against *S. aureus* and *S. hæmoliticus*. The dihalogen derivatives are also highly bactericidal. The presence of 1 or 2 Me groups causes a considerable increase in germicidal potency towards the cocci only. Me and Pr$^\beta$ together reduce the bactericidal action on all 4 micro-organisms. The above substances appear to show a typically bactericidal rather than a bacteriostatic behaviour, when compared, *e.g.*, with bacteriostatic dyes. The effect of EtOH used in the prep. of solutions employed in the bacteriological tests is studied. Concns. not germicidal *per se* impair the antibacterial action of the 5-chloro-2-derivative; an explanation for this is suggested on the basis of an assumed shift of the partition equilibrium of the dissolved substance between the bacteria and the H_2O–EtOH phase. The effect of using dil. alkali in the prep. of the solutions on their germicidal action is also studied. C. J. W. (*b*)

Thiophenols. Action of benzhydrol, triphenyl-carbinol, and the corresponding chlorides. C. Finzi and V. Bellavita (Gazzetta, 1932, **62**, 699—709).—Thiophenols combine with CHPh$_2$·OH or CPh$_3$·OH in H_2SO_4, or with CHPh$_2$Cl or CPh$_3$Cl in acid, alkali, or pyridine, to products in which primary substitution in each case is in the SH group. The following are described : *Ph CHPh$_2$ sulphide*, m.p. 78°; S : *p-bisdiphenylmethylthiophenol*, m.p. 121° (using CHPh$_2$·OH with hot H_2SO_4, or AlCl$_3$; α- and β-*naphthyl CHPh$_2$ sulphides*, m.p. 77·5° and 123°, respectively; S : 4-*bisdiphenylmethyl-α-thionaphthol*, m.p. 148°; *Ph CPh$_3$ sulphide*, m.p. 106°; α- and β-*naphthyl CPh$_3$ sulphides*, m.p. 121° and 134°; S : 1-*bistriphenylmethyl-β-thionaphthol*, m.p. 82°; *o-* and *p-tolyl CPh$_3$ sulphides*, m.p. 145° and 147°, respectively; 2 : 4-*dinitrophenyl CPh$_3$ sulphide*, m.p. 190° (from 4-chloro-*m*-dinitrobenzene and CPh$_3$·SH or from 2 : 4-dinitrothiophenol and CPh$_3$Cl); 2 : 4 : 2′ : 4′-*tetramethylthioltriphenylcarbinol*, m.p. 141° [from *m*-C$_6$H$_4$(SMe)$_2$, CPh$_3$Cl, and AlCl$_3$], and 2 : 4-*dimethylthioltriphenylcarbinol*, m.p. 144—145° [from *m*-C$_6$H$_4$(SMe)$_2$, CPh$_3$Cl, and AlCl$_3$]. E. W. W.

Constitution of tribromoguaiacol. A. Zangirolami (Gazzetta, 1932, **62**, 570—575).—Tribromoguaiacol, m.p. 117° (cf. A., 1893, i, 313), must be the 4 : 5 : 6-compound, since it is obtainable from 6-bromoguaiacol (J.C.S., 1908, **93**, 792) and Br. It is also apparently obtained when 6-bromo-5-nitroguaiacol (J.C.S., 1917, **111**, 917) is reduced to 6-*bromo-5-aminoguaiacol* (*hydrochloride*, decomp. 230°; *sulphate*, decomp. 200°), diazotised, treated with KBr, and the mixed product brominated. E. W. W.

Decomposition of acyl derivatives of 3 : 5 : 3′ : 5′ - tetranitro - 2 : 2′-dihydroxydiphenyl into 1 : 3 : 6 : 8-tetranitrodiphenylene oxide and an acid anhydride. J. van Alphen (Rec. trav.

chim., 1932, **51**, 715—725).—The following diacyl derivatives of 3 : 5 : 3′ : 5′-tetranitro-2 : 2′-dihydroxydiphenyl are decomposed by heating alone or in PhNO$_2$ to the corresponding acid anhydride and 1 : 3 : 6 : 8-tetranitrodiphenylene oxide (I) (cf. this vol., 267) : *dipropionate*, m. p. 139°; *diisobutyrate*, m.p. 133°; *di-p-chlorobenzoate*, m.p. 233°; *di-p-bromobenzoate*, m.p. 204°; *di-p-anisate*, m.p. 199°; *di-m-ethoxybenzoate*, m.p. 118°; *di-p-ethoxybenzoate*, m.p. 188° (impure); *di(phenylacetate)*, m.p. 174·5°; *phthalate*, m.p. > 200° (indef.; decomp.), and *di-p-nitrobenzoate*, m.p. 221°. The action of *p*-toluenesulphonyl chloride on the diphenol in aq. NaOH at 95—100°, or on its K salt in COMe$_2$ at the b.p. gave (I) unaccompanied by any acyl derivative; ClCO$_2$Et and the K salt at 100° gave a similar result. (I) was not formed, however, by the action of conc. H_2SO_4 at 140° or of 7% oleum at 15° on the diphenol. 3 : 5 : 3′ : 5′-*Tetrabromo*-2 : 2′-*diacetoxydiphenyl*, m.p. 118°, is stable at 250° and at higher temp. decomposes without formation of the corresponding diphenylene oxide. No other formation was observed on heating 2 : 2′-diacetoxydiphenyl, its 5 : 5′-(NO$_2$)$_2$-derivative, m.p. 204°, 3 : 5 : 3′ : 5′-tetranitro-4 : 4′-diacetoxydiphenyl, or 2 : 4-dinitro- or 2 : 4 : 6-trinitro-phenyl acetates. H. A. P.

Configurative relationships of phenylmethyl-, *cyclo*hexylmethyl-, and methylhexyl-carbinols and of their homologues. P. A. Levene and R. E. Marker (J. Biol. Chem., 1932, **97**, 379—391).—Previous conclusions (A., 1930, 1178) are in part confirmed and in part corrected. Freudenberg's rule is not universally true. The contribution of the *cyclo*hexyl group has an opposite direction of rotation from that of the hexyl group when the members of the two series are configuratively related. The following substances were prepared, mainly by the Grignard (A) or malonic ester (B) syntheses : *cyclohexylmethylcarbinol* (A), resolved by the *strychnine* salt, [α]$_D^{10}$ +48·6° in abs. EtOH, of the *H phthalate*, gives the d-*carbinol*, b.p. 105°/35 mm., [α]$_D^{10}$ +5·11°; cyclo-hexyl-n-*propylcarbinol* (A), resolved by the *strychnine* salt, [α]$_D^{30}$ −1·55° in abs. EtOH, of the *H phthalate*, gives the l-*carbinol*, b.p. 127°/25 mm., [α]$_D^{29}$ −17·03°; cyclohexylethylcarbinol (A), resolved by the *strychnine* salt, [α]$_D^{29}$ +13·3° in abs. EtOH, of the *H phthalate*, gives the l-*carbinol*, b.p. 106°/19 mm., [α]$_D^{30}$ −8·09°; cyclohexyl-n-*butylcarbinol* (A), resolved by the *strychnine* salt, [α]$_D^{29}$ −2·06° in abs. EtOH, of the *H phthalate*, gives the l-*carbinol*, b.p. 135°/25 mm., [α]$_D^{30}$ −12·87°; CHPhPr·OH, resolved similarly, gives the *l*-carbinol, b.p. 120°/15 mm., [α]$_D^{24}$ −23·3° (homogeneous) and −35·8° in C$_6$H$_6$ [*acetate*, b.p. 134°/30 mm., [α]$_D^{24}$ −55·1° in C$_6$H$_6$ and −57·32° (homogeneous)]; the *cinchonidine* salt of d-*phenyl-n-butyl-carbinol H phthalate*, [α]$_D^{25}$ +11·5° in Et$_2$O, gives the d-*carbinol*, b.p. 130°/15 mm., [α]$_D^{24}$ +17·2° (homogeneous) and +31·3° in C$_6$H$_6$; l-α-*phenylethyl chloride*, b.p. 90°/26 mm., [α]$_D^{24}$ −16·9° (from CHPhMe·OH and SOCl$_2$), yields (B) d-β-*phenylbutyric acid*, b.p. 134°/4 mm., [α]$_D^{25}$ +2·85°; d-α-*phenylpropyl chloride*, b.p. 86°/14 mm., [α]$_D^{24}$ +19·82° (similarly prepared), yields (B) d-β-*phenylvaleric acid*, solid, b.p. 150°/6 mm., [α]$_D^{24}$ +5·44° in C$_6$H$_6$; l-α-*phenyl-n-butyl chloride*, b.p.

115°/30 mm., $[\alpha]_D^{24}$ −26·19°, yields (B) d-β-*phenyl-n-hexoic acid*, b.p. 155°/4 mm., $[\alpha]_D^{25}$ +7·95°; l-α-*phenyl-n-amyl chloride*, b.p. 120°/15 mm., $[\alpha]_D^{25}$ −24·62°; α-*phenylethyl acetate*, b.p. 120°/35 mm., $[\alpha]_D^{25}$ +26·8° (homogeneous) and +28·9° in C_6H_6; d-α-*phenylpropyl acetate*, b.p. 130°/35 mm., $[\alpha]_D^{24}$ +53·7° in C_6H_6 and +55·34° (homogeneous); l-α-*phenyl-n-amyl acetate*, b.p. 140°/20 mm., $[\alpha]_D^{24}$ −37·3° in C_6H_6 and −37·9° (homogeneous). R. S. C.

Tautomerism of hydroxytriarylcarbinols. III. L. C. ANDERSON and M. B. GEIGER (J. Amer. Chem. Soc., 1932, 54, 3058—3064).—The effect of substitution is shown in the absorption spectra curves of the corresponding methane, coloured carbinol, and fuchsone of 3-chloro-, 3-bromo-, 3 : 5-dichloro-, and 3 : 5-dibromo-4-hydroxytriphenylcarbinols, together with the curves of the colourless carbinols of the last three compounds. F. S. (b)

Heteropolarity. XVI. Diphenyl-green dyes. W. DILTHEY, W. BRANDT, W. BRAUN, and W. SCHOMMER (J. pr. Chem., 1932, [ii], 134, 188—208).— A p-Ph substituent in the aldehyde component of malachite-green and similar dyes has a bathochromic influence on shade, apparently due to an absorption band not present in the visible spectrum of the parent type, the main band being altered but little in position. The dye salts ($RClO_4$) are less stable to hydrolysis, and the halochromism in H_2SO_4 is abnormal. 4'-*Aminophenyl-4-diphenylylcarbinol*, m.p. 189—190° (Ac_2 derivative, m.p. 157—158°), is prepared by reduction of the corresponding ketone with Zn and NaOH in MeOH. p-*Dimethylaminophenyl 4-diphenylyl ketone* (I), m.p. 127—128° [*picrate*, m.p. 159—160° (decomp.); *oxime*, m.p. 225—230°], is prepared by interaction of p-dimethylaminobenzoyl chloride, Ph_2, and $AlCl_3$ in $PhNO_2$. It is reduced as above to the corresponding *carbinol*, m.p. 139—141°. pp'-*Tetramethyldiaminodiphenyl-4-diphenylylcarbinol*, m.p. 145°, is prepared by condensation of (I) with $NPhMe_2$ and $POCl_3$ or by oxidation of pp'-*tetramethyldiaminodiphenyl-4-diphenylylmethane* (II), m.p. 191°, with PbO_2 and HCl. It is reduced to (II) by Zn and AcOH, and with acids gives diphenyl-green-*A* [*perchlorate*, m.p. 222° (decomp.); *chloride*]. (II) is prepared by interaction of diphenyl-4-aldehyde with $NPhMe_2$ and $POCl_3$ at 100°. The following methane bases are similarly prepared and oxidised to dyes. *Bis-4-diethylaminophenyl-*, dimorphic, m.p. 132°, 143—144° [*carbinol base*, m.p. 148°; diphenyl-green-*B* (*perchlorate*, m.p. 205°)], *bis-4-benzylmethylaminophenyl-*, m.p. 113° {diphenyl-green-*C* [*perchlorate*, m.p. 200° (decomp.)]}, and *bis-4-benzylethylaminophenyl-4'-diphenylylmethane*, m.p. 97° {diphenyl-green-*D* [*perchlorate*, m.p. 210° (decomp.)]}. H. A. P.

Manufacture of alkamines of the type Ar·CH(OH)·CHR·NR'R''. I. G. FARBENIND. A.-G.—See B., 1932, 792.

Chemical structure and optical rotation. III. Configurative relationship of disubstituted propionic acids containing a cyclohexyl group. Correction of previous work. P. A. LEVENE and R. A. MARKER (J. Biol. Chem., 1932, 97, 563—583; cf. A., 1931, 1413).—The sign of [α] given previously

(*loc. cit.*) for γ-phenylhexoic acid (A) and the substances prepared from it should be changed from − to +. The lævorotation of γ-phenylhexane, obtained by reduction of the bromide prepared from (A), is due to partial unsaturation; the hydrocarbon is dextrorotatory after catalytic reduction (colloidal Pd). Other hydrocarbons, similarly prepared, are, however, saturated. These corrections lead to the conclusion that all β-phenyl-β-alkylpropionic acids rotate in the same direction (contrast *loc. cit.*). Reduction of β-phenylbutyric acid, but not of the homologues, to the *cyclo*hexyl compound results in a change of direction of rotation; all the carbinols, halides, and hydrocarbons of the *cyclo*hexyl series rotate in the opposite direction to the corresponding phenyl compounds. Unless otherwise stated, reductions reported below were carried out by H_2 and PtO_2 in AcOH. Reduction of β-phenylbutyric acid gives l-β-*cyclohexylbutyric acid* (I), b.p. 145°/4 mm., $[\alpha]_D^{24}$ −0·26°; β-phenylbutyl alcohol gives d-β-*cyclohexylbutyl alcohol*, b.p. 128°/15 mm., $[\alpha]_D^{25}$ +2·71°, which with PBr_3 yields the d-*bromide*, b.p. 126°/15 mm., $[\alpha]_D^{25}$ +5·20°. d-β-*Phenylbutane* (II), $[\alpha]_D^{25}$ −6·82°, gives d-β-*cyclohexylbutane*, b.p. 174°, $[\alpha]_D^{25}$ +0·79°. Crystallisation of the quinine salt of the dl-acid obtained from α-*cyclo*hexylethyl bromide and Et_2 malonate gives (I), having $[\alpha]_D^{24}$ −0·75°, the *Et ester*, b.p. 104°/3 mm., $[\alpha]_D^{23}$ −1·44°, of which with Na and EtOH gives l-β-*cyclohexylbutyl alcohol*, b.p. 128°/15 mm., $[\alpha]_D^{27}$ −2·69°; this with PBr_3 gives the corresponding *bromide*, b.p. 135°/15 mm., $[\alpha]_D^{27}$ −6·6°, which by Grignard reactions affords d-β-*cyclohexylbutane*, b.p. 174°, $[\alpha]_D^{27}$ +0·45°, and l-γ-*cyclohexylvaleric acid*, b.p. 149°/3 mm., $[\alpha]_D^{25}$ −2·17°. The *Et ester*, b.p. 133°/7 mm., $[\alpha]_D^{27}$ −2·14°, of this with Na and EtOH gives l-δ-*cyclohexyl-n-amyl alcohol*, b.p. 134°/15 mm., $[\alpha]_D^{27}$ −2·98°, giving with PBr_3 the *bromide*, b.p. 146°/16 mm., $[\alpha]_D^{27}$ −6·56°, whence (Grignard) l-β-*cyclohexylpentane*, b.p. 88°/15 mm., $[\alpha]_D^{27}$ −0·81°, was obtained. β-Phenylhexane, $[\alpha]_D^{25}$ +1·96°, gives l-β-*cyclohexylhexane*, b.p. 101°/18 mm., $[\alpha]_D^{25}$ −0·90°. β-Phenylvaleric acid, $[\alpha]_D^{27}$ −14·2° in C_6H_6, gives l-β-*cyclohexylvaleric acid* (III), b.p. 153°/5 mm., $[\alpha]_D^{27}$ −1·53°. γ-Phenyl-n-amyl alcohol, $[\alpha]_D^{25}$ −4·54°, gives d-γ-*cyclohexyl-n-amyl alcohol* (IV), b.p. 135°/15 mm., $[\alpha]_D^{25}$ +2·22°, yielding with PBr_3 the *bromide*, b.p. 135°/15 mm., $[\alpha]_D^{25}$ +2·76°. γ-Phenylhexane, $[M]_D^{21}$ +0·92°, gives d-γ-*cyclohexylhexane* (V), b.p. 111°/28 mm., $[\alpha]_D^{23}$ −0·89°. γ-Phenylheptane, $[\alpha]_D^{25}$ +0·97°, gives l-γ-*cyclohexylheptane*, b.p. 112°/15 mm., $[\alpha]_D^{25}$ −0·68°. α-Phenylpropyl bromide and Et_2 malonate give dl-β-*cyclohexylvaleric acid*, resolved by the quinine salt into (III), b.p. 148°/4 mm., $[\alpha]_D^{25}$ −1·38°, the *Et ester*, b.p. 118°/6 mm., $[\alpha]_D^{27}$ −0·82°, of which with Na and EtOH yields (IV), b.p. 119°/5 mm., $[\alpha]_D^{27}$ 2·00°. β-Phenylhexoic acid, $[\alpha]_D^{24}$ −2·48°, gives l-β-*cyclohexylhexoic acid* (VI), b.p. 155°/4 mm., $[\alpha]_D^{24}$ −0·39°. γ-Phenylhexan-α-ol, $[\alpha]_D^{25}$ +2·51°, gives l-γ-*cyclohexylhexan-α-ol*, b.p. 141°/15 mm., $[\alpha]_D^{23}$ −0·19°, yielding with PBr_3 the *bromide*, b.p. 145°/15 mm., $[\alpha]_D^{23}$ −0·62°. δ-Phenyloctane, $[M]_D^{23}$ +1·18°, gives δ-*cyclohexyloctane*, b.p. 123°/15 mm., $[\alpha]_D^{25}$ −0·29°. α-*cyclo*Hexylbutyl bromide and Et_2 malonate give dl-β-*cyclohexylhexoic acid*, resolved with difficulty by the quinine salt to (VI), $[\alpha]_D^{24}$ +2·04°, the

Et ester, b.p. 126°/4 mm., $[\alpha]_D^{27}$ +1·54°, of which led to d-γ-cyclo*hexan-α-ol*, b.p. 127°/4 mm., $[\alpha]_D^{17}$ −0·79°, the corresponding *bromide*, b.p. 145°/15 mm., $[\alpha]_D^{25}$ −1·38°, and (V), $[\alpha]_D^{27}$ +0·57°. d-β-*Phenylheptoic acid* (VII), $[M]_D^{27}$ +47·6°, gives d-β-cyclo*hexylheptoic acid*, b.p. 155°/2 mm., $[\alpha]_D^{27}$ +4·6°. α-Phenylpropyl chloride, $[M]_D^{17}$ +30·62°, and MgMeI give (II), b.p. 63°/15 mm., $[\alpha]_D^{17}$ +1·18°. α-Phenyl-n-amyl chloride, $[M]_D^{25}$ −45·06°, and Et$_2$ malonate give (VII), b.p. 165°/4 mm., $[\alpha]_D^{25}$ +8·00°, the Et ester, b.p. 128°/2 mm., $[\alpha]_D^{15}$ −2·98°, of the l-isomeride of which led to l-γ-*phenylheptan-α-ol*, b.p. 150°/10 mm., $[\alpha]_D^{27}$ −1·45°, the corresponding *bromide*, b.p. 132°/4 mm., $[\alpha]_D^{27}$ −10·4°, d-γ-*phenylheptane*, b.p. 112°/15 mm., $[\alpha]_D^{15}$ +0·75°, and l-γ-cyclo*hexylheptane*, b.p. 112°/15 mm., $[\alpha]_D^{25}$ −0·54°. R. S. C.

o-Chlorobenzoic acid by the action of chlorine on saccharin. P. BERTOLO and A. BERTOLO (Gazzetta, 1932, **62**, 487—493).—Saccharin is oxidised by KClO$_3$ and dil. HCl (1 in 4) at the b.p. to o-chlorobenzoic acid, free from m- and p-isomerides.

E. W. W.

Absorption in ultra-violet and chemical reactivity of organic compounds. (MME.) RAMART-LUCAS and J. HOCH (Bull. Soc. chim., 1932, [iv], **51**, 824—838).—A detailed description of work already published (cf. this vol., 211). In the series Ph·[CH$_2$]$_n$·CO$_2$H the effect of o-Me groups (mesityl in place of Ph) is to diminish the mutual effect of the chromophores. γ-*Mesitylpropyl bromide* (I), b.p. 163°/20 mm. [prepared by the route C$_6$H$_2$Me$_3$·[CH$_2$]$_2$·CO$_2$H→·COCl →·CO·NH$_2$→·CH$_2$·OH (Na and EtOH)→ ·CH$_2$Br (PBr$_3$)], is converted by KCN into γ-*mesitylbutyronitrile*, b.p. 177°/18 mm., which on alkaline hydrolysis gives the corresponding *acid*, m.p. 87°. δ-*Mesityl-n-valeric acid*, m.p. 64°, b.p. 213°/18 mm. (*amide*, m.p. 131°), is prepared by condensation of (I) with CHNa(CO$_2$Et)$_2$, hydrolysis of the resulting Et_2 γ-*mesitylpropylmalonate*, b.p. 222°/18 mm., with KOH in EtOH, and decarboxylation of the resulting *acid*, m.p. 140°, by heat. Reduction of δ-mesitylvaleramide with Na and abs. EtOH gives ε-*mesitylpentan-α-ol*, b.p. 183—184°/16 mm. (*phenylurethane*, m.p. 97°), the corresponding *bromide*, b.p. 185°/18 mm., of which is converted by KCN and subsequent hydrolysis into ε-*mesityl-n-hexoic acid*, m.p. 70°. Interaction of $\alpha\kappa$-dibromodecane in excess with NaOPh gives mainly $\alpha\kappa$-*diphenoxydecane*, m.p. 85°, and a little α-*bromo-κ-phenoxydecane*, b.p. 230—245°/35 mm., converted by the malonate synthesis into λ-*phenoxylauric acid*, m.p. 81°. The action of AlCl$_3$ on phenoxyacetyl chloride in C$_6$H$_6$ gives, in addition to coumarone (15% of theory), ω-phenoxyacetophenone, b.p. 210—215°/15 mm.; the yield of coumarone is not increased by carrying out the reaction in CS$_2$. H. A. P.

Nuclei of cis-cinnamic acid. II. A. W. K. DE JONG (Rec. trav. chim., 1932, **51**, 695—698; cf. this vol., 612).—Crystal nucleus formation in liquid cis-cinnamic acid is favoured by light and by the $trans$-acid; the cryst. forms that separate depend to some extent on the temp. Light petroleum (b.p. 40—50°) and H$_2$O have little or no effect. H. A. P.

New choladienic acid. V. DEULOFEU (Z. physiol. Chem., 1932, **210**, 30—32).—Catalytic hydro-

genation (PtO$_2$) of 7 : 12-diketocholanic acid at 60° gives 7 : 12-dihydroxycholanic acid, m.p. 206—208°. The latter, on distillation in vac., affords ε-*choladienic acid*, m.p. 184—185°, which on catalytic hydrogenation takes up 2H$_2$ yielding cholanic acid.

J. H. B.

Bromination of dehydrodeoxycholic acid and of dehydrocholic acid. II. T. NOGUCHI (Z. physiol. Chem., 1932, **209**, 249—252; cf. A., 1931, 1293).—Hydrolysis of monobromodehydrodeoxycholic acid (I) with dil. aq. KOH gives 2-*hydroxydehydrodeoxycholic acid* (II), m.p. 197° (decomp.) (*Ac* derivative, m.p. 235°). Oxidation of (II) with CrO$_3$ in AcOH opens the ring between C$_2$ and C$_3$ giving deoxybilianic acid. Hence the Br in (I) is attached at C$_2$ of ring I. Similarly CrO$_3$ oxidation of 2-hydroxydehydrocholic acid gives bilianic acid, indicating a similar position for Br in monobromodehydrocholic acid.

J. H. B.

Phenanthrene series. II. Phenanthrenecarboxylic acids and 9-bromophenanthrene derivatives. E. MOSETTIG and J. VAN DE KAMP (J. Amer. Chem. Soc., 1932, **54**, 3328—3337; cf. A., 1930, 1438).—Phenanthrene (I), (COCl)$_2$, and AlCl$_3$ in CS$_2$ at −15° give a *compound*, m.p. 232—234°, phenanthrene-3-carboxylic acid (II), small amounts of the -2- and -9- (III) -carboxylic acids, and an *acid*, m.p. 123—125°, the structure of which has not been determined; these results are contrary to those of Liebermann and Zsuffa (A., 1911, i, 202). Acids are not produced from (I), COCl$_2$ (or CNBr), and AlCl$_3$. 9-Bromophenanthrene (IV) and a slight excess of CuCN at 260° give 93% of the nitrile, hydrolysed to 90% of (III). (IV), (COCl)$_2$, and AlCl$_3$ in CS$_2$ give 85% of a mixture of acids, separable through the Me esters; 9-*bromophenanthrene-3(or 6)-carboxylic acid* (V), m.p. 283—284° (*Me* ester, m.p. 155—155·5°, oxidised to Me phenanthraquinone-3-carboxylate), and at least two other acids are formed. Debromination of the Me ester by H (Pd) gives the Me ester of (II). (IV), AcCl, and AlCl$_3$ give 70% of 9-*bromo-3(or 6)-acetylphenanthrene*, m.p. 150—151° (*semicarbazone*, m.p. 265—265·5°; *oxime*, m.p. 142·5—143°), oxidised (NaOCl) to (V). C. J. W. (b)

Retene. II. α-Retenecarboxylic acid and its derivatives. M. T. BOGERT and T. HASSELSTRÖM (Proc. Nat. Acad. Sci., 1932, **18**, 417—421).—Acetylretene (A., 1931, 1297) and alkaline NaOBr in MeOH give the (α-)retenecarboxylic acid (I), m.p. 237·5—238·5° (all m.p. are corr.) (*anilide*, m.p. 224·5—225·5°), of Komppa and Wahlforss (*ibid.*, 226), which is oxidised by CrO$_3$–AcOH to α-retenequinonecarboxylic acid, decomp. above 252° (lit. m.p. 237—240°) [*quinoxaline*, decomp. above 272°, from o-C$_6$H$_4$(NH$_2$)$_2$; *Me* ester, m.p. 197·5—198·5° (*quinoxaline*, m.p. 187—188·5°)], and reduced (as Na salt) by Na and isoamyl alcohol to α-*octahydroretenecarboxylic acid*, m.p. 181—182°, the alkali salts of which behave as true resinates. An amorphous compound, hydrolysed by aq. Na$_2$CO$_3$ to the Na salt of (I), is also formed during the prep. of (I) by Komppa and Wahlforss' method (*loc. cit.*).

H. B.

Theory of ring-contraction and related rearrangements. F. SCHENCK (J. pr. Chem., 1932,

[ii], **134**, 215—248).—The hypothesis tentatively advanced (A., 1928, 174) in explanation of the conversion of the stereoisomeric truxillamic and truxinamic acids (cf. this vol., 158, 159) by NOBr or HNO$_2$ into corresponding forms of 2-phenyl-3-hydroxybenzyl-*cyclo*propane-1-carboxylic acid (I) is inadequate; thus, it should lead to the same intermediate form in the case of both α- and γ-truxillic acids, whereas actually different end-products are obtained. It is now suggested that the conversion of ·NH$_2$ into ·N$_2$·OH lessens the attraction of C for N, and that the resulting partial-valency adjustments lead successively to a strengthening of the 2:3- and 2:4-linkings and weakening of the 1:2- and 1:4-linkings, compensated by a partial-valency linking between the 1:3-positions. Elimination of N$_2$ then leads to formation of the *cyclo*propane ring by fission of the 1:2- or 1:4-linking, the –CHPh·OH groups thus formed taking the place of the original NH$_2$ group. In the truxillic series fission takes place in both directions, but in the truxinic series it occurs between the Ph
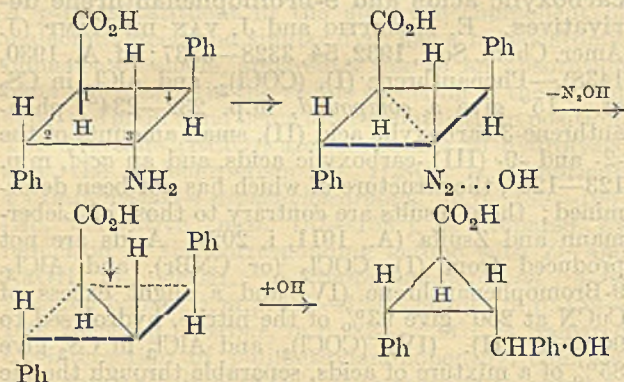
groups only. The hypothesis is generally applicable to rearrangements involving the migration of hydrocarbon radicals, and explanations of the retropinacolin, pinacone–pinacolin, semipinacolin, and benzil–benzilic acid transformations are given.

The three remaining isomerides of (I) demanded by theory are isolated by reduction of the Me esters of the 3-benzoyl-2-phenyl*cyclo*propane-1-carboxylic acids (for brevity the former are referred to as "oxyacids," and the latter as "ketonic acids"; for numeration cf. A., 1928, 174 *et seq.*) with Al(OPr$^\beta$)$_3$ in Pr$^\beta$OH. Reduction of ketonic acid I Me ester gives the *lactone*, m.p. 168—169°, of oxy-acid Ib, m.p. 171—172° (decomp.) [*Me* ester, m.p. 171—172° (CH$_2$N$_2$)], and a small amount of the Pr$^\beta$ ester of oxy-acid IVa. Oxy-acid Ib is isomerised to IIIb by fusion with KOH, and to the lactone of Ia by 15% HCl at room temp. Ketonic acid II gives OH-acids IIa and IIb as lactones, the latter in preponderating amount. From ketonic acid III the Pr$^\beta$ ester, m.p. 125·5—126·5°, of *oxy-acid* IIIb (2^t-*phenyl-3^t-hydroxybenzylcyclopropane-1^c-carboxylic acid*), m.p. 188—189° (*Me* ester, m.p. 104—105°), alone is obtained; it does not give any appreciable amount of lactone with Ac$_2$O at 100°. Reduction of the Me ester of ketonic acid IV, and hydrolysis of the product gives a mixture of oxy-acids IVa and IVb (2^c-*phenyl-3^t-hydroxybenzylcyclopropane-1^c-carboxylic acid*) [*oxyacid* IVa, m.p. 152—153° (*Me* ester, m.p. 125—126°;

Pr$^\beta$ ester, m.p. 125—126°); *oxy-acid* IVb, m.p. 151—152° (*Me* ester, m.p. 82—83°)]; on reoxidation both give the original ketonic acid. The relative configurations of Ph and CO$_2$H in the new isomerides are confirmed by ring-fission with AcOH–H$_2$SO$_4$, which gives the stereoisomeric forms of α-(acetoxybenzyl)-β-benzylidenepropionic acid (Pr$^\beta$ ester of acid, m.p. 151·5—152·5°, has m.p. 109—110°). H. A. P.

Substitution products of o-α-naphthoylbenzoic acid. E. H. JOHNSON, V. WEINMAYR, and R. ADAMS (J. Amer. Chem. Soc., 1932, **54**, 3289—3295).—o-α-Naphthoylbenzoic acid (I) and Br in boiling AcOH give 69·5% of o-5'-*bromo-1'-naphthoylbenzoic acid* (II), m.p. 203—204°; the 5'-*Cl*-derivative (III) has m.p. 179—180° (94·4% yield). Bromination of (I) in presence of a trace of FeCl$_3$ and Fe at room temp. gives 57·3% of the 5':8'-*Br$_2$*-derivative (IV), m.p. 260—261°, also formed by brominating in 93% H$_2$SO$_4$ at 50° or by further bromination of (II); the 5':8'-*Cl$_2$*-derivative (V) has m.p. 242°. Fusion of (II) with alkali affords 5-hydroxy-α-naphthoic acid. (II) and conc. H$_2$SO$_4$ at 115—117° give Bz-4-*bromo-1:2-benzanthraquinone*, m.p. 231—232° (oxidised to anthraquinone-1:2-dicarboxylic acid); (IV) similarly affords the 1:4-*Br$_2$*-derivative, m.p. 265—266°, whilst (III) and (V) give the 4-*Cl*-, m.p. 232°, and the *Cl$_2$*-derivative, two forms, m.p. 267—268° and 304°, respectively. (II) and HNO$_3$ in H$_2$SO$_4$ give the 8'-*NO$_2$*-derivative, m.p. 228—230°; reduction (catalytic or with Fe and acid) gives a light brown amorphous product characteristic of 8-amino-1-ketonaphthalene. (III) gives an 8'-*NO$_2$*-derivative, m.p. 233—234°. (II) and conc. HNO$_3$ in Ac$_2$O give 32% of o-5':8'-*dinitro-1'-naphthoylbenzoic acid*, m.p. 262—263° (decomp.).

C. J. W. (b)

Preparation of amines from carboxylic acids by means of azoimide. M. OESTERLIN (Angew. Chem., 1932, **45**, 536—537).—p-Methoxyhydrocinnamic acid reacts readily with N$_3$H in presence of conc. H$_2$SO$_4$, the 2:4-dimethoxy-compound reacts but slightly, and the trimethoxy- not at all. With benzoic, phenylacetic, and hydrocinnamic acids, 85%, 75%, and 70% yields of the corresponding amines are obtained. o-, m-, and p-Nitrobenzoic acids react readily, with o- and p-aminobenzoic acids only traces of the diamines are formed. Phthalic acid yields only anthranilic acid. With aliphatic dicarboxylic acids the yield of amine depends on the distance between the two CO$_2$H groups; adipic acid yields 80% of putrescine and succinic acid only 8% of C$_2$H$_4$(NH$_2$)$_2$, whilst CH$_2$(CO$_2$H)$_2$ and its aromatic derivatives do not react. Lævulic acid reacts explosively, yielding NH$_2$Me. NH$_2$-acids cannot be further aminated with N$_3$H, and heterocyclic acids such as the pyridine- and quinoline-carboxylic acids do not react. With cinnamic acid styrylamine is most probably formed, but it decomposes immediately into phenylacetaldehyde and NH$_3$; a considerable quantity of NH$_2$Ph is formed also.

H. F. G.

Synthesis of depsides. T. CURRIE and A. RUSSELL (J.C.S., 1932, 2263—2265).—Excellent yields of depsides are readily obtained by condensing

an acid chloride with the Na salt of a hydroxy-aldehyde in $COMe_2$ and oxidation of the resulting aldehyde by $KMnO_4$ in aq. MeOH. The name *p*-dibenzoic acid is assigned to *p*-benzoyloxybenzoic acid. The following compounds were thus prepared : 3 : 3' : 4'-*trimethoxy*-p-, m.p. 124°, 3' : 4'-*dimethoxy*-o-, m.p. 102°, -m-, m.p. 120°, and -p-, m.p. 109°, 4'-*methoxy*-o-, m.p. 85°, -m-, m.p. 102°, and -p-, m.p. 113°, and 3 : 4'-*dimethoxy*-p-benzoyloxybenzalde-hyde, m.p. 136°; 3 : 3' : 4'-*trimethoxy*-p- (II), m.p. 216—218°, 3' : 4'-*dimethoxy*-o-, m.p. 152°, -m-, m.p. 167°, and -p-, m.p. 211—212°, 4'-*methoxy*-o-, m.p. 132°, -m-, m.p. 196°, and -p-, m.p. 212°, and 3' : 4'-*dimethoxy*-p-benzoyloxybenzoic acid, m.p. 171°. The *acid chloride* of (II) has m.p. 129°.　　R. S. C.

Condensation of certain γ-ketonic esters with aromatic aldehydes. C. F. H. ALLEN and G. F. FRAME (Canad. J. Res., 1932, 6, 605—613).—The preps. of benzylidene-*p*-chloro-, -*p*-bromo-, and -*p*-methoxy-acetophenone are modified. KCN, AcOH, and the appropriate ketone in EtOH at 35° give γ-*keto*-α-*phenyl*-γ-*p*-*bromo*-, m.p. 124°, and -*p*-*methoxy*-*phenylbutyronitrile*, m.p. 62° (*Me* esters, m.p. 129° and 97°, respectively); the *Et* ester of the corresponding *p*-Cl-compound has m.p. 63°. These esters, the appropriate aldehyde, and NaOMe (not piperidine or $NPhEt_2$) in hot MeOH yield the following *lactols* (A), $\begin{array}{c} CO\text{——}CPh \\ O\cdot CR'(OH) \end{array}\!\!>\!\!C\cdot CH_2R$, of substituted γ-*keto*-αγ-*diphenyl*-β-*benzyl*-Δ^α-*butenoic acid* : R=Ph, and R'= p-C_6H_4Cl (I), m.p. 134°, p-C_6H_4Br, m.p. 155°, and p-*anisyl*, m.p. 119°; R=*piperonyl*, and R'=p-C_6H_4Cl (II), m.p. 174°, p-C_6H_4Br, m.p. 171°, and p-*anisyl*, m.p. 162°. (A) are insol. in $NaHCO_3$, sol. in cold, aq. NaOH (pptd. unchanged by acids), unchanged by O_3 or dissolution in conc. H_2SO_4, do not give aromatic acyl derivatives or phenylurethanes, react with 3 mols. of MgMeI to evolve 1 mol. of CH_4, and are oxidised by $KMnO_4$ to the substituted benzoic acids, whilst with CrO_3 in AcOH 1 : 2-diketones are also formed, of which the following are new (m.p. in parentheses being those of the *quinoxaline* deriv-atives) : p-*chloro*-, m.p. 103° (m.p. 132°), p-*bromo*-phenyl, m.p. 122° (m.p. 143°), and p-*anisyl benzyl* 1 : 2-*diketone*, m.p. 96° (m.p. 138°); p-*chlorophenyl piperonyl* 1 : 2-*diketone*, m.p. 161·5° (decomp.) (m.p. 161°). (I) with $SOCl_2$ or AcCl gives γ-*chloro*-α-*phenyl* - γ - *p* - *chlorophenyl* - β-*benzyl*-Δ^α-γ-*butenolactone* (III), m.p. 137°; the corresponding p-*bromophenyl* com-pound (IV) has m.p. 132°. (III) with AgOAc gives the γ-*aceto*-compound, m.p. 157° [hydrolysed to (I) by conc. aq. NH_3 at 30°], also formed from (I), Ac_2O, and a trace of H_2SO_4, and with MeOH gives the γ-OMe-compound, cryst., rapidly hydrolysed by hot KOH–MeOH to the *K* salt of the acid (V) cor-responding with (I). (IV) yields similarly the corresponding γ-OMe-compound, m.p. 75°. The *Ag* salt of (V) and MeI in dry Et_2O give the *Me* ester, m.p. 87°, hydrolysed to (I) by hot KOH–MeOH. The constitution of (A) is proved by the above re-actions, but the open-chain form also exists, as (I) forms an *oxime*, m.p. 160°. (A) is presumed to be formed by elimination of H_2O from the aldehyde and the β-CH_2 group of the keto-ester, followed by

migration of the ethylenic linking, thus indicating that in arylated γ-keto-esters the CO group confers greater mobility on the α-H atom than does the CO_2Me group. The stability of the lactol is con-sidered to be due to the branching of the chain.
　　R. S. C.

Friedel–Crafts reaction with phenolic acids. P. C. MITTER and H. C. RAY (J. Indian Chem. Soc., 1932, 9, 247—250).—Me salicylate, o-$C_6H_4(CO)_2O$ (I), and $AlCl_3$ in s-$C_2H_2Cl_4$ give o-4'-*hydroxy*-3'-*carboxy*-*benzoylbenzoic* (4-*hydroxybenzophenone*-3 : 2'-*dicarb*-*oxylic*) *acid*, m.p. 248° [*Me₂ ester*, m.p. 130—131°; *Me ether* (II), m.p. 232° (*Me₂ ester*, m.p. 105—106°)], identical with the phthalylsalicylic acid of Limpricht (A., 1899, i, 292) and reduced by Zn dust and AcOH–conc. HCl to α-*p*-*hydroxyphenylphthalide*-3'-*carboxylic acid*, m.p. 211—212° [*Me ether*, m.p. 164°, prepared by similar reduction of (II)]. Me *o*-cresotate and (I) similarly give 4-*hydroxy*-5-*methylbenzophenone*-3 : 2'-*di*-*carboxylic acid*, m.p. 258—261° (decomp.) [*Me₂ ester*, m.p. 103—104°; *Me ether*, m.p. 197—198° (*Me₂ ester*, m.p. 90°)], reduced to α-4'-*hydroxy*-5'-*methylphenyl*-*phthalide*-3'-*carboxylic acid*, m.p. 204—205° (*Me* ester, m.p. 114—115°; *Me ether*, m.p. 160°). Me *p*-cresotate and *m*- and p-OH·C_6H_4·CO_2Me do not react with (I) under the above conditions.　　H. B.

Displacement of atoms and groups in the naphthalene nucleus. J. G. KERKHOF (Rec. trav. chim., 1932, 51, 739—754).—The displacement of substituents in the $C_{10}H_8$ series follows the rules postulated by Blanksma (A., 1902, i, 600, 715; 1904, i, 565) for the C_6H_6 series, e.g., OH, NH_2, and alkyl groups promote replacement in the *o*- and *p*-positions. The ready replacement of groups in the α- but not β-positions may then be regarded as due to the behaviour of the fused ring as an *o*-substituent to the former. These principles are illustrated by the bromination and nitration of 1-hydroxy-4-naphth-aldehyde (I), and the α- and β-naphthoic acids and 1-and 2-$C_{10}H_7$·SO_3H.
Bromination of (I) [azine ($+6H_2O$), m.p. 225—235°; p-*nitrophenylhydrazone*, m.p. 238—239° (decomp.); *semicarbazone*, m.p. 225°; *semioxamazone*, m.p. 268° (decomp.)] in AcOH gives the 2-*Br*-derivative (II), m.p. 144° [azine, m.p. 246° (decomp.); *phenylhydr*-*azone*, m.p. 122° (decomp.); p-*nitrophenylhydrazone*, m.p. 218—219° (decomp.); *semicarbazone*, decomp. 219—222° (no m.p.); *semioxamazone*, m.p. 247—248°]; further bromination gives 2 : 4-dibromo-α-naphthol. Nitration (HNO_3, d 1·4, in AcOH) of (I) or (II) gives 2 : 4-dinitro-α-naphthol only. α-Naphthoic acid gives the 5-Br-derivative without loss of CO_2; nitration of this, however, gives an indefinite product, m.p. 140—145°, from which the CO_2H group has been com-pletely eliminated. Bromination of 1-$C_{10}H_7$·SO_3H in H_2O results in partial replacement of the 1-SO_3H group with formation of 1 : 6-$C_{10}H_6Br_2$ (?) (about 33%); nitration, similarly, gives 1 : 8-dinitro- or 1 : 3 : 8-trinitro-naphthalene according to conditions, and nitronaphthalenesulphonic acids. Little or no loss of SO_3H was observed in the nitration or bromin-ation of 2-$C_{10}H_7$·SO_3H. Nitration of 1-$C_{10}H_7$·Br occurred without replacement of Br and gave the 4 : 5-, m.p. 174°, and 4 : 8-$(NO_2)_2$-derivatives. The

literature m.p. of 4 : 5-dinitro-α-naphthylamine (245°) (*Ac* derivative, 245°) and -α-naphthylmethylamine (259°) are confirmed (cf. A., 1902, i, 753). 4 : 8-*Dinitro-α-naphthylmethylamine*, m.p. 145°, is similarly prepared.   H. A. P.

Hydrolysis of lignin with 12% hydrochloric acid. M. Phillips and M. J. Goss (J. Amer. Chem. Soc., 1932, **54**, 3374—3377).—Lignin is isolated from maize cobs, oat hulls, and spruce wood by the method of Willstätter and Zechmeister (A., 1913, i, 955), by the EtOH and aq. NaOH methods, and by Freudenberg and Harder's modification (A., 1927, 342) of Urban's method. Distillation with 12% HCl gives CH_2O (in appreciable quantity) only with the lignins isolated from oat hulls and spruce wood by Freudenberg and Harder's method (cf. *loc. cit.*). The results are discussed from the point of view of the probable presence of the methylenedioxy-group in the lignin mol.   C. J. W. (*b*)

Manufacture of aldehydes and intermediate products [perfumes]. W. W. Groves. From I. G. Farbenind. A.-G.—See B., 1932, 793.

Cyclic ketones. III. R. Poggi and P. Saltini (Gazzetta, 1932, **62**, 678—686; cf. A., 1931, 1057).— 6-Benzylidene-2-methyl*cyclo*hexanone forms an *oxime*, m.p. 147—148·5°; 6-benzylidene-3-methyl*cyclo*hexanone a *semicarbazone*, m.p. 173—180°. 4-Methyl*cyclo*hexanone yields 6-*benzylidene-*, m.p. 51—52° (*semicarbazone*, m.p. 190—191°; *oxime*, m.p. 144·5—145·5°), and 2 : 6-*dibenzylidene-4-methyl*cyclohexanone [*Br₄*-derivative, m.p. 192° (decomp.)]. 2-Benzyl-*cyclo*hexanone [oxime, new m.p. 133—135° (cf. A., 1926, 744)] gives 6-*benzylidene-2-benzyl*cyclo*hexanone*, m.p. 77°. 2-Benzylidene-4-methyl*cyclo*hexanone is hydrogenated (Pt-black) to 2-*benzyl-4-methyl*cyclo*hexanone* [*semicarbazone*, m.p. 186° (decomp.); *oxime*, m.p. 131°; 6-*benzylidene* derivative, m.p. 50—75°].
                                                E. W. W.

Triphenylmethane derivatives with linked benzene nuclei. VII. Ketomethylenephenyldiphenylenemethane. R. Weiss and E. Knapp (Monatsh., 1932, **61**, 61—68).—Fluorenone and o-C_6H_4Me·MgBr give 9-*hydroxy-9-o-tolylfluorene* (I), m.p. 121—123° (*acetate*, m.p. 174—177°) [in one case 9-o-*tolylfluorene* (+0·25H_2O), m.p. 129—130·5°, m.p. (anhyd.) 133° (*NO₂*-derivative, m.p. 156—157°), was produced], oxidised by alkaline $KMnO_4$ to o-*diphenylenephthalide* (the *lactone* of 9-hydroxy-9-phenylfluorene-2′-carboxylic acid), m.p. 226—229°. This is reduced (Na–Hg, EtOH) to 9-*phenylfluorene-2′-carboxylic acid*, m.p. 243—246° (*Me* ester, m.p. 112—114°), converted by P_2O_5 in C_6H_6 into *ketomethylenephenyldiphenylenemethane* (II), decomp. 249°. (I) and (II) fuming HNO_3 in cold AcOH give a *NO₂*-derivative, m.p. 155—157° [(*NO₂*)₂-derivative, m.p. 222—223°], reduced (SnCl₂, conc. HCl, AcOH) to an *amino-9-o-tolylfluorene*, m.p. 131—134° [isolated by addition of aq. NH₃ and (NH₄)₂S to the evaporated reaction mixture; when the mixture is basified with aq. NaOH, an oily product (*hydrochloride*, decomp. 200°) is obtained].   H. B.
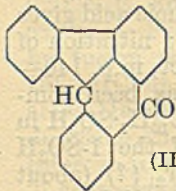
Three-carbon tautomerism in dicyclic systems. I. Comparison of corresponding compounds of trans-β-decalin and cyclohexane. II. Effect of an α-methyl group on tautomerism in trans-β-decalin compounds. III. Comparison between corresponding compounds of trans-hexahydrohydrindene and cyclopentane. IV. Effect of an α-methyl group on tautomerism in trans-hexahydrohydrindene compounds. R. S. Thakur (J.C.S., 1932, 2120—2138, 2139—2147, 2147—2157, 2157—2167).—I. Isomerides of the types (A), (B), and (C), in which X=CO₂H, Me, and Ac, are prepared.
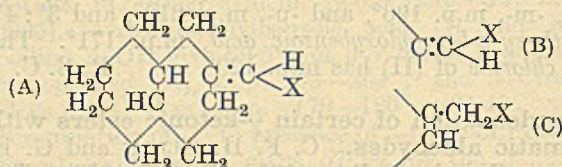
Their interconversions take place to an extent and (excepting the acids) at a rate very similar to those of the corresponding *cyclo*hexane compounds, thus indicating that the strain factor either operates with equal force in both series or plays no determining part in the equilibrations. The apparent mobility of the acids in the *trans*-β-decalin series is lowered by the insolubility of the K salts in conc. aq. KOH. The percentage of Δ^2-form (C) in mixtures can in all cases be determined by I (modified method in some cases). *trans*-β-Decalone (modified prep.; yield 86%) gives by the Reformatsky reaction a mixture of two isomeric forms of *Et* 2-*hydroxy-trans-decalin-2-acetate*, b.p. 140—150°/1 mm. (average yield 67%), hydrolysed by cold 10% NaOH–MeOH to $\Delta^{2 \text{ (or 1)}}$-*trans-octahydronaphthyl-2-trans-β-decalone*, m.p. 125—126° [*semicarbazone*, m.p. 209—210° (decomp.); *oximes*, m.p. 180—190° and 198—203° (decomp.)], and three forms of 2-*hydroxy-trans-decalin-2-acetic acid*, (I) m.p. 140—141° after sintering, (II) m.p. 116—118° (lit. 102°), and (III) m.p. 88°. (III) is possibly a eutectic mixture of (I) and (II). The crude mixture of acids and boiling Ac_2O give a liquid and a mixture of *trans-decahydronaphthylidene-2-acetic acids*, separable by partial esterification into αβ-*acids*, (IV), m.p. 143° (lit. 145°) (*dibromide*, m.p. 155°; *amide*, m.p. 187—188°; *Et* ester, b.p. 160°/7 mm.), and (V), m.p. 95—96° (*dibromide*, m.p. 143—144°; *amide*, m.p. 145—147°; *Et* ester, b.p. 160°/9 mm., converted by O_3 into *trans*-β-decalone). The *acid chlorides* of (IV) and (V) (prepared by $SOCl_2$ below 40°) isomerise when distilled, but give nearly pure amides with NH_3 in Et_2O if not heated. Under certain conditions, instead of (IV) and (V), there were obtained 2-*methylene-trans-decalin*, b.p. 81—83°/9 mm. [nitrosochloride gives *nitrolpiperidides*, m.p. 197—198° (decomp.) and 153—154°], and Δ^2-*trans*-octahydronaphthalene-2-acetic acid [cf. (C)] (VI), m.p. 99—100° (lit. 100—101°) (*Et* ester, b.p. 153—154°/9 mm.) (also obtained from the αβ-acid, pyridine, and Ac_2O, first at 100° and then at 130°). The crude hydroxy-ester with boiling $POCl_3$–C_6H_6 or cold pyridine–$SOCl_2$ gives a mixture, whence (VI) [*dibromide*, m.p. 99—100° (lit. 100—101°); *amide* (prepared from distilled acid chloride), m.p. 181—182°] was isolated. The pure ester of (VI) with O_3 in $CHCl_3$ gives *trans-cyclo*hexane-2-γ-

carbethoxyacetone-1-acetic acid (*semicarbazone*, m.p. 164°), and (in another experiment) *trans-cyclo*hexane-1 : 2-diacetic acid (VII), *trans*-cyclohexane-2-acetone-1-acetic acid [*semicarbazone*, m.p. 195—196° (decomp.)], and a liquid acid, further oxidised by hot, dil. HNO$_3$ to (VII). Equilibrium mixtures of (IV), (V), and (VI) (boiling 20—25% aq. KOH) contain 12$\pm$1% of $\alpha\beta$-acid. Partial esterification of (V) gives (IV) and the ester of (VI), but not (V). (IV) and (V) in CHCl$_3$ are slowly (? and partly) converted into (VI) by ultra-violet light. The esters of (IV), (V), and (VI) give with NaOEt no OEt-compound, but an equilibrium mixture containing 40% of $\alpha\beta$-esters. The distilled acid chloride, b.p. 154—155°/8 mm., of (IV) with ZnMeI in PhMe gives the *semicarbazone* (VIII), m.p. 186—187°, of trans-*deca-hydronaphthylidene*-2-*acetone*, a small amount of an *isomeride*, m.p. 199°, and a mixture of (IV) and (VI), but often a low-melting, inseparable, possibly eutectic mixture (IX) of semicarbazones is obtained. The distilled acid chloride of (V) gives similar products, but in one experiment the *semicarbazone* (X), m.p. 134—135°, of Δ^2-trans-*octahydronaphthyl*-2-*acetone* was obtained, whilst (II) gives also (VIII) and (IX). Use of MgMeI and ZnMe$_2$ led to similar products. By the Blaise–Maire reaction the acid chloride, b.p. 145—146°/11 mm., of (VI) gave (X), whilst some (VI) was regenerated. (VIII), best with H$_2$C$_2$O$_4$, yields the *ketone*, b.p. 149—150/15 mm., oxidised to decalone by 3% KMnO$_4$. (X) and an *isomeride*, m.p. 175° (obtained from an $\alpha\beta$-acid chloride in one Blaise–Maire reaction), with H$_2$C$_2$O$_4$ or Al–Hg give the *ketone*, b.p. 145°/15 mm. The equilibrated (NaOPr) mixture of these ketones contains 35% of the $\alpha\beta$-components. This mixture with Et$_2$ sodiomalonate gives a gum, changed by hot 20% aq. KOH to *decalin*-2-spirocyclo*hexane*-2' : 6'-*dione*, decomp. 185°. *trans*-β-Decalone, COMe$_2$, and NaOEt give a mixture of ketones, yielding (IX), whereas, when Mg(OBu)$_2$ is used, the product gives gummy semicarbazones.

II. As in the *cyclo*hexane series, substitution by an α-Me group to give type (D) $\diagdown$C:CMeX from type (A) greatly retards the tautomeric mobility of the acids and esters of the *trans*-β-decalin series, and displaces the equilibrium largely to the $\alpha\beta$-side. *trans*-β-Decalone, Et α-bromopropionate, and Zn in hot C$_6$H$_6$ give a mixture of isomeric *Et* 2-*hydroxy*-trans-*decalin*-2-α-*propionates*, b.p. 170—172°/9 mm. (76% yield), hydrolysed by cold 10% NaOH–MeOH–H$_2$O to the corresponding acids, (I) m.p. 156—157°, and (II) m.p. 110—114°, and Δ^2-*trans*-octahydro-naphthyl-2-β-decalone. The mixed ester with cold pyridine and SOCl$_2$ gives *Et* Δ^2-*octahydronaphthalene*-2-α-*propionate* (III), b.p. 163—164°/19—20 mm., hydrolysed by cold NaOH–MeOH–H$_2$O to the corresponding *acid* (IV), b.p. 148—149°/approx. 1 mm. (acid chloride, b.p. 155—156°/17 mm.; *amide*, m.p. 133—134° after sintering). The constitution of (III) is proved by ozonolysis to *trans-cyclo*hexane-1-acetic acid-2-methyl Et ketone [*semicarbazone*, m.p. 203° (decomp.)]. The crude mixture of (I) and (II) with boiling Ac$_2$O yields trans-*decahydronaphthylidene*-2-α-*propionic acid* (V), m.p. 95—96° [*amide*, m.p. 206—207°, gives with Br in CHCl$_3$ the *dibromide*, m.p.

175—176° (decomp.), and (?) α-bromo-Δ^2-*octahydro-naphthalene*-2-α-*propionic acid*, m.p. 145—146° (decomp.); *Et* ester (VI), b.p. 169°/16 mm.]. The undistilled chloride of (V) and ZnMeI in Et$_2$O at $-40°$ give the anhydride and a little α-methyl-*trans*-decahydronaphthylidene-2-acetone (VII) (*semicarbazone*, m.p. 209—210°), whereas the distilled chloride gives a product containing mostly the $\beta\gamma$-isomeride. The acid chloride, b.p. 159—161°/19 mm., of (III) with ZnMeI gives pure α-*methyl*-Δ^2-trans-*octahydronaphthyl*-2-*acetone* (VIII), b.p. 153—154° (*semicarbazone*, m.p. 194°), also obtained from Δ^2-*trans*-octahydronaphthyl-2-acetone, MeI, and " mol." Na in Et$_2$O, and with a little (VII) from (I) [? or (II)]. Equilibration of (IV) and (V) is too slow for measurement; the equilibrium mixture (NaOEt) of (III) and (VI) contains 10% of (VI), the mobility of the substances being one hundredth of that of the unsubstituted esters; heating (VIII) with NaOEt indicated at most a trace of isomerisation.

(E) ... (F)
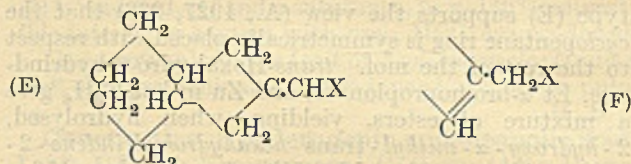
III. Substances of types (E) and (F) (X=CO$_2$H, CO$_2$Et, and Ac) are prepared and found to show very high mobility, equilibrium being very much on the $\alpha\beta$-side. The *cyclo*pentane series is the only series resembling these compounds, but the large amount of $\beta\gamma$-form in the equilibrium mixture of *cyclo*pentane acids is anomalous. The prep. of *trans-cyclo*hexane-1 : 2-diacetic acid from *trans*-β-decalol and -decalone, and thence of *trans*-hexahydro-2-hydrindone (I) is modified. (I) is purified by hydrolysis of the semicarbazone by H$_2$C$_2$O$_4$ or dil. H$_2$SO$_4$; when 50% aq. HCl is used, this gives also a substance, m.p. 150—152°, possibly *di*-trans-*hexahydro*-2-*hydrindylidene-hydrazine*, yielding the semicarbazone of (I) and, with dil. acids, (I). (I) yields by the Reformatsky reaction Et 2-hydroxy-*trans*-hexahydrohydrindyl-2-acetate (II), b.p. 167°/20 mm., and *trans*-hexahydrohydrindyl-idenehexahydro-2-hydrindone, m.p. 115—116° after sintering [*oximes*, m.p. 211—212° after sintering and decomp., and (in small amount), m.p. 206°]; hydrolysis of (II) gives the corresponding acid, m.p. 87—88°, which with boiling Ac$_2$O does not give an AcO-compound, but yields *trans*-hexahydrohydrindyl-idene-2-acetic acid (III), m.p. 151—152° [dibromide, m.p. 147—148°; acid chloride, b.p. 153—154°/16 mm.; *amide*, m.p. 154—155°; *anhydride*, m.p. 116—118°; *Et* ester (IV), b.p. 158°/19 mm.]. (II) with P$_2$O$_5$ (with or without C$_6$H$_6$), POCl$_3$ and C$_6$H$_6$, or pyridine and SOCl$_2$ gives mixtures of esters, hydrolysed by 10% NaOH–MeOH–H$_2$O to mixtures of (III) and *trans*-hexahydrohydrindenyl-2-acetic acid (V), m.p. 66—67° [dibromide, m.p. 135°; *amide*, m.p. 160—161° after sintering; *Et* ester (VI), b.p. 133—135°/11—13 mm.]. The acid chloride of (III) with ZnMeI gives *trans*-hexahydrohydrindylidene-2-acetone (VII), b.p. 134°/10 mm. [semicarbazone, m.p. 221—222° (decomp.)], oxidised in AcOEt by O$_3$ to *trans*-hexahydrohomophthalic acid and *trans*-hexa-

hydro-2-hydrindone, and giving with Et_2 sodio-malonate *Et* cyclohexane-3 : 5-*dione*-1(2')-*spiro-trans-hexahydrohydrindene*-2-*carboxylate*, m.p. 156—157° [hydrolysed by 20% aq. KOH to *cyclo*hexane-3 : 5-dione-1(2')-*spiro-trans*-hexahydrohydrindene]. (VII) is unchanged by *N*-NaOEt. The equilibrium mixture of (IV) and (VI) contains 98·5±0·5% of (IV), that of (III) and (V) about 90% of (III). Kandiah's data (A., 1931, 728) for many of the above compounds are corrected.

IV. Substitution of an α-Me group in substances of types (E) and (F) shifts the position of the equilibrium to the αβ-side and retards the mobility of the system. The mobility of the ketones cannot, however, be measured. The resemblance between the *trans*-hexahydrindene and the *cyclo*pentane compounds is less than that between the *trans*-β-decalin and *cyclo*hexane compounds, but this is inexplicable, as is also the high mobility of the first-mentioned series. The absence of isomerides amongst compounds of type (E) supports the view (A., 1927, 238) that the *cyclo*pentane ring is symmetrically placed with respect to the rest of the mol. *trans*-Hexahydro-2-hydrindone, Et α-bromopropionate, and Zn in hot C_6H_6 give a mixture of esters, yielding, when hydrolysed, 2 - *hydroxy* - α - *methyl* - trans - *hexahydrohydrindene* - 2 - *acetic acid*, m.p. 119—120° [*Et* ester (II), b.p. 156—157°/11 mm.], dehydrated by boiling Ac_2O to α-*methyl*-trans-*hexahydrohydrindylidene*-2-*acetic acid* (I), m.p. 196—197° [*Me* ester (II), m.p. 43—45°; *Et* ester (III), b.p. 154°/10 mm.; acid chloride, b.p. 163°/10 mm.; *amide*, m.p. 205°; *dibromide*, m.p. 182—183° (decomp.)], oxidised by $KMnO_4$ to *trans*-hexahydro-hydrindone. (II) with P_2O_5 in C_6H_6 or pyridine and $SOCl_2$ gives a mixture of esters, hydrolysed to (I) and impure α-*methyl*-trans-*hexahydroindenyl*-2-*acetic acid* (IV), b.p. 154—155°/1—2 mm. [*Et* ester (V), b.p. 134°/10 mm.]; the last acid contained some *isomeride*, (VI) or (VII) (R=·CHMe·CO_2H), m.p. 89—90° after sintering (*amide*, m.p. 185—186° after
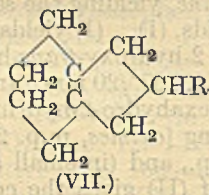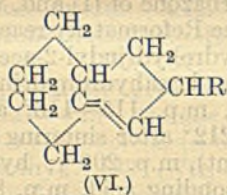
sintering), best separated by partial esterification. The acid *chloride*, b.p. 163°/10 mm., cryst., with ZnMeI gives α-*methyl*-trans-*hexahydrindylidene*-2-*acetone* (VIII), b.p. 144—148°/9 mm. [*semicarbazone*, m.p. 206—208° (decomp.)], converted by O_3 into *trans*-hexahydro-2-hydrindone, and yielding with Et_2 sodiomalonate an oily ester, hydrolysed by 20% aq. KOH to 2-*methylcyclo*hexane-3 : 5-*dione*-1(2')-*spiro-transhexahydrohydrindene*, m.p. 164—165°. The sodio-derivative of (VIII) with BzOH gives a product yielding a *semicarbazone*, m.p. 213°, or trans-*hexahydrohydrindyl*-2-*acetonesemicarbazone*, m.p. 180°, according to the conditions used. trans-*Hexahydrohydrindylidene*-2-*acetone*, "mol." Na, and MeI or EtI in hot Et_2O give a mixture of αβ- and βγ-unsaturated ketones [*semicarbazone* of (?) βγ-form, m.p. 175—177°]. (VIII) is unaffected by *N*-NaOEt—

EtOH. Equilibrium mixtures of (I) and (IV) and of (III) and (V) contain 90 and 98%, respectively, of the αβ-form. Hydrolysis of (V) by NaOH—MeOH—H_2O gives a mixture of (I) and (II).   R. S. C.

Mixed benzoins. VIII. Determinations of structures. Question of isomerides. J. S. BUCK and W. S. IDE (*J. Amer. Chem. Soc.*, 1932, **54**, 3302—3309; cf. A., 1931, 1294).—The following new benzoins are reported : 3 : 4-*diethoxybenzoyl-o-chlorophenylcarbinol*, m.p. 63° [from *o*-C_6H_4Cl·CHO and 3 : 4-$(OEt)_2C_6H_3$·CHO] [*oxime* (I), m.p. 61°], and its 4'-*methoxy*-3'-*ethoxy*-, m.p. 103° [*oxime* (II), m.p. 113°], and 3'-*methoxy*-4'-*ethoxy*-, m.p. 120° [*oxime* (III), m.p. 114°], analogues; p - *dimethylaminobenzoyl* - 3 : 4-*methylenedioxyphenylcarbinol*, m.p. 136° [*oxime* (IV), m.p. 145°]. Oxidation of the benzoins (in EtOH) with a slight excess of Fehling's solution gives 2-*chloro*-3' : 4'-*diethoxy*-, m.p. 110°; 2-*chloro*-4'-*methoxy*-3'-*ethoxy*-, m.p. 150°; 2-*chloro*-3'-*methoxy*-4'-*ethoxy*-, m.p. 132°, and 4'-*dimethylamino*-3 : 4-*methylenedioxy*-, m.p. 174°, -*benzils*. The following deoxy-compounds are prepared by the method previously described : 3' : 4'-*diethoxyphenyl o-chlorobenzyl ketone*, m.p. 95° (anti-*oxime*, m.p. 105°); 4'-*methoxy*-3'-*ethoxy*-, m.p. 98° (anti-*oxime*, m.p. 130°), and 3'-*methoxy*-4'-*ethoxy*-, m.p. 121° (anti-*oxime*, m.p. 167°) -*phenyl o-chlorobenzyl ketones*; 4'-*dimethylaminophenyl* 3 : 4-*methylenedioxybenzyl ketone*, m.p. 140° (anti-*oxime*, m.p. 152°). anti-4' - *Dimethylaminophenyl* m - *chlorobenzyl ketoxime*, m.p. 146°; anti-3' : 4'-*methylenedioxyphenyl p-chlorobenzyl ketoxime*, m.p. 119°; *o-chlorophenylacet*-3' : 4'-*diethoxyanilide*, m.p. 178°, -4'-*methoxy*-3'-*ethoxyanilide*, m.p. 165°, and -3'-*methoxy*-4'-*ethoxyanilide*, m.p. 166°; m-*chlorophenylacet*-4'-*dimethylaminoanilide*, m.p. 178°; p-*chlorophenylacet*-3' : 4'-*methylenedioxyanilide*, m.p. 195°; 3 : 4-*methylenedioxyphenylacet*-4'-*dimethylaminoanilide*, m.p. 170°; p-*dimethylaminobenzoyl* - m - *chlorophenylcarbinoloxime* (V), m.p. 148°, and 3 : 4-*methylenedioxybenzoyl-p-chlorophenylcarbinoloxime* (VI), m.p. 178°, are described. The Beckmann reaction (PhSO$_2$Cl and alkali) with the oximes (I)—(VI) gives : (I) *o*-C_6H_4Cl·CHO (88%) and 3 : 4-$(EtO)_2C_6H_3$·CN (87%); (II) *o*-C_6H_4Cl·CHO (73%) and 3 : 4-EtO(MeO)C_6H_3·CN (44%); (III) *o*-C_6H_4Cl·CHO (65%) and 3 : 4-MeO(EtO)C_6H_3·CN (60%); (V) *m*-C_6H_4Cl·CHO (52%) and *p*-NMe$_2$·C_6H_4·CN (62%); (VI) *p*-C_6H_4Cl·CHO (38%) and piperonitrile (47%); (IV) piperonal (77%) and *p*-NMe$_2$·C_6H_4·CN (63%). *m*-C_6H_4Cl·CHO, hippuric acid, Ac_2O, and NaOAc give the *azlactone*, m.p. 164°, hydrolysed by 10% NaOH to m-*chlorophenylpyruvic acid*, m.p. 145°, oxidised by alkaline H_2O_2 to m-*chlorophenylacetic acid*, m.p. 74°. 3 : 4-*Diethoxybenzaldoxime*, m.p. 98°, is dehydrated by Ac_2O to 3 : 4-*diethoxybenzonitrile*, m.p. 68°. 4-*Methoxy*-3-*ethoxybenzaldoxime*, m.p. 98°, 4-*methoxy*-3-*ethoxybenzonitrile*, m.p. 70°, and 3-*methoxy*-4-*ethoxybenzaldoxime*, m.p. 100°, are prepared. The question of the formation of pairs of isomeric mixed benzoins (by the KCN condensation) is discussed; it is considered that reported cases of the occurrence of such pairs of isomerides require further substantiation. In naming benzoins the authors suggest using primes for the numbered substituents

on the C_6H_6 ring next to the CO group (in the case of oximes, the C:NOH group); thus o-chlorobenz-veratroin is 2-chloro-3′ : 4′-dimethoxybenzoin.

C. J. W. (b)

Complex salts of hydroxyquinones. II. A. MANGINI and R. STRATTA (Gazzetta, 1932, **62**, 686—699; cf. this vol., 164).—The following are described: the Co, decomp. 210—215°, Cu (+2H_2O), decomp. above 300°, UO_2, Ni, Zn (+H_2O), Pb (+H_2O), Cd (+2½H_2O), Hg (+H_2O), and basic Fe salts of 2-hydroxy-α-naphthaquinone; the neutral Ni salt of naphthazarin; the acid Ni (+1⅓H_2O), and neutral Ni (+½H_2O) and Cu salts of 1 : 8-dihydroxyanthraquinone; the neutral Cu (+H_2O) and Co (+½H_2O), and the acid Ni (+3H_2O) salts of chrysophanic acid [1 : 8-dihydroxy-2-(or 3)-methylanthraquinone]. The colours of salts of these hydroxyquinones are tabulated; spectroscopic examination shows that salt-formation involves chelation. E. W. W.

Perylene and its derivatives. XXXVI. A. ZINKE (Monatsh., 1932, **61**, 1—14).—Perylene dissolves in cold conc. H_2SO_4 with the following colour changes: green, bluish-green, blue (red fluorescence), bluish-violet, reddish-violet; perylenesulphonic acids and perylene-3 : 10-quinone (I) (probably formed by way of the 3 : 10-disulphonic acid) are produced. (I) is formed in quant. yield from perylene and traces of HNO_3 and $FeSO_4$ in cold conc. H_2SO_4.

[With G. HAUSWIRTH.] Dichloroperylene-3 : 10-quinone heated with PhOH, K_2CO_3, and Cu powder gives diphenoxyperylene-3 : 10-quinone; di-(3-methyl-4-isopropylphenoxy)- and di-p-chlorophenoxyperylene-3 : 10-quinones are prepared similarly. A compound, $C_{40}H_{20}O_3$, not reducible (vat), is obtained using β-$C_{10}H_7$·OH. Perylene-3 : 9-quinone (II) and Cl_2 in $PhNO_2$ containing a little I give an unstable adduct, which when crystallised from $PhNO_2$ passes into a violet substance [probably a mixture of Cl_2- and Cl_3-derivatives of (II)], oxidised by MnO_2 and conc. H_2SO_4 to anthraquinone-1 : 5-dicarboxylic acid (III); substitution occurs in the quinonoid nuclei. Analogous results are obtained using Br. (II) and HNO_3-AcOH give a $(NO_2)_2$-derivative [corresponding $(NH_2)_2$-derivative], also oxidised (bleaching powder) to (III).

1-Hydroxyperylene, BzCl, and $AlCl_3$ in CS_2 give a 1-hydroxydibenzoylperylene, m.p. 227—228°, which is not converted into a dye (isoviolanthrone) when heated with $AlCl_3$ in absence or presence of MnO_2.

[With W. BLANK.] 3 : 9-Dibenzoylperylene (IV) does not react with p-OMe·C_6H_4·MgI nor does (?) 3 : 9-dianisoylperylene with MgPhI. (IV) and MgPhBr give 3 : 9-di-(α-hydroxydiphenylmethyl)perylene, m.p. 327—328°. (I) is reduced (partly) to the quinol by MgMeI and MgPhBr.

[With V. GRIMM.] Phenanthrene-1 : 8 : 9 : 10-tetracarboxylic dianhydride (A., 1931, 730) and fuming HNO_3 at 250° give mellitic acid. H. B.

Manufacture of 1-aldehydroanthraquinone and its nuclear substitution products. A. CARPMAEL. From I. G. FARBENIND. A.-G.—See B., 1932, 764.

Manufacture of alkyl ethers of amino-β-hydroxyanthraquinones. J. Y. JOHNSON. From I. G. FARBENIND. A.-G.—See B., 1932, 765.

Manufacture of vat dyes [dibenzopyrene-quinones; dibenzoylnaphthalene derivatives]. I. G. FARBENIND. A.-G.—See B., 1932, 765.

Constitution of marmelosin. I. B. B. L. DIKSHIT and S. DUTT (J. Indian Chem. Soc., 1932, **9**, 271—279).—Marmelosin (I) (A., 1930, 1628), $C_{13}H_{12}O_3$, m.p. 103°, [α] +36° in EtOH (Ac, m.p. 214°, Bz, m.p. 119—120°, and NO_2-, m.p. 97°, derivatives; phenylurethane, m.p. 245°; Br-derivative dibromide, m.p. 82°), is reduced by Zn dust and AcOH to dihydromarmelosin, m.p. 238° [Ac derivative, m.p. 176°, formed by reductive acetylation of (I)], gives an additive compound, m.p. 156°, with HBr (1 mol.), and is dehydrated by warm 75% H_2SO_4 or with PCl_5 to anhydromarmelosin, m.p. 76°. KOH-fusion of (I) gives $H_2C_2O_4$ and an acid, $C_{13}H_{18}O_6$, m.p. 245°, which is also formed (together with a little succinic acid) by oxidation of (I) with alkaline $KMnO_4$. (I) may be an αβ-unsaturated lactone. When an alkaline solution of (I) is acidified, (I) and a substance, m.p. 146° [convertible into (I) in contact with conc. HCl], are produced.

(I) occurs only in the fruit of Aegle marmelos (Indian Bel) and predominates in the inner layer of the pulp.

H. B.

Constitution of hederagenin and oleanolic acid. I, II, III. Z. KITASATO and C. SONE (Acta Phytochim., 1932, **6**, 179—222, 223—225, 305—314).— I. Hederagenin, $C_{31}H_{50}O_4$, is isolated from the saponin of Sapindus mukurossi (cf. A., 1925, i, 947, 948; 1930, 1293; 1931, 1159) [diphenylurethane, m.p. 155—158°; thionylethyl derivative, m.p. 269°; -oxychlorophosphine, m.p. 275°; -phosphoric acid, m.p. 286° (decomp.); γ-keto-methyl derivative, m.p. 190—193°, and its oxime, m.p. about 190° (decomp.); γ-keto-derivative, m.p. > 300°, and its oxime; bromo-methyl derivative, m.p. 147°; bromodiacetyldehydrolactone, m.p. 223° (decomp.); bromodehydrolactone, m.p. 210°; dibromolactone, m.p. 251—253° (decomp.); dibromodiacetyl-lactone, m.p. 216—217° (decomp.); tribromolactone, m.p. 217°; bromothionyldehydrolactone, m.p. 212—213° (decomp.); "bromothionyl-lactone," $C_{31}H_{47}SBr$, m.p. 257°; nitrode-(6)-hydrodinitrate, m.p. 229°]. Acetyloleanolic acid on oxidation yields the δ-keto-acetyl-lactone, m.p. 227—280° [oxime, m.p. 222° (decomp.); Br-derivative, m.p. 225—226° (decomp.)], hydrolysis of which gives the δ-ketolactone, m.p. >300°, which on reduction yields the δ-ketodehydrolactone, m.p. 277° [dioxime, m.p. 223° (decomp.); Br-derivative, m.p. 225° (decomp.)]. Similarly were prepared δ-ketohederageninlactone, m.p. >300° [diacetyl oxime, m.p. about 200° (decomp.); Me derivative, m.p. 220°], δ-ketoacetylmethyloleanolic acid, m.p. 224°, and δ-ketomethyloleanolic acid, m.p. 197°. Oxidation of bromohederageninlactone yields bromohedragone-lactone (with 1½ mol. AcOH), m.p. 200—202° [oxime, (+1½ mol. AcOH), m.p. 225° (decomp.)], which is reduced (Zn dust, AcOH) to hedragone, $C_{33}H_{46}O_3$, m.p. 253—255° [oxime, m.p. 245—246° (decomp.); dibromolactone, m.p. 203—204° (decomp.)], the Me derivative and oxime being identical with substances described by Jacobs (A., 1926, 1250). Hedragone on further reduction gives hedragenin, m.p. 261—263° (Ac derivative, m.p. 247—250°; acetylmethyl derivative, m.p. 175°). Dehydrogenation of hederagenin

by Se yields $C_{10}H_5Me_3$. The sapogenin from *Panax* is identical with oleanolic acid. The hæmolytic and toxic properties of the saponin of *S. mukurossi* were determined.

II. δ-Ketoacetyloleanolic acid lactone oxidised with $HNO_3 + AcOH$ yields a *di-acid* (I), $C_{33}H_{50}O_8$, m.p. >300° (*Me* ester, m.p. 269—270°). Similarly, δ-keto-diacetylhederageninlactone yields a *dinitrodi-acid*, m.p. 274° (decomp.).

III. Hydrolysis of (I) yields oleanolic acid lactone di-acid, m.p. >300°. MeOH–KOH converts ε-bromo-δ-ketodehydro-oleanolic acid lactone into *ε-oxy-δ-keto-oleanolic acid lactone*, m.p. 285°. Hedragone treated with $HNO_3 + AcOH$ followed by reduction with Zn dust yields *ketohedragone di-acid*, m.p. >300° (decomp.), whilst treatment with KOBr gives a *substance*, m.p. >300°, which is either hedragone di-acid or hedragilic acid. Oxidation of hedragone gives the *δ-ketolactone*, m.p. 234—236° [*oxime*, m.p. 208—210° (decomp.)], which with KOBr yields *hedragil-lactone tri-acid*, m.p. 288—289° (decomp.). The above data are applied to a consideration of the structural formulæ of hederagenin and oleanolic acid, based on a picene ring structure. F. O. H.

Constitution of abietic acid. F. VOCKE (Annalen, 1932, **497**, 247—264).—Reduction (H_2, PtO_2, AcOH) of abietic acid (I) gives tetrahydroabietic acid (II), m.p. 190° (not sharp), $[\alpha]_D +11\cdot1°$ in 96% EtOH, the Me ester of which with MgPhBr affords a *carbinol*, $C_{32}H_{44}O$, m.p. 155°, oxidised (CrO_3, AcOH) to BzOH and $COPh_2$. (II) and conc. H_2SO_4 at 60° give CO (about 70%), CO_2 (about 30%), a *hydrocarbon*, $C_{19}H_{34}$, b.p. 128°/1 mm., and a viscous oil (sol. in H_2SO_4). The formation of CO from (I) and conc. H_2SO_4 at 50—60° indicates that the CO_2H of (I) is attached to a *tert.*-C atom. The acid $C_{11}H_{16}O_6$ (III), prepared from (I) by Levy's method (A., 1929, 1448), and conc. H_2SO_4 at 100—140° give 2 mols. of CO; 1-*methylhexahydrophthalic acid*, m.p. 165° [prepared by reduction (H_2, Pd-black, AcOH) of the adduct from citraconic anhydride and butadiene], similarly gives 1 mol. of CO at 100—140°, whilst *cis*- and *trans*-hexahydrophthalic acids afford about 1 mol. of CO at 195—250° and 230—250°, respectively. (III), Br, and red P at 100° (bath) (after mixing in the cold) give a mixture of the *bromoanhydrotricarboxylic acid* (IV), m.p. 215° (slight decomp.), its *acid bromide*, (V), m.p. 207° (not sharp) (stable to cold H_2O), the anhydrotricarboxylic acid (IV, Br =H), m.p. 178° (cf. Ruzicka *et al.*, A., 1931, 736), and its *acid bromide*, m.p. 160° (also stable to cold H_2O); the chloride of (III) and Br at 100° (tube) afford (after treatment with moist HCO_2H) a *compound*, $C_{11}H_{13}O_5Br_3$, m.p. 150°. (IV) and (V) heated with 2N-NaOH give (by loss of HBr and CO_2) 1 : 3-*dimethyl - Δ² - tetrahydro - phthalic acid*, m.p. 183° (decomp.) (*Me* ester, m.p. 132°), converted by aq. H_2SO_4 (1 : 1) at 120—100° into the *lactone* (VI), m.p. 146°, and oxidised (O_3 and then CrO_3 in AcOH) to a malonic acid derivative, the Me ester, b.p. about 150° (bath)/12 mm., of which is hydrolysed by 2N-HCl at 160—180° to α-methyl-

glutaric acid. (III) is probably 1 : 3-dimethyl*cyclo*hexane-1 : 2 : 3-tricarboxylic acid. The formation of methylretene from methylabietin (Ruzicka and Meyer, A., 1922, i, 829) may involve migration of Me. (I) appears to be best represented by the annexed constitution.
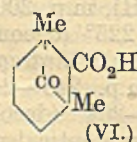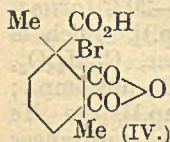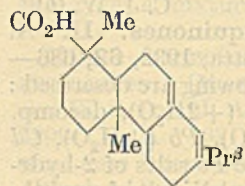
trans-Hexahydrophthalic acid, Br, and red P at 70—80° give a little *Br*-derivative, m.p. 172°, also formed similarly from, and reduced (Zn dust, AcOH) to, *cis*-hexahydrophthalic acid. H. B.

Thermal decomposition of natural and artificial caoutchouc in presence of aluminium chloride. N. D. ZELINSKI and N. S. KOSLOV (Annalen, 1932, **497**, 160—170).—Caoutchouc ("pale crêpe") heated with 10% of $AlCl_3$ gives saturated ($KMnO_4$), b.p. 34—240°, and unsaturated (*A*), b.p. 70—250°/9 mm., hydrocarbons; with 20% of $AlCl_3$, saturated hydrocarbons, b.p. 34—300°, are produced. (*A*) heated with 10% of $AlCl_3$ also gives saturated hydrocarbons, b.p. 29—290°. Dehydrogenation of the "benzine" fraction (*B*), b.p. 70—150°, with Pt-asbestos at 300° affords a product containing 13% of aromatic hydrocarbons [by absorption in oleum (7% SO_3)]; (*B*) contains *cyclo*-alkanes other than -hexanes. A fraction, b.p. 120—126°, is similarly dehydrogenated to a product containing 41% of xylenes. The gaseous products of the original decomp. are saturated. Caoutchouc from *Scorzonera Tau-Sagis* with 10% of $AlCl_3$ gives a mixture, b.p. 22—235° to 70—250°/15 mm., of hydrocarbons all the fractions of which contain unsaturated ($KMnO_4$) material; further treatment with 10% of $AlCl_3$ affords a saturated mixture, b.p. 30—267°. The original mixture contains *cyclo*hexane derivatives, other *cyclo*alkanes, unsaturated hydrocarbons possessing a terpene odour, and a fraction resembling dipentene. Synthetic caoutchouc (from butadiene and Na) also gives a mixture of *cyclo*hexane derivatives and other *cyclo*alkanes when heated with $AlCl_3$. H. B.

Modifications of guttapercha hydrocarbon. II. A. W. K. DE JONG (Rec. trav. chim., 1932, **51**, 699—705; cf. this vol., 275).—On heating, the spongy modification contracts markedly in vol. between 61° and 64·5° (55—63° in less pure samples), after which it expands normally at the same rate as the α-modification, of which it is composed. The contraction represents the m.p. range, but is not observed if the hydrocarbon has been previously pulverised. The β-form is less dense than the α-, and both expand on melting. The spongy form was purified by crystallisation from C_6H_6; it undergoes autoxidation. H. A. P.

Natural and synthetic rubber. X. Constituents of rubber hydrocarbon. XI. Constituents of milled rubber hydrocarbon. T. MIDGLEY, jun., A. L. HENNE, and M. W. RENOLL (J. Amer. Chem. Soc., 1932, **54**, 3343—3348, 3381—3383).—X. By means of fractional pptn. (B., 1931, 853) and by the use of a "standard pptn. point" (the temp. at which a sudden increase of turbidity occurs in a slowly-cooled solution of 0·85% rubber, 28·55% abs. EtOH,

and 70·6% of C_6H_6) it is concluded that the original rubber specimen consisted of a sol. portion (>20%) containing several individuals, a single sol. component (>50%), and an insol. portion (<20%). The larger portion is characterised by a " standard pptn. point " of 35°. It is suggested that the more sol. fractions are generated during the washing and sheeting of the original coagulum.

XI. Investigation of the composition of milled rubber by a method based on fractional pptn. from C_6H_6–EtOH shows that it consists of a continuous serious of undefined components, without a single predominating individual. C. J. W. (b)

Asymmetric synthesis. XI. A. McKenzie and P. D. Ritchie (Biochem. Z., 1932, 250, 376—384).— (—)Menthyl anisoylformate, m.p. 62·5—63°, has $[\alpha]_{5461}^{20}$ −58·6° in $CHCl_3$, −44·2° in $COMe_2$, −45·0° in C_6H_6, −30·6° in CS_2, and −45·9° in EtOH. Mutarotation was not observed in these solutions, a striking difference from (—)menthyl benzoylformate. The asymmetric syntheses by Grignard reactions of (—)methylanisylglycollic acid, m.p. 146—147°, $[\alpha]_{5461}^{25}$ −61·7° in EtOH, from (—)menthyl anisoylformate and of (+)methylanisylglycollic acid, m.p. 146—147°, $[\alpha]_{5461}^{25}$ +61·0°, from (—)menthyl pyruvate are described. P. W. C.

Studies in stereochemical structure. IV. Esters of (—)menthol and the (—), (+), and r-mandelic acids. R. Roger (J.C.S., 1932, 2168—2180).—The rotatory dispersions of d-mandelic acid, Et d(−)-, and (—)menthyl d(−)-mandelate are normal and complex, that of (—)menthyl r- is simple, and that of (—)menthyl l(+)-mandelate is complex and anomalous in certain solvents. The dispersions of (—)menthyl d(−)- and l(+)-mandelates may be complicated by induced asymmetry in the C·COR group. The evidence for the existence of (—)menthyl r-mandelate as a true racemic compound in solution is examined. F. R. S.

The enzyme model of Bredig and Fajans. P. Rona and F. Reuter.—See this vol., 966.

Hydrocarbons corresponding with particular camphor-like substances. II. apoiso Fenchene (camphenilene), apocyclene, and apobornylene. G. Komppa and T. Hasselström (Annalen, 1932, 497, 116—130).—dl-apoBornyl (=dl-α-fenchocamphoryl) chloride (I) heated with NH_2Ph gives a mixture of hydrocarbons containing apocyclene (not affected by $KMnO_4$) and apoisofenchene (II, R'=Me, R=H) (oxidised by $KMnO_4$ to trans-apofenchocamphoric acid). (I) and amyl-alcoholic K amyloxide at 230° give apobornylene (II, R=Me, R'=H), oxidised to apocamphoric acid. Treatment of α - fenchocamphoronehydrazone with EtOH–HgCl₂ in cold EtOH–KOH affords apocyclene, b.p. 137·5°/756 mm., m.p. 41—42° (cf. A., 1922, i, 1167), whilst reduction of (I) with Na and EtOH gives apobornylene and apocamphane. dl-β-Fenchocamphoryl chloride does not undergo rearrangement when heated with aq. $Ca(OH)_2$ and is converted by K amyloxide at 230° into apoisofenchene, b.p. 134·5—135·5°/762 mm., m.p. 24·5—25° [nitrosochloride, m.p. 144—145° (decomp.)].
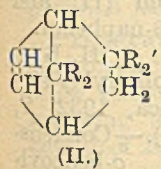
Camphenilonehydrazone and EtOH–HgCl₂ in EtOH–KOH give apocyclene, the hydrochloride (III), b. p. 76—77°/11 mm., m.p. 44—46°, of which is probably a stereoisomeride of (I). (III) and KOPh at 150° afford pure apocyclene (m.p. 38·5—39·5°), whilst (III) and aq. $Ca(OH)_2$ at 80° give (probably) a stereoisomeride (IV), b.p. 196—198°, m.p. 85·5—86·5°, of α-fenchocamphorol. (IV) is oxidised by $KMnO_4$ to apocamphoric acid and by $K_2Cr_2O_7$–dil. H_2SO_4 to α-fenchocamphorone. The acetate from (III) and AgOAc in AcOH is hydrolysed by EtOH–KOH to a product, b.p. 78—81°/6·5 mm., containing isofenchyl alcohol; the acetate from (I) [which reacts less readily than (III)] is hydrolysed to solid (impure) α-fenchocamphorol. H. B.

Catalytic action of silica gel in the reaction of camphene and oxalic acid. Synthesis of isoborneol. T. Kuwata and S. Tategai (J. Soc. Chem. Ind. Japan, 1932, 35, 303—304b).—Camphene (I) and anhyd. $H_2C_2O_4$ react thus : (I) (2 mols.) $+2H_2C_2O_4$ $\rightleftharpoons$ isobornyl H oxalate (m.p. 40·5°) (2 mols.) $\rightleftharpoons$ isobornyl oxalate (m.p. 114—115°) $+H_2C_2O_4$. Reaction is extremely slow below 100° and polymerised material results above 150°; a 65% yield of isoborneol (II) is obtained only with difficulty (cf. G.P. 193,301). Reaction occurs below 100° with silica gel as catalyst ; the yield of (II) is increased to 75%. The yield of borneol from pinene and $H_2C_2O_4$ is <75% ; polymerised material is formed from the intermediate bornyl H oxalate. H. B.

Constitution of bornylaniline. J. J. Ritter and H. O. Mottern (J. Amer. Chem. Soc., 1932, 54, 3458).—Lipp and Stutzinger's observation (this vol., 398) that the " bornylaniline " of Ullmann and Schmid (A., 1911, i, 70) is identical with the product from camphene and NH_2Ph is confirmed. Reduction of camphoranil with Na and NH_2Ph gives a sec.-amine, the Ac derivative of which has m.p. 112—113° (Lipp and Stutzinger give 123°). C. J. W. (b)

Higher β-homologues of camphoric acid, and β-homocamphor. F. Salmon-Legagneur (Bull. Soc. chim., 1932, 51, [iv], 807—824).—A fuller account of work already published (cf. A., 1931, 626; this vol., 399). The Me ester (I) of camphoceanaldehydic acid [Et ester, b.p. 144—145°/13 mm. (semicarbazone, m.p. 158—160°)] gives with Zn and Et bromoacetate Et β-campholide-β-acetate, C_8H_{14}<$\begin{smallmatrix}CO\\CH(CH_2 \cdot CO_2Et)\end{smallmatrix}$>O, m.p. 52—53° (cf. A., 1931, 626), hydrolysed by 20% H_2SO_4 at 100° to the corresponding acid, m.p. 213°, but by aq. KOH to α-carboxycamphocean-β-acrylic acid (Me_2 ester, b.p. 188°/15 mm.). Reduction of (I) with H_2–PtO_2 gives the ester $C_8H_{14}(CH_2 \cdot OH) \cdot CO_2Me$, b.p. 158—162°/19 mm., cyclised by aq. KOH to β-campholide, m.p. 218°. The oxime of (I) is converted by $SOCl_2$ into camphoric acid mononitrile. Interaction of $SOCl_2$ (1 mol.) with oximino-β-homocamphor (1 mol.) (cf. this vol., 399) gives a compound, $C_{22}H_{32}O_3N_2$, m.p. 200—205°. The thermal decomp. of Pb α-carboxycamphocean-β-propionate gives, in addition to β-homocamphor, a diketone, $C_{22}H_{32}O_2$ (or $C_{22}H_{36}O_2$?), m.p. 290—291° (block), probably C_8H_{14}<$\begin{smallmatrix}CO \cdot CH_2 \cdot CH_2\\CH_2 \cdot CH_2 \cdot CO\end{smallmatrix}$>$C_8H_{14}$, or a dehydrogenation product. H. A. P.

Sulphur compounds of terpenes. II. Constitution of sulphur compound from the action of sulphur on dipentene. III. Action of sulphur on cyclic terpene alcohols. IV. Action of sulphur on linalyl acetate and linalool. A. NAKAT-SUCHI (J. Soc. Chem. Ind., Japan, 1932, **35**, 376—379B).—II. Under the conditions previously used (A., 1931, 95) dipentene heated with S gives a *sulphide*, $C_{10}H_{18}S$ (I), b. p. 223°/759 mm., m.p. —23° (*dibromide*, m.p. 143°), which gives additive *compounds* with $AuCl_3$ and MeI. Oxidation of (I) with $KMnO_4$ gives successively the cryst. *compounds*, $C_{10}H_{18}O_2S$, m.p. 65·5°, $C_{10}H_{18}O_3S$, m.p. 150°, and $C_{10}H_{18}O_4S$, m.p. 227·5°.
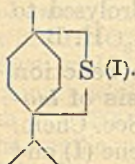
III. Dihydro-α-terpineol heated with S at 160° first eliminates H_2O, further treatment giving the same result as $\Delta^{8(9)}$-*p*-menthene; the product gives a *compound* $C_{10}H_{17}SAu$ with $AuCl_3$. α-Terpineol and terpinyl acetate similarly lose H_2O or AcOH, giving, finally, *p*-cymene and (?) (I). No reaction occurs with menthol.

IV. Linalool and its acetate similarly heated with S eliminate H_2O or AcOH and afford *p*-cymene, dipentene, a *terpene*, $C_{10}H_{16(14)}$, b.p. 186—187°/774 mm., m.p. —26·81°, a *compound*, $C_{10}H_{18}S$ ($AuCl_3$ and MeI additive *compounds*) (probably a mixture of different types containing the C·S·C and C:S groups), and higher S derivatives.　　　　　J. W. B.

Ethyl 5-nitrofurfurylidenemalonate and α-cyano-β-5-bromofurylmalonate. Stability of furan compounds towards acids. H. GILMAN and R. V. YOUNG (Rec. trav. chim., 1932, **57**, 761—768).—The product of nitration of Et furfurylidenemalonate (I) (A., 1895, i, 651) is the 5-NO_2-derivative [synthesis from 5-nitrofurfuraldehyde (II) and Et malonate]. The product of bromination of Et α-cyano-β-furylacrylate (A., 1894, i, 488) is identical with the product of interaction of (II) and $CN·CH_2·CO_2Et$ in presence of NaOEt, and is therefore the 5-, and not the β-Br-derivative. Many negatively substituted furan derivatives have good stability towards acids (including the halogen acids); thus, (I) may be nitrated with HNO_3 (d 1·5).　　H. A. P.

Dimethylfuroic acids. H. GILMAN and R. B. BURTNER (Rec. trav. chim., 1932, **51**, 667—672).—Details are given for the prep. of 2 : 5-dimethylfuran-3-carboxylic acid [4-*Br*-derivative, m.p. 181° (decomp.); α-*naphthalide*, m.p. 148°]. Nitration of its Et ester in Ac_2O gives the 4-NO_2-ester, b.p. 119—120°/20 mm., hydrolysed by 20% HCl to the free *acid*, m.p. 176°, and 3-*nitro*-2 : 5-*dimethylfuran*, b.p. 88—92°/9 mm. (also formed by nitration of 2 : 5-dimethylfuran). The 5-NO_2-, m.p. 182°, and 5-*Br*-, m.p. 104° (decomp.), derivatives of 2 : 4-dimethylfuran-3-carboxylic acid [best prepared by the method of Anschütz (A., 1891, 172)] are similarly prepared. It is decarboxylated by Cu-bronze and quinoline to 2 : 4-dimethylfuran (*HgCl*-derivative, m.p. 112°).　　H. A. P.

Experiments on the synthesis of anthocyanins. XIV. Cyanenin chloride, malvenin chloride, and an indication of the synthesis of cyanin chloride. A. LÉON and R. ROBINSON (J.C.S., 1932, 2221—2224).—*Cyanenin* and *malvenin chlorides* (also

picrates), the 5-glucosidyl derivatives of cyanidin and malvidin chlorides, have been synthesised by the method used for pelargonenin chloride (A., 1931, 1423) and are identical with the products of hydrolysis of cyanin and malvin chlorides. Condensation of crude 2-*o*-benzoylphloroglucinaldehyde with the intermediate for chrysanthemin (*loc. cit.*) gives traces of (probably) cyanin chloride.　　E. E. J. M.

Stability of coumarinic acids derived from 1 : 2-βα-naphthapyrones. B. B. DEY, R. H. R. RAO, and Y. SANKARANARAYANAN (J. Indian Chem. Soc., 1932, **9**, 281—289).—Acidification of alkaline solutions of 1 : 2-βα-naphthapyrone (I) (modified prep. given) and its 3-Me and 3-$CO_2H·CH_2$· derivatives regenerates the pyrones, *i.e.*, the intermediate coumarinic acids are unstable. The 4-Me and 4-$CO_2H·CH_2$· derivatives similarly afford stable (*i.e.*, isolable) coumarinic acids which are not convertible into the *trans*-forms (coumaric acids) by the usual methods, but which pass into the original pyrones at the m.p. when crystallised from hot AcOH, or when kept in a desiccator for several days. The pyrone ring is rendered unstable by Cl, Br, or NO_2 in the 3-position; these groups are removed by boiling alkali when the 4-position is unsubstituted. The following are prepared : trans-β-2-*hydroxy*-1-*naphthylacrylic acid* (II), m.p. 165° (decomp.), in small amount from (I) and 40% KOH; cis-β-2-*hydroxy*-1-*naphthylcrotonic acid* (III), m.p. 146° (decomp.), from 4-methyl-1 : 2-βα-naphthapyrone; cis-α-*chloro*-β-2-*hydroxy*-1-*naphthylcrotonic acid*, m.p. 148° (decomp.), from 3-chloro-4-methyl-1 : 2-βα-naphthapyrone; cis-β-2-hydroxy-1-naphthylglutaconic acid, m.p. 174° (decomp.) (cf. Dey, J.C.S., 1915, **107**, 1606), from 1 : 2-βα-naphthapyrone-4-acetic acid; trans-β-2-*hydroxy*-1-*naphthylitaconic acid*, m.p. 79°, from 1 : 2-βα-naphthapyrone-3-acetic acid by Sen and Chakravarti's method (A., 1930, 913); cis-β-2-*hydroxy*-1-*naphthyl*-β-*methylitaconic acid*, m.p. 154° (decomp.), from 4-methyl-1 : 2-βα-naphthapyrone-3-acetic acid; trans-β-2-*hydroxy*-1-*naphthyl*-α-*methylacrylic acid*, m.p. 138° (*Me* ester, m.p. 130°), from 3-methyl-1 : 2-βα-naphthapyrone by Sen and Chakravarti's method; cis-β-(?)-*nitro*-2-*hydroxy*-1-*naphthylcrotonic acid*, m.p. 271° (decomp.), from (?)-*nitro*-4-*methyl*-1 : 2-βα-*naphthapyrone*, m.p. 273° (sinters at 268°) [prepared from (III) and fuming HNO_3 in Ac_2O]. 3-*Bromo*-1 : 2-βα-*naphthapyrone*, m.p. 165° (decomp.), from (I) and Br in CS_2 and sunlight, is converted by 30% KOH in EtOH into β-*naphthafurancarboxylic acid*, m.p. 192°. 3-*Nitro*-1 : 2-βα-*naphthapyrone*, m.p. 244°, from (II) and HNO_3, and 30% KOH give 1-aldehydo-β-naphthol.　　H. B.

Dye derived from 10-hydroxy-9-phenyl-γ-anthranol. T. PAVOLINI (L'Ind. Chimica, 1932, **7**, 877—879). — Condensation of *o*-benzoyl-benzoic acid with resorcinol yields a *compound*, named *rodonine*, m.p. 157—158°, of the probable constitution annexed. In slightly acid solution it dyes wool and silk yellow and in slightly
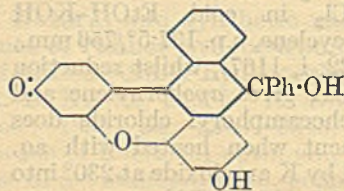
alkaline solution coral-pink. It serves as an indicator, changing sharply from yellow in neutral or acid solution to pink with green fluorescence in alkaline solution; its use for determining the acidity of coloured liquids like wine, beer, and vinegar is suggested.　T. H. P.

Rotenone. XXIII. Structure of rotenonone. F. B. LaForge (J. Amer. Chem. Soc., 1932, 54, 3377—3380).—Rotenonone, the lactone corresponding with rotenononic acid (I), is partly converted into derritol (II) by Zn and EtOH–KOH. (I) and Me_2SO_4 in 5% KOH give the *Me* ester, m.p. 138°, of *methylrotenononic acid*, m.p. 179—180° (*tetrahydro*-derivative, m.p. 184—186°). (II) and $CO_2Et \cdot COCl$ in pyridine give rotenonone; this is a convenient method of prep. A structure is proposed for rotenonone; it is identical with that of Butenandt and McCartney (this vol., 619).　C. J. W. (*b*)

Ring fission of pyridine. A. Treibs (Annalen, 1932, 497, 297—301).—Pyridine (1 mol.) and $CHCl_3$ (1 mol.) in cold 15% NaOH (3—5 mols.) give first an unstable red dye and then (after 1—7 months) HCN and a little β-vinylacrylic acid : $C_5H_5N +$ $CHCl_3 + 5NaOH = C_5H_5O_2Na + NaCN + 3NaCl + 3H_2O$; glutacondialdehyde is not an intermediate. Red dyes are similarly produced using $CHBr_3$, CHI_3, CCl_4, $CPhCl_3$, and $CCl_3 \cdot CO_2H$, but not with 2 : 6-dimethyl- and 2 : 4 : 6-trimethyl-pyridine, quinoline, and 2-methylquinoline. 2-Methylpyridine, $CCl_3 \cdot CO_2H$, and aq. NaOH give HCN and sorbic acid.　H. B.

The Rosenmund aldehyde synthesis in the pyridine series. R. Graf (J. pr. Chem., 1932, [ii], 134, 177—187).—4 : 6 - *Dichloropyridine* - 2 - *aldehyde*, m.p. 74° (*phenylhydrazone*, m.p. 195—197°), 5 : 6-*dichloropyridine*-3-*aldehyde*, m.p. 69—70° (*phenylhydrazone*, m.p. 158°), and 2 : 6-*dichloropyridine*-4-*aldehyde*, m.p. 46—47° (*phenylhydrazone*, m.p. 157—158°), are obtained, together with some of the corresponding dichloropyridines, from the appropriate carboxyl chlorides (H_2–Pd–$BaSO_4$). The reaction fails with less highly negatively substituted derivatives, *e.g.*, nicotinic, 4-chloropicolinic, dipicolinic, isocinchomeronic, quinaldinic, and 2-chloroquinoline-4-carboxylic acids. The aldehydes are converted by 50% aq. KOH into the corresponding alcohols, viz., 4 : 6-*dichloro*-2-*pyridylcarbinol*, m.p. 84° (*Bz* derivative, m.p. 53—54°), 5 : 6-*dichloro*-3-*pyridylcarbinol*, m.p. 76—78° (*Bz* derivative, m.p. 103—104°), and 2 : 6-*dichloro*-4-*pyridylcarbinol*, m.p. 131—132° (*Bz* derivative, m.p. 119—120°). 2 : 3-Dichloropyridine has m.p. 69°.　H. A. P.

Preparation of pyridine-o-thiol- and -o-sulphocarboxylic acids. E. Sucharda and C. Troszkiewicz (Rocz. Chem., 1932, 12, 493—499).—The following substances have been prepared by the action of KSH on the corresponding chloropyridinecarboxylic acids : 2-*thiolpyridine*-3-*carboxylic acid*, m.p. 270°, yielding on oxidation 2-*sulphopyridine*-3-*carboxylic acid*, m.p. 282°, 3-*thiolpyridine*-2-*carboxylic acid*, m.p. 183·5°, 2 : 2'-*dicarboxy*-3 : 3'-*dipyridyl disulphide*, m.p. 206°, yielding on oxidation the corresponding 3-*sulphonic acid*, m.p. 343°, 3-*thiolpyridine*-4-*carboxylic acid*, m.p. 225°, and 4 : 4'-*dicarboxy*-3 : 3'-*dipyridyl disulphide*, m.p. 307—308°,

giving on oxidation the corresponding 3-*sulphonic acid*, m.p. 318°.　R. T.

Action of halogens on polycyclic indole derivatives. II. Bromination of the acyl derivatives of 8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole and 7 : 8 : 9 : 10 - tetrahydro - αβ - naphthacarbazole. S. G. P. Plant and (Miss) M. L. Tomlinson (J.C.S., 1932, 2192—2195).—Bromination of 7-acetyl-8 : 9 :10 : 11-tetrahydro-α′β′-naphthacarbazole in AcOH gives the 5-*Br*-compound, m.p. 199°, hydrolysed to 5-*bromo*-8 : 9 : 10 : 11-α′β′-*naphthacarbazole*, m.p. 115—120°, also prepared from *cyclo*hexanone-4-bromo-2-naphthylhydrazone (corresponding Bz compounds similarly obtained ; 5-*bromo*-7-*benzoyl*-, m.p. 158—159°). *Et* 8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole*-7-*carboxylate*, m.p. 121°, is brominated to the 5-*Br*-derivative, m.p. 180—181°; the 5-*bromo*-11-*acetyl*, m.p. 126—127°, and 5-*bromo*-11-*benzoyl*, m.p. 115°, derivatives are hydrolysed to 5-*bromo*-7 : 8 : 9 : 10-*tetrahydro*-αβ-*naphthacarbazole*, m.p. 116° (prepared by the indole synthesis from *cyclo*hexanone and 4-*bromo*-1-*naphthylhydrazine*, m.p. 139°). Orientation problems arising from these results are discussed.　F. R. S.

Platinum with a co-valency of four : diquinolinoplatinous chlorides. E. G. Cox, H. Saenger, and W. Wardlaw (J.C.S., 1932, 2216—2221).—Cold aq. K_2PtCl_4 with quinoline gives a solid which when extracted with $CHCl_3$ gives the β-*dichloride*, $Pt(C_9H_7N)_2Cl_2,2CHCl_3$ (I), for which crystallographic data are given ; this in boiling quinoline gives the α-*dichloride* $Pt(C_9H_7N)_2Cl_2$ (II) but no tetraquinilinosalt. (I) with C_5H_5N gives quantitatively *tetrapyridinoplatinous chloride* $[Pt(C_5H_5N)_4]Cl_2$ (III), giving with K_2PtCl_4 a *plato*-salt, $[Pt(C_5H_5N)_4][PtCl_4]$ and with dil. HCl α-*dipyridinoplatinous chloride*; with aq. C_5H_5N (I) gives mixtures of (III) with β-*dipyridinodiquinilinoplatinous chloride*, $Pt(C_5H_5N)_2(C_9H_7N)_2Cl_2$, (*plato*-salt ; α-*pyridinoquinolinoplatinous chloride*). (II) reacts similarly but much less rapidly ; α-*tetrapyridino*- and α-*dipyridinodiquinilino*-*platinous chlorides* and their *plato*-salts are described. With moist Ag_2O (I) gives the β-*base* $Pt(C_9H_7N)_2(OH)_2$ (β-*dibromide*) ; (II) reacts very slowly, giving only traces of the α-*base*.
　E. E. J. M.

Synthesis of quinoline derivatives. K. Dziewoński and J. Moszew (Rocz. Chem., 1932, 12, 482—492).—The chief product of reaction of $CS(NHPh)_2$ or $CO(NHPh)_2$ with COPhMe is 4-anilino-2-phenylquinoline, m.p. 190° [*hydrochloride*, m.p. 265—266°; *picrate*, m.p. 235—236°; *NO*-derivative, m.p. 203°; *Ac* derivative, m.p. 160°; *compound* with 0·5 mol. $C_2H_4Br_2$, m.p. 297—298°; 1 : 2 : 3 : 4-*tetrahydro*-derivative, m.p. 138—139° (*picrate*, m.p. 163°)]. $COMe_2$ and di-*p*-tolylthiocarbamide yield 4-*p*-*tolylamino*-2-*phenyl*-6-*methylquinoline*, m.p. 162° [*hydrochloride*, m.p. 324°; *nitrate*, m.p. 171°; *picrate*, m.p. 241°; *NO*-derivative, m.p. 189°; *Ac* derivative, m.p. 154°; *compound* with $C_2H_4Br_2$, m.p. 262—263°; *tetrahydro*-derivative, m.p. 113° (*picrate*, m.p. 203°)].
　R. T.

Molecular dissymmetry dependent on restriction of rotation about a single linking. II. Opti-

cally active **8-benzenesulphonylethylamino-1-
ethylquinolinium salts.** W. H. MILLS amd J. G.
BRECKENRIDGE (J.C.S., 1932, 2209—2216).—The fol-
lowing 8-*benzenesulphonyl* compounds having the
annexed formula are described : -*aminoquinoline* (I),
m.p. 133·5°; -*ethylaminoquinoline*
(II), m.p. 136·5° [prep. by mixing
EtOH solutions of (I) and KOEt
and heating the resulting K deriv-
ative (III) with EtI at 115°]; -*ethyl-
amino-1-methylquinolinium iodide* (IV), m.p. 169·5°
[prep. by heating (II) with Me$_2$SO$_4$ at 100° and treat-
ing the resulting methosulphate, m.p. 192°, with aq.
KI] [d-α-*bromocamphor-π-sulphonate* (V), [α]$_{5461}^{17·5}$ +59·4°
in CHCl$_3$]; -*ethylamino-1-ethylquinolinium iodide*, m.p.
173°, from (II) and Et$_2$SO$_4$, giving a gummy d-*bromo-
camphorsulphonate* (VI), the cryst, anhyd. form of
which was obtained by pptn. of its EtOH solution
with Et$_2$O [*dihydrate* (VII), m.p. 104—107°]; -d-*ethyl-
amino-1-ethylquinolinium iodide* (VIII), from (VII) and
conc. aq. KI; -l-*ethylamino-1-ethylquinolinium* d-
bromocamphorsulphonate (IX), prep. by evaporation of
a solution of (VI) in EtOAc–MeOH [l-*iodide* (X)];
-n-*propylaminoquinoline*, m.p. 66·5°, from (III) and
PrI at 120° {*methosulphate*, m.p. 168°; *methiodide*,
m.p. 162°; d-*bromocamphorsulphonate*, m.p. 170° [*tri-
hydrate* (XI), m.p. 105°, [α]$_{5461}$ +58·8° in CHCl$_3$)]};
-*benzylaminoquinoline*, m.p. 124°, from (III) and
CH$_2$PhBr at 160° (*methosulphate*, m.p. 219°; meth-
iodide, m.p. 176°). (VII), (VIII), (IX), and (X) in
which R′ is Et all show mutarotation, which is described
in detail; (V) and (XI) in which R′ is Me do not.
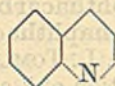
E. E. J. M.

Oxidation of optochin. C. C. VERNON and H. U.
RESCH (J. Amer. Chem. Soc., 1932, 54, 3455—3456).—
Oxidation of optochin with CrO$_3$ in acid solution
gives 6-*ethoxyquinoline-4-carboxylic acid*, m.p. 288·5°.

C. J. W.*(b)

Quinoline compounds. VII. U. BRAHMACHARI
and J. M. DAS-GUPTA (J. Indian Chem. Soc., 1932,
9, 203—206).—β-6-Methoxy-8-quinolylamino-α-di-
methylamino- and -α-diethylamino-propane (*dihydro-
chlorides*, m.p. 180° and 175°, respectively) are pre-
pared from the α-NH$_2$-compound (this vol., 281, 522)
and MeI and EtI, respectively. β-8-*Quinolylamino-*,
β-6-*methyl-8-quinolylamino-*, and β-6-*methoxy-2-methyl-
8-quinolylamino-α-dimethylaminopropane dihydrochlor-
ides*, m.p. 200—205°, 210°, and 218°, respectively, are
similarly prepared. These compounds could not be
prepared from aminoquinolines and β-bromo-α-dialkyl-
aminopropanes. 8-Allylaminoquinoline and fuming
HBr at 100° (bath) give 8-β-bromopropylaminoquinol-
ine, hydrolysed by aq. Na$_2$CO$_3$ to 8-β-hydroxypropyl-
aminoquinoline (*hydrochloride*, m.p. 170—172°), also
formed from 8-aminoquinoline and CH$_2$Cl·CHMe·OH;
8-β-hydroxypropylamino-6-ethoxyquinoline (*hydro-
chloride*, m.p. 165°) is similarly prepared. 8-Amino-
quinoline and Et lactate at 130° give 8-α-hydroxy-
propionamidoquinoline (*hydrochloride*, m.p. 182—
185°), also formed when 8-aminoquinoline lactate is
heated at 175°. 8-α-Hydroxypropionamido-6-ethoxy-
quinoline (*hydrochloride*, m.p. 177°) is similarly prepared.

H. B.

**Synthetic experiments in the benzyl*iso*quinol-
ine series. I.** C. SCHÖPF, H. PERREY, and I.

JÄCKH. **II. Preparation of 6-hydroxy-1-3′-
hydroxy-4′-methoxybenzyl-N-methyltetrahydro-
*iso*quinoline and laudanosoline 4′-methyl ether.**
C. SCHÖPF, I. JÄCKH, and H. PERREY (Annalen, 1932,
497, 47—58, 59—68).—I. β-3 : 4-*Dimethoxyphenyl-
propionhydrazide*, m.p. 132—133°, is converted by
the usual method into the azide, which when heated
with CH$_2$Ph·CO$_2$H in C$_6$H$_6$ gives phenylacet-β-3 : 4-
dimethoxyphenylethylamide. Rapid treatment of
β-m-*benzyloxyphenylpropionhydrazide* (I), m.p. 135—
137° (sinters at 130°), with aq. NaNO$_2$ in cold AcOH–
C$_6$H$_6$ affords the azide, which with CH$_2$Ph·CO$_2$H and
3-*benzyloxy-4-methoxyphenylacetic acid*, m.p. 126—
130° (prepared from benzyl*iso*vanillin by way of the
azlactone and pyruvic acid), gives *phenylacet-*, m.p.
81—86°, and 3-*benzyloxy-4-methoxyphenylacet-* (II),
m.p. 101—106°, -β-m-*benzyloxyphenylethylamide*, re-
spectively. Slow treatment of (I) with NaNO$_2$ gives
some sec.-β-m-*benzyloxyphenylpropionhydrazide*, m.p.
190—192°, as a by-product. (II) and PCl$_5$ in CHCl$_3$
give 6-*benzyloxy-1-3′-benzyloxy-4′-methoxybenzyl-3 : 4-
dihydroisoquinoline hydrochloride* (III) (+2H$_2$O), m.p.
127—128° (decomp.); the free base (IV) undergoes
ready autoxidation and with MeI affords a *compound*,
probably C$_{32}$H$_{30}$O$_4$NI, m.p. 188—190°. The follow-
ing compounds are described : s-*di-(β-m-benzyloxy-
phenylethyl)carbamide*, m.p. 166—168°; β-3-*benzyloxy-
4-methoxyphenylpropionhydrazide*, m.p. 138—140°;
3 : 4-*dibenzyloxyphenylacetic acid*, m.p. 109°.

II. β-3 : 4-*Dibenzyloxyphenylpropionhydrazide*, m.p.
138°, is converted [as (I)] into the azide which with
3-benzyloxy-4-methoxyphenylacetic acid gives 3-
*benzyloxy - 4 - methoxyphenylacet - β - 3 : 4 - dibenzyloxy-
phenylethylamide*, m.p. 137° (sinters at 124°), cyclised
by PCl$_5$ in CHCl$_3$ to 6 : 7-*dibenzyloxy-1-3′-benzyloxy-
4′ - methoxybenzyl - 3 : 4 - dihydroisoquinoline hydro-
chloride*, m.p. 179—181°. Successive treatment of
this with NaOEt and MeI in EtOH and N$_2$ gives
the *methiodide*, m.p. 185—187°, of the free base;
treatment of this with AgOAc in aq. AcOH and
subsequent reduction (Zn dust) affords 6 : 7 - *di-
benzyloxy-1-3′-benzyloxy - 4′ - methoxybenzyl - N -methyl-
tetrahydroisoquinoline (laudanosoline 6 : 7 : 3′ - tri-
benzyl 4′-methyl ether)*, m.p. 86—87°, debenzylated
by HCl (d 1·12) in 2N-AcOH to *laudanosoline 4′-Me
ether*, m.p. 120—122° (decomp.) (sinters at 110°)
(demethylated by 48% HBr to laudanosoline). 6-
*Benzyloxy-1-3′-benzyloxy - 4′ - methoxybenzyl - 3 : 4 - di-
hydroisoquinoline methiodide*, m.p. 120° (sinters at
100°) [obtained by successive treatment of (III) with
NaOEt and MeI in EtOH and N$_2$], is converted into
the *methochloride* (+H$_2$O), m.p. 145—147°, which is
debenzylated to the 6 : 3′-dihydroxy-analogue (V)
[corresponding *methopicrate*, m.p. 208—209° (sinters
at 198°)] and reduced by Zn dust and 50% AcOH to
the 6 : 3′-dibenzyl ether of 6-hydroxy-1-3′-hydroxy-
4′-methoxybenzyl-N-methyl-1 : 2 : 3 : 4-tetrahydro*iso*-
quinoline [*picrate*, m.p. 183—184° (sinters at 175°)]
[also prepared by reduction of (V) with Zn dust and
30% AcOH or catalytically]. Debenzylation of (IV)
gives 6-hydroxy-1-3′-hydroxy-4′-methoxybenzyl-3 : 4-
dihydroisoquinoline [*picrate*, m.p. 148—152° (sinters
at 140°)], reduced (H$_2$, PtO$_2$, dil. HCl, or Zn dust,
30% AcOH) to 6-*hydroxy-1-3′-hydroxy-4′-methoxy-
benzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline* (VI), m.p.

210—212° (sinters at 206°) [*picrate*, m.p. 130—132° (sinters at 120°); Ac_3 derivative, m.p. 103—105° (sinters at 95°)], also obtained by reduction (H_2, PtO_2, AcOH) of (III) and subsequent debenzylation. (VI) and keten in *N*-AcOH give an impure *N*-Ac derivative. Reduction of (IV) (as acetate) with Zn dust and 50% AcOH gives a *compound*, $C_{31}H_{31(29)}O_3N(+3H_2O\ ?)$, m.p. 140—142°, hydrolysed by 20% HCl to 50% of (VI) and resinous material; with 60% AcOH, a *substance*, $C_{26}H_{27}O_4N$, m.p. 166—168°, is also produced, whilst the use of 30% AcOH leads to 6% of a *compound*, $C_{31}H_{31}O_3N$, m.p. 150—152°, and a mixture of substances [hydrolysed to (VI) in 15% yield].

A *hydrochloride*, $C_{31}H_{28}O_4NCl,H_2O$, of the autoxidation product of (IV) is described. H. B.

Phenanthridine series. II. Nitro- and aminophenanthridines. G. T. Morgan and L. P. Walls (J.C.S., 1932, 2225—2231).—5-Nitro- and 4-nitro-2-acetamidodiphenyls and 2-*o-nitrobenzamido*-5-*nitrodiphenyl*, m.p. 167° (prep. from 5-nitro-2-xenylamine and *o*-nitrobenzoyl chloride), give with $POCl_3$ 3-*nitro*-(I) and 7-*nitro-9-methylphenanthridines* and 3-*nitro*-9-*o-nitrophenylphenanthridine*, m.p. 210°, 243—245°, and 227°, respectively; the yield of the last two is small. Reduction (Fe) of (I) gives 3-*amino-9-methylphenanthridine*, m.p. 152°, the *Ac* derivative of which with Me_2SO_4 gives 4-*acetamido-9 : 10-dimethylphenanthridinium methosulphate*, decomp. about 225°, hydrolysis of which with 5*N*-HCl gives the *chloride*, m.p. about 275° (decomp.) (*dihydrate*), which has no therapeutic val.

An improvement in Pictet and Hubert's process for preparing phenanthridine (IV) is described. The *dinitrate* and *nitrate*, m.p. 169—171°, with conc. H_2SO_4 give three *mononitro*-derivatives, m.p. 260—262°, 160—163°, and 156—158°, and a *substance* subliming at 220/6 mm. (IV) reacts with $NaNH_2$ or with NH_3 in hot $NPhMe_2$ in presence of Na to give 9-*aminophenanthridine* (V), m.p. 195·5° [*acetate*, m.p. 206—209°; *lactate*, m.p. 202—204° (decomp.); *Ac* derivative, m.p. 193·5° (does not form quaternary salts)], together with a brown *base* which gives highly-coloured solutions in acids. With HNO_2 (V) is not diazotised, but gives only phenanthridone identical with that obtained when either *o-xenylcarbamide* [2-*diphenylylcarbamide*], m.p. 157—158·5°, or *methyl-o-xenyl* [*methyl-2-diphenylyl*] *carbamate*, m.p. 61°, obtained from *o*-xenylcarbimide with NH_3 or MeOH, respectively, is fused with $ZnCl_2$. E. E. J. M.

Acenaphthenone. II. Indole and acridine derivatives. A. C. Sircar and M. D. R. Gopalan (J. Indian Chem. Soc., 1932, 9, 297—301).—*Acenaphthindole*, m.p. 235°, and its N-*Me* derivative, m.p. 204°, are prepared by Robinson and Thornley's method (A., 1927, 158) from acenaphthenone (I) and NHPh·NH₂

(II.)

and NPhMe·NH₂, respectively. *Pheno - αβ - acenaphthacridine* [2 : 3-1 : 8-*naphthquinoline*] (II), m.p. 181°, is obtained from (I) and *o*-NH₂·C₆H₄·CHO by Friedländer's method (A., 1883, 1148; 1892, 1106). Reduction of *o-nitrobenzylidene-acenaphthenone*, m.p. 157°, with Fe and fuming HCl in
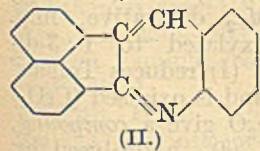
EtOH gives a little (II) and a *substance*, decomp. 236—240°. H. B.

Syntheses of 19-ketophenanthridindocoline, 3-benzoylcarbazole, and 3 : 6-dibenzoylcarbazole. S. G. P. Plant and (Miss) M. L. Tomlinson (J.C.S., 1932, 2188—2192).—Carbazole and *o*-NO₂·C₆H₄·COCl afford 9-*o-nitro*-, m.p. 148—150°, reduced to 9-*o-aminobenzoylcarbazole*, m.p. 160—162°, which on diazotisation in MeOH–H₂SO₄ gives 19-ketophenanthridindocoline (cf. this vol., 168). 9-Benzoylcarbazole heated with AlCl₃ at 120° is isomerised to the 3-Bz compound (*phenylhydrazone*, m.p. 219°), converted by Ac₂O and BzCl, respectively, into 3-*benzoyl-9-acetyl*-, m.p. 154°, and 3 : 9-*dibenzoyl-carbazole*, m.p. 170°. 3-Benzoylcarbazole has been synthesised by oxidising with S 6-*benzoyltetrahydrocarbazole*, m.p. 167—168°, obtained by heating the product of condensing *cyclo*hexanone and *p*-hydrazinobenzophenone with H₂SO₄. Benzoylation of carbazole in CS₂ in presence of AlCl₃ gives 3 : 6-*dibenzoylcarbazole* (I), m.p. 258°, which forms 3 : 6 : 9-*tribenzoyl*-, m.p. 224°, 3 : 6-*dibenzoyl-9-acetyl*-, m.p. 270°, and -9-*phenacetyl-carbazole*, m.p. 190—191°, with the appropriate reagent. 4-Bromo-3-nitrobenzophenone, *p*-aminobenzophenone, and K₂CO₃ yield 2-*nitro*-, m.p. 150°, reduced to 2-*amino*-4 : 4'-*dibenzoyldiphenylamine*, m.p. 153°, converted by NaNO₂ into 5 : 4'-*dibenzoyl-1-phenylbenzotriazole*, m.p. 195°, which is decomposed at 380° to (I). 2-Bromo-3-nitrobenzophenone, m.p. 76° (lit. 115°), and NH₂Ph give 2-nitro-, reduced to 2-*amino-6-benzoyldiphenylamine*, m.p. 118—119°, forming with NaNO₂, 7-*benzoyl-1-phenylbenzotriazole*, m.p. 154°, which could not be converted into 1-benzoylcarbazole. F. R. S.

Structure of C-substituted derivatives of barbituric acid. D. Marotta and G. Rosanova (Atti R. Accad. Lincei, 1932, [vi], 15, 753—755).—Diazomethane converts 5 : 5-diethylbarbituric acid into a mixture of an O-*ether* (a syrup) and the *N*-ether obtained by Fischer and Dilthey (A., 1905, i, 35). T. H. P.

*iso*Violuric acid (alloxan-6-oxime). D. Davidson and M. T. Bogert (Proc. Nat. Acad. Sci., 1932, 18, 490—496).—*iso*Barbituric acid (A., 1925, i, 1188) and HNO₂ give iso*violuric acid* (*alloxan-6-oxime*) (+2H₂O), m.p. (anhyd.) about 250° (decomp.) [5-*phenylhydrazone*, m.p. 268° (decomp.)], rearranged by dil. HCl to violuric acid, oximated to *alloxan-5 : 6-dioxime*, m.p. 242° (decomp.) [reduced by 20% (NH₄)₂S to 5 : 6-diaminouracil], and reduced [(NH₄)₂S] to iso*uramil*, not melted at 290° (5-O-*Ac* derivative, not melted at 275°), which is hydrolysed by dil. HCl to dialuric acid and oxidised by dil. HNO₃ to alloxan. H. B.

Creatine and creatinine. II. Alleged acyl derivatives of creatine. H. R. Ing (J.C.S., 1932, 2198—2200).—Acetylation of creatine gives *s*-(N-acetylsarcosyl)acetylcarbamide (I), m.p. 177—178°, and 1-methylhydantoin, and not diacetylcreatine (cf. Erlenmeyer, A., 1895, i, 310), since (I) reacts with aq. NH₃ to form acetylcarbamide and N-*acetylsarcosine amide*, m.p. 140—141°. Phthalyldicreatine (Urano, A., 1907, i, 192) is *dicreatinine phthalate*, m.p. 223° (decomp.). F. R. S.

Formation of the piperazine ring. K. H. SLOTTA and R. BEHNISCH (Annalen, 1932, **497**, 170—180).—β-Dimethylaminoethyl alcohol (I), p-$C_6H_4Me\cdot SO_2Cl$, and Na_2CO_3 in C_6H_6 give 1 : 1 : 4 : 4-*tetramethylpiperazinium di-p-toluenesulphonate* (II), decomp. 335° (corresponding *dipicrate*, decomp. 315°), also obtained from p-$C_6H_4Me\cdot SO_3Ag$ and 1 : 1 : 4 : 4-tetramethylpiperazinium di-iodide or dichloride [prepared from $NMe_2\cdot CH_2\cdot CH_2Cl$ (cf. Knorr, A., 1904, i, 938)]. β-Diethylaminoethyl alcohol (III) similarly affords 1 : 1 : 4 : 4-*tetraethylpiperazinium di-p-toluenesulphonate* (IV), m.p. 285° (corresponding *dipicrate*, m.p. 277°, and *dichloroaurate*, decomp. 236—237°), also formed from β-chloroethyl p-toluenesulphonate and $NHEt_2$ at 120°. Similarly, $PhSO_2Cl$ with (I) and (III) gives 1 : 1 : 4 : 4-*tetramethyl*-, decomp. above 340° (*dipicrate*, decomp. 315°), and 1 : 1 : 4 : 4-*tetraethyl*-, m.p. 258—260° (*dipicrate*, m.p. 277°), -*piperazinium dibenzenesulphonates*, respectively. β-N-Methyl- and -ethyl-anilinoethyl alcohols with $ArSO_2Cl$ give deep blue products. (II) and (IV) are converted by EtOH–KOH into 1 : 4-dimethyl- and -diethyl-piperazine, respectively. PhOH, (II), and EtOH–KOH at 130° give ω-dimethylaminophenetole; ω-*diethylaminophenetole*, b.p. 120°/10 mm., and o-anisyl β-diethylaminoethyl ether are similarly prepared from (IV) and PhOH and guaiacol, respectively. p-$C_6H_4Me\cdot SO_2Cl$ and (III) in pyridine give β-*diethylaminoethylpyridinium* p-*toluenesulphonate*, m.p. 166° (not sharp) (corresponding *picrate*, m.p. 143°, and *chloroaurate*, m.p. 212°). H. B.

Substituted piperazines. IV. Stereoisomeric bispentamethylenepiperazines. GODCHOT and MOUSSERON. **V. Aminoalcohols.** MOUSSERON (Bull. Soc. chim., 1932, [iv], **51**, 774—782, 782—807).—IV. 2-*Chlorocycloheptanone*, b.p. 98—100°/1 atm., prepared by chlorination of suberone in presence of $CaCO_3$, gives with cold NH_3–EtOH *bispentamethylenepyrazine*, m.p. 137—138° [*picrate*; *chloroplatinate*; *hydrochloride* ($+2H_2O$)], in 12% yield. Unlike the corresponding tetramethylene compound (this vol., 625), this is not reduced by Na and EtOH or Na and $C_5H_{11}\cdot OH$, but with H_2–Pt gives three of the five possible stereoisomeric piperazines, isolated as $(NO)_2$-derivatives, viz., α-, m.p. 74—75° [*chloroplatinate*; $(NO)_2$-derivative, decomp. 230° without melting], β-, m.p. 100—101° [*dipicrate*, m.p. 165°; *chloroplatinate*, decomp. 250°; *dihydrochloride* ($+8H_2O$); $(NO)_2$-derivative, m.p. 186—187°; solubility of urate 1 in 1510 of H_2O at 15°], and γ-*bispentamethylenepiperazine*, m.p. 58—59° [*dipicrate*, decomp. 220°; *chloroplatinate*, decomp. 230°; *dihydrochloride* ($+8H_2O$), decomp. 250°; $(NO)_2$-derivative, m.p. 148—149°; solubility of urate 1 in 24·6 of H_2O at 15°]. α-*Chlorocyclooctanone*, b.p. 96—98°/6 mm., similarly prepared, did not give a pyrazine derivative with NH_3.

V. Interaction of α-halogeno-alcohols or the corresponding ethylene oxides with piperazine and its C-substituted derivatives gives a mixture of mono- and bis-N-substitution products. These are separated either by crystallisation from the aq. reaction mixture, and recovery of the more sol. mono-derivative by steam-distillation and pptn. as $HgCl_2$ derivative, or by action of CS_2, which combines with the former only to give a dithiocarbamate, which is decomposed by boiling aq. KOH. The following are described : N-(2-*hydroxycyclopentyl*)-, m.p. 83—84° [*picrate*; *dithiocarbamate*, decomp. 200°; *chloroplatinate*, decomp. 250°; *dihydrochloride* ($+3H_2O$), decomp. 230°; *mercurichloride*]; NN'-*bis-2-hydroxycyclopentyl*-, m.p. 202—203° [*picrate*; *chloroplatinate*, decomp. 250°; *dihydrochloride* ($+3H_2O$), decomp. 200°]; N-2-*hydroxycyclohexyl*- (I), m.p. 67—68° [*picrate*, decomp. 200°; *dithiocarbamate*, m.p. 205° (decomp.); *chloroplatinate*, decomp. 250°; *dihydrochloride* ($+1H_2O$); *mercurichloride* ($C_{10}H_{20}ON_2,2HCl,2HgCl_2$)]; NN'-*bis-2-hydroxycyclohexyl*- (II), m.p. 204—206° [*picrate*, m.p. 215° (decomp.); *chloroplatinate*, decomp. 270°; *dihydrochloride* ($+4H_2O$), decomp. 240°]; NN'-*bis-2'-hydroxycyclohexyl-2 : 5-dimethyl*-, m.p. 225° (*chloroplatinate*, decomp. 260°); N-2-*hydroxycycloheptyl*-, m.p. 41—42° [*picrate*, decomp. 225°; *dithiocarbamate*, decomp. 235°; *chloroplatinate*; *dihydrochloride* ($+4H_2O$), m.p. 220°]; NN'-*bis-2-hydroxycycloheptyl*-, m.p. 78—79° [*dipicrate*; *chloroplatinate*; *dihydrochloride* ($+6H_2O$), m.p. 225°]; N-2-*hydroxycyclooctyl*-, m.p. 39° [*dipicrate*, decomp. 250°; *dithiocarbamate*, decomp. 220°; *chloroplatinate*, decomp. 260°]; NN'-*bis-2-hydroxycyclooctyl*-, m.p. 84—85° [*dipicrate*, decomp. 270°; *chloroplatinate*, decomp. 270°]; N-1-*hydroxy-2-indanyl*-, m.p. 72—73° (*dipicrate*, decomp. 240°; *dithiocarbamate*, decomp. 220°; *chloroplatinate*, decomp. 245°], and NN'-*bis-(1-hydroxy-2-indanyl)-piperazine*, decomp. 200° without melting (*dipicrate*; *chloroplatinate*]. The C_6, C_7, and C_8 derivatives possess marked local anæsthetic action. It was not found possible to condense tetramethyl- or bistetramethylene-piperazines with o-chlorocyclohexanol or with cyclohexene oxide. Interaction of 2-chlorocyclohexanone with excess of piperazine hydrate at 140° gives N-2-*ketocyclohexylpiperazine*, m.p. 4° [*dithiocarbamate*, m.p. 165° (decomp.); *chloroplatinate*, decomp. 210°], and NN'-*bis-2-ketocyclohexylpiperazine*, m.p. 113—114° (*picrate*, decomp. 140°; *dihydrochloride*, m.p. 185°; *chloroplatinate*). The former is reduced by Na and EtOH to the corresponding alcohol (I), but by H_2–Pt to a *stereoisomeride* of (I), m.p. 105—106° (*dithiocarbamate*, m.p. 155°; *picrate*, m.p. 150°; *chloroplatinate*, decomp. 225°); from the latter both (II) and its *stereoisomeride*, m.p. 160—161° (*picrate*, m.p. 180°), are formed by either method, Na and EtOH giving mainly (II), and Pt–H_2 mainly its stereoisomeride. H. A. P.

Syntheses of 2-iminazolone-4-carboxylic acid and 2-iminazolone. G. E. HILBERT (J. Amer. Chem. Soc., 1932, **54**, 3413—3419).—Anhyd. tartaric acid is added to oleum (13% SO_3) below 10° and the mixture treated with $CO(NH_2)_2$ at 80°, whereby 2-*iminazolone-4-carboxylic acid* (I), m.p. 261° (decomp.) (*Et* ester, m.p. 255°; 1 : 3-*Me*$_2$ derivative, m.p. 229—230° (decomp.), decarboxylated to 1 : 3-dimethyl-2-iminazolone), results. (I) reduces Tollens' reagent and Ag_2O in aq. NH_3, and is oxidised (CrO_3) to parabanic acid. (I) and Ac_2O give a *compound*, $C_{12}H_8O_6N_4$ (?), not melted at 300°, hydrolysed by KOH to a *salt*, $C_8H_2O_4N_4K_2$. (I) heated at 220°/2 mm. for 6 hr. gives 2-iminazolone, decomp. 250—251°

(1 : 3-Ac_2 derivative, m.p. 105—106°), which is probably identical with the "*isoiminazolone*" of Fenton and Wilks (J.C.S., 1909, **95**, 1329).

C. J. W. (*b*)

NN'-Substituted pyrimidine and purine derivatives. IV. 5-Substitution products of 3-phenyl-1-methylbarbituric acid. B. HEPNER and S. FRENKENBERG (J. pr. Chem., 1932, [ii], **134**, 249—256). —3-Phenyl-1-methylbarbituric acid reacts with PhCHO, PhN_2Cl, and HNO_2 to give the *CHPh*: derivative, m.p. 102—104°, *3-phenyl-1-methylalloxan-5-phenyl-hydrazone*, m.p. 210—214°, and *3-phenyl-1-methyl-violuric acid* ($+1H_2O$), m.p. 91° (decomp.), respectively. The last-named is reduced by Zn and HCO_2H (*d* 1·22) to *5-formamido-3-phenyl-1-methylbarbituric acid*, m.p. 248° (decomp.). The 5-bromo-5-alkyl derivatives of phenylmethylbarbituric acid, prepared by bromination in $CHCl_3$ (*5-bromo-3-phenyl-1-methyl-*, m.p. 161°, *5-bromo-3-phenyl-1-methyl-5-n-propyl-*, m.p. 89°, and *-5-iso*propyl-, m.p. 95°, *-barbituric acids*) are converted by aq. alkalis, NH_3, or amines into hydantoin derivatives with elimination of HBr and CO_2: *N-phenyl-N'-methyl-5-isopropylhydantoin*, m.p. 170° (*Br*-derivative, m.p. 127°, stable to alkalis), is thus prepared. The *dibromides*, m.p. 118—120° and 108°, respectively, of 3-phenyl-5-allyl-1-methyl-5-*n*-propyl-, and -5-*iso*propyl-barbituric acid, and the *tetrabromide*, m.p. 168°, of 3-phenyl-5 : 5-diallyl-1-methylbarbituric acid are described. *N'-*Phenyl-*N'-*methylcarbamide is conveniently prepared by de-sulphurisation of the thiocarbamide with H_2O_2 and the calc. quantity of NaOH. H. A. P.

Gluciminazole and its thiol. H. PAULY and E. LUDWIG (Z. physiol. Chem., 1932, **209**, 247—248).— Gluciminazole (A., 1922, i, 953) forms crystals ($+2\frac{1}{2}H_2O$), m.p. 120°, $[\alpha]_D^{20}$ —19·6°. The corresponding thiol has m.p. 205° (temp. raised 1° in 10 sec.). J. H. B.

Colouring matters of bacteria. II. Chlororaphin and "xanthoraphin," a contribution to the chemistry of quinhydrones. F. KÖGL and B. TÖNNIS (Annalen, 1932, **497**, 265—289).—The identity of chlororaphin (I), m.p. 228—229° (in N_2), with a quinhydrone-like complex of mol. proportions of phenazine-1-carboxylamide (II) and dihydrophenazine-1-carboxylamide (III) is confirmed (cf. A., 1930, 929). Zerevitinov determinations of active H give the following vals.: (I) 3, (II) 1, (III) variable results, phenazine 0, dihydrophenazine 2; the val. for (I) indicates that (III) possesses an unsym. structure (cf. *loc. cit.*). o-$C_6H_4Br\cdot NO_2$, 3 : 4-$(NH_2)_2\cdot C_6H_3\cdot CO_2H$, Na_2CO_3, and CuCl in amyl alcohol and N_2 at 185—190° give (probably) a *mixture*, m.p. 228—229°, of 4-amino-3-*o*-nitroanilino- and 3-amino-4-*o*-nitroanilino-benzoic acids, which when reduced ($SnCl_2$, conc. HCl, AcOH) and then oxidised (H_2O_2) affords *phenazine-2-carboxylic acid*, m.p. 292—293° (*amide*, m.p. 312°, which forms a green "quinhydrone," chars at 240°, with its H_2-derivative).

[With H. J. GROENEWEGEN.] "Xanthoraphin," the H_2O-sol. intermediate in the production of (I), is identical with oxychlororaphin [*i.e.* (II)] (cf. *loc. cit.*). Addition of phenazine-1-carboxylic acid to the culture solution (asparagine, glycerol, $MgSO_4$, Na

phosphate, $CaCl_2$, and $FeSO_4$ in H_2O) causes approx. twelve- and five-fold increases in the amount of (II) after 4 and 10 days, respectively; the use of K phenazine-1-carboxylate leads to an approx. eleven-fold increase of (II) after 4 days and about 71% of the salt is consumed. KOBz has little effect, K nicotinate causes decreases in the amount of (II) and the wt. of the bacteria (*B. chlororaphis*), but K picolinate increases the amount of (II) by 387% and the wt. of the bacteria by 46% [whilst picolinic acid (51%) is recovered and 3% of picolinamide is formed]. The amount of (II) is doubled by addition of o-$C_6H_4(OH)_2$ and pyrocatechol-o-carboxylic acid. H. B.

Dyes derived from phenanthraquinone : fluorenophenanthrazines. P. C. DUTTA, D. PRASAD, and S. C. DE (J. Indian Chem. Soc., 1932, **9**, 211—213).—The following are prepared from 1 : 2-diaminofluorene and the appropriate phenanthraquinone (the colour given is the shade on wool) : *fluoreno-phenanthrazine*, m.p. 279—280° (yellow) ; *-2-* (this and the following compounds have m.p. above 290°) (chocolate-brown) and -4-*nitro-* (deep brown), -2 : 7- (yellow) and -4 : 5-*dinitro-* (chocolate), -2-*bromo-* (brown), -2- (chocolate-brown) and -4-*amino-* (deep brown), -2 : 7-*diamino-* (yellowish-brown), -2- (chocolate) and -4-*hydroxy-* (greenish-brown), and -2 : 7-*dihydroxy-phenanthrazines* (greenish-brown). The compounds are pptd. unchanged from their deep blue solutions in conc. H_2SO_4 by H_2O; they possess deeper shades than the corresponding phenanthra-phenazines and -naphthazines. H. B

Prodigiosin, the red pigment of *Bacillus prodigiosus*. II. F. WREDE (Z. physiol. Chem., 1932, **210**, 125—128; cf. A., 1929, 1469).—Analyses of prodigiosin and of its perchlorate confirm the formula $C_{20}H_{25}ON_3$ It contains one OMe group and 2 active H atoms [Zn salt, $(C_{20}H_{21}ON_3)_2Zn$, m.p. 176°] and resembles a dipyrrylmethene. J. H. B.

Ring structure of guanosine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1932, **97**, 491—495).—Guanosine hydrate, NaOAc, and boiling Ac_2O give triacetylguanosine, m.p. 224—225°, which with Me_2SO_4 and NaOH in aq. $COMe_2$ affords *trimethyl-N-methylguanosine* (*hydrochloride*, amorphous, decomp. 98°). This with 4% HCl (85°; 8 hr.) gives 2 : 3 : 5-trimethylribose, oxidised by hot, conc. HNO_3 to *i*-dimethoxysuccinic acid. Guanosine is, therefore, a ribofuranoside :

$$\text{NH—CO-C·N}{\scriptstyle >}\text{CH—CH·(CH·OH)}_2\text{·CH·CH}_2\text{·OH}$$
$$\dot{\text{C}}(\text{NH}_2)\text{:N·C·N} \quad \underline{\quad\quad\text{O}\quad\quad}$$

R. S. C.

Tetrazole derivatives. R. STOLLÉ [with K. EHRMANN, D. RIEDER, H. WILLE, H. WINTER, and F. HENKE-STARK] (J. pr. Chem., 1932, [ii], **134**, 282—309; cf. A., 1922, i, 689).—Interaction of $NHMe\cdot CS\cdot NH_2$ with Pb carbonate and NaN_3 in EtOH in CO_2 gives 5-amino-1-methyltetrazole, m.p. 222° (*Ac*, m.p. 164°, *CHPh*:, m.p. 157°, and N-*NO-*, explodes 177°, -derivatives). It is converted by $Ca(OCl)_2$ in warm H_2O into 1 : 1'-*dimethyl-5 : 5'-azotetrazole*, m.p. 182° (decomp.), which is reduced by H_2S in faintly acid solution to the *hydrazo-*compound ($+1H_2O$), m.p. 158° (decomp.). *5-Amino-1-phenyltetrazole* [*hydrochloride*, m.p. 155—165° (de-

4 A

comp.); $+AgNO_3$, m.p. 183° (decomp.); $CHPh$:, m.p. 119°, N-$(CH_2Ph)_2$, m.p. 107°, and N-NPh:N, decomp. 130°, derivatives], is similarly formed from NHPh·CS·NH_2, and converted into 1 : 1'-*diphenyl*-5 : 5'-*azo*-, m.p. 228° (decomp.), and -5 : 5'-*hydrazo-tetrazole* ($+2EtOH$), m.p. 190° (decomp.) (Ac_2 derivative, m.p. 195°). Its N-NO-derivative (Ag salt, decomp. 224°) is decomposed to 5-hydroxy-1-phenyl-tetrazole (I) by hot aq. NaOH, and reduced by Zn and 10% aq. AcOH or by Na–Hg to 5-*hydrazino*-1-*phenyltetrazole*, m.p. 125° (decomp.) [$CHPh$:, m.p. 205°, and CMe_2:, m.p. 146° (decomp.), derivatives], which is also the product of interaction of (II) (below) with N_2H_4,H_2O, and is converted by HNO_2 into 5-*azido*-1-*phenyltetrazole*, m.p. 99° [hydrolysed by NaOH in aq. EtOH to (I)]. 5-*Chloro*-1-*phenyltetrazole*, m.p. 124°, is prepared from the 5-NH_2-compound with HNO_2 in warm HCl (Cu is beneficial), or from (I) and $POCl_3$ at the b.p. The 5-*Br*-compound (II), m.p. 151°, is prepared similarly, and also by bromin-ation of 1-phenyltetrazole (accompanied by a by-product, m.p. 225°, when Fe is used as catalyst) or (in H_2O) of 5-thiol-1-phenyltetrazole or the correspond-ing disulphide, and is hydrolysed to (I) by conc. aq. KOH. 5-Phenylhydrazino-1-phenyltetrazole (*loc. cit.*), prepared from (II) and NHPh·NH_2, is oxidised by HgO in xylene to 5-*benzeneazo*-1-*phenyltetrazole*, m.p. 168°. 5-*Allylamino*-1-*phenyltetrazole*, m.p. 108°, is prepared from NHPh·CS·NH·C_3H_5 by the general method, or from (II) and allylamine at 100°. p-*Chlorophenylthiocarbamide*, m.p. 183°, prepared by heating $C_6H_4Cl·NH_2,HSCN$ at 100°, is converted by NaN_3 and PbO into 5-*amino*-p-*chlorophenyltetrazole*, m.p. 213° (decomp.).

The following are prepared by similar methods : 1 : 1'-*bis*-p-*chlorophenyl*-5 : 5'-*azotetrazole*, m.p. 228° (decomp.); 5-*amino*-m-*chlorophenyl*-, m.p. 173° (de-comp.); 5-*amino*-p-*aminophenyl*-, m.p. 200° (decomp.); 5-*amino*-o-*anisyl*-, m.p. 172°; 1 : 1'-*bis*-o-*anisyl*-5 : 5'-*azo*-, m.p. 190° (decomp.); 5-*amino*-1-p-*phenetyl*-, m.p. 197° (*hydrochloride*, decomp. 190°; Ac_2, m.p. 145°, and NO-, decomp. 117°, derivatives); 1-p-*phenetyl*-5-*hydrazino*-, m.p. 158° (decomp.) (*hydro-chloride*, decomp. 180°; *sulphate*; $CHPh$: derivative, m.p. 171°); 1-p-*phenetyl*-5-*azido*-, m.p. 72°; 5-*chloro*-1-p-*phenetyl*-, m.p. 99°; 5-*hydroxy*-1-p-*phenetyl*-, m.p. 168°; 1 : 1'-*bis*-p-*phenetyl*-5 : 5'-*azo*-, m.p. 223° (decomp.) (converted by O_2 or H_2O_2 in warm aq.-alcoholic NaOH into 5-amino- and 5-hydroxy-1-p-phenetyltetrazoles); 1 : 1'-*bis*-p-*phenetyl*-5 : 5'-*hydrazo*- ($+2EtOH$), m.p. 167° (decomp.); 5-p-*phenetylamino*-1-p-*phenetyl*-, m.p. 197° (from the thio-carbamide); 5-*amino*-1-m-*xylyl*-, m.p. 198°; 5-*amino*-1-α-*naphthyl*-, m.p. 194° (Ac derivative, m.p. 214°); 1 : 1'-*bis*-α-*naphthyl*-5 : 5'-*azo*-, m.p. 180° (decomp.) (stable to H_2O_2 in AcOH); 5-*amino*-1-β-*naphthyl*-, m.p. 193°; and 1 : 1'-*bis*-β-*naphthyl*-5 : 5'-*azotetrazole*, decomp. 204°. The product of interaction of 1-phenyltetrazole and MgMeI gives with BzCl, not the expected 5-Bz derivative, but benzoylphenyl-cyanamide, a fission product. H. A. P.

Oxidation of uric acid by iodine. J. MORE (J. Pharm. Chim., 1932, [viii], **15**, 545—550).—When uric acid is oxidised by aq. I containing $Na_2B_4O_7$

and NH_4 salts, an unstable compound, $C_4H_{10}O_3N_6$ is formed, readily decomposing into NH_4 oxalurate. A. L.

Acetylation of uric acid [and methyl deriv-atives]. H. BILTZ and H. PARDON (J. pr. Chem., 1932, [ii], **134**, 310—334).—Acetylation of methyluric acids with hot Ac_2O occurs in position 7 if this is free; an 8-acetoxyxanthine derivative is formed if this is substituted, but either position 3 or 9 is free, otherwise no action takes place. Thus 1 : 3 : 9-trimethyluric acid gives the 7-Ac derivative (I), dimorphic, m.p. 235°, whilst the three isomeric trimethyluric acids are unaffected. Similarly, 3-methyl- and 1 : 3-dimethyl-uric acids give 7-Ac derivatives, m.p. 300° (decomp.), and 304° (decomp.), respectively, the structure of which is confirmed by their methylation by CH_2N_2 (carefully freed from H_2O and MeOH) to (I).

9-Methyluric acid is conveniently prepared by action of Me_2SO_4 and alkali on uric acid and separ-ation of the mixed 3- and 9-Me derivatives by the usual means. With Ac_2O it gives the 7-Ac derivative, slow decomp. >300°, converted quantitatively by pure CH_2N_2 into 6 : 8-*dihydroxy*-2-*methoxy*-7-*acetyl*-1 : 9-*dimethylpurine* (II), m.p. 150°; this on heating at 180° isomerises to (I), and on hydrolysis with HCl in EtOH at the b.p. gives 6 : 8-*dihydroxy*-2-*methoxy*-1 : 9-*dimethylpurine*, m.p. 275°, which, when heated above its m.p., similarly gives 1 : 3 : 9-tri-methyluric acid among other products. 7-*Acetyl*-1 : 9-*dimethyluric acid*, m.p. 282° (decomp.), also gives (II) with CH_2N_2.

The Ac derivative of 7-methyluric acid (A., 1921, i, 606) is converted by CH_2N_2 into 8-*acetoxycaffeine* (III), m.p. 135° [re-solidifies and re-melts 340° (de-comp.)], identified by deacetylation by heat or by alcoholic HCl to 1 : 3 : 7-trimethyluric acid; it is therefore 8-*acetoxy*-7-*methylxanthine*. 1 : 7-Dimethyl-uric acid, similarly, gives 8-*acetoxy*-1 : 7-*dimethyl-xanthine*, m.p. 272° (decomp.), which with CH_2N_2 gives (III). Acetylation of 1-methyluric acid gives 8-*acetoxy*-7-*acetyl*-1-*methylxanthine*, decomp. >300°, which on methylation with pure CH_2N_2 gives 8-*acetoxy*-7-*acetyl*-1 : 3-*dimethylxanthine*, m.p. 125° (identity confirmed by alkaline hydrolysis to 1 : 3-dimethyluric acid); CH_2N_2 in presence of MeOH, however, removes the 7-Ac group and gives (I), whilst in presence of piperidine this group is replaced by Me and 8-methoxycaffeine, m.p. 176°, is produced. Uric acid is slowly converted by 2000 parts of Ac_2O at 100° into 8-*acetoxy*-7-*acetylxanthine*, from which the OAc group is displaced by cold H_2O, and 7-*acetyluric acid*; the former gives (I) with CH_2N_2. Methylation of acetyl-3 : 9-dimethyluric acid (A., 1921, i, 614) with Me_2SO_4 and NaOH (CH_2N_2 is without action) gives a mixture of 3 : 9-dimethyl-, 3 : 7 : 9-trimethyl-, and tetramethyl-uric acids, and thus affords no evidence of structure (cf. following abstract). H. A. P.

Reactions of 7-acetyl-3 : 9-dimethyluric acid H. BILTZ and H. PARDON (J. pr. Chem., 1932, [ii], **134**, 335—352).—Chlorination of 7-acetyl-3 : 9-di-methyluric acid (I) in $CHCl_3$ gives 4-*chloro*-3 : 9-

dimethyl-$\Delta^{5:7}$-isouric acid (II), m.p. 175° (decomp., sinters at 80°), but in pure, dry AcOH 4-chloro-5-acetoxy-7-acetyl-3 : 9-dimethyl-4 : 5-dihydrouric acid (III), m.p. 171° (decomp.) (previously described as the 1-Ac compound; cf. A., 1921, i, 609), is formed, whilst from the mother-liquors the corresponding 5-OH-compound (IV) is slowly pptd. on addition of H_2O. (IV) is also formed by chlorination in wet AcOH or by hydrolysis of (III); it is unaffected by cold H_2O, but at the b.p., or with 30% aq. AcOH or NH_3 in boiling EtOH gives 1 : 7-dimethylspiro-dihydantoin, m.p. 265° ("4-hydroxy-3 : 9-dimethyl-$\Delta^{5:7}$-isouric acid," loc. cit.); it is stable to EtOH, not reducible to 3 : 9-dimethyluric acid (V), and, unlike the corresponding 3 : 7-Me_2 compound, is completely decomposed by NaOEt. With warm Ac_2O in AcOH it gives a Cl-free compound, m.p. 202°. (III) liberates I from HI with formation of (V), and is converted by warm EtOH into 3 : 9-dimethyluric acid glycol monoethyl ether, m.p. 174°; with CH_2N_2 it gives 4-chloro-5-acetoxy-7-acetyl-1 : 3 : 9-trimethyldihydrouric acid (VI), m.p. 185° (decomp.), the structure of which, and, therefore, of (I) also, is proved by its formation by chlorination of 7-acetyl-1 : 3 : 9-trimethyluric acid in Ac_2O. Hydrolysis of (VI) with warm H_2O gives 1-acetylisoapocaffeine, and reduction with HI in AcOH gives 1 : 3 : 9-trimethyluric acid.

Methylation of (IV) with CH_2N_2 gives the 5-Me ether, m.p. 143°, hydrolysed by conc. HCl at room temp. to 7-acetyl-3 : 9-dimethyluric acid glycol mono-methyl ether, m.p. 205° (decomp.), which is further hydrolysed by NH_3 in EtOH to the Ac-free ether, m.p. 214°. Replacement of the 4-Cl group of (IV) occurs on treatment with amines in EtOH at room temp.; at the b.p., or where interaction is vigorous, simultaneous removal of the 7-Ac group occurs. 5-Hydroxy-4-piperidyl-, m.p. 208° [hydrochloride, m.p. 200° (decomp.); chloroaurate, m.p. 174° (decomp.); 7-Ac derivative, m.p. 198°], 5-hydroxy-4-anilino-7-acetyl-, m.p. 182°, 5-hydroxy-4-methylamino-, m.p. 186° [picrate, m.p. 186° (decomp.)], and 5-hydroxy-4-amino-7-acetyl-3 : 9-dimethyl-4 : 5-dihydrouric acid, m.p. 218° [picrate, m.p. 298° (decomp.)] (not hydrolysed by NH_3 in EtOH or by HCl), are thus prepared.　　H. A. P.

Chlorophyll. XXIII. Synthesis of phylloerythrin. Conversion of phæoporphyrin a_5 into phæoporphyrin a_7. H. Fischer and J. Riedmair (Annalen, 1932, 497, 181—193; cf. this vol., 625).—Deoxophylloerythrin (I) (improved prep. given; cf. A., 1930, 932, where it is termed isophæoporphyrin a_3) in conc. H_2SO_4 treated with oleum (50% SO_3) containing S, gives about 10% of phylloerythrin (II) (Me ester, m.p. 264°), identical with the natural product. (I) is oxidised by CrO_3–AcOH to phylloporphyrin (III) and by K_2CrO_7–conc. H_2SO_4 to (III) and a trace of (II). Treatment of phæoporphyrin a_5 with oleum-S [as for (I)] gives phæoporphyrin a_7; ring fission accompanies oxidation.　　H. B.

Constitution of bile pigments. VIII. Synthesis of a coprobilirubin and work preliminary to a bilirubin synthesis. H. Fischer and E. Adler (Z. physiol. Chem., 1932, 210, 139—167;

cf. this vol., 627).—5-Bromo-3 : 4'-di-β-carboxyethyl-4 : 3' : 5'-trimethylpyrromethene hydrobromide when heated with KOAc in AcOH gives 5-hydroxy-3 : 4'-di-β-carboxyethyl-4 : 3' : 5'-trimethylpyrromethene (I), m.p. 265°, and coprobilirubin (II), decomp. 292° (Me_4 ester dihydrochloride, m.p. 199—200°; Cu salt, m.p. 300°). Treatment of (I) with Br in AcOH affords an acid (III), $C_{18}H_{20}O_5N_2$, m.p. 275° (Me_2 ester hydrochloride, m.p. 239—240°; Me_2 ester, m.p. 243°). Fusion of (III) with resorcinol had no effect, but (II) gave 5-hydroxy-3 : 4'-di-β-carboxyethyl-4 : 3'-dimethylmethene (IV), m.p. 225°. Treatment of (IV) with CH_2O regenerated (II). Reduction of (II) with HI gave cryptopyrrolecarboxylic acid. Reduction of (IV) or of (I) with Na–Hg gave leuco-derivatives. Reduction of 5-hydroxy-4 : 3' : 5'-trimethyl-3 : 4'-diethylpyrromethene with HI gave the corresponding methane (V), m.p. 149°. Fusion of the blue stage (VI) (Cu salt) of ætiomesobilirubin with resorcinol afforded 5-hydroxy-4 : 3'-dimethyl-3 : 4'-diethylpyrromethene (VII), m.p. 197°, which again gave ætiomesobilirubin with CH_2O–HCl. Gentle reduction of (VI) with HI afforded the methane (V) and the methane, m.p. 115°, corresponding with (VII).

The brominated acetylpyrromethene (VIII) (A., 1924, i, 80) with NaOAc in AcOH exchanges one Br for OH, giving a product (IX), $C_{14}H_{15}O_2N_2Br_3$, m.p. not below 300°. With Zn dust–AcOH (IX) gives a product, $C_{14}H_{15}O_2N_2Br$, m.p. 297° (decomp.). Treatment of Et α-methyl-lævulate with NH_3 in EtOH gave a substance, m.p. 245—260°, probably bis-5-hydroxy-2 : 4-dimethylpyrrole. Mesobilirubin forms a Cu salt. SO_2Cl_2 converts 3-acetyl-5-carbethoxy-2 : 4-dimethylpyrrole (X) into 3-acetyl-5-carbethoxy-4-methyl-2-chloromethylpyrrole (XI), m.p. 119°. In boiling H_2O, (XI) gives the corresponding 2-hydroxymethyl derivative, m.p. 123°, and 3 : 3'-diacetyl-5 : 5'-dicarbethoxy-4 : 4'-dimethylpyrromethane, m.p. 200°. With EtOH, (XI) gives the corresponding 2-ethoxymethyl derivative, m.p. 92°. When warmed with NH_2Ph (XI) affords a substance, $C_{17}H_{18}O_3N_2$, m.p. 204—205°. With 3 mols. of SO_2Cl_2 (X) yields 3-acetyl-5-carbethoxy-4-methyl-2-dichloromethylpyrrole (XII), m.p. 158°, which in hot H_2O gives 2-formyl-3-acetyl-5-carbethoxy-4-methylpyrrole (XIII), m.p. 103° (dioxime, m.p. 193°). With hydrazine hydrate, (XIII) affords a pyridazine derivative (hydrazide in position 5). With 4 mol. of SO_2Cl_2, (X) gave no cryst. Cl-derivative, but on boiling with EtOH there was obtained probably 3 : 3'-dichloro-5 : 5'-dicarbethoxy-4 : 4'-dimethylpyrromethene (XIV), m.p. 193°. With Br and (X) a product, m.p. 229° (decomp.), was obtained, possibly the analogue of the product formed with 4 mols. of SO_2Cl_2. Bromination of (XII) in AcOH gave a substance, $C_9H_{10}O_2NCl_2Br$, m.p. 112°, which when boiled with EtOH gave the product, $C_{11}H_{12}O_3NBr$, m.p. 108—109°.

Condensation of (XI) with cryptopyrrole afforded a product, $C_{19}H_{25}O_2N_2Cl$, decomp. at 282°, with crypto-pyrrolecarboxylic acid, a product, $C_{22}H_{31}O_4N_2Cl$, decomp. at 200°, and with opsopyrrole a product, $C_{18}H_{23}O_2N_2Cl$, m.p. 337° (decomp.). The last is hydrolysed by NaOH, yielding a substance, $C_{16}H_{19}O_2N_2Cl$.　　J. H. B.

Fluorescence spectra of bilipurpurin. C. DHÉRÉ (Compt. rend., 1932, **195**, 336—338).—By crushing the crystals of bilipurpurin Me ether against the inside of a test-tube dark red rays are visible. The fluorescence spectrum of bilipurpurin in pyridine or $CHCl_3$ resembles that of protoporphyrin. The spectrum in CS_2, and the effect of alkalis, EtOH, and AcOH on it, are described. H. D.

Acetylcarnitine. R. KRIMBERG and W. WITTANDT (Biochem. Z., 1932, **251**, 229—234; cf. A., 1927, 1058).—*Acetylcarnitine*, $C_7H_{14}O_3NAc$, m.p. 145° (decomp.), $[\alpha]_{D}^{23}$ —19·52° [*chloride*, m.p. 181° (decomp.); *chloroaurate*, m.p. 128°; *chloroplatinate*, m.p. 187°], obtained in 70% yield by cold acetylation of *l*-carnitine (from meat extract) and treatment of the chloride so obtained with Ag_2O, yields betaine on oxidation with $Ba(MnO_4)_2$. With $HgCl_2$ acetylcarnitine yields a mixture of cryst. substances. Acetylcarnitine chloride is stable in air. W. McC.

Thiazoles. XVIII. Synthesis of 2-phenylbenzthiazole-5-carboxylic acid and derivatives. M. T. BOGERT and H. G. HUSTED (J. Amer. Chem. Soc., 1932, **54**, 3394—3397).—$o\text{-SH·}C_6H_4\text{·}NH_2,HCl$ is most conveniently prepared from the Zn salt and conc. HCl. The $3\text{-}NO_2$-derivative, m.p. 100—101° (all m.p. are corr.), of $p\text{-}C_6H_4Cl\text{·}CN$ and Na_2S_2 give 86% of *di-2-nitro-4-cyanophenyl disulphide*, chars about 235° and liquefies about 335°, reduced to 2-*amino-4-cyanothiophenol* (I), decomp. about 250°. 2-Anilinobenzthiazole is best prepared from di-*o*-aminophenyl disulphide and PhNCO. 5-*Cyano-phenylbenzthiazole* (II), m.p. 196·6—197·7° (*NO₂*-derivative, m.p. 256°), obtained in 20% yield from the Zn salt of (I) and BzCl or in 30% yield using PhCHO, is hydrolysed by 75% H_2SO_4 at 80° to 23% of the *amide*, m.p. 247·2°, of 2-*phenylbenzthiazole-5-carboxylic acid*, m.p. 273° (*Me* ester, m.p. 171—172°, obtained in 5% yield from the Ag salt and MeI). C. J. W. (*b*)

Aminobenzthiazoles. XIII. Corrected data for the 2-alkylamino-β-naphthathiazole series. G. M. DYSON, R. F. HUNTER, and R. W. MORRIS (J.C.S., 1932, 2282—2283).—The revised m.p. of the *s*-α-naphthylalkylthiocarbamides previously described (A., 1926, 718) are: methyl-, 198°; ethyl-, 121°; *n*-propyl-, 101—102°; *n*-butyl-, 100°; *n*-amyl-, 104°; *iso*amyl-, 95°; *n*-heptyl-, 65—66°. The alleged 2-alkylamino-β-naphthathiazoles (A., 1927, 263) obtained by bromination of naphthylalkylthiocarbamides are mixtures containing probably 8-bromo-2-alkylamino-β-naphthathiazoles. Pure 2-alkylamino-β-naphthathiazoles are obtained by refluxing the naphthylalkylthiocarbamides in $CHCl_3$ with slight excess of Br, and have the following m.p.: 2-methyl-, 161°; 2-ethyl-, 107°; 2-*n*-propyl-, 86°; 2-*n*-butyl-, 67°; 2-*iso*butyl-, 70°; 2-*n*-amyl-, 78°; 2-*iso*amyl-, 90°; 2-*n*-hexyl-, 70°; and 2-*n*-heptyl-, 72°. E. E. J. M.

Electrolytic reduction of saccharin. I. Electrolysis in acid and alkaline solutions. M. MATSUI, T. SAWAMURA, and T. ADACHI (Mem. Coll. Sci. Kyōto, 1932, **A**, **15**, 151—155).—Saccharin, suspended in a mixture of EtOH and dil. H_2SO_4, is reduced at a cathode of Pb, Zn, Hg, or Zn–Hg, below 30°, using 5·5 amp. per 70 sq. cm. to a *substance*, $C_{14}H_{12}O_4N_2S_2$, m.p. 141°, regarded as a condensation product of hydroxybenzylsultam and benzylsultam, $SO_2{<}^{C_6H_4}_{NH-}{>}CH\text{·}N{<}^{CH_2}_{SO_2}{>}C_6H_4$ (result not affected by varying c. d. or concn. of H_2SO_4); and at 50° and 1 amp. per 10 sq. cm., to benzylsultam. If the catholyte contains $NHPh\text{·}NH_2$, ψ-*o*-sulphamidobenzaldehydephenylhydrazone is pptd. under the former conditions. In presence of aq. NaOH at 15—18° and 3 amp. per 70 sq. cm., NH_2Bz, Na_2SO_3, NH_3, PhCHO, benzoin, and hydrobenzoin are obtained. D. R. D.

Syntheses and transformations of natural substances under physiological conditions (biogenesis of natural substances). [Introduction.] C. SCHÖPF. **I. Alkaloids of *Angostura* bark. Synthesis of 2-methyl- and 2-*n*-amyl-quinoline under physiological conditions.** C. SCHÖPF and G. LEHMANN. **II. Dehydrogenation of laudanosoline and laudanosoline 3′ : 4′-dimethyl ether.** C. SCHÖPF and K. THIERFELDER (Annalen, 1932, **497**, 1—6, 7—21, 22—46).—[Introduction.] Three types of biosynthesis are differentiated : (*a*) through a highly sp. enzyme action (*e.g.*, starch from CO_2), (*b*) intermediate enzyme action on cell constituents, and (*c*) changes involving no enzyme action. Syntheses of natural substances under conditions of type (*c*) are investigated.

I. $o\text{-}NH_2\text{·}C_6H_4\text{·}CHO$ (*M*/200) and $COMe_2$ (*M*/100) in aq. solution at p_H 12 and 13 at 25° give (after 7 days) 11 and 86%, respectively, of 2-methylquinoline (I), which is not produced below p_H 12 even with more conc. solutions. The aldehyde and Me amyl ketone similarly give (at p_H 13) 98% of 2-*methyl-3-n-butyl-quinoline*, m.p. 61—62° (*picrate*, m.p. 206°) [oxidised (CrO_3–dil. H_2SO_4) to 2-methylquinoline-3-carboxylic acid (II)], whilst 2-phenylquinoline (III) is produced in quant. yield with COPhMe. It is unlikely that (I) and 2-*n*-amylquinoline (IV) [picrate, m.p. 110—111° (lit. 125—127°)] are produced in nature by such condensation; they are probably formed by processes analogous to the following. $o\text{-}NH_2\text{·}C_6H_4\text{·}CHO$ (*M*/200) and $CH_2Ac\text{·}CO_2H$ (*M*/125) at p_H 5—11 and 25° for 8 days give (I), the yield being a max. (66%) at p_H 9; with *M*/50-acid (to overcome self-decomp.) a 90% yield of (I) results after 16 days. Anhydrotris-*o*-aminobenzaldehyde [and no (I)] is produced at p_H 3, whilst (II) is the sole product at p_H 13. (III) and (IV) are similarly formed using $CH_2Bz\text{·}CO_2H$ (95% yield at p_H 9) and hexoylacetic acid (70—75% yield at p_H 7—9), respectively; at p_H 13, 2-phenyl-, m.p. 234° (lit. 230°), and 2-*n*-*amyl-quinoline-3-carboxylic acid*, m.p. 148° [decarboxylated to (IV)], result. The velocity coeff. (*k*) for the reactions with $CH_2Ac\text{·}CO_2H$ at p_H 9, $CH_2Bz\text{·}CO_2H$ at p_H 7—9, and hexoylacetic acid at p_H 7—9 are 0·028, about 0·14, and at least 0·01, respectively; *k* decreases with time owing to self-decomp. of the acids.

II. Treatment of papaverine methiodide with NaOEt and subsequent reduction (H_2, Pt) gives
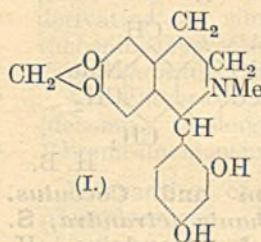
N-*methyl*-3 : 4-*dihydroisopapaverine*, m.p. 129—130°, reduced (H₂, PtO₂, EtOH–AcOH) to *dl*-laudanosine, which is demethylated by 48% HBr to *dl*-laudanosoline (I) (+0·5H₂O), m.p. 192—194° (becoming red) (sinters at 188—190°) [hydrobromide (II) (+3H₂O), m.p. 230—232° (lit. 230°); *Ac*₄ derivative *picrate*, m.p. 178—179° (sinters at 163°), and *picrolonate*, m.p. 224° (sinters at 220°)]. (II) is dehydrogenated by tetrabromo-*o*-benzoquinone in AcOH to 2 : 3 : 11 : 12-*tetrahydroxy* - 8 - *methyldibenzotetrahydro* - *pyrrocolinium hydrobromide* (III) (+H₂O), m.p. 262°, m.p. (anhyd.) 275—276° (decomp.) (cf. Robinson and Sugasawa, this vol., 527), decomposed by aq. NaHCO₃ to the corresponding *phenol-betaine* (IV) (+H₂O), m.p. 251° [*Ac*₄ derivative *hydrobromide*, m.p. 170—172°, and *picrolonate*, m.p. 207° (decomp.) (sinters at 204°)]; a by-product is a *compound*, $(C_6HO_2Br_3)_x$ (+0·5H₂O), m.p. 297—300°. (IV) is also produced from (I) by the action of O₂ and Pt-black in *N*-AcOH, O₂, and Pd–C in dil. Na₂CO₃, and K₃Fe(CN)₆ at p_H 6·9—7·1 (phosphate buffer). (IV) and BzCl in cold pyridine give 2 : 3 : 11 : 12-*tetrabenzoyloxydibenzotetra-hydropyrrocoline*, m.p. 225—227° (sinters at 220°). Methylation (Me₂SO₄, aq. NaOH) of (IV) affords 2 : 3 : 11 : 12-*tetramethoxy* - 8 - *methyldibenzotetrahydro-pyrrocolinium methosulphate* (+2·5H₂O), m.p. 228° (sinters at 115°), degraded (Hofmann) to 5 : 6-di-methoxy - 2 - (3′ : 4′ - dimethoxy - 6′ - vinylphenyl) - 1 - methyldihydroindole, m.p. 128—129° (lit. 124—127°), the methiodide, m.p. 210°, of which is degraded further to 6-dimethylamino-3 : 4 : 3′ : 4′-tetrameth-oxy-6′-vinylstilbene, m.p. 112° (lit. 109—110°), and an *isomeride* (? cis-*form*), m.p. 92° (sinters at 87°). The former stilbene is oxidised by O₃ in 2*N*-H₂SO₄ to *m*-opianic acid, *m*-hemipinic acid, 6-*dimethylaminovera-traldehyde*, m.p. 72—73° [also prepared by methylation (MeI, 20% K₂CO₃) of 6-aminoveratrylideneaniline and subsequent hydrolysis], and 6-*dimethylamino*-6′-*aldehydo*-3 : 4 : 3′ : 4′-*tetramethoxystilbene*, m.p. 144—146°.

Laudanosoline 3′ : 4′-Me₂ ether (V) (+EtOH), m.p. 100—105° (decomp.), m.p. (EtOH-free) 143—145°, prepared by reduction (H₂, PtO₂, EtOH) of protopapaverine, is oxidised by O₂ and Pt in *N*-AcOH to probably the 6 : 7-quinone which is reduced to (V). *dl*-Glaucine heated with aq. HBr gives the hydrobromide, m.p. 238—242° (decomp.), of *dl*-nor-glaucine {*Ac*₄ derivative, m.p. 176—178° [*hydro-bromide*, m.p. 202° (decomp.) (sinters at 191°); *picrolon-ate*, m.p. 210° (sinters at 178°, softens at 185—186°)]}. Successive treatment of corytuberine with 48% HBr and Ac₂O–pyridine gives *tetra-acetylcorytuberoline hydrobromide*, m.p. 230—231° (decomp.) [*picrolonate*, decomp. 209° (sinters at 162°, softens at 180—182°)]. *N*-Methyl-3 : 4-dihydro*iso*papaverine and 48% HBr give 3 : 4-*dihydropapaveroline methobromide* (+2H₂O), sinters at 190—194°, melts to a turbid liquid at 226—228°, and becomes yellow at 280—285° [correspond-ing betaine, m.p. 238—239° (decomp.) (darkens at 200°)]. H. B.

Chemotherapy. III. (Attempts to prepare antimalarials.) Derivatives of cotarnine. G. S. AHLUWALIA, B. D. KOCHHAR, and J. N. RAY (J. Indian Chem. Soc., 1932, 9, 215—223).—Cotarnine (modified prep. given; cf. J.C.S., 1918, 113, 469) and *m*-C₆H₄(OH)₂ in abs. EtOH at 40—45° give *anhydro-cotarninoresorcinol* (1 - 2′ : 4′ - *dihydroxyphenylhydro* - *cotarnine*) (I) (*hydrochloride*, m.p. 240°). The follow-ing are prepared similarly : *anhydrocotarnino-pyro-gallol*, m.p. 211°; -*phloro-glucinol*, m.p. 170° [*hydro-chloride*, m.p. 185° (decomp.)]; -1 - *phenyl* -3- *methylpyrazolone*, m.p. 177°; -3-*methylpyrazol-one*, m.p. 199° (decomp.); -3 : 5-*dimethylpyrazole*, m.p. 140°; -5-*phenyl*-3-*methylpyr-azole*, m.p. 146°; -1 : 5-*di-phenyl*-3-*methylpyrazole*, m.p. 148°; -*o*-, m.p. 126°, and -*p*-*phenetidine*, m.p. 126° (*hydrochloride*, m.p. 239°), and -*o*-, m.p. 134°, and -*p*-*anisidine*, m.p. 124°. The anhydrocotarnino-*p*-nitrotoluene of Hope and Robinson (J.C.S., 1911, 99, 2114) (modified prep. given) is reduced by SnCl₂ and aq. HCl at 28—32° to the *NH₂*-derivative, m.p. 95°, converted by the usual method into *anhydrocotarnino*-p-*cresol*, m.p. 191°.

[With K. S. GRAVAL.] Various pharmacological data for some of the above compounds are given. H. B.

Constitution of isochondodendrine. V. F. FALTIS, S. WRANN, and E. KÜHAS (Annalen, 1932, 497, 69—90).—Experiments on the formation of ethers (Ullmann method) from α-*o*- and -*m*-bromo-phenyl-β-*p*-hydroxyphenylethane derivatives are de-scribed. *m*-C₆H₄Br·CHO and *p*-OMe·C₆H₄·CH₂·CO₂Na in Ac₂O at 100—110° give m-*bromo-α-anisylcinnamic acid*, m.p. 169—170°, reduced and demethylated by red P and HI (b.p. 127°) to β-m-*bromophenyl-α*-p-*hydroxyphenylpropionic acid* (I), m.p. 173—174° (*NH*₄ salt, m.p. 175°; *Me* ester, m.p. 102—103°), also prepared by reduction of m-*bromo-α-p-hydroxy-phenylcinnamic acid*, m.p. 211—212° (O-*Ac* derivative, m.p. 168—169°), and by way of *m*-nitro-, m.p. 187—189°, and *m*-amino-, m.p. 215—218°, -α-*p*-hydroxy-phenylcinnamic acids and β-*m*-aminophenyl-α-*p*-hydroxyphenylpropionic acid, m.p. 196—198°. The K salt of (I) heated with Cu powder gives a non-cryst. Br-containing complex mixture. Anisaldehyde and *o*-C₆H₄Br·CH₂·CO₂Na afford p-*methoxy-α-o-bromo-phenylcinnamic acid*, m.p. 167—168°, reduced (H₂, Pd-black, dil. NaOH) to α-*phenyl-β-anisylpropionic acid*, m.p. 120—121° (*Me* ester, m.p. 59—60°).

Treatment of hemipinic acid in cold 10% KOH with Cl₂ gives 5 : 6-*dichlorohemipinic acid*, m.p. 132—133° (*anhydride*, m.p. 122—123°), and its K H salt; with 2*N*-KOCl in 20% KOH, 5-*chlorohemipinic acid*, (II), m.p. 168—169° (slight decomp.), results. 4(?) : 6-*Dibromo-2 : 3-dimethoxybenzoic acid*, m.p. 154°, and a little 5-*bromohemipinic anhydride*, m.p. 150°, are obtained using KOBr. (II) could not be condensed with p-OH·C₆H₄·CO₂R.

Mol. wt. determinations, mainly by Pirsch's method (this vol., 713), on various derivatives of *iso*chondo-dendrine (III) indicate that (III) is $C_{36}H_{38}O_6N_2$ and not $C_{18}H_{19}O_3N$ (A., 1922, i, 569; 1928, 433); Rast's method gives low results. The structures of (III),

oxyacanthine, berbamine, and phæanthine are discussed; the following is preferred for (III).
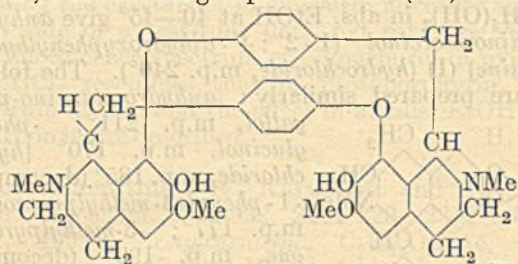

H. B.

Alkaloids of *Sinomenium* and *Cocculus*. XXXIV. Alkaloids of *Stephania tetrandra*, S. Moore. IV. Constitution of tetrandrine. H. KONDO and K. YANO. XXXV. Constitution of trilobine and *isotrilobine*. VI. H. KONDO and M. TOMITA (Annalen, 1932, 497, 90—104, 104—115).— XXXIV. Tetrandrine (I), $C_{38}H_{42}O_6N_2$ [and not $C_{19}H_{23}O_3N$ as previously reported (J. Pharm. Soc. Japan, 1928, 552, 108)] [*dimethiodide* (+2H_2O), m.p. 269° (decomp.)], is converted by the energetic action of HBr into *demethylotetrandrine* (II) (previously designated demethyltetrandrinol), $C_{34}H_{34}O_6N_2,2H_2O$, m.p. 228° [*hydrobromide* (+2H_2O)]. (I) and HBr (d 1·58) at 100° (bath) give (II), a *compound*, $C_{34}H_{30}O_2N_2(OH)_3(OMe)$, m.p. 190—200°, and a *substance*, $C_{34}H_{30}O_3N_2(OMe)_2,2H_2O$, m.p. 130—140°, $[\alpha]_D^{31}$ +204·4° in $CHCl_3$; shorter treatment affords a *compound*, $C_{34}H_{31}O_3N_2\cdot OMe,2H_2O$, m.p. 240°, $[\alpha]_D^{31}$ +238° in $CHCl_3$. α-Tetrandrinemethylmethine, $C_{40}H_{46}O_6N_2$, m.p. 172° [*dimethiodide* (+2H_2O), decomp. 235°], and O_3 in cold, very dil. AcOH give 5 : 4′-dialdehydo-2-methoxydiphenyl ether (III) and a dialdehydotrimethoxybis-(β-dimethylaminoethyl)-diphenyl ether [the dimethiodide, decomp. 250°, is degraded (Hofmann) to a dialdehydotrimethoxy-divinyldiphenyl ether (IV), m.p. 138—140° (*disemi-carbazone*, decomp. 230—245°)], identical with the ethers obtained similarly from the methylmethine from methyloxyacanthine (V) (cf. von Bruchhausen and Gericke, A., 1931, 636). (I) and (V) are isomerides. Further oxidation of (IV) with O_3 in Et_2O affords a *tetracarboxytrimethoxydiphenyl ether*, decomp. 184—220° (Me_2, m.p. 150°, and Me_4, m.p. 152—153°, esters) [also obtained with (III) by ozonolysis of de-N-methyltetrandrine, $C_{36}H_{32}O_6$, m.p. 221°], which with KOH at 300—350° gives *m*-hemipinic acid and an *acid*, $C_{12}H_{14}O(OMe)_3(CO_2H)_3$, m.p. 270—275° ($Me_3$ ester, m.p. 150°). Oxidation of (IV) with O_3 in $CHCl_3$ and subsequent hydrolysis with H_2O affords a hydroxytetra-aldehydodimethoxydiphenyl ether [*diquinoxaline* (+H_2O), m.p. 245—250° (decomp.), from o-$C_6H_4(NH_2)_2$], converted by alkali into a *hydroxydicarboxydimethoxydi(hydroxymethyl)diphenyl ether*, m.p. 160—190°. β-Tetrandrinemethylmethine, $C_{40}H_{46}O_6N_2$, has m.p. 140°.

(I) and (V) contain the same diphenyl ether grouping (see A); they differ in the configuration (alternatives suggested) of the trimethoxydi-(N-methyl-tetrahydro*iso*quinoline) ether residue.

XXXV. Trilobine (VI), m.p. 235°, $[\alpha]_D^{12}$ +296·3° in $CHCl_3$, and *isotrilobine* (VII), m.p. 215°, $[\alpha]_D^8$ +314·8° in $CHCl_3$ [previously designated homotri-
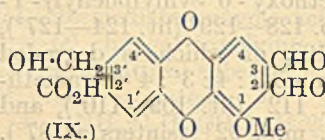
lobine (J. Pharm. Soc. Japan, 1930, 585, 1041)], both $C_{36}H_{36}O_5N_2$ (cf. *loc. cit.*), like methyloxy-

(A.)
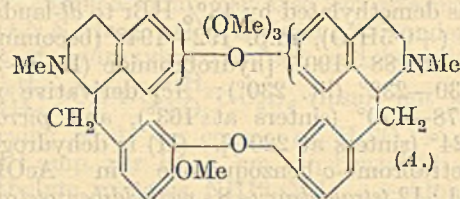
acanthin and tetrandrine, are oxidised by $KMnO_4$ to 5 : 4′-dicarboxy-2-methoxydiphenyl ether. Treatment of (VI) with Me_2SO_4 and alkali gives *trilobine-methylmethine*, $C_{38}H_{40}O_5N_2$, m.p. 106°, oxidised by O_3 in very dil. AcOH to (III) (above) and the *dialdehyde* (VIII), m.p. 124°. The *dimethiodide* (+H_2O), m.p.
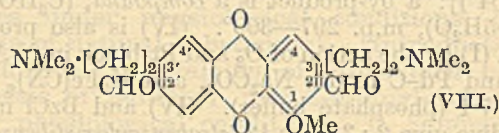

(VIII.)

230° (decomp.), of (VIII) is degraded (Hofmann) to the 3 : 3′-*divinyl* 2 : 2′-*dialdehyde* (+0·5H_2O), m.p. 195° or above 300° (slow heating) [*dioxime* (+0·5H_2O), m.p. 206° (decomp.)] [the anil methiodide of which is degraded (Hofmann) to a phenol], oxidised by O_3 in $CHCl_3$ (and subsequent hydrolysis) to the *dialdehydo-acid* (IX), m.p. 90—91° (decomp.) (*disemicarb-azone*, m.p. > 300°;

(IX.)

azine, m.p. <300°; Ac derivative, m.p. 165—168°), which is converted by 10% KOH into the corresponding (2 : 3-)*phthalide* m.p. 286°, and oxidised by $KMnO_4$ to the 2 : 3 : 2′ : 3′-*tetracarboxylic acid*, m.p. 192—197° (decomp.) (Ag_4 salt; Me_4 ester, m.p. 85°). This with KOH at 250° gives protocatechuic and a trace of gallic (?) acid. *iso*Trilobinemethylmethine, m.p. 115°, α_D^{29} ±0°, is also oxidised by O_3 to (III) and (VIII).

(VI) and (VII) are represented by the following structure; in one case R=OMe and R′=H, whilst in the other R=H and R′=OMe.
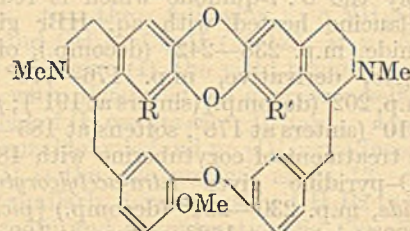
H. B.

Sinomenine and disinomenine. XXXII. Hofmann degradation of 1-bromosinomeninone di-oxime, and bromination of the sinomeninone-furazan derivatives. K. GOTO and S. MITSUI (Bull. Chem. Soc. Japan, 1932, 7, 223—233).—Like sino-meninone dioxime (A., 1931, 1172), the corresponding 1-Br-compound when heated with 16·5% KOH gives 1-*bromosinomeninonefurazan* (I), decomp. 262° [also obtained from sinomeninonefurazan (*loc. cit.*) by the action of Br in AcOH], whilst its *methiodide*, sinters 220°, decomp. 254°, similarly affords 1-*bromo*-

de-N-*methylsinomeninonefurazan* (II, X=Br), decomp. 225° [also obtained, in small yield, by bromination of de-N-methylsinomeninonefurazan]. The oily methiodide of (II) is converted by 16·5% KOH into NMe₃ and 1-*bromodehydro*-l-*thebenone ketone-*(7)-*furazan* (III, X=Br), m.p. 191°. With Br (2 mols.) in AcOH

MeO—Br, HO— (I.) NMe N: O—N

MeO—X, HO— Me₂N— (II.) ¹⁰/₉ N: O—N

MeO—X, CH₂·O— (III.) CH₂ N: O—N

MeO—, HO— Me₂N— (VIII.) H₂ H₂ H₂ H₂
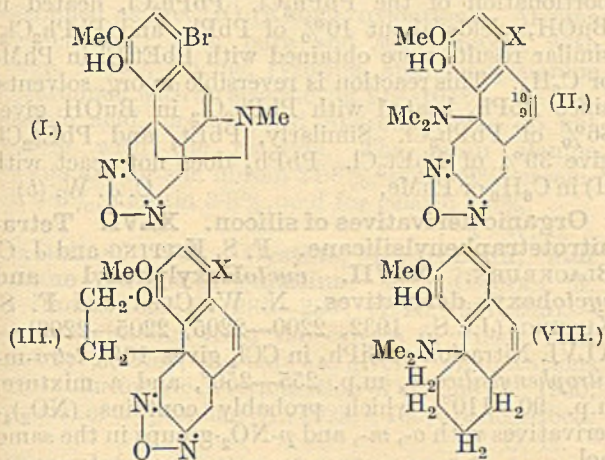
de-N-methylsinomeninonefurazan (II, X=H) gives the 1 : 9(?)-*Br₂*-derivative (IV), sinters 194°, decomp. 212°, bromination occurring also at the 9- or 10-position, whilst with 3 Br₂ is obtained a *perbromide*, decomp. 146°, converted by either COMe₂ or H₂SO₃ into (IV). The oily methiodide (not characterised) of (IV) with 16·5% KOH gives 1 : 9(?)-*dibromodehydro*-l-*thebenone ketone-*(7)-*furazan* (V), m.p. 210—211°, also obtained by bromination of either (VI), (VII), or (III)]. Since (V) is stable towards AgOAc–AcOH or KOH–MeOH, the Br is not in the reduced phenanthrene nucleus. Similar bromination (1 mol.) of dehydro-l-thebenone ketone-(7)-furazan (VI) (loc. cit., as III, X=H) gives its 9-*Br*-derivative (VII), m.p. 152—153°, which is different from (III). Similarly de-N-methyldemethoxydeoxodihydrosinomenine (VIII) with Br (3 mols.) affords the *perbromide* (IX), decomp. 112—113°, of the 1 : 9-*Br₂*-derivative, decomp. 205°, which is obtained by the action of COMe₂. Treatment of dihydrode-N-methylsinomeninone-furazan (as II, X=H and 9 : 10 double linking reduced) with 1, 2, or 3 Br₂ gives only the 1-*Br*-derivative, sinters 207°, decomp. 221—223° [*hydrobromide*, m.p. 259° (decomp.)], the methiodide of which readily affords 1-*bromo*-l-*thebenone ketone*-(7)-*furazan*, m.p. 202—203°, also obtained by bromination of l-thebenone ketone-(7)-furazan (loc. cit.). (II), (IV), (VII), and (IX) exhibit halochromism in conc. H₂SO₄. J. W. B.

Sinomenine. XXXIII. Acetolysis of sinomeninone and 1-bromosinomeninone. K. GOTO, H. SHISHIDO, and K. TAKUBO (Annalen, 1932, 497, 289—296).—Sinomeninone methyl-alcoholate (previously described as sinomenine hydrate) is converted by boiling with Ac₂O and NaOAc into 20% of 4 : 6-diacetoxy-3-methoxyphenanthrene (I) and 10% of *triacetyl*isothebenine (II), m.p. 167° (sinters at 164°). 1-Bromosinomeninone is similarly converted into 25% of 1-bromo-4 : 6-diacetoxy-3-methoxyphenanthrene [reduced catalytically to (I)]

and 20% of 1-*bromotriacetyl*isothebenine (III), m.p. 191° (converted by 2N-MeOH–NaOH at 80° into 7% of a *compound*, C₂₀H₂₀O₄NBr, m.p. 253°). Reduction (H₂, Pd–BaSO₄, PdCl₂, AcOH–NaOAc) of (II) or (III) gives *triacetyl*-9 : 10-*dihydroiso*thebenine (IV), m.p. 182°: the triacetylisothebenine of Schöpf et al. (this vol., 290) is (IV). Thebenine and its Ac₃ derivative are similarly reduced to 9 : 10-dihydrothebenine (*hydrochloride*, m.p. 261°) and *triacetyl*-9 : 10-*dihydrothebenine*, m.p. 120° (decomp.), respectively.

1 : 5-*Dibromosinomeninone hydrobromide*, m.p. 197° (decomp.), undergoes conversion (in EtOH) into 1-bromosinomeneine hydrobromide. H. B.

Interaction of phenylarsines with halogenophenylarsines. F. F. BLICKE and L. D. POWERS (J. Amer. Chem. Soc., 1932, 54, 3353—3360).— Contrary to Steinkopf and Smie (Ber., 1926, 59, B, 1453), AsPhCl₂ and AsHPh₂ give AsPh₂Cl and arseno-benzene. AsPhCl₂ (2 mols.) and AsHPh₂ (4 mols.) give arsenobenzene (1 mol.) and (AsPh₂)₂ (2 mols.); the latter and an equiv. of AsPhCl₂ give AsPh₂Cl and arsenobenzene. No reaction takes place at room temp. between AsPh₂Cl (or AsHPh₂) and arsenobenzene. AsPhI₂ and AsHPh₂ give di-iododiphenyldiarsyl and (AsPh₂)₂; AsPhI₂ and (AsPh₂)₂ give di-iododiphenyldiarsyl and AsPh₂I. AsPh₂Cl and AsHPh₂ in Et₂O afford (AsPh₂)₂ (which is a satisfactory method of prep.); AsPh₂I reacts similarly. AsPhCl₂ (or AsPhI₂) and AsH₂Ph give arsenobenzene; when 3 mols. of AsPhI₂ are used, the product is di-iododiphenyldiarsyl. AsPh₂Cl (or AsPh₂I) (4 mols.) and AsH₂Ph (2 mols.) give arsenobenzene (1 mol.) and (AsPh₂)₂ (2 mols.). C. J. W. (b)

Compounds of arsinic acids and hydrochloric acid. J. PRAT (Compt. rend., 1932, 195, 489—491). —Solubility curves of phenyl-, o-tolyl-, and p-acetamidophenyl-arsinic acids in aq. HCl show the formation of additive *compounds*, which may be isolated using anhyd. conditions : PhAsO₃H₂,HCl ; o-C₇H₇·AsO₃H₂,HCl, p-NHAc·C₆H₄·AsO₃H₂,HCl. F. R. S.

Condensation of 4-halogeno-3-nitrophenyl-arsinic acids with aliphatic amino-compounds and phenols. W. D. MACLAY and C. S. HAMILTON (J. Amer. Chem. Soc., 1932, 54, 3310—3315).—The following 3-*nitro*-4-*alkylaminophenylarsinic acids*, which do not melt or decompose below 250°, were prepared from 4-chloro-3-nitrophenylarsinic acid, NH₂Alk, and aq. NaOH at 125—135° : *Pr, Bu, Bu*β, *amyl*, iso*amyl*, and β-*hydroxyethyl*. Reduction with alkaline Fe(OH)₂ gives the corresponding 3-*amino*-4-*alkylaminophenylarsinic acids*. 2-*Nitro*-4-*arsinophenylglycine*, decomp. 230—235°, is reduced to 2-hydroxy-3-dihydroquinoxaline-7-arsinic acid. 4-Bromo-3-nitrophenylarsinic acid and ArOH in presence of K₂CO₃, Cu powder, and amyl alcohol at 140—150° give 3-*nitro*-4-*aryloxyphenylarsinic acids*, do not melt or decompose below 250°; the following are described : 4-*phenoxy*-, 4-p-*chlorophenoxy*-, 4-p-*tolyloxy*-, 4-p-*carboxyphenoxy*-, 4-o-*tolyloxy*-, 4-o-*carboxyphenoxy*-, and 4-p-*nitrophenoxy*-. 3-*Amino*-4-*phenoxy*-, -4-o- (I) and -p-*carboxyphenoxy*-, -4-p-*chlorophenoxy*-, and -4-o-*tolyloxy*-*phenylarsinic acids* are prepared. The above CO₂H derivatives are prepared by oxidation of the

Me analogues. (I) passes at 200—210°/20 min. into the *lactam*, not melted at 250°. 4-p-*Tolyloxyphenylarsinic acid*, not melted at 250°, prepared in 70% yield from its 3-NH$_2$-derivative through the diazo-reaction, is oxidised to 4-p-*carboxyphenoxyphenylarsinic acid*. Condensation products are not obtained with BuOH, *n*- or *iso*-amyl alcohol, or NH$_2$Ph.

C. J. W. (*b*).

Quinoline compounds containing arsenic. IV. Synthesis of derivatives of quinoline-5- and -8-arsinic acids. V. Synthesis of 7 : 8-triazolquinoline-5-arsinic acid. R. H. SLATER (J.C.S., 1932, 2104—2108, 2196—2197).—IV. 5-*Nitro*-, m.p. 95—96°, obtained by replacement of Br by piperidine, is reduced to 5-*amino-8-piperidinoquinoline*, m.p. 182—183° (*Ac* derivative, m.p. 210—211°), which cannot be converted into the corresponding arsinic acid. 8-*Bromo-5-aminoquinoline*, m.p. 156—157° (*Ac* derivative, m.p. 179—180°), gives 8-*bromoquinoline-5-arsinic acid*, m.p. 234—235° (decomp.), in which the Br is unaffected by piperidine [8-chloro-5-amino-quinoline, m.p. 154—155° (*Ac* derivative, m.p. 172—173°), and 8-*chloroquinoline-5-arsinic acid*, m.p. 226—227° (decomp.), are similarly obtained]. 5-*Chloroquinoline-8-arsinic acid*, m.p. 284—285° (decomp.), prepared from 5-nitro-8-aminoquinoline, with oleum and KNO$_3$ yields the 6-*NO$_2$*-compound, m.p. 233—234° (decomp.), which gives with piperidine 6-*nitro-5-piperidino*-, m.p. 259—260° (decomp.), and with aq. KOH, 6-*nitro-5-hydroxy-quinoline-8-arsinic acid*, m.p. 226—227° (decomp.).

V. 5 : 7-Dinitro- is reduced by NH$_4$SH to 5 : 7-*diamino*-8-*p-toluenesulphonamidoquinoline*, m.p. 207—208° (decomp.), which, after bis-diazotisation and treatment with Na$_3$AsO$_3$, gives a mixture of 7 : 8-*triazolquinoline-5-arsinic acid*, m.p. above 310°, and 7 : 8-*triazolquinoline*, m.p. 256—257°. F. R. S.

Replacement reactions with the diazonium and acetoxymercuri-groups. J. G. KERKHOF (Rec. trav. chim., 1932, 51, 755—760; cf. this vol., 1031).—In the naphthalene series, the normal displacement reactions are shown by the diazonium and Hg·OAc groups, the latter occupying a position intermediately between the CHO and CO$_2$H groups. Mercuration of β-hydroxy-1-naphthoic acid in glacial AcOH at room temp. gives CO$_2$ and 1-acetoxy-mercuri-β-naphthol (I), identified by conversion into 1-bromo- and 1-iodo-β-naphthol. The Hg·OAc group in (I) was not replaced by nitration; HNO$_3$ (*d* 1·4) in EtOH gave the *nitrate* (?), m.p. >260°. Contrary to lit., 3-bromo-4-hydroxy-1-naphthaldehyde is not mercurated by Hg(OAc)$_2$ in AcOH at the b.p.

H. A. P.

Organic lead compounds. III. Reaction of organic lead salts on mercury and lead aryls. P. R. AUSTIN (J. Amer. Chem. Soc., 1932, 54, 3287—3289; cf. A., 1931, 1317).—Pb diaryl dichlorides react in some cases with Hg diaryls to form the mercuric aryl chlorides and a Pb triaryl chloride. PbPh$_2$Cl$_2$ and HgPh$_2$ give 21% of PbPh$_3$Cl and 57% of HgPhCl when heated in pyridine for 10 hr. Pb di-o-tolyl dichloride and HgPh$_2$ afford 38% of HgPhCl, but the expected (I) (below) could not be isolated; some PbPh$_2$Cl$_2$ is isolated, showing that a further

reaction had taken place. *Pb phenyl di-o-tolyl chloride* (I), m.p. 113—114°, is prepared in 70% yield from the bromide using the method previously described (*loc. cit.*). PbPh$_3$Cl did not react with HgPh$_2$ or Hg(CH$_2$Ph)$_2$ when heated in various solvents; a small quantity of PbPh$_4$ resulted from disproportionation of the PbPh$_3$Cl. PbPh$_3$Cl, heated in BuOH, yields about 10% of PbPh$_4$ and PbPh$_2$Cl$_2$; similar results were obtained with PbEt$_3$Cl in PhMe or C$_6$H$_6$. This reaction is reversible in org. solvents, since PbPh$_4$ heated with PbPh$_2$Cl$_2$ in BuOH gives 86% of PbPh$_3$Cl. Similarly, PbEt$_4$ and PbEt$_2$Cl$_2$ give 39% of PbEt$_3$Cl. PbPh$_4$ does not react with (I) in C$_6$H$_6$ or PhMe. C. J. W. (*b*)

Organic derivatives of silicon. XLVI. Tetra-nitrotetraphenylsilicane. F. S. KIPPING and J. C. BLACKBURN. **XLVII.** *cyclo*Hexylphenyl and *cyclo*hexyl derivatives. N. W. CUSA and F. S. KIPPING (J.C.S., 1932, 2200—2205, 2205—2209).—XLVI. Nitration of SiPh$_4$ in CCl$_4$ gives 10% *tetra-m-nitrophenylsilicane*, m.p. 255—256°, and a mixture, m.p. 90—110°, which probably contains (NO$_2$)$_4$-derivatives with o-, m-, and p-NO$_2$-groups in the same mol.

XLVII. Mg *cyclo*hexyl bromide and PhSiCl$_3$ give *dicyclohexylphenylsilicyl chloride*, b.p. 188—192°/2 mm., m.p. 45—48°, forming with aq. alkali *dicyclo-hexylphenylsilicol* (I), m.p. 145—146°, and *cyclo-hexylphenylsilicon dichloride*, b.p. 123—125°/0·5 mm., hydrolysed to *dicyclo*-, m.p. 164—165°, and *cyclo-hexylphenylsilicanediol*, m.p. 123—124° (efferv.), which condenses readily to *trianhydrotriscyclohexylphenyl-silicanediol*, m.p. 117—118°. (I) cannot be converted into the corresponding oxide or a compound containing Si:C, but gives with HNO$_3$ or with Br in AcOH, *trianhydrotrisdicyclohexylsilicanediol*, m.p. 237—239°. F. R. S.

Rearrangement and hydrogenation of metal alkyls. W. H. ZARTMAN and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 3398—3401).—Ni catalyses the reaction, PbPh$_4$ ⟶ Pb + 2Ph$_2$, which occurs at 200°/100 atm. of H$_2$. A similar reaction occurs with Pb tetra-p-tolyl and Pb tetra-n-heptyl and to a very limited extent with ZnBu$_2$. Ni also catalyses the cleavage of ZnBu$_2$ and MgPh$_2$ to C$_4$H$_{10}$ and C$_6$H$_6$, respectively. Sb(Ph)$_3$ is recovered unchanged. C. J. W. (*b*)

Degradation of proteins. III. Proline and hydroxyproline contents of certain proteins. O. FÜRTH and H. MINNIBECK (Biochem. Z., 1932, 250, 18—34).—A method is described which combines those of Van Slyke (determination of non-NH$_2$-N of the phosphotungstic acid filtrate), Dakin (fractional extraction of the protein hydrolysate with butyl and propyl alcohols), and Kapfhammer and Eck (pptn. of proline with CdCl$_2$) which permits the determination (in a few g. of protein) of proline and hydroxyproline. The % of proline and hydroxyproline respectively are for gelatin 9·0 and 14·7, for zein 8·4 and 0·8, and for caseinogen 5·7 and 2·1. The method also gives good results for mixtures of proline and hydroxyproline with zein and caseinogen hydrolysates. P. W. C.

Degradation of proteins. IV. Micro-determination of alanine in protein. O. FÜRTH, R.

SCHOLL, and H. HERRMANN (Biochem. Z., 1932, **251**, 404—417).—After removal from protein hydrolysates of the dicarboxylic acids by pptn. of the Ca salts with EtOH and of the phosphotungstic acid ppt., the residual NH_2-acids are converted by HNO_2 into the OH-acids (alanine to lactic acid). The alanine is then determined as MeCHO ($KMnO_4$ oxidation). Alanine (0·1—0·5 mg.) both pure and when mixed with glycine, valine, leucine, tyrosine, and phenylalanine is determined with an accuracy of 91—104%. Serine, glutamic acid, proline, and hydroxyproline do not interfere with the reaction. The mean alanine contents are for silk fibroin 21·8%, zein 8·9%, casein-ogen 5·3%, keratin 3·8%, and for gelatin 2·5%.

P. W. C.

Glutelins. VII. Cystine, tryptophan, and tyrosine content of glutelins. F. A. CSONKA (J. Biol. Chem., 1932, **97**, 281—286; cf. A., 1931, 245).—Vals. for glutelins from the cereals of wheat, rice, maize, rye, barley, and oats are given. Modifications for the colorimetric determination of cystine (A., 1930, 1604) and of tryptophan (A., 1923, i, 160) are described.

F. O. H.

Micro-determination of carbon and hydrogen in an atmosphere of nitrogen. J. B. NIEDERL and B. WHITMAN (Mikrochem., 1932, **11**, 274—300).—The combustion tube is packed with Ag for removal of halogen, $PbCrO_4$ and CuO for removal of S, Cu for reduction of N oxides, and CuO (no PbO_2), and the combustion is performed in N_2. Two heating burners are used, and a const.-temp. device is replaced by an arrangement of Cu tube and sheet which conducts enough heat from the burner to prevent condensation in the end of the combustion tube. Full details and results are given. The method requires 22 min., compared with 44 min. for the original Pregl method, and 100 c.c. of N_2.

H. F. G.

Determination of carbon and hydrogen by the Pregl method applied to explosive liquids. M. FRERI (Gazzetta, 1932, **62**, 606—609).—Explosive liquids such as the azide $(C_3H_2ON)N_3$ (A., 1931, 1170) and glyceryl nitrate can be analysed for C and H by the Pregl method if the tube is extended and a long charge of CuO included and progressively heated, and if the sample is gradually heated by a Cu sleeve provided with a thermometer.

E. W. W.

Nitrogen not determined by Kjeldahl method. F. SERIO and S. FIANDACA (Biochem. Z., 1932, **250**, 408—413).—The Kjeldahl method determines ureide-, purine-, and guanidine-N quantitatively; gives vals. for pyrrole and pyridine rings and for certain NH_2-acids (lysine) which are 10—27% lower than by the Dumas method, does not determine NO- and NO_2-N, and gives vals. for diabetic urine 15% lower than by Dumas and for normal urine and urine of diabetics after treatment with insulin 2—6% lower.

P. W. C.

Determination of the halogen content of organic compounds. P. T. MILLER and C. B. JOHN-SON (J. Colo.-Wyo. Acad. Sci., 1929, **1**, No. 1, 55).—Reduction with Na in $EtOH$-C_6H_6 is followed by titration with $AgNO_3$ (Mohr).

CH. ABS.

Micro-acetyl determination. A. FRIEDRICH and S. RAPOPORT (Biochem. Z., 1932, **251**, 432—446).—

The apparatus and method depending on hydrolysis with p-toluenesulphonic acid and determination of AcOH are described. The method is applicable to all compounds which give non-volatile hydrolytic products and substances containing NAc groups, since the base unites with the excess of sulphonic acid.

P. W. C.

Determination of propionic acid. J. B. McNAIR (J. Amer. Chem. Soc., 1932, **54**, 3249—3250).—$EtCO_2H$ is converted into $H_2C_2O_4$ when a mixture of $EtCO_2H$ (5·94 c.c. of 0·1N), Na_2CO_3 (1·5 g.), 3·12% $KMnO_4$ (17·5 c.c.), and H_2O (27 c.c.) is heated at 100° (bath)/4 hr.; excess of $KMnO_4$ is removed with EtOH, the MnO_2 filtered off, and C_2O_4'' pptd. as CaC_2O_4 (in aq. AcOH solution). $EtCO_2H$ can thus be determined in presence of HCO_2H and AcOH.

W. T. H. (b)

Characterisation of acetone in the presence of aldehydes (formaldehyde, acetaldehyde, prop-aldehyde). L. KLINC (Bull. Soc. Chim. biol., 1932, **14**, 885—895).—The method previously described (A., 1931, 1273) has been modified to avoid loss of $COMe_2$ during destruction of the aldehyde. The mixture is treated with 5 c.c. of Scott–Wilson reagent, and the mixed ppts. formed are distilled with 5 c.c. of 3% H_2O_2 through boiling 30% KOH solution. Aldehyde is thus oxidised, and the $COMe_2$ is collected in a further 5 c.c. of Scott–Wilson reagent. The descriptions of the turbidities or ppts. given by various amounts of $COMe_2$ with different proportions of the above aldehydes present are tabulated.

A. C.

Sensitivity of reagents in the test for phenols. J. CONTZEN (Chem.-Ztg., 1932, **56**, 683).—Of 11 tests for phenols all were sensitive in a concn. of 10 mg. phenol per c.c., all but one (the $FeCl_3$ test) in 1 mg. per c.c., only 2, Landolt's aq. Br test and Udransky's furfuraldehyde test, in 0·1 mg. per c.c., and none in 0·01 mg. per c.c.

M. S. B.

Micro-acidimetry of nitrophenols using the glass electrode. H. M. PARTRIDGE and J. A. C. BOWLES (Mikrochem., 1932, **11**, 326—336).—A rapid potentiometric method, using a thermionic valve galvanometer (cf. this vol., 1013), is suitable for titrating nitrophenols having an acid ionisation const. $> 10^{-8}$. Probable error using 9-mg. sample about 0·2%.

H. F. G.

Picrolonates of the alkaline-earth metals. P. L. ROBINSON and W. E. SCOTT (Z. anal. Chem., 1932, **88**, 417—431).—From aq. solutions Ca and Sr picrolonates crystallise with $7H_2O$, the Mg salt with $2H_2O$, and the Ba salt with $4H_2O$; the Ca and Sr compounds are isomorphous. From EtOH Ba and Sr picrolonates crystallise with EtOH and are iso-morphous, but the Ca compound is quite distinct in cryst. habit. The saturated aq. solution contains per litre, 1·5 mg. of the Ca, 3 mg. of the Mg, 14 mg. of the Sr, and 25 mg. of the Ba salt; excess of Na picrolonate reduces these vals. by about 60%. The use of Na picrolonate in microchemical tests for the alkaline earths is discussed (cf. A., 1931, 1259).

A. R. P.

Sensitivity of some methods for determining adrenaline. H. SATO (Tôhoku J. Exp. Med., 1932, **18**, 463—474).—The following concns. (mg. per c.c.) can be determined accurately: perfusion of toad

legs 10^{-4}—10^{-3}, perfusion of rabbit's ear 10^{-5}—10^{-4}, rabbit intestine segment 4×10^{-5}—8×10^{-4}, paradoxical cat pupil reaction 10^{-4}—10^{-3}, blood pressure of pithed frog 5×10^{-3}—$2\cdot5\times10^{-2}$, Suto–Kojima colorimetric 4×10^{-4}—5×10^{-3}, Kodama's modification of Folin–Cannon–Denis method 2×10^{-3}—4×10^{-3}. The min. detectable difference and the probable error are given. CH. ABS.

Palladous chloride as a reagent for the detection and determination of purine derivatives and as an oxidising agent. J. M. GULLAND and T. F. MACRAE (J.C.S., 1932, 2231—2236).—$PdCl_2$ with many purines and alkaloids forms almost quantitatively sparingly sol. complexes from which the bases are easily regenerated by the action of Ag in aq. suspension. Pptn. depends on the p_H of the solution. The caffeine and theobromine complexes have the formula R_2PdCl_2. The uses of $PdCl_2$ as an oxidising agent are described. E. E. J. M.

Determination of arsenic in organo-arsenic derivatives. II. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1932, 9, 203—206).—Compounds containing $As^{...}$ are oxidised by warm H_2O_2, any mineral acid produced (e.g., HCl from chloroarsines) is neutralised with $0\cdot1N$-Na_2CO_3, the mixture then treated with excess of KI, and the liberated I (from H_2O_2) removed with $Na_2S_2O_3$. As^v in the resulting solution is then determined as previously described (this vol., 763). The above method can be used as a qual. test for As. H. B.

Biochemistry.

Crystalline hæmoglobin from human blood. Z. ASZÓDI (Biochem. Z., 1932, 252, 212—214).—By means of a method described, up to 4 g. of cryst. hæmoglobin can be obtained from 100 c.c. of the blood. W. McC.

Uniformity of the prosthetic group of hæmoglobins of various sources. J. POLDERMANN (Biochem. Z., 1932, 251, 452—457).—The differences in light absorption (both of intensity and of position of max. and min. absorption bands) of a series of chlorohæmin preps. from the bloods both of different animals of the same kind and of different kinds of animals (horse, ox, pig, dog, cat, man) are never greater than the experimental error, and spectrophotometric investigation of these chlorohæmins gives no evidence in favour of difference of prosthetic groups of these hæmoglobins. P. W. C.

Action of parenterally administered iron on blood formation. W. LINTZEL and T. RADEFF (Biochem. Z., 1932, 250, 519—524).—Repeated subcutaneous injection of small amounts of Na $Fe^{...}$ citrate into rats, accelerates hæmoglobin formation. The substance acts more slowly with parenteral administration than when given by mouth. P. W. C.

Action of manganese and plant ash on growth and on the synthesis of hæmoglobin. J. T. SKINNER, W. H. PETERSON, and H. STEENBOCK (Biochem. Z., 1932, 250, 392—404).—Addition of Mn to a milk diet containing Fe+Cu accelerates considerably the growth of young rats, growth being stimulated equally by $0\cdot0041$ mg. as by $0\cdot25$ mg. Mn per rat per day. The element appears to stimulate appetite. Such addition of Fe, Cu, and Mn is as active as an acid extract of lucerne containing these three elements in equiv. amounts. Mn exerts no influence on the regeneration of hæmoglobin in anæmic rats and the ash of lucerne is not more active in curing alimentary anæmia than is the equiv. amount of Fe and Cu. P. W. C.

Cryptohæmin. E. NEGELEIN (Biochem. Z., 1932, 250, 577).—The cryptoporphyrin reported by the author as formed on shaking the porphyrin of bloodhæmin in HCl solution with air and irradiating (this vol., 763) is more probably an artefact arising during isolation. P. W. C.

Relationship between respiration and the pyrophosphate exchange in bird's erythrocytes. W. A. ENGELHARDT (Biochem. Z., 1932, 251, 343—368).—Decomp. of pyrophosphate occurs under anaërobic conditions in nucleated blood corpuscles, resynthesis taking place under aërobic conditions. Not only is the hydrolysis of pyrophosphate reversed by respiration, but the hydrolytic products themselves increase respiration. Adenylpyrophosphate is a constituent of the co-enzyme complex of respiration. P. W. C.

Calcium content of the red corpuscles of human blood. I. Z. VON GULÁCSY. **II.** S. SCHÖNBERGER (Biochem. Z., 1932, 251, 162—166, 167—172).—The red corpuscles contain only traces of or no Ca. W. McC.

Micro-determination of chloride in plasma and corpuscles of human blood. S. RASZEJA (Bull. Soc. Chim. biol., 1932, 14, 873—884).—Low results in determining small amounts of Cl′ by Volhard's method, due to interaction of AgCl and CNS′, are prevented by centrifuging the AgCl before titrating the excess $AgNO_3$. With the technique described, Cl′ added to plasma is determined within $0\cdot57\%$, and the sum of separately determined plasma- and corpuscular Cl′ ($3\cdot562$ and $1\cdot922$ mg. per c.c., respectively) is only $1\cdot38\%$ below that for whole blood ($2\cdot854$ mg. per c.c.). A val. of $0\cdot711$ is deduced for the ratio corpuscle- : plasma-vol., the ratio of the chloride concns. being $0\cdot54$. The former val. is in agreement with the results of conductivity measurements by Slawinski's method (A., 1929, 1142). The analyses were made at p_H $7\cdot6$—$7\cdot75$ on blood in the fasting state. A. C.

Animal proteases. VIII. Proteolytic enzymes of the white blood-corpuscles of different kinds of animals. H. KLEINMANN and G. SCHARR (Biochem. Z., 1932, 251, 275—328).—The proteinases of aq. and glycerol extracts of horse and rabbit leucocytes were investigated by nephelometric and colorimetric methods, using caseinogen, edestin, gelatin, etc. as substrates. Acid and alkaline glycerol and

acid aq. extracts contain cathepsin and trypsin in approx. equal amounts, whereas alkaline aq. extracts contain chiefly trypsin. By treatment with $CHCl_3$ (48 hr. at 37°) the ereptic activity of the extracts is destroyed, whilst the tryptic activity is unchanged. Separation of erepsin and trypsin is also effected by kaolin adsorption, the residual solution containing almost all the erepsin and the eluate of the adsorbate containing the proteinases, especially trypsin. Extraction for a short time with neutral glycerol gives almost pure cathepsin. Investigation of exudates shows that whereas horse lymphocytes contain only cathepsin, myelocytes contain also trypsin. Rabbit's mono- and poly-nuclear leucocytes contain cathepsin but no trypsin. The proteolytic activity of cathepsin is increased by H_2S and HCN only when gelatin is used as substrate. The trypsin of horse leucocytes cannot be activated by intestinal enterokinase. Glycerol and to a smaller extent aq. extracts contain dipeptidase, the p_H optimum for leucylglycine being 8 and for glycylglycine 7. Autolysis with $CHCl_3$ destroys dipeptidase activity.   P. W. C.

Animal proteases. IX. Proteases in horse and rabbit sera. H. KLEINMANN and G. SCHARR (Biochem. Z., 1932, **252**, 145—184; cf. preceding abstract).—The sera contain cathepsin which probably exists combined with the globulin fraction of the serum-protein, but cannot be activated by shaking with $CHCl_3$, PhMe, or Et_2O. No diminution in the activity of the protease is caused by treating the sera with kaolin, but when caseinogen is the adsorbent a tryptic enzyme is adsorbed. Edestin adsorbs no enzyme from the sera. As regards activation with HCN and H_2S the cathepsin of the sera resembles that from the blood-corpuscles and organs. Enterokinase (from intestinal mucous membrane) has no effect on the activity of the tryptic enzyme. In the sera the cathepsin exists in an active, the trypsin in an inactive, state. Adsorption on caseinogen activates the tryptic enzyme.   W. McC.

Maintenance of a normal plasma-protein concentration in spite of repeated protein loss by bleeding. C. W. BARNETT, R. B. JONES, and R. B. COHN (J. Exp. Med., 1932, **55**, 683—693).—Removal of blood-plasma from dogs, followed by return of the red cells, does not lead to a fall in plasma-protein.   CH. ABS.

Occurrence of β-h-fructosidase in the plasma of horse blood. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1932, **82**, 318—319; cf. A., 1930, 499, 1065).—The plasma of horse blood contains an enzyme inactive towards maltose, but capable of inverting sucrose and converting raffinose into melibiose and fructose, with optimum p_H 4·7. It is therefore β-h-fructosidase, hitherto found only in vegetable organisms.   J. H. L.

Extent of noticeable variation in the amount of diastase in blood and urine (Wohlgemuth) under different physiological conditions. K. GERMER (Hospitalstid., 1931, **74**, 951—959).—The normal diastase content of 24 hr.-urine lies between 16 and 128, and depends but little on sex or age. Normal blood-diastase lies between 8·8 and 22·8; it is somewhat higher in men than in women and is

independent of the time of day and the ordinary mixed diet.   CH. ABS.

Quantitative and reversible reaction of serum with ether and the dependence on temperature. F. SEELICH (Biochem. Z., 1932, **250**, 549—559).—Serum unites with large amounts of Et_2O during shaking, forming a gel from which, on keeping, the Et_2O again separates. The amount of Et_2O so absorbed depends on the pretreatment of the serum.   P. W. C.

Diffusible serum-calcium by high-pressure ultrafiltration. H. O. NICHOLAS (J. Biol. Chem., 1932, **97**, 457—464).—Such filtration through cellophane membranes shows 64% of the total Ca of normal serum to be diffusible. The results at such pressures (150 lb. per sq. in.) are higher but more const. than those obtained at low pressures.   F. O. H.

Organic phosphorus compounds in blood. C. BOMSKOV (Z. physiol. Chem., 1932, **210**, 67—78).—The various P fractions in the blood of man, dog, and rabbit were determined, making use of the step-photometer. The total org. acid-sol. P compounds are esters from which the P can be eliminated by prolonged hydrolysis.   J. H. B.

Determination of bilirubin. E. HERZFELD (Biochem. Z., 1932, **251**, 394—403).—A detailed study of the Van den Bergh reaction for determination of bilirubin in serum is described. The tint obtained in the direct determination is often not comparable with that of the standard Co solution, and even after EtOH pptn. although the tint is comparable the results vary from $\frac{1}{10}$ to $\frac{1}{3}$ of those by other methods.   P. W. C.

Determination of blood-bile acids. I. Method of Aldrich. K. KUSUI (J. Biochem. Japan, 1932, **15**, 399—411).—The method of Aldrich and Bledsoe (A., 1928, 788) was investigated. Adsorption of bile acids occurs during treatment of the filtrate from deproteinised blood with C and $Ba(OH)_2$. Hence the method gives low vals. (viz., 2·56—5·26 mg. per 100 c.c. of normal human blood).   F. O. H.

Determination of blood-glutathione. G. E. WOODWARD and E. G. FRY (J. Biol. Chem., 1932, **97**, 465—482).—Sulphosalicylic acid (I) but not tungstic acid is suitable for deproteinising blood for glutathione determinations. Following the addition of a further quantity of (I) and of KI, the filtrate is titrated against 0·001N-KIO_3. Normal human blood gave 0·025—0·041%, whilst 5 cancer cases gave 0·026—0·036%. Reduction of the filtrate by Zn gave an increase of 0·003—0·011%, probably due to oxidised glutathione. Ergothioneine is the only blood constituent to interfere, giving an error of approx. 0·003% in the actual vals.   F. O. H.

Optical activity of blood filtrates. I. Preparation and investigation of blood filtrates. H. N. NAUMANN (Biochem. Z., 1932, **251**, 266—274).—For the prep. of blood filtrates, neither dialysis nor ultra-filtration can be used without loss of sugar by adsorption, and protein pptn. methods must be relied on. A table summarises the abs. and % errors in the prep. of the filtrates, in polarisation and

determination of sugar by the Hagedorn–Jensen method. Modifications of the method are described and the probable error is reduced to 0·01 c.c. 0·005N-thiosulphate, equiv. to 4% on the normal blood-sugar content.   P. W. C.

Micro-determination of true blood-sugar. N. Doi (J. Biochem. Japan, 1932, **15**, 427—438).—The determination of the reducing val. of 0·2 c.c. of blood by the Hagedorn–Jensen method before and after fermentation by yeast was investigated. Deproteinisation by the Folin–Wu reagent and due regard to the conditions for fermentation are recommended.
F. O. H.

Micro-determination of fructose in blood. H. Steinitz and I. von Riesen (Biochem. Z., 1932, **252**, 201—204).—The fructose in 0·2 c.c. of blood can be determined by the method described.   W. McC.

Influence of proteins, amino-acids, and their derivatives on the regulation of blood-sugar. E. G. Schenck (Arch. exp. Path. Pharm., 1932, **167**, 201—215).—The changes in the blood-sugar of rabbits after ingestion of NH_2-acids, glutathione, peptone, and proteins were determined. Glycine is the NH_2-acid most effective in lowering the blood-sugar, a lowering which summates with that due to simultaneous injection of insulin. Alimentary hyperglycæmia is eliminated by administration of glycine. Valine exhibits the greatest hyperglycæmic activity of the NH_2-acids investigated. Glutathione, which has practically no action on the blood-sugar level, inactivates insulin *in vitro*, but not *in vivo*. A consideration of the correlation of the structure of the substances with their action on the blood-sugar indicates that the sp. action of insulin depends to some extent on its constituent NH_2-acids.
F. O. H.

Effect of intravenous injection of diastase on the blood-sugar in normal and depancreatised animals. H. E. C. Wilson and F. Strieck (Biochem. Z., 1932, **251**, 199—203).—Since extra pure (but not ordinary) diastase has no hypoglycæmic effect when intravenously injected into rabbits, dogs, or depancreatised dogs, it follows that the reduction in blood-sugar produced both by active and by heat-inactivated diastase is caused by admixtures of unknown nature.   W. McC.

Ammonia formation in tortoise blood. II. Formation of a phenolic substance which accompanies the formation of ammonia in hæmolysed tortoise blood. W. Mozolovski and T. Mann (Biochem. Z., 1932, **250**, 487—488).—In the protein-free filtrate of tortoise blood, a substance is present which gives a bluish-green $FeCl_3$ reaction and on making alkaline a red pigment. The NH_3 formation after hæmolysis is attributed to deamination of an aromatic NH_2-acid with the formation of the phenolic substance.   P. W. C.

Nature of antibody reactions. H. Sachs and H. O. Behrens (Biochem. Z., 1932, **250**, 352—375).—Addition of tannin to the cholesterolised ox-heart extracts ordinarily employed in the Wassermann test causes either no or only a fleeting increase of the anti-complement action of tannin. Union with comple-

ment on addition of tannin to EtOH extracts of organs is, however, confirmed, using guinea-pig heart extracts. The reaction with tannin is concerned not with antigenic functions but with the colloidal nature of the carriers of antigenic activity. Storage of extract dilutions at a higher temp. effects some change in the colloidal nature of the carrier, so that under suitable conditions an extremely strong reaction with tannin is obtained. Maturing in this way at 56° is much more effective than at 37°. The combinations of complement with tannin and with antibodies are quite different processes.   P. W. C.

Significance of the structure of antigens for their production and for the specificity of antibodies. H. Erlenmeyer and E. Berger (Biochem. Z., 1932, **252**, 22—36).—Since no As could be detected in horse sera specifically immunised with the antigen obtained from diazotised atoxyl and the sera it is concluded that antibodies are not in any way produced from antigens. It is impossible to distinguish serologically between antigens produced from p-$NH_2 \cdot C_6H_4 \cdot OPh$, p-$NH_2 \cdot C_6H_4 \cdot NHPh$,   or p-$NH_2 \cdot C_6H_4 \cdot CH_2Ph$,   but the antigen from p-$NH_2 \cdot C_6H_4Bz$ can be so differentiated. This shows the importance for serological specificity of the "field" effect of mols.   W. McC.

Distribution of protective principle in different protein fractions of horse serum immunised against snake venom. S. M. K. Mallick and G. C. Maitra (Indian J. Med. Res., 1932, **19**, 951—955).—The active antibody is recovered quantitatively in the pseudoglobulin fraction; the euglobulin and albumin fractions are inactive.   Ch. Abs.

Effect of hyperthermia, acidosis, and alkalosis on the production of agglutinins. J. Davesne and P. Haber (Ann. Inst. Pasteur, 1932, **49**, 220—233).—Increase of hyperthermia induced in rabbits by tetrahydro-β-naphthylamine simultaneously with, and after, the immunisation of the animals coincides with an increase in the amount of agglutinins. Acidosis and alkalosis have no effect on the temp. change produced by the injection of the antigen.   A. L.

Substances involved in the coagulation of the blood of the new-born. II. Effect of ultra-violet radiation and viosterol. III. Effect of withholding protein and fat from the diet. H. N. Sanford, T. H. Gasteyer, and L. Wyat (Amer. J. Dis. Children, 1932, **43**, 566—568, 569—571).—II. The blood-fibrinogen is increased and the antithrombin decreased in both cases.

II. The blood-fibrinogen is decreased.   Ch. Abs.

Chemical nature of heparin. I. Determination of heparin. A. Fischer and A. Schmitz (Z. physiol. Chem., 1932, **210**, 129—133).—Two methods are developed for comparing the heparin content of preps. depending on its power of (a) preventing pptn. of caseinogen solutions and (b) clotting blood, respectively.   J. H. B.

Crystalline myoglobin. I. Crystallisation and purification; mol. wt. A. H. T. Theorell (Biochem. Z., 1932, **252**, 1—7).—Although myoglobin (from horse heart or ox; yield 0·5 g. per kg.) has the same Fe content as has hæmoglobin, there are

important differences between the two pigments. Myoglobin has mol. wt. 35,000 or 17,500, is stable within the p_H range 5·5—13, and has isoelectric point at p_H 6·99. The prep. of the cryst. substance (prisms from horse, plates from ox) is described. W. McC.

Titrimetric fat determination in small amounts of organ. P. KIMMELSTIEL and H. BECKER (Z. physiol. Chem., 1932, **209**, 166—175).— The Kumagawa and Suto method (A., 1908, ii, 331) is modified by direct extraction of the fat with light petroleum. Slightly lower ($1\frac{1}{2}\%$) but more correct vals. are thus obtained. J. H. B.

Preparation of inosic acid. G. EMBDEN (Z. physiol. Chem., 1932, **210**, 194—196).—On keeping liver pulp in distilled H_2O at room temp. adenylic acid is rapidly deaminated; inosic acid accumulates and is readily isolated from the solution. J. H. B.

Skin and the nitroprusside reaction. E. NISHI-MURA (Japan. J. Dermat., 1931, **31**, 1015—1028).— The nitroprusside reaction was practically the same for man, cats, rabbits, guinea-pigs, mice, and frogs. SH-compounds are present in almost all the internal organs. CH. ABS.

Age changes in inorganic constituents of sound human teeth. H. M. LUNDSTROM (Amer. J. Med. Sci., 1931, **182**, 152).—The Mg : Ca and PO_4 : CO_3 ratios increase with age. CH. ABS.

Reaction of mastic in cerebrospinal fluid. L. G. CORDERO (Anal. quím. farm., Chile, 1931, **1**, 105—113).—Colloidal mastic coloured with Sudan III is readily prepared and gives trustworthy results.
CH. ABS.

Gastric secretion. IV. Variations in the chlorine content of gastric juice and their significance. F. HOLLANDER (J. Biol. Chem., 1932, **97**, 585—604).—For pure gastric juice collected from dogs with Pavlov pouches an abs. parallelism exists between the total and neutral Cl' on the one hand and the total acidity on the other. This fact indicates that pure gastric juice is a mixture of a parietal secretion of isotonic HCl containing no fixed base with an alkaline mucous secretion of an isotonic fluid, the principal constituents of which are neutral chlorides and H carbonates. Thus the max. acidity attained by gastric juice under normal conditions is that of a solution of HCl which contains no neutral Cl' and is isotonic with the blood. F. O. H.

Self-protective mechanism of the stomach against the corrosive action of hydrochloric acid. N. HENNING and L. NORPOTH (Arch. exp. Path. Pharm., 1932, **167**, 224—236).—Aq. HCl of concn. up to $0·045\%$ causes a marked corrosion of the mucous lining of the rat's stomach to an extent not exceeded by that due to normal human gastric juice containing 5—6 times this HCl concn.
F. O. H.

Colorimetric determination of hydrogen-ion concentration in milk. A. C. GALLETTI (Arch. Farm. sperim., 1932, **54**, 229—236).—The p_H of milk can be determined rapidly and simply by dialysis into indicator solutions. The non-dialysable portion of the milk does not affect its reaction. R. N. C.

Milk of the American buffalo. F. T. SHUTT (Analyst, 1932, **57**, 454).—Analyses of the milk of *Bison americanus* are given. W. J. B.

Human milk. IX. Variations in composition. B. NIMS, I. G. MACY, M. BROWN, and H. A. HUNSCHER (Amer. J. Dis. Children, 1932, **43**, 828—844).—Variations are independent of diet, activity, climate, and stage of lactation. The fat and total solids are max. at 10 a.m. and decrease until 2 p.m. Total ash, Ca, and P are min. at 6—10 a.m. and max. at 2 p.m. Cl' is highest in the early morning; N is max. at 2 and 6 p.m. CH. ABS.

Dietary of the human mother with respect to the nutrients secreted into breast milk. C. F. SHUKERS, I. C. MACY, B. NIMS, E. DONELSON, and H. A. HUNSCHER (J. Nutrition, 1932, **5**, 127—139).— The intake in food and the output in milk of protein, fat, carbohydrate, Ca, and P for 3 lactating women are recorded and discussed. A. G. P.

Influence of certain balanced rations on chemical and physical properties of milk-fat. O. R. OVERMAN and O. F. GARRETT (J. Agric. Res., 1932, **45**, 51—58).—Cotton-seed, linseed, and soya-bean meals produce slight variations in the physical consts. of the corresponding milk-fats when fed to dairy cows. These are too small to be of practical interest. H. G. R.

Determination of bile acids with the help of the step-photometer. H. SÜLLMANN and L. SCHAUB (Biochem. Z., 1932, **251**, 369—383).— Investigation of the absorption by the step-photo-meter of the colours obtained by carrying out the Pettenkofer reaction with bile acids leads to a method for their determination, the ratio of the concns. of the unknown to a known solution of bile acid being directly as their extinction coeffs. The purification of the bile acid becomes extremely important when the method is adapted for determinations in organs, blood, urine, etc. P. W. C.

Anion-cation studies in liver and gall-bladder bile. I. S. RAVDIN, C. G. JOHNSTON, C. RIEGEL, and J. H. AUSTIN (Amer. J. Med. Sci., 1932, **183**, 148—150).—The hepatic bile of different animals and of the same animal at different times is more variable than serum in its electrolyte content. The base, total anion, Ca, and usually HCO_3' are higher, and Cl' is lower. The bile salt varies from 15·6 to 66 milli-equiv. per litre, and the p_H is 7·1—8·6. Unknown anions account for about 12 milliequiv. per litre. The composition of bile after a period in the gall bladder is the resultant of absorption of H_2O, some bile salts, and much Cl' and HCO_3'. CH. ABS.

Determination of cholesterol in the bile. R. ELMAN and J. B. TAUSSIG (J. Lab. Clin. Med., 1931, **17**, 274—279).—The production of a green colour by non-cholesterol substances is avoided by saponific-ation with KOH before extraction with light petroleum. CH. ABS.

Stalagmometric determination of bile acids in urine. M. TAKEDA, T. OHO, and T. YOSHINARE (J. Biochem. Japan, 1932, **15**, 413—425).—The urine is filtered, the sp. gr. adjusted to 1·010, and

the p_H to 9·0, 7·0, or 4·0. For each reaction the "drop no." is determined by the stalagmometer, the vals. obtained forming a criterion of the amount of bile acids present.   F. O. H.

Is blood-protein amide-nitrogen a source of urinary ammonia? II. T. P. NASH, jun., and E. F. WILLIAMS, jun. (J. Pharm. Exp. Ther., 1932, 45, 487—492).—A reply to criticisms by Bliss (this vol., 635) of previous work by the authors (ibid., 295).   A. L.

Effect of grapes and grape products on urinary acidity. L. G. SAYWELL (J. Nutrition, 1932, 5, 103—120).—Addition of grapes, grape-juice, raisins, etc. to a basal diet resulted in a decrease in NH_3 excreted and a corresponding decrease in total acidity and a rise in p_H (0·8—1·2 units) in the urine. The alkalinity of the ash of the grape is correlated with the physiological reaction. The increased excretion of org. acids is attributed to the presence of incompletely oxidised tartaric acid. Approx. 94% of the ingested org. acids were oxidised.   A. G. P.

Determination of magnesium in urine by the step-photometer. II. C. URBACH (Biochem. Z., 1932, 252, 74—80; cf. A., 1931, 1444).—An improved micro-method is described.   W. McC.

Relation of neutral sulphur content and of "iodic acid value" to the appearance of ether-insoluble phenols in urine. O. FÜRTH, R. SCHOLL, and H. HERRMANN (Biochem. Z., 1932, 251, 148—161; cf. this vol., 186).—The neutral S (total S — total sulphate S) in urine (and in other body-fluids) is best determined iodometrically by a modification of Lang's method (A., 1929, 1500). Increased excretion of neutral S in (pathological) urine is usually accompanied by increased excretion of the phenols which are found in the Mörner and Sjöquist fraction. The "iodic acid val." (Chikano, A., 1929, 474) of this fraction of the urine is probably a measure of the amount of easily oxidised substances, and these are related to polyphenols. In the Mörner and Sjöquist fraction about half of the N is loosely bound and can be eliminated as NH_3 by hydrolysis and almost all of the N can be converted by energetic hydrolysis into free NH_2-groups. Possibly the fraction contains carbamido-acids in addition to NH_2-acids and polypeptides.   W. McC.

Microphotometric method for determination of chlorine. Rapid determination of chlorine in biological media. E. OBERMER and R. MILTON (Biochem. Z., 1932, 251, 329—342).—The method is described and adapted to determination of Cl in urine.   P. W. C.

Causes of errors in investigations of urine. K. BECHER (Pharm. Ztg., 1932, 77, 784—785).—An account is given of the precautions necessary in the collection of urine, and examination of its sediment. Photomicrographs of different types of foreign matter are given.   A. C.

Acid–base balance in sweat. E. H. FISHBERG and W. BIERMAN (J. Biol. Chem., 1932, 97, 433—441).—In diseased man a rise of body temp. to approx. 41° induced by radiothermal treatment causes a loss of sweat almost equal to the blood-vol. The skin exerts a base-sparing function by excreting the sweat at a much lower p_H than that of the plasma and by a part of the excreted lactate being non-ionised. The presence of lactic acid (which possibly functions as a stimulus to the sweat glands) and lactates prevents, by their buffering action, a p_H of < 4 and hence protects the skin from damage.
F. O. H.

Azotæmia. II—IV. R. A. IZZO (Semana méd., 1932, i, 387—398, 522—551, 619—654).—Blood-urea is normally 0·036—0·0398%. The distribution of blood-N in relation to disease is discussed.
CH. ABS.

Value of some vegetables in nutritional anæmia. H. LEVINE, F. P. CULP, and C. B. ANDERSON (J. Nutrition, 1932, 5, 295—306).—Lettuce, lettuce and tomato, asparagus, spinach, and broccoli supplied in amounts to produce the same Fe intake induced blood regeneration in periods varying inversely with the Cu contents. Solutions of inorg. salts of Cu alone or of Fe alone permitted only partial regeneration, but mixed solutions effected a rapid recovery of hæmoglobin.   A. G. P.

Plasma-catalase in artificially induced anæmia of rabbits and the origin of normal plasma-catalase. Y. TAKIZAWA (Tohoku J. Exp. Med., 1932, 18, 512—525).—There is no definite relationship between the state of the blood and the amount of plasma-catalase.   CH. ABS.

Is tissue respiration depressed in beriberi? H. G. K. WESTENBRINK (Arch. Néerl. Physiol., 1932, 17, 239—256).—On statistical examination only 2 out of 15 investigations on the cell metabolism of normal and beriberi animals point to a significant difference.   W. O. K.

Influence of the geological nature of the soil and of the mineral content of the drinking water on the frequency of cancer in man. F. BLANCHET and L. BETHOUX (Compt. rend., 1932, 195, 469—472).—In France the rate of mortality from cancer is higher in those districts in which the rocks are chiefly cryst. (granite, schists, etc.) than in those in which sedimentary rocks predominate. In the former regions the drinking H_2O is relatively pure and low in mineral content.   W. O. K.

Action of glutathione on the Pasteur reaction. E. BUMM and H. APPEL (Z. physiol. Chem., 1932, 210, 79—86).—Neither oxidised (I) nor reduced glutathione (II) has any effect on the respiration or anaërobic glycolysis of rat sarcoma tissue. Under aërobic conditions, glycolysis (lactic acid formation) is reversibly increased by (II) and almost reaches the normal anaërobic val., whilst (I) has no action.
J. H. B.

Anaërobic activation of glycolysis in tumour tissue. F. DICKENS and G. D. GREVILLE (Nature, 1932, 130, 206).—A spontaneous increase occurs in the anaërobic conversion of glucose into lactic acid by the Jensen rat sarcoma, but the pre-activation period is shorter than is the case with fructose. $0·001M$-$AcCO_2Na$ (I) abolishes the pre-activation period in both cases. Mill Hill fowl tumour attacks

fructose with the same vigour as the Jensen sarcoma, but without the spontaneous increase in lactic acid formation; (I) has no effect in this case. (I) may be able to replace the anaërobic activator in partly activated tissues, but has no effect when activation is complete. L. S. T.

Failure to produce dental caries in the white rat with high-carbohydrate diet and *B. acidophilus* or with vitamin-*D* deficiency. C. A. LILLY (J. Nutrition, 1932, 5, 175—181).—Administration of these abnormal diets for a year failed to induce experimental caries. A. G. P.

Muscle-creatine in nutritional muscular dystrophy of the rabbit. M. GOETTSCH and E. F. BROWN (J. Biol. Chem., 1932, 97, 549—561).—The abs. and relative creatine contents of the skeletal muscle, but not of the heart or brain, decrease. Both white muscle (which normally contains 0·42—0·50%) and red muscle (normally 0·26—0·36%), at the final stages of degeneration, contain 0·11—0·25%, the normal level of the cardiac muscle-creatine. The content of the degenerated muscle is independent of the fat content (0·5—48·0%). Degeneration is accompanied by an increase in H_2O content. The extent of pathological lesion appears to be parallel with the degree of diminution in creatine. F. O. H.

Glucose-tolerance curve in epilepsy. G. W. J. MACKAY and H. BARBASH (J. Mental Sci., 1931, 77, 83—85).—A high percentage of epileptic patients present a glucose-tolerance curve of a subnormal type. J. H. Q.

Metabolism of fats during experimental yellow fever in monkeys. P. GERARD, (MLLE.) MOISSONIER, and (MLLE.) WELTI (Bull. Soc. Chim. biol., 1932, 14, 916—928).—Lipin fractions have been determined in various organs of monkeys after death from yellow fever. Vals. for one healthy animal serve as normals. The disease is marked by decreases in lipoid P, lipocytic coeff., and in the unsaponifiable matter of the heart, suprarenals, kidney, and ganglions. The proportion of fatty acids to total lipins is increased. There is little or no change in the content of phosphatide-fatty acids and their I vals. A. C.

Carbohydrate metabolism in a case of hæmochromatosis. R. P. STETSON and J. P. PETERS (Arch. Int. Med., 1932, 50, 226—231). J. B. B.

Cholesterol of the blood-plasma in hepatic and biliary diseases. E. Z. EPSTEIN (Arch. Int. Med., 1932, 50, 203—222).—Hypercholesterolæmia generally occurs in obstructive jaundice, but in degenerative liver diseases jaundice is accompanied by a decrease in cholesterol. In atrophic cirrhosis of the liver and in cholecystitis and cholelithiasis without bile duct obstruction the cholesterol figures are practically normal. J. B. B.

Influence on carbohydrate metabolism of experimentally-induced hepatic changes. III. Chloroform poisoning. T. L. ALTHAUSEN and E. THOENES (Arch. Int. Med., 1932, 50, 257—268).—Rabbits were injected with a large dose of $CHCl_3$ and the effects of the resulting injury to the liver were studied. Blood-sugar and glucose tolerance were reduced. Adrenaline caused no hyperglycæmia. Re-

covery was associated with increased utilisation of glucose. That injury to the pancreas was not involved was shown by glucose injections without insulin. J. B. B.

Malarial pigment (hæmozoin) in the spleen. R. C. WATS and W. J. WHITE (Indian J. Med. Res., 1932, 19, 945—950).—The pigment is bleached by conc. H_2O_2. The alkaline solution has no sp. absorption bands, nor does it yield hæmatin. An alkaline extract of minced spleen does not give flocculation or complement fixation with malarial sera. CH. ABS.

Determination of the isoelectric point of crystalline Bence-Jones protein. O. JERVELL and R. NICOLAYSEN (Biochem. Z., 1932, 250, 308—311).—Crystallisation occurs only in acid reaction and the isoelectric point of the cryst. material as determined by electrometric titration is at p_H 4·0—4·25. P. W. C.

Organic acids of the cerebrospinal fluid [in general paralysis]. R. H. HURST (J. Mental Sci., 1931, 77, 119—126).—There is no increase in lactic acid of the cerebrospinal fluid in general paralysis, but a definite increase in " total org. acids." J. H. Q.

Boltz acetic anhydride test [in general paralysis]. J. E. NICOLE and E. J. FITZGERALD (J. Mental Sci., 1931, 77, 321—331).—The Boltz test (carried out with Ac_2O and H_2SO_4 on cerebrospinal fluid) is rarely positive in nonparetic cases except in certain conditions of meningeal involvement. It is usually positive in general paralysis and becomes negative after malarial treatment, especially after some years have elapsed since the first malarial attack. The test appears to be associated with, if it is not identical with, the glyoxylic acid test for tryptophan. J. H. Q.

Parallel study of the psycho-galvanic reflex and the hyperglycæmic index in psychotics. M. R. LOCKWOOD (J. Mental Sci., 1932, 78, 288—301).—A close parallelism exists, in psychotics, between the hyperglycæmic index (cf. McCowan and Quastel, *ibid.*, 1931, 77, 525) and the psychogalvanic reflex. J. H. Q.

Solvent action of the blood-serum of healthy and rachitic young pigs on the bone salts. J. MAREK, O. WELLMANN, and L. URBANEK (Biochem. Z., 1932, 252, 131—144).—Blood-serum from healthy young pigs deposits salts when shaken with bone-powder, bone ash, $Ca_3(PO_4)_2$, or $CaCO_3$ (or mixtures of these salts), whereas that from young pigs suffering from experimental rickets due to acidosis or alkalosis produced by appropriately unsuitable or unbalanced mineral content in the diet dissolves these materials. The nature of the deposition or dissolution depends on the prevailing composition of the serum and of the bone; acidosis in the bone causes deposition chiefly of $CaCO_3$, alkalosis causes deposition chiefly of $Ca_3(PO_4)_2$. Ca and P contents and also the Ca/P quotient are greatly affected by the digestive processes. W. McC.

Phosphorus partition in the blood of rachitic and non-rachitic calves. F. J. STARE and C. A. ELVEHJEM (J. Biol. Chem., 1932, 97, 511—524).—Experimental rickets in calves is accompanied by a decrease in inorg., acid-sol., and total P. The

decrease in total P is slightly greater than that in the inorg. P, indicating small decreases in ester-P and possibly in lipin-P. The distribution of the fractions between corpuscles and plasma also appears to be affected by the disease, and for this reason, together with the possible change in P distribution during separation, the plasma-inorg. P is not truly indicative of the total change in the inorg. P fraction during rickets.   F. O. H.

Sodium iodobismuthite for use in the treatment of syphilis. C. GURCHOT, P. J. HANZLIK, and J. SPAULDING (J. Pharm. Exp. Ther., 1932, **45**, 427—467).—The prep. of cryst. Na iodobismuthite (I), $Na_2BiI_5,4H_2O$, and its properties are described. In aq. and glycol solutions the Bi is combined with I as electronegative complex. Glycol and especially NaI inhibit the hydrolysis of (I) by H_2O and its pptn. by horse and ox sera and ovalbumin. (I) dialyses slowly through celloidin and frog's skin. Serum-proteins increase, whilst NaI has no effect on, the rate of dialysis. A 6% solution of (I) in glycol containing 12% NaI is recommended for the treatment of syphilis.   A. L.

Standardisation of colloidal gold sols in the Lange test. W. A. KREIDLER and J. C. SMALL (J. Lab. Clin. Med., 1931, **17**, 259—268).—The sols are standardised against a cerebrospinal fluid with a val. of 4 and the required sensitiveness is obtained by adjustment of the p_H.   CH. ABS.

Standardisation of colloidal gold sols by utilising a standard solution of globulin. W. A. KREIDLER and J. C. SMALL (J. Lab. Clin. Med., 1931, **17**, 269—271).—A solution of edestin is employed.
                                        CH. ABS.

Animal calorimetry. XLII. Respiratory metabolism of exercise and recovery in depancreatised dogs. W. H. CHAMBERS, M. A. KENNARD, H. POLLACK, and M. DANN (J. Biol. Chem., 1932, **97**, 525—547).—The elevation of the R.Q. occurring in depancreatised dogs during exercise is followed by a compensatory fall during rest such that the combined periods of activity and recovery show no increase over the basal level. The recovery process is slightly slower in the diabetic than in the normal fasting dog. No significant differences occur in the contents of glycogen, sugar, and lactic acid of the tissues of diabetic dogs before and after work. The data indicate that the rise in R.Q. is due to changes in the CO_2 equilibrium in the body rather than to carbohydrate oxidation and favour the theory that fat is the fuel utilised in the depancreatised dog during exercise.   F. O. H.

Effects of low environmental temperature on metabolism. I. Technique and respiratory quotient. II. Influence of shivering, subcutaneous fat, and skin temperature on heat production. R. W. SWIFT (J. Nutrition, 1932, **5**, 213—225, 227—249).—I. Exposure to cold does not favour any preferential oxidation of carbohydrate in man. Depletion of glycogen stores is proportional to the increased total metabolism.

II. Exposure at 2° for 1 hr. resulted in no change in protein metabolism or blood-sugar level. In general reaction to cold varied inversely to the amount of subcutaneous fat.   A. G. P.

Analysis of the curve of heat production in relation to the plane of nutrition. E. B. FORBES and M. KRISS (J. Nutrition, 1932, **5**, 183—197).—The heat derived from body substance and from nutrient constituents at various levels of intake from fasting up to thrice the maintenance ratio is examined. The heat contribution from protein has approx. the same proportion of the total heat at all levels of feeding. The fat contribution is approx. 83—86% of the total at fasting and falls to zero at the maintenance level. Between fasting and maintenance the carbohydrate contribution is the complement of that of the fat, and above the maintenance level does not vary greatly.   A. G. P.

Manometric measurement of the metabolism of growing tissue cultures. H. LASER (Biochem. Z., 1932, **251**, 2—9).—A method and apparatus for measuring the gaseous metabolism are described. The respiration of the cultures (osteoblast) increases with time. The initially very extensive anaërobic glycolysis decreases and the aërobic glycolysis is not always const.   W. McC.

Alleged evidence for an α-oxidation of fatty acids [in muscle]. F. KNOOP (Z. physiol. Chem., 1932, **209**, 277—279).—The figures of Hahn (A., 1930, 1064), from which he concludes conversion of $EtCO_2H$ into $AcCO_2H$, are within the limits of experimental error.   J. H. B.

α-Oxidation of fatty acids. A. HAHN (Z. physiol. Chem., 1932, **209**, 279—280).—A reply to Knoop (see preceding abstract).   J. H. B.

Behaviour of the phosphatides and cholesterol of whole blood, plasma, and erythrocytes in normal men after taking olive oil with and without previous administration of phosphate. H. WENDT (Biochem. Z., 1932, **250**, 212—219).—Administration of olive oil to healthy man and animals causes, 4 hr. later, an increase in blood-phosphatide and -cholesterol, the increase occurring only in the serum and plasma and not in the corpuscles. Previous administration of PO_4''' or addition of PO_4''' to the olive oil has no influence on the result. Prolonged administration of PO_4''' increases the plasma-phosphatide val.   P. W. C.

Destruction of cholesterol by the animal organism. I. H. PAGE and W. MENSCHICK (J. Biol. Chem., 1932, **97**, 359—368).—Rabbits were fed on large amounts of cholesterol and the fæcal cholesterol and, after death, the body distribution of the sterol were determined. Deposition of cholesterol occurred in all organs except the brain. A deficiency in the balance indicated a destruction of cholesterol of 0·8—1·8 g. per week. The bearing of the results on cholesterol arteriosclerosis is discussed.
                                        F. O. H.

Fate of orally administered cholesterol in the human intestine. H. SALOMON (Z. physiol. Chem., 1932, **209**, 276).—Polemical in reply to Bürger and Winterseel (this vol., 85).   J. H. B.

Fate of orally administered cholesterol in the human intestine. M. BÜRGER (Z. physiol. Chem., 1932, **209**, 276).—A reply to Salomon (cf. preceding abstract). J. H. B.

Carbohydrate metabolism of resting and active mammary glands. H. K. BARRENSCHEEN and N. ALDERS (Biochem. Z., 1932, **252**, 97—112).—The phosphate content of the lactating mammary gland (I) (guinea-pig, rabbit) is considerably higher than that of the resting gland (II), the increase being chiefly in the org. acid-insol. fraction. The acid-sol. org. P (hexosephosphoric ester) of (I) also is greater than that of (II). Since the glands contain a pyrophosphate fraction (adenosinetriphosphoric acid), and since added hexosediphosphate is converted into methylglyoxal when glycolysis in them is inhibited with $CH_2Br \cdot CO_2H$, it seems that the hexosephosphoric ester is an intermediate product in the production of lactose in the glands. (I) and (II) contain the same (very small) amount of glycogen, but the glycolytic power of (I), which seems necessarily to involve intermediary phosphorylation, is much greater than that of (II). (I) produces lactic acid from added lactose and galactose [(II) does not] and only (I) can produce the acid in pure O_2. Glucose, glycogen, lactose, galactose, and hexosediphosphate are decomposed to equal extents by (I). W. McC.

Bile acids and carbohydrate metabolism. XXII. Influence of loss of bile on sugar tolerance in dogs with biliary fistulæ. T. TANAKA (J. Biochem. Japan, 1932, **15**, 381—398).—The tolerance is increased on parenteral administration of cholic acid and decreased on withdrawal of bile, the two effects being mutually dependent. On the other hand, the tolerance of such dogs injected with very small amounts of adrenaline together with glucose is greater when accompanied by withdrawal of bile. F. O. H.

Changes in colloidal condition of muscle-proteins in muscle activity. H. J. DEUTICKE (Z. physiol. Chem., 1932, **210**, 97—124).—Changes in solubility of the proteins were determined by extraction with buffer solutions, after electrical stimulation of the isolated frog's muscle. The decreases run parallel with the development of tension. The solubility changes are reversed after keeping the isolated muscle in O_2, but not in N_2. Resting muscle, on keeping in O_2, develops only a slight increase in protein solubility. The reversion shown by fatigued muscle in O_2 is a relatively slow process. Neither a high degree of tension nor a subminimal stimulus produces a measurable change in protein solubility. The colloidal changes probably occur at the moment of muscle contraction, and are an important cause of fatigue. J. H. B.

Influence of the sympathetics on the biochemical processes of fatigued muscle. P. JACKY (Biochem. Z., 1932, **250**, 178—192).—With fresh frog's muscle and with muscle fatigued by stimulation of the sciatic and curarised, stimulation of the sympathetics on one side did not increase the creatinephosphoric acid content of that side, but when the muscle was severely fatigued by stimulation

of the anterior roots, stimulation of the sympathetics always gave an increase of creatinephosphoric acid. P. W. C.

Elimination of purines in fatigue of isolated frog's muscle. S. E. KERR (Z. physiol. Chem., 1932, **210**, 181—193).—Small amounts of purines, apparently not in the form of nucleotides, are present in fresh frog's muscle. The purine fraction is considerably increased by fatigue induced by electrical stimulation. J. H. B.

Urea formation in the animal body. H. A. KREBS and K. HENSELEIT (Z. physiol. Chem., 1932, **210**, 33—66).—The rate of synthesis of urea from CO_2 and NH_3 in surviving tissue sections of rat's organs was measured under varying conditions. The liver is the only organ in which urea is synthesised. The synthesis is greatly accelerated by ornithine, which acts like a catalyst in that it is not used up, and small amounts can effect a large conversion. No other substance examined had a similar action. Citrulline accelerates urea formation from NH_3, but is consumed in the process, furnishing 1 atom of N per mol. of urea. Urea formation is intimately linked with respiration; its object is apparently to detoxicate NH_3 in the body. Urea is not formed by liver pulp, in which the cell structure is destroyed. The reactions are explained as follows : ornithine takes up CO_2 and NH_3 to form citrulline, which reacts with NH_3 to give arginine. The latter is decomposed by arginase into ornithine and urea :

$$R \cdot CH_2 \cdot NH_2 + CO_2 + NH_3 \xrightarrow{} R \cdot CH_2 \cdot NH \cdot CO \cdot NH_2 \xrightarrow{NH_3}$$
$$R \cdot CH_2 \cdot NH \cdot C(\colon NH) \cdot NH_2 \xrightarrow{H_2O} R \cdot CH_2 \cdot NH_2 + CO(NH_2)_2$$
$$[R = CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H]. \quad \text{J. H. B.}$$

Ammonia in human brain. H. SCHWARZ and H. DIBOLD (Biochem. Z., 1932, **251**, 187—189).—Fresh diseased (tumours) human brain-tissue (5 cases examined) contains, on the average, 0·204 mg. of NH_3 per 100 g. and there may be a relation between pathological (or physiological) condition and NH_3 content. At room temp. the tissue produces NH_3 rapidly. W. McC.

Production of ammonia in brain. Effect of alteration of the circulation and of administration of insulin on this production. H. SCHWARZ and H. DIBOLD (Biochem. Z., 1932, **251**, 190—198; cf. preceding abstract).—Fresh rabbit's brain contains, on the average, 0·4 mg. of NH_3 per 100 g. and produces NH_3 rapidly at room temp. Ligature of the carotid frequently leads to increase in the NH_3 content of the brain, especially when there is accompanying section of the vagus nerves. Administration of insulin irreversibly reduces the NH_3 content of brain, since counteraction of the hypoglycæmia by administration of sugar is not accompanied by restoration of the original NH_3 val. W. McC.

Protein metabolism in men and animals. E. VOIT (Z. Biol., 1932, **93**, 15—41).—Cell wear and tear, physiological protein decomp., and min. requirements are related to each other and have separate vals. Min. protein requirements acquire significance in the dieting of men and animals only when measured during an exact diet, in which case the val. obtained

is higher than when measured on animals fed on excessive diets. H. D.

Determination of the biological value of protein in the study of avian nutrition. J. L. ST. JOHN, O. JOHNSON, J. S. CARVER, and S. A. MOORE (J. Nutrition, 1932, 5, 267—276).—During 12 weeks following the hatching of chickens the % of total N and uric acid eliminated varied from day to day, but the total quantity per day remained practically the same throughout. The total fæcal N was comparatively small. No relationship was observed between either fæcal or urinary N and the age of the chicks. A. G. P.

Changes in the weights of various organs and systems of young rats maintained on a low-protein diet. M. LIMSON and C. M. JACKSON (J. Nutrition, 1932, 5, 163—174).—Low-protein diets fed to rats increased the wt. of some organs and decreased that of others. The effect is ascribed to deficiency of sp. nutrients for certain organs the growth of which is suppressed while other organs develop more or less normally. A. G. P.

Effects of restricted protein intake on the œstrous cycle and gestation in the rat. H. R. GUILBERT and H. GOSS (J. Nutrition, 1932, 5, 251—265).—Protein-deficient diets produced either a cessation of œstrus or long and irregular cycles together with infertility. A. G. P.

Feeding experiments with decomposition products of proteins. U. SUZUKI and N. HASHIMOTO (Proc. Imp. Acad. Tokyo, 1932, 8, 292—295).—Mayeda's experiment (this vol., 643) is repeated and the results are confirmed. The mixed acid and alkaline hydrolysis products of the horse-meat protein of a rat's diet can replace the protein entirely without affecting growth, but the acid products alone require addition of 3% r-tryptophan. P. W. C.

Feeding experiments with decomposition products of proteins. II. S. MAYEDA (Proc. Imp. Acad. Tokyo, 1932, 8, 296—299).—The protein of a rat's diet can be replaced completely by either a mixture of alkaline and acid hydrolysis products or by acid hydrolysis products with 3% of tryptophan, but cannot be replaced by either acid or alkaline hydrolysis products separately. The baryta hydrolysis product was fractionated with $HgSO_4$ into the tryptophan-containing ppt. and the tryptophan-free filtrate. The baryta filtrate has no supplementary effect on the acid hydrolysis product, and omission of the filtrate from a sufficient diet of acid hydrolysis product + tryptophan + filtrate did not effect growth. P. W. C.

Utilisation by human subjects of the nitrogen, calcium, and phosphorus of the navy bean (*Phaseolus vulgaris*), with and without a supplement of cystine. M. A. PITTMAN (J. Nutrition, 1932, 5, 277—294).—With diets of which navy bean formed the chief source of N the balance became increasingly negative. Addition of cystine slightly increased N retention. The Ca and P of the beans were insufficient to maintain the normal balance. There was better utilisation of P than of Ca. Improvement in the utilisation of P corresponded with greater retention of N. A. G. P.

Calcium retention on a diet containing American cheddar cheese. M. G. MALLON, L. M. JOHNSON, and C. R. DARBY (J. Nutrition, 1932, 5, 121—126).—The Ca of this cheese is as well utilised as that from pasteurised whole milk. A. G. P.

Iron requirement of the pre-school child. J. M. LEICHSENRING and I. H. FLOR (J. Nutrition, 1932, 5, 141—146).—The maintenance requirement of Fe for children was similar to that for adults (average 0·12 mg. per kg.) and the growth requirement was approx. 0·2 mg. per kg. A. G. P.

Corrosive action of hydrofluoric acid [on the skin etc.]. K. FREDENHAGEN and M. WELLMANN (Angew. Chem., 1932, 45, 537—538).—The action of HF on the skin is due to the rapid diffusion of F' into the underlying tissue. Application of a paste of MgO and glycerol, or, in severe cases, subcutaneous injection of 20% aq. $MgSO_4$ or of certain non-toxic Ca compounds, is recommended. H. F. G.

Physiological action of aluminium. J. H. BURN (Analyst, 1932, 57, 428—440).—From a review of the literature it is concluded that when Al compounds are given by mouth, only traces of Al are absorbed from the intestine and that no effect other than mild catharsis follows the feeding of Al salts to man even when this is continued for 6 months. W. J. B.

Influence of industrial poisons on antibody formation. I. Lead. II. Benzene and turpentine. F. W. BICKERT (Arch. Hyg., 1931, 106, 271—298; 107, 1—10).—Subcutaneous administration to rabbits of $Pb(OAc)_2$ or other Pb salts stimulates the production of hæmolysins for sheep erythrocytes, of agglutinins for typhus bacilli, and of an antitoxin for diphtheria toxin. Administration of $Pb(OAc)_2$ inhibits the formation of precipitins for sheep serum. Hæmolysin production appears to be inhibited by subcutaneous injections of C_6H_6 and to be stimulated by injections of turpentine. CH. ABS.

Zinc content of internal organs in two cases of poisoning by zinc phosphide. A. MONTEFREDINE (Arch. Farm. sperim., 1932, 54, 223—228).—The organs analysed showed high Zn contents, ranging from 10 to 60 times the normal val. The kidney was an exception, showing only a slight increase, owing to its excretory activity. The livers showed a high fat content, due to fatty degeneration. R. N. C.

Action of thorium on the metabolism [of rabbits]. J. Z. DOMINGUEZ (Biochem. Z., 1932, 251, 141—147).—In rabbits parenteral administration of small amounts (0·1—0·2 g. per kg.) of $ThCl_4$ has slight irregular effects on the metabolism (oxidations, excretion of C, O, and N), but larger doses (0·2—0·6 g. per kg.) stimulate oxidations. W. McC.

Biochemical action of arsinic acids of the pyridine series. VI. Excretion of organic halogen compounds in the urine. A. BINZ and H. MAIER-BODE (Biochem. Z., 1932, 252, 16—21; cf. A., 1931, 1454).—The max. urinary concn. of combined Br or I which can be attained as a result of injection of aliphatic or aromatic I or Br compounds is not proportional to the amount of halogen injected. The diuretic effect, the time required for attaining this

max., and the long time which elapses before excretion of halogen ceases, vary greatly from substance to substance, and no relationship can be traced between these factors and the halogen content of the substances. Within the observed time $CHI(SO_3Na)_2$ was almost quantitatively excreted and the excretion of other I compounds exceeded 80%, but $CHBr(SO_3Na)_2$ and $CH_2Br\cdot SO_3Na$ as well as certain I compounds were excreted less completely (or more slowly).

W. McC.

Relationship between chemical structure and physiological response. II. Conjugation of hydroxy- and methoxy-benzoic acids. A. J. Quick [with M. A. Cooper] (J. Biol. Chem., 1932, **97**, 403—419).—The principal conjugated product excreted in the urine of dogs fed with $p\text{-}OH\cdot C_6H_4\cdot CO_2H$ (I) is the *diglycuronic acid* derivative, m.p. 200—201° (decomp.), $[\alpha]_{11}^{20}$ —15° to —16° (1% aq. solution), exhibiting mutarotation in alkaline solution. Conjugation with 2 mols. of glycuronic acid also occurs in dogs with o- and $m\text{-}OH\cdot C_6H_4\cdot CO_2H$. Ingestion of (I)–diglycuronic acid by man is not followed by excretion of this compound, only (I) and its glycine derivative appearing in the urine. m- and p-Hydroxy- and -methoxy-hippuric acids were isolated from human urine following ingestion of the corresponding benzoic acids, which, however, are also excreted free or, in some cases, combined with glycuronic acid. In man $o\text{-}OH\cdot C_6H_4\cdot CO_2H$ is excreted as the free acid. The theory is advanced that, in a conjugation process of detoxication, a weak acid is converted into a strong acid which can be eliminated through the kidney.

F. O. H.

Ethyl alcohol. III. Combustion of ethyl alcohol by a homeotherm (mouse) at the neutral temperature. M. Nicloux (Bull. Soc. Chim. biol., 1932, **14**, 861—872; cf. A., 1931, 1327).—The combustion of EtOH in mice at 30° after subcutaneous injection of quantities varying between 0·18 and 4·9 mg. per g. of mouse is proportional to time, and is almost complete in 3 hr. The amount of EtOH oxidised per g. of body-wt. per hr. is approx. const. This " coeff. of ethyloxidation " has a mean val. of 0·65 mg. for the mouse at 30°.

A. C.

Esters of dialkylaminomethanols as local anæsthetics. E. V. Lynn and F. V. Lofgren (J. Amer. Pharm. Assoc., 1932, **21**, 761—764).—Of 16 cinnamyl, m- and p-aminobenzoyl, and Bz esters of a series of dialkylaminomethyl alcohols together with their salts, all the sol. salts possessed local anæsthetic properties. Some of the bases showed local anæsthetic properties. The sol. salts, especially those of high mol. wt., were readily hydrolysed and very irritating when applied to the cornea of a rabbit. E. H. S.

Conditions for novocaine action. A. Weiss (Arch. exp. Path. Pharm., 1932, **167**, 177—190).—The anæsthetic action of novocaine on the rabbit's cornea is increased by parenteral administration of $CaCl_2$ or morphine and is accelerated by that of KCl. With morphine the duration of anæsthesia can be increased eightfold and this phenomenon is used as a method of assay of morphine preps. Other opium alkaloids also possess this synergising action, but generally to a smaller extent. Heroin and

dilaudid, however, increase the anæsthesia to the extent of, respectively, 280 and 500% of that of morphine.

F. O. H.

Effect of phloridzin on the rate of absorption from the gastro-intestinal tract of the white rat. R. H. Wilson (J. Biol. Chem., 1932, **97**, 497—502).—Rats continuously subcutaneously injected with phloridzin absorb glucose, glycine, and alanine at 70, 137, and 134% of the normal rate, respectively. These changes afford an explanation of the equal rates of glucose excretion in phloridzin glycosuria of dogs after the ingestion of these substances.

F. O. H.

Variations of alkaline reserve in organisms stimulated by pharmacodynamic substances. —R. Messina (Arch. Farm. sperim., 1932, **54**, 207—213).—Subcutaneous injection of morphine and pilocarpine in the dog caused a marked fall in alkaline reserve, the effect lasting several hr. Atropine had the same effect to a smaller degree. With all three alkaloids, small doses caused a greater fall than larger doses. It is suggested that the rise in blood-Ca following the injections results in an increased production of $H^{\cdot}$.

R. N. C.

Influence of pharmacodynamic substances on calcium–potassium equilibrium. R. Messina (Arch. Farm. sperim., 1932, **54**, 214—222).—Subcutaneous injection of small quantities of morphine, pilocarpine, and atropine in the dog resulted in a rise of blood-Ca together with a corresponding fall in blood-K. Results obtained with larger quantities were irregular. These variations are attributed to secondary effects following the disturbance of the sympatheticotonic state by morphine and pilocarpine, or vagal paralysis by atropine.

R. N. C.

Colloid chemistry of nervous systems. V. W. D. Bancroft, R. S. Gutsell, and J. E. Rutzler, jun. (J. Physical Chem., 1932, **36**, 2011—2082).—Administration of large amounts of NaCNS to four morphine addicts during morphine withdrawal alleviated withdrawal symptoms, and mental rehabilitation was accomplished in three cases. Overdosage of NaCNS can be counteracted by Na amytal, an agglomerating agent.

C. T. S. (b)

New class of choline esters (carbamylcholine chloride or "lentine"). II. Action on the blood-pressure, intestine, digestive glands, and its fate in the organism. H. Nöll (Arch. exp. Path. Pharm., 1932, **167**, 158—170; cf. this vol., 301).—Carbamylcholine chloride (I) is 1000 times as powerful as acetylcholine (II) in its action on the blood-pressure of the decapitated cat, whilst in their action on the isolated small intestine both the two substances are approx. equal. In contrast to (II), intravenous injection of (I) results in a contraction of the intestine *in situ*. (I) excites salivation, approaches histamine in its promotion of the flow of gastric juice, does not influence the excretion of bile, and, unlike choline or (II), is stable in the body.

F. O. H.

Depressor substances of yeast. U. S. von Euler (Arch. exp. Path. Pharm., 1932, **167**, 171—176).—The depressor substance obtained by von

Euler and Gaddum (J. Physiol., 1931, **72**, 74) is not present in EtOH extracts of fresh, frozen, or heated yeast. The depressor substances of yeast fall into two groups, choline-like substances and adenyl compounds. Acetylcholine does not occur in yeast. The actions of adenylthiomethylpentose and of a vitamin-B_1 prep. on the blood-pressure and on the isolated intestine of the rabbit are similar to, but much weaker than, those of yeast-adenylic acid.

F. O. H.

Protective action of optical desensitisers towards photo-biological processes. E. SZŐRÉNYI (Biochem. Z., 1932, **252**, 113—125).—Photographic desensitisers (dyes) protect sensitised blood-corpuscles and *Paramecia* from the detrimental action of light, the protective effect being much greater than that of resorcinol or of serum. The toxicity of hæmatoporphyrin as an optical sensitiser is greater at acid than at alkaline reaction, that of rose-Bengal 3B (tetrachlorotetraiodofluorescein) is greater at alkaline than at acid. White mice sensitised to light are protected against its harmful effects by subcutaneous injection of serum.

W. McC.

Mitogenetic radiation. III. Induction in onion roots with yeast and blood. M. MOISEJEVA (Biochem. Z., 1932, **251**, 133—140; cf. this vol., 201).—Since no mitogenetic effects can be produced in onion roots by induction with yeast, blood from healthy or tuberculous persons, or rat's blood, such roots cannot serve as detectors of mitogenetic radiation and the results of all investigations in which the roots were so used are erroneous.

W. McC.

Mitogenetic radiation from white blood-cells, J. KLENITZKY (Biochem. Z., 1932, **252**, 126—130).—Mitogenetic radiation characteristic of glycolysis (I), oxidation, and phosphatase action is emitted by white polynuclear blood-corpuscles and such rays, characteristic of proteolytic processes (II), are probably also emitted. Most of the rays are of intra-cellular origin. The cell-free liquid emits only the rays characteristic of (I) and possibly also those of (II).

W. McC.

Catalase. III. Types of inhibition and mechanism of the catalase reaction. K. G. STERN (Z. physiol. Chem., 1932, **209**, 176—206; cf. this vol., 775).—The mechanism of the inhibition of catalase by various methods is discussed. EtO_2H has an affinity for catalase and hence acts as inhibitor; Et_2O_2 has no such affinity and shows no inhibition. The comparative activity of a no. of inhibitors is given. The theory of action of catalase is based on the assumption of the breakdown of the H_2O_2 into two OH groups, yielding O_2 and H_2O as end-products.

J. H. B.

Biological reduction. I. Active hydrogen-donator from heart-muscle. K. KODAMA. **II. Distribution of "biosugar"-dehydrogenase in various tissues and the co-enzymic action of extract of suprarenal cortex.** M. TSUKANO. **III. Oxidation–reduction potential of "biosugar" with its dehydrogenase.** M. TSUKANO. **IV. Biological reduction of cystine.** M. TSUKANO (J. Biochem. Japan, 1932, **15**, 473—476, 477—485, 487—490, 491—496).—I. Ox heart-muscle was ex-

tracted with boiling 70% aq. EtOH, the extract pptd. by $HgCl_2$, and the filtrate treated with $Ba(OH)_2$ followed by pptn. with EtOH. The salt thus obtained corresponded with a Ba hexosemonophosphate, $[\alpha]_D^{20}$ +7·82° (phenylhydrazone, m.p. 138°). The identity of the ester with that of Embden (A., 1927, 749) or that of Robison (A., 1923, i, 86) was doubtful and it was therefore designated "biosugar." "Biosugar" acts as a H-donator to a dehydrogenase.

II. The distribution of the dehydrogenase in various ox and rabbit tissues was determined. Suprarenal cortex has an outstanding activity due to the presence of a "co-donator" which resembles adenylpyrophosphate and does not itself reduce methylene-blue but promotes the action of the dehydrogenase as donator.

III. The reduction potentials of systems containing "biosugar" and heart-muscle, suprarenal cortex, or suprarenal cortex + heart-muscle + hexosediphosphate were determined. The vals. obtained were in agreement with the biochemical behaviour of such systems.

IV. The system "biosugar"–heart-muscle emulsion can reduce cystine to cysteine to an extent greater than succinate-dehydrogenase can, the optimum p_H being approx. 7·4.

F. O. H.

Hexosediphosphatedehydrogenase and carboxylase in plant seeds. B. ANDERSSON (Z. physiol. Chem., 1932, **210**, 15—29).—A hexosediphosphatedehydrogenase occurs in several plant seeds from which Thunberg reported its absence. The inactivity of these seeds is not due to lack of enzyme, but to the absence in sufficient amount of cozymase. The activity of certain seeds (oats, rye, wheat) is much increased during the first days of germination. This is due not to an increase in enzyme but to the production of cozymase. The enzyme of peas fermenting $AcCO_2H$ requires a co-enzyme identical in its action with cocarboxylase. Mg also activates this fermentation.

J. H. B.

Asymmetric catalysis with organic fibres (a new enzyme model). G. BREDIG and F. GERSTNER (Biochem. Z., 1932, **250**, 414—429).—Cotton fibres are converted by introduction of a NEt_2 group into a very active catalyst, which is able to decarboxylate β-keto-acids and to catalyse the formation of mandelonitrile from HCN and PhCHO, a considerable amount of the product being lævorotatory.

P. W. C.

Specificity of polysaccharide-splitting enzymes. W. GRASSMANN, L. ZECHMEISTER, G. TÓTH, and R. STADLER (Naturwiss., 1932, **20**, 639).

W. R. A.

Specificity of amylases. I. Separation and properties of the two malt amylases. G. A. VAN KLINKENBERG (Z. physiol. Chem., 1932, **209**, 253—268).—The Wijsman diffusion experiment (A., 1890, 998) offers a good method for studying amylases. Dry preps. of α- and β-amylase were obtained each free from the other form. β-Amylase shows optimal activity at p_H 4·55—5·15, α-amylase at 5·65—5·85 with citrate buffer. The I reaction disappears completely with α-amylase, but changes to purple with β-amylase, corresponding with the formation of

erythrogranulose. The reaction of α-amylase is inhibited more by α-maltose, that of β-amylase by β-maltose. J. H. B.

Effect of the colloidal condition of starch and of amylase solution on the rate of the enzymic hydrolysis. E. A. Sym (Biochem. Z., 1932, 251, 116—132).—The colloidal condition of starch has no effect on its reaction with amylase, but that of the amylase influences its activity and is affected by such factors as the protective action of starch against inactivation by H˙ or by salts and the high temp. coeff. of the inactivating process. The lower is the concn. of the starch the greater is the degree of hydrolysis by amylase. Free amylase is much less stable than amylase–starch compound. The inactivation of amylase by salts (NaCl, $CaCl_2$, Na_2SO_4) is partly an ionic phenomenon (at optimum acid reaction anions act, at optimum alkaline reaction, cations), but also partly dependent on the colloidal condition of the enzyme. In acid solutions amylase is very labile and very readily affected by all inactivating factors. The way in which hydrolysis proceeds is probably determined by the intermediate products in the reaction. Amylase apparently does not combine with the end-products. W. McC.

Activity of the amylase in the leaves of the sugar-beet. A. Oparin and S. Risskina (Biochem. Z., 1932, 252, 8—15; cf. A., 1929, 1106).—When the fresh or dried leaves of the sugar-beet are mixed with H_2O (or with buffer solutions) part of the amylase present dissolves and part remains bound to (or adsorbed on) the leaves in an inactive state. The amount of active (dissolved) amylase attains an equilibrium with that of the bound. Most of the latter can be extracted gradually from the leaves by repeated washing with H_2O, and extraction with McIlvaine's buffer solution removes most of the amylase from the leaves in the active (dissolved) state. Autolysis in the leaves is accompanied by rapid inactivation of the amylase. W. McC.

Glutathione as a complement of amylases. H. Pringsheim, H. Borchardt, and H. Hupfer (Biochem. Z., 1932, 250, 109—124).—Glutathione behaves very similarly to yeast-complement in the activation of pancreatic amylase. The complement action of solutions containing equimol. amounts of oxidised and reduced glutathione and of cysteine are approx. the same. Dithioglycollic acid has no complement action. The action of glutathione is the same with and without the addition of NaCl. Glutathione and yeast-complement do not activate yeast-amylase. Whereas addition of glutathione and yeast-complement to the starch–pancreatic amylase mixture after attainment of equilibrium takes the amylolysis further, no such action is obtained with yeast-amylase. Salivary amylase behaves like pancreatic amylase. P. W. C.

Separation of α-glucosidase and β-*h*-fructosidase in yeast autolysates, and the hydrolysis of sucrose. R. Weidenhagen (Z. Ver. deut. Zucker-Ind., 1932, 82, 503—519).—The author restates his theory of the sp. action of sugar enzymes (A., 1928, 1157, 1281; 1929, 352, 722) and describes the separation of the two sucrose-splitting enzymes, which are both present in yeast, by preferential adsorption of α-glucosidase (maltase) on β-$Al(OH)_3$ (cf. A., 1930, 1065; 1931, 653). α-Glucosidase hydrolyses sucrose about twice as rapidly as it does maltose. J. H. L.

Emulsin. VIII. B. Helferich and S. Winkler (Z. physiol. Chim., 1932, 209, 269—275).—*Phenol-α-d-mannoside*, m.p. 132—133°, $[\alpha]_D^{23}$ +113·5°, is hydrolysed by preps. of emulsin at substantially the same rate ratios as the -β-*d*-glucoside and -β-*d*-mannoside whereas *phenol-β-d-mannoside*, m.p. 175—176·5°, $[\alpha]_D^{20}$ −71·6°, is not attacked. The decisive factor in hydrolysis by β-*d*-glucosidase is probably the *trans*-position of the O atoms at C_1 and C_2. J. H. B.

Pectolase. I. F. Ehrlich (Biochem. Z., 1932, 250, 525—534).—A theoretical paper announcing the prep. of a highly-active enzymic system, pectolase, from mould cultures which is able to hydrolyse the complex tetragalacturonic acid of pectin to unimol. *d*-galacturonic acid. P. W. C.

Pectolase. II. F. Ehrlich (Biochem. Z., 1932, 251, 204—222).—Examples of the action of samples of pectolase from various sources (takadiastase, emulsin, moulds) are given. W. McC.

Enzymic hydrolysis and synthesis of aspartic acid. A. I. Virtanen and J. Tarnanen (Biochem. Z., 1932, 250, 193—211).—A very sp. enzyme, *aspartase*, is isolated from cultures of *B. fluorescens liquefaciens* which effects the interconversion *l*-aspartic acid ⇌ fumaric acid + NH_3 at p_H 7, but not below p_H 6. The reaction follows the mass law; the synthetic action is increased by addition of NH_3, and the equilibrium is reached from both sides. The enzyme solution also contains fumarase and asparaginase. It does not cause addition of NH_3 to fumaric acid diamide, nor to mesaconic, aconitic, and sorbic acids. It does not cause deamination of NH_2-acids (except asparagine). Aspartase is much more sensitive to acids and EtOH than is asparaginase. Its p_H optimum is 7—7·5. It occurs widely in plants (pea seedlings, young grass), but was not detected either in yeast or in animal organs. P. W. C.

Activation and inhibition of arginase preparations by oxygen, carbon dioxide, cysteine, and salts of heavy metals. II. S. Salaskin and L. Soloviev (Biochem. Z., 1932, 250, 503—518).—Arginase prepared by different methods is differently affected by gases. The $COMe_2$ prep. is affected most strongly with O_2 and the glycerol prep. with CO_2. The glycerol prep. after partial loss of activity by the action of gases is completely reactivated by addition of cysteine, whereas the $COMe_2$ prep. and the AcOH prep. under the same conditions are inhibited. After treatment with salts of heavy metals (Fe, Cu) all the arginase preps. are activated by cysteine. P. W. C.

Liver autolysis. W. Laves and E. Schadendorff (Z. physiol. Chem., 1932, 210, 168—180).—In progressive autolysis of cell and tissue structures, the morphological changes are accompanied by a displacement of the isoelectric point of the colloids to the alkaline side. These changes in liver tissue extracted with EtOH correspond with an increase

of protein degradation products and a higher acidity in the extracts.   J. H. B.

Quinones as enzyme models. V. Comparison of the deamination of di- and tri-peptides with that of glycine. B. KISCH (Biochem. Z., 1932, **250**, 135—148).—Catalytic oxidative deamination of glycylglycine (I) and glycyl-leucine by hydroxyquinol is not preceded by splitting of the substrate. Leucylglycylglycine is not deaminised at p_H 6—12. Whereas deamination at p_H 7—9 of (I) by a series of quinones and resorcinol occurs less readily than with glycine, insertion of a p-OH group in the catalyst enables deamination to occur more readily than with glycine. The reverse is the case at p_H 9—11. The p_H optimum for deamination of (I) is much lower than for glycine and serine (cf. this vol., 578).   P. W. C.

Proteases of insectivorous plants. K. G. STERN and E. STERN (Biochem. Z., 1932, **252**, 81—96).—The secretion in the trap and the extract from its glandular tissue of *Nepenthes Hibberdii* and of *N. mixta* contain a catheptic (I) (optimum activity at p_H 4—5) and a tryptic (II) (optimum activity at about p_H 7) protease. Since the p_H of the secretion is about 7 (II) is more active under natural conditions than is (I). The action of (I) on gelatin is not stimulated by HCN, H_2S, or cysteine nor that of (II) by enterokinase.   W. McC.

Tyndallometric determination of pepsin. E. HERZFELD (Biochem. Z., 1932, **251**, 384—393).—A method is described for the rapid determination of small amounts of pepsin in terms of the turbidity of the protein degradation products, obtained under standard conditions.   P. W. C.

Action of pancreatin on gelatin surfaces. M. BERGMANN and F. FÖHR (Biochem. Z., 1932, **250**, 568—576).—The gelatin with which is incorporated some black material is spread in layers of known thickness on glass and the extent of digestion by pancreatin is measured optically in terms of decrease in blackness by comparison with a standard wedge made of the same substances. Curves showing the dissolution of gelatin as a function of the digestion time closely approximate to straight lines.
     P. W. C.

Enzymic fission of proline peptides. II. W. GRASSMANN, O. VON SCHOENEBECK, and G. AUERBACH (Z. physiol. Chem., 1932, **210**, 1—14; cf. A., 1929, 848).—The new substrates were prepared by treating the corresponding αδ-dibromovaleryl compounds with 25% aq. NH_3, avoiding the use of Ag. The following were employed : dl-*prolylglycine*, m.p. 225—227° (decomp.), dl-*prolylglycylglycine*, m.p. 217° (from αδ-*dibromovalerylglycylglycine*, m.p. 153°), prolylalanine, and prolyl-leucylglycine. In confirmation of previous work all the proline peptides were hydrolysed by crude erepsin solutions, also by peptidase solutions from spleen, liver, kidney, lung, and yeast. Dried preps. of amino- and poly-peptidase were inactive towards the proline peptides. The divergent results of Abderhalden and Zumstein (A., 1931, 767) may be due to traces of Ag in their polypeptides, since the metal is a powerful inhibitor. Prolinase was obtained almost free from polypeptidase, but not from dipeptidase. It differs from dipeptidase in being less sensitive to HCN and more readily adsorbed by kaolin and $Al(OH)_3$ Cy.   J. H. B.

Formation of lysolecithin from egg-yolk lecithin by pancreas extract. Z. NIKUNI (Proc. Imp. Acad. Tokyo, 1932, **8**, 300—303).—When egg-yolk lecithin is digested with pancreas extract a powerful hæmolytic substance identical with the lysolecithin formed from lecithin by the action of snake venom is obtained.   P. W. C.

Nuclein metabolism. XXIX. Enzymic fission of pus-nucleic acid with nucleotidase from intestinal mucosa and a new carbohydrate from animal nucleic acid. F. BIELSCHOVSKY (Z. physiol. Chem., 1932, **210**, 134—138; cf. this vol., 776).—From the products of enzymic hydrolysis of pus-nucleic acid were isolated guanosine, inosine, thymosine, cytidine (as picrate), and a *carbohydrate*, darkens at 150°, m.p. 204° (decomp.), giving negative $NHPh_2$, Kiliani, fuchsin-H_2SO_4, and Angeli–Rimini tests.
     J. H. B.

Urea formation in the animal body. VI. A.4. Urea formation in surviving organs and in their press-juice. L. SOLOVIEV and S. MARDASCHEV (Z. physiol. Chem., 1932, **209**, 239—246; cf. this vol., 544).—In liver autolysis neither NH_4 salts nor NH_2-acids give rise to urea, the only source of which is arginine.   J. H. B.

Urease. II. Action of neutral chlorides on urease. A. RUCHELMANN (Biochem. Z., 1932, **251**, 51—59; cf. this vol., 777).—At p_H 7·1 (7·4 for LiCl) the activity of urease and the rate at which it decomposes urea are affected by the presence of the chloride of Na, K, Rb, or Li usually according to the amount of buffer present. The salts diminish the activity of the enzyme to some extent in proportion to their concn., but other factors (accumulation of NH_3, effects on the two phases of the reaction, binding of the enzyme or of the substrate) are also involved.   W. McC.

Influence of hydrogen-ion concentration on the phosphorylation and lactic acid formation in muscle. B. TANKÓ (Biochem. Z., 1932, **250**, 7—17). In fresh muscle-pulp the p_H optimum of $OH\cdot CHMe\cdot CO_2H$ formation, using PO_4'''+glycogen+ pulp at room temp., is 7·6 (corrected for phosphatese action 7·3), whilst in muscle-powder the vals. are 7·3—7·4 (corr. 7·2). The displacement of p_H with muscle-powder is probably related to the action of glycogenase. The p_H optima for phosphatese are with fresh pulp 7·2—7·3 and with muscle-powder 7·1.   P. W. C.

Co-enzyme action. II. Adenosinetriphosphoric acid. H. K. BARRENSCHEEN and W. FILZ (Biochem. Z., 1932, **250**, 281—304).—A method for the prep. of adenosinetriphosphoric acid by pptn. with alkaline $CaCl_2$ or $Ca(OAc)_2$–NaOAc is described. The Ag salt from mammalian muscle has the formula $C_{10}H_{13}O_{13}N_5P_3Ag_3$. The carbohydrate component on distillation with HCl gave only traces of furfuraldehyde and no lævulic acid. The velocity of hydrolysis as followed by Van Slyke's method was much smaller than for Embden's muscle-adenylic acid and in the hydrolysate inorg. PO_4''' and inosic acid were detected,

whilst inosinepyrophosphoric acid was not found. After 4 hr. hydrolysis, an *adenosinetriphosphoric acid* was also isolated which differed from the original material in that it was much more sol., it contained 6 OH groups titratable potentiometrically (the original substance contained only 5), and it gave a Ag salt containing Ag_4. Muscle-deaminase did not separate NH_3 from either of these acids, but a mixture of adenylic acid deaminase and pyrophosphatase separated both P and N in the ratio 2 : 1. Liver-nucleophosphatase did not separate P from these acids. The structural formula is discussed. P. W. C.

Effect of phosphatases in lactic and alcoholic fermentations and on the relationship of cozymase. C. ARNAUDI and M. FRANCIOLI (Biochem. Z., 1932, **250**, 125—134).—Small amounts of the phosphatases of *Aspergillus niger*, *A. oryzœ*, of yeast, and of phytase accelerate alcoholic fermentation. These phosphatases are not all able to protect pigeons fed on rice from polyneuritis. The enzymic power of *B. bulgaricus* can be increased by addition of phytase and by the phosphatase of *A. oryzœ*, the increase being pronounced in presence of inorg. PO_4'''. Fermentation of glucose can be effected by an enzymic system in which the cozymase is replaced by the phosphatases of *A. oryzœ* or *A. niger*, and by phytase. P. W. C.

Zygosaccharomyces. M. SACCHETTI (Atti R. Accad. Lincei, 1932, [vi], **15**, 762—765).—Various conjugating yeasts were isolated from Italian products, two new species being named *Zygosaccharomyces gracilis italicus* and *Z. felsineus*. T. H. P.

Biological action of arsenate. II. Influence of arsenate on phosphorylation by muscular tissue. L. R. SUBKOVA and A. E. BRAUNSTEIN (Biochem. Z., 1932, **250**, 496—502).—Tables show the extent of inhibition by arsenate of phosphorylation by pigeon's breast muscle (pulp and dried powder preps.) with and without addition of NaF and of glycogen and the mechanism of the inhibition is discussed. P. W. C.

Biological action of arsenate. III. Biochemical esterification of arsenic acid by yeast. A. E. BRAUNSTEIN and M. M. LEVITOV (Biochem. Z., 1932, **252**, 56—63; cf. this vol., 882).—During the esterification of H_3AsO_4 by yeast labile hexosearsenic esters are very probably produced. $CH_2Br\cdot CO_2H$ inhibits the production of the esters. W. McC.

Action of halogenoacetic acids on hydrolysis and oxidative metabolism. E. LUNDSGAARD (Biochem. Z., 1932, **250**, 61—88).—In experiments of short duration at p_H 4·5—5, fermentation by yeast is completely inhibited, but respiration is unaffected by $0.001M$ solutions of $CH_2I\cdot CO_2H$ and $CH_2Br\cdot CO_2H$. $CHBr_2\cdot CO_2H$ has some, $CBr_3\cdot CO_2H$, $CHMeI\cdot CO_2H$, $CH_2I\cdot CH_2\cdot CO_2H$, $CHMeBr\cdot CO_2H$, $CH_2Br\cdot CH_2\cdot CO_2H$, $CH_2Cl\cdot CO_2H$, and $CH_2Ph\cdot CO_2H$ have only a fleeting or no effect on fermentation. The conditions for maintaining respiration (R.Q. about 1) for a long time are given, fermentation being excluded. EtOH and $AcCO_2H$ are more readily oxidised by poisoned yeast than is carbo-

hydrate. Synthesis of carbohydrate from EtOH does not occur with poisoned yeast. Oxidation with poisoned yeast in glucose solution is essentially similar to that in EtOH solution, but the CO_2 development is about twice as great as that obtainable from the EtOH formed in fermentation and the R.Q. is much greater than when EtOH is oxidised. It appears that a direct oxidation of glucose occurs. P. W. C.

Is the nutrilite for " Gebrüde Mayer " yeast of universal biological importance? R. J. WILLIAMS, C. M. LYMAN, G. H. GOODYEAR, and J. H. TRUESDAIL (J. Amer. Chem. Soc., 1932, **54**, 3462—3463).—An unknown hydroxy-acid, M about 200, is the responsible agent for a remarkable growth stimulation of " Gebrüde Mayer " yeast. It is found in a great variety of living tissues; its esters are not basic, it contains several OH groups, is not olefinic, and does not contain CHO, CO, or aromatic groups. C. J. W. (*b*)

Biochemical conversion of ethyl alcohol into citric acid by moulds. T. CHRZASZCZ, D. TIUKOV, and M. ZAKOMORNY (Biochem. Z., 1932, **250**, 254—269).—During the conversion by various species of *Penicillium* of EtOH into citric acid, the following products arise : acetic, succinic, fumaric, *l*-malic, glycollic, oxalic, and other acids. These products arise also from sugar, but only after the sugar is completely degraded to EtOH. The mechanism suggested is, therefore, sugar—→EtOH—→ AcOH —→ glycollic —→ *l*-malic —→ citric acids. The influence of the medium and of the particular strain determines the relative amounts of these products and the extent of the conversion of glycollic into oxalic acid. P. W. C.

Ergosterol and mannitol from *Aspergillus fischeri*. L. M. PRUESS, W. H. PETERSON, and E. B. FRED (J. Biol. Chem., 1932, **97**, 483—489).— The dried mycelium of *A. fischeri* (Thom 5041) on extraction with 96% EtOH yields mannitol (0·4%) and ergosterol (0·1%). These substances are also produced by *A. oryzœ*. F. O. H.

Formation and biological significance of a growth regulator by *Aspergillus niger*. P. BOYSEN-JENSEN (Biochem. Z., 1932, **250**, 270—280). —A method is described for the prep. of a metabolic product of *A. niger*, which, although unnecessary for the growth of the organism itself, is able to accelerate the growth of *Avena* coleptile. The formation of this substance occurs only when certain NH_2-acids of high mol. wt. are present in the medium. P. W. C.

Biochemistry of luminous bacteria. II. Influence of sugars with sodium chloride on luminosity. F. FUHRMANN (Monatsh., 1932, **60**, 414—430).—Under the experimental conditions, glucose, fructose, and galactose do not cause appreciable increase of luminosity; the two first-named sugars are generally restrictive whether the NaCl content is optimal or less. With $0.5M$-NaCl in the initial stages up to 24 hr., galactose and fructose in particular exercise a marked impulse on the luminosity if the amounts used are small. In these small amounts, glucose has an appreciably

slower action, since, as when other hexoses are employed in larger amount, the max. luminosity is attained only after 36 hr. When judged by the amount of acid produced, galactose is least attacked, although it produces the greatest luminosity. Generally, in presence of the hexoses larger amounts of NaCl lead to greater light max. followed by rapid decline. In the initial stages of growth sucrose and lactose in all amounts employed strongly excite the luminous process, the max. being lower with lactose. In $0.25M$-NaCl lactose restricts the luminosity more or less, since the max. attained are lower than in the sugar-free controls. In $0.5M$-NaCl additions of sucrose are without marked effect on the luminescence, whereas analogous additions of medium amounts of lactose have a favouring action. Development of acidity is not marked with the disaccharides and is absent at the optimal NaCl content. Very small additions of maltose facilitate the development of light. Small amounts, in solutions of much less than the optimal NaCl concn., cause a very rapid increase of the luminosity to a high max. in the first 24 hr., followed by an extremely rapid decline.   H. W.

Hemicellulose-decomposing bacteria. A. G. NORMAN (J. Bact., 1932, 23, 72—73; cf. this vol., 195).—Soil bacteria fermenting hemicellulose at 65°, but more rapidly at 25—35°, were examined. Lactobionic acid was utilised by all strains and maltobionic acid by many. Gum arabic, mesquite gum, and tetragalacturonic acid were fermented. In liquid media the fermentation of complex hemicelluloses proceeded slowly.   A. G. P.

Thermophilic fermentation of beet pulp. C. H. WERKMAN and J. STRITAR (J. Bact., 1932, 23, 70—71).—Soil organisms ferment pulp at 56—58°. Sugars, pentosans, pectins, and, later, cellulose are decomposed. Lignin is very resistant. CH_4 is among the products from cellulose. Small amounts of HCO_2H are produced.   A. G. P.

Bacterial decomposition of glucose, fructose, and glucosamine. F. LIEBEN and L. LÖWE (Biochem. Z., 1932, 252, 70—73; cf. A., 1930, 251).—Fructose by itself is more extensively decomposed by *B. proteus vulgatus* (I), and by *B. prodigiosus* (II) than is glucose by itself, but (I) decomposes the two sugars to the same extent and (II) decomposes glucose to a much greater extent than fructose in a mixture of equal parts of the two sugars. (II) decomposes glucosamine to the same extent as it does glucose.   W. McC.

Lactobacillus acidophilus. **I. Occurrence of free, optically active, dihydroxystearic acid in the fatty extract.** J. A. CROWDER and R. J. ANDERSON (J. Biol. Chem., 1932, 97, 393—401).—Treatment of the fat, extracted from the bacteria by $Et_2O+EtOH$, with Et_2O leaves an insol. residue (2·6%) which, on crystallisation from suitable solvents, yields dihydroxystearic acid, m.p. 108° (softening at 105°), $[\alpha]_D^{20} +7.78°$ in MeOH (recrystallisation from EtOAc gives m.p. 106—107°, but $[\alpha]_D^{20} +2.92°$, indicating racemisation by contact with hot solvents); Ac derivative, an oil at 0°; Ba salt, m.p. 208—209°.   F. O. H.

Effect of associated growth on the forms of lactic acid produced by certain bacteria. E. L. TATUM, E. B. FRED, and W. H. PETERSON (J. Bact., 1932, 23, 73—74).—Many organisms normally producing specifically *d*- or *l*-lactic acid when grown in association with *Cl. acetobutylicum* yield inactive forms. This effect is due to the production of a heat-labile substance by the latter organism. A disarrangement of the normal enzymic system of the lactic organisms is suggested.   A. G. P.

Propionic acid bacteria. E. R. HITCHNER (J. Bact., 1932, 23, 40—41).—Variations in the characteristics of numerous cultures are recorded. Pigmentation occurred in certain cases in which a neutral reaction was maintained throughout growth. Stimulated growth occurring in association with other organisms is ascribed to modification of the oxidation-reduction potential of the medium. Catalase activity of cultures varied considerably and was extremely low in many cases. All cultures fermented hexoses and glycerol but not inulin or dulcitol. $EtCO_2H$, AcOH, and CO_2 were the chief fermentation products of glucose. Small amounts of succinic acid were also formed.   A. G. P.

Factors involved in the biological production of acetone and butyl alcohol. L. WEINSTEIN and L. F. RETTGER (J. Bact., 1932, 23, 74—75).—The presence of EtOH-sol. protein in the medium is essential for the normal production of BuOH by *Cl. acetobutylicum*. Acid hydrolysates of sawdust, cotton-seed hulls, maize cobs, etc. yielded normal amounts of $COMe_2$ but no BuOH. The latter was formed only after the addition of prolamine.   A. G. P.

Activity of the enzyme dismuting acetaldehyde in aerobic cell metabolism. F. WINDISCH (Biochem. Z., 1932, 250, 466—486).—The conversion of MeCHO into AcOH and EtOH by bacteria (*B. ascendens*, *B. pasteurianum*, *B. aceti*, Hansen) under aerobic conditions is examined and methods for the macro-determination of O_2 utilisation and AcOH and EtOH production are described. The results are discussed from the viewpoint of mechanism of reaction.   P. W. C.

Nitrogen metabolism of bacteria as affected by colloids and replaceable bases in soil. H. J. CONN (J. Bact., 1932, 23, 77).—Certain non-sporing, humifying soil bacteria fail to develop in soils rich in total N, without the addition of N compounds, or salts or hydroxides of strong bases. This apparent deficiency of available N is characteristic of soils having high ratios of colloids to Ca. The presence of much adsorbed N liberated by the addition of strong bases is suggested.   A. G. P.

Synthesis of amino-acid by animal tissue and bacteria *in vitro*. T. ISHIHARA (Fukuoka-Ikwad.-Zasshi, 1931, 24, 1231—1304).—Aspartic acid was synthesised by many bacteria from a mixture of fumaric acid and NH_4 salt. The fumaric acid could not be replaced by crotonic, β-hydroxybutyric, or pyruvic acid. No animal tissues, even embryonic or neoplastic, synthesised NH_2-acid *in vitro*.   CH. ABS.

Growth of *Rhizobia* on rich nitrogenous media. A. W. HOFER and I. L. BALDWIN (J.

Bact., 1932, **23**, 65—66).—In high-N media marked physiological differences between *R. meliloti* and other nodule organisms are apparent.   A. G. P.

Dependence of the respiration of nitrogen bacteria on the oxygen tension. O. MEYERHOF and W. SCHULZ (Biochem. Z., 1932, **250**, 35—49).—Curves show the variation of the respiration of cultures of *Azotobacter chroöcoccum* in N-free salt solutions with the Q_{O_2} vals. at O_2 concns. of 0·3, 1, and 4%. Corresponding with the incomplete saturation of the respiratory enzyme at lower O_2 tensions, the CO inhibition decreases with decreasing O_2 tension.
                                                            P. W. C.

Effect of lecithin and cholesterol on the biology of the human tubercle bacillus. I. LOMINSKY (Ann. Inst. Pasteur, 1932, **49**, 194—219).—A comparison of the development of the bacilli grown on potato media containing (a) 0·07% cholesterol, (b) without addition, (c) 0·1% lecithin, (d) 0·07% cholesterol and 0·1% lecithin showed that the rate of growth increased in this order. The order of toxicity of such cultures for white mice was (c), (b), (d), (a), and for guinea-pigs, (d), (c), (b), (a), (c) and (d) being the most toxic, respectively.   A. L.

Chemical, microscopical, and serological properties of filtrates of *B. tuberculosis* and *B. phlei*. C. NINNI (Ann. Inst. Pasteur, 1932, **49**, 186—193).—The filtrates from the bacilli grown on Sauton medium contain protein and lipins, the amount of ultra-virus present depending on the amount of protein and colloidal material. The fats and lipins which will not pass through the Chamberland L_2 filter are present as complex lipo-proteins and are pptd. from the filtrates dried at 38° by EtOH at 96°. Filtrates after such treatment are antigenic.   A. L.

Presence of bacteria in coal seams. R. LIESKE (Biochem. Z., 1932, **250**, 339—351).—The bacterial content of seams of coal does not vary inversely with the density of the coal, anthracite often giving a large and porous coal a small count. The natural flora is not the same as that of the air of the mine. Very frequently gas-rich coal contains a greater no. of bacteria than gas-poor coal.
                                                            P. W. C.

Occurrence of micro-organisms in peat bogs and their rôle in peat formation. S. A. WAKSMAN and E. R. PURVIS (J. Bact., 1932, 23, 76).—Profiles of forest and sedge peats contain high bacterial nos. irrespective of the age of the various layers. Cellulose-decomposing bacteria are more concerned in peat formation than is usually supposed and are active in transformation processes long after the peat is laid down. Many organisms concerned are facultative anaërobes capable of developing at fairly high acidity.   A. G. P.

Microflora of old volcanic ash with special reference to nitrogen-fixing bacteria. N. R. SMITH (J. Bact., 1932, **23**, 75—76).—No evidence of N fixation by *B. radiobacter* in volcanic ash was obtained, although the organism was present. *Azotobacter* was not observed.   A. G. P.

Influence of dyes on the formation of catalase in certain bacteria. I. A. VOLFSON (Arch. sci.

biol., Russia, 1931, **31**, 161—172).—The production of catalase by Gram-positive bacteria was affected much more than that by Gram-negative bacteria on treatment of the medium with methylene-blue, neutral-red, gentian-violet, acid-fuchsin, or eosin. The basic dyes were more effective than the acid dyes. The presence of dyes had no appreciable effect on the decomp. of H_2O_2.   CH. ABS.

Use of reduced iron in the cultivation of anaërobic bacteria. E. G. HASTINGS and E. McCOY (J. Bact., 1932, **23**, 54—56).—Addition of reduced Fe to milk prior to routine tests for anaërobic organisms renders these tests much more definite.
                                                            A. G. P.

Soya-bean culture media. E. T. H. TSEN and S. SUNG (Chinese Med. J., 1932, **46**, 603—606).—The soya-bean media described give as good bacterial growth, with the same morphological and antigenic properties, as meat-peptone agar.   H. G. R.

Relation of temperature to the germicidal efficiency of lye solutions. E. C. McCULLOCH (J. Bact., 1932, **23**, 50—51).—A high-grade household lye effectively destroyed *B. abortus* and *E. coli*, a 1 : 800 solution having PhOH coeff. 8. Between 2° and 25° temp. had little influence on toxicity, which is associated with the activity of OH'.
                                                            A. G. P.

Oligodynamic action of metals. H. LANGWELL (Chem. and Ind., 1932, 701—702).—The oligodynamic action of metals may inactivate extra-cellular enzymes without causing injury to the organisms. Where fermentation is unaffected by oligodynamic action no extracellular enzymes are present.   T. McL.

Oligodynamic action of silver. F. L. HAHN (Biochem. Z., 1932, **251**, 101—104; cf. Egg and Jung, A., 1929, 1494).—Although the bactericidal effect of solutions of normal Ag salts depends on [Ag·], solutions of complex Ag salts need contain, initially, only sufficient of the ions to permit adsorption of them by the bacteria. Subsequent decomp. of complex ions and repetition of the process carry on the reaction.   W. McC.

Perfusion fluid for rabbit-ear vessels in determining blood-adrenaline. Z. KANOWOKA (Tohoku J. Exp. Med., 1932, **18**, 553—558).—Na citrate (10 g.) and old serum (100 c.c.) are diluted with "Tyrode" or "normosal" to 1000 c.c.   CH. ABS.

Threshold sensitivity of the rabbit ear method for determining adrenaline. H. SATO (Tohoku J. Exp. Med., 1932, **18**, 475—481).—Poor results were obtained with Schlossmann's perfusion fluid.
                                                            CH. ABS.

Standardisation of secretin. O. WILANDER and G. ÅGREN (Biochem. Z., 1932, **250**, 489—495).—The method is described. The active substance behaves like a base; it does not contain histamine and has no influence on the secretion of bile.   P. W. C.

Protection of insulin by antiproteases and its absorption from the intestine. B. K. HARNED and T. P. NASH, jun. (J. Biol. Chem., 1932, **97**, 443—456).—From *Ascaris lumbricoides* was obtained an antitryptic prep. which almost entirely prevented the

action of trypsin on insulin *in vitro*. Small amounts of the prep., however, did not afford protection against very large amounts of trypsin, indicating a stoicheiometric relation between trypsin and antitrypsin. The introduction of antitrypsin–insulin mixtures into the duodenum of normal dogs had no influence on the blood-sugar, whereas introduction into the stomach (where the antitrypsin functions as antipepsin) or duodenum of depancreatised dogs abolished the sugar excretion for short periods and produced an increase in the D : N ratio sufficient to indicate a temporary storage of glycogen. The relation between dosage and effect, however, indicated that the absorption of insulin from the intestine is small. F. O. H.

Physiology of glands. CXXVI. Relationship of the spleen and thyroid to iron metabolism. L. Asher and H. Tschumi (Biochem. Z., 1932, 251, 418—431).—The excretion of Fe by normal rabbits is investigated under const. conditions. After injection of thyroxine a considerable increase, and after splenectomy a decrease, of excretion of Fe occurs, but injection of thyroxine into splenectomised animals causes an even greater increase of Fe excretion than in the case of normal animals. P. W. C.

Effect of thyroid administration on blood-cholesterol. A. G. Duncan (J. Mental Sci., 1931, 77, 332—340).—The administration of thyroid to patients suffering from a wide variety of mental disorders results in a rapid lowering of blood-cholesterol. After cessation of the thyroid administration the blood-cholesterol rises gradually to a figure considerably above the former resting val. This phenomenon probably applies also to normal individuals. J. H. Q.

Direct measurements of the oxygen consumption of isolated, beating auricles from normal and thyrotoxic guinea-pigs. D. McEachern (Bull. Johns Hopkins Hosp., 1932, 50, 287—294).—The O_2 consumption is (7—20%) higher in the latter. Ch. Abs.

Respiratory metabolism in infancy and in childhood. XIII. Calorigenic action of thyroid extracts in normal infants. T. C. Wyatt, L. E. Weymuller, and S. Z. Levine (Amer. J. Dis. Children, 1932, 43, 845—864). Ch. Abs.

Relation of the blood-silica to the parathyroid gland and to the blood-calcium. J. Gürsching and H. Kraut (Arch. exp. Path. Pharm., 1932, 167, 146—157).—The ash of normal dog's blood contains 1—6·1% SiO_2. During tetany due to parathyroidectomy the Si contents of whole blood and serum decrease. Introduction of parathyroid hormone in such dogs and also in normal dogs effects an increase in the blood-Si. Hence the parathyroid gland regulates both the Ca and Si levels of the blood. Both Ca and Si are increased by administration of calcinosis factor. On subcutaneous injection of the one substance the blood level of the other also increases, both levels subsequently decreasing at approx. the same rate. F. O. H.

Comparative pharmacology of calcinosis factor and parathyroid hormone. T. von Brand, F. Holtz, and W. Putschar (Arch. exp. Path. Pharm., 1932, 167, 113—145).—Whilst the injection of calcinosis factor (irradiated ergosterol in which vitamin-*D* is either left intact or destroyed by heat or hydrogenation) is attended by symptoms resembling those due to injection of parathyroid hormone, differences occur in the type of calcification, in the changes in the serum-Ca, and in the relative sensitivity of different animals. Hence the mechanism of the action of the two substances must be different, despite the fact that, in the alleviation of tetany due to parathyroidectomy, the hormone may be completely replaced by the calcinosis factor. F. O. H.

Carotenoids and sex hormones. I. H. von Euler and E. Klussmann (Biochem. Z., 1932, 250, 1—6).—The presence of β-carotene in cows' corpus luteum and placenta, and of xanthophyll in human placenta, is detected. P. W. C.

Detection of sex hormones in totally castrated animals. S. Loewe, W. Raudenbusch, H. E. Voss, and F. Lange (Biochem. Z., 1932, 250, 50—52).—Sex hormones are detected in the excretions of castrated animals (ox and cock). P. W. C.

Androkinin content of the fæces. S. Loewe, F. Rothschild, and H. E. Voss (Biochem. Z., 1932, 251, 246—247).—The fæces of young men contain 2 mouse units of androkinin per kg. P. W. C.

Concentration–action curve for the follicular hormone (menformon). S. E. de Jongh, E. Laqueur, and P. de Fremery (Biochem. Z., 1932, 250, 448—465).—A more accurate method using the morphological examination of vaginal smears in the determination of the degree of action is employed for the construction of concn.–action curves for menformon, six concns. of the prep. being injected into 1200 mice in two different laboratories. The importance of the curves for evaluation of the prep. is indicated. P. W. C.

Action of the follicular hormone on plants. II. Action of crystalline β-follicular hormone. W. Schoeller and H. Goebel (Biochem. Z., 1932, 251, 223—228; cf. A., 1931, 1337).—The flowering of plants (*Calla œthiopica*) is accelerated by treatment with cryst. β-follicular hormone (Butenandt, this vol., 781) (300 mouse units per week) which also causes the growth of a second crop of flowers. The cryst. hormone, however, has none of the effects on the coleoptile of *Avena* which both the " auxin " of Went and Kögl (cf. this vol., 661) and commercial progynon solutions have. These solutions therefore contain " auxin." W. McC.

Magnesium content of blood-corpuscles after injection of prolan. L. Cannavò and R. Indovina (Biochem. Z., 1932, 250, 405—407).—When prolan is subcutaneously injected into man, a considerable increase in serum-Mg occurs (cf. this vol., 432) without any corresponding decrease in the corpuscle-Mg and the excess Mg must be derived from reserves in the tissues. Intramuscular injection of $MgCl_2$ solution causes a large increase of serum-Mg which is of only short duration and is not comparable with the effect of prolan. P. W. C.

Recent researches on the nature and function of vitamins. J. C. DRUMMOND (J. Roy. Soc. Arts, 1932, **80**, 949—957, 959—965, 974—980, 983—990).—Cantor lectures.

Carotene and vitamin-*A*. H. VON EULER (Bull. Soc. Chim. biol., 1932, **14**, 838—860).—A lecture.

Carotene and vitamin-*A*. H. VON EULER and E. KLUSSMANN (Svensk Kem. Tidskr., 1932, **44**, 223—224).—In cow-liver extracts (physiological salt solution) to which colloidal carotene has been added the characteristic absorption at 328 mμ is three times as strong as in those to which only H_2O has been added, but with blood extracts there is no such increase in strength. The content of carotenoid substances of the livers of rats to which carotene and thyroxine are administered is < that of the livers of rats receiving carotene alone. Spectroscopic examination shows that although the vitamin-*A* contents are the same, there is less carotene in extracts from the livers of rats which receive thyroxine than in those from the livers of rats which receive only carotene. W. McC.

Prophylactic dose of vitamin-*A* in the form of carotene. A. POLAK and J. A. STOKVIS (Arch. Néerl. Physiol., 1932, **17**, 299—306).—0.5—1.0×10^{-6} g. of carotene per day (dissolved in arachis oil) administered to young rats on a diet otherwise lacking vitamin-*A* prevents xerophthalmia and ensures normal growth. W. O. K.

Specific effect of vitamin-*B* on growth. B. SURE, M. C. KIK, and M. E. SMITH (J. Nutrition, 1932, **5**, 155—162).—The sp. effect of vitamin-*B* on growth is produced by raising the level of nutrition by a stimulation of the appetite. A. G. P.

Dietary requirements for fertility and lactation. XXIV. Specific effect of vitamin-*B* on lactation. B. SURE and M. E. SMITH (J. Nutrition, 1932, **5**, 147—153; cf. A., 1931, 772).—Data from experiments with rats indicate that vitamin-*B*, in addition to stimulating the appetite, exerts a sp. influence on lactation unrelated to the food and H_2O intake. A. G. P.

Is the vitamin-*B* content of milk under physiological control? F. L. GUNDERSON and H. STEENBOCK (J. Nutrition, 1932, **5**, 199—212).—No essential differences were apparent in the vitamin-*B* content of milk from cows or goats of different breeds, or in different stages of lactation, or receiving rations in which the vitamin-*B* content was varied in relation to the amount of milk produced. A. G. P.

Vitamin-*B*₁. H. MISAWA (J. Biochem. Japan, 1932, **15**, 439—471).—The prep. of vitamin-B_1 by a method based on that of Jansen and Donath (A., 1927, 382) yielded 13·38—23·0 mg. of cryst. material from 10 kg. of rice germ. The purest prep. had a protective dose against polyneuritis in pigeons of 0·007 mg. per day, whilst 0·02 mg. per day maintained normal growth in rats on a vitamin-B_1-free diet. Aq. extraction of these preps. yielded a cryst. substance and a less active amorphous substance. The cryst. preps. contained no P, were optically inactive, gave positive Jendrassik (A., 1923, ii, 892), Pauly, and Folin–Denis (phenol) tests, and in EtOH solution showed absorption bands at 250—280 and 310—360 mμ. F. O. H.

Antineuritic vitamin. III. Removal of impurities by fractional precipitation. R. J. BLOCK and G. R. COWGILL (J. Biol. Chem., 1932, **97**, 421—431).—Extracts of rice polishings with cold H_2O or of yeast with hot aq. HCl were conc. and treated by the CCl_4 technique (this vol., 309, 657). Treatment of the solutions thus obtained with HNO_2 did not reduce the total N content, but considerably decreased the potency. Fractionation by addition of picric, flavianic, or rufianic acid followed by BuOH–Et_2O (1 : 1) extraction was not satisfactory. More favourable was fractional pptn. by org. solvents. The vitamin was destroyed by AcOH and Ac_2O. Of 50 inorg. salts only $CuCl_2$ and $Hg(NO_3)_2$ gave ppts. which contained the vitamin in a conc. form without considerable loss of potency. $SnCl_2$ caused extensive destruction. Animal tests indicated that the preps. lacked some substance other than the antidermatitis factor which was supplied in the diet by crude yeast and by liver-preps. F. O. H.

Influence of vitamin-*B*₂ on carbohydrate metabolism. J. A. COLLAZO and C. PI-SUÑER BAYO (Biochem. Z., 1932, **250**, 89—108).—When natural fluids rich in the *B* group of vitamins are heated for 3 hr. at 100—120°, vitamin-B_1 and various enzymes are destroyed but vitamin-B_2 is unaffected. The glycogen and glutathione contents of muscle and liver and the sugar, uric and lactic acid, and glutathione contents of the blood of pigeons are investigated under varying conditions of *B*-avitaminosis. Vitamin-B_2 is the carrier of the enzyme complex responsible for glycogen formation and disappearance of sugar and lactic acid and increases the oxido–reduction power of the tissues. P. W. C.

Vitamin-*C*. E. OTT and K. PACKENDORFF (Z. physiol. Chem., 1932, **210**, 94—96).—A review. J. H. B.

Vitamin-*C*. J. TILLMANS and P. HIRSCH (Biochem. Z., 1932, **250**, 312—320).—A discussion. P. W. C.

Narcotine and vitamin-*C*. O. DALMER and T. MOLL (Z. physiol. Chem., 1932, **209**, 211—230; **211**, 284).—Methylnornarcotine (I) prepared from the natural alkaloid was not cryst. and had no antiscorbutic action (cf. this vol., 310). Attempts to synthesise (I) by condensation of cotarnine and normeconine failed. Narcotine could not be isolated from unripe orange juice or from potatoes. The Et_2O extract of ripe orange juice was not antiscorbutic and the extracted juice was as active as the original material. Hexuronic acid concentrates prepared by the method of Szent-Györgyi (A., 1929, 98) had definite antiscorbutic action. J. H. B.

Vitamin-*C*. V. Vitamin-*C* in seeds germinating in a dark place. T. MATSUOKA (J. Agric. Chem. Soc. Japan, 1931, **7**, 1070—1081).—Vitamin-*C* was not produced until the third day of germination; after 10 days the quantity was <50% of that of seeds germinated in (artificial) light. CH. ABS.

Vitamin-*C* in cranberries. O. M. BOGOLIUBOVA (Arch. sci. biol., Russia, 1931, **31**, 322—329).—Preservation, at a low temp. without freezing, for 4 months did not impair the vitamin-*C* content;

fermentation, freezing, and drying destroy the vitamin-*C*. Vitamin-*A* is probably present.

CH. ABS.

Vitasterol-*D*. IV. Activation of ergosterol by irradiation with natural light. A. JENDRASSIK (Biochem. Z., 1932, **252**, 205—211).—Antirachitic activity (equal to 0·02 or more of that produced by ultra-violet rays) is developed in ergosterol solutions on irradiation with direct or diffuse sunlight at 3450 m. and also at much lower altitudes. Although the absorption decreases continuously as the irradiation continues, no relation between the former and vitamin-*D* production can be traced. W. McC.

Chemical nature of vitamin-*D*. I. REMESOV (Biochem. Z., 1932, **250**, 560—563).—It is suggested that cholesterol exists in keto- and enol forms, the enol form being provitamin-*D*, which on irradiation passes to the keto-form, vitamin-*D*. Identity of ergosterol and provitamin-*D* is discredited.

P. W. C.

Irradiated cholesterol. R. G. GUSTAVSON (J. Colo. Wyo. Acad. Sci., 1929, **1**, No. 1, 23).—Extraction of irradiated cholesterol with liquid NH_3 gives a yellow, resinous, antirachitic material. CH. ABS.

Toxicity of irradiated ergosterol. G. TIXIER (Bull. Soc. Chim. biol., 1932, **14**, 896—899).—No abnormal calcification was observed in the viscera of rats which received in addition to a normal diet daily doses of 5, 10, or 20 mg. of a commercial prep. of irradiated ergosterol for 90 days, corresponding with 750, 1500, and 3000 times the therapeutic dose, respectively. The highest of these doses was fatal in 87 days to 1 of 2 rats which showed only hæmorrhage of the renal parenchyma. Any toxicity of antirachitic preps. is due to incorrect irradiation or contaminated ergosterol. A. C.

(A) Reduction in the blood-calcium content of parathyroidectomised dogs to which irradiated ergosterol has previously been administered. (B) Reduction in the calcium content resulting from subcutaneous injection of turpentine with production of abscesses. J. CHEYMOL and A. QUINQUAUD (J. Pharm. Chim., 1932, [viii], **16**, 185—190, 190—194).—A. The life of parathyroidectomised dogs is prolonged, sometimes very greatly, by administration of irradiated ergosterol in doses of about 0·005—0·01 g. per kg. for periods of 17 days to one month prior to the operation. At the same time the Ca content of their blood is reduced by amounts up to 50%.

B. Subcutaneous injection of turpentine (2—4 c.c.) (with production of abscesses) into dogs treated as in A sometimes produces further small reductions in the Ca content of the blood-serum. W. McC.

Physiology of apples. XII. Ripening processes in the apple and the relation of time of gathering to chemical changes in cold storage. H. K. ARCHBOLD. **XIII. Starch and hemicellulose content of developing apples.** E. M. WIDDOWSON (Ann. Bot., 1932, **46**, 407—459, 597–631;

cf. A., 1929, 362).—XII. The total growth rate of apples increased during the first 3 weeks of development and subsequently remained practically const. In the first 3 weeks no starch was present and 53% of the dry matter consisted of EtOH-insol. material and acids, together with 15% of sugars. During the period of starch synthesis the proportion of insol. matter and acids fell to 17% and that of total sugars rose to 55%. During the final ripening stages starch was hydrolysed, the sugar content rose to approx. 80%, and the acids and insol. matter declined to 14%. The rate of N intake reached a max. after 2 weeks of development and subsequently decreased steadily. During the storage of packed fruit any remaining starch is hydrolysed and sucrose inverted. Oxidation of sugars and the inversion of sucrose did not always occur at corresponding rates and differences were manifest by variations in the proportion of fructose. The glucose content remained practically const. throughout. Acid and a portion of the insol. matter were lost continuously during storage. Only a portion of the products of hydrolysis of the insol. matter was oxidised and the balance accumulated as (undetermined) nonreducing substances. Late gathering is associated with a low rate of loss of total sugars, a high rate of sugar inversion, a higher level of concn. at which sucrose inversion ceases, greater changes in reducing sugar contents, and low initial acidity.

XIII. Starch in the EtOH-insol. residue from apple tissue is determined by hydrolysis with taka-diastase after the partial removal of pectins by extraction with $K_2C_2O_4$ solution. Starch formation begins about mid-June and reaches a max. (1·5—2% of green wt.) in July—August, disappearing by the end of October. Apple tissue contains a readily hydrolysable polysaccharide other than starch or pectin. From the residue not hydrolysed by taka-diastase two H_2O-sol. substances, a polyuronide and a polysaccharide, were isolated. Both yield arabinose on hydrolysis and are classed as hemicelluloses. Both the hemicellulose and pectin contents of the growing apple increase steadily to a const. val. which persists during storage. Hemicelluloses do not act as reserve carbohydrates, but in structure and function are closely related to pectins. A. G. P.

Determination of lipin-soluble bismuth in oil solutions. F. ROTHÉA (J. Pharm. Chim., 1932, [viii], **16**, 110—112).—2 c.c. of the solution are heated, finally in a muffle furnace, and the residue is treated with HNO_3 and re-ignited. The residual Bi_2O_3 is weighed. R. S. C.

Colorimetric determination of sulphate in biological fluids. S. MORGULIS and M. G. HEMPHILL (Biochem. Z., 1932, **249**, 409—411).—Lang's technique (A., 1929, 1500) is unsatisfactory, but if the H_2CrO_4 is determined by titration with I after addition of KI and H_2SO_4 results which differ by only 0·6% from gravimetric are obtained provided that phosphates are first removed with $Ca(OH)_2$ and reducing substances destroyed with H_2O_2 and $FeCl_3$.

W. McC.