BRITISH CHEMICAL ABSTRACTS

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A.-PURE CHEMISTRY

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BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1933.

General, Physical, and Inorganic Chemistry.

Light excitation and emission in hydrogen sparks under increased pressure. W. FINKELN-BURG (Physikal. Z., 1932, 33, 888–889). A. J. M.

Bands due to the hydrogen molecule: $2p^{3}\Pi$ bands of hydrogen. I. SANDEMAN (Proc. Roy. Soc., 1932, A, 138, 395-411).—The proposed arrangement of the new H₂ bands described by Richardson and Davidson (A., 1931, 887) is criticised, and a simpler scheme is suggested. L. L. B.

Optical investigations of the accommodation coefficient and distribution function for molecular translation at low pressures. L. S. ORN-STEIN and W. R. VAN WIJK (Z. Physik, 1932, 78, 734—743).—A Fabry-Perot etalon was used to measure the distribution of intensity in a spectral line of He, and calculations are given relating this distribution to the distribution of velocities in the gas; the calculations give an accommodation coeff. of 0.3 for He colliding with a glass wall at 650°.

A. B. D. C.

Optical investigation of the collisions of gas molecules with a wall. L. S. ORNSTEIN and W. R. VAN WIJK (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 722—726).—The problem of the collision of gas mols. with a wall has been investigated by spectroscopic observation of an electrical discharge in He at 0.01 cm. pressure, contained in an annular space between two walls, the inner cooled, and the outer heated to 320°. J. W. S.

Quantum defect for highly excited S states of para- and ortho-helium. L. P. SMITH (Physical Rev., 1932, [ii], 42, 176–181).—Calc. vals. of the quantum defects for the o- and p-systems are 0.289 and 0.160, respectively, compared with 0.230 and 0.122 obtained by Hylleraas (cf. A., 1930, 1487) uncorrected for polarisation of the atom core, and 0.298 and 0.140 needed to yield the experimental term vals. N. M. B.

Photometric investigation of the most intense emission bands of fluorine. J. AARS (Z. Physik, 1932, 79, 122–138).—A discussion of the intensities of F_2 lines in bands at 17,439, 16,379, and 18,548 cm.⁻¹ A. B. D. C.

Spectrum of doubly-ionised neon (Ne III). T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 819—826).—Ne III spectrum has been photographed to 2000 Å., and new lines have been measured and classified. J. W. S.

Lifetime of the metastable ³P₂ neon atom. E. MATUYAMA (Physical Rev., 1932, [ii], 42, 373378).—Measurements of the rate of decrease of absorption of the 6402 Å. line of Ne excited by a high-frequency oscillatory current gave the val. 0.005 sec. at 5.2 mm. pressure. N. M. B.

Duration of metastable states : neon. J. M. ANDERSON (Canad. J. Res., 1932, 7, 434 - 443; cf. A., 1931, 781).—Decay curves for the absorption lines $\lambda\lambda 6402$, 6334, 6266, 6163, 6143, and 5945 at room and liquid air temp. are shown for a series of pressures, and half life-pressure curves are recorded. At the same pressure and temp. the rate of decay varies for different lines. N. M. B.

Energy balance of a positive column of sodium vapour. M. J. DRUYVESTEYN (Physikal. Z., 1932, 33, 822—823).—The distribution of radiation between the *D* lines and the infra-red bands of Na vapour has been measured for a column of Na vapour. W. R. A.

Continuous spectrum of sodium. H. HAMADA (Nature, 1932, 130, 811—812). L. S. T.

Vibrational and rotational structure of yellowred emission band spectrum of sodium molecule. Y. UCHIDA (Japan. J. Physics, 1932, 8, 25–50; cf. A., 1932, 667).—Full data for rotational lines of the first five order groups are given, and lines are identified with the wave nos. calc., with the mol. consts. obtained from absorption data, and their quantum transitions are fixed. The mol. consts. of Na₂ were $B_0^{"}$ 0.15399, α_1 0.0007, and α_2 0.00003 cm.⁻¹

N. M. B. Spectral lines of Cl v and Cl IV. S. C. DEB (Bull. Acad. Sci. Agra and Oudh, 1932, 2, 43—50).—The spectral lines of Cl IV and Cl v are classified. The ionisation potentials are, respectively, 55·17 and 69·36 volts, which are larger than Bowen's vals. (A., 1928, 210) M. S. B.

Continuous spectrum of pure argon. S. P. McCALLUM, L. KLATZOW, and J. E. KEYSTON (Nature, 1932, 130, 810—811).—The special characteristics which appear in the spectrum of highly-purified A are described. L. S. T.

Spectrum of potassium hydride. G. M. ALMY and C. D. HAUSE (Physical Rev., 1932, [ii], 42, 242—266).—Full data and analyses for the lines of 29 bands in the range 4100—6600 Å. are tabulated. Absorption bands were masked by alkali bands except in the region 4600—4800 Å. Heats of dissociation are 1.25 and 2.06 volts for the excited and ground states, respectively. A Franck-Condon intensity diagram is in good agreement with observed intensities. N. M. B.

Change of wave-length and intensity in iron, nickel, and titanium lines by disruptive discharge. H. NAGAOKA, T. FUTAGAMI, and I. MACHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 169–184).—Line shifts are characteristic of different spectral series, and are classified into several types. Relation with stellar spectra is discussed. N. M. B.

Interferometer measurements in the extreme ultra-violet region of copper. J. C. McLENNAN and (MISS) F. M. QUINLAN (Phil. Mag., 1932, [vii], 14, 823—829).—Cu arc lines between λ 2276 and 1980 Å. were measured. H. J. E.

Hyperfine structure of arc lines and the nuclear moment of copper. R. RITSCHL (Z. Physik, 1932, 79, 1—25).—Both Cu isotopes have nuclear moment 3/2. A. B. D. C.

Spark spectra of copper, silver, and gold between 1300 and 300 A. L. BLOCH, E. BLOCH, and J. FARINEAU (J. Phys. Radium, 1932, [vii], 3, 437— 451).—Wave-lengths and intensities are tabulated for approx. 400 lines of Cu, 640 lines of Ag, and 540 lines of Au, in the ranges 1377.48—385.94, 1321.02— 260.17, and 1341.58—296.13 Å., respectively.

N. M. B.

Spark spectrum of rubidium in the ultraviolet. J. JANIN (Compt. rend., 1932, 195, 1010– 1012).—Using the electrodeless discharge and Rb prepared from RbN_3 , 96 lines between λ 2400 and 2150 Å. have been measured, of which 20 are assigned to Rb II, 29 to Rb III, and 5 to Rb IV.

C. A. S.

First spark spectrum of antimony. R. J. LANG and E. H. VESTINE (Physical Rev., 1932, [ii], 42, 233-241).—Full data and analyses for about 200 lines in the range 7000-600 Å. are tabulated. N. M. B.

Hyperfine structure in the antimony spark spectrum and the nuclear moment of antimony isotopes. J. S. BADAMI (Z. Physik, 1932, 79, 206— 223).—Hyperfine structure of a series of Sb II lines indicates the moment 3/2 for Sb¹²¹ and 7/2 for Sb¹²³. A. B. D. C.

Hyperfine structure in the antimony arc spectrum, Sb I. J. S. BADAMI (Z. Physik, 1932, 79, 224-230). A. B. D. C.

Spectrum of iodine in adsorbed state. D. CHILTON and E. RABINOWITSCH (Z. physikal. Chem., 1932, B, **19**, 107—112).—The absorption spectrum of I sorbed on a chabasite crystal is similar to that of I dissolved in C_6H_6 or that of I vapour, except that it exhibits two, or possibly three, max. It is concluded that sorption is mol., and that the sorbate consists of several layers differing in the firmness with which they are attached to the surface. The spectrum is widened somewhat towards the ultraviolet, compared with the other two; this is ascribed to sorptive forces. R. C.

Extinction of iodine fluorescence by magnetic fields and foreign gases. W. BERG (Z. Physik, 1932, 79, 89-107).—An investigation of extinction

by magnetic fields and foreign gases shows that the magnetic field not only itself extinguishes the fluorescence, but also increases the effective cross-section of the mols. for collision with I, N_2 , O_2 , and A.

A. B. D. C.

Absorption of the fluorescent light of iodine by its vapour. I. I. AGARBICEANU (Compt. rend., 1932, 195, 947—949; cf. A., 1932, 891).—The temp. absorption curves of six lines of the fluorescence spectrum of I by I vapour in air at temp. $23-270^{\circ}$ show that increase of absorption with rise of temp. is due both to the gases of the air and also to increase in collisions bringing I₂ mols. into various states.

C. A. S.

Lanthanum spectra (La I, La II, La III). H. N. RUSSELL and W. F. MEGGERS (Bur. Stand. J. Res., 1932, 9, 625-668).—The available data on the La spectrum have been analysed and the lines classified as belonging to the La I, La Π , and La III series. The ionisation potentials are 5.59 volts for La, 11.38 volts for La⁺, and 19.1 volts for La⁺⁺. D. R. D.

Collision phenomena on optical excitation of various mercury isotopes. S. MROZOWSKI (Z. Physik, 1932, 78, 826—843).—Improved apparatus confirms the result that a non-extinguishing inert gas exerts a selective effect on the intensities of hyperfine lines of the Hg isotopes. A. B. D. C.

Emission life of the mercury resonance line at 2537 A. S. MROZOWSKI (Z. Physik, 1932, 78, 844– 846).—Measurements of the emission life of the Hg resonance line 2537 Å. do not agree with observations on absorption. A. B. D. C.

Spectra of high-frequency discharges. I. Comparison of damped with undamped electrodeless excitation. J. K. ROBERTSON (Phil. Mag., 1932, [vii], 14, 795-806).—The spectra of the discharges in Hg and Cd vapours are compared.

H. J. E.

Isotope displacement in hyperfine structure. G. BREIT (Physical Rev., 1932, [ii], 42, 348—354).— The order of magnitude of isotope displacements can be explained as due to small changes in nuclear radii. Data for Hg, Tl, and Pb arc and spark spectra are in agreement with this theory. N. M. B.

Mercury vapour discharge. E. LÜBCKE (Physikal. Z., 1932, 32, 890—895).—The probability of ionisation in the Hg discharge is calc. In the Hg arc at low pressures the concn. of electrons is smaller than that of positive ions. There must be heavier negative carriers present. A. J. M.

Spectrum of trebly-ionised lead. J. KISHEN (Nature, 1932, 130, 739).—A necessary modification of this spectrum gives $6s^2S$ a val. of 340,180, yielding an ionisation potential of 41.9 volts. L. S. T.

Hyperfine structure of arc lines in vacuum of bismuth in the visible and the ultra-violet regions. W. MOHAMMAD and P. N. SHARMA (Phil. Mag., 1932, [vii], 14, 977–990).—The hyperfine structure of 13 Bi lines in the violet and ultra-violet regions has been examined, using two Lummer plates. J. W. S. Cold cathode vacuum arc. F. H. NEWMAN (Phil. Mag., 1932, [vii], 14, 788—794).—The mechanism of starting and maintaining the arcs is discussed. H. J. E.

Structures in the K absorption spectra of Cu and Zn in brass. S. KAWATA (Japan. J. Physics, 1932, 8. 51—56).—The structures for the pure elements and in some kinds of brass were largely influenced by the phases of the absorbing atoms, and showed no satisfactory agreement with Kronig's theory (cf. A., 1931, 993). N. M. B.

N-Series for the elements 73 Ta to 81 Tl. I. T. MAGNUSSON (Z. Physik, 1932, 79, 161–169).— The lines $N_{IV}N_{VI}$ and N_VN_{VI} , v_{II} were measured for Ta, W, Os, Ir, Pt, Au, and Tl, and the K-absorption edge was determined for C. A. B. D. C.

Measurements of the absorption coefficient for X-rays in the neighbourhood of the L-edges of the elements Pt and Au. M. WOLF (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 547-550)... The results are used to calculate the no. of dispersion electrons connected with each of the 3 L-levels.

H. J. E.

X-Ray study of the density distribution in the discharge tube. Y. ISHIDA and T. SUETSUGU (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 185—188).—Qual. investigations of pressure variations in the positive column of various Hg discharge tubes were made by means of X-ray photographs.

N. M. B.

Origin of the spectral selective photo-electric effect in thin alkali metal films. R. SUHRMANN and A. SCHALLAMACH (Z. Physik, 1932, 79, 153— 160).—An investigation of the spectral selective photo-effect for K films on Ag surfaces with films greater and less than the monoat. layer shows that the layer of K atoms can reduce the energy required to extract electrons from the Ag. No barrier layer photo-effect need be postulated.

A. B. D. C.

Long-wave limit of the photo-electric effect determined from atomic volume of the elements. G. SCHWEIKERT (Z. Physik, 1932, 79, 248—253).— Theoretical. The long-wave photo-electric limit is shown to be proportional to the 2/3 power of the at. vol. A. B. D. C.

Diffraction of fast protons by gold foil. E. RUPP (Z. Physik, 1932, 78, 722—727).—Protons traversing gold foil gave X-ray interference patterns for the wave-length 6.4×10^{-12} cm. corresponding with the accelerating potential of 200 kv. Atom factors for protons were determined. A. B. D. C.

Emission of positive ions from cold surfaces under the influence of strong electric fields. W. R. HARPER (Nature, 1932, 130, 775). L. S. T.

Reflexion of atomic beams from sodium chloride crystals. R. M. ZABEL (Physical Rev., 1932, [ii], 42, 218—228).—The wave nature of He, Ne, and A was investigated by the reflexion of beams of these gases from natural NaCl, and laboratorygrown NaCl crystals cleaved under various conditions; evidence of diffraction was obtained in all cases.

N. M. B.

Diffusion of positive ions of salts through copper at high temperature. Mass spectrograph analysis of the emitted ions. J. CICHOCKI (J. Phys. Radium, 1932, [vii], 3, 478—485).—When the chlorides of Li, Na, K, Mg, Cu, Sr, and Ba enclosed in a Cu film are heated to a high temp., the positive ions of the salt diffuse through the film and become a source of complex ions consisting of combinations of the metal of the salt with the Cu or the Pt forming the supporting electrode. N. M. B.

Magnetic spectra of secondary electrons from silver. S. CHYLINSKI (Physical Rev., 1932, [ii], 42, 393—399).—Kinetic energy distribution curves are given for Ag bombarded with cathode rays in the energy range 2.1—30 equiv. kv. Peak locations vary somewhat with the primary voltage; the curve forms are similar to those of the continuous X-ray spectrum. N. M. B.

Kinematographic electron microscopy of oxide cathodes. E. BRÜCHE and H. JOHANNSON (Ann. Physik, 1932, [v], 15, 145—166).—Film exposures of emitting oxide cathodes are examined by an electric electron microscope and results are discussed.

W. R. A. New cathode investigations with the electrical electron microscope. E. BRÜCHE and H. JOHANNson (Physikal. Z., 1932, 33, 898—899).—The electron microscope (cf. A., 1932, 209) has been used to study cathodes of pure W, and of Th and W. The former differs considerably from an oxide cathode in its behaviour, whilst the latter occupies a position between the two types. A. J. M.

Polarisation of electrons. E. RUPP (Physikal. Z., 1932, 33, 937—940).—The earlier experiments (A., 1932, 317) have been extended and a new one is described for double scattering at 90°. Polarisation brought about by this method must be due to a different cause from that in the earlier experiments. It may result from polarisation of the nucleus.

A. J. M.

Large-angle scattering of electrons in gases. II. C. B. O. MOHR and F. H. NICOLL (Proc. Roy. Soc., 1932, A, 138, 469–478; cf. A., 1932, 1185).— Angular distributions of scattered electrons in H_2 , CO_2 , CH_4 , N_2 , Ne, PH_3 , and H_2S have been measured to 160° for 30–150 volt electrons. The elastic and inelastic scattering curves are found to be closely similar. The elastic scattering curves show a gradual change in form for successive elements in the periodic table. L. B.

Motion of an electron in a crystalline lattice. G. C. WICK (Atti R. Accad. Lincei, 1932, [vi], 16, 142-149).—Theoretical. Taking into account the resonance forces between a conducting electron and the bound electrons of the lattice, the energy levels of the former are calc. approx. There is an energy max. for zero velocity of the electron. O. J. W.

Velocity distribution of electrons in the positive column. M. J. DRUYVESTEYN (Physikal. Z., 1932, 33, 856-863).—The diffusion of electrons in the positive column is investigated for small c.d. The gradient of the column is calc., and the formulæ are applied to the positive column in Ne. A. J. M. Quantum theory of diffusion of electrons. L. GOLDSTEIN (Compt. rend., 1932, 195, 864-866).

Quantum mechanics [applied to] the formation of negative ions. Y. ROCARD (Compt. rend., 1932, 195, 945-947).—Calculation of the nature of the spectrum emitted on the fixation of an electron by H_2 or He shows that this process may be the origin of some of the light of the night sky. C. A. S.

Revision of at. wt. of silicon. Ratio $SiCl_4:SiO_2$. P. F. WEATHERILL and P. S. BRUNDAGE (J. Amer. Chem. Soc., 1932, 54, 3932—3938).— This ratio, determined by hydrolysis of $SiCl_4$ in dil. HCl, gives $28\cdot103\pm0\cdot003$ for the at. wt. of Si.

L. P. H. (c)

Method of separation of isotope mixtures and its application to the isotopes of neon. G. HERTZ (Z. Physik, 1932, 79, 108—121).—Diffusion through porous walls in vac. gave partial separation of the Ne isotopes. A. B. D. C.

New isotopes of mercury. F. W. ASTON (Nature, 1932, 130, 846).—Definite traces of new lines 197 and 203 have been obtained in the mass spectrum of Hg. The former is due to a new isotope, but the latter may be due to the hydride of 202, although this is considered improbable. The proportions of Hg¹⁹⁷ and Hg²⁰³ are 0.01 and 0.006%, respectively, and their effect on the mean at. wt. is therefore negligible. L. S. T.

Atomic disruption by means of hydrogen canal rays. F. KIRCHNER (Physikal. Z., 1932, 33, 777).— The at. disruption of Li has been studied by an apparatus essentially simpler than the apparatus of Cockroft and Walton (cf. A., 1932, 893), whose results are confirmed. W. R. A.

Period of radium. E. GLEDITSCH and E. FOYN (Amer. J. Sci., 1932, [v], 24, 387–393).—Boltwood's method on a Norwegian broeggenite gives 1691 years. C. W. G.

Passage of neutrons through matter. H. S. W. MASSEY (Proc. Roy. Soc., 1932, A, 138, 460-469; cf. A., 1932, 443).—Mathematical. Born's quantum theory of collisions is applied to the elastic collisions of neutrons with material particles. A neutron model consisting of a H atom in a nearly zero quantum state is considered. The experimental evidence indicates that the radius of such an atom must be $< 2.0 \times 10^{-13}$ cm. L. B.

Radioactivity of samarium. G. VON HEVESY and M. PAHL (Nature, 1932, 130, 846–847).—Sm is radioactive, emitting a radiation of the α -ray type, the intensity of which is reduced to half its val. by 1.3 μ of Al. L. S. T.

Ionising effect of α -rays in solid dielectrics. H. FOLMER (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 636—642).—An improved technique has shown that α -radiation influences the conduction of paraffin exposed to Po radiation and suggests the probability of ionisation in solid dielectrics.

W. R. A.

Temperature variation of the total currentcarrying elements in air. A. BECKER and I. SCHAPER (Z. Physik, 1932, 79, 186-193).-Saturation current due to complete absorption of Po α -rays by a vol. of air increased as the temp. of the air rose from -80° to 250° ; the increase must be due to variation of the energy required for formation of the current-carrying elements. A. B. D. C.

β-Rays of active deposit of actinium. S. Y. SZE (Compt. rend., 1932, 195, 773—775; cf. A., 1932, 790).—H_ρ and the energies and origins of the groups in the β-ray spectrum of this deposit, relative to the Th-B line H_ρ 1398, have been redetermined with substantially different results (cf. A., 1926, 105). Three groups, H_ρ 2418, 2670, 2772, were not found, two, 2149, 2456, are shown to be due to the transition Ac-B $_{B}$ Ac-C, and three, 1953, 2252, 2304, to Ac-C $_{a}$ Ac-C". C. A. S.

Radiations from radium-D and -E. J. A. GRAY (Nature, 1932, 130, 738).—Ranges of the β -rays of Ra-E in various substances are given. Absorption of the γ -rays in Pb has been measured and a soft type of γ -ray, presumed to be the M-rays characteristic of at. no. 83, detected. L-Rays are emitted by approx. 30% of Ra-D atoms and primary rays by < 4%; the primary rays consist apparently of a band extending from $\lambda < 0.28$ Å. to $\lambda < 0.30$ Å. The properties of the hard γ -rays of Ra-E indicate that they are excited by some of the β -rays after their escape from the nucleus. L. S. T.

Gamma-ray ionisation chamber. G. C. LAU-RENCE (Canad. J. Res., 1932, 7, 103—105).—The chamber described is claimed to be as sensitive as a good gold-leaf electroscope, but the scale length is longer, permitting fewer readings each of longer duration. A. G.

 γ -Rays of thorium-B and of the thorium-C bodies. C. D. ELLIS (Proc. Roy. Soc., 1932, A, 138, 318—339).—The β -ray spectrum of Th-B+C has been studied and new measurements have been made of the energies of the β -ray groups. The relative H_{ρ} of the different groups were determined, also the abs. H_{ρ} of certain strong groups. The intensities of the groups were measured photometrically. The γ -rays associated with the disintegrating bodies have been deduced from these results. L. B.

Average life of activated atomic nuclei: probable cases of impossibility of γ -ray emission. F. PERRIN (Compt. rend., 1932, 195, 775—778; cf. A., 1932, 5, 790).—Theoretical. Considering that oscillation of one constituent of a nucleus involves oscillation of the remainder, the calc. mean life of a state, e.g., of Ra-C', is greatly increased. Nuclei consisting of helions, Be⁸, C¹², etc., or of helions and demihelions, Li⁶, B¹⁰, etc., ought not to emit γ -rays. C. A. S.

Ionisation by γ - and cosmic rays in oxygen and xenon. V. MASUCH (Z. Physik, 1932, 79, 264—265).—Ionisation of O₂ and Xe is proportional to the density of the gas for the harder components of cosmic rays, but not for rays of smaller energy.

A. B. D. C.

Secondary radiation produced by cosmic rays. J. M. BENADE (Nature, 1932, 130, 699). L. S. T. Light emission caused by electronic, ionic, and atomic collision. W. HANLE and K. LARCHE (Physikal. Z., 1932, 33, 884—887).—The directional distribution of intensity for the three types of collision is investigated, and an arrangement of apparatus for studying this in ionic and at. collision is described.

A. J. M.

Atomic eigenfunctions and energies. C. W. UFFORD and G. H. SHORTLEY (Physical Rev., 1932, [ii], 42, 167—175; cf. A., 1931, 781).—Mathematical. N. M. B.

Breakdown discharge as statical ionisation. H. EISLER (Z. Physik, 1932, 79, 266—274).—Breakdown discharge may be explained by a purely statical ionisation of the atoms or mols. of the dielectric.

A. B. D. C.

Space charge and its relation to the chemical components of the atmosphere. R. STOPPEL (Z. Physik, 1932, 78, 849—853).—Short-circuited electrometers show considerable variations of zero varying with the gas $(H_2, N_2, O_2, \text{ and } CO_2)$ surrounding the instrument. A. B. D. C.

Cosmic-ray ionisation as a function of pressure, temperature, and dimensions of the ionisation chamber. J. W. BROXON (Physical Rev., 1932, [ii], 42, 321-335).—Investigations over a pressure range did not support the subsidiary radiation theory of cosmic-ray ionisation (cf. A., 1931, 3). N. M. B.

Magnetic spectrum of cosmic rays. P. KUNZE (Z. Physik, 1932, 79, 203-205).—A Wilson chamber in an intense magnetic field showed curved traces of cosmic rays, positive particles being more frequent than negative; an energy spectrum is shown.

A. B. D. C.

Air afterglow and active nitrogen. J. K. ROBERTSON (Canad. J. Res., 1932, 7, 444-450).— The air afterglow spectrum in the visible range consists of a continuous faintly banded region 4400— 5000 Å., and a pure continuum in the yellow and red. Evidence indicates that the yellow-red afterglow is due to N; the addition of Hg vapour at once destroys the glow. N. M. B.

Value of b_k and atomic radii of elements in relation to the periodic system. J. A. M. VAN LITEMPT (Rec. trav. chim., 1932, 51, 1117—1130). b_k is a periodic function of the at. no. Hence, in cases where its val. is unknown, b_k may be determined by interpolation in the b_k -at. no. curve. The vals. obtained are closely correlated with the at. and ionic radii. For any one element, the radius of the positive ion at. no. of the element. The vals. with Ce^{•••}, Ce^{•••}, and Ce suggest that free Ce has the electronic structure 2 8 18 18 10 2, analogous to that of Ce^{••••} (2 8 18 18 8), whilst the Ce^{•••} ion has the structure 2 8 18 19 8. An attempt is made to correlate these at. radius relationships with superconductivity phenomena.

D. R. D.

Eddington's theory and physical constants. G. S. R. KRISHNAN (Nature, 1932, 130, 776).—Vals. have been calc. for the physical consts. Selected vals. are: at. wt. of H, 1.00774 ± 0.00002 , e/m_0 $1.77001\pm0.00013\times10^7$ c.m.u., e $4.81209\pm0.00037\times10^{-10}$ e.m.u., $N 6.01132 \pm 0.00089 \times 10^{23}$, and $h 6.64879 \pm 10^{-27}$.

Determination of e/m for "thread "ine at 169 SIEBERTZ (Physikal. Z., 1932, 33, 895—897^{m.-1} were are obtained for e/m greater than for elecalogy with N. M. B.

Structure of line spectra in cryane, ali-TOMASCHEK (Nature, 1932, 130, 740).—(Relative binations for Pr, Nd, Sm, and Er have bin Raman es. (Miss)

Regularities in the line spectra of s, 54, 4199 R. TOMASCHEK (Physikal. Z., 1932, 33, of the lines The phosphorescence spectra of the re $n-C_6H_{13}Br$, CaO and MgO are investigated.

Spectrum of chromium in c^{s} character-DEUTSCHBEIN (Physikal. Z., 1932, 33,gs. The re-The absorption and emission spectra of Obrations are room temp. and at -180° to -190° werans, and the Cr is capable of producing phosphors of 2575 cm.⁻¹, isomorphous with the principal material O-H freitself as larger mols. in the principal crorce and ex-H₂S and the

Line spectrum of samarium ion is its variation with the temperatu a 5% change and J. G. HARWELL (Proc. K. Akad. e detected. sterdam, 1932, 35, 979—994).—The ab: J. G. A. G. of Sm^{***} in hexagonal cryst. Sm(EtSCROFT and C. been determined parallel to the optic 2575-2587). and 169° abs. Absorption lines in th of H₂O drops 2200 Å. are tabulated. y with varying

2200 Å. are tabulated. Doublet separation of the BRUNETTI and Z. OLLANO (Nuovo Separation of Chemical Science Solution of Ce(NO₃)₃ gives a Raman cm.⁻¹ and a 5.6M solution of CeCl₃ cm.⁻¹ These are ascribed to the Cent transition ${}^{2}F_{5/2} - {}^{2}F_{7/2}$, in agreement magnetic measurements, but not v L J. P. (c) barrent for the transition to the cent transition to the transition

Absorption spectrum of o(J. Amer. Chem. pressures and the existence of 'light scattering I. Ultra-violet bands between is is contrary to W. FINKELNBURG and W. STEINE, the discrepancy 79, 69—88).—The absorption specs. L. O. (c) atm. indicates that the O_4 mol. ex. mols. united by van der Waals for hanisms for the

mois, united by van der waars for pours by air. Significance of ultra-violet sull. Soc. chim., of alkali halides. M. BORN (Z he luminiscence 62-68).—The hypothesis that ul330, 1255; 1931, bands of alkali halide crystals are unds. The temp. of two neighbouring ions within are given for many to contradictions in the theory and ethers. With removed by assuming that the ne low 300° probably an internal surface.

Molecular absorption of miliate products are cules in the vacuum ultra D. R. D. and H. SPONER (Z. Physik, ¹)er the influence of

Absorption spectra were measu Elektrochem., 1932, 1560 Å. for ICl, IBr, and BrCl. it Brüninghaus (A.,

Absorption spectrum o: D. R. D. W. G. BROWN (Physical Rev., S. ROTHSCHILD 363).—Vibrational analysis leases. S. ROTHSCHILD of the IBr absorption spectrum 51).—The addition CaS-Sm or SrS-Sm

phosphors greatly increases their efficiency, so that they can be excited by an ordinary electric lamp. The Bi must be fused with the phosphor, and probably acts as a sensitiser, taking up the incident radiation and passing it on to the phosphor. A. J. M.

Reflecting power of thin metallic films. P. ROUARD (Compt. rend., 1932, 195, 869-870).-The reflecting power of the glass-metal surface of a Au film 9.5-10.4 mµ for $\lambda\lambda$ 5780, 5461, and 4358 Å. decreases with increasing thickness to min. for thicknesses $< 5.2 \text{ m}\mu$, and then rises rapidly. Films of Ag and Pt behave similarly. C. A. S.

Variation of reflecting power of bismuth on magnetisation. E. ENGLERT and K. SCHUSTER (Z. Physik, 1932, 79, 194-196).-Variation of resistance of Bi with temp. does not affect reflecting power. A. B. D. C.

Ionised gases in a magnetic field at pressures below 10⁻³ mm. Hg. T. V. IONESCU and C. MIHUL (Compt. rend., 1932, 195, 765-767; cf. A., 1931, 285; 1932, 554).—The effects of pressure and H₂O vapour are examined. In the atm. waves of length > 10 m. are reflected where pressure is $< 10^{-4}$ mm. Hg, *i.e.*, at heights > 150 km. C. A. S.

Scattering of light by sound waves. P. DEBYE (Physikal. Z., 1932, 32, 849-856).-Theoretical. A. J. M.

Selenium or selenide rectifier ? W.S. GRIPEN-BERG (Physikal. Z., 1932, 33, 778).-Certain facts indicate that the rectifying properties of a Se rectifier are really attributable to a very thin surface layer of Fe selenide. W. R. A.

Selective photo-effect and optical absorption at composite photo-cathodes. W. KLUGE (Physikal. Z., 1932, 33, 873-874).-The composite cathodes are made up of a layer of Ag, on which is deposited a layer of alkali oxide with alkali metal adsorbed. With such a cathode there are two max., one in the short-wave, the other in the long-wave region. By making the M₂O-M layer very thin, the long-wave max. gets weaker. It is also possible in this case to study both the photo-effect and optical reflexion. There is no min. of reflexion corresponding with max. of photo-electric efficiency. A. J. M.

Spectral sensitivity of [photo-electric]cells with copper electrodes covered with cuprous oxide. G. ATHANASIU (Compt. rend., 1932, 195, 767-769).—Using electrodes of electrolytic Cu covered with Cu₂O prepared by (a) the author's method (cf. A., 1925, ii, 1067), (b) Garrisson's method (cf. A., 1923, ii, 728), and (c) heating to 1000° and cooling rapidly, and as electrolyte 0.1N-CuSO4, -KCl, or -KNO₃, the e.m.f. of the photo-electric cell is with (a) negative, but with (b) and (c) positive or negative. The positive effect is due to CuO, which when alone produces an e.m.f. of sign opposite to that produced by Cu₂O. A similar explanation holds for the varying position of the max. sensitivity, that for Cu_2O being at 4600–4800 Å., but displaced towards red by CuO, the max. for (b) being at 5100-5800 Å.

C. A. S.

Electrical and optical behaviour of semiconductors. VII. Photo-electric properties of

semi-conductor unidirectional layers. W. LEO (Ann. Physik, 1932, [v], 15, 129-144).-The capacity and resistance of unidirectional layers of Cu₂O and Ag₂S are considered. W. R. A.

Relation of optical transparency of cuprous oxide to electrical conductivity. G. MÖNCH (Z. Physik, 1932, 78, 728-733) .- The absorption edge of Cu_oO lies at 638 mµ and is independent of the conductivity of the sample; the transparency of the sample was used to measure the O2 content of the layer. A. B. D. C.

Electrostatic theory of the dependence on frequency of ionic mobility and dielectric constant in mixed solutions of strong electrolytes. I. General theory. H. FALKENHAGEN and W. FISCHER (Physikal. Z., 1932, 33, 941-945).-The general solution of the differential equation connecting ionic mobility, dielectric const., and frequency is considered. A. J. M.

Dielectric constant. I. Variation of dielectric constant of quartz with applied potential. H. SAEGUSA and K. NAKAMURA (Sci. Rep. Tôhoku, 1932, 21, 411-438) .- Apparatus and technique for the accurate determination of dielectric const. are de-The dielectric const. of a quartz plate cut scribed. perpendicular to its optical axis increases exponentially with applied potential from about 2000 volts per cm. thickness, and increases rapidly with rising temp. When the quartz plate is cut parallel to the optical axis, no such effect is observed up to 12,000 volts per cm. E. S. H.

Electric moment of hydrogen peroxide. E. P. LINTON and O. MAASS (Canad. J. Res., 1932, 7, 81-85).—The electric moments of H_2O_2 and of H_2O were measured by determinations of the dielectric consts. of solutions in dioxan at 25° and in Et₂O at 10° or 0°. The vals. obtained were 2.13 and 2.06×10^{-18} for $H_{2}O_{2}$ and 1.90 and 1.71×10^{-18} for $H_{2}O_{2}$. The lower val. obtained for H₂O in Et₂O may be due to its association being greater at the lower temp. or to experimental errors. The val. obtained for H₂O₂ favours the formula $H_2 O \rightarrow O$. A. G.

Connexion between dipole moment and cohesive forces. A. E. VAN ARKEL (Rec. trav. chim., 1932, 51, 1081-1107).-Calc. and observed vals. of b.p., dipole moment, and van der Waals a and b for org. liquids are compared. London's theory (A., 1930, 1239) is extended to more complicated mols. van Laar's law concerning the additivity of b (A., 1916, ii, 386) is obtained as a first approximation for sub-It, 580) is obtained as a first approximation for sub-stances of zero moment. For halogen atoms a/V^2 is const. (V=at. or mol. vol. at b.p.). For C tetra-halides (e.g., CBr₃Cl) $T=(V_{compound}-V_C)^2/V_{compound}$ approx., where T=b.p. abs. It follows that the val. of the b.p. is approx. additive. For partly halogenated compounds (e.g., CHCl₃) the b.p. is 45° > theory for compounds containing 1 H 85° higher for theory for compounds containing 1 H, 85° higher for those with 2 H, and 81° higher for those with 3 H, the val. of this increment increasing with dipole moment. The val. of a depends on the sum of the abs. partial moments and not on the total moment. For isomeric derivatives of C_6H_6 the b.p. rises with dipole moment. Of disubstituted C_2H_4 derivatives, the $\alpha\alpha$ -compounds

have the lowest b.p.; when both substituents are the same, the *trans*-isomerides have lower b.p. than the cis. A study of C_2H_6 and C_3H_8 derivatives indicates that the more a group is surrounded by other atoms, the smaller is its effect on the cohesive forces. The b.p. of CF_4 is about -130° , and not -15° as stated by Moissan (A., 1890, 944). D. R. D.

Dielectric constant of ethyl alcohol vapour and possible effect of conductivity. H. L. KNOWLES (J. Physical Chem., 1932, 36, 2554—2566).—Except near the saturation pressure 3(K-1)/(K+2), where K is the dielectric const., varies linearly with P, the ideal v.p. Near saturation the slope of the graph of K against P increases markedly. The val. of K, calc. from the slopes of the lower part of these curves, is 1.686×10^{-18} . S. L. (c)

Dipole moments of quinoline and isoquinoline. R. J. W. LE Fèvre and J. W. SMITH (J.C.S., 1932, 2810–2811).—New determinations of the dipole moments of quinoline and isoquinoline give vals. of $2 \cdot 18$ and $2 \cdot 52 \times 10^{-18}$ e.s.u., respectively. H. A. P.

Dielectric constants of liquid and solid ethyl ether and nitrobenzene. J. MAZUR (Spraw. Prace Polsk. Towarz. Ficyz., 1931, 5, 181–200; Chem. Zentr., 1932, ii, 352–353).—For Et₂O, ε rises with fall of temp. and is max. (12·39) at $-105\cdot4^{\circ}$, thereafter falling rapidly until at $-117\cdot2^{\circ}$ (solidification) it suffers sudden change. For solid Et₂O ε approaches 2·04 as the temp. falls below $-118\cdot9^{\circ}$. For PhNO₂, ε (35·41 at 30·01°) becomes max. at 9·6° (38·15) and then falls rapidly to 11·82 at 7·71°, finally approaching the val. 2·709. An anomalous val. is again obtained near the f.p. (Cf. this vol., 11.) A. A. E.

Ionised gases in a magnetic field at pressures above 10^{-3} mm. Hg. T. V. IONESCU and C. MIHUL (Compt. rend., 1932, 195, 1008—1010).—The effects of pressures >10⁻³ mm. Hg on the conductivity of ionised H₂, N₂, and air in fields >80 gauss for λ 250— 660 cm. are examined, as also is the relation between conductivity and electronic current in various fields, and between dielectric const. and field at various pressures. Marked changes occur at pressures of 0.02— 0.15 mm. Hg, which would favour propagation in the atm. of waves of λ 5—6 m. at 50—80 km. height at the expense of longer waves. C. A. S.

Electrical conductivity of palladium with occluded oxygen. D. P. SMITH (Z. Physik, 1932, 78, 815–823).— O_2 lowers the electrical resistance of Pd independently of the presence of H_2 .

A. B. D. C.

Electricity transport by oxygen in metals. A. COEHN (Z. Physik, 1932, 78, 824—825).—Polemical against Smith (cf. preceding abstract). A. B. D. C.

Electrical resistance of titanium and zirconium nitrides and a new resistance effect. P. CLAUSING (Z. anorg. Chem., 1932, 208, 401-419; cf. A., 1931, 921).—The nitrogenation of filaments of Ti or Zr can be followed by measuring the resistance for various filament currents. The formula ZrN has been established by synthesis. Resistivities of TiN and ZrN and their temp. coeffs. have been measured. Peculiar hysteresis effects in the change of resistance

with temp. are described and attributed to traces of free metal in the nitrides. F. L. U.

Conductivity of corundum. H. VON WARTEN-BERG and E. PROPHET (Z. Elektrochem., 1932, 38, 849—850).—The conductivity of corundum rises from $\kappa = 1.3 \times 10^{-7}$ at 1500° abs. to 5.0×10^{-6} at 1800° abs. Data are given for ruby. Artificial ruby may be prepared by heating Al₂O₃ with Cr₂O₃ (1%) at 1600° abs. D. R. D.

Temperature coefficient of resistivity of silicon and a [new] thermo-electric phenomenon of unipolar substances. C. BEDEL (Compt. rend., 1932, 195, 871-873).—The ends of a fragment of Si heated to a const. temp. exhibit p.d., e.g., with pure Si in fragments 0.4 mv. at 100°, in crystal 8.6 mv. at 330°. Carborundum, pyrites, and galena behave similarly (cf. A., 1930, 402). This is due to the equal and opposite currents produced at the ends by the thermoelectric effect combined with the rectifying power of a unipolar substance. It is impossible therefore to determine the temp. coeff. of resistance of Si, as there are three superposed actions : the thermoelectric effect, dielectric conductivity at the contacts, and conductivity proper of Si; it is, however, certainly negative for pure Si. The resistivity of Si containing 0.1% Fe decreases continuously to 400°, but with 1.8% Fe there is a min. at 210°, above which it is positive (cf. A., 1910, ii, 481; 1931, 30). C. A. S.

Variation of the true and apparent electrical resistivity of quartz with temperature. S. SHIMIZU (Sci. Rep. Tohoku, 1932, 21, 439-454).— The causes of the variation of resistivity with time have been investigated at different temp. (cf. A., 1932, 560). E. S. H.

Electrical conductivity of mercury at high temperatures and pressures. W. BRAUNBER (Physikal. Z., 1932, 33, 830–831). W. R. A.

Rotation of Rochelle salt in alkaline media. A. N. CAMPBELL and A. J. R. CAMPBELL (J. Physical Chem., 1932, 36, 2610—2614).—The marked variation of rotation with [OH'], the reduction in [OH']of aq. NaOH caused by the salt, the decrease in conductivity on mixing aq. Rochelle salt and NaOH, and the form of the equilibrium diagram point to complex formation. S. L. (c)

Spectrochemistry of compounds of the sterol group. K. von Auwers and E. Wolter (Nachr. Gcs. Wiss. Göttingen, 1931, 101-119; Chem. Zentr., 1932, i, 2595-2596).—Solutions of linalool (I), geraniol (II), farnesol (III), cinnamyl alcohol (IV), and their Ac derivatives, and triolein (V) in quinoline and 1-C10H7Me were examined. Of the homogeneous substances only (I), and its acetate, and (V) were normal. The solvents have a moderate effect; the exaltations of n are usually 0.2-0.3 and of the scattering power 5-10% > for the homogeneous materials; with (III) these are unchanged in solution, and with (IV) and its acetate somewhat diminished. Vals. for (II) in quinoline differed from those in Cholestane, cholestene, 4-cholestene, 1-C₁₀H₇Me. a-cholesterylene, cholesterol, and cholesteryl butyrate and oleate were also examined; vals. of n in solution and in the fused state correspond, but those of dis-

persion exhibit variations. All the compounds tend towards depression of the mol. and sp. refractory power. Ergosterol (VI), ergosteryl acetate, palmitate, and benzoate, ergosteryl- B_3 acetate (VII), ergotetraene (VIII), suprasterol-I and -II, suprasteryl-I acetate, and an irradiation dihydro-derivative C₂₇H₄₄O were studied. Ergosterol and its esters differ optically from the suprasterol group, the latter belonging to the cholesterol group and the former exhibiting exaltation. Hence (VI) contains a conjugated linking; two double linkings are considered to be conjugated and the third isolated. Windaus' formula (A., 1930, 1578) is not excluded. (VII) is also conjugated; in (VIII) either two double linkings are conjugated and the third is isolated, or three lie in a ring and the fourth is remote. In the suprasterols the three double linkings are isolated, whilst C27H44O contains a conjugation. Hydroxycholestenone and dehydroergosteryl acetate were also examined. A. A. E

Refraction of gaseous acetaldehyde and ethyl acetate. H. LOWERY (Phil. Mag., 1932, [vii], 14, 743-745).—The gaseous refractive indices of MeCHO (for λ 5461 Å.) and of EtOAc (for λ 5461, 5893 Å.), and the dispersion of MeCHO between λ 4358 and 6708 Å., have been measured. H. J. E.

Dispersion of gases and vapours and its representation by the dispersion theory. III. Dispersion of oxygen between 6000 and 1920 Å. R. LADENBURG and G. WOLFSOHN (Z. Physik, 1932, 79, 42-61).—Interferometer dispersion measurements give vals. which can be represented by a dispersion formula with three characteristic frequencies at 1899, 1468, and 544 Å. A. B. D. C.

Optical properties of carbonates. H. BRAS-SEUR (Z. Krist., 1932, 83, 493-495).—The ionic refraction, R, of CO_3'' is taken as 10.88 or 8.38 according as the electric vector of the incident light is \parallel or \perp to the plane of the CO_3'' groups (cf. A., 1924, ii, 373). The birefringence of fourteen normal or basic carbonates is calc. as the difference between the vals. of n deduced from $R=M(n^2-1)/d(n^2+2)$ through use of the two vals. of R for CO_3'' . The calc. birefringence exceeds the actual only for

 $(MgOH)_2Mg_2(CO_3)_3,3H_2O$ and $Na_2Ca(CO_3)_2,2H_2O$, but is less for all others, indicating respectively nonparallelism and parallelism of the CO_3'' groups.

C. A. S.

Magnetic circular dichroism and anomalous magnetic rotatory dispersion in cobalt chloride solutions. M. SCHÉRER (Compt. rend., 1932, 195, 950—952).—With a field of 50 kilogauss and aq. CoCl₂ of d^{19} 1·122 positive magnetic circular dichroism and anomalous magnetic rotatory dispersion were detected. The ellipticity– λ curve shows a max. of 2β =1·50° for λ 5100 Å. (the wave-length for which absorption in the band λ 4350—5700 is a max.), and is steeper on the long-wave side. The rotation– λ curve has a point of inflexion at λ 5050, rotation being positive or negative as λ is > or < 5050 Å. (cf. A., 1925, ii, 478). C. A. S.

Magnetic circular dichroism and rotatory dispersion. A. COTTON (Compt. rend., 1932, 195, 915-919).—The results reported in the preceding abstract are discussed with reference to the previous work of the author and others (cf. A., 1906, ii, 146; 1930, 668). The assumption that only paramagnetic atoms can give rise to the effects is questioned. C. A. S.

Magneto-optic rotation by condenser discharge. F. G. SLACK and W. M. BREAZEALE (Physical Rev., 1932, [ii], 42, 305–311; cf. Allison, A., 1930, 1541). N. M. B.

Mechanical double refraction of oils in relationship to the molecular form and association. III. D. VORLANDER and J. FISCHER (Ber., 1932, 65, [B], 1756-1762; cf. A., 1931, 286).-Observations are recorded for many org. liquids of known mol. composition. The sp. double refraction $[D]_t$ vals. are much lower for aliphatic than for aromatic derivatives even when the internal friction of the oils is of the same order of magnitude. The $[D]_t$ vals. are regarded as an approx. mathematical expression of the relative tendency of the mols. towards association. With paraffin hydrocarbons, aliphatic dibromides, and dicarboxylic esters of the malonic series the influence of linear structure of normal C chains is obvious. The longer C chain of Me₂ succinate imparts a greater directive stability to the mol. than does the shorter C chain of the isomeric $(CH_2 \cdot OAc)_2$. *n*-Pentane and Et_2O show no D effect under the experimental conditions. C₆H₆ becomes positively double refractive, but no effect is observed with cyclobexane. Homologues and substituted derivatives of C_6H_6 show a greater D effect than C_6H_6 . Hydrogenation of homologues of C_6H_6 causes the disappearance of all D effect, which falls in the sequence $1-C_{10}H_7Me$, tetra-and deca-hydronaphthalene. Cyclic hydroaromatic and open-chained, strongly-branched hydrocarbons cannot be distinguished from one another. The greater effect with $C_{10}H_8$ derivatives in comparison with C_6H_6 compounds shows that the two C_6 rings in $C_{10}H_8$ lie approx. in the same plane. The preponderating importance of the linear para position is observed. With PhCl, PhBr, PhI, the val. 1/M-[D] diminishes with increasing at. wt. of the halogen. The contrast between positive and negative substituents in C₆H₆ does not find expression. H. W.

Theory of diamagnetism of conductivity electrons. R. PEIERLS (Physikal. Z., 1932, 33, 864).— A method of calculating diamagnetism of free electrons is indicated, which is free from the restriction that the wave-length of the electron must be small compared with the orbit radius. A. J. M.

Magnetic constants of benzene, naphthalene, and anthracene molecules. K. S. KRISHNAN (Nature, 1932, 130, 698–699).—The principal susceptibilities of mols. of C_6H_6 , $C_{10}H_8$, and anthracene have been calc. by a method previously given (A., 1932, 1078). The increase in susceptibility from C_6H_6 to $C_{10}H_8$ to anthracene is practically confined to a direction normal to the plane of the mols., which is also an axis of approx. magnetic symmetry.

L. S. T.

Influence of light on paramagnetic susceptibility. O. SPECCHIA (Nature, 1932, 130, 697-698). L. S. T. Transition from ferromagnetic to paramagnetic form for manganese arsenide and phosphide. A. SMITS, H. GERDING, and F. VER-MAST (Rec. trav. chim., 1932, 51, 1178—1192).— V-T curves indicate that the transition from ferroto para-magnetic form in the case of MnAs and MnP is gradual. In the case of MnAs there is a temp. hysteresis. The equilibrium potentials of MnAs and MnP in aq. MnCl₂ containing HCl rise continuously with temp., but, in the case of MnAs, the potential obtained on rapid heating or cooling passes through a min. and temp. hysteresis is observed. D. R. D.

Diamagnetic susceptibilities of some sulphur compounds. J. FARQUHARSON (Phil. Mag., 1932, [vii], 14, 1003—1012).—The mol. magnetic susceptibilities of SO₃, KHSO₄, K₂SO₃, K₂S₂O₃, K₂S₃O₇, K₂S₂O₈, and K₂S₄O₈ have been measured. The % differences between the experimental figures and those calc. by Pauling's and Slater's methods are in good agreement with each other and with theory. The changes in magnetic susceptibility which accompany the various stages in building up the mol. agree with theory and give the polarities of some of the linkings. J. W. S.

Dia- and para-magnetism of the metals. E. Vogr (Physikal. Z., 1932, 33, 864-869).—There are two types of paramagnetism in metals, one dependent on temp., the other weak, and independent of temp. In the case of the transition metals the two types are not differentiated. The magnetism, in these metals, varies little with temp., with the exception of Pt and Pd, which can be explained by considering their at. structure. To test the views put forward, the susceptibility of mixed crystals of Au with Fe, Ni, Pd, and Pt is investigated. A. J. M.

Magnetic properties of some compounds of molybdenum, tungsten, and chromium in various states of valency of these elements. B. T. T. JABBES (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 693—700).—Twenty-two substances containing Mo, W, or Cr have been measured. MoCl₄, MoCl₅, and K₃CrO₈ are strongly paramagnetic; MoS₂ and Mo₃Br₆ are diamagnetic. Observed vals. for χ_A are compared with vals. deduced from the Hund and Bose–Stoner theories for Mo⁺⁶, Mo⁺⁵, Mo⁺⁴, Mo⁺³, Mo⁺², and discrepancies are discussed. Complex compounds in which the metal (M) is quinquevalent are strongly paramagnetic when they are of the MOX₃ type and diamagnetic when they are of the MO₂X type. Metallic Mo shows anomalous paramagnetism.

W. R. A.

Magnetic behaviour of the oxygen molecule. R. EINAUDI (Atti R. Accad. Lincei, 1932, [vi], 16, 133-139).—Mathematical. The behaviour of O_2 in magnetic fields of the order of 10^4 gauss is calc. O. J. W.

Compact molecules. J. J. VAN LAAR (Chem. Weekblad, 1932, 29, 587).—A criticism of Backer's views (A., 1932, 679), and a claim for priority.

H. F. G.

Polar valencies of carbon. T. MIŁOBEDZKI (Rocz. Chem., 1932, 12, 635-637).—The polar valencies of C in various compounds are classified with regard to their degree of oxidation, from $C^{-IV}H_i$ to $C^{+IV}Cl_4$, free C having the polar valency C^0 . R. T.

Semi-classical theory of chemical binding. W. HEITLER (Z. Physik, 1932, 79, 143-152).—A summary of a general theory of homopolar linkings which shows that the no. of linkings between two atoms is quantised as are the no. of light quanta according to Dirac's theory; the energy of linking is additive with respect to the no. of linkings. A. B. D. C.

Relationship between electrical potentials and chemical reactivity. L. KAHLENBERG (Science, 1932, 76, 353-358).—An address. L. S. T.

Formation of double molecules in gases under the influence of an electric field. H. SENFTLEBEN (Physikal. Z., 1932, 33, 826—829).—The influence of pressure, temp., and field strength on the effect has been investigated. The degree of association of $COMc_2$ and NO_2 is considered. W. R. A.

Five-electron problem in quantum mechanics, and its application to hydrogen-chlorine reaction. G. E. KIMBALL and H. EYRING (J. Amer. Chem. Soc., 1932, 54, 3876—3885).—Slater's method (A., 1931, 1356) is used to solve the problem of five electrons with spin degeneracy. Rules are given for finding the proper functions corresponding with an arbitrary no. of valency linkings between atoms. The calc. activation energies of the reactions Cl_3+ $H_2 \longrightarrow Cl_2+HCl+H$, $H+Cl_2+H_2 \longrightarrow 2HCl+H$, and $Cl+H_2O+H_2 \longrightarrow HCl+H_2O+H$ indicate that none of them takes part in the photochemical reaction between H_2 and Cl_2 , and that the reaction proceeds through the Nernst chain. G. M. M. (c)

Single electron linking. R. F. HUNTER (Chem. and Ind., 1932, 939).—A review of published work supports the view of singlet sharing. E. S. H.

Spectroscopic determination of electron affinities. H. KUHN (Z. physikal. Chem., 1932, B, 19, 217—218).—Lederle's theoretical methods (A., 1932, 791) are criticised. R. C.

Quantum mechanics treatment of the water molecule. A. S. COOLIDGE (Physical Rev., 1932, [ii], 42, 189–209).—Mathematical. The interaction of the atoms in the H₂O mol., and the sources of the binding energy in various types of resonance or electron interchange, are investigated. N. M. B.

Angle between the oxygen linkings by the collision area method. W. A. HARE and E. MACK, jun. (J. Amer. Chem. Soc., 1932, 54, 4272—4277; cf. A., 1932, 563, 566).—The viscosity of the vapours of Ph₂O and CH₂Ph₂ at temp. between 165° and 363° corresponds with the collision areas (theoretically almost equal) 36·13 and 36·40 Å.², and the Sutherland consts. 400 and 387, whilst the shadowgraphic collision areas of various mol. models agree with the angles 107° and 110°, respectively, between the O linkings. The Sutherland const. and collision area of Et₂O are 380 and 18·18 Å.², respectively, and the mol. is tightly coiled. The significance of these results is discussed. J. G. A. G.

Behaviour of liquid nitrobenzene in vicinity of m.p. J. WELLM (Z. physikal. Chem., 1932, B, 19, 113—116; cf. A., 1932, 329).—The viscosity, d, and the dielectric const. are normal near the m.p. (Cf. this vol., 9.) R. C.

Supposed allotropy of liquid nitrobenzene. E. COHEN and L. C. J. TE BOEKHORST (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 1016—1023).— Between 2° and 20° the sp. vol. and the fluidity of PhNO₂ (m.p. 5.77°) are expressed by $V=0.81759_3+$ $0.000663t+0.000,000,48t^2$ and $\phi=31.98_9+0.80348t$ $+0.002742t^2$ with errors of $\Rightarrow 2 \times 10^{-5}$ and $\Rightarrow 3 \times 10^{-2}$, respectively. No discontinuities are shown by the pure substance or when a trace of H₂O is added.

A. G. Parachor of rhenium. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (J.C.S., 1932, 2673— 2676; cf. A., 1932, 585).—Measurements of density and surface tension (by capillary rise) on Re_2O_7 , ReO_2Cl_3 , and ReO_3Cl , at respective approx. temp. of 300°, 50°, and 30°, lead to vals. for the parachor of Re of 68.9, 78.9, and 76.4, respectively.

N. M. B.

New X-ray interference method for complex crystals, in particular rolled and fibrous materials (object between two slits). H. SEEMANN (Physikal. Z., 1932, 33, 755-763). W. R. A.

Use of monochromatic radiation in X-ray scattering in gases. W. VAN DER GRINTEN (Physikal. Z., 1932, 33, 769—770).—Results obtained using monochromatic radiation and filtered radiation with CCl₄ are compared. W. R. A.

Influence of temperature on the scattering of X-rays by gas molecules. R. W. JAMES (Physikal. Z., 1932, 33, 737-754).—The scattering curves for SiCl₄ vapour at 100° and 300° have been determined; no temp. effect has been observed. The curves substantiate the tetrahedral model for SiCl₄, and interat. distances, Cl-Cl 3·35, Si-Cl 2·17 Å., have been evaluated. The theory of the scattering of X-rays by a mol. with vibrating atoms has been considered. W. R. A.

New methods of mass-spectrometry. J. MAT-TAUCH (Physikal. Z., 1932, 33, 899–903). A. J. M.

Corrections for Debye-Scherrer X-ray photographs. Z. NISHIYAMA (Sci. Rep. Tohoku, 1932, 21, 364—384).—Different correction formulæ for the thickness of the specimen have been applied to results for Armco Fe and Al (99.95%). The author's formula (A., 1930, 148) gives the best agreement. The lattice consts. determined are Fe 2.861, Al 4.041 Å.

E. S. H.

Determination of crystallographic constants. G. KALB (Z. Krist., 1932, 83, 362-373).—Observed variations in such determinations far exceed experimental errors, and are due to vicinal faces (cf. A., 1903, ii, 472; 1932, 450). Averaging does not give a correct result, which is obtainable only by taking these faces into individual consideration.

C. A. S.

Calculation methods in fine structure investigations. M. VON SCHWARZ and O. SUMMA (Z. Krist., 1932, 83, 499-500). C. A. S.

Thermal dilation in crystals and Haüy's law. A. CAVINATO (Atti R. Accad. Lincei, 1932, [vi], 16, 163—165).—A proof of the validity of Haüv's law for the thermal dilation of a crystal. O. J. W.

Atomic arrangement in glass. W. H. ZACHA-RIASEN (J. Amer. Chem. Soc., 1932, 54, 3841— 3851).—The atoms in a glass are linked by essentially the same forces as in a crystal. In both cases the linkings form three-dimensional networks, but the glass network is irregular in that it lacks the symmetry and periodicity of the crystal lattice. A glass network with an energy content comparable with that of the corresponding crystal can be formed only when the co-ordination nos. of the atoms involved are suitable. L. O. (c)

Carbon with metallic lustre; new form of carbon? S. B. HENDRICKS (Z. Krist., 1932, 83, 503-504).—A grey, somewhat porous form of C (C 98.76-98.92, H 0.73-0.91%, no ash) is deposited in hot C tubes (800°) through which C_6H_6 vapour is passed; it is sometimes harder than corundum and takes a high polish (cf. A., 1892, 565; 1923, ii, 757). X-Ray examination shows patterns similar to those found in finely-divided graphite by Raman and Krishnamurti (cf. A., 1929, 984), which are, however, attributed to a modification of the ideal graphite lattice and not to "free electrons." C. A. S.

Unidimensional swelling of graphitic acid and graphite. U. HOFMANN [with A. FRENZEL, D. WILM, and E. CSALÁN] (Kolloid-Z., 1932, **61**, 297– 304).—A summary of published work. E. S. H.

Madelung constants for some cubic crystal lattices. J. SHERMAN (Phil. Mag., 1932, [vii], 14, 745-746; cf. Wheeler, A., 1932, 793).—The const. for cuprite has been corrected. H. J. E.

Tetragonal and cubic martensites. K. HONDA and Z. NISHIYAMA (Sci. Rep. Tôhoku, 1932, 21, 299-331).—Tetragonal (α) martensite is the first product of quenching C steel and consists of an interstitial solid solution of C in Fe. Tempering the product at 100—150°, or shock such as grinding, converts it into cubic (β) martensite. X-Ray analysis shows that the lattice const. of β -martensite increases slightly with the content of C; it is therefore a solid solution of C in Fe and not a decomp. product of α -martensite. β -Martensite can also be obtained directly by quenching steel in rapeseed oil at 140°. A mechanism of the changes involved in quenching and tempering is suggested. E. S. H.

Blue sodium-tungsten bronze. W. F. DE JONG and H. J. STEK (Z. Krist., 1932, 83, 496; cf. A., 1932, 450).—Blue Na–W bronze, probably $Na_2(WO_3)_5$, is tetragonal, with a 17.5, b 3.80 Å., d 7.3. C. A. S.

Crystal structure of hydrated cadmium sulphate. L. EGARTNER, F. HALLA, and E. SCHWARZ (Z. Krist., 1932, 83, 422–425).—3CdSO₄,8H₂O has a 14.65, b 11.84, c 16.35 Å., β 34° 48′, with 4 mols. in the unit cell, space-group C_{2h}^{ϵ} . It is not piezo-electric. C. A. S.

Crystal structure and dehydration figures of alkali halide hydrates. W. A. WOOSTER (Nature, 1932, 130, 698).—Weissenberg and oscillation photographs give for NaBr,2H₂O *a* 6.59, *b* 10.20, *c* 6.51 Å., β 112.5°, *a*: *b*: *c* 0.646: 1:0.638, d_{calc}, 2.28, 4 mols.

per unit cell; space-group $C_{2h}^{\bullet} - P2_{1/a}$; and for NaI,2H₂O a 6.85, b 5.76, c 7.16 Å., a 98°, β 119°, γ 68.5°, a:b:c 1.190:1:1.243, $d_{calc.}$ 2.67, 2 mols. per unit cell; space-group $C_{1}^{i} - P_{1}$. L.S. T.

X-Ray examination of ammonium hydrogen fluoride. O. HASSEL and N. LUZANSKI (Z. Krist., 1932, 83, 448-459).—NH₄F,HF is rhombic with a 8.14, b 8.33, c 3.68 Å., d (by suspension method) 1.50, space-group V_{*}^{*3} . It is not piezoelectric.

C. A. S.

Structure of potassium osmiamate. F. M. JAEGER and J. E. ZANSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 610—624).—From aq. solution KOsNO₃ crystallises as yellow, hemihedral, tetragonalbipyramidal crystals, $a: c=1:2\cdot3123$, space-group C_{4H}^{6} ; $d^{18} 4\cdot 49$ —4.51. Results for rotation, oscillation, and powder spectrograms are recorded and discussed. KOsNO₃ is a complex salt built up entirely of ions all of which have inert gas electronic configurations. The O and N ions are arranged around the Os ions at the corners of a tetragonal bisphenoid, disagreeing with structures suggested by Werner and Dinklage.

W. R. A.

Structure of the ammonium, rubidium, and thallium osmiamates. F. M. JAEGER and J. E. ZANSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 787-798; cf. preceding abstract).----NH₄OsNO₃, RbOsNO₃, and TlOsNO₃ have each a rhombic-bisphenoidal pseudo-tetragonal structure, space-group V^4 , the lattice consisting of the simple rhombic cell. There are 4 mols. in the unit cell, the dimensions of which are : NH₄OsNO₃ a 5.53, b 5.86, c 13.54 Å.; RbOsNO₃, a 5.57, b 5.84, c 13.64 Å.; TlOsNO₃, a 5.42, b 5.68, c 13.45 Å. J. W. S.

Structure of cerium osmiamate. F. M. JAEGER and J. E. ZANSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1932. 35, 779-786).—CsOsNO₃ is rhombic-bisphenoidal and pseudo-tetragonal in structure, a 8.08, b 8.35, c 7.22 Å. The space-group is V^2 , and the unit cell contains 4 mols. (see preceding abstract). J. W. S.

Crystal structure of calcium metaborate. W. H. ZACHARIASEN and G. E. ZIEGLER (Z. Krist., 1932, 83, 354-361).—Ca(BO₂)₂ is rhombic, with a 6·19, b 11·60, c 4·28 Å., and 4 mols. in the unit cell, d 2·65, space group V_1^{14} (*Pnca*). Each Ca atom is surrounded by 8 O atoms at average distance 2·52 Å., each B by 3 O at 1·36 Å., two of the latter being shared by two BO₃ groups so that the BO₃ groups form endless chains. C. A. S.

Structure of potassium dithionate and measurement of integrated reflexion from a small crystal. G. V. HELWIG (Z. Krist., 1932, 83, 485-492; cf. A., 1931, 1115).—Further examination of small crystals by a new method for measuring the integrated reflexion and of a large crystal shows that the space-group is definitely D_s^2 (cf. A., 1932, 1079). A satisfactory structure similar to, but more symmetrical than, that of Huggins and Frank (cf. J. Min. Soc. Amer., 1931, 16, 580) is deduced.

C. A. S.

X-Ray analysis of iron pyrites by the method of Fourier series. H. M. PARKER and W. J. WHITE- HOUSE (Phil. Mag., 1932, [vii], 14, 939–961).—The lattice spacing in FeS₂ is 5.405 Å., the parameter of the S atom 0.114, the distance S—S 2.14 Å., and the distance S—Fe 2.26 Å. The predictions of Bragg and West (A., 1931, 26) concerning the diffraction effects in a Fourier analysis and the possibility of counting electrons are confirmed. The diffraction rings surrounding each peak were found to have the predicted radii. The Fe atom is found to have its full complement of 26 electrons, indicating the nonionic nature of FeS₂. J. W. S.

Crystal structure of goethite. S. GOLDSTAUB (Compt. rend., 1932, 195, 964—967; cf. A., 1931, 1390).—The unit cell contains 2 mols. of Fe_2O_3, H_2O . The structure consists substantially of hexagonally close-packed O atoms with the Fe atoms in the octahedral interspaces, being closely related to hæmatite. C. A. S.

Crystal structure of bertrandite. T. Ito and J. WEST (Z. Krist., 1932, 83, 384–393).—Bertrandite, $H_2Be_4Si_2O_9$, is rhombic pyramidal, with a 15-19, $b \ 8.67$, $c \ 4.53$ Å., and 4 mols. in the unit cell : spacegroup $C_{2^{cl}}^{tr}$. The structure differs fundamentally from that of hemimorphite (cf. A., 1889, 471; 1932, 987), and is represented by $Be_2(BeOH)_2SiO_3SiO_4$, the Si and Be atoms forming chains of Si with O and Be with O or O and OH, parallel to the c axis, thus explaining the predominating cleavage. C. A. S.

Structure of minerals of sodalite family. T. F. W. BARTH (Z. Krist., 1932, 83, 405-414).-The structures of sodalite, noselite, and hauynite all consist primarily of Si-Al-O chains forming a network of composition $(Al_6Si_6O_{21})^{VI}$, with internal spaces in which the larger ions Na⁻, Ca⁺⁺, Cl', and SO₄" can be packed. In sodalite all such are occupied by Cl' (with the Na⁺ tetrahedrally around each $\hat{C}l'$; in noselite alternate spaces by SO_4'' (similarly surrounded); hauynite is intermediate with part of the Na2O replaced by CaO, but also with more of the vacant spaces occupied by SO_4'' necessitating for electrovalent balance a further replacement of Na⁺ by Ca⁺⁺. The formulæ for the unit cubes are Na₂Al₆Si₆O₂₄Cl₂, Na₈Al₆Si₆O₂₄SO₄, and (NaCa)₄₋₈Al₆Si₆O₂₄(SO₄)₁₋₂, respectively. They are isomorphous, space-group T_{d} , which for sodalite gives a structure almost identical with T_{d}^{4} (cf. A., 1931, 289). A variate atom equipoint arrangement, similar to that in hauynite, applies to Al and Si in ultramarine (cf. A., 1929, 749), the framework of which is [(AlSi)₁₂O₂₄]ⁿ, where the valency n, and consequently the content of Na and S, depend on the ratio Al : Si. C. A. S.

Structure of lead formate. F. HALLA and L. ZIMMERMANN (Z. Krist., 1932, 83, 497–498; cf. A., 1929, 16).—Previous results are confirmed. The crystal is not piczoelectric; a structure is proposed. C. A. S.

X-Ray examination of mono- and poly-meric butenesulphones. E. SAUTER (Z. Krist., 1932, 83, 340—353).—The identity of polybutenesulphone before and after dissolution in H_2SO_4 or HNO_3 and repptn. by H_2O is confirmed. Δ^{β} -Butene- $\alpha\delta$ -sulphone, d^{17} 1.50, is monoclinic, a 9.55, b 11.35, c 6.23 Å., β 131° 14', 4 mols. in the unit cell, space-group C_{2M}^{5} ; corresponding data for β -methyl- Δ^{β} -butene- $\alpha\delta$ -sulphone (cf. A., 1930, 1405) are 1.36, monoclinic sphenoidal, 6.60, 7.62, 6.67 Å., 110° 34', 2, C_z^* ; and for $\delta\gamma$ -dimethyl- Δ^{β} -butene- $\alpha\delta$ -sulphone, 1.34, rhombic, 7.55, 12.12, 7.39 Å., 90°, 4, V_{1}^{16} . All are non-piezoelectric.

C. A. S.

X-Ray diffraction in ethyl ether near the critical point. F. H. W. NoLL (Physical Rev., 1932, [ii], 42, 336—339).—In the higher regions of the temp. range $25-210^{\circ}$ at $43\cdot5\pm0\cdot7$ kg. per sq. cm. pressure the ionisation curves are a combination of the liquid and polyat. gas types, the liquid type decreasing up to 155° . There is strong evidence of liquid, semi-orderly, cybotactic groups from room temp. to 199° .

N. M. B.

Crystallographic relations of methylglucoses. E. VON SZADECZKY (Z. Krist., 1932, 83, 501-50°). 4-Methylglucose dibenzylmercaptal, m.p. 96° (cf. A., 1932, 369), is monoclinic, a:b:c=1.8230:1:1.8467, β 100° 50'; the crystals are pseudo-hexagonal. The 2-Me derivative, m.p. 190-191°, is rhombic bipyramidal, a:b:c=0.5331:1:1.0755, in tabular crystals. C. A. S.

What causes the different X-ray spectra of natural starches? J. R. KATZ and J. C. DERKSEN (Naturwiss., 1932, 20, 851).—Natural starches give three types of X-ray spectra, designated A, B, and C, respectively. The C spectrum is probably a transition or mixed spectrum of A and B. Sol. starch was dissolved at 100° to form a 1 : 1 solution, and evaporated at 20°; the product gave the B spectrum. The same solution evaporated at 60° gave the A spectrum. The difference may arise owing to the existence of a different stereoisomeric form of the pyranoid ring in the starch crystals. A. J. M.

Röntgen diagram of stretched myosin threads. G. BOEHM and H. H. WEBER (Kolloid-Z., 1932, 61, 269—270).—Myosin threads, made by spraying from a capillary tube, give an X-ray diagram which is identical with that obtained from stretched frogmuscle. E. S. H.

Crystal threads and fibrous aggregation forms. H. W. KOHLSCHÜTTER (Kolloid-Z., 1932, 61, 270—280).—A discussion of the relations between the dendritic and similar crystal growths of metals and inorg. compounds and the thread-like structure of complex org. substances. E. S. H.

Linear and laminar fine structures. R. O. HERZOG (Kolloid-Z., 1932, 61, 280—297).—A lecture, in which is discussed the evolution of one- and twodimensional structures from mols., through mol. aggregates, to the structural elements of histological specimens. E. S. H.

Polyoxymethylene films and threads. W. KERN (Kolloid-Z., 1932, 61, 308—310).—A review of published work, particularly on elasticity and plasticity. E. S. H.

Dependence of the susceptibility of bismuth single crystals on the field. W. J DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 454-458; cf. A., 1931, 411).—At 20.4° and 14.2° abs. the relation between diamagnetic magnetisation and field strength is linear except with fields of 12.5-14.5 and 21-28 kilogauss. H. J. E. Spontaneous magnetisation and thermoremanence in ferromagnetic single crystals. J. KOENIGSBERGER (Physikal. Z., 1932, 33, 763-767). W. R. A.

Ferromagnetic single crystals. R. GANS (Physikal. Z., 1932, 33, 924–928).—The ferromagnetic properties of single crystals can be most casily explained from (1) consideration of the symmetry of the crystal, and (2) Heisenberg's principle. A. J. M.

Elastic forces and magnetic properties. R. BECKER (Physikal. Z., 1932, 33, 905-913).

A. J. M.

Permeability and hysteresis for magnetisation in the preferential direction for energy. F. PREISACH (Physikal. Z., 1932, 33, 913—923).—Experiments with permalloy are described and discussed. Preferential directions produced by directed cryst. and elastic forces affect the magnetisation in the same way. A. J. M.

Joule magnetostrictive effect in a group of cobalt-iron alloys. S. R. WILLIAMS (Rev. Sci. Instr., 1932, [ii], 3, 675-683).—A group of ferromagnetic rods, including Fe, Ni, Co, and Fe-Co alloys, has been found having a wide variation in change of length when magnetised longitudinally. A new extensometer and recording camera are described. C. W. G.

Resistivity of polycrystalline wires in relation to plastic deformation, and the mechanism of plastic flow. E. N. DA C. ANDRADE and B. CHALMERS (Proc. Roy. Soc., 1932, A, 138, 348-374).-Measurements have been made of the sp. resistivities of Cd, Cu, Al, and Sn wires at various stages of the plastic flow under large stresses. The sp. resistance of metals which crystallise in the cubic system is unaffected by the flow, but with metals crystallising with a unique axis of symmetry it changes by approx. 2% during the intermediate stage of flow at diminishing rate (the β -flow), although it remains unchanged during the immediate extension and during the final flow at const. rate. It is considered that the first immediate stretch takes place by break-up of the crystallites and movements of the fragments without distortion; that during the β -flow, rotation of the crystallites takes place with change of sp. resistance; and that in the final stage of steady flow slipping without rotation occurs. This hypothesis explains why an increase of sp. resistance with extension is found in metals of which the crystals have the slipplanes parallel to the unique axis, whilst there is a decrease with crystallites having the slip-plane normal to the unique axis. Further evidence in favour of this theory is afforded by low-temp. experiments, where there is marked immediate stretch but no β-stretch. Under these conditions, an extensive twinning takes place in the case of Cd, causing an increase of resistivity as opposed to the decrease found at room temp. L. L. B.

Rotatory magnetisation. H. BRION (Ann. Physik, 1932, [v], 15, 167–197).—The Barkhausen effect has been studied in relation to the position of the coil, to the density, and material of the target for layers of Ni, Fe, Fe-Si, and Cu-Ni-Fe alloys. The rotatory moment of hysteresis can be approx. computed from the period of vibration. W. R. A.

Propagation of large Barkhausen discon-tinuities. II. K. J. SIXTUS and L. TONKS (Physical Rev., 1932, [ii], 42, 419-435; cf. A., 1931, 791).—A new formula for the penetration time of large Barkhausen discontinuities is found. The behaviour of the discontinuity in a 15% Ni-Fe wire under various conditions was investigated.

N. M. B. Plasticity and creep in solids. H. JEFFREYS (Proc. Roy. Soc., 1932, A, 138, 283-297) .- A new derivation of the equations of plastic flow is given. A theory of creep is developed, and its relation to experimental evidence is discussed. The results are applied to certain geophysical problems. L. L. B.

Heat of loosening of the lead lattice. G. von HEVESY, W. SEITH, and A. KEIL (Z. Physik, 1932, 79, 197-202).-The heat of activation for the reaction constituted by interchange of lattice elements was determined from the temp. coeff. of diffusion velocity of a radioactive Pb isotope into Pb; its val. is 27,830 g.-cal. per mol., and it is no more sensitive to structure changes than the A const. of the diffusion equation.

A. B. D. C.

Persistence of anisotropic structure in silica obtained from the action of acids on leucite. G. A. BLANC (Atti R. Accad. Lincei, 1932, [vi], 16, 3-6; cf. A., 1931, 1253).—The crystal of hydrated SiO₂ obtained by the action of mineral acids on leucite retains under certain conditions the original eryst. form and structure of the complex $KAlSi_2O_6$. O. J. W.

Structural constant relative to changes of state. R. BIGAZZI (Atti R. Accad. Lincei, 1932, [vi], 16, 48-53).-For a large no. of substances the relationship $TM/p^2 = K$ is found to hold; T = abs. temp. of a change of state, b.p. or f.p., M = mol. wt., $p = d^{15}$. For substances having a similar structure but different composition K is approx. const. provided no change in M occurs during the change of state. If K is divided by a factor c, which depends on structural complexity of a particular mol., then K' = K/ccan be regarded as an approx. const. for a change of state. K' varies between 2 and 10 approx. for the O. J. W. substances tabulated.

Theory of superconductivity. R. DE L. KRONIG (Z. Physik, 1932, 78, 744-750).-A metal conductor is represented as an electron lattice which " melts " at the temp, where superconductivity suddenly sets in. A. B. D. C.

Explanation of certain results on superconductivity. M. VON LAUE (Physikal. Z., 1932, 33, 793-796).-The influence of a magnetic field on superconductivity and two experiments by Sizoo W. R. A. (cf. A., 1926, 667) are discussed.

Dispersion of sound in several gases, and its relation to the frequency of molecular collisions. W. T. RICHARDS and J. A. REID (Nature, 1932, 130, 739).—The dispersion of sound in CO_2 , CS_2 , SO_2 , and C₂H₄ is sensitive to pressure, and the velocity of sound at a given frequency increases as pressure is decreased until a const. val. is reached. Dispersion

in mixtures of C₂H₄ and A or C₂H₄ and N₂ indicates that the vibrational energy of C_2H_4 is not excited by collisions with mols. of N_2 or A. In mixtures of C_2H_4 and H_2 it is necessary to suppose that a collision with a H_2 mol. is 10 times as likely to excite C_2H_4 as is a collision with another C_2H_4 mol. Air, N_2 , A, C_3H_8 , and C_5H_{12} appear to show no dispersion between 9 and 451 kilocycles. L. S. T.

Velocity of sound in nitrogen. W. H. KEESOM and J. A. VAN LAMMEREN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 727-736).-Using the method described previously (A., 1931, 792) the velocity of sound in $\dot{N_2}$ has been measured over the temp. range -200° to 0° , and at different pressures. The Kirchhoff-Helmholtz formula holds very closely.

J. W. S.

Optical properties of solid and liquid media under ultrasonic elastic vibrations. R. LUCAS and P. BIQUARD (J. Phys. Radium, 1932, [vii], 3, 464-477).—Observations on Et₂O, paraffin, H₂O, and quartz as diffracting media show grating type diffraction patterns broadening into a mirage effect with increase of the elastic wave-length. N. M. B.

Heat capacity of iron. J. B. AUSTIN (Ind. Eng. Chem., 1932, 24, 1225-1235).-The available data on the heat capacity of Fe are discussed thermodynamically. A heat capacity-temp. curve is given from 20° abs. to the m.p. of Fe, and is satisfactory up to 900°. There appears to be no discontinuous change in heat capacity at the magnetic inversion point, 768°, but there is a cusp in the heat capacity curve, and therefore a point of inflexion in the heat contenttemp. curve, indicating that there is no latent heat of transformation in the ordinary sense. M. S. B.

Exact measurement of specific heats of solid substances at high temperatures. VI. Metals in stabilised and non-stabilised condition : platinum and silver. VII. Metals in stabilised and non-stabilised condition : copper and gold. F. M. JAEGER, E. ROSENBOHM, and J. A. BOTTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 763-771,772-779).-VI. The sp. heat of Pt which has been heated to a high temp. and quenched is much < in the stable condition. The sp. heat of cold-plated Ag is also much < that of the fused and slowly cooled metal. The data obtained are compared with recorded vals.

VII. The sp. heat of rolled Cu is > that of the stabilised metal, and the sp. heat of cold-plated Au is slightly < that of the fused and solidified Au.

J. W. S.

Change of the specific heat of tin when becoming superconducting. W. H. KEESOM and J. A. KOK (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 743-748).-Between 3.70° and 3.72° abs. the at. heat of Sn decreases from 0.0078 to 0.0054, the change coinciding with the transition of the superconducting to the non-superconducting state. A magnetic field impeding the production of superconductivity prevents also the change in sp. heat. Transition to the superconducting state is not associated with a heat of transition. J. W. S.

Exact measurement of specific heats of solid substances at high temperatures. XI. The

remarkable behaviour of beryllium after preliminary heating above 420°. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 1055—1061).—The loss of heat from Be heated above 420° is abnormally slow, and this peculiarity is retained for several months at room temp. Other physical properties are also affected and there are unexplained lines in the X-ray spectrum. A. G.

Anomaly in the specific heat of liquid helium. W. H. KEESOM and (MISS) A. P. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 736—742).— The sp. heat of liquid He has a max. val. of about 3.0at 2.19° abs., but falls to 1.1 certainly within 0.02° and probably within 0.002° . J. W. S.

Calculation of specific heats of diatomic gases by quantum statistics. C. GREGORY (Z. Physik, 1932, 78, 791-800).—Quantum statistics are used to calculate the sp. heats from spectral data.

A. B. D. C.

Specific heat and dissociation of gases at high temperatures. K. WOHL and M. MAGAT (Z. physikal. Chem., 1932, B, 19, 117–138).—The effectiveness of the addition of H_2O vapour as a means of reducing heat losses in the explosion method of sp. heat determination (A., 1929, 1394) has been confirmed. The observed sp. heats of H_2O and H_2 agree within 1% with theoretical vals., whereas the observed vals. for N₂ and O₂ may be as much as 2.2% too small, probably because the time in which the exploding mixture is heated to and at its max. temp. is too short for the mol. vibrations to be fully excited. The thermal dissociation of H_2O into $\frac{1}{2}H_2$ and OH has been calc. from explosion data. The most probable heat effect of the reaction $2H_2O=H_2+2OH$ is -124kg.-cal. R. C.

Specific heat of superheated water vapour for pressures of 120–200 atmospheres and for saturation temperatures up to 450°. W. KOCH (Forsch. Gebiet Ingenieurwesens, 1932, 3, 1–10; Chem. Zentr., 1932, i, 1763).—Between 120 and 200 atm. c_p falls continuously with a rise in temp., and falls sharply at first with a rise in pressure. $c_p=0.49+$ $(1.55 \times 10^7 p+0.14 \times 10^9) T^{-3/5}+6.036 \times 10^{39} (p+80)^{5:58}$ $\times T^{-10}+7.4302 \times 10^{130} (p-71)^{4.41} \times T^{-50}+7.9652 \times 10^{315}$ $(p-19)^{21.79} \times T^{-130}$. The greatest measured val. is 4.249 at 200 atm. and 368.5°. L. S. T.

Definition and measurement of the distillation coefficient and the volatility constant of volatile substances in dilute solution. P. JAULMES (J. Chim. phys., 1932, 29, 403—417).—Distillation coeff. is defined as the relation between the titre of a volatile acid in the distillate and that in the boiling liquid at the same instant. Volatility const. is defined as the corresponding relation between the vapour and the boiling liquid. Methods for determining these vals. are described. E. S. H.

Free energy of transition of iron $(\alpha \rightleftharpoons \gamma)$. C. P. YAP (Trans. Faraday Soc., 1932, 28, 781-788). —From published data for the sp. heat of Fe, the free energy of transition is calc. as 822 g.-cal. per g.-atom at 25°. The allotropy of Fe is discussed. E. S. H. Fluorides of low b.p. M. MAGAT (Z. anorg. Chem., 1932, 209, 11-12).—A reply to criticisms by Ruff, Ebert, and Menzel (A., 1932, 902). F. L. U.

Fusion curve of hydrogen up to 610 kg. per sq. cm. W. H. KEESOM and J. H. C. LISMAN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 607— 610).—The fusion curve of H₂ up to 610 kg. per sq. cm. and in the temp. range $13.95-26.95^{\circ}$ abs. is represented by log $(a+p)=c \log T+b$, where a=245, b=0.28771, and c=1.83435. The difference between calc. and observed vals. of pressure is a function of temp. W. R. A.

Equation of the fusion curve. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 624-635).—Theoretical. The fusion curve of He is considered. W. R. A.

Thermal expansion of lead. P. HIDNERT and W. T. SWEENEY (Bur. Stand. J. Res., 1932, 9, 703).— A curve is given indicating the thermal expansion of Pb from -253° to 300°, combining fresh data over the range 20—300° with published data. Cast Pb expands equally in all directions. D. R. D.

Origin of zero-point entropy. K. CLUSIUS (Nature, 1932, 130, 775-776).

Density curve of liquid carbon monoxide and its saturated vapour, and the rectilinear diameter. E. MATHIAS, C. A. CROMMELIN, W. J. BIJLEVELD, and P. P. GRIGG (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 551-553).-CO obeys the law of rectilinear diameters approx. The crit. density is 0.3010. The results are tabulated. H. J. E.

Application of J. J. van Laar's theory concerning the additivity of b and \sqrt{a} to boron, iron, nickel, osmium, and iridium compounds. J. A. M. VAN LIEMPT (Rec. trav. chim., 1932, 51, 1108—1116; cf. A., 1916, ii, 386).—From published v.-p. and crit. point data for BF₃, Fe(CO)₅, Ni(CO)₄, OsO₄, and IrF₆, the at. consts. for B, Fe, Ni, Os, and Ir are deduced. The results indicate that BF₃, IrF₆, Fe(CO)₅, and Ni(CO)₄ have complete electron shells, but that OsO₄ has not, and that in the carbonyls the CO groups are linked directly to the central atom, cyclic formulæ being untenable. D. R. D.

Application of J. J. van Laar's theory concerning the additivity of b and \sqrt{a} to aluminium compounds. J. A. M. VAN LIEMPT (Rec. trav. chim., 1932, 51, 1131–1133).— $b_k=102\times10^{-5}$ for Al in Al₂Cl₆. The electron shells of the Al are complete, the structure being two tetrahedra with a common edge. D. R. D.

Properties of volatile hydrides. II. Preparation, [vapour] tensions, and densities of pure hydrogen sulphide. (At. wt. of sulphur.) A. KLEMENC and O. BANKOVSKI (Z. anorg. Chem., 1932, 208, 348-366).—H₂S was prepared from H₂ and S and purified by fractional distillation. V.p. were determined between -120° and -60° . M.p. $-85 \cdot 6^{\circ}$, b.p. $-60 \cdot 7^{\circ}$. Gaseous H₂S does not attack Hg, but the liquid does. The dry gas does not react with solid KOH in absence of O₂. Density of liquid between 190° and 212° abs. is given by $d=0.9496 \times$ $[1+0.0018397(212\cdot45-T)]$. The density of the gas was determined at 0° and the wt. of a normal litre is given as 1.53623 ± 0.00007 g. The corresponding at. wt. of S, calc. by using a linear extrapolation of the accepted compressibility to p=0, is $32.065 \pm$ 0.0016. F. L. U.

Densities of saturated vapours. R. WRIGHT (J. Physical Chem., 1932, 36, 2793—2795).—Apparatus and procedure are described for the determination of d. The results indicate that there is no union between the mols. of COMe₂ and CHCl₃ in the vapour. E. S. H.

Thermal properties of substances of high mol. wt. A. W. HSIA (Z. ges. Kälte-Ind., 1931, 38, 150–154, 167–169; Chem. Zentr., 1932, ii, 344).— MeBr vapour is stable towards light. The v.p. $(-76^{\circ} \text{ to } 30^{\circ})$ is given by : $\log p = 10\cdot3344 - 1375\cdot625/T - 1\cdot11078 \log T + 8\cdot559 \times 10^{-4}T$. Between -60° and $0^{\circ} d_{\text{liq.}} = 624\cdot98 + 1\cdot1132(t_{\text{crft.}} - t) + 153\cdot72 \times (t_{\text{crit.}} - t)^{\dagger}$: $t_{\text{crit.}} = 194^{\circ}$. The d of the gas was determined; the equation of state is $v = 8\cdot932T/P - 0\cdot1913/(T/100)^{4\cdot9}$. The heat of volatilisation (at $50^{\circ} 60\cdot46$; $0^{\circ} 62\cdot06$, $-50^{\circ} 62\cdot92$, at b.p. $61\cdot94$ g.-cal. per g.), enthalpy, and entropy were determined. For $cis-C_2H_2Cl_2 \log p = 11\cdot23645 - 1702\cdot5468/T - 1\cdot25137 \log T + 0\cdot0023807T$; for $trans \cdot C_2H_2Cl_2 \log p = 1711\cdot4651 - 11\cdot9275/T - 1\cdot4394 \log T + 0\cdot000569T$. The heats of vaporisation at the b.p. are $73\cdot01$ and $73\cdot65_5$ g.-cal. per g., respectively. A. A. E.

Measurement of the total radiation of water vapour at temperatures up to 1000°. E. SCHMIDT (Forsch. Gebiet Ingenieurwesens, 1932, A, 3, 57—70; Chem. Zentr., 1932, ii, 832—833).

Glycerol viscosity tables. M. L. SHEELY (Ind. Eng. Chem., 1932, 24, 1060—1064).—Abs. viscosities for glycerol solutions at 20°, 25°, and 30° have been determined and tabulated for every 1% from 0 to 100% glycerol (interpolated from 55 experimental determinations). Vals. for 22.5° and 27.5° are given over the range 55—100% glycerol. The figures agree well with the experimental data of Archbutt and Deeley (within $\pm 1.8\%$), but differ considerably from those of Herz and Wegner (B., 1925, 964).

É. L.

Equation relating viscosity and surface tension. D. SILVERMAN and W. E. ROSEVEARE (J. Amer. Chem. Soc., 1932, 54, 4460).—By combining the equations of Batchinski (A., 1913, ii, 928) and of McLeod the equation $\gamma^{-1/4} = A/\eta + B$ is obtained, where γ is the surface tension, η is the viscosity, and A and B are consts. characteristic of the liquid. The curve of $\gamma^{-1/4}$ against fluidity for 25 liquids affords straight lines except in the cases of Et₂O and the alcohols. J. G. A. G.

Effect of a magnetic field on the viscosity of oxygen. M. TRAUTZ and E. FRÖSCHEL (Physikal. Z., 1932, 33, 947).—Using a transpiration method to measure the viscosity, $\Delta \eta/\eta$ was found to be -0.003for fields of 10—15 kilogauss, a result agreeing with that of Engelhardt and Sack (A., 1932, 1081).

A. J. M.

Viscosity, thermal conductivity, and diffusion in gas mixtures. XXI. Absolute η -effective cross-section, molecular theoretical significance of critical temperature, and the calculation of critical pressure from η . M. TRAUTZ (Ann. Physik, 1932, [v], 15, 198–218).—Theoretical.

W. R. A. Diffusion in liquids. I. R. FURTH. II. Micro-diffusion apparatus for colourless liquids. III. Diffusion measurements on electrically neutral liquid mixtures and solutions. R. ZUBER. IV. Diffusion measurements on electrolytic solutions. R. ZUBER and K. SITTE. V. Theory of diffusion in solutions of strong electrolytes. K. SITTE (Z. Physik, 1932, 79, 275—279, 280—290, 291—305, 306—319, 320—344).—I. A summary of present views on diffusion, and of possible applications of diffusion measurements to determine the mol. mechanism and states of aggregation in liquids.

II. Diffusion can be conveniently followed by observing in a low-power microscope the limit of the region of total reflexion.

III. The micro-diffusion method (see above) has been applied to aq. solutions of sucrose, carbamide, glycerol, and formamide. The results conform to Boltzmann's diffusion law, and show the dependence of the diffusion coeff. on the concn.; the size of the particles and its dependence on concn. are also deduced.

IV. The behaviour of aq. solutions of alkali halides agrees with Boltzmann's law, and this is shown to be expected theoretically. The diffusion coeff. first decreases and then increases with concn.; characteristic inflexions of the curve are subsequently shown. The experimental curve is explained by reference to Born's theory of ionic motion and to Bjerrum's theory of ionic association.

V. The formation of ionic clusters is considered with reference to Born's theory of ionic motion in dipolar liquids, the Nernst-Planck theory of diffusion of electrolytes in dil. solutions, and the diffusion of electrolytes in conc. solutions. The theoretical deductions agree well with observed results (see above), and are applied to obtain the degree of association of ions in aq. solutions of alkali halides at various conens. A. B. D. C.

Theory of diffusion. B. BRUŽS (Z. physikal. Chem., 1932, 162, 31-43).—By means of the theory previously elaborated (A., 1932, 123, 1000) and a thermodynamic treatment of osmotic pressure which takes into account the osmotic pressures of both solvent and solute and is applicable at all concns., an equation for diffusion coeffs. is obtained, which at low concns. agrees with Nernst's equation. Equations for liquid-junction potentials and Hittorf coeffs. are derived. R. C.

Diffusion of metals in the solid state. VI. Copper and aluminium. G. GRUBE and R. HAEF-NER (Z. Elektrochem., 1932, 38, 835-842).—The diffusion of Cu and Al has been examined by microanalysis of thin shavings after heating an Al cylinder electroplated with Cu at various temp. for a known time. Rapid diffusion occurs at 600°, being almost complete within 2 hr. If the metal be examined before diffusion is complete, the following layers are found : pure Cu, CuAl₂, eutectic with 32% Cu, η mixed crystals, pure Al. α Mixed crystals are formed more slowly by diffusion of Al into Cu. In order to form a hard surface layer on Al, only η mixed crystals must be formed. For this purpose, the Al may be heated in a powdered mixture of CuCl₂ and Cu. Cu may be surface-hardened by heating it in a powdered mixture of NH₄Cl and Cu–Al alloy containing 80% Cu. D. R. D.

Law of additive atomic heats in intermetallic compounds. IX. Compounds of tin and gold, and of gold and antimony. X. Silver and gold. J. A. B. BOTTEMA and F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 916-928, 929-931).—IX. The existence of AuSn has been confirmed by X-ray analysis. Its structure is analogous to that of PtSn and the sp. vol. is about 12% the mean of the sp. vols. of its components. Its true sp. heat is given by $c_p = 0.039649 - 0.3356 \times 10^{-6}t + 2.9337 \times 10^{-8}t^2$. The mol. heat is < the sum of the at. heats of the components. The compound $AuSb_2$ exists in a γ form (below 358°), a β form (355-405°), and an α form (above 405°). The true sp. heats of these are given by: $\gamma c_{\rm p} = 0.043626 - 0.189064 \times 10^{-4}t + 0.79563 \times 10^{-7}t^2$, $\beta c_{\rm p} = -0.169785 + 0.22014 \times 10^{-2}t - 0.42252 \times 10^{-7}t^2$ $10^{-5}t^2$, $\alpha c_p = 0.45389 - 0.39127 \times 10^{-2}t + 0.70257 \times 10^{-5}t^2$. The sp. heats of Sb are given by : βc_{μ} (below 413°)= $0.0535656 - 0.46635 \times 10^{-4}t + 0.15497 \times 10^{-6}t^2, \quad \alpha c_p$ $(above 413^\circ) = 0.534496 - 0.4522 \times 10^{-2}t + 0.7944 \times$ $10^{-5}t^2$. In this case the mol. heat of AuSb₂ is > the sum of the at. heats of the constituents.

X. The sp. heat of the Au–Ag alloy containing 25.56 at.-% Au shows that the at. heat is not additive even in mixed crystals. The deviations increase with rise of temp. and are not appreciable below 600° .

E. S. H.

Electrical conductivity and phase-rule diagrams of binary alloys. VII. System lithiumcadmium. G. GRUBE, H. VOSSKÜHLER, and H. VOGT (Z. Elektrochem., 1932, 38, 869—880).—The equilibrium diagram and the conductivity as well as the thermal expansion have been examined. Li melts at 179°, Cd at 321°, and LiCd at 549°. There are five series of mixed crystals, from two of which the compounds LiCd₃ and Li₃Cd separate on cooling.

D. R. D.

Electrical properties of very dilute mixedcrystal alloys. III. Resistance of copper and gold alloys. Regularity of resistance increments. J. O. LINDE (Ann. Physik, 1932, [v], 15, 219—248).—Metals having at. nos. between 25 and 33, 45 and 51, and 77 and 80 were alloyed with Cu and the increase in resistance at 18° was measured. The solubility of Os, Ru, and Mo in Cu has been investigated. Similar experiments were conducted with Ag and Au. W. R. A,

Superconductivity of gold-bismuth [alloys]. W. J. DE HAAS and T. JURRIAANSE (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 748—750; cf. A., 1931, 1224).—X-Ray diffraction measurements and chemical analysis show the presence of a phase Au_2Bi in Au-Bi alloys. This phase is responsible for the superconductivity in this system. The elementary cell of the cubic crystals has an edge of 7.94 Å. and contains 24 atoms. The sp. gr. is 15.46, which compares with 15.70 according to the X-ray measurements. J. W. S.

Magnetostriction of iron-cobalt alloys. Y. MASIYAMA (Sci. Rep. Tôhoku, 1932, 21, 394-410).— The longitudinal and transverse effects for the whole series of alloys are opposite in character and the observed vol. change is a differential effect. A marked discontinuity at about 80% Co corresponds with the change of phase from α to γ solid solution. E. S. H.

Magnetic properties of the system Mn-Cu-Al. S. VALENTINER and G. BECKER (Physikal. Z., 1932, 33, 872).—The unique position of the alloy MnAlCu₂ is shown also in its magnetic properties. A. J. M.

Lithium alloys. I. Thermal and X-ray analysis of the system lithium-tin. A. BARONI (Atti R. Accad. Lincei, 1932, [vi], 16, 153—158).— Thermal data show the existence of Li_4 Sn (m.p. 684°), Li_3 Sn₂ (m.p. 483°), and LiSn_4 , with eutectic points at 458°, 320°, and 214°, corresponding with 35, 58, and 94 at.-% Sn, respectively. X-Ray examination by the powder method confirms the first two, but not the third. The structures could not be determined. O. J. W.

Palladium-nickel alloys. A. T. GRIGORIEV (Ann. Inst. Platine, 1932, No. 9, 13—22).—The hardnesscomposition curve has a max. at 60 at.-% Pd, whilst the temp. coeff. of conductivity curve has two min., at 20.3 and at 80.8 at.-% Pd. The above data, in conjunction with the microcryst. structure of the etched alloys, indicate that the system consists of an unbroken series of solid solutions. R. T.

Platinum-cobalt alloys. V. A. NEMILOV (Ann. Inst. Platine, 1932, No. 9, 23-30).—The fusion diagram indicates that the system consists of an unbroken series of solid solutions, with a min. m.p. for 25 at.-% Pt. Alloys of max. hardness contain 11.6 and 50.6 at.-% Pt. The microcryst. structure and the temp. coeff. of conductivity curve afford evidence for the transformation of one solid solution into another in alloys rich in Co. R. T.

Equilibrium diagram of the system ironnickel-tungsten. K. WINKLER and R. VOCEL (Arch. Eisenhüttenw., 1932–1933, 6, 165–172).—The space diagram of the ternary system shows four saturation surfaces corresponding with the separation of ternary α , ternary γ , Fe₃W₂, and a ternary W-rich solid solution, respectively. There are two planes of 4-phase equilibrium : (a) at 1455°, Fe₃W₂+liquid $\Rightarrow \gamma$ +W-rich solid solution, co-ordinates (i) 31·3% Fe, 68·7% W, (ii) 1% Fe, 1% Ni, 98% W, (iii) 52·5% Fe, 22% Ni, 25·5% W, (iv) 42·5% Fe, 27·5% Ni, 30% W; and (b) at 1465°, α +liquid $\Rightarrow \gamma$ +Fe₃W₂, coordinates (i) 56% Fe, 15% Ni, 29% W, (ii) 58·5% Fe, 10·5% Ni, 31% W, (iii) 61% Fe, 14% Ni, 25% W, (iv) 31·3% Fe, 68·7% W. The complete ternary diagram and many sections through it are shown and the structure and magnetic properties of the solid alloys are discussed. A. R. P.

Solid solutions [obtained] by precipitation and isomorphism between complexes of platinum and of quadrivalent tellurium. II. Cæsium chlorotellurite _and the systems $Cs_2PtCl_6-Cs_2TeCl_6$ and $Rb_2PtCl_6-Cs_2PtCl_6$. G. NATTA and R. PIRANI (Atti R. Accad. Lincei, 1932, [vi], 16, 265–270; cf. A., 1932, 564).—X-Ray investigation shows that Cs_2TeCl_6 crystallises in the cubic system, with 4 mols. in the unit cell: $a \ 10.45\pm0.01$ Å., $v \ 1141.2\times10^{-24}$ c.c., $d \ 3.51$. The space-group is O_h^s , and for u=0.25 the distances for Cl—Cs, Cl—Te, and Cl—Cl are 3.71, 2.62, and 3.72 Å., respectively. Crystallographic data for the two series of solid solutions show that Vegard's law is obeyed. O. J. W.

Binary mixtures. II. Viscosity of naphthalene solutions. L. PIATTI (Angew. Chem., 1932, 45, 719-720).—The viscosities at 20° of solutions of $C_{10}H_8$ in C_6H_6 , xylene, EtOH, 1- $C_{10}H_7$ Cl, *m*-cresol, tolyl phosphate, and scrubbing oil have been determined. The influence of $C_{10}H_8$ in reducing the viscosity of the second component is greatest for liquids of high viscosity and is reversed for very mobile liquids. In the case of the oil the viscosity curve is very steep and the $C_{10}H_8$ content may be determined approx. from the viscosity. H. F. G.

Determination of facility of fractional distillation of liquid binary mixtures. I. RABCE-WICZ-ZUBKOWSKI (Rocz. Chem., 1932, 12, 832–835). —Fractionation in its dependence on the relative v.p. is considered. R. T.

Dielectric constants of organic solvent-water mixtures at various temperatures. G. ÅKERLÖF (J. Amer. Chem. Soc., 1932, 54, 4125–4139).—By means of a resonance method the dielectric consts. of 0-100% mixtures have been determined at temp. between 20° and 100° for MeOH, EtOH, Pr^aOH, Pr^gOH, CMe₃·OH, glycol, glycerol, COMe₂, mannitol, and sucrose. The variation of dielectric const., D, with abs. temp. is given by $D=ae^{-bT}$, where a and b are characteristic consts. J. G. A. G.

Partial molecular polarisation in solutions. W. J. C. ORR and J. A. V. BUTLER (Nature, 1932, 130, 930–931).—Experimental and calc. vals. for Bu^aOH in C₇H₁₆ are compared. L. S. T.

Magnetic susceptibility of binary liquid mixtures. K. KIDO (Sci. Rep. Tôhoku, 1932, 21, 385– 393).—The diamagnetic susceptibility of the mixtures H_2O -EtOH, H_2O -MeOH, H_2O -COMe₂, H_2O -HCO₂H, C_6H_6 -EtOH, C_6H_6 -COMe₂, $SnCl_4$ -AcOH, and $SnCl_4$ -HCO₂Et is a linear function of composition. Susceptibility is apparently not influenced by association or compound formation. E. S. H.

Solutions of ethyl alcohol in cyclohexane, in water, and in cyclohexane and water. R. D. VOLD and E. R. WASHBURN (J. Amer. Chem. Soc., 1932, 54, 4217—4225; cf. A., 1931, 1225).—Equilibrium concess. and refractivities of single-phase saturated solutions have been determined at 25°. Cryoscopic data show that the mols. of EtOH are highly associated in cyclohexane, whilst the distribution ratio of EtOH between H_2O and cyclohexane indicates that EtOH has the same mol. form in the two phases. The results are discussed.

J. G. A. G. New equilibria at room temperature with three or four liquids together. E. JANECKE (Z. Elektrochem., 1932, 38, 860-861).-HCO·NH₂-PhNO₂-paraffin oil, and HCO·NH₂-PhNO₂-C₆H₁₄ form systems with three liquid phases. $HCO \cdot NH_2 - H_2O - K_3PO_4$ forms two phases. This mixture forms four liquid phases on mixing with $PhNO_2$ -paraffin oil or $PhNO_2 - C_6H_{14}$. These systems are not stable, since the $HCO \cdot NH_2$ is slowly hydrolysed, forming HCO_2NH_4 , which reacts with K_3PO_4 , forming a ppt. which is probably a solid solution of the *trihydrate* $K_3PO_4, 3H_2O$ in $(NH_4)_3PO_4, 3H_2O$. D. R. D.

Influence of degree of dispersion on physicochemical constants. E. COHEN and C. THÖNNESSEN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 441–453; cf. A., 1931, 677).—The solubility of salicylic acid in H_2O may be raised 15% by increasing the degree of dispersion, there being no evidence of a more sol. modification. *o*-Nitrobenzoic acid, acetylsalicylic acid, and phthalic acid behave similarly. H. J. E.

Influence of degree of dispersion on physicochemical constants. E. COHEN and C. THONNES-SEN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 798—802; cf. preceding abstract).—The influence of dispersion on the solubility of salicylic acid decreases with rise of temp. and finally disappears. This is attributed to the acceleration of recrystallisation at higher temp. The solubility data of Walker and Wood (J.C.S., 1898, 73, 619) are inaccurate.

J. W. S.

Solubility of succinic acid in binary mixtures. W. D. BANCROFT and F. J. C. BUTLER (J. Physical Chem., 1932, 36, 2515—2520).—The max. solubility in $COMe_2-H_2O$ mixtures alters with temp. The solubility does not change much with varying polymerisation of the alcohols. Some data for adipic acid have been obtained. Succinic and adipic acids are probably more sol. in depolymerised H_2O and $COMe_2$ than in the polymerised liquids. I. J. P. (c)

Hydrazine : solubility of hydrazinium salts in mixed solvents. E. C. GILBERT and E. H. HUFF-MAN (J. Physical Chem., 1932, 36, 2789–2792).—The solubilities of N_2H_4 picrate and trinitro-*m*-tolyloxide (I) have been determined in EtOH-H₂O mixtures at 20° and that of (I) in H₂O at temp. from 15° to 30°. The solubility eurves show max. and min. and do not resemble those of the corresponding free acids; there is no evidence for the existence of a stable alcoholate. The salts retain H₂O of hydration even in 99.8% EtOH and the anhyd. salts take up H₂O from aq. EtOH. E. S. H.

Systems potassium stearate (palmitate)-alcohol-water. Separation of stearic and palmitic acids. K. SCHERINGA (Chem. Weekblad, 1932, 29, 605-606).—At 18° the solubilities of K stearate in 94 and 66 wt.-% EtOH are 0.62% and 2.6%, respectively, and those of K palmitate 1.4% and 19%, respectively. In 49% EtOH K palmitate forms a colloidal solution. The solubility isotherms are very steep and indicate that rapid separation of the two acids may be effected by fractional crystallisation of the K salts from aq. EtOH. H. F. G.

Unusual crystal growth. H. G. TANNER (J. Physical Chem., 1932, 36, 2639-2640).—By dissolving Al(NO₃)₃ in MeOH and adding NH₂Ph a gel was obtained from which a large tuft of white,

lustrous, hair-like crystals of NH_2Ph,HNO_3 was formed. The crystals grew in the gel to a certain size, when the gel shrank suddenly away from their sides, but the ends remaining in the gel continued to grow. F. L. B. (c)

Distribution ratios and association of carboxylic acids. A. E. SMITH and J. W. NORTON (J. Amer. Chem. Soc., 1932, 54, 3811–3818).—The distribution at 0° between $\beta\beta\delta$ -trimethylpentane (I) and MeOH of HCO₂H, AcOH, BuOH, and octoic, lauric, palmitic, oleic, and 50% oleic-50% linoleic acids, and between (I) and MeCN of lauric, oleic, maleic, fumaric, and the phthalic acids indicates that CO₂H groups tend to associate in pairs.

L. P. H. (c)

Distribution of solute between crystalline solid and liquid phases. VII. V. G. CHLOPIN and P. I. TOLMATSCHEV (Bull. Acad. Sci. U.R.S.S., 1932, No. 1, 43-49).—The partition of Ra between cryst. Ba(NO_3)₂ and its saturated solution acidified with HNO₃ is in accordance with the simple distribution law. R. T.

Rare gases. I. Permeability of various glasses to helium. W. D. URRY (J. Amer. Chem. Soc., 1932, 54, 3887—3901).—The rate of diffusion of He, Ne, and H₂ through various glasses at comparatively low temp. and pressures has been determined. It seems that He is first adsorbed and H₂ absorbed on the glass surface. L. K. (c)

Diffusion of gases through fused quartz. L. S. T'SAI and T. R. HOGNESS (J. Physical Chem., 1932, **36**, 2595—2600).—Determinations of the rate of diffusion and permeability of quartz membranes for Ne and He at $180-980^{\circ}$ suggest that quartz glass possesses channels which increase in clearance with rise in temp. SiO₂ glass, heated at high temp., undergoes a permanent change accompanied by an increase in permeability for He. The permeability of quartz glass for gases is greatest for atoms or mols. of small cross-section. S. L. (c)

Adsorption of platinum metals by active carbon. H. WÖLBLING (Angew. Chem., 1932, 45, 720—721).—Unlike "base" metals, Pt, Pd, and Os are adsorbed readily from dil. slightly acid solutions by active C, whilst Ir and Ru are incompletely adsorbed and 90—95% of any Rh present remains in solution. The adsorbed Pt may be extracted with hot conc. HCl or NaCl solutions, without detriment to the C, but after 1—2 days' treatment with H₂ this is no longer possible. Adsorbed Ir, Os, and Ru are but sparingly soluble in NaCl solution. Rh alone of the Pt metals is adsorbed rapidly and completely from ammoniacal solutions. Pt, Pd, and Os are completely adsorbed from solutions containing an excess of alkali iodide. From colloidal solutions prepared with SnCl₂, Pt and Pd are completely adsorbed in the cold; Os is partly adsorbed, and Rh is removed only on warming. Technical and analytical applications of these results are noted.

H. F. G. Precipitation and adsorption of small amounts of substances. VI. Inclusion of small amounts of lead in alkali halides. H. KADING (Z. physikal. Chem., 1932, 162, 174—186; cf. A., 1930, 1365).—In the crystallisation of aq. NaCl, KCl, or KBr containing a very small amount of Pb (Th-B) the latter forms a solid solution, the distribution between the solid and liquid phases conforming to the simple distribution law. That solid solution formation rather than adsorption occurs is shown by radiographs and by the failure of attempts to realise adsorption displacement. The Pb enters into the solid phase as a complex anion, such as $PbCl_3'$; the plumbite complex is unable to do this. Pb is appreciably included only in halides with the rocksalt lattice; NaCl,2H₂O and NaBr,2H₂O take up no Pb. R. C.

Adsorption of crystal solution interfaces. VI. Macroscopic sodium nitrate crystals grown in the presence of dyes and other foreign materials. L. A. WEINLAND, sen., and W. G. FRANCE (J. Physical Chem., 1932, 36, 2832—2839; cf. A., 1930, 1514).— The experiments indicate that the adsorption depends on the residual valency force fields, the interionic distances in the crystal face, and the polar nature of the adsorbed material. Adsorption is selective for crystal faces having stronger fields of force and modifies the crystal habit; the (100) faces are developed at the expense of the (111). X-Ray data indicate that the dye is adsorbed interstitially. Adsorption is independent of the degree of dispersion of the dye. E. S. H.

Sorption of tannic acid by proteins and the mechanism of vegetable tanning. W. GALLAY (Canad. J. Res., 1932, 7, 349–363).—The sorption of tannic acid by gelatin and casein from aq. solution agrees with Freundlich's formula, the temp. coeff. being negative; from aq. EtOH and aq. COMe₂ the sorption follows Henry's law. Effects observed with hide powder as sorbent are also described. The viscosities of EtOH-H₂O mixtures are related to the sorption effects which are observed with these liquids. N. M. B.

Theory of adsorption of gases on solids. R. S. BRADLEY (J. Physical Chem., 1932, 36, 2674—2682).— The potential energy of an adsorbed mol. is considered to be represented by a simple harmonic formula, which corresponds with a "Morse curve." Formulæ are given for the no. of adsorbed mols. and for the correction for the finite size of the adsorbed mols. Frenkel's deduction of the mean life of an adsorbed mol. and the adsorption isotherm are revised. S. L. (c)

Adsorption. Availability and accessibility. (SIR) W. HARDY and (MISS) M. NOTTAGE (Proc. Roy. Soc., 1932, A, 138, 259–283).—Measurements are recorded of the variation of static friction (μ) with temp. for solutions of a wax, $C_{15}H_{31}$ ·CO₂H, and $C_{16}H_{33}$ ·OH in B.P. paraffin, over the range 10–106°. Variation is limited to a narrow temp. range (of about 15–20°), outside which μ is const. The limits of variation are the frictions of the pure solvent and solute, respectively, showing that the proportions of solvent and solute mols. in the adsorbed layer could be approx. determined from measurements of μ . At a given temp. μ is affected by the previous history and composition of the solution. The phenomena are influenced by two changes : change in state of the bulk solution which fixes the "availability" of the solute for adsorption, and a change in the capacity of the solute for replacing adsorbed solvent, which is the "accessibility" of the solute. L. L. B.

Surface tension of caoutchouc solutions. E. VELLINGER (Compt. rend., 1932, 195, 788—790).— The interfacial tensions between C_6H_6 solutions of caoutchoue (0.3%), and of its resin (0.02%) and an aq. solution of an electrolyte plotted against the $p_{\rm H}$ of the aq. solution show a max. at $p_{\rm H}$ 7 followed by rapid falls to zero at about $p_{\rm H}$ 11 and 12, respectively. The behaviour of caoutchouc closely resembles that of mineral oils. C. A. S.

Influence of cation exchange on the capillary rise of water in soil. O. BOTTINI (Atti Accad. Lincei, 1932, [vi], 15, 883-887).—The rate of ascent of H_2O through specimens of a soil saturated, by the base-exchange method, with Na^{*}, NH₄^{*}, K^{*}, Mg^{**}, Ca^{**}, Al^{***}, Ba^{**}, or H^{*} varies according to the nature of the ion, being least for Na^{*} and rising to a max. at H^{*} in the order given. The effect is concerned primarily with the influence of the ions on the dispersion and swelling of the soil particles. H. F. G.

Surface films. XVI. Surface potential measurements on fatty acids on dilute hydrochloric acid. N. K. ADAM and J. B. HARDING (Proc. Roy. Soc., 1932, A, 138, 411-430).-A description is given of apparatus for the simultaneous determination of the change in contact potential, ΔV , at the interface between aq. solutions and air, caused by a surface film, and the surface pressure of the film. With the acids $C_{13}H_{27}$ ·CO₂H, $C_{15}H_{13}$ ·CO₂H, $C_{17}H_{35}$ ·CO₂H, and $C_{21}H_{43}$ ·CO₂H, ΔV increases slightly with increasing length of the chain and shows a steady rise nearly proportional to the increasing no. of mols. in the film as the liquid-expanded film is compressed. The rise on compressing the condensed films is <that corresponding with the no. of mols. in the film. The small change in the vertical component of the dipole moment per mol. (μ) as the expanded film is compressed indicates an approx. const. orientation of the CO₂H groups in the film throughout this region. A fall in μ of about 40% takes place on passing to the vapour state of the films, indicating some re-orientation of the CO2H groups in the flat L. L. B. chains.

Surface potentials of unimolecular films. IV. Effect of underlying solution and transition phenomena in the film. J. H. SCHULMAN and A. H. HUGHES (Proc. Roy. Soc., 1932, A, 138, 430— 450).—The effect of the underlying solution on the surface potentials of unimol. films of several longchain fatty compounds has been studied over a wide $p_{\rm II}$ range, with special reference to the mutual influence of the solution and the polar head-group of the filmforming material. Two-dimensional transitions of state are discussed in detail. L. L. B.

Measurement of superficial pressure of superficial solutions of soluble substances. A. MAR-CELIN and D. G. DERVICHAN (Compt. rend., 1932, 195, 866-869),—A method is described for deducing the superficial pressure in the unimol. film formed by an insol. substance, e.g., by oleic acid on H_2O , from the diameter of the clear circular space which is formed by a current of air of definite strength and width impinging vertically on the talc-powder covered film. The method is applicable to superficial solutions of sol. substances (the Gibbs layer). C. A. S.

Weakening of fine-structural cohesion by water and aqueous solutions. F. RINNE (Kolloid-Z., 1932, 61, 304–308).—The high H_2O content of biological systems is regarded as the cause of their chemical lability. The high dielectric const. of H_2O causes a weakening of the electrical fields of the finestructural units. This effect is illustrated by the influence of H_2O on the fine structure of cryst. bromophenanthrenesulphonic acid. E. S. H.

Spreading of ovalburnin. E. GORTER, J. VAN ORMONDT, and F. J. P. DOM (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 838-843).—Like caseinogen (cf. A., 1926, 1094) ovalburnin shows max. spreading on a solution of $p_{\rm n} 4$ —5, and min. spreading at about $p_{\rm H} 3$. The effects of Cl', SO₄", CH(SO₃)₃"', K', Ba", and Co(NH₃)₆" ions on the spreading favour the view that at the isoelectric point the neutral protein mol. spreads out in a thin layer, but addition of H^{*} or OH' ions diminishes the area occupied. The addition of negative ions on the acid side of the isoelectric point (below $p_{\rm H} 3$) increases the surface by eliminating the charge of the protein ions. The same holds for the addition of positive ions in alkaline medium. The activity of ions is in the order ter-> bi-> uni-valent. J. W. S.

Proteins in unimolecular films. Measurements by the methods of du Nouy and Langmuir. E. GORTER and W. A. SEEDER (Kolloid-Z., 1932, 61, 246—249).—Results obtained by the two methods are in agreement. E. S. H.

Films, threads, and colloid science. Wo. Ost-WALD (Kolloid-Z., 1932, 61, 136-140).—Films and threads are discussed as difform systems, representing a transitional stage between massive and mol. matter. E. S. H.

Unimolecular surface films. N. K. ADAM (Kolloid-Z., 1932, 61, 168—177).—A lecture on recent published work. E. S. H.

Examination of film structures by electrical and optical methods. E. K. RIDEAL (Kolloid-Z., 1932, 61, 177-180).—A lecture. E. S. H.

Unimolecular layers of proteins. E. K. RIDEAL (Kolloid-Z., 1932, 61, 218-222).-Resistance to compression is first observed in a film of gliadin when its concn. reaches 0.36×10^{-7} g. per sq. cm. The film is then easily compressible up to the val. 0.7×10^{-7} , after which the compression rises rapidly to a conen. of about 1.5×10^{-7} g. per sq. cm., at which the film apparently assumes a two-dimensional gel structure. These data agree with vals. calc. on the assumption that the side-chains of the mol. contain $\cdot [CH_2]_2 \cdot CO_2H$. The surface-potential method of examining the protein films is illustrated by experiments on the degradation of albumin by proteolytic enzymes, and the effect of irradiating a film of albumin by ultra-violet light is also described. E. S. H.

Gum surfaces. III. F. V. VON HAHN (Kolloid-Z., 1932, 61, 222—234; cf. A., 1932, 1085).—The spreading of 37 org. substances and plant products on a surface of starch paste is related to the surface activity of the spreading solution by an S-shaped curve. Exceptions are noted in the case of substances having very high surface activity at low concens. (e.g., soaps, saponin). E. S. H.

Solid properties and structure of cellulose nitrate films. A. V. BLOM (Kolloid-Z., 1932, 61, 234-239).—Under increasing degree of stretching, films of cellulose nitrate pass through (a) an elastic region, (b) a transitional region, (c) a plastic region, (d) a region in which solid properties are developed as a result of increasing orientation of the micelles. Finally the films break. The breaking tension is not sufficient to characterise the cohesive forces operating in the chains of mols., but must be considered in relation to the whole of the stress-strain curve. The region (d)is more extended for samples of high viscosity than for those of low viscosity, and appears only in films of thickness > 60 μ . The development of birefringence supports the conclusions reached. E. S. H.

Physics of membranes. E. MANEGOLD (Kolloid-Z., 1932, 61, 140—160).—Published work is summarised (cf. A., 1931, 905, 1007, 1128; 1932, 119, 691). E. S. H.

Membrane equilibria. F. G. DONNAN (Kolloid-Z., 1932, 61, 160-167).—A lecture, with special reference to the biological significance. E. S. H.

Phase equilibrium in systems subdivided by membranes. R. EISENSCHITZ (Z. physikal. Chem., 1932, 162, 216—222).—Equations are obtained which give the no. of degrees of freedom in systems subdivided by rigid impermeable and semipermeable membranes. R. C.

Osmotic pressure, and permeability of membranes. W. W. LEPESCHKIN (J. Physical Chem., 1932, **36**, 2625—2638).—The permeability of a membrane to a solute is expressed by $P_0 = P(1-\mu)$, where P_0 is the suction of the solution, P its osmotic pressure, and μ the permeability factor, proportional to the permeability of the membrane to solute. The max. hydrostatic pressure, P_m , in an osmometer depends on the permeability of the membrane to both solute and H_2O , in accordance with $P_m = P(1-\mu)(1-\mu/\sigma)$, where σ is the H₂O-permeability factor. I. J. P. (c)

Osmotic systems in which non-diffusing substances may occur. I. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 1038—1045).—If, in addition to diffusing substances, an osmotic system includes on the two sides of the membrane n and n' non-diffusing substances, respectively, it possesses n+n' additional degrees of freedom. If the composition of the first side is fixed it still has n' degrees of freedom. A. G.

Osmosis in systems consisting of water and tartaric acid. III. F. A. H. SCHREINEMAKERS and J. P. WERRE (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 477–485; cf. A., 1932, 691).— Theoretical. H. J. E.

Osmotic systems containing water, sodium chloride, and sodium carbonate with one in-

variant liquid. F. A. H. SCHREINEMAKERS and L. J. VAN DER WOLK (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 938-947).—Theoretical. E. S. H.

Osmotic systems containing water, sodium chloride, and sodium carbonate with one invariant liquid. II. F. A. H. SCHREINEMAKERS and L. J. VAN DER WOLK (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 1046—1054).—Osmotic effects with a membrane of pig's bladder are described.

A. G. Preparation and properties of proteo-cellulose membranes. J. LOISELEUR and L. VELLUZ (Bull. Soc. Chim. biol., 1932, 14, 1210-1217; cf. A., 1931, 167).—Mixed solutions of (a) protein and cellulose acetate in glacial AcOH or 96—98% HCO_2H , and (b) protein in HCO₂H and cellulose acetate in COMe, with or without CH₂O, when evaporated at low temp. give rise to homogeneous membranes which are rendered static by the cellulose and show the xanthoproteic and biuret reactions. They adsorb reduced metals (Au, Ag) in colloidal form, dyes, and metallic ions. The adsorptive power increases with the proportion of protein to cellulose and varies with the nature of the protein. Membranes of caseinogen or ovalbumin adsorb dyes far more effectively than those containing gelatin, and this is attributed to the aromatic NH₂acids which are present in the former but not in the latter. A. C.

Phenyl phosphate as a solvent in cryoscopy. I. F. GARELLI and G. RACCIU (Atti R. Accad. Lincei, 1932, [vi], 15, 976–980).—Ph₃PO₄, m.p. 48.25° , is recommended as a cryoscopic solvent. The mean observed val. of K is 120 (calc. 117.6). The latent heat of fusion is 17.56 and the sp. heat 0.381. D. R. D.

Phenyl phosphate as a cryoscopic solvent. F. GARELLI and G. RACCIU (Atti R. Accad. Lincei, 1932, [vi], 16, 54—56).—The lowering of the f.p. of Ph₃PO₄ leads to the formulæ : S_{10} ; I_2 ; trimethylenetrinitrotetramine, $(CH_2:N\cdot NO_2)_3$, and indigotin, $C_{16}H_{10}O_2N_2$. O. J. W.

Cryoscopy of some electrolytes in molten CaCl₂,6H₂O. E. DARMOIS and R. CHALIN (Compt. rend., 1932, 195, 786-788; cf. A., 1931, 35).—Data are recorded for KNO₃, Mg(NO₃)₂, La(NO₃)₃, Th(NO₃)₄, KI, CdI₂, Na H and Na₂ malates, NH₄Br, CdBr₂, and LiI. C. A. S.

Determination of paramagnetic ionic moments in solutions. H. AUER (Physikal. Z., 1932, 33, 869—872).—A crit. investigation of Quincke's method for determining paramagnetism has been made and the results are applied to salt solutions. The magnetic investigation of a salt solution is a sensitive test for inner mol. interaction, but the extrapolated vals. for moments of free ions derived in this way are doubtful. A. J. M.

Faraday effect of some uni-univalent electrolytes in aqueous solutions. I, II. E. B. ANDER-SEN and R. W. ASMUSSEN (J. Physical Chem., 1932, 36, 2819—2826, 2827—2831).—I. Technique for determining the magnetic rotation of the plane of polarisation of light by aq. salt solutions is described. Data are given for solutions containing different compounds of H[•], Li[•], Na[•], Rb[•], Cs[•], and NH₄[•] with F[•], Cl[•], I[•], OH[•], ClO₃[•], BrO₃[•], and IO₃[•], which are all diamagnetic. The results indicate that the rotation of the compound is approx. equal to the sum of the rotations of the constituent ions. A change of the anion with the same cation gives a large change in the rotation, whilst only a slight effect is produced by a change of cation with the same anion. The rotation of H₂O is approx. one half the sum of that of H[•] and OH[•], whilst that of aq. NH₃ is equal to the sum of rotations for NH₄[•] and OH[•].

II. Further measurements have been made, using mainly salts of alkali metals with oxy-acids of S. These results show that the effect of adding O or S to a mol. varies with the constitution. E. S. H.

Dusts, smokes, mists, and fogs. S. C. BLACK-TIN (Chem. and Ind., 1932, 1006—1007).—Suspensions in gases may be classified as dusts, smokes, etc., according to their mode of formation, tendency of the particles to grow larger or smaller, and physical state of the particles. Abs. particle size is of minor importance. D. R. D.

Migration velocity of suspended dust particles in electro-filters. G. MIERDEL (Physikal. Z., 1932, 33, 823-824). W. R. A.

Influence of time on conductivity of colloid [suspensions] at different levels. PAPAYANNO (Compt. rend., 1932, 195, 1012—1014).—The conductivities at levels differing by 5—8 cm. of suspensions of mastic, collodion, and colloidal Ag plotted against time show that (S-I)/I, where S and I are the conductivities at the upper and lower level, respectively, is increasingly positive for mastic suspensions, whilst the reverse is true for collodion and colloidal Ag. It is zero for optically clear, but not for ordinary, conductivity H₂O. C. A. S.

Viscosity of lyophilic colloids. I, II. I. SAKURADA (J. Soc. Chem. Ind. Japan, 1932, 35, 445— 453B).—I. Viscosity formulæ are discussed and relations between them are indicated.

II. Published data are used to derive the sp. vol. of colloid particles of cellulose nitrate in various dispersion media from the observed viscosity. The results obtained from different formulæ are compared and their relative validity is discussed. E. S. H.

Lyophilic colloids. XVI. Viscosity and sol concentration. H. G. B. DE JONG, H. R. KRUYT, and J. LENS (Kolloid-Beih., 1932, 36, 429-462; cf. A., 1932, 465).-The experiments show that gum arabic sols up to 30%, gelatin sols up to 17%, and coacervates of gum arabic-gelatin and gelatin-PrOH behave at 42° in accordance with the Hagen-Poiseuille law. Carragheen sols show a marked deviation. The relation between the viscosity of the hydrophilic sol, η_s , and the concn., C, is given by $\log \left[(\eta_s - \eta_0) / \eta_0 C \right] =$ aC+b, where η_0 is the viscosity of the dispersion medium, and a and b are consts. The best agreement is found when considerable quantities of electrolyte are present, or at the isoelectric point, when the capillary-electric charge does not predominate. Application of the formula to published work shows that it is valid for organosols. The consts. a and b vary

with the electrolytes present and with temp., but there is no simple relation between them. E. S. H.

Highly-polymerised compounds. LXXIII. Viscosity measurements with silicic acid solutions. R. SIGNER and H. GROSS (Annalen, 1932, 499, 158-168) .- The viscosities of solutions obtained by hydrolysis of Me pentasilicate (A., 1930, 461) with 75% MeOH and containing 1.67-3.03% SiO₂ remain almost const. for a considerable time, then increase rapidly prior to gelation, and decrease immediately before complete gelation. The relation between max. viscosity and conen. $(K = \log \eta_r/c)$ holds for solutions of varying concn. prepared from Me pyro-, penta-, and nona-silicates. Solutions of the same concn. prepared from different esters give the same curves for viscosity plotted against K_c (=log η_r); the gelation times differ (the solution from the more highly polymerised ester gels more rapidly). The increase in particle size (leading to gelation) is probably due to the exclusive formation of thread-like mols. H. B.

Colloid-chemical study of a technical, high-molecular azo-dye. K. BRASS and K. EISNER (Kolloid-Beih., 1932, 37, 56-90).—The prep. of a black triazo-dye (no. 669 in Schultz-Lehmann's Tables, Berlin, 1931) and of some of its derivatives is described. Measurements of surface tension and viscosity failed to give characteristic results for the solutions. Diffusion experiments show that the particle size decreases progressively as the solution is purified, and increases with age. The technical preps. have a lower degree of dispersion than those prepared by the method described. The particle size of the acid dyes is about twice that of their Na and NH₄ salts. The acid dyes are adsorbed by cotton, wool, and animal C to a greater extent than are the NH₄ salts. The degree of adsorption decreases as the dyes are purified. Wool is coloured reversibly by these dyes at room temp., but irreversibly at higher temp. Addition of salts increases the adsorption and multivalent cations E. S. H. have a coagulating effect.

Electrical factors of colloid stability. E. S. HEDGES (Chem. and Ind., 1932, 937–938).—A crit. review of recent work on the influence of non-electrolytes on electrokinetic potential, dielectric polarisation, and the relation between charge and hydration. E. S. H.

Emulsion persistence. W. CLAYTON (Soc. Chem. Ind., Chem. Eng. Group, Nov. 25, 1932, advance proof, 19 pp.).—A survey and crit. discussion of published work on emulsifying agents, wetting, the "Bodenkörperregel," stability, viscosity, and electric charge, creaming (especially of milk), frothing, centrifugal separation, inversion, electro-osmotic behaviour (especially dehydration of crude petroleum), tests (especially for bituminous road emulsions).

E. S. H.

Mechanism of the coagulation of sols by electrolytes. IV. Arsenic trisulphide sol. H. B. WEISER and G. R. GRAY (J. Physical Chem., 1932, 36, 2796—2812; cf. A., 1932, 994).—The changes in [H^{*}] in the titration of As_2S_3 sol with aq. BaCl₂, SrCl₂, CaCl₂, AlCl₃, or NH₄Cl have been followed by means of the glass electrode. The H^{*} displacement curve is similar in form to the adsorption curve. The displacement is relatively greater at lower concns. and reaches a max. at or below the pptn. val. The amount of displaced H^{*} is 20-40% of the total [H^{*}] of the liquid after coagulation of the sol, and is determined by the concn., size, and form of the particles; it is always < the amount of pptg. ion adsorbed. The order Al>Ba, Sr>Ca>NH₄ represents the displacing power, pptg. power, and adsorption of the several chlorides. E. S. H.

Influence of the anion on flocculation of colloidal clay by potassium salts. A. DEMOLON and E. BASTISSE (Compt. rend., 1932, 195, 790-792).--Experiments have been made with (a) colloidal clay from brick earth treated with 0.05N-HCl, and (b) the same freed from Fe₂O₃ by H₂C₂O₄. In the case of (a) the limiting val. for all K salts increases rapidly from neutrality to $p_{\rm H} 8.5$ (cf. B., 1924, 721). OH ions show an optimum peptising concn. differing according to the base, e.g., $p_{\rm H} 7.6$ for K⁺, 8.8-9 for Na⁺. With fine kaolin the limiting val. increases continuously with $p_{\rm H}$. In the case of (b) a higher limiting val. is found, but the fixing power for P₂O₅ is only 1/3 that of (a). C. A. S.

Lyotropic numbers and the properties of ions. E. H. BUCHNER, A. VOET, and E. M. BRUINS (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 563— 569; cf. A., 1932, 692).—Both cations and anions may be characterised by lyotropic nos., expressing their coagulating properties. These show a linear relation with the influence of the ions on the electrokinetic potentials of sols, with their catalytic activity in the inversion of sucrose and the hydrolysis of esters, and with their influence on the swelling of gelatin. H. J. E.

Lyotropic numbers and viscosity. E. H. BUCHNER, E. M. BRUINS, and J. H. C. MERCKEL (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 569-575).—For concns. up to 1N there is a linear relation between the viscosity of dil. acids, or of salt solutions with a common cation, and the lyotropic nos. of the anions. The same holds for different cations with a common anion. Deviations occur in more conc. solutions. H. J. E.

Ionic interchange in sulphur sols. Lyotropic series and the mechanism of coagulation. T. R. BOLAM and G. BOWDEN (J.C.S., 1932, 2684-2694).-The order of facility of replacement of H by cations, from the micelles of S sols stabilised by polythionic acid is Mg">K'>Na'>Li'. Adsorption of total salt may also occur, the order for the alkali chlorides being K>Na>Li. If the concn. of acid is not too high, coagulation takes place at the concn. of salt which is just sufficient to liberate the whole of the H'; the concns. of LiCl and KCl which produce the first sign of coagulation liberate the same amount of H^{*}. The occurrence of the lyotropic series observed in these phenomena is interpreted by reference to the Donnan equilibrium and the theory of surface M. S. B. dissociation.

Rhythmic precipitation of dyes by electrolytes. (MLLE.) S. VEIL (Compt. rend., 1932, 195, 781– 783; cf. A., 1932, 693).—Neutral-red and toluidineblue in presence of $K_2Cr_2O_7$ behave similarly to methylene-blue. Aq. $K_2Cr_2O_7$ dropped on gelatin impregnated with either forms Liesegang rings (cf. A., 1930, 1506). C. A. S.

Behaviour of metallic soaps with organic solvents. J. W. MCBAIN and W. L. MCCLATCHIE (J. Physical Chem., 1932, 36, 2567-2574).-The formation of jellies from soaps and org. solvents has been examined. For the Ag and Al soaps the best solvents are in general the least polar compounds. The Na soaps, although sol. in polar solvents, also dissolve and form jellies in the non-polar solvents. Swelling of jellies is attributed to direct combination, sorption, or polarisation of mols. or groups of mols. of solvent with exposed groups of the jelly for which the solvent has affinity, as well as to penetration of free mols. of solvent between the interlacing structure to release strains in the structure. The former factor corresponds with the thermodynamic properties represented by the v.p., whilst the latter is purely mechanical. F. L. B. (c)

Effect of X-radiation on viscosity of gelatin. H. Q. WOODARD (J. Physical Chem., 1932, 36, 2543— 2553).—The viscosity, η , of dil. gelatin sols is decreased by intense irradiation by X-rays. When for a given sol η is reduced by heat, by $p_{\rm II}$ change, or by salts, the % reduction (A) due to subsequent irradiation is decreased. When η is reduced by ageing or by irradiation, (A) is decreased, but in a manner too irregular for quant. interpretation. When η is reduced by dilution, A is not changed. F. L. B. (c)

Effect of addition of salts on the isoelectric point of proteins. III. H. ANDRZEJEWSKI (Biochem J., 1932, 26, 1397—1405).—The concn. (c) of EtOH necessary for the flocculation of purified gelatin sols is smallest at the isoelectric point. Negatively-charged micelles are more readily coagulated by EtOH than are positively-charged ones. The val. of c at the isoelectric point is increased in the presence of MgCl₂ or Na₂SO₄, whilst MgSO₄ is without effect. At all $p_{\rm H}$ vals. salts giving rise to ions of the same valency do not affect the val. of c. At $p_{\rm H} < 4.8$ salts yielding multivalent anions and univalent cations lower c at small concns. and slightly raise it at $p_{\rm H} > 4.8$. This effect is due to the charge of the colloidal particles; the greater is the original charge the greater is the percentage recorded. Observations relating to anti- and isoions are also recorded. S. S. Z.

Heats of wetting of silica gel. R. BERTHON (Compt. rend., 1932, 195, 1019—1021).—Patrick and Grimm's hypothesis (cf. A., 1922, ii, 122) is incorrect; that of Bartell and Fu (A., 1930, 1246) errs in neglecting the effect of the curved surfaces of small capillaries in which the adsorption pressure P_a is > that on a plane surface. The energies of wetting, Q, have been determined for H₂O and 12 org. liquids, and compared with $W_a - W_c$ deduced from Bartell and Merrill's results (cf. A., 1932, 690), where W_a is the energy of adhesion of solid to liquid, W_b that of cohesion of the liquid. $W_a - W_c$ is much > Q for polar liquids such as MeOH, EtOH, and AcOH, for which the compression in the capillaries should be greatest. A thermodynamic theory of wetting must take into consideration the geometry of the surface. C. A. S.

Alkali cellulose. II. Application of phase theory to gel reactions. K. HESS, C. TROGUS, and O. SCHWARZKOPF (Z. physikal. Chem., 1932, 162, 187-215; cf. A., 1932, 836).-Thermodynamic considerations applied to the system cellulose-NaOH-H_oO show that two solid phases may coexist in equilibrium with a liquid phase of variable composition and a vapour phase (cf. this vol., 22). Analytical and X-ray data show that two phases of const. composition (cryst. compounds) must be accompanied by at least one phase of variable composition. In the reaction between cellulose and NaOH changes on the micelle surfaces are accompanied by changes in the interior, so that the determination of the composition of a solid phase by analysis gives an average val., whilst X-ray methods can follow only the changes in the interior. Depending on the NaOH concn. there are formed several compounds for which Na/C=1/6. The formation of alkali cellulose is not covered by the theory of the Donnan equilibria, although the reaction of small parts of the cellulose agrees with this theory (cf. B., 1931, 920). As a whole the reaction may probably be regarded as a heterogeneous reaction on which are superimposed surface changes which probably have the character R. C. of Donnan equilibria.

Methane-carbon dioxide and carbon monoxide-hydrogen equilibrium. J. SCHMIDT and B. NEUMANN (Z. Elektrochem., 1932, 38, 925-933).-The equilibrium $2CO+2H_2 \implies CH_4+CO_2$ has been investigated by a streaming method, using Ni pptd. on SiO2 gel as catalyst. The results agree with theory above 600°. Various side-reactions occur. H₂O is formed by the reaction $CO_2+H_2 \implies H_2O+CO$ and reacts with CH_4 , forming CO and H_2 . Probably NiO is formed. The reaction $CH_4+CO_2=2CO+2H_2$ can be made to occur without pptn. of C. D. R. D.

Equilibrium between dimethyl ether, methyl alcohol, and water. N. G. GAJENDRAGAD, S. K. K. JATKAR, and H. E. WATSON (J. Indian Inst. Sci., 1932, 15A, 59-69; cf. B., 1926, 565, 963).-For the conversion of MeOH into Me2O an alum catalyst can be used at $170-250^{\circ}$ or H_2SO_4 at 130° . In the former case the rate is much lower than with EtOH. The equilibrium const. is 15.4 at 230° and 48.5 at 130°. Equilibrium was approached from both sides.

F.L.U.

Intermolecular force effects. III. Heat of combination and mode of combination of organic molecular compounds. G. BRIEGLEB and T. Schachowsкоу (Ž. physikal. Chem., 1932, В, 19, 255—277; cf. A., 1932, 563).—From the extinction coeffs. for solutions of the binary compounds of s-trinitrobenzene (I) with Ph_2 , $C_{10}H_8$, phenanthrene, and anthracene at various temp. in spectral regions in which the components do not absorb, the heats of dissociation have been calc. Combination is not due to any particular NO₂ group, but to the joint action of all such groups, and leads to the preferential formation of an average constellation in which the max. moment induced in the hydrocarbon lies in the direction of max. polarisability. The order of diminishing energy of combination is the same as the order of diminishing max. polarisability, as deduced from the

Kerr const. The f.-p. diagram for Ph₂ and (I) shows that these combine to form an incongruently melting 1:1 compound. R. C.

Incomplete dissociation of typical binary salts and application of dilution law to their solutions in non-aqueous solvents. II. P. WALDEN (Z. physikal. Chem., 1932, 162, 1-30; cf. A., 1930, 995).-Conductivity measurements over wide concn. ranges for salts behaving as typical strong electrolytes in aq. solution have shown that in solvents for which the dielectric const. is not too large these salts behave as weak electrolytes in respect of the validity of the dilution law. Various homopolar substances behave as weak electrolytes when dissolved in solvents such as N₂H₄, which by virtue of basic or acid properties are able to exert a sp. influence on the solute; such solvents usually have a fairly high dielectric const. The degree of dissociation as measured by the conductivity ratio seems to depend, not only on the dielectric const. of the solvent, but also on a mutual interaction of solvent and undissociated solute mols. R. C.

Absorption spectrum and dissociation constants of arsenious acid. P. GOLDFINGER and H. D. GRAF VON SCHWEINITZ (Z.

physikal. Chem., 1932, B, 19, 219-227; cf. A., 1932, 1006).-According to the titration curve the first dissociation const. is 2×10^{-10} to 8×10^{-10} , and spectroscopic measurements of the ionic concns. in presence of varying amounts of alkali give 1×10^{-14} to 6×10^{-14} for the second dissociation const. These vals. show that $HAsO_3''$ is responsible for the autoxidation of H_3AsO_3 (cf. A., 1925, ii, 308). The long-wave limit of continuous absorption in 1*M* solution is 2680 for H₂AsO₃' and 2800 Å. for HAsO₃". R. C.

VII.

Autoxidation.

Acidity of thiophenol and of the isomeric dithiophenols. G. SCHWARZENBACH (Helv. Chim. Acta, 1932, 15, 1468-1481).-The acidities determined potentiometrically in 60-100% aq. EtOH show that all the substances are stronger acids than the corresponding phenols, o-dithiophenol (I) being almost as strong as AcOH. The strengths decrease in the order o-, m-, p-, mono-. The results are discussed theoretically. In its behaviour towards solutions of metal salts, (I) shows a close resemblance to F. L. U. H.S.

Acidic properties of metal salt hydrates. F. REIFF (Z. anorg. Chem., 1932, 208, 321-347).-Acidities of aq. solutions of metal halides at various concns. have been determined electrometrically. The quotient [H]/concn. in general increases with concn., and the acidity is attributed mainly to the formation of aquo-acids, e.g., [ZnCl₂(OH)H₂O]H. Metal salts of these acids cannot usually be isolated, but cryst. oxonium salts with cineole (=Ci), or more readily with 1:4-dioxan (=D), have been prepared. The following compounds are described :

 $[MCl_2(OH)H_2O]H,D$ (M=Cu, Mn, Ni, or Co), [CaCl.(OH)]H,D, [LiCl(OH)]H,D, [(LiBr)2O](H,D)2, $[LiI(OH)_2](H,D)_2, [NaI(OH)_2](H,D)_2,$ $[SnCl_4(OH)_2](H,D)_2, [ZnCl_2(OH)_2]H_2, H_2O, Ci, 2ZnBr_2, 2H_2O, 3Ci, (ZnI_2)_2, 3H_2O, 3H$ [ZnBr₂(OH)H₂O]H,D, [(ZnI₂)₂O](H,D)₂, [AuCl₃(OH)]H,D, [AuCl₃O](H,Ci)₂,

 $[PtCl_4(OH)H_2O]H,D.$ The acidity of equimol. solutions of chlorides increases with decreasing polarity and is parallel with the electrode potential of the metal. Acid properties of halide hydrates increase from chloride to iodide and with the valency of the metal. The suggested formation of an aquo-base by CsF in aq. solution is supported by the prep. of the compound CsF,2AcOH. The results are discussed. F. L. U.

Strength of semicarbazide—and a correction. N. F. HALL (J. Amer. Chem. Soc., 1932, 54, 3961— 3962).—Recalculation of Wood's val. gives 3.07 at 25° for the acid dissociation const. $(pK_{\rm A})$. L. K. (c)

Simple basic indicators. II. Solutions in formic acid. L. P. HAMMETT and A. J. DEYRUP (J. Amer. Chem. Soc., 1932, 54, 4239—4247; cf. A., 1932, 921).—Relative vals. of the basicity of a series of basic indicators in pure HCO₂H agree closely with those for aq. solutions. H₂SO₄ is a strong monobasic acid and PhSO₃H is moderately strong, whilst HCO₂Na and NH₂Ph are strong bases. Ionisation consts. of HSO₄', EtCN, NHAcPh, and H₂O have been determined, and the ion product of the solvent corresponds with $-\log C_{H^+} \cdot C_{CO_3H'} = 6\cdot17$. J. G. A. G.

Existence of the phosphorus hexafluoride ion. W. LANGE (Z. anorg. Chem., 1932, 208, 387–391; cf. A., 1930, 877).—Solutions of KPF_6 and of $KClO_4$ of the same concn. give the same depression of f.p. between 0.019 and 0.066M. The ion PF_6' is stable in aq. solution and its structure is regarded as symmetrical. F. L. U.

Compounds of tartaric acid and chromium. J. P. MATHIEU (Compt. rend., 1932, 195, 1017–1019; cf. A., 1932, 111).—Changes in p_{fr} , conductivity, and rotatory power when NaOH is added to solutions containing a fixed amount of tartaric acid with varying amounts of $Cr(OH)_3$ which have attained equilibrium by keeping for several months, indicate that the neutralisation of any excess tartaric acid is followed by the neutralisation of a very weak (violet) dibasic acid, H₂[TCr], with formation of the (green) salt Na₂[TCr]; there is no pptn. of $Cr(OH)_3$. C. A. S.

Relation between the higher charge ions and the deviations from the first approximation of the Debye-Hückel theory. J. B. CHLOUPEK, V. Z. DANES, and B. A. DANESOVA (Coll. Czech. Chem. Comm., 1932, 4, 473—479).—To test the validity of La Mer's development of the Debye-Hückel theory (A., 1928, 841; 1929, 1386, 1387), precise determinations of the solubility of Ce(IO₃)₃ from three different sources have been made in H₂O and in aq. solutions of KNO₃, K₂SO₄, MgSO₄, and MgCl₂ at $25\cdot00\pm0\cdot02^{\circ}$. M. S. B.

Glycine in water solution. J. Y. CANN (J. Physical Chem., 1932, 36, 2813—2816).—Thermodynamic functions calc. from (unpublished) experimental data suggest that glycine in conc. aq. solutions is associated. E. S. H.

Activity coefficients of ions. K. HASS and K. JELLINEK (Z. physikal. Chem., 1932, 162, 153—173). —The activity coeffs. of Cl', Br', I', SO₄'', CrO₄'', and C_2O_4'' for a wide range of conens. have been obtained from e.m.f. measurements with various salts at 25°, and the activity coeffs. of many of the salt cations have been deduced. Solubility products have been determined at 25°. R. C.

Behaviour of electrolytes in mixed solvents. IV. Free energy of zinc chloride in wateralcohol solutions. R. T. HAMILTON and J. A. V. BUTLER (Proc. Roy. Soc., 1932, A, 138, 450-459; cf. A., 1930, 35).—The partial free energies of ZnCl₂ in H₂O-EtOH solutions, with ZnCl₂ concns. from 0.01 to 1.0M, have been measured at 15°. The vals. show that ZnCl₂ is almost completely ionised in H₂O and undissociated in EtOH. L. L. B.

Thermodynamic studies in silver chloride and silver bromide. F. L. E. SHIBATA and T. TAKETA (J. Sci. Hiroshima Univ., 1932, 2, 243—268).—From measurements of the c.m.f. of cells of the type $H_2(Pt)$ | aq. HCl(HBr)|AgCl(AgBr)|Ag between 4° and 30° the entropy of AgCl is calc. to be 24·3, and of AgBr 26·9 g.-cal. per degree at 25°. The effect on the c.m.f. of illuminating the cells was also studied. F. L. U.

Thermodynamic properties of liquid solutions of silver bromide with alkali bromides. J. H. HILDEBRAND and E. J. SALSTROM (J. Amer. Chem. Soc., 1932, 54, 4257—4261).—The data obtained for AgBr diluted with LiBr, NaBr, KBr, and RbBr are interpreted on the view that the linking in the alkali bromides is completely ionic, whilst that in AgBr is incompletely ionic and is tightened by a large alkali ion, e.g., Rb⁺, in the AgBr liquid lattice, whereas a small alkali ion has the opposite effect. J. G. A. G.

Thermodynamic properties of fused salt solutions. VI. Rubidium bromide in silver bromide. E. J. SALSTROM (J. Amer. Chem. Soc., 1932, 54, 4252—4256; cf. A., 1931, 1234).—The e.m.f. of the cell Ag(s)|AgBr(l), $RbBr(l)|Br_2(g)$ has been determined between 456° and 622°, the mol. fraction of AgBr being varied between 0.352 and 1.0. Density data for the equimolar mixture are given for 514— 624°. Free energies of formation and dilution, heats of formation, entropy changes, activities, and activity coeffs. are calc. The system shows a large negative deviation from Raoult's law. J. G. A. G.

Significance of solvent for solubility of salts, and activity coefficients of ions. J. N. BRÖNSTED, A. DELBANCO, and K. VOLQVARTZ (Z. physikal. Chem., 1932, 162, 128-146; cf. A., 1929, 649).-The solubilities of several cobaltammine salts in MeOH solutions of various uni-univalent salts agree with Debye and Hückel's theory, but the solubilities in solutions of bi-bivalent salts do not. From the ratio of the solubilities of cobaltammine salts in H₂O and MeOH ionic distribution ratios have been calc. The relation between the solubility of [Co(NO₂)₃,3NH₃] and that of flavotetranitrodiamminocobaltate in various solvents indicates that the solubilities of both substances are determined essentially by electric forces. Born's electrostatic formula is not generally valid for the ionic distribution ratio. R. C.

Thermodynamics of concentrated solutions. II. Calculation of entire crystallisation curves in binary eutectic systems. E. KORDES (Z. physikal. Chem., 1932, 162, 103—127; cf. A., 1932, 228).—An equation has been derived for the calculation of the above curves and its validity confirmed by reference to existing data. The equation contains three consts., of which two can be calc., for f.-p. depressions in dil. solutions, from the latent heats of fusion and m.p. of the pure components, and the third is a factor which corrects for the positive or negative heats of mixture of the components in the molten state and can be calc. from a determination of crystallisation temp. at a single high concn. The equation is applicable to systems having a miscibility gap in the liquid state. R. C.

Thermochemistry and the periodic table. Energy of transfer of electrons on oxidation. T. C. SUTTON (Nature, 1932, 130, 474—475).—The energy of linking with O is a periodic function of the at. no. in the two series C, N, O, and F, and Si, P, S, and Cl. It is proportional to the covalency of the atom, depends on the no. of electron shells in the atom, and is not directly affected by the nature of the nucleus. The energy of transfer of an electron on oxidation is approx. the same for all atoms with the same no. of electron shells and decreases as this no. increases. L. S. T.

Co-ordination. IV. Fluorides and chlorides and their complex ions. F. J. GARRICK (Phil. Mag., 1932, [vii], 14, 914—937; cf. A., 1931, 547).— The energy of co-ordination (referred to abs. zero) in terms of the sizes, charges, and polarisabilities of the ions, is derived for the fluorides and chlorides of several metals and non-metals. In the case of those of B, Al, Cr^{••}, Si, Ti^{••}, and Sn^{•••}, and for PF₅ and SF₆ the same quantity is calc. from thermochemical data. There is satisfactory agreement between the two series of results. Conclusions are reached with regard to the stabilities of various known and hypothetical complex ions and salts, from considerations of the energies of hydration of complex ions, the lattice energies of complex salts, and the energies of co-ordination. E. S. H.

Heat of formation of hydrochloric acid and some related thermodynamic data. F. D. Ros-SINI (Bur. Stand. J. Res., 1932, 9, 679–702).—The heat of formation of gaseous HCl from H_2+Cl_2 is given by $H_{298\cdot1}=-22,063\pm12$ g.-cal.¹⁵ per mol. of HCl. Existing thermodynamic data for HCl and its aq. solution are compared and correlated. D. R. D.

Thermal data. I. Heat capacities, entropies, and free energies of seven organic compounds containing nitrogen. H. M. HUFFMAN and H. BORSOOK (J. Amer. Chem. Soc., 1932, 54, 4297— 4301).—Data are recorded for *d*-alanine, *l*-asparagine, *l*-asparagine hydrate, *l*-aspartic acid, *d*-glutamic acid, creatine, and creatinine. J. G. A. G.

Vapour pressure of water over aqueous solutions of potassium hydroxide. Y. KOBAYASHI (J. Sci. Hiroshima Univ., 1932, 2, 269-274).-V.p. of aq. KOH at 25° have been calc. for concns. up to 20*M*. Tables and a curve are given. F. L. U.

Fusion diagrams of highly-refractory oxides. V. Systems with magnesium oxide. H. VON WARTENBERG and E. PROPHET. VI. Correction. H. VON WARTENBERG and H. J. REUSCH (Z. anorg. Chem., 1932, 208, 369-379, 380-381; cf. A., 1932, 913).—V. Revised m.p. of NiO, CoO, and Mn_3O_4 are 1990°, 1810°, and 1560°, respectively. Data for mixtures of MgO with Cu₂O, BeO, CaO, SrO, BaO, TiO₂, CeO₂, Cr₂O₃, Mn₃O₄, Fe₃O₄, NiO, and CoO are given. TiO₂ forms compounds, 2TiO₂,MgO, m.p. 1680°, and TiO₂,MgO, m.p. 1840°. Mixed crystals are formed with NiO, CoO, Mn₃O₄, Fe₃O₄, and Cr₃O₄, the last-named being formed from Cr₂O₃ by loss of O₃ above 2300°.

 Cr_2O_3 by loss of O_2 above 2300°. VI. Fusion curves for mixtures of ZrO_2 and of Al_2O_3 with NiO, CoO, and Mn_3O_4 have been redetermined. F. L. U.

Iron nitrides. S. SATOH (Bull. Chem. Soc. Japan, 1932, 7, 315-333).—The structures of a series of Fe nitrides have been determined by X-ray analysis. The heat of formation of Fe₄N, cale. from the measured heat of dissolution in dil. H₂SO₄, is 4460 g.-cal. per g.-mol. Mol. heats of Fe₂N and Fe₄N have been calc., assuming Neumann and Kopp's law, and the equilibrium relations of the systems Fe-Fe₄N-NH₃-H₂ and Fe₄N-Fe₂N-NH₃-H₂ have been worked out. Fe nitride (containing no Fe) gives a potential -0.448 volt in N-FeSO₄ (free from Fe⁻), but in presence of 7% Fe⁻⁻ the potential is +0.5708 volt. The presence of O₂ or Fe⁻⁻ appears to convert the nitride into a passive state. Fe nitride does not provide a reversible electrode in solutions of NH₃ in MeOH, EtOH, or liquid NH₃ containing KNH₂.

Two-component salt mixtures of lead nitrate with thallium or silver nitrate. H. M. GLASS, K. LAYBOURN, and W. M. MADGIN (J.C.S., 1932, 2713— 2715).—The f.-p. curves of the systems $Pb(NO_3)_2$ -AgNO₃ and $Pb(NO_3)_2$ -TlNO₃ both have a simple eutectic at 200·2° and 175·5°, respectively. The curves are limited by the decomp. of $Pb(NO_3)_2$ in mixtures containing < 60% AgNO₃ or 50% TlNO₃ (cf. A., 1932, 468). The decomp. temp. of $Pb(NO_3)_2$ rises with dilution. M. S. B.

Thermal dissociation of sodium hydrogen sulphate. F. ISHIKAWA, K. MASUDA, and H. HAGISAWA (Bull. Inst. Phys. Chem. Res., Japan, 1932, 11, 1244—1253).—The dissociation pressure resulting from the reaction $2NaHSO_4 \implies Na_2S_2O_7 +$ H_2O has been measured from 130° to 280° . The m.p. of NaHSO₄ is 182° and is not affected by addition of $Na_2S_2O_7$. $Na_2S_2O_7$ decomposes very slowly at 300° and rapidly above 400° . D. R. D.

Limits of the admissibility of co-ordinative and constitutional inferences from the composition of crystalline phases. E. HERTEL and A. DEMMER (Annalen, 1932, 499, 134—143).—The equilibrium diagram for TiCl₄ (24—50 mol.-%) and EtCN shows the existence of six solid compounds and is more complex than would be expected from preparative results. The diagram for TiCl₄ (30—50 mol.-%) and PhCN indicates five compounds, whilst that for TiCl₄ (10—80 mol.-%) and m-C₆H₄(NO₂)₂ indicates six and these do not include the 2 : 1 compound (which can be isolated) owing to the metastability of this. Investigations on the mol. compounds of metal chlorides and NO₂-derivatives do not show whether N₂O₄ has a s- or as-constitution (cf. Reihlen and Hake, A., 1927, 219). The following compounds are prepared: TiCl₄,3EtCN, m.p. 108° ; TiCl₄,2PhCN, 173·5°; TiCl₄,3PhCN, 168°; $4TiCl_4,m^{-}C_{6}H_4(NO_2)_2$, 115°; TiCl₄, $m^{-}C_{6}H_4(NO_2)_2$, 116°; TiCl₄,3 $p^{-}C_{6}H_4(NO_2)_2$, 115°; 2TiCl₄, $p^{-}C_{6}H_4(NO_2)_2$, 130°; TiCl₄,2COPh₂, 150°. TiCl₄ forms 2:1, 1:1, and 1:2 compounds, m.p. 175°, 163°, and 136°, respectively, with Me fumarate; the use of an excess of the ester in cold C₆H₆ gives the 1:1 compound (+2C₆H₆), which when freed from C₆H₆ (in vac. during 4 weeks) affords the substance, $\frac{CH^{-}CO_2}{CH^{-}CO_2}$ TiCl₂ (?), m.p. 140°. Other mol. compounds (not new) are also described. H. B.

System $CS(NH_2)_2$ -NH₃-H₂O. E. JĀNECKE and A. HOFFMANN (Z. Elektrochem., 1932, 38, 880— 883).—Solubility and v.-p. data are given over the range -78° to 181° . The compounds $CS(NH_2)_2$, $3NH_3$ and $CS(NH_2)_2$, NH_3 are stable at low temp. (decompose at -10° and 8° , respectively). D. R. D.

Reduction of zinc oxide by hydrogen. F. SCHACHERL (Gazzetta, 1932, 62, 839-843).—The equilibrium const. $(1\cdot3\times10^{-4} \text{ at } 583^\circ, 2\cdot67\times10^{-6} \text{ at} 393^\circ)$ is not influenced by the presence of 33 mol.-% MgO in the ZnO. H. F. G.

Ternary system K_2SiO_3 -Na₂SiO₃-SiO₂. F. C. KRACEK (J. Physical Chem., 1932, 36, 2529-2542).— The ternary system is of the simple eutectoid type with respect to the binary systems K_2SiO_3 -SiO₂ and Na₂SiO₃-SiO₂, and no ternary compounds occur. In the disilicate region both $K_2Si_2O_5$ and Na₂Si₂O₅ take up a limited excess of K_2O , Na₂O, and SiO₂, depending on the composition of the liquid in equilibrium with the crystals. I. J. P. (c)

Solubility isotherms of complex inorganic thiocyanates. I. A. DE SWEEMER (Natuurwetensch. Tijds., 1932, 14, 231--244).--The 25° isotherm of the system KCNS-Co(CNS)₂-H₂O indicates the existence of only one complex, viz., $K_2Co(CNS)_4H_2O$, the saturated solution of which contains 60.7%. The region in which the solid complex can exist is large compared with that of $K_4Ni(SCN)_64H_2O$, the only complex salt in the system KCNS-Ni(CNS)₂-H₂O at 25°. No complexes are formed in the system Co(CNS)₂-Ni(CNS)₂-H₂O at 25°. The analytical significance of the results is discussed. H. F. G.

Equilibrium in systems composed of sulphur dioxide and sodium, potassium, or ammonium thiocyanate. H. W. FOOTE and J. FLEISCHER (J. Amer. Chem. Soc., 1932, 54, 3902—3906; cf. A., 1931, 799). G. M. M. (c)

Vapour lines of three-phase systems for the co-existence of two solid components with the vapour of a binary system. A. SMITS and E. J. HARMSEN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 700-705).—In the region in which the vapour behaves as an ideal gas the mol. heat of sublimation of the least volatile component increases, thereby confirming the predictions of Wuite.

W. R. A. Limiting mobilities of some univalent ions and the dissociation constant of acetic acid at 25°. D. A. MACINNES, T. SHEDLOVSKY, and L. G. LONGS-WORTH (Nature, 1932, 130, 774–775).—A criticism (cf. A., 1932, 1089). The val. $K=1.753\times10^{-5}$ for AcOH (*ibid.*, 695) and not 1.776×10^{-5} (*ibid.*, 1089) has been independently confirmed (*ibid.*, 695). L. S. T.

Irreversible processes in electrolytes. Diffusion, conductance, and viscous flow in arbitrary mixtures of strong electrolytes. L. ON-SAGER and R. M. FUOSS (J. Physical Chem., 1932, 36, 2689-2778).—Theoretical. The effects of the Coulomb forces on diffusion, electrolytic conduction, and viscous flow are considered from a common viewpoint. Previous results for simple electrolytes can be extended to mixtures containing an arbitrary no. of ionic species, and general limiting laws are derived. The electrostatic effects are proportional to the sq. root of the conen. The electrostatic contribution to viscosity is computed and the mechanism of force transfer is investigated. Kohlrausch's rule relating to the independent migration of ions is not valid for mixtures and the conductances are not additive. The general laws of diffusion are discussed. The rate of production of entropy in transport processes is a quadratic function of the velocities. Laws of combined diffusion and electrical conduction are formulated.

E. S. H.

Influence of picric acid on the electro-capillary curve of mercury. H. BREINDL and K. SÖLLNER (Z. Elektrochem., 1932, 38, 843—846).—Electrocapillary curves are given for Hg in contact with N/110-KCl, in H₂O, in N/1100-picric acid, and in N/1100-salicylic acid. Surface tension and e.m.f. data are also given for Hg in contact with dil. aq. HgNO₃ containing HNO₃ and KNO₃. D. R. D.

Electrokinetic phenomena. VIII. Surface conductance of cellulose and Smoluchowski's theory. H. A. ABRAMSON (J. Physical Chem., 1932, 36, 2141—2144).—Data for alkali chlorides and HCl show the classical theory to be inadequate. For Li', Na', and K', but not for Mg'' and Ba'', the quotient of the sp. surface conductance of cellulose by the ionic mobility is const. A modification of the theory is proposed which makes the surface conductance partly dependent on the abs. mobilities of the anions and cations (cf. A., 1931, 429). C. H. R. (c)

Unique electrode potential characteristic of a metal, and a theory for the mechanism of electrode potential. A. L. MCAULAY and E. C. R. SPOONER (Proc. Roy. Soc., 1932, A, 138, 494-501).-A theory is advanced for the origin of the electrode potential of a metal immersed in an aq. solution. The bombardment, owing to heat motion, of polar H₂O mols. on the metal results in a stream of ions being drawn into the solution to a distance t from the electrode surface, and equilibrium is attained when their removal is balanced by their return under the field so produced. This results in a layer of ions of thickness t, surrounding the metal. Certain consequences of the theory which have been verified by experiment are described. L. L. B.

Potential [at metallic electrodes] in electrolytes with foreign ions. II. A. SCHMID, P. VÖGELE, and W. WINKELMANN (Helv. Chim. Acta, 1932, 15, 1393—1398; cf. A., 1930, 705).—Potentials of Ag, Pb, and Cu in aq. solutions of their respective nitrates (Cu also in CuSO₄) have been determined at progressive dilutions of electrolyte. Ag behaves in accordance with Nernst's law down to about $10^{-5}N$, but is less negative at higher dilutions. Cu shows a similar deviation between 0·1 and 0·01N, whilst Pb is more negative from the start. In all three cases the potential-dilution curves possess a well-defined max. Potentials of Cu in Cu-free solutions of several acids and alkali salts are found to depend largely on the anion and very little on the cation present. Potentials in very dil. solutions and even in pure H₂O are definite and reproducible. F. L. U.

Influence of gases on normal potential of zinc electrode. F. H. GETMAN (J. Physical Chem., 1932, 36, 2655—2663).—The initial val. of the potential of a Zn electrode in aq. ZnCl₂ is increased by air, N₂, and H₂, and decreased by O₂. This influence diminishes with time. The change in potential is much smaller than that produced by the same gases when the metal is immersed in aq. KCl. S. L. (c)

Normal potential and heat of dissolution of gallium. E. S. VON BERGKAMPF (Z. Elektrochem., 1932, 38, 847–848).—Measurements with the cell Ga | $KGa(SO_4)_2|Hg_4SO_4|Hg$ indicate that $E_0=-0.52$ volt. Hence the heat of formation of Ga^{***} from Ga (solid) is 36 kg.-cal. The heat of dissolution of Ga in aq. HCl (1 mol. HCl: 8.81 mols. H₂O) is 32 kg.-cal.

D. R. D.

Electrical measurement of cyanide solution activity. W. E. JOHN and E. BEYERS (J. Chem. Met. Soc. S. Africa, 1932, 35, 27—34).—Measurements have been made of the potential of Au in 0.02-0.06%aq. KCN and the effect thereon of CaO, Hg⁻⁻, Fe⁻⁻, Zn⁻⁻, and Pb⁻⁻ was determined. With increasing concn. of KCN the potential becomes less negative, and finally reaches a positive val. in 0.037% aq. KCN. Hg⁻⁻ in minute quantities raises the potential to a positive val. in all concens. of KCN, whereas CaO, Fe⁻⁻, Zn⁻⁻, and Pb⁻⁻ depress it to more negative vals. than in pure KCN. A. R. P.

Electrochemical investigation of solid cadmium-gold alloys. A. OLANDER (J. Amer. Chem. Soc., 1932, 54, 3819—3833).—The e.m.f. of the cell Cd liquid|K(Rb)Cl,LiCl,CdCl₂|(Cd,Au) solid above 340° and the cell Cd solid|(K,Na,Cd)OAc|(Cd,Au) solid at 250—300° and the temp. coeffs. have been determined. With the completion of the phase diagram of the Au-Cd system three new transitions have been found. L. P. H. (c)

E.m.f. in liquid ammonia. G. I. COSTEANU (Compt. rend., 1932, 195, 778—779).—For 0.1Nsolutions of the electrolytes the e.m.f. of the cells Pb|Pb(NO₃)₂,AgNO₃|Ag and Cd|Cd(NO₃)₂,4H₂O,AgNO₃| Ag between -65° and -35° are expressed by 0.462+0.0005(t+35°) and 0.963-0.00033(t+35°), respectively. C. A. S.

[Ammonium acetate as a buffer.] R. J. WIL-LIAMS and C. M. LYMAN (J. Amer. Chem. Soc., 1932, 54, 4458; cf. A., 1932, 709).—The $p_{\rm H}$ of the solutions is liable to be < 7. J. G. A. G. Indicators. XIX. Existence and significance of the "hydrogen effect." A. THIEL and G. COCH (Z. anorg. Chem., 1932, 208, 397—400; cf. A., 1931, 1383).—When CO_2 is rigorously excluded an extremely small displacement of the $p_{\rm H}$ of solutions buffered to different extents is observed. This displacement, which may be of either sign, is independent of the presence of neutral salt. The contrary result obtained by Wolf is attributed to excessive platinising of the electrodes used. F. L. U.

Hydrogen over-voltage on mercury cathodes in presence of small amounts of platinum metals. I. SLENDYK and P. HERASYMENKO (Z. physikal. Chem., 1932, 162, 223-240).-The current-voltage curves for the simultaneous separation of H and Pt on a dropping Hg electrode exhibit two periods of rapidly increasing current. The first corresponds with the separation of mol. H_2 catalysed by Pt already deposited, and the second with the discharge of H on the uncontaminated Hg surface. Even minute traces of Pt have an appreciable catalytic effect, and many published measurements of H over-voltage are doubtless in error as a consequence of this effect. Neutral salts cause considerable reduction in the catalysed separation of H. The variation with [H'] of the limiting current and cathode potential for the catalysed separation can be accounted for by means of Langmuir's adsorption isotherm. Some other Pt metals, but not Pd or Rh, behave similarly to Pt.

R. C.

Hydrogen over-voltage. T. ERDEY-GRUZ and H. WICK (Z. physikal. Chem., 1932, 162, 53—62).— The slope, b, of the graph of the logarithm of the c.d. against the over-voltage of H on a C electrode with an uncontaminated surface is the same as for an indifferent metal electrode, and thus agrees with the theory (A., 1930, 1376). Compared with other metals, Pb and Ta give abnormal vals. of b, which is perhaps connected with the persistence on them of an adsorbed film even at H discharge potentials. R. C.

Discharge voltage of mercury on foreign electrodes. T. ERDEY-GRÖZ and H. WICK (Z. physikal. Chem., 1932, 162, 63—70; cf. A., 1932, 24).—The potential at which Hg starts to separate electrolytically on an electrode which it does not wet is cale. theoretically to be -0.34 volt, relative to the reversible potential of Hg in the same solution. With C electrodes coated with lustrous C separation begins at some parts of the surface of even the most inactive C at -0.21 volt, and this is ascribed to the presence of active spots. Discharge on the most inactive parts of the surface requires a potential of -0.23 to -0.27volt. For Pt and Ta the discharge voltage is much smaller than for C. R. C.

Anodic film of aluminium. I. Effect of concentration of the electrolyte on the formation of anodic film. II. Anodic behaviour of aluminium in aqueous solutions of oxalic acid. S. SETOH and A. MIYATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **19**, 189–236, 237–291).—Experiments have been made with $H_2C_2O_4$ solutions and the influence of the conen. of the electrolyte on film formation has been examined. The thickness and electrical resistance of the Al₂O₃ film, resistance to corrosion, and energy efficiency of film formation with d.c. and with superposed d.c. and a.c. have been measured. With a.c. no film is formed.

II. The porous active layer of Al_2O_3 is continuously renewed by combination of nascent O in the pores with the Al. At const. c.d. the rise of terminal voltage and the growth of the active layer are almost independent of the electrolyte used. The destructive power of the electrolyte on the active layer varies with the anion. Retardation of anodic corrosion by the electrolyte is effected by the screening action of O_2 occluded in the pores of the active layer.

N. M. B.

Theory of passivity phenomena. XVII. Comparison of E. Müller and Schwabe's new theory of passivity and W. J. Müller's protective film theory with the experimental results of researches on passivity. W. J. Müller (Z. Elektrochem., 1932, 38, 850-860; cf. A., 1932, 473).—Experimental data for the electrolytic passivation of Pb, Cd, Cu, and Zn in saturated aq. solutions of their perchlorates and sulphates support W. Müller's theory. E. Müller and Schwabe's c.m.f.-c.d. curves (*ibid.*, 814) cannot be used as a basis for a theory of passivity. D. R. D.

Photovoltaic effect. R. T. DUFFORD (Trans. Electrochem. Soc., 1932, 62, 345—351).—Work of the author and others on photovoltaic effects in cells containing ethereal solutions of Grignard compounds (A., 1927, 918; 1929, 1364; 1930, 846, 1126; 1931, 802) is reviewed and discussed. H. J. T. E.

Crossing of potential thresholds in chemical reactions. E. WIGNER (Z. physikal. Chem., 1932, B, 19, 203-216).—The case where the reacting mols. have almost sufficient energy to cross the threshold mechanically, but a finite fraction of them have rather less energy and pass through the upper part of the energy hill non-mechanically, is worked out. The result is compared with Eckart's calculations (Physical Rev., 1930, [ii], 35, 1303). Application of the quantum correction to the rate of transformation of para-H₂ into normal H₂ increases somewhat the deviation of the observed from the calc. vals. R. C.

Electrical ignition of explosive gaseous mixtures. G. I. FINCH (Nature, 1932, 130, 929).— Crit. of the thermal theory of electrical ignition.

L. S. T. Lower pressure limit in the chain reaction between hydrogen and oxygen. C. N. HINSHELwood and E. A. MOELWYN-HUGHES (Proc. Roy. Soc., 1932, A, 138, 311-317).—The influence of temp., H_2 -O₂ ratio, presence of inert gases, and diameter of the explosion vessel on the lower limit of the low-pressure explosion region in the combination of H₂ and O₂ has been explored in detail (cf. A., 1931, 1244). The results can be explained on the hypothesis that the lower limit is determined by a balance between the branching of reaction chains and the destruction of chain carriers by diffusion to the walls of the vessel. L. L. B.

Internal energy of gases after explosion. W. T. DAVID, J. R. BROWN, and A. H. EL DIN (Phil. Mag., 1932, [vii], 14, 764–777).—In CO-air and H_2 -air explosions in spherical vessels 6 in. and 17.45 in. internal diameter with central ignition, heat losses up to the moment of max. pressure were approx. the same for each vessel. The higher pressure developed in the larger vessel is attributed to more complete combustion at the moment of max. pressure. Explosion experiments give too high vals. for sp. heats. H. J. E.

Explosive oxidation of carbon monoxide at lower pressures. G. HADMAN, H. W. THOMPSON, and C. N. HINSHELWOOD (Proc. Roy. Soc., 1932, A, 138, 297-311).-Dry CO and O₂ combine explosively in SiO₂ vessels between certain pressure limits in the region of 700°. Outside these limits, which are independent of the degree of dryness, the reaction rate is very small. The effect of inert gases shows that the lower limit is determined by the diffusion of active centres of some kind to the vessel wall, and the upper limit to gas-phase deactivation. The lower limit is independent of temp., whilst the upper moves rapidly towards higher pressures as the temp. rises. CO may affect the wall of the vessel so that no explosion takes place, leading to a metastable state. The mechanism of the change is discussed. L. L. B.

Mechanism of flame movement. II. Fundamental speed of flame in mixtures of methane and air. H. F. COWARD and F. J. HARTWELL (J.C.S., 1932, 2676—2684).—During the uniform movement of flame, the vol. of gas burnt in unit time in the explosion of a given CH_4 -air mixture is proportional to the area of the flame front. This relation holds for all inflammable CH_4 -air mixtures and for all the explosion tubes used (diameters $2 \cdot 5$ — 10 cm.). From the results the speed of propagation in the direction normal to the flame front for a stationary gas mixture (the fundamental speed of flame) is calc. and a comparison made with the results given by Gouy's Bunsen flame method.

F. J. W. Propagation of flame in electric fields. II. Effects of transverse fields. E. M. GUENAULT and R. V. WHEELER (J.C.S., 1932, 2788-2793).— Changes in the speed of flames due to the imposition of a transverse electric field are caused by an increase in the surface area of the flame front. The field has no effect on the character or speed of the chemical reactions taking place in the flame. All changes in shape of the flame can be explained as due to a mechanical drag exerted by the field on the flame, which behaves as a positively-charged mass of gas. CO-air and C_2H_2 -air mixtures were used. F. J. W.

Thermal decomposition of nitrous oxide. M. VOLMER and H. FROEHLICH (Z. physikal. Chem., 1932, B, 19, 85-88; cf. A., 1931, 174).—At a temp. between 625° and 680° the graph of the reciprocal of the velocity coeff. against the reciprocal of the pressure between 2 and 300 mm. exhibits the curvature predicted theoretically, due to variation with pressure of the average mean life of the active mols. (A., 1927, 833). R. C.

Thermal decomposition of nitrous oxide. Effect of helium, argon, and oxygen. M. VOLMER and H. FROEHLICH (Z. physikal. Chem., 1932, B, 19, 89–96).—Measurements have been made at 625–670° with initial N₂O pressures of about 1— 50 mm. The probabilities of activation per collision are: N₂O, 1/190; A, 1/1600; N₂, 1/800; He, 1/290; O₂, 1/830; CO₂, 1/145. R. C.

Reactions of hydrogen atoms with hydrazine and with ammonia. J. K. DIXON (J. Amer. Chem. Soc., 1932, 54, 4262—4271; cf. A., 1932, 820).— Approx. 1 mol. of NH₃ and 1 mol. of permanent gas are produced in the decomp. of 1 mol. of N₂H₄ by a stream of at. H. The temp. coeff. between 0° and 22° is zero. With const. initial [N₂H₄], the % of N₂H₄ decomposed and that of NH₃ produced decreases with [H]. H was, however, always in excess. With const. [H], the abs. wt. of N₂H₄ decomposed and of NH₃ formed decreased with initial [N₂H₄], although the % decomp. increased. H₂O vapour does not affect the results. A weak green fluorescence occurs near the point of mixing of N₂H₄ and at. H; some of the lines in the spectrum were identified with the α -bands of the NH₃ flame. The reaction mechanism is probably H+N₂H₄ \longrightarrow H₂+N₂H₃, 2N₂H₃ \longrightarrow 2NH₃+N₂, and the relation to the photochemical and electrical decomp. of NH₃ is discussed (cf. A., 1932, 705). Results observed with NH₃ may be due to the action of O atoms from the H₃O mixed with the at. H. J. G. A. G.

Reaction velocity of chloroalkyls with sodium vapour. H. VON HARTEL, N. MEER, and M. POLANYI (Z. physikal. Chem., 1932, B, 19, 139-163).—The diffusion method for the determination of the velocity of gas reactions of Na vapour (cf. A., 1931, 174) does not give accurate vals. of the abs. velocity coeff., but is satisfactory for comparative purposes. The results show that the reaction inertia decreases in the order F, Cl, Br, I for the halides of a given radical, with increase in length of the C chain, with increase in the no. of Cl atoms, and the more so the closer these are together, and with introduction of carbonyl-O. It decreases in the order primary, sec., tert., but is not affected by branching of the C chain. The reaction is retarded by a double linking at the C atom to which the Cl is attached, but the inertia is reduced if the double linking occurs at the next C atom. A small reaction inertia seems to be associated with a large dipole R. C. moment.

Comparison of sodium vapour reaction with other organic chemical reactions. N. MEER and M. PÓLANYI (Z. physikal. Chem., 1932, B, 19, 164-189; cf. preceding abstract).-The comparison is with published data for the ionic reactions (1) $A_{I}'+RA_{II} \longrightarrow RA_{I}+A_{II}'$ and (2) $R_{I}OR+H \longrightarrow R_{I}OH+R'$. Disregarding cases where there is possibly steric hindrance, the relations between reactivity and constitution are similar to those for Na vapour, except that lengthening the C chain causes considerable retardation. Assuming that under the influence of the electric forces of the dipole the reacting ion attacks that side of the atom to which it is to be attached which is remote from the linking to be severed, it may be deduced (a) that in (1), but not in (2), steric hindrance may operate, D

and (b) that in (1) optical inversion will occur when optically-active substances are involved. Of these (b) accords with the experimental data and explains the racemising action of halogen ions, assuming this to be based on atom-exchange reactions causing inversion and leading to equilibrium between the antipodes, and (a) probably accounts for the fact that in (1) the reactivity diminishes in the order primary, *sec.*, *tert.*, whereas the order for (2) is the same as for Na vapour. R. C.

Rate of fourth-order reaction between bromic and hydrobromic acids. Kinetic salt effect. H. A. YOUNG and W. C. BRAY (J. Amer. Chem. Soc., 1932, 54, 4284—4296; cf. A., 1930, 713).—The velocity of the reaction $\text{BrO}_3'+3\text{H}_2\text{O}_2=3\text{O}_2+\text{Br}'+$ $3\text{H}_2\text{O}$ between 0.0125-0.5M·H^{*}, 0.005-0.01M· BrO_3' , and 0.013-0.062M·H $_2\text{O}_2$, alone, and with the addition of 0.0008—0.008M·Br' and 0.07-0.7M· NaClO_4 , at 25°, 45°, and 65°, is given by $-d[\text{BrO}_3']/$ $dt = k_1[\text{H}_2\text{O}_2][\text{BrO}_3'][\text{H}'] + k[\text{BrO}_3'][\text{Br}'][\text{H}']^2$. The heat of activation of the fourth-order reaction is $16,000\pm300$ g.-cal. and that of the third-order $15,000\pm1000$ g.-cal. The limiting law of the kinetic salt effect of the fourth-order reaction at 65° is k/γ^2_{TBr} , $\gamma^2_{\text{TBr}O_4}=\gamma$, and the velocity at 25° for ionic strengths < 0.2 in HClO₄ or H_2SO_4 solutions is given by $-d[\text{BrO}_3']/dt = 540\pm15[\text{BrO}_3'][\text{Br}'][\text{H}']^2\gamma^4_{\text{TBr}}$. The mechanism proposed for the autocatalytic reduction of BrO_3' by H_2O_2 involves a series of steps including the reduction of the intermediate compounds HBrO₂ and HOBr by H_2O_2 . J. G. A. G.

Rate of reaction of disubstituted aminomethylsulphonic acids with iodine. T. D. STEWART and W. E. BRADLEY (J. Amer. Chem. Soc., 1932, 54, 4183—4188).—The velocity of the reaction $R_2N^+H\cdot CH_2\cdot SO_3^-+I_3' \rightarrow R_2N^+:CH_2+SO_4''+3I'+3H'$ is independent of [I], is of first order with respect to NH_2 -acid, and decreases with increasing acidity. With a particular substituent group, R, the reaction velocity is the same whether I, Br, or H_2O_2 is used and the rate-determining step is probably an ionisation process, for which velocity coeff. and heats of activation are recorded for a no. of cases. J. G. A. G.

Kinetics of reaction between arsenious acid and iodine. II. Influence of neutral salts on velocity of reaction and equilibrium point. E. JÓZEFOWICZ (Rocz. Chem., 1932, 12, 787—798).— K, Na, Li, Ba, Sr, Ca, and Mg chlorides and bromides (0.5-3N) and NaNO₃ and KNO₃ considerably reduce the velocity of oxidation of H₃AsO₃ by I, and slightly augment that of oxidation of HI by H₃AsO₄, thereby shifting the equilibrium point in the direction of H₃AsO₃ formation. This effect is due to reversal of the reaction I₂+H₂O = HOI+HI in the presence of neutral salts. R. T.

Aldehyde hydrogen sulphites. II. Effect of varying temperature on equilibrium between benzaldehyde and hydrogen sulphite ion. III. Effect of changing hydrogen-ion concentration on specific reaction rate of addition of sodium hydrogen sulphite to benzaldehyde. IV. Discussion of equilibrium, rates, and temperature coefficients as affected by hydrogen-ion concentration. T. D. STEWART and L. H. DONNALLY (J. Amer. Chem. Soc., 1932, 54, 3555-3558, 3559-3569; cf. A., 1932, 818).-II. Equilibrium data are given for $p_{\rm II}$ 0.0—13 at 0—58°. III—IV. Data are given for the rate of reaction of

PhCHO and NaHSO₃ at 21° for $p_{\rm H}$ 1.9 and 5.2. These permit the calculation at 21° for $p_{\rm H}$ 0—13 of the sp. rates of the reactions of PhCHO with SO₃", HSO₃', and H₂SO₃, the sp. rates of dissociation of OH•CHPh•SO₃H (I) and its uni- and bi-valent ions, and the overall equilibrium const. (I) is a very strong monobasic acid, with a second dissociation const. of 7×10^{-10} ; the activation energies and heats of dissociation are calc. The first dissociation const. of PhCHO as an acid is 5×10^{-13} .

H. A. B. (c)

Mechanism of oxidation process. XXXII. Enzymic oxidation of acetic acid by yeast. H. WIELAND and R. SONDERHOFF (Annalen, 1932, 499; 213–228).—Oxidation of AcOH [as NaOAc or Ba(OAc)₂ in buffered solutions] by "impoverished" yeast (I) (A., 1932, 303) and O₂ during about 24 hr. gives a solution containing unchanged AcOH, succinic acid (II) (= about 5% of AcOH consumed), and citric acid (III) (= about 10% of AcOH used). The oxid-ation is more dependent on the substrate conen. than in the case of EtOH (cf. loc. cit.); the velocity with M/128 solutions is about 75% of that with M/4solutions. The time-O2-consumption curves show that reaction undergoes self-acceleration owing to the intermediate products being oxidised faster than AcOH. The ratio CO_2 produced : O_2 consumed is approx. 1, whilst the mol. ratio O_2 : AcOH is 1.7-1.8. The intermediate production of glycollic acid or $H_2C_2O_4$ is improbable, since these acids are little or not affected by $(I)+O_2$. (II) is oxidised at a much slower rate than AcOH; it is considered that this does not disprove the intermediate formation of (II) from AcOH and it is suggested that the (II) produced during the dehydrogenation is "activated." Fumaric acid is oxidised by (I) and O, at about the same rate as (II). AcOH, (II), and malic acid are not dehydrogenated by (I) and methylene-blue. (III) may be produced by an aldol-like condensation of AcOH and oxaloacetic acid [formed from (II)]; this is supported by the observation that (III) is not produced from (II) and $(I)+O_2$. Oxidation of (III) by $(I)+O_2$ also proceeds slowly; the velocity of CO₂ evolution is very small during the initial stages, but subsequently increases rapidly. H. B.

Velocity of dissolution of carbon dioxide and ammonia in water and aqueous solutions. A. N. SCHUKAREV and M. V. BONDAREVA (Ukrain. Chem. J., 1932, 7, [Sci.], 1-11).—The velocity of dissolution (V) of \dot{CO}_2 in H_2O is proportional to the velocity of stirring. For equiv. concns. of alkali $V_{N_4OH} > V_{NH_3}$; the velocity coeff. diminishes with increasing conen. of alkali to N, above which it remains const. The velocity of dissolution of NH3 in aq. acids (HCl, H₂SO₄, HNO₃) at first rises rapidly and then slowly with the concn. of acid; alkalis reduce the val. of V. R. T.

Thermal decomposition of methane by a carbon filament. H. H. STORCH (J. Amer. Chem. Soc., 1932, 54, 4188—4198).—The decomp. of CH₄ by C

filaments at 1457-2000° in bulbs cooled by liquid N2, and at -183° , -78° , and 0° , has been investigated. The earliest products isolated are C₂H₆ and H₂, of which 95% yield is achieved with liquid N₂. At -183° , C₂H₄ and C₂H₂ are also obtained, whilst at the higher temp. the products are C and H₂. With < 8 cm. of CH₄, the reaction is of approx. first order and has a heat of activation of $77,170\pm10,000$ g.-cal. At higher pressures, the reaction becomes of approx. second order, possibly owing to temp. gradient effects near the filament. The effect of H_2 on the reaction is in accord with the equation derived by Kassel (A., 1932, 1209) on the assumption of a series of dehydrogenations following the initial synthesis of C_2H_6 . J. G. A. G.

Oxidation of sulphur at low pressures. A. RITCHIE and E. B. LUDLAM (Proc. Roy. Soc., 1932, A, 138, 635-643).-The low-pressure oxidation of S, initiated on a hot surface and accompanied by a visible glow, has been studied experimentally. The rate is independent of the pressure of O_2 , due to two compensating factors: (1) the rate of oxidation is proportional to the pressure of O_2 , and (2) the rate of inhibition by SO₂ is inversely proportional to the pressure of O_2 . A residual pressure is observed and an explanation is offered. L. L. B.

Kinetics of reactions governed by diffusion. J. PALACIOS (Anal. Fis. Quim., 1932, 30, 695-700).-The kinetics of reactions between a solid and a gas in which the velocity is determined by the relatively slow rate of diffusion of the gas through the layer of reaction product is considered. Such reactions proceed to completion in a finite time; if the surface is plane the velocity diminishes with time at a decreasing rate and then falls abruptly to zero at the instant of completion, whereas for cylindrical or spherical surfaces it falls continuously. H. F. G.

Intensive drying. I. Reaction between ammonia and phosphorus pentoxide. J. SANCHO and E. Moles (Anal. Fis. Quim., 1932, 30, 701-719). -Very pure and dry NH₃ and P₂O₅ react vigorously at first, but after a few min. the velocity diminishes and several days are required for completion of the reaction. If more NH3 is admitted to the vessel further absorption takes place. The composition of the product of the first reaction approximates to NH_3, P_2O_5 , but with further NH_3 $(NH_3)_{1-2}, P_2O_5$ is formed. The absorption obeys an equation of the Freundlich type, viz., $S = 58t^{-17.6}$. H. F. G.

Kinetics of peptisation of hydrated chromic oxide. J. LISIECKI (Rocz. Chem., 1932, 12, 817-831).—Aq. HCl dissolves or peptises Cr₂O₃ hydrate gels, according to the structure and relative concn. of the gel and to [HCl]. NaOH in excess of the theoretical amount is required for peptisation, indicating the existence of the equilibrium CrO·ONa+H₂O CrO·OH+NaOH. Peptisation by HCl or CrCl₃ leads to the production of CrCl₂OH. The reaction of peptisation by NaOH is of the autocatalytic type, and proceeds according to Ostwald's, Zawidzki's, and von Buzagh's kinetic equations. The velocity coeff. of the reaction is 0.133 at 18° and 0.525 at 38° ; the temp. coeff. is 1.97 over the range $18-38^{\circ}$.

R. T.

Kinetics of the systems $CaO-CO_2$ and $Cd-CO_2$. S. BRETSZNAJDER (Rocz. Chem., 1932, 12, 799-815).—The velocities of the reactions $CaO + CO_2 \Longrightarrow$ $CaCO_3$ and $CdO+CO_2 \longrightarrow CdCO_3$ vary with the pressure, temp., reacting surface (S) of the solid phase, and difference between the equilibrium pressure of CO₂ and that of the systems. At pressures considerably different from that of equilibrium the velocity is > theoretical, owing to the presence of active nuclei in the solid phase. The reaction is retarded by the formation of layers of reaction products on the oxides; the inhibitive action of these layers depends on their thickness and structure, and on previous treatment of the oxides. The val. of S depends on the dimensions and structure of the crystals of oxide. The velocity of reaction is not a simple function of the composition of the solid R. T. phase at a given temp. and pressure.

Galvano- and potentio-metric determination of corrosion. M. T. MICHAILOV (Korrosion u. Metallschutz, 1932, 8, 85–89; Chem. Zentr., 1932, ii, 607).—Potential and c.d. measurements are inadequate. Todt's test is not universally applicable. A. A. E.

Methods for investigating the corrosion of metals. E. V. TZEKHNOVITZER (Soobshch. Vsesoy. Inst. Met., 1931, No. 1-2, 45-49).-A discussion. CH. ABS.

Corrosion of iron in mixtures of water vapour and air. E. I. DUIRMONT (Soobshch. Vsesoy. Inst. Met., 1931, No. 1-2, 37-45).—Corrosion is more rapid at higher temp. and in presence of CO_2 and O_2 . The properties of the product depend on the temp. CH. ABS.

Rate of dissolution of carbonyl iron in hydrochloric and sulphuric acids. M. CENTNERSZWER and M. STRAUMANIS (Z. physikal. Chem., 1932, 162, 94—102).—Dissolution in 10—11.45*N*-HCl is very slow, and there is a period of induction with one or more well-defined velocity max. Dissolution in H_2SO_4 is more rapid than in HCl of the same normality, but is qualitatively similar. The velocity fluctuations are ascribed to impurities, perhaps C. R. C.

Explosibility of systems of base metals and halogen compounds. F. LENZE and L. METZ (Chem.-Ztg., 1932, 56, 921-923).—Mixtures of alkali or alkaline-earth metals with halogenated hydrocarbons are sensitive to shock, especially as the no. of halogen atoms is increased. Probably unstable intermediate compounds, such as C_2HCl and C_2Cl_2 , are formed and lead to explosive decomp. of the whole. E. S. H.

Catalytic decomposition of hydrogen peroxide by ferric ions. W. LIMANOWSKI (Rocz. Chem., 1932, 12, 782—786).—Fe^{•••} catalyses the reduction of KMnO₄ by H_2O_2 ; H_2O_2 reduces Fe^{•••} to Fe^{••}, which is oxidised by KMnO₄. R. T.

Chemical reactions in concentrated electrolytes. XIV. Reaction between vanadic acid and hydrogen bromide, and the effect on it of acids, salts, and catalysts (2). M. BOBTELSKY and L. CHAJKIN (Z. anorg. Chem., 1932, 209, 95—104; cf. A., 1932, 576).—When the Br formed is removed at a const. rate the influence of added substances is the more pronounced the smaller is the conen. of HBr. The reaction velocity increases with conen. of added H_2SO_4 , being measurable only between the limits 35% and 48% H_2SO_4 . All chlorides except ZnCl₂ and CdCl₂ accelerate the reaction. Sulphates exert little effect. F. L. U.

Catalytic effects produced by tartaric acid, sodium hydrogen tartrate, and by first- and second-stage tartrate buffers. H. M. DAWSON and E. SPIVEY (J.C.S., 1932, 2612-2620).—The catalytic coeffs. for the tartaric acid mol., the H tartrate ion, and the tartrate ion for the COMe₂-I reaction are $26 \cdot 0 \times 10^{-6}$, $8 \cdot 5 \times 10^{-6}$, and $1 \cdot 0 \times 10^{-6}$, respectively. The first-stage ionisation coeff. for tartaric acid is $k_1=8 \cdot 5 \times 10^{-4}$ in salt-free solutions. The influence of [NaCl] on k_1 is given by log $k_1^x = \log k_1^0 + 0 \cdot 54 \sqrt{x} 0 \cdot 24x$, where k_1^x is the ionisation coeff. in xM-NaCl solution. The catalytic effects of first- and secondstage tartrate buffers can be represented by $v=v_h+$ $v_{n_xT}+v_{nT'}+v_{T'}+v_{n_y}+v_{on'}$, where the successive partial velocities are due respectively to H', the tartaric acid mol., the H tartrate ion, the tartrate ion, the H₂O mol., and OH'. F. J. W.

[Effect of] hydrogen-ion concentration on degradation of uric acid. F. ROSENTHAL (Biochem. Z., 1932, 255, 200–204).—Decomp. of uric acid, which increases with increasing $p_{\rm fl}$, can be detected in aq. solutions at $p_{\rm fl}$ 7.5. The extent of decomp. is independent of concn. and is unaffected by the state of the dissolved acid. Inorg. catalysts (FeCl₃, CuSO₄, KMnO₄), methylene-blue, and glutathione do not accelerate the decomp., which does not take place between $p_{\rm fl}$ 7.5 and 10.8 if O₂ (air) is absent. W.McC.

Effect of ions in sugar solutions and solvent mixtures. F. TÖDT (Z. Ver. deut. Zuckerind., 1932, 82, 817–849).—The neutral-salt effect and the high activity of H^{*} in sugar solutions (especially with addition of EtOH) lead to the suggestion that these and allied effects are due to removal of H_2O of solvation from H^{*}. E. S. H.

Decomposition of nitrous oxide on glowing platinum. G. M. SCHWAB and B. EBERLE (Z. physikal. Chem., 1932, B, 19, 102—106; cf. A., 1932, 819).— O_2 formed by the reaction has a retarding action and is strongly adsorbed by the Pt wire, whereas added O_2 has no retarding action. R. C.

Catalysed hydrogenation of ethylene. M. TAUBER (Z. physikal. Chem., 1932, B, 19, 97-101).— There seems to be no connexion between the activity of a Pt-black film and its volta potential. The activity is destroyed when the catalyst is exposed to a high vac., probably because of dehydration or the decomp. of surface oxides. R. C.

Heterogeneous chemical reactions in the silent electric discharge. I. S. MIYAMOTO (J. Sci. Hiroshima Univ., 1932, 2, 217-242).—The following solid substances are reduced by gaseous H_2 in the silent discharge : S. I. FeCl₃, CuCl₂, CuCl, HgCl₂, Hg₂Cl₂, SnCl₄, NaNO₃, AgNO₃, K₄Fe(CN)₆, KMnO₄, KClO₃, KIO₃, HIO₃, CuSO₄, KBrO₃, As₂O₅,

As₂O₃, As₂S₃. Details with regard to the experiments and reaction products are given. F. L. U.

Boron hydrides. XVII. Electrolysis of solutions of boron hydrides in anhydrous ammonia. A. STOCK and E. WIBERG [with H. MARTINI and A. NICKLAS] (Ber., 1932, 65, [B], 1711-1724; cf. A., 1931, 1248).—The initial reactions involved in the electrolysis of B_2H_6 in anhyd. NH_3 at -75° are $[B_2H_4]H_2+NH_3 \longrightarrow [B_2H_3(NH_2)]H_2$ (I) $+H_2$ and (I) $+NH_3 \longrightarrow [B_2H_2(NH_2)_2]H_2+H_2$. After this stage the reaction becomes very difficult, probably owing to internal salt formation of the compound. The second change, initially very slight but gradually increasing in importance and ultimately occurring almost exclusively, results in decomp. of NH₃ into N_2 and $3H_2$; its course as far as (I) is concerned is given by the scheme : $3(I) \longrightarrow 3B_2H_3(NH_3)' + 3H';$ the residue left after electrolysis yields B₂O₃ and H₂, the total vol. of the latter being six times that of the B_2H_6 . Electrolysis of solutions of B_4H_{10} is similarly accompanied by substitution and re-formation reactions. If the e.m.f. is sufficiently high all the H atoms of the anion B_4H_6 can be replaced with production of $[B_4(NH_2)_6]H_4$, but further replace-ment does not occur. Continued electrolysis at 10—16 volts results in slow evolution of H_2 without alteration in the B: NH_2 ratio until finally $B_4(NH_2)_6$ remains as a colourless, non-volatile substance, sol. in liquid NH₃. With medium voltages the first stage of the reaction ceases after introduction of about $4NH_2$ into the B_4H_{10} mol., and ultimately with small current practically only the mixture of 25% N_2 and 75% H_2 is evolved. Similar observations are made with $B_{10}H_{14}$. At 2-4 volts ammination appears to proceed to the stage $B_{10}(NH_2)_6H_8$, whereas at higher voltages 12 or more H atoms can be replaced at higher voltages 12 or more H atoms can be replaced. H. W.

H. W. Electrolytic oxidation. II. Electrolyte oxid-ation of sodium thiosulphate. S. GLASSTONE and A. HICKLING (J.C.S., 1932, 2800—2807).—(NH₄)₂MoO₄ increases the yield of Na₂SO₄ obtained from the electrolytic oxidation of Na₂S₂O₃; MoO₃ similarly increases the formation of SO₄" when Na₂S₂O₃ is oxidised by H₂O₂. During the oxidation of Na₂S₂O₃ is oxidised by H₂O₂. During the oxidation of Na₂S₂O₃ at platinised Pt, Au, Ni, and gas-C anodes increase of $p_{\rm H}$ decreases the current efficiency for oxidation, but increases the ratio of Na₂SO, to Na₂SO, formed. but increases the ratio of Na_2SO_4 to $Na_2S_4O_6$ formed. MnSO₄ and CoSO₄, which catalyse the decomp. of H_2O_2 , reduce markedly the oxidation efficiency at all the electrodes used. The results are in harmony with the view that the anodic oxidation of Na₂S₂O₃ is a secondary process in which H_2O_2 is the effective oxidising agent. F. J. W.

Theory of electrolytic formation of sodium persulphate. O. ESSIN and E. ALFIMOVA (Z. physikal. Chem., 1932, 162, 44-52).—Compared with the formation of $(NH_4)_2S_2O_8$ (A., 1926, 804) the formation of Na₂S₂O₈ is complicated by the production of H_2SO_5 , which is responsible for the re-actions $SO_5''-2\Theta \longrightarrow SO_4+1O_2$ and $SO_4+H_2O \longrightarrow$ $SO_5''+2H'$, and $H_2SO_5+O \longrightarrow H_2SO_4+O_2$. The observed variation of current yield of active O with the concess. of SO4", SO5", and S2O8" agrees with this view. R. C.

Electrolytic preparation of some complex salts of bivalent silver. G. A. BARBIERI (Atti R. Accad. Lincei, 1932, [vi], 16, 44–47).—Attempts to repeat Morgan and Burstall's prep. (cf. A., 1931, 234) of [Ag 3 dipy](NO₃)₂ failed, the complex never con-taining more than 2 mols. of dipyridyl for 1 atom of Ag. By the anodic oxidation of Ag salts in acid solution in presence of dipyridyl the following complex solution in protocol dipylagities of Ag^{Π} were obtained : [Ag 2 dipy](N \hat{O}_3)₂, [Ag 2 dipy](ClO₄)₂, and [Ag 2 dipy](SO₄H)₂. O. J. W.

Silver plating. E. B. SANIGAR.-See B., 1932, 1085.

Influence of magnetic field on electrolysis of nickel salts. H. FORESTIER (Compt. rend., 1932, 195, 954-957; cf. A., 1930, 1002).-A field of 5200 gauss causes considerable retardation in the rate of deposition of Ni from 0.61% aq. NiSO₄ when $p_{\rm fl} < 2.3$, and stops it entirely for $p_{\rm fl} < 1$. For higher $p_{\rm fl}$ there is slight acceleration. With increasing field and $p_{\rm H}$ 1.2 the rate decreases asymptotically to a min. With salts of Zn or Cu there is slight acceleration for all $p_{\rm H}$. This enables Ni and Cu to be separated in solutions of $p_{\rm H}$ 1—2. C. A. S.

Gold plating solutions. O. SIZELOVE.-See B., 1932, 1085.

Possibility of use of chromium anodes in chromium plating. J. KORPIUM.-See B., 1932, 1085.

High-acid chromium [electrodeposition] process. RASSOW and L. WOLF.-See B., 1932, 1085.

Distillation cathodes. W. HINSCH (Z. tech. Physik, 1931, 12, 528—541; Chem. Zentr., 1932, i, 1757).—The emission of cathodes of Ba-coated Pt wires has been investigated. L. S. T.

Photochemical reaction of hydrogen and chlorine. A. J. ALLMAND and H. C. CRAGGS (Nature, 1932, 130, 927).-Normal reaction rates are obtained even when special precautions to eliminate H₂O L. S. T. are taken.

Photochemical formation of hydrogen peroxide. A. L. MARSHALL (J. Amer. Chem. Soc., 1932, 54, 4460–4461).—The quantum efficiency of the formation of H_2O_2 photosensitised by Hg is 2.5 and not 6.6 as previously reported (A., 1928, 30). Contrary to the observations of Frankenburger and Klinkhardt (A., 1932, 348), at least 75% of the product from moist H_2-O_2 mixtures is H_2O_2 . J. G. A. G.

Photochemical reaction between bromine and potassium oxalate in visible and ultra-violet light. A. K. BHATTACHARYA, O. PRAKASH, and N. R. DHAR (Z. anorg. Chem., 1932, 209, 139-144).-The reaction velocity is proportional to $I^{1/5} - I$ (where I is the intensity of the light), the temp. coeff. is > 1, and the quantum yield high. With increasing acceleration of the reaction the temp. coeff. falls, the quantum yield is increased, and the index of I reduced. Infra-red and red radiations accelerate the reaction probably by loosening the Br-Br linking. A. R. P.

Photochemical reduction of carbon dioxide. M. REGGIANI (Helv. Chim. Acta, 1932, 15, 1383— 1390).—Contrary to the observations of Rajvansi and Dhar (A., 1932, 480), exposure of CO_2 to sunlight or artificial light in presence of different optical sensitisers and of various inorg. and org. reducing agents for periods up to 48 hr. did not lead to the production of detectable quantities of CH_2O , HCO_2H , or CO. Negative results were also obtained when the CO_2 was in the form of K or Ca H carbonates or an aromatic org. acid. F. L. U.

Photochemical studies. XV. Germane. Decomposition of ammonia sensitised by mercury vapour. H. ROMEYN, jun., and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1932, 54, 4143—4154).— GeH₄ does not absorb light of λ 7000—2100 Å., but radiation transmitted by a thin layer of quartz causes decomp. The unsensitised and Hg-sensitised decomp. conform approx. to the equation GeH₄= Ge+2H₂, but there is a deficiency of H₂ evolved, probably owing to adsorption. The sensitised reaction is approx. of first order and is not affected by added H₂ or N₂. The mechanism is discussed, and probably involves the initial formation of GeH₃ and H. J. G. A. G.

Photochemistry of phosphine. H. W. MEL-studied and the kinetics of the reaction are compared with those of NH_3 . From an investigation of the influence of the pressure of PH_3 , H_2 , O_2 , and A on the reaction the following mechanism is suggested : the PH₃ mol. is dissociated, in the first place, by collision with excited Hg atoms into at. H and a residue which is probably PH_2 . The dissociation products diffuse to the walls of the vessel, where they may recombine, as is shown by the fact that the reaction is retarded by at. H. Formation of PH₃ from red P or P vapour and at. H could not be detected. The lowering of the explosion limit of PH3-O2 mixtures by illumination with a Hg arc is due to a surface effect. The O2 first attacks the products of dissociation, thus accelerating the rate of decomp., and the oxide mol. so formed (probably a P oxide) initiates a stable chain reaction between the remaining PH₃ and O₂, as is shown by the acceleration of this reaction by A. The effect can be reproduced by pretreatment of the walls of the tube with at. H. L. L. B.

"After effect" and "induction period" in the reversible photochemical reduction of tungstic acid sol. S. GHOSH and A. K. BHATTACHARYA (Bull. Acad. Sci. Agra and Oudh, 1932, 2, 29–32).—A period of induction is observed in the photochemical reduction of tungstic acid by glucose and the reaction is of zero order (cf. A., 1930, 1533). On placing the reduction product in the dark, reoxidation takes place, but the rate of reaction, also zero-mol., is at first reduced owing to the "after effect" (cf. A., 1928, 720) or continuation of reduction in the dark after exposure to light. In an atm. of CO_2 the reaction is still zero-mol., but the rate is considerably increased. There is no reoxidation in the dark, but the "after effect" continues for some time, a stationary state being reached before reduction is complete. Reoxidation in the first case is apparently due to the presence of air and not to a reversal of the reaction. M. S. B.

Photoanisotropic effect (Weigert effect) with dyes. II. T. KONDO (Z. wiss. Phot., 1932, 31, 185-199; cf. A., 1932, 1214).-Benzopurpurin, rhodulin-violet, orthochrome, pinacyanol, and metanilyellow in collodion or gelatin emulsions have been examined in detail. With decreasing wave-length of activating polarised light, the max. of dichroism moves to shorter wave-lengths, but the max. dichroism obtainable is at a longer wave-length than the spectral absorption max. With orthochrome, the shape of the dichroism curve alters with the wave-length of activation. Metanil-yellow shows both dichroism and strong double refraction, the max. of the latter being at a longer wave-length. Circularly polarised light has no effect. The effects vary greatly from collodion to gelatin emulsions. J. L.

Activation of nuclei. LUPPO-CRAMER (Z. wiss. Phot., 1932, 31, 200-202).—So-called "Siedeemulsionen" (neutral, *i.e.*, free from NH₃, during ripening) and certain special emulsions (cf. A., 1931, 579, 806) are activated by immersing, before exposure, in 0.5% aq. NaOH, or in 1% aq. NH₃ (then washing for 1 hr. and drying). Treatment of these activated plates, after exposure and before development, with a solution of 2% KBr+2% H₂SO₄, or 2% KBr+0.3% H₂O₂, or with (NH₄)₂S₂O₈ solution causes some destruction of the latent image and considerable fog. J. L.

Desensitising [with] sensitisers. LUPPO-CRAMER (Z. wiss. Phot., 1932, 31, 203-207).—The Capri-blue effect (cf. B., 1932, 162; A., 1931, 806) also appears with physical development; methylene-blue, phenosafranine, and Janus-green B behave similarly. Ordinary diapositive plates treated with Capri-blue solutions are increasingly desensitised to white light at conens. $> 1:10^7$, but they are sensitised to red light at conens. $> 1:10^7$, but they are sensitised to red light at conens. of 1:20,000 to $1:10^9$, with a max. between $1:2 \times 10^6$ and $1:10^7$. Erythrosin and neocyanine (allocyanine) solutions behave similarly, the latter sensitising to a high degree for red and infra-red light at a conen. of $1:10^6$. J. L.

Lattice disturbances. LUPPO-CRAMER (Z. wiss. Phot., 1932, 31, 208—209). Gelatin emulsions of HgI₂ are only slightly light-sensitive; addition of TII sensitises the emulsion up to 50° E.-H., developed in metol-quinol, or, better, amidol. Addition of Na_2CO_3 to amidol developer causes fogging and reversal. Immersing plates in 3% NaNO₂ or NaHSO₃ solution has no sensitising effect. J. L.

Hypersensitisation. III. Influence of silver ions on the spectral sensitivity of dyed [sensitised] silver bromide plates [emulsions]. J. I. BOKINIK and Z. A. ILJINA (Z. wiss. Phot., 1932, 31, 210-215; cf. A., 1932, 581).—Slow plates were sensitised with dyes and hypersensitised with 0.01% AgNO₃ solution. Acid dyes, which do not sensitise, are not hypersensitisable. Plates sensitised with basic dyes, *e.g.*, pinacyanol, pinachrome, fuchsin, auramine, etc., are mostly hypersensitised with pinacryptol-yellow or -green are nevertheless resensitised and hypersensitised by $AgNO_3$. These results support the theory that metallic Ag is produced by photochemical decomp. of Ag ion-dye complex. J. L.

Photochemical reaction involving zinc oxide and oxygen. J. MCMORRIS and R. G. DICKINSON (J. Amer. Chem. Soc., 1932, 54, 4248—4252).—NO₂ and not O₃ (A., 1932, 130) was found in O₂ which had passed over ZnO [prepared from $Zn(NO_3)_2$] strongly irradiated with near ultra-violet light from a Hg arc. Visible radiation is ineffective. J. G. A. G.

Decompositions by light in aqueous solutions. I. Decomposition of trichloroacetic acid and ferric thiocyanate. A. K. BHATTACHARYA and N. R. DHAR (Z. anorg. Chem., 1932, 209, 123—128).— The rate of decomp. of $CCl_3 \cdot CO_2H$ (I) and $Fe(CNS)_3$ (II) in light of various wave-lengths has been measured at $15-55^\circ$; the temp. coeff. is > 1, but decreases with increasing rate of decomp. The quantum yields of photochemical decomp. are high and increase with rise in temp. and acceleration of the reaction. The relation between the rate of decomp. and the light intensity or absorbed radiation varies from $I^{1/3}$ to I for (I) and from $I^{1/4}$ to I for (II). In presence of H_2O light seems to loosen the C·Cl, C·O, and C:N (in presence of Fe^{***}) linkings, so that decomp of (I) is accelerated in visible, and decomp. of (II) in red and infra-red, light. A. R. P.

Photobromination of benzene. E. RABINO-WITSCH (Z. physikal. Chem., 1932, B, 19, 190-202).-The quantum yield is 0.4-0.9 at room temp., and its temp. coeff. is 1.6. It varies little with the light intensity or the wave-length between 3000 and 5500 Å., although there is a fall on approaching the dissociation limit of Br, and it increases with the Br concn. The dissolved Br mols. are attached to C₆H₆ mols., with which they react on light absorption. C6H6Br6 is formed chiefly by reaction of the activated Br mols. PhBr results from the reaction with free Br atoms : $C_6H_6+Br=Ph+HBr$, $Ph+Br_2=PhBr+Br$, the former of these requiring thermal activation, which accounts for the high temp. coeff. of the photochemical reaction and the disappearance of the temp. coeff. on dilution with CCl₄ (cf. A., 1929, 1153). A monochromator giving light of considerable intensity is described. R. C.

Radio-sensitivity from a chemical viewpoint. G. HARKER (J. Cancer Res. Comm., Sydney, 1932, 4, 109-117).—When Pd deposited on C is exposed to X-rays in an atm. of H_2 a reaction is sometimes initiated which yields MeNC. Once started, the reaction proceeds to completion after the rays are switched off if conditions are favourable, and under some conditions it occurs without X-ray treatment.

A. G.

Liquefaction of helium. F. SIMON (Z. ges. Kälte-Ind., 1932, 39, 89–90; Chem. Zentr., 1932, ii, 578).—He released from an insulated vessel at 50 atm./ 12° abs. is quickly cooled to the b.p. and about 50° /o of the He remains liquefied in the vessel. By diminution of pressure a temp. of $< 2^{\circ}$ abs. is easily reached.

A. A. E. Preparation of liquid hydrogen with neon as intermediary. K. CLUSIUS (Z. gcs. Kälte-Ind., 1932, 39, 94–97; Chem. Zentr., 1932, ii, 579). Ne is cooled in liquid air and expanded from 190 atm., whereby it is partly liquefied and is used to effect the liquefaction of H_2 . The process is considered thermodynamically. A. A. E.

Fixation of hydrogen by highly-dispersed metals. Synthesis of ammonia. E. MÜLLER and K. SCHWABE (Z. Elektrochem., 1932, 38, 861–868).— On shaking with H₂, liquid Zn amalgam absorbs H₂, forming a greyish-vellow solid. Zn also combines with H₂, when it is distilled with NaCl in H₂ at low pressure, using Frankenburger's method (A., 1931, 1120) with improved technique. Under these conditions, W did not distil and no H₂ was absorbed. Frankenburger's results on Fe were confirmed. Traces of NH₃ are formed when the experiment is conducted in an atm. of N₂+H₂. Palladised BaSO₄ catalyses the reaction N₂+3H₂=2NH₃ at room temp. D. R. D.

Relative stability of copper derivatives of β diketo-compounds. T. S. MOORE and (MISS) M. W. YOUNG (J.C.S., 1932, 2694—2709).—The equilibria existing between β -diketo-compounds and the Cu derivatives of other diketo-compounds, together with the equilibria between two Cu derivatives, have been studied mainly in C₆H₆ solution. The results are quantitatively consistent with the equations CuA₂+ HB = CuAB+HA; CuAB+HB = CuB₂+HA, and CuA₂+CuB₂ = 2CuAB. The vals. of the equilibrium consts. indicate that the co-ordinating affinity of the β -diketo-compounds in their Cu derivatives follows the same order as the percentage of enol contained in the pure compounds. No evidence was obtained of the existence of compounds, such as CuA₂,HB, containing 6-covalent Cu.

F. J. W.

[Explosive decomposition of alkaline ammoniacal silver solutions.] W. COLTOF (Chem. Weekblad, 1932, 29, 737).—An alkaline NH_3 -Ag solution prepared exactly as described by Tollens (A., 1882, 1329) exploded violently within 1 hr., when the containing vessel was moved, although no ppt. and the merest trace of film were present (cf. A., 1932, 582). S. C.

New complex compounds of silver cyanide with sodium cyanide. G. A. BARBIERI and A. TETTAMANZI (Atti R. Accad. Lincei, 1932, [vi], 15, 965-967).—NaAg(CN)₂ and the compounds Na₂Ag(CN)₃,3H₂O and Na₃Ag(CN)₄,5H₂O separate on crystallising a solution of AgCN in aq. NaCN.

D. R. D.

Cæsium polybromides. I. W. H. HARRIS (J.C.S., 1932, 2709—2713).—The system CsBr–Br–H₂O has been examined at 0° and 25°. The only polybromide existing at both temp. is CsBr₃. Fresh evidence is given confirming the formula $Br_2, 10H_2O$ for Br hydrate. F. J. W.

Ternary compound $4CaO,Al_2O_3,Fe_2O_3$. S. SOLACOLU (Zement, 1932, 21, 301–305; Chem. Zentr., 1932, ii, 851).—The existence of brownmillerite, $4CaO,Al_2O_3,Fe_2O_3$, is confirmed. The substance is stable in presence of excess of CaO. Its isomorphism with $2CaO,Fe_2O_3$ is confirmed.

A. A. E.

Reaction between calcium oxide and silica in relation to the hardening of Portland cement. A. J. P. VAN DER BURGH (Chem. Weekblad, 1932, 29, 616—618).—When CaO is added to SiO_2 gel in contact with H_2O the CaO conen. of the solution remains approx. const. at 0.002*M* until the gel has absorbed about 0.9 mol. of CaO per mol., and thereafter rises rapidly until the ratio CaO: SiO_2 in the solid phase is about 1.4:1. The voluminous product does not change with time. The reactions at the membrane formed when Ca(OH)₂ solution is brought into contact with SiO_2 are discussed in their bearing on the hardening of Portland cement. H. F. G.

Hydrothermal synthesis of calcium silicates under ordinary pressure. VI. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 439—443B; cf. A., 1932, 1007, 1008).—CaSiO₃ is obtained by heating CaO and SiO₂ (1:1) at or above 1200°. Ca₂SiO₄ is produced by heating CaO and SiO₂ (2:1) at or above 1250°. Ca₃Si₂O₅ is formed under intermediate conditions, but is mixed with other silicates from which separation is difficult. E. S. H.

Synthetic bianchite. C. ANDREATTA (Atti R. Accad. Lincei, 1932, [vi], 16, 62-69; cf. A., 1930, 1397).—By crystallisation at 30° from a solution containing ZnSO_4 , FeSO₄, and H_2SO_4 , (Zn,Fe)SO₄,6H₂O, which has approx. the composition of natural bianchite, was obtained. The green transparent monoclinic crystals have H 2-3, d 2.031±0.005. Crystallographic and optical data are given. O. J. W.

Alkaline-earth silicides. L. WÖHLER and W. SCHUFF (Z. anorg. Chem., 1932, 209, 33-59; cf. A., 1926, 368).—The compounds SrSi and BaSi are obtained from the elements by brief heating at 1000° and subsequent quenching. By heating at 1200— 1400° the above are converted slowly, and CaSi readily, into the disilicides. The latter are also produced from Si and the corresponding oxides or peroxides by Goldschmidt's method. Ba also forms the compound BaSi₃, and the existence of still higher silicides is probable. The chemical behaviour of the compounds has been studied. The following heats of formation were determined: CaSi 85·3, CaSi₂ 161·5, SrSi 112·8, SrSi₂ 147·4, BaSi 181·5, BaSi₃ 399·2 kg.-cal. Observations on the thermal decomp. of Ca, Sr, and Ba oxalates are recorded. F. L. U.

Action of ammonia on mercurous chloride. C. RENZ (Helv. Chim. Acta, 1932, 15, 1316–1320).— The grey residue left after dissolving NH_2HgCl by aq. HCl from Hg_2Cl_2 which has been blackened in aq. NH_3 is but slightly attacked by dil. or conc. HNO_3 . A second treatment with aq. NH_3 produces further blackening. The product is regarded as a "photochloride" consisting of Hg finely dispersed in unchanged Hg_2Cl_2 . F. L. U.

Potassium iodomercurate. F. GALLAIS (Compt. rend., 1932, 195, 875—878).—The conductivity curve of mixed solutions, 0.01M, of KI and HgCl₂ indicates a min. for KI+0.22HgCl₂ when the solvent is H₂O, but for KI+0.25HgCl₂ in EtOH, and in both cases a second discontinuity for KI+0.50HgCl₂. It is concluded that K₂HgI₄ is formed but destroyed immediately without formation of KHgI₃ (cf. A., 1928, 20): $0.25 K_2 Hg I_4 + 0.25 Hg Cl_2 = 0.50 Hg I_2 + 0.50 KCl.$ The limit mol. conductivity of the iodomercurate indicates formation of three ions, $2K' + Hg I_4''$ (cf. A., 1921, ii, 57; 1925, ii, 887); moreover, $Ag NO_3$ ppts. $Ag_2 Hg I_4$ from EtOH solution of the iodomercurate. Although the anion $Hg I_4''$ predominates in a solution of iodomercurate it must be capable of furnishing compounds in which the anion contains only I_3 (cf. A., 1931, 1318). C. A. S.

Chlorination of aluminium oxide with chlorine and carbon monoxide. W. D. TREADWELL and L. TEREBESI (Helv. Chim. Acta, 1932, 15, 1353—1362). —The rate of chlorination of γ -Al₂O₃ has been studied in the range 325—980°. The course is autocatalytic up to 800°, the more markedly so the lower is the temp. Above 800° the curve is linear until the solid is nearly used up. The velocity-temp. curves show a max. at about 550° and a min. at about 650°, the latter corresponding with transformation of γ -Al₂O₃ into the less reactive α -form. The observed autocatalysis is attributed to formation of active C at the reacting surface. When COCl₂ is used the reaction is more rapid and also shows max. velocity at 550°. F. L. U.

Structure of kaolins from the viewpoint of the chemistry of ultramarine. I. Action of dealkalising factors on sodium kaolinates. M. DOMINIKIEWICZ (Rocz. Chem., 1932, 12, 836-853). ---Na₆Al₆Si₆O₂₄ (I) and Na₁₂Al₆Si₆O₂₇ (II) have been prepared from kaolin and Na₂CO₃. Thugutt's nepheline hydrate (cf. A., 1911, ii, 298) is identical with the trihydrate of (I). Na cannot be removed from (I) by treatment with SO_2Cl_2 , AcCl, Ac₂O, AcOH, S, NH₄Cl, SO_2 , and H₂S at red heat; HCl at 175° converts it into $Na_4Al_6Si_6O_{23}$ (III). (II) is converted by SO_2Cl_2 , AcCl, and Ac_2O into $Na_8Al_6Si_6O_{24}$, which yields (I) with S, NH_4Cl , or HCl at 110°, and this, as before, gives (III) on treatment with HCl at 175°, whilst the trihydrate of (I) yields that of (III) under similar conditions. The above results support the view that the basis of all aluminosilicates is hexa-aluminosilicic acid, and that this acid possesses three types of OH groups, of different acidity. The existence of the compound $Na_3Al_5Si_6O_{22.5}$, described by Silber (A., 1981, 684) is 1881, 684) is not confirmed. R. T.

Separation of rare earths by basic precipitation. X. Preparation of pure ytterbium oxide. W. PRANDTL (Z. anorg. Chem., 1932, 209, 13-16; cf. A., 1931, 813).—Yb can be separated from Tm and Lu by repeated electro-reduction of $Yb_2(SO_4)_3$ to the slightly sol. YbSO₄. Details are given. F. L. U.

Acid fluorides of thallium and ammonium and their mixed crystals. O. HASSEL and H. KRING-STAD (Z. anorg. Chem., 1932, 208, 382–386; cf. A., 1930, 1099).—The substance obtained by crystallising a solution of TIF in excess of aq. HF at room temp. is shown by analysis to be $H_2TIF_3,0.5H_2O$. The compound $H_2(NH_4)F_3,0.5H_2O$ can be similarly prepared. The two salts form a continuous series of mixed crystals. F. L. U.

Active charcoal. E. LANDT (Kolloid-Beih., 1932, 37, 1-55).—A survey of published work on prep.,
chemical composition, electrical conductivity, wettability, apparent and true sp. gr., heat of wetting, sedimentation vol., porosity, surface development, electric charge, isoelectric point, coagulation and peptisation, and adsorption of acids, bases, salts, org. electrolytes, and non-electrolytes. Application to the sugar industry is discussed. E. S. H.

Transformation of amorphous carbon into graphite. H. ISHIKAWA (Elec. Rev., Japan, 1931, 19, 419, 493, 690, 726, 824, 884).—Graphitisation of amorphous C with 8% SiO₂ at 1850° for 24 hr. affords 77—80% of graphite. Experiments with C and 5% of SiO₂, Al₂O₃, Fe₂O₃, and WO₃ gave higher % of graphitisation than those with C free from these oxides (about 30% yield). Transformation of amorphous C into graphite probably takes place around impurities as nuclei. CH. ABS.

Nitrogen compounds of germanium. III. Germanous imide. W. C. JOHNSON, G. H. MOREY, and A. E. KOTT (J. Amer. Chem. Soc., 1932, 54, 4278-4284).—GeI₂ is prepared by the interaction of GeS with conc. HI, and crystallised from the solution at -80° . With precautions, gaseous NH₃ at $-33 \cdot 5^{\circ}$ reacts quantitatively with GeI₂ thus : GeI₂+3NH₃= GeNH+2NH₄I. GeNH is insol. in liquid NH₃, reacts with H₂O or dil. NaOH to give NH₃ and Ge(OH)₂, and reacts violently with O₂. J. G. A. G.

Separation of hafnium and zirconium. I. W. PRANDTL (Z. anorg. Chem., 1932, 208, 420-426; cf. A., 1931, 813).—A solution of mixed ZrO_2 and HfO₂ in dil. H₂SO₄ containing H₂C₂O₄ is treated with Na₄Fe(CN)₆, when the ppt. contains a greater proportion of Hf than the original mixture. F. L. U.

Basic lead salts. P. JOLIBOIS and L. CLOUTIER (Compt. rend., 1932, 195, 795—796).—Using the method previously described (cf. A., 1920, ii, 107) addition of aq. Pb(NO₃)₂ to aq. $K_2Cr_2O_7$ containing increasing amounts of KOH gives successively PbCrO₄, PbCrO₄, Pb(OH)₂, and PbCrO₄, 2Pb(OH)₂ (cf. A., 1906, ii, 757). Similarly the following only were obtainable: 2PbCO₃, Pb(OH)₂, PbCl₂, Pb(OH)₂, PbCl₂, 6Pb(OH)₂, PbSO₄, 3Pb(OH)₂, 2SiO₂, 3Pb(OH)₂, PbCl₂, 6Pb(OH)₂, and 2B₂O₃, 7Pb(OH)₂. No basic iodide was obtained (cf. A., 1904, ii, 258). C. A. S.

Principles of the genetic development of material. VII. Conversion of lead oxide into carbonate. Chemistry and morphology of white lead. V. KOHLSCHÜTTER [with H. HOSTETTLER] (Helv. Chim. Acta, 1932, 15, 1425-1449; cf. A., 1932, 131).-The course of the reaction and the nature of the product obtained when PbO is acted on by CO₂ and H₂O under various conditions have been studied by measurements of vol. change, $p_{\rm H}$ of liquid, by chemical and X-ray analysis, and by microscopical examination. Products approximating to white lead were obtained only when the PbO was in a finely-dispersed form. The reaction is considered to take place in a layer of solution adherent to the particles, and to be preceded by a local peptisation of the PbO. The character of the product is largely determined by the concn. of CO₂. F. L. U.

Thorium sulphide. PICON (Compt. rend., 1932, 195, 957-959; cf. A., 1930, 582).-ThS₂, prepared by passing H_2S over ThO_2 in a graphite boat at 1600°, black, vitreous, has d_0° 7.234, m.p. $1925\pm25^\circ$, at which temp. it is slightly volatile. On heating in vac., S is evolved at 2800°, ThC₂ being formed from the graphite of the crucible. Cl_2 attacks it at 250°; Br, if moist, slowly at room temp.; O_2 at 400°; aq. HF and (slowly) aq. HCl at room temp.; dry HCl at 300°; SO_2 at 400° forms S and ThO₂; conc. H_2SO_4 has no action, but dil. acid gives $Th(SO_4)_2$; 10% HNO₃ gives $Th(NO_3)_4$; CO_2 above 440° gives $ThO_2 + 2CO+S$; Mg has no action at 800°. Aq. NaOH has very little action in the cold; fused NaOH attacks it rapidly. $K_4Fe(CN)_6$ at room temp. gives ThO_2 and S, but H_2O_2 and KMnO₄ form $Th(SO_4)_2$. C. A. S.

Hyponitrites. II. Metallic salts. III. Esters. J. R. PARTINGTON and C. C. SHAH (J.C.S., 1932, 2589-2597).-The hyponitrites of Ca, Sr, and Ba decompose on heating, forming chiefly the monoxide, N_2 , and N_2O , together with some nitrite and nitrate, and NO. The hyponitrites of Pb and Cu do not give any nitrite or nitrate. Alkalis convert them partly into hydroxides; acids give chiefly N₂O. KMnO₄ and NaOCl oxidise them incompletely to nitrates. Mol. wt. determinations on C₆H₆ solutions of Et, Pr, Bu, and CH₂Ph esters of $H_2N_2O_2$ indicate the formula $R_2N_2O_2$. They decompose at temp. as low as 15°, giving N₂. H_2O , alkalis, and acids produce hydrolysis to the alcohol, aldehyde, and N2. Reducing agents give alcohol and N_2 . **F**. J. W.

Basic phosphates. P. JOLIBOIS and L. CLOUTIER (Compt. rend., 1932, 195, 1027—1029; cf. this vol., 38).—Similar methods failed to yield any basic phosphate of Pb, Cu^{II}, Fe^{III}, Al, Zn, Ag, Mn, Cr, or U, the tribasic salt only being formed mixed with varying amounts of the hydroxide, or, if NaOH was in great excess, the hydroxide only. C. A. S.

Ammonolysis of antimony trichloride. R. SCHWARZ and A. JEANMAIRE (Ber., 1932, 65, [B], 1662—1664; cf. A., 1932, 1100).—SbCl₃ absorbs rather more than 3 mols. of NH₃ without appearing to yield a definite ammonate. The initial product appears to be Sb(NH)Cl which, when washed with liquid NH₃ (for removal of NH₄Cl), continuously loses Cl until finally orange SbN remains. It is unusually sensitive to moisture. Decomp. into Sb and N commences at 500° and is complete at 750°. H. W.

Desulphurisation of antimony trisulphide with carbon monoxide. E. V. BRITZKE and M. V. ZAETEV.—See B., 1932, 1077.

Sulphurous acid and its salts. XII. Action of hydrogen sulphide on potassium hydrogen sulphite solutions. F. FOERSTER and O. SCHMITT (Z. anorg. Chem., 1932, 209, 145—174).—The reaction products of H₂S and 0.5*M*-KHSO₃ under various conditions comprise S_2O_3'' , S_3O_6'' , S_4O_6'' , S_5O_6'' , SO_4'' , S (ppt.), and H', and evidence is adduced to show that their formation can be explained on the assumption of the existence of the intermediate compound SO. Curves showing the proportion of the above substances produced under different conditions and methods of analysing the solutions are given.

A. R. P.

Thionitrososulphonium chloride, (SN)₃SCl (thiotrithiazyl chloride). A. MEUWSEN (Ber., 1932, 65, [B], 1724-1733).-(SN)₃SCl is obtained in 90% yield by digestion of S_4N_4 (purified by sub-limation in high vac.) with S_2Cl_2 in CCl₄ or by the action of excess of SOCl₂ on S_4N_4 ; poor yields of impure product are obtained from S_4N_4 and AcCl. Since the presence of 4 SN groups in S_4N_4 and (HSN)₄ is regarded as established and these do not suffer disruption under the action of Cl, it is assumed that they are present in S_4N_3Cl formed by the much milder action of S_2Cl_2 . The product is therefore considered to be thionitroso- or isothiazyl-sulphonium chloride. This conclusion is strengthened by its stability to Cl, which demonstrates the absence of SS linkings, by the quant. evolution of N as NH3 when acted on by alkali and by absence of separation of I after addition of KI. Cautious warming of (NSCl)₃ with S_2Cl_2 gives the very unstable, rust-brown $N_2S_3Cl_2$, which regenerates (NSCl)₃ when treated with Cl_2 in CCl_4 and passes, when heated with S_2Cl_2 in CCl_4 , into (SN)₃SCl; the last-named sub-stance is also obtained directly by prolonged warming of $(NSCI)_3$ with S_2Cl_2 in CCl_4 . The reactions of $N_2S_3Cl_2$ are readily explained by the constitution (NS)₂SCl₂. H. W.

Chemically different and differently-coloured chromic hydroxides. A. HANTZSCH and E. TORKE (Z. anorg. Chem., 1932, 209, 60–94).—When aq. $[Cr(H_2O)_6]Cl_3$ is added to 2N aq. NH₃ containing 25% NH₄Cl at room temp. a bright bluish-green ppt. (A), readily sol. in dil. HCl, AcOH, or NaOH, is obtained. Similar treatment of aq. [Cr(H₂O)₄Cl₂]Cl,2H₂O yields a dark green ppt. (B) of the same empirical composition, Cr(OH)3,3H2O, but less readily sol. in the above reagents. The acid solutions of (A) are blue, of (B) green. On dehydration both (A) and (B) give the same green Cr(OH)3,H2O, but the isobaric dehydration curve is stepped with (A) and continuous with (B). (A) is completely converted into (B) when left for 8-10months at room temp. (A) does and (B) does not react with 100% AcOH or Ac₂O. From their chemical behaviour the constitution of (A) appears to be Cr(OH)₃,3H₂O, and of (B) [Cr(H₂O)(OH)₃],2H₂O. No hydrate with a larger proportion of H₂O could be F. L. U. isolated.

Bivalent chromium compounds. G. A. BAR-BIERI and A. TETTAMANZI (Atti Accad. Lincei, 1932, [vi], 15, 877–882).—The following compounds are described : $[Cr(C_{10}H_8N_2)_3]Br_2,6H_2O$, from 2:2'-dipy-ridyl, $Cr(OAc)_2$, and NaBr; $[Cr(C_{10}H_8N_2)_3](ClO_4)_3$; $Cr(SCN)_2,2(C_6H_{12}N_4,HSCN)$, from $(CH_2)_6N_4$.HSCN and $Cr(OAc)_2$, and the analogous *Fe* and *Mn* deriv-atives; $CrCl_2,2HCl,C_6H_{12}N_4,4H_2O$, and the corre-sponding *Mn*, *Ni*, *Fe*, and *Co* compounds.

H. F. G.

Permolybdates and pertungstates and the structure of perchromates. A. ROSENHEIM, M. HAKKI, and O. KRAUSE (Z. anorg. Chem., 1932, 209, 175-203).-Alkali and alkaline-earth molybdates and tungstates dissolved readily in 30% H₂O₂ at 0°, giving blood-red and pale yellow solutions, respectively, from which the following compounds have been isolated : K_2MoO_8 , $K_2WO_8, 0.5H_2O$, $Rb_2WO_8, 3H_2O$, Na_2WO_8, H_2O , $BaWO_8, 4H_2O$; all these compounds explode on rubbing or warming. The following stable compounds have been prepared in a similar way from polymolybdates and polytungstates :

5(NH₄)₂O,12MoO₃,12O,21H₂O,

- 5(NH₄)₂O,12MoO₃,3O,12H₂O,

 $\begin{array}{c} 5(\mathrm{NH}_4)_2\mathrm{O}, 12\mathrm{MoO}_3, 3\mathrm{O}, 12\mathrm{H}_2\mathrm{O}, \\ 5(\mathrm{CH}_8\mathrm{N}_3)_2\mathrm{O}, 12\mathrm{MoO}_3, 3\mathrm{O}, 11\mathrm{H}_4\mathrm{O}, \\ 5(\mathrm{CH}_8\mathrm{N}_3)_2\mathrm{O}, 2\mathrm{MoO}_3, 3\mathrm{O}, 11\mathrm{H}_4\mathrm{O}, \\ 5(\mathrm{CH}_8\mathrm{N}_3)_2\mathrm{O}, 2\mathrm{MoO}_3, 3\mathrm{O}, 3\mathrm{H}_2\mathrm{O}, \\ 5\mathrm{BaO}, 12\mathrm{MoO}_3, 3\mathrm{O}, 18\mathrm{H}_2\mathrm{O}, 5\mathrm{Ag}_2\mathrm{O}, 12\mathrm{MoO}_3, 3\mathrm{O}, 12\mathrm{H}_2\mathrm{O}, \\ \mathrm{BaO}, 2\mathrm{MoO}_3, 4\mathrm{O}, 4\mathrm{H}_2\mathrm{O}, \mathrm{K}_2\mathrm{O}, 2\mathrm{MoO}_3, 4\mathrm{O}, 4\mathrm{H}_2\mathrm{O}, \\ \mathrm{K}_2\mathrm{O}, 3\mathrm{MoO}_3, 4\mathrm{O}, 4\mathrm{H}_2\mathrm{O}, \mathrm{K}_2\mathrm{O}, 3\mathrm{MoO}_3, 0, 4\mathrm{H}_2\mathrm{O}, \\ \mathrm{K}_2\mathrm{O}, 2\mathrm{WO}_3, 4\mathrm{O}, 4\mathrm{H}_2\mathrm{O}, \mathrm{BaO}, 2\mathrm{WO}_3, 4\mathrm{O}, 8\mathrm{H}_2\mathrm{O}, \\ (\mathrm{CH}_6\mathrm{N}_3)_2\mathrm{O}, 2\mathrm{WO}_3, 4\mathrm{O}, 4\mathrm{H}_2\mathrm{O}. \mathrm{From RC}_2\mathrm{O}_4, \mathrm{H}_2\mathrm{MoO}_4, \mathrm{and} \\ \mathrm{H}_2\mathrm{O}_2 \mathrm{at} \ 0^\circ \ compounds \ of \ the \ type \ \mathrm{RC}_2\mathrm{O}_4, \mathrm{H}_2\mathrm{MoO}_4, 2\mathrm{O} \\ [\mathrm{R}=\mathrm{Ba}, \ \mathrm{K}_2, \ or \ (\mathrm{NH}_4)_2] \ \mathrm{and} \ \mathrm{K}_2\mathrm{C}_2\mathrm{O}_4, \mathrm{MoO}_5, \ \mathrm{have} \\ \mathrm{been \ prepared}. \ \mathrm{Corresponding} \ W \ derivatives \ of \ \mathrm{K}_2, \\ (\mathrm{NH}_4)_2, \ \mathrm{Rb}_2, \ \mathrm{Ba}, \ \mathrm{and} \ (\mathrm{CH}_6\mathrm{N}_3)_2 \ \mathrm{arc} \ \mathrm{also} \ \mathrm{described}. \\ \mathrm{The \ constitution \ of \ the \ above \ compounds \ \mathrm{and} \ \mathrm{of} \\ \mathrm{perchromates \ is \ discussed \ \mathrm{and} \ it \ is \ concluded \ that} \end{array}$ perchromates is discussed and it is concluded that in all cases the metal atom is sexavalent, the permolybdates and pertungstates having the formula $(O_2)_2$: M: $(O_2R)_2$, the perchromates the formula (O_2) : [Cr(:O): $(O_2K)_3$]₂, and the oxalato-complexes the formula $R_2[(O_2)_2M(C_2O_4)(H_2O_2)]$ (M=W or Mo).

A. R. P. Oxidations with fluorine. XIX. Action of fluorine on aqueous solutions of ammonia and of ammonium carbonate. F. FICHTER and A. GOLD-ACH (Helv. Chim. Acta, 1932, 15, 1511-1520; cf. A., 1931, 1022).-Passage of F₂ through aq. NH₃ at temp. between -8° and 35° gives rise to O_2 , N_2 , N_2O , NH_4NO_2 , and N_2H_4 . Aq. $(NH_4)_2CO_3$ yields NH_4NO_3 in addition to the above. No NH_2OH could be detected. Yields of all products were quantitatively determined. A mechanism is suggested whereby all the observed products can be accounted for by assuming the initial reaction NH3+ $F_2 = 2HF + NH$. F. L. U.

 $p_{\rm H}$ values of hypochlorite solutions. L. P. LYNCH and C. R. NODDER (J. Text. Inst., 1932, 23, 309-318T).-The excess of alkali present in stock solutions of NaOCI may be determined after decomp. of the OCl' with neutral H_2O_2 , but the p_{11} val. of dil. solutions cannot, in general, be determined after such decomp. A simple method of finding the approx. $p_{\rm H}$ vals. of dil. hypochlorite liquors is described. Equations are evolved from which the shift in $p_{\rm H}$ val. produced by adding the Na or K salt of a weak acid to a buffer solution may be determined. The shifts observed on addition of several of such salts to OAc' and $PO_4^{\prime\prime\prime}$ buffers, and the calc. vals. for the effect of the addition of NaOCl, are recorded. A method of determining the dissociation const. of a weak acid is indicated. B. P. R.

Anti-corrosive effect of addition of water-glass to bromine water, chlorine water, or bleachingpowder solutions. H. BOHNER (Hausz. V.A.W. Erftw. Aluminium, 1931, 3, 347-348; Chem. Zentr., 1932, i, 1823).-The corrosion of Al, silumin, or lautal by Cl₂-H₂O or Br-H₂O is markedly diminished by the presence of 0.5 or 5%, respectively, of Na silicate. Attack by bleaching-powder solution is

also considerably repressed by the presence of Na silicate. A. A. E.

Thioper-rhenates. H. V. A. BRISCOE, P. L. ROBINSON, and E. M. STODDART (J.C.S., 1932, 2811-2812).—A correction. F. J. W.

Fluorination of rhenium. O. RUFF and W. KWASNIK [with E. ASCHER] (Z. anorg. Chem., 1932, 209, 113-122).-In a current of F at 125° Re forms ReF₆ as a colourless gas, which solidifies to light yellow crystals, m.p. 26.4° . Moisture hydrolyses ReF₆ to HReO₄ and ReO₂, H₂O and in contact with quartz at 20° it is slowly converted into an oxyfluoridc. Most metals reduce ReF₆ to lower fluorides at 500° and eventually to metal at higher temp. No higher fluoride could be prepared. A. R. P.

Effect of silica on the dissociation of ferric oxide. J. KLEFFNER and E. J. KOHLMEYER (Metall u. Erz, 1932, 29, 189-194; Chem. Zentr., 1932, ii, 974).—The conversion $Fe_2O_3 \longrightarrow Fe_3O_4$ at 1600° is unaffected by SiO_2 , but Fe_3O_4 reacts with it under these conditions. Fe₃O₄ has m.p. 1580°. A. A. E.

Calcium salt of a complex ferriphosphoric acid. A. SANFOURCHE and B. FOCET (Compt. rend., 1932, 195, 873-875).-On adding 14 g. of FePO₄ to 145 g. of aq. solution of 35.4 g. of $CaH_4(PO_4)_2$ and 8.1 g. of H_3PO_4 the liquid rapidly gelatinises, but soon deposits white crystals of the complex $Ca[H_2Fe(PO_4)_2]_2$, containing 3-6% CaHPO₄. With less FePO₄ the above transformations occur less rapidly, but more so with rise in temp. The stability of the gel stage is much increased if AlPO₄ is substituted for part of the $FePO_4$ (cf. A., 1923, ii, 31). C. A. S.

Preparation of nickel-free cobalt salts through cobalt complexes. J. V. DUBSKY and V. DOSTAL

cobalt complexes. J. V. DUBSKY and V. DUSTAL (Chem. Listy, 1932, **26**, 593—595).—The salts $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5OH_2]_2(SO_4)_3$, $[Co(NH_3)_4(NO_2)_2]Cl$, $[Co(NH_3)_4CO_3]_9SO_4$, $[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_3(NO_2)_3]$, $[Co(NH_3)_2(NO_2)_4]K$, and $[Co(CN)_6]K_3$, prepared from Co salts containing Ni, were free from Ni, whilst $[Co(C_2O_4)_3]K_3$ and $[Co(CN)_S)$ IK were contaminated with Ni B. T $[Co(CNS)_4]K_2$ were contaminated with Ni. R. T.

cobalticyanides. I. Substituted complex dicobalti-µ-sulphito-decacyan-Hexapotassium ide. P. RAY (Z. anorg. Chem., 1932, 208, 392-396; cf. A., 1931, 1140) .--- An orange-red cryst. compound, to which the formula $K_6[(CN)_5 \cdot Co \cdot SO_3 \cdot Co \cdot (CN)_5]$ is assigned, is obtained by adding a solution of CoCl₂ saturated with SO₂ to aq. KCN cooled to -10° . The Pb, Hg^{II}, Cu^{II}, Cd, Zn, Fe^{III}, Mn^{II}, Co^{II}, and Ni^{II} salts are described. F. L. U.

Cobaltic pentammines. (MME.) R. DUVAL (Ann. Chim., 1932, [x], 18, 241-301).—In part a more detailed account of previous results (A., 1929, 1254; 1931, 53), including a reply to Klement (A., 1931, 1140), showing that persulphatopentamminecobaltic sulphate must possess the structure originally assigned. By application of the method previously described (loc. cit.) 30 types of pentamminecobaltic compounds have been prepared and are described, the following being new: formatopentamminecobaltic dithionate and chloride, $[CoCO_2H(NH_3)_5]Cl_2$; oxalatopentamminecobaltic oxalate, $[CoC_2O_4(NH_3)_5]C_2O_4$, $3H_2C_2O_4$; tartropentamminecobaltic nitrate, $[CoC_4H_4O_6(NH_3)_5]NO_3$, citratopentamminecobaltic citrate, probably and $\begin{array}{l} [\text{CoX}(\text{NH}_3)_5] + [\text{Co}(\text{XH}_2)_3(\text{NH}_3)_5] + [\text{Co}(\text{XH}_2)_3(\text{NH}_3)_5] \\ (\text{X} = \text{C}_6\text{H}_5\text{O}_7) \quad (\text{cf. Duff, J.C.S., 1923, 123, 568}); \end{array}$ chloratopentamminecobaltic chlorate,

[CoClO₃(NH₃)₅](ClO₃)₂,2H₂O, and cobaltinitrite; perchloratopentamminecobaltic perchlorate,

 $[CoClO_4(NH_3)_5](ClO_4)_2$, differing from the compound $[Co(H_2O)(NH_3)_5](ClO_4)_3$ obtained by Hassel (A., 1929, 18); bromatopentamminecobaltic bromate, $[CoBrO_3(NH_3)_5](BrO_3)_2$, obtained by loss of $2H_2O$ from $[Co(H_2O)(NH_3)_5](BrO_3)_3, H_2O$; iodatopentam-minecobaltic iodate, $[CoIO_3(NH_3)_5](IO_3)_2, HIO_3$; dithionatopentamminecobaltic dithionate,

[CoS₂O₆(NH₃)₅]S₂O₆,2H₂O, which reacts with [Co(NH₃)₅Cl]Cl₂ \longrightarrow 2[CoS₂O₆(NH₃)₅]Cl (+3H₂O) + [CoCl(NH₃)₅]S₂O₆. With Na₃PO₄ [Co(H₂O)(NH₃)₅](OH)₃ (I) gives [CoPO₄(NH₃)₅] (cf. Duff, *loc. cit.*, and Klement, A., 1926, 1219), but with

 H_3PO_4 followed by NH_4NO_3 is obtained the double salt $[CoH_2PO_4(NH_3)_5](H_2PO_4)_2, 3NH_4NO_3.$ (I) with K chromioxalate gives a compound, which may be $[Co(H_2O)(NH_3)_5][Cr(C_2O_4)_3], [Cr(C_2O_4)_3]K_3,6H_2O, or <math>[Co(NH_3)_5Cr(C_2O_4)_3][Cr(C_2O_4)_3]K_3,6H_2O, and with K cobaltioxalate are obtained$

 $[Co(C_2O_4)_3][Co(H_2O)(NH_3)_5],$ $[Co(H_2O)(NH_3)_5],$

 $\begin{bmatrix} \operatorname{Co}(C_2O_4)_3 \\ [\operatorname{Co}(C_2O_4)_3 \\ [\operatorname{Co}(H_2O)(\operatorname{NH}_3)_5], 10 \\ [\operatorname{Co}(H_2O)(\operatorname{NH}_3)_5], 10 \\ [\operatorname{Co}(H_2O)(\operatorname{NH}_3)_5], 0 \\ [\operatorname{Co}(\operatorname{NO}_2)_6], \\ \end{bmatrix}$ and hexamminecobaltic formate, [Co(NH3)6](CO2H)3, are J. W. B. also described.

Phosphides of nickel : reaction between phosphorus and nickel carbonyl. C. M. W. GRIEB and R. H. JONES (J.C.S., 1932, 2543-2546).-P does not react with liquid Ni(CO)₄, but with the vapour forms a black cryst. substance, NiP, m.p. $> 50^{\circ}$. It is sol. in HNO₃ and aqua regia, but insol. in HCl. Heating in air causes the loss of P and the formation of $Ni_3(PO_4)_2$. Bubbling $Ni(CO)_4$ vapour through liquid P or a solution of P in turpentine gives a black unstable substance containing NiP₄. F. J. W.

Nickelo-hexanitrites. M. MOUSSERON and R. CARITEAU (J. Pharm. Chim., 1932, [viii], 16, 382-387).—The following salts were prepared from Ni (freed from Co and AcOH) $[X = Ni(NO_2)_6]$: (a) hydrolysed by cold H_2O , K_4X , Na_4X , Li_4X , K_2Li_2X , and K₃NaX; (b) stable to cold, but hydrolysed by hot, H₂O, Ca₂X, Ba₂X, Sr₂X, SrCaX, BaSrX, CaBaX, K₂CaX (+3H₂O, lost at 180° in vac.), K₂BaX, K_2 SrX, and Ca(NH₄)₂X; (c) stability not defined, K₂MgX, K₂CdX, K₂PbX, K₂HgX, and Na₂HgX. All these salts form orange to red octahedra, and are best washed with COMe2. Cuttica's results (A., 1923, ii, 77) were vitiated by washing the ppts. with EtOH-Et₂O, in which KNO₂ is insol. R. S. C.

Iridium tetrahydroxide. N. K. PSCHENITSIN and C. E. KRASIKOV (Ann. Inst. Platine, 1932, No. 9, 135-136).-Ir(OH), is prepared from KOH and K₂IrCl₆. **R**. **T**.

Preparation of iridium tetrachloride. N. K. PSCHENITSIN and C. E. KRASIKOV (Ann. Inst. Platine, 1932, No. 9, 133–134).—IrCl₄ is prepared from Cl_2 and $(NH_4)_2IrCl_6$. R. T.

Thermal decomposition of bivalent platinammines. A. A. GRÜNBERG and B. V. PTITSIN (Ann. Inst. Platine, 1932, No. 9, 73–90).—The decomp. temp. of a no. of salts of the type $[Pt4NH_3]X_2$ diminish in the order $SO_4 < CrO_4 < Cl_2 < Br_2 <$ $(NO_2)_2 < I_2 < (CNS)_2$, and of the type $[Pt2NH_3X_2]$ in the order : *cis*-isomeride : $Cl_2 < Br_2 < (NO_2)_2 < I_2$; *trans*-isomeride : $Br_2 < Cl_2 < I_2$. The *trans*- are more stable than are the corresponding *cis*-isomerides. Traces of H_2O greatly reduce the thermostability of the above compounds. R. T.

Green salt of Magnus and some related compounds. E. G. COX, F. W. PINKARD, W. WARD-LAW, and G. H. PRESTON (J.C.S., 1932, 2527— 2535).—Magnus' green salt [Pt,4NH₃][PtCl₄] is pyramidal, space-group C_4^{\prime} (P4), a 6·29, c 6·42 \pm 0·02 Å., with 1 mol. per unit cell; the salt is therefore not polymerised. The ions [PtCl₄] and [Pt4NH₃] have the same form as in K₂PtCl₄ and [Pt,4NH₃]Cl₂, except that the NH₃ groups in the cation are not rotating. The Pd analogue has the same structure. The supposed pink isomeride of Magnus' green salt is actually Cleve's salt, [Pt,3NH₃,Cl]₂[PtCl₄]. Under experimental conditions not fully understood, the true pink isomeride is obtained; this is orthorhombic, a 7·9, b 8·2, c 7·9 Å., with 2 mols. of [Pt,4NH₃][PtCl₄] in the unit cell. Both pink forms are convertible into the green salt. F. J. W.

Systematic measuring out of samples as a practical help in volumetric and gravimetric analysis. P. FUCHS (Chem.-Ztg., 1932, 56, 941—943).—In order that burette readings may be numerically equal to the percentage of the substance under determination present in the sample, the mass of sample taken should be equal to the quantity of the pure substance which would react with 100 c.c. of the solution in the burette. A similar relationship applies in gravimetric analysis, in order that the mass of ppt.=% of substance in the sample.

D. R. D.

Equilibria in reduction, oxidation, and carbonisation processes in iron. XII. R. SCHENCK and T. DINGMANN (Z. anorg. Chem., 1932, 209, 1–10).— Technique of micro-analysis of gas mixtures is described. F. L. U.

Determination of hydrogen-ion concentration. B. ELEMA (Chem. Weekblad, 1932, 29, 638—643).— Largely a review of the characteristics of the MacInnes and Dole glass electrode. Details are given of the prep. of the electrode and of its use for small vols. of liquid. The use of the Ag|AgCl electrode is recommended; if the HCl is covered with paraffin to prevent evaporation, the potential of the glass electrode remains const. for at least 6 months.

H. F. G.

New indicators for the determination of halogens by Fajans' method. L. BELLADEN and G. PIAZZA (Annali Chim. Appl., 1932, 22, 631-637).--Using Orsella brillante C and Chromotrop F.4 C as indicators, halogen ions may be determined by Fajans' method (A., 1924, ii, 60, 776) with zero error at dilutions down to about 0.01N and with an error >0.2% at dilutions to 0.003N. I' in presence of Cl' may be determined with zero error when KCl:KI is >1 and with 0.3% error when KCl:KI=3. In presence of Orsellab rillante C, Ag is determinable exactly with standard KBr solution, either in neutral solution or in presence of HNO₃ up to N/3 conen. T. H. P.

Determination of very small quantities of bromide. Z. SZABÓ (Z. anal. Chem., 1932, 90, 189—193).—The Br' solution is treated with 1 g. of KHCO₃ and a measured vol. of Cl₂-H₂O (5 mg. Cl₂ per c.c.), the solution evaporated to dryness, and the residue dissolved in H₂O; 5 c.c. of 1% PhOH, 2—5 mg. of KI, and 5 c.c. of 20% H₂SO₄ are added, and the liberated I is titrated with 0.001N-Na₂S₂O₃. A correction is applied for the amount of Cl₂ used (table given). A. R. P.

Use of calcium carbonate in the determination of iodides. C. STAINIER and L. LECLERCQ (J. Pharm. Belg., 1932, 14, 265–270; Chem. Zentr., 1932, ii, 1049).—Na phosphate interferes with the titration of I with $Na_2S_2O_3$. The solution is conveniently neutralised with $CaCO_3$. A. A. E.

Colorimetric determination of fluorine in [natural] water with ferric thiocyanate. (MISS) M. D. FOSTER (J. Amer. Chem. Soc., 1932, 54, 4464— 4465).—The complex ion formed by interaction of a fluoride and FeCl₃ does not give the characteristic Fe colour with NH₄CNS. By careful control of acidity, temp., and conen., the bleaching produced in FeCl₃–NH₄CNS solution by 0.025 mg. of F' in 100 c.c. H₂O can be determined. J. G. A. G.

Thiosulphate solutions of permanent titre. R. A. KÖLLIKER (Z. anal. Chem., 1932, 90, 272– 277).—The storage bottle, burette, and $Na_2S_2O_3$ solution are sterilised by live steam and maintained under aseptic conditions. Apparatus and procedure are described. The change in normality of solutions so prepared was 0.1% after 500 days. F. L. U.

Analytical notes. L. ROSENTHALER (Pharm. Zentr., 1932, 73, 737–738).—CH₂O can be detected in presence of $(CH_2)_6N_4$ by phloroglucinol and NaOH. α -Naphthoflavone can be used as indicator for I-Na₂S₂O₃ titrations in acid, but not in NaHCO₃ solution. R. S. C.

Determination of arsenic, antimony, tin, and zinc in ores and alloys by titration with potassium iodate. Y. Y. LURE.—See B., 1932, 1083.

Determination of silicon, aluminium, fluorine, and orthophosphoric acid in the presence of one another. I. T. MILLNER and F. KUNOS (Z. anal. Chem., 1932, 90, 161—170).—For the determination of SiO₂ and Al₂O₃ in alkali fluorides, fluosilicates, or cryolite the substance is evaporated to dryness in a Pt crucible with HCl, H₃BO₃, and Na₂HPO₄ to expel F as BF₃, and the residue heated at 130° to dehydrate SiO₂. The filtrate from the SiO₂ is evaporated with HNO₃ and the P₂O₅ removed with (NH₄)₂MOO₄: Al₂O₃ is then determined in the usual way with or without a preliminary separation of Mo. A. R. P.

Volumetric determination of alkali sulphates. J. FIALKOV and M. STSCHIGOL (Pharm. Zentr., 1932, 73, 563—566).—The neutral solution is treated with an excess of 0.1N-BaCl₂, the excess of Ba^{**} is pptd. from the boiling solution by an excess of 0.1N-alkali $(1:2 \text{ mixture of Na}_2\text{CO}_3 \text{ and NaOH})$, and an aliquot part of the solution is filtered and titrated with 0.1N-HCl. A. R. P.

Determination of potassium, using lead-containing complexes. II. Na₂PbCo(NO₂)₆. P. S. SERGIENKO (Ukrain. Chem. J., 1932, 7, [Sci.], 36— 41).—The reagent (A) is prepared by adding a saturated solution of 11.5 g. of Pb(NO₂)₂ to 15 g. of NaNO₂ and 10 g. of Co(NO₃)₂,6H₂O, adding H₂O to 100 c.c., and filtering from the ppt. which forms after a time. The neutral solution under examination is freed from NH₃, and 15 c.c. of (A) are added per 20 mg. of K, when a dark green ppt. of K₂PbCo(NO₂)₆ separates. The washed ppt. is boiled with 50—100 c.c. of 0·1N-KMnO₄ and 15—20 c.c. of 30% H₂SO₄, and then with 0·1N-Na₂C₂O₄, excess of which is titrated with 0·1N-KMnO₄. The experimental error is ± 1 —2% for 0·1—0·3 g. of K. R. T.

Volumetric determination of small quantities of sodium. S. RUSZNYÁK and E. HATZ (Z. anal. Chem., 1932, 90, 186—189).—See A., 1932, 1152. A. R. P.

Rapid macro- and micro-determination of silver. G. SPACU and P. SPACU (Z. anal. Chem., 1932, 90, 182–185).—The hot neutral or slightly ammoniacal AgNO₃ solution is treated with KI sufficient to redissolve the AgI ppt., then with an excess of aq. [Cu pn₂]SO₄ (pn=propylenediamine), whereby on cooling the whole of the Ag separates as pale violet crystals of the *compound* [Cu pn₂](AgI₂)₂. The crystals are washed with 1% aq. KI containing 0.5% of the precipitant, then with 96% EtOH and Et₂O, and dried in vac. for weighing; they contain 23.07% Ag. The sensitivity of the test is 1 part of Ag in 200,000 parts. A. R. P.

Volumetric determination of calcium and magnesium in presence of each other. E. VON MIGRAY (Chem.-Ztg., 1932, 56, 924).—The boiling solution is treated with N-(NH₄)₂C₂O₄ and aq. NH₃, and acidified with 2N-AcOH; Na₂HPO₄ is added and the solution made alkaline with NH₃. The ppt. is suspended in H₂O, and the liquid titrated at 80—90° with 0·1N-HCl, using Me-red to determine Mg. 0·1N-KMnO₄ is then added to determine Ca. E. S. H.

Potentiometric determination of zinc. I. TANAEV.—See B., 1932, 1084.

Separation of group III metals. R. RIPAN (Bul. Soc. Stiinte Cluj, 1931, 6, 280–285; Chem. Zentr., 1932, i, 1806).—Zn, Al, Cr, Mn, and Fe are separated from Co and Ni by treating the sulphides pptd. by alkaline $(NH_4)_2S$ with 10% HCl, and Co is confirmed by the blue colour formed when a drop of KCNS and EtOH or COMe₂ is added to the Co and Ni solution. The HCl extract is neutralised with Na₂CO₃ and the Zn removed as $[Zn(NH_3)_4]Cl_2$ by boiling with a small amount of Cl_2 -H₂O and excess of NH₃. Boiling with conc. NaOH removes Al from the residue, whilst boiling with KOH and Cl_2 -H₂O removes Cr as chromate. The residual Fe and Mn are dissolved in HCl and the Fe is pptd. with NaOAc. Al is best identified by pptn. with $(NH_4)_2CO_3$. L. S. T. Separation of common elements into groups. II. Separation by means of sodium hydroxide and sodium peroxide. E. H. SWIFT and R. C. BARTON. III. Separation of zinc, cobalt, nickel, and iron from aluminium, chromium, and manganese. E. H. SWIFT, R. C. BARTON, and H. S. BACKURS (J. Amer. Chem. Soc., 1932, 54, 4155-4161, 4161-4172; cf. A., 1932, 827).-II. Details of two procedures for separating Mn, Fe, Co, and Ni from Al, Cr, and Zn by means of NaOH and Na₂O₂ are given. With solutions of pairs of metals the separation of Zn or of Cr, unless originally present as CrO_4'' , is very unsatisfactory, but that of Al from Fe or Mn is nearly complete.

III. By the following method, < 1 mg. of Al, Cr, or Mn is carried down with ppts. of Zn, Co, Ni, or Fe from solutions containing 250 mg. each of two metals, one from each "group," in 100 c.c. of 0.3M-HCl. The solution is almost neutralised with 6N-aq. NH₃ 10 g. of $(NH_4)_2C_2O_4$ are added, and the solution is exactly neutralised with NaHCO₃. H₂S is passed for 3-5 min. and the temp. is then raised to 60°. Acidity is neutralised by adding 1 g. of NaHCO₃ and H₂S is again passed, the process being repeated until the solution remains alkaline. 1 mg. of a metal of one "group" can be separated from 500 mg. of one from the other. J. G. A. G.

Simultaneous electrolytic determination of lead and copper. H. BILTZ (Z. anal. Chem., 1932, 90, 277—278).—A claim for priority over Bjørn-Andersen (A., 1932, 1011). F. L. U.

Registering potentiometric determination of small quantities of dissolved copper. L. TRON-STAD (K. Norske Vidensk. Selsk. Forhandl., 1931, 4, 20-23; Chem. Zentr., 1932, ii, 575).—Vals. from the empirical e.m.f.-Cu concn. curve are subject to a relative error of about 10%. Hence for 0.002-0.05 g. per litre they are at least as accurate as iodometric vals. Variations in the total concn. of the electrolytic bath and small temp. variations do not greatly affect the error. Other e.m.f. vals. are obtained, however, in 0.002N-Na₂SO₄, but they are reproducible, and Cu can be determined potentiometrically.

A. A. E.

Quantitative emission-spectral analysis. III. Determination of copper in high-grade aluminium. J. CLERMONT.—See B., 1932, 1083.

Micro-chemical reaction of copper salts. I. M. KORENMAN (Pharm. Zentr., 1932, 73, 738—741). —NH₂Ph in H₂O (A) or conc. aq. NH₂Ph,HCl (B), saturated with NH₄CNS, gives a characteristic cryst. ppt. with Cu salts. (A) is most suitable for conc. solutions or in presence of Cd, (B) for dil. solutions (min., 0.00000005 g. Cu). Cd salts give a ppt. with (B) only, readily distinguished from the Cu ppt., but much Cd obscures the crystal form of the latter. The ppt. is not formed in presence of Bi, Sb, or Sn, but (A) and (B) are the only reagents sp. for Cu. A solution of cinchonine and NH₄CNS in dil. HNO₃ gives a cryst. ppt. only with Cu salts, but certain other salts interfere. R. S. C.

Gasometric determination with a ureometer of calcimeter type. G. D ESTE (Boll. Chim. farm., 1932, 71, 717–728):—Full details are given of the application of the author's apparatus (A., 1932, 550) to the determination of CeO_2 , MnO_2 , and MnO_4' , with H_2O_2 ; H_2O_2 , BaO_2 , etc., and HBO_3 , with $KMnO_4$; Pb_3O_4 , with HNO_3 ; Fe, Zn, etc. and $CaCO_3$ etc. with HCl; and V_2O_5 and S_2O_8'' with N_2H_4 . H. F. G.

Determination of indium and gallium with 8-hydroxyquinoline. W. GEILMANN and F. W. WRIGGE (Z. anorg. Chem., 1932, 209, 129–138).—In is completely pptd. as $In(C_9H_6NO)_3$ at 70–80° from a solution containing 2% NaOAc and 2% AcOH, and Ga as $Ga(C_9H_6NO)_3$ from feebly ammoniacal tartrate solution. The ppts, are dried at 105–120° for weighing. Both compounds are volatile, so that the metals can be recovered only by destroying org. matter with H_2SO_4 and HNO_3 and treating the solution with aq. NH₃. A. R. P.

Colour reaction between rhenium heptoxide and hydrogen peroxide. Rhenium peroxide. H. HAGEN and A. SIEVERTS (Z. anorg. Chem., 1932, 208, 367—368).—Solid Re_2O_7 gives with conc. H_2O_2 a deep red solution. The coloured product is stable except towards H_2O , and is sol. in EtOH or Et₂O, but not in hydrocarbons, CHCl₃, CCl₄, or COMe₂. The white oxide formulated by I. Noddack and W. Noddack (A., 1929, 411) as Re_2O_8 did not yield the red compound except with H_2O . This and other experiments indicate that the white oxide is a modification of Re_2O_7 . F. L. U.

Colorimetric determination of iron with 2:2'dipyridyl. F. FEIGL, P. KRUMHOLZ, and H. HAM-BURG (Z. anal. Chem., 1932, 90, 199—202).—A 1% solution of 2:2'-dipyridyl in 0·1N-HCl gives an intense red colour with Fe^{*} salts. Fe^{**} salts must first be reduced with Na₂SO₃. In presence of Mn the solution must be at least 0·2N-HCl, and in presence of Zn, which gives a colourless complex with the reagent, a large excess of a 2·5% solution of reagent must be used. Hg^{**} forms an insol. complex with dipyridyl, but this is converted into a complex Hg sulphite if the acidity of the solution does not exceed 0·1N. A. R. P.

7-Iodo-8-hydroxyquinoline-5-sulphonic acid as a reagent for colorimetric determination of ferric iron. J. H. YOE (J. Amer. Chem. Soc., 1932, 54, 4139-4143).—The addition of 0.1 p.p.m. of Fe^{***} to aq. 7-iodo-8-hydroxyquinoline-5-sulphonic acid (2 g. per litre) changes the colour from yellow to blue or green. The sensitivity is greatest in solutions slightly acid to Me-orange and the colour is stable to light. A large no. of colourless ions give no colour reaction, and coloured ions at sufficiently low conen. do not interfere. Salts of Sn, Ti, and especially Cu interfere.

J. G. A. G.

Micro-electrolytic determination of iron. A. OKAC (Chem. Listy, 1932, 26, 595–597).—0.3—0.5 g. of $(NH_4)_2C_2O_4$ is added to a small vol. of H_2O , the solution (1—10 mg. Fe) is added, and the vessel is warmed to complete dissolution of oxalate. The electrodes are then placed in the vessel, and H_2O is added to allow complete immersion of the cathode (total vol. of electrolyte 6 c.c.). A current of 0.3— 0.6 amp. is passed during 10—20 min. to decolorise the electrolyte, and 5 min. later H_2O is gradually added to 150 c.c., when the current is cut off. The cathode is washed with H_2O and EtOH, dried during 15 min. at 80°, and weighed. The analytical error is 0.1-1%. R. T.

Determination of iron carbonyl in gases. E. POHLAND and W. HARLOS (Z. anal. Chem., 1932, 90, 193—199).—For small quantities of gas the $Fe(CO)_5$ is converted into Fc_2O_3 by exposing a mixture of the gas and O_2 to direct sunlight or to the light of the Hg vapour lamp. The Fc_2O_3 is dissolved in HCl and determined volumetrically or colorimetrically. The $Fe(CO)_5$ may also be converted into FeBr₃ by shaking the gas with Br-H₂O. To determine $Fe(CO)_5$ in a gas stream the gas is passed through MeOH or H₂SO₄. $Fe(CO)_5$ has been found in compressed H₂ and always in CO stored in Fe cylinders. A. R. P.

Electrographic determination of nickel in nickel steels. A. GLAZUNOV and J. KÄIVOIILAVY.— See B., 1932, 1121.

Rapid colorimetric determination of nickel in alloys. I. V. P. OCHOTIN and A. P. SYSTCHOV.— See B., 1932, 1121.

Colorimetry of titanium. II. General colorimetric procedure. H. GINSBERG (Z. anorg. Chem., 1932, 209, 105—112; cf. A., 1931, 814).—Systematic errors in the colorimetric determination of Ti in solutions containing < 3 mg. Ti per 100 c.c. have been traced to the optical behaviour of the solid glass dipping rods of the Duboscq colorimeter. Similar errors are to be expected when dealing with other solutions having very slight colour. F. L. U.

Precipitation method for determining vanadium [in steel]. S. M. GUTMAN.—See B., 1932, 1083.

Electrometric determination of vanadium in self-hardening steels. S. M. GUTMAN and N. V. MIKEEVA.—See B., 1932, 1083.

Determination of antimony in commercial copper. H. BLUMENTHAL.—See B., 1932, 1121.

Ceric sulphate in volumetric analysis. X. Determination of antimony and arsenic. N. H. FURMAN (J. Amer. Chem. Soc., 1932, 54, 4235–4238). —Contrary to Willard and Young (A., 1928, 725), but in agreement with Rathsburg (*ibid.*, 1207), Sb is oxidised rapidly by Ce(SO₄)₂ at room temp., in absence of a catalyst, if 30—50 vol.-% of HCl (d 1·19) is initially present. As in relatively high conen. interferes, but in lower conens. may be determined, after the end-point of oxidation of Sb has been found, by adding ICl as eatalyst and continuing the Ce(SO₄)₂ titration to the second end-point. J. G. A. G.

Electrolytic determination of bismuth in lead alloys. L. LUCCHI and A. BARTOCCI.—See B., 1932, 1121.

Drop method of approximate determination of gold. N. A. TANANAEV and E. V. VASILIEVA (Ukrain. Chem. J., 1932, 7, [Sci.], 50–54).—The coloration given by a drop of solution on benzidine paper is matched with those given by a series of standard Au solutions. The error rises from $\pm 2\%$ for 0.1 mg. to $\pm 20\%$ for 0.06 mg. of Au. R. T.

Heat loss from Dewar flasks. K. S. COLE and R. H. COLE (Rev. Sci. Instr., 1932, [ii], 3, 684-686).— Newton's law of cooling is obeyed if the contents are stirred. The heat loss coeff. is independent of the vol. of the contents between 50% and 90% capacity. C. W. G.

Reduction of platinum resistance thermometers to the international temperature scale. G. S. CALLENDAR (Phil. Mag., 1932, [vii], 14, 729— 742).—The reduction of measurements and their accuracy are discussed. H. J. E.

Constancy of the rotatory power of quartz plates. K. SANDERA (Z. Zuckerind. Czechoslov., 1932, 57, 41-44).—To investigate the cause of variations in the rotatory power of quartz control plates, a set of four plates first calibrated in 1914 were read in March, 1931, August, 1931, and March, 1932. Inappreciable differences were observed in the readings, the mean of all being about 0.005° V. Severe mechanical effects, as grinding and compression, caused some variation of the readings, but these reverted to the original val. J. P. O.

Optical-electric colorimeter. B. LANGE (Chem. Fabr., 1932, 457—459).—A lamp is placed between two test glasses, the light passing through suitable filters, then through the liquids to be compared, and on photo-electric cells. The instrument is particularly suitable for matching faint colorations, being much more sensitive than the eye. If a mirror galvanometer is used for current measurement the colour of $10^{-5}N$ -KMnO₄ can be detected. Turbidities may be readily compared even when rapidly settling ppts. are concerned. The apparatus may be used for the determination of one component in a coloured solution, *e.g.*, Fe in a dye, or of the $p_{\rm II}$ val. of coloured solutions. C. I.

Surface microscopy. H. WAGNER and M. ZIPFEL (Chem. Fabr., 1932, 421-423).—Various methods of illuminating opaque objects are described, and their application to the study of paint films etc. is discussed. H. F. G.

Christiansen filter for ultra-violet light. H. KOHN and K. VON FRAGSTEIN (Physikal. Z., 1932, 33, 929–931).—The filter is made by mixing a solution containing 56% C_6H_6 and 44% EtOH with amorphous SiO₂. The point of intersection of the dispersion curves of the liquid mixture and the SiO₂ is at 360 mµ at 20°, and this is the wave-length of the light transmitted. The filter is very sensitive to temp.

A. J. M.

Photochemical technique. III. Quartz capillary arc lamps of bismuth, cadmium, lead, mercury, thallium, and zinc. R. M. HOFFMAN and F. DANIELS (J. Amer. Chem. Soc., 1932, 54, 4226—4235; cf. A., 1932, 827).—Full details of the construction and operation of an inexpensive, easily repaired, quartz capillary lamp containing molten Bi, Cd, Pb, Tl, or Zn are given. Energy distribution curves were determined by a modified method for recording thermopile–galvanometer deflexions.

J. G. A. G.

Quantitative crystal analysis by X-rays. M. E. NAHMIAS (Z. Krist., 1932, 83, 329–339).—Sources of error in previous methods (cf. B., 1925, 546; 1931, 350) are discussed, and improvements suggested. The essential difference in the new method is that the intensities of the lines of the substance to be determined are not compared directly with those of that pure substance, but both are compared with the lines of a third substance, e.g., Al. The powdered materials are stuck on fine (0.03 cm. diam.) Al wire which is moved helicoidally, thus averaging the composition of the material examined and diminishing errors due to heterogeneity. With quartz and kaolin and quartz and mullite results accurate to 10%, or with practice to 5%, are readily obtained. C. A. S.

Simple photographic method of measuring the persistence of spectral lines. A. OCCHIALINI and G. M. RANGHIASCI (Atti Accad. Lincei, 1932, [vi], 15, 875—876).—A series of photographs is taken at short time intervals on one plate as the source of light is gradually moved away from the slit. The no. of spectra in which the line in question is visible gives a measure of the intensity. The method is applicable to the analysis of alloys. H. F. G.

Thermionic potentiometer for the measurement of $p_{\rm H}$. A. E. J. VICKERS, J. A. SUGDEN, and R. A. BELL (J.C.S., 1932, 2812).—A reply to Morton (A., 1932, 1105). F. J. W.

Fractional distillation. G. O. THACKER.—See B., 1932, 1107.

Extractors and condensers. O. HAGEN (Chem. Fabr., 1932, 424-427).—Several modified types of Soxhlet extraction apparatus are described, and an account is given of a condenser in which the vapour is caused to follow a helical path by means of a screwshaped central portion through which the cooling H₂O flows. The loss of solvent with this type is about 50% of that with the ordinary Allihn condenser.

H. F. G. Soxhlet with three-way tap. H. WASSERFUHR (Asphalt u. Teer, 1932, 32, 358—360; Chem. Zentr., 1932, ii, 1109).—The lower part of the siphon tube is fitted with a 3-way tap so that the apparatus can be used in the usual way, there is a continuous flow of solvent into the flask, or the solvent can be removed during extraction. A. A. E.

Check valve for water filter-pumps. G. BALZ (Z. Elektrochem, 1932, 38, 868—869).—A Hg trap is employed, the sucking-back of Hg being prevented by means of a sintered glass filter plate. D. R. D.

Experiments with capillary jets. E. TYLER and F. WATKIN (Phil. Mag., 1932, [vii], 14, 849-881). J. W. S.

Measurement of vapour pressure by transference and its application to the pneumatolytic transference of aluminium oxide by hydrogen chloride or chlorine. W. FISCHER and R. GEWEHR (Z. anorg. Chem., 1932, 209, 17—32; cf. A., 1929, 31).—Apparatus for the quant. collection of volatile solid products arising from the interaction of Al_2O_3 and HCl or Cl₂ is described. Results obtained at temp. between 1000° and 1200° indicate that with HCl the reaction is $Al_2O_3+6HCl = 2AlCl_3+3H_2O$, but that with Cl₂ at least one oxychloride is formed.

F. L. U.

Dissociation pressures of nitrates and sulphates. I. Apparatus. B. NEUMANN and A. SONNTAG (Z. Elektrochem., 1932, 38, 934–936).— The ordinary type of apparatus with a paraffin oil or H_3PO_4 trap and Hg manometer is described.

D. R. D.

Theory of drying. J. FRITH and F. BUCKING-HAM.—See B., 1932, 1107.

Measurement of viscosity. K. FISCHER (Chem. Fabr., 1932, 459—461, 471—473).—Capillary viscosimeters are best operated under pressure, in which case the effect of the changing liquid head becomes negligible. These instruments give only kinematic viscosities which often cannot be converted into abs. units. Falling-ball or -cylinder viscosimeters also require a knowledge of d; they are limited in that they cannot be used with corrosive liquids. Fifteen types of viscosimeter are tabulated, the accuracy, time required, and other particulars being given. C. I.

Use of Wilson cloud chamber for measuring the range of α -particles from weak sources. F. N. D. KURIE (Rev. Sci. Instr., 1932, [ii], **3**, 655—667).— Two photographs of the chamber are taken simultaneously at right angles by means of a single lens, and are examined after development by using the camera as a projector. C. W. G.

Physico-chemical and physiological researches relating to organic colouring matters. A. MEYER (Bull. Soc. chim., 1932, [iv], 51, 1202—1205). —The use of impure and inadequately defined dyes in physico-chemical and physiological work is deprecated. H. B.

Early chemistry of gold. A. KENT (Proc. Roy. Phil. Soc. Glasgow, 1932, 60, 101-112).

Geochemistry.

Determination of atmospheric ozone by visual photometry. J. GAUZIT (Compt rend., 1932, 195, 892-894).—A spectrophotometer enabling the optical density, and thence the O_2 content, of the atm. to be determined photometrically by means of visual rays ($\lambda = 6800-4900$) is described. The equiv. thickness of the O_3 layer at Montpellier on Jan. 30 and 31, and Sept. 14, 1932, thus determined was 0.31, 0.35, and 0.235 cm. $\pm 10\%$, respectively (cf. A., 1926, 1080; 1927, 808). C. A. S.

Inert gas content and radioactivity of natural Italian hydrocarbon gases. M. G. LEVI, A. G. NASINI, and P. DE CORI (Gazzetta, 1932, 62, 799– 821).—Analyses are given of 23 samples of natural gas from different districts. The total inert gas content (vol.-%) ranged from 0.004 to 1.4, the content of A from 0.003 to 1.28, and that of He from 0.0005 to 0.12. The radioactivity varied from 0.02 to 17.8 millimicrocuries per litre. H. F. G.

Helium content of beryllium. W. D. URRY (Nature, 1932, 130, 777-778).—The possible mechanisms discussed are all insufficient to account for the abnormally high He content of several palæozoic beryls (A., 1910, ii, 920; 1928, 1341). L. S. T.

Tian-Shan gaseous springs. P. I. TOLMATSCHEV (Bull. Acad. Sci. U.R.S.S., 1932, No. 1, 51–64).— The gases associated with 55 Tian-Shan (Turkestan) thermal springs contained H_2S 0–1.6, CO_2 0–7.3, CO 0–13.6, O_2 0–18.8, CH_4 0–35.4, C_2H_6 0–41.3, higher paraffins 0–11.7, and N_2 and inert gases 15–100%. Apart from the above springs, the Bezbeltschir spring gas had CO_2 93.5, O_2 0.4, and N_2 6.5%, a Shor-Su spring H_2S 47.7, CO_2 2.3, CO 2.5, O_2 1.1, CH_4 20.6, and higher hydrocarbons 11.7%, and a Tschadai spring CO_2 1.0, CO 0.4, O_2 1.2, CH_4 69.1, and N_2 28.3%. R. T.

Analysis of the acid water of Slatina Radenci. S. S. MIHOLIC (Jub. Fest. 50 Slatina Radenci, 1932, 16 pp.).—Analyses of various waters, made during the last 60 years, are summarised. Little change in composition appears to have occurred during the period. The dissolved substances in the waters are of mixed origins. H. F. G.

Cruz del Aire meteorites. R. E. S. HEINEMAN (Amer. J. Sci., 1932, [v], 24, 465–470).—A description and analysis are given. C. W. G.

Occurrence of potassium in Tarapacá province [Chile]. K. V. AREND (Bol. min. Soc. Nac. Min., 1931, 43, 784—790; Chem. Zentr., 1932, ii, 853).

Crystal morphology of faujasite and linnæite. W. WITTEBORG and W. BARMEN (Z. Krist., 1932, 83, 374–381).—Examination of recently-found crystals of faujasite (a variety of analcite) and of linnæite, CoS, Co_2S_3 , and in particular of their vicinal faces, confirm them as holohedral cubic, O^h . C. A. S.

Crystal structure of dickite. J. W. GRUNER (Z. Krist., 1932, 83, 394–404; cf. B., 1930, 832; A., 1932, 987).—Dickite is monoclinic with a 5·14, b 8·94, c 15·42 Å., β 96° 50′, and 4 mols. of Al₂Si₂O₅(OH)₄ in the unit cell, d_{theor}. 2·589, space-group C⁴.

C. A. S.

Structural relations between phosphates (triphylite) and silicates (olivine): composition of ardennite. B. GOSSNER and H. STRUNZ (Z. Krist., 1932, 83, 415–421).—Triphylite has $a \cdot 4.67$, $b \cdot 10.34$, $c \cdot 6.00$ Å., $d \cdot 3.56$; 4 mols. of Li(FeMn)PO₄ in the unit cell; space-group v_1^{k} (cf. olivine; A., 1926, 995); The mean of two closely agreeing analyses of ardennite gives SiO₂ 28.76, As₂O₅ 4.30, V₂O₅ 4.90, Al₂O₃ 24.65, Fe₂O₃ 0.08, FeO 0.96, MnO 26.41, MgO 2.08, CaO 2.56, H₂O 5.08%, corresponding with (SiO₄)₅(AsO₄)Al₃Mn(AlOH)₂Mn₄,2H₄O, with which is compared zoisite, (SiO₄)₆Al₄(AlOH)₂Ca₄, indicating equivalence between Si^{1V} + Al^{1II} and As^V + Mn^{1I}. Ardennite has a 18.56, b 5.83, c 8.72, d 3.610–3.645, with 2 mols. in the unit cell, space-group v_1^{ls} , showing some similarity to zoisite. C. A. S.

Twin structure of amethyst quartz with reference to the temperature of origin. O. MÜGGE (Z. Krist., 1932, 83, 460–484).—From the character and interrelations of the different forms of twinning exhibited by such quartz it can be determined whether it has been formed below or above 573° . C. A. S.

Mixed crystals in the ternary system An-Ab-Cg. E. DITTLER and A. KÖHLER (Tsch. Min. Petr. Mitt., 1932, 43, 352—361).—Fusions of various composition ranging from $An_{80}Ab_{10}Cg_{10}$ to $An_{50}Ab_{10}Cg_{40}$ yielded crystals of basic plagioclase in which no appreciable amount of the carnegieite mol. (NaAlSiO₄) could be detected. This separated out in the groundmass as nepheline. When this mol. is present in larger amount the nepheline takes up some anorthite and becomes isotropic or optically positive, and the crystals show signs of unmixing. L. J. S.

Peridotite of Kaersut (Greenland) and associated dyke rocks. F. K. DRESCHER (Tsch. Min. Petr. Mitt., 1932, 43, 207—270).—The residual liquid from the crystallisation of the peridotite has penetrated along veins, giving kaersutite- and augitepegmatites which are relatively richer in alkalis than the parent rock. Analyses are given of the rocks and their constituent minerals. L. J. S.

Scapolite, zoisite, and secondary albite from the Lampi-Varaka (N. Karelia) pegmatite vein. S. M. KURBATOV (Bull. Acad. Sci. U.R.S.S., 1932, No. 2, 241-257).—The vein originally consisted of plagioclase, which as a result of autopneumolysis underwent conversion into scapolite, and this, in turn, under the influence of hydrothermal factors, yielded zoisite, calcite, and albite. R. T.

Stanniferous region of Nam Pha Thène (Laos). J. FROMAGET (Compt. rend., 1932, 195, 967—969).— The chief feature is an intrusive mass of monzonitic granite containing SiO₂ 67·14, Al₂O₃ 15·71, Fe₂O₃ 0·96, FeO 2·83, MgO 1·20, CaO 4·18, Na₂O 3·21, K₂O 3·60, TiO₂ 0·46, P₂O₅ 0·16, H₂O+ 0·61, H₂O- 0·22, MnO 0·12%. This is in close relationship with quartzitic microdiorite. Both are traversed by veins of microgranite containing up to 2% cassiterite which has resulted from metallic emanations which have also converted the felspar of the microgranite into damourite. C. A. S.

Sierra Nevada as a co-magmatic region. A. A. FITCH (Amer. J. Sci., 1932, [v], 24, 481—495).—The Sierra Nevada province has been characterised since the early Mcsozoic by a suite of rocks for which Al, Fe+Mg, and Ca+Na+K are sensibly invariant, Ca showing a progressive decrease with time and Na+K an increase. C. W. G. Calcareous rock of the apex of the black stones in the Gargano region. M. COPPOLA (Annali Chim. Appl., 1932, 22, 638—641).—This contains about 20% of clay, 65.5% CaCO₃, 7.9% MgCO₃, etc., together with $2\cdot2\%$ C, which may have been produced either from CO or CO₂ or by profound igneous distillation. T. H. P.

Sp. gr. of Japanese acid clay. K. YAMAMOTO and H. ISHIKAWA (Bull. Waseda Appl. Chem. Soc., 1932, 17, 1-8).—The clay has d^{25} 2.4-2.5; after acid treatment it has d^{25} 2.2-2.4. d increases above 120°, is max. at 200°, and decreases slowly to 400° and rapidly from 600° to 800°. The change at 120-200° is attributed to the effect of adsorbed H₂O, and that at 600-800° to structural change. CH. Aps.

Physico-chemical properties of Japanese acid clay. VI. X-Ray studies. II. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 482–486B; cf. A., 1931, 1266).—The clay contains cryst. $Al_2O_3, 4SiO_2, H_2O$. The lattice consts. of the hexagonal crystals have been determined. The clay has $d \ 2 \cdot 4 - 2 \cdot 6$; after treatment with alkali it is higher, but lower after treatment with acids. These effects are due to the content of colloidal SiO₂. d increases by heating the clay up to 200°, through loss of H_2O ; above 400° d decreases through a change in structure. After heating at 1200° for 4-5 hr. the diffraction pattern is changed completely and then is identical with that of opal. E. S. H.

Microbiological characteristics of certain Crimean and Caucasian hill and steppe soils. T. L. SIMAKOVA (Bull. Acad. Sci. U.R.S.S., 1932, No. 1, 71-83).—Nitrifying bacteria and Azotobacter are present in the surface layers of Crimean soils (A) but not in Caucasian mountain soils (B); this is ascribed to the low CaCO₃ content and high acidity of (B). Denitrifying bacteria are present only in the upper 25 cm. of (B), and at all depths examined of (A). Clostridium pasteurianum and anaërobic but not aërobic cellulose-destroying bacteria were present in both (A) and (B). R. T.

Chemical and morphological examination of the origin of forest humus. W. GROSSKOPF (Proc. 2nd Internat. Cong. Soil Sci., 1932, 3, 176—178).— Forest humus consists largely of lignin or its transition products. A. G. P.

Swedish soils. O. TAMM (Ernähr. Pflanze, 1932, 28, 297–308).—Geological formations are described and profiles of typical soils recorded. A. G. P.

Geochemistry of oil formation. S. ZUBER (Petroleum, 1932, 28, 1-5).—A discussion of theories. E. S. H.

Organic Chemistry.

Graphical study of the composition of organic compounds. IV. T. HIGASI (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 1254—1265).—The compositions of C-H-O compounds are indicated on a trilinear diagram and certain deductions made. D. R. D. Two "methyl" groups of normal saturated hydrocarbons. R. REINECKE (Chem.-Ztg., 1932, 56, 932—933).—The van 't Hoff conception of the C tetrahedron can be brought into harmony with recent discoveries if the two tetrahedra in, e.g., C_2H_6 are conceived of as united, not corner to corner, but one corner to the centre of a face. For many purposes it is more convenient to represent mols. by cubes of which the diagonals of the faces form the tetrahedra. The theory is developed and illustrated by the properties of substituted derivatives of C_2H_6 , and its possibility of extension to ring mols. such as graphite, C_6Me_6 , and to such compounds as stearic acid is pointed out. C. I.

Absorption in the ultra-violet of methane, ethane, and butane. W. KEMULA and S. MRAZEK. --See this vol., 6.

Action of sulphur on hydrocarbons. F. J. NELLENSTEYN and D. THOENES (Chem. Weekblad, 1932, 29, 582—587).—The reaction between S and paraffins, paraffin oils, and lubricating oils at 260— 300° yields C and almost all the S as H_2S , only traces of org. compounds of S being formed; it involves the complete breaking down of \cdot CH₃, \cdot CH₂, and \cdot CH groups. The mechanism of the reaction is discussed. H. F. G.

Synthesis of highly-chlorinated hydrocarbons and the catalytic action of aluminium chloride. H. J. PRINS (Rec. trav. chim., 1932, 51, 1065-1080). -Certain chloro-methanes, -ethanes (less readily), -ethylenes, and -propylenes, and C₃H₃Cl₅ in presence of AlCl₃ condense with polychlorohydrocarbons containing a double linking and a neighbouring CCl, or CCl₃ group. $C_3H_2Cl_6$ reacts only at higher temp. with previous loss of HCl. The action is ascribed to the formation, e.g., from $CHCl_3$, of $[AlCl_4]^-$ and $[CHCl_3]^+$, the latter being the active agent. The formation of higher condensation products in certain cases is due to loss of HCl from the saturated chlorohydrocarbons first produced. The action may be reversed. Octachloropentadiene is converted by AlCl₃ into octachlorocyclopentene. Reagents which remove halogens give with polychlorohydrocarbons, besides the normal coupled products, coloured unsaturated substances containing only C and Cl. The colour intensity of AlCl₃ complexes with chlorohydrocarbons passes through a max. with increasing Cl content.

A. A. L.

Action of chlorine on acetylene and the preparation of tetrachloroethane and trichloroethylene. N. A. VALIASCHKO and K. G. KOSENKO (Ukrain. Chem. J., 1932, 7, [Sci.], 12-35).—The yield of $C_2H_2Cl_4$ from C_2H_2 and Cl_2 is 71-81%, and 88% when the catalysts are respectively Fe or Fe oxides and SbCl₅. 87% yields of C_2HCl_3 are obtained by treating $C_2H_2Cl_4$ with Ca(OH)₂. R. T.

Derivatives of tribromoethanol (avertin). II. S. CHECHIK (J. Amer. Pharm. Assoc., 1932, 21, 1007— 1009; cf. A., 1932, 367).—Benzyl βββ-tribromoethyl ether, b.p. 172—174°, and β-bromo-ββ-dibenzyloxyethyl alcohol, b.p. 194—196° (Ac derivative), are described. E. H. S.

Dehydration of $\beta\gamma\delta$ -trimethylpentan- γ -ol. F. C. WHITMORE and K. C. LAUGHLIN (J. Amer. Chem. Soc., 1932, 54, 4392-4393).—Dehydration of $\beta\gamma\delta$ -trimethylpentan- γ -ol with a little I at the b.p. gives the normal products, β -isopropyl- Δ^{α} -isopentene and $\beta\gamma\delta$ -trimethyl- Δ^{β} -pentene, in the ratio 1:2; the structures are determined by ozonolysis. H. B. Rearrangement of unsaturated $\alpha\delta$ -glycols. β -Methyl- $\Delta\beta$ -butene- $\alpha\delta$ -diol. A. F. SHEPARD and J. R. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 4385— 4391).— $\alpha\delta$ -Dibromo- β -methyl- $\Delta\beta$ -butene (isoprene dibromide) and KOAc in AcOH at 100° give the diacetate (I), b.p. 120·5—122·5°/10 mm., of β -methyl- $\Delta\beta$ -butene- $\alpha\delta$ -diol (II), b.p. 127·5—128°/7 mm. (II) is reduced catalytically (PtO₂) to β -methylbutanediol, the diacetate of which is obtained by similar reduction of (I). (II) is readily converted by halogen acids or ZnCl₂ into tiglic aldehyde (α -methyl- Δ^{α} -butenal) [mixture of dibromides, b.p. 71—73° (corr.)/3·5 mm.], also formed from (I) and MeOH-HCl; the suggested mechanism is: OH·CH₂·CH:CMe·CH₂·OH — CH₂:CH·CMe:CH·OH —> CHMe:CMe·CHO.

H. B.

Octadecane- $\alpha\kappa$ -diol. W. SECK and F. DITTMAR (Chem. Umschau, 1932, 39, 226—229).—Octadecane- $\alpha\kappa$ -diol, m.p. 65° (corr.) (diacetate, b.p. 201°/0·2 mm.), has been prepared by hydrolysing $\alpha\kappa$ -dibromo-octadecane (cf. A., 1932, 1109) with KOAc and AcOH, or with AgOAc (yield 90%). Smaller yields of the glycol (16—20%) are obtainable by the reduction of Et ι -hydroxystearate, or its acetate with NaOBu.

E. L.

Synthesis of allodulcitol. LESPIEAU and WIE-MANN (Compt. rend., 1932, 195, 886—888).—Griner's mixture (I) of divinyl glycols and Br give two solid dibromides and a liquid. The higher-melting dibromide (m.p. 174°) with Zn dust and EtOH gives a pure divinyl glycol (II), m.p. 18°, b.p. 100°/14 mm., hydrogenated (Pd) to γ 8-dihydroxy-*n*-hexane, m.p. 88.5° H H

(A., 1928, 151). The formula CH_:CH·C—C·CH:CH_ OH OH

for (II) is proved by the higher m.p. of the dibromide and the oxidation of (II) by $AgClO_3$ and osmic acid to allodulcitol (III), m.p. 144—146° [dibenzylidene derivative, m.p. 246° (block)]. Oxidation of an erythritol (A., 1930, 450) probably gives the corresponding dicarboxylic acid. Oxidation of (I) gives a mixture of (III), mannitol, and a third isomeride. R. S. C.

Identity of volemitol (α -sedoheptitol) and β -*d*-mannoheptitol. V. ETTEL (Coll. Čzech. Chem. Comm., 1932, 4, 504—512).—Epimerisation of α -*d*mannoheptonic acid affords the β -acid, m.p. 155°, $[\alpha]_D^{\infty} - 2 \cdot 9^{\circ}$ in H₂O (*Ca* and *Ba* salts), reduced by Na-Hg to β -mannoheptose, m.p. 140°, $[\alpha]_D^{\infty} - 7 \cdot 61^{\circ}$ in H₂O [p-bromophenylhydrazone, m.p. 191—193° (decomp.)], and to β -*d*-mannoheptitol (I), m.p. 150°,

 $\begin{array}{c} (H_2 \cdot OH & [\alpha]_D^m + 1 \cdot 9^\circ \text{ in } H_2O, \text{ which with PhCHO} \\ (HO \cdot C \cdot H)_3 & \text{and } 50\% & H_2SO_4 \text{ gives a } tribenzylidene \\ (H \cdot C \cdot OH)_2 & ether, \text{ m.p. } 210^\circ, [\alpha]_D^m - 42 \cdot 8^\circ \text{ in } C_5H_5N, \\ (H \cdot C \cdot OH)_2 & \text{and an } ether \text{ (not pure), m.p. } 190-195^\circ, \\ CH_2 \cdot OH & [\alpha]_D^m - 72 \cdot 60^\circ \text{ in } C_5H_5N. \end{array}$

of these derivatives with those similarly obtained from volemitol (A., 1929, 798) proves the identity of this alcohol with (I). Interaction of volemitol with MeCHO under conditions used by La Forge for α -sedoheptitol (A., 1917, i, 118) gives, in addition to the triethylidene ether, m.p. 161—162°, $[\alpha]_{3}^{\infty}$ —74·3° in CHCl₃, previously obtained (*loc. cit.*), an isomeric *ether*, m.p. 210°, $[\alpha]_{3}^{\infty}$ —51·9° in CHCl₃, identical with that obtained by Bougault and Allard (A., 1903, i, 62), thus removing the discrepancy previously observed, and confirming the identity of volemitol with α -sedoheptitol (A., 1928, 1213).

J. W. B.

Aromatic esters of monoalkyl ethers of ethylene and diethylene glycols. R. C. CONN, A. R. COLLETT, and C. L. LAZZELL (J. Amer. Chem. Soc., 1932, 54, 4370—4372).—The following esters are prepared from OH·CH₂·CH₂·OAlk and

repared from OH·CH₂·CH₂·OAlk and OH·CH₂·CH₂·O·CH₂·CH₂·OAlk by the C₅H₅N method: β-methoxyethyl benzoate, b.p. 251·6—252·6°/738·5 mm., and p-nitrobenzoate, b.p. 158·3—160·3°/4 mm., m.p. 50·5°; β-ethoxyethyl benzoate, b.p. 260—261°/ 738·5 mm., and p-nitrobenzoate, b.p. 163·5—164·5°/4 mm.; β-butoxyethyl benzoate, b.p. 156·5—157°/14·5 mm., 131·6—132·6°/3 mm., and p-nitrobenzoate, b.p. 179—180°/3·5 mm.; β-β·ethoxyethoxyethyl benzoate, b.p. 160—161°/14·5 mm., 141—143°/2 mm., and p-nitrobenzoate, b.p. 179·3—181·3°/4 mm., and p-nitrobenzoate, b.p. 230—232°/4 mm. Various physical data are given. H. B.

Interaction of etherates of magnesium halides and ethylene oxides. II. Interaction of magnesium bromide etherate and some monosubstituted aliphatic ethylene oxides. I. RIBAS and E. TAPIA (Anal. Fis. Quim., 1932, 30, 778-791; cf. A., 1930, 1403).-Ethylene oxide, epichlorohydrin, and $\alpha\beta$ -oxido- γ -methoxypropane react in Et₂O with MgBr₂ to give products CH₂Br·CHR·O·MgBr,Et₂O (R=H, CH₂Cl, or CH₂·OMe), white cryst. substances decomposed by moisture with formation of the compounds CH2Br·CHR·OH and MgBr2+Mg(OH)2. Apparently identical products are formed by interaction of MgEtBr and the compounds CH_Br CHR OH. Half the Br in these products appears as Br' ion when dissolved in dil. HNO₃ under conditions in which the interaction of MgBr₂ with the ethylene oxide to give the bromohydrin is negligible. Confirmatory determinations are made of the Mg(OH), formed.

MgBr₂ reacts with excess of the above ethylene oxide derivatives to give *products* $(CH_2Br\cdot CHR\cdot O)_2Mg$. No evidence was obtained of the formation of additive compounds of the type MgBr₂+ethylene oxide+ Et₂O even at -21° . R. K. C.

Mechanism of hydrolysis of dialkylaminomethyl ethers. T. D. STEWART and W. E. BRADLEY (J. Amer. Chem. Soc., 1932, 54, 4172—4183).—The preps. of the following are described : diethylaminomethyl Me, Et, Bu^a, and n-heptyl ethers, b.p 115— 115·8°/755 mm., 132—134°/756 mm., 172—173°/758 mm., and 112·5°/15 mm., respectively, and di-npropyl-, b.p. 87°/42 mm., diisopropyl-, di-n-butyl-, b.p. 116°/11 mm., diisobutyl-, b.p. 92°/5 mm., di-namyl-, b.p. 28°/5 mm., phenylmethyl-, diallyl-, b.p. 89°/11 mm., and dimethyl-, b.p. 128°/756 mm., -aminomethyl Bu^a ethers. n-Butoxymethylpiperidine, b.p. 82°/5 mm., and 3-β-hydroxyethyloxazolidine, b.p. 78°/2 mm., were prepared. That the hydrolysis of these ethers to CH₂O,

That the hydrolysis of these ethers to CH_2O , alcohol, and sec.-amine probably involves the primary formation of the N-dialkylmethyleneiminium ion, which subsequently adds OH' to form the amine and CH_2O , is supported by the isolation of

Chlorides of arylsulphurous acids and the mixed aryl alkyl sulphites. P. CARRÉ and D. LIBERMANN (Compt. rend., 1932, 195, 799-801).— SOCl₂ and diaryl sulphites afford the chlorides of arylsulphurous acids which are not purified, but afford with alcohols, in presence of C_5H_5N , arylalkyl sulphites. The following are described: Ph Me, b.p. 128-130°/20 mm., Ph Et, b.p. 142-144°/25 mm., Ph Bu^a, b.p. 170-173°/20 mm., o-tolyl Me, Et, b.p. 145-147°/20 mm., and Bu^a, b.p. 170-173°/13 mm., m-tolyl Me, b.p. 137-140°/25 mm., Et, b.p. 147-150°/25 mm., and Bu^a, b.p. 178-180°/20 mm., p-tolyl Me, b.p. 134-136°/20 mm., Et, b.p. 146-149°/20 mm., and Bu^a, b.p. 175-177°/25 mm., sulphite. J. L. D.

Action of acid chlorides on orthoformic ester. Preparation of symmetrical esters of sulphuric acid. R. LEVAILLANT (Compt. rend., 1932, 195, 882—884).—CH(OEt)₃ (I) (1 mol.) and CCl₃·COCl (1 mol.) at 95—100°, and later at 160°, give EtCl, HCO₂Et, and CCl₃·CO₂Et (yield > 90%). CH₂Cl·COCl at 100—110° gives similarly CH₂Cl·CO₂Et, and BzCl at 125—130° in presence of a little ZnCl₂ gives BzOEt (92% yield). p·Ce₆H₄Me·SO₂Cl at 110°, and PhSO₂Cl at 150—155° (ZnCl₂) give good yields of the Et esters. Addition of SOCl₂ (1 mol.) to (I) (2 mols.) at 0° and gradual heating to 100° yields SO₂Et₂ (80% yield). SO₂Cl₂ (1 mol.) and (I) (1 mol.) give CISO₃Et and a little Et₂SO₄. Esters of ClSO₃H give good yields of symmetrical esters of H₂SO₄, *e.g.*, CISO₃Et (1 mol.) and (I) (1 mol.) give a 90% yield of Et₂SO₄. R. S. C.

Reaction between neutral lead mercaptides and sulphur. W. E. DUNCAN and E. OTT (J. Amer. Chem. Soc., 1932, 54, 4463).—The basic Pb derivative of sec.-BuSH and S in C_6H_6 give (cf. A., 1930, 1405) a mixture of basic Pb polysulphides; individual compounds could not be isolated. H. B.

Thioethers of pentaerythritol. II. H. J. BAOKER, P. TERPSTRA, and N. D. DIJKSTRA (Rec. trav. chim., 1932, 51, 1166—1172).—The following tetrathioethers of pentaerythritol are prepared as previously described (A., 1932, 363), % yields being given in parentheses: Bu^{β} , b.p. 221—223°/2 mm. (80), n-amyl, b.p. 241—243°/2 mm. (80), n-hexyl, b.p. 206—208°/0.0001 mm. (80), n-heyyl, b.p. 222— 224°/0.0001 mm. (93), n-octyl, b.p. 238—240°/0.0001 mm. (77), n-nonyl, b.p. 251—253°/0.0001 mm. (79), n-decyl, m.p. 19°, b.p. 259—261°/0.0001 mm. (87), n-undecyl, m.p. 28° (74), and n-dodecyl, m.p. 35— 36° (92). The tert.-Bu ether exists in two forms, m.p. 116.4° and 123.6°. X-Ray data are given for this substance and the Ph, and tetrabenzyl ethers. A. A. L.

Tetrasulphones derived from carbontetramethanethiol. H. J. BACKER and N. D. DIJKSTRA (Rec. trav. chim., 1932, 51, 1173—1177).—Tetrathioethers of pentaerythritol (cf. preceding abstract) with H_2O_2 in AcOH give the following tetrasulphones : Me, decomp. > 300°, Et, m.p. 185.5°, Pr^a , m.p. 126.5°, Pr^{β} , m.p. 220.5°, Bu° , m.p. 111.5°, Bu^{β} , m.p. 134°, sec.-Bu, m.p. 115°, tert.-Bu, decomp. > 300°, n-amyl, m.p. 83.5°, n-hexyl, m.p. 85.5°, n-heptyl, m.p. 72°, n-octyl, m.p. 80°, n-nonyl, m.p. 76°, n-decyl, m.p. 78.8°, n-undecyl, m.p. 72.5°, n-dodecyl, m.p. 78.3°, Ph, m.p. 244°, benzyl, m.p. 179.5°, β -phenylethyl, m.p. 183°. A. A. L.

Resolution of chloroiodomethanesulphonic acid. J. READ and (MISS) A. M. MCMATH (J.C.S., 1932, 2723-2727).—Optically impure NH₄ d- and *l*-chloroiodomethanesulphonate (J.C.S., 1914, 105, 811) in H₂O when repeatedly pptd. with brucine sulphate affords, after treatment with dil. NH₃, NH₄ d-chloroiodomethanesulphonate, m.p. 229-230° (decomp.), $[\alpha]_0$ +13·2° in H₂O {Ba salt, $[\alpha]_0$ +11·0°; strychnine salt, m.p. about 227° (decomp.), $[\alpha]_0$ -14·6°; 1-hydroxyhydrindamine salt, m.p. 204° (decomp.), $[\alpha]_0$ -6·0°; d-hydroxyhydrindamine salt, m.p. 194° (decomp.), $[\alpha]_0$ +23·6°}, and NH₄ 1-chloroiodomethanesulphonate, $[\alpha]_0$ -13·0° in H₂O [strychnine salt, m.p. about 227° (decomp.), $[\alpha]_0$ -26·5°; 1hydroxyhydrindamine salt, m.p. 194° (decomp.), $[\alpha]_0$ -46·9° in COMe₂]. The NH₄ salts described are less easily racemised than the chloroiodoacetates (A., 1927, 445). J. L. D.

Conductometric determination of small amounts of fatty acids by the visual method. G. JANDER and K. F. WEITENDORF (Angew. Chem., 1932, 45, 705-707).—Small amounts (10-25 mg.) of fatty acids are determined by extraction from H_2O with light petroleum, evaporation to dryness, dissolution in EtOH purified over CaO and H_2O , and conductometric titration with 0·1*N*-NaOH in MeOH after addition of a little HCl. CO₂ must be excluded. A. G.

Reaction of carboxylic acids with phosphorus pentoxide. K. C. LAUGHLIN and F. C. WHITMORE (J. Amer. Chem. Soc., 1932, 54, 4462).—CMe₃·CO₂H and P₂O₅ give CO and polymerides of *iso*butene; PrCO₂H gives CO and CO₂ in the ratio 1:5 and tar, whilst Pr^βCO₂H gives CO and CO₂ in the ratio 5:1 and tar (in presence of xylene the ratios of CO and CO₂ remain the same, but the yield is diminished to 0·07 and 0·14%, respectively). Gas is not evolved when BzOH is heated with an excess of P₂O₅ in xylene. H. B.

n-Decyl series. G. KOMPPA and Y. TALVITIE (J. pr. Chem., 1932, [ii], 135, 193-203).—The following are described : n-decyl chloride, b.p. 223-223.5°/760 mm., 105-105.5°/15.5 mm., from the alcohol and PCl₅ in CCl₄; n-decyl bromide (I), b.p. 117.6—118°/15.5 mm., 104-104.4°/8 mm., from the alcohol, Br, and red P; Et n-decylacetoacetate, b.p. 171-171.5°/9 mm., from CHNaAc·CO₂Et, (I), and NaI in EtOH, hydrolysed (very dil. H₂SO₄ at 200°) to Me n-undecyl ketone; Me n-decyl ether, b.p. 213.3—213.5°/760 mm., 100.5°/15.5 mm., from Na decyloxide (II) and Me₂SO₄ in C₆H₆; Et n-decyl ether, b.p. 223:5—224°, 99:6—99:8°/8 mm., from NaOEt and n-decyl iodido (III); Pr^a n-decyl ether, b.p. 242.5°/760 mm., 122.5°/15.5 mm., from NaOPr and (III); di-n-decyl ether, b.p. 196°/15.5 mm., in poor yield from (II) and (III) in xylene; Ph n-decyl

ether, b.p. 178°/15 mm., m.p. 8-10°, from NaOPh and (III); n-decyl formate, b.p. 105·1-105·3°/9 mm., acetate, b.p. 244°/760 mm., 125·6-125·8°/15·5 mm. (lit. 125-126°/15 mm. and 187-190°/720 mm.), propionate, b.p. 138.2-138.6°/15.5 mm., 123.9-124.3°/8 mm., n-butyrate, b.p. 149.8°/15.5 mm., 134.8-135°/8 mm., palmitate, m.p. 30°, pyruvate, decomp. on attempted distillation (semicarbazone, m.p. 143°), benzoate, b.p. 195.8°/8 mm., p-nitrobenzoate, m.p. 30.2°, p-aminobenzoate hydrochloride, m.p. 161° (not sharp), cinnamate, b.p. 224°/11 mm., m.p. 7°, phenylcarbamate, m.p. 59.6°, and naphthyl-carbamate, m.p. 71.4°; N-n-decylphthalimide, m.p. 56°, from o-C₆H₄(CO)₂NK and (III) at 200°, hydrolysed (conc. HCl at 200°) to n-decylamine (phenylcarbamyl, m.p. 84.2°, and a-naphthylcarbamyl, m.p. 129.5°, derivatives). Numerous spectrochemical data are H. B. recorded.

a-Bromo-n-butyric acid. I. Preparation, purity, and velocity of hydrolysis. R. AHLBERG (J. pr. Chem., 1932, [ii], 135, 282-304).-Partly a more detailed account of work previously reviewed (A., 1931, 574). The reaction, which proceeds 500 times as rapidly as the other (cf. loc. cit.) during the hydrolysis of an aq. solution of Ba α-bromobutyrate, is due to the presence of an unstable impurity in the α -bromobutyric acid (I) used. Such impurity is found when the PrCO, H used is prepared by fermentation (not with the synthetic acid); it is removable by neutralisation of the Br-acid with aq. Na₂CO₃, keeping the solution for 3-4 days, and then acidifying. The rate of hydrolysis of pure (I) (details of prep. by the Hell-Volhard method given) (as neutral salt) is practically independent of the concn. and is $k \times 10^6 =$ 16.8—17.2 at 25° and 511—527 at 45°; the temp. coeff. in the range $25-45^{\circ}$ is 5.53. **H**. **B**.

Esters of α -hexabromostearic acid. K. E. STANFIELD and E. R. SCHIERZ (J. Amer. Chem. Soc., 1932, 54, 4356—4359).—The following esters are new : n-, m.p. 143—143·1°, and tert.-, m.p. 162—162·5°, -Bu; α -ethylpropyl, m.p. 135·8—135·9°; isoamyl, m.p. 135—135·1°; α -methylbutyl, m.p. 135·7—135·9°; dimethylethylcarbinyl, m.p. 159—159·5°; β -methylbutyl (?), m.p. 133·4—133·8°; hexyl, m.p. 132·6— 132·8°; heptyl, m.p. 130·6—130·8°; α -propylbutyl, m.p. 135·1—135·2°; octyl, m.p. 128—129°; α -methylheptyl, m.p. 129·1—129·2°; benzyl, m.p. 140·4— 140·5°. The m.p. of the esters decreases with increase in the no. of C atoms of the alkyl group; the esters from tert.-alcohols have abnormally high m.p. and are less sol. in org. solvents than those from primary and sec.alcohols. H. B.

Autoxidation of unsaturated fatty acids. II. Action of carotenoids. W. FRANKE (Z. physiol. Chem., 1932, 212, 234—255; cf. A., 1932, 1112).— Carotenoids, including vitamin-A and carotene, accelerate the oxidation of fatty acids but not of the glycerides. In presence of hamin the lipochromes produce considerable autoxidation not in the free fatty acids, but in the neutral oils, which may be due to the formation of an additive compound between hamin and carotenoid. In C_5H_5N but not in other solvents the lipochromes restrict autoxidation of unsaturated fats and fatty acids. In NPhMe₂ in presence of hæmin autoxidation of the lipochromes and of the unsaturated fatty acids is extremely rapid. The autoxidation was also studied in xylene with and without hæmin. J. H. B.

Composition of illipé butter. Study of $\alpha\alpha$ dilauro- β -azelain and $\alpha\alpha$ -dilaurin. G. SHUSTER (J. Pharm. Chim., 1932, [viii], 16, 421–431; cf. A., 1931, 712, 1199).—The Hilditch process for the examination of fats has been modified by pre-oxidation of the fat in COMe₂ solution by KMnO₄. Illipé butter contains tristearin 1.4%, palmitodistearin 5.2%, dilauro- β -olein 21.3%, distearo- β -olein 40.2%, β -monostearo- $\alpha\alpha$ -diolein 5.4%, β -palmito- $\alpha\alpha$ -diolein 3.5%, and triolein 12.22%. The following have been synthesised : $\alpha\alpha$ -distearo- β -azelain, m.p. 67°; β -stearo- $\alpha\alpha$ -diazelain, m.p. 61°; β -palmito- $\alpha\alpha$ -diazelain, m.p. 57°. $\alpha\alpha$ -Dilauro- β -azelain, m.p. 44°, can be partly hydrolysed to $\alpha\alpha$ -dilaurin, m.p. 22–23°. T. McL.

Elæostearic acids. I. Isomerism of the elæostearic acids. E. ROSSMANN (Chem. Umschau, 1932, 39, 220—224).—The properties of the isomeric acids and their esters, and the irreversible isomerism of the α - to the β -form, support a conception of the β -acid as an extended *trans*-form chain mol., whilst the α -acid is regarded as a *cis*-form coiled chain. It is improbable that couepic acid is a geometrical isomeride of elæostearic acid. E. L.

Acylacetic esters. J. DÉCOMBE (Ann. Chim., 1932, [x], 18, 81-187).-Distillation of acylacetic esters in specially washed Pyrex flasks at a rate of 6-8 drops a min., termed "slow distillation," gives distillates containing much enolic form, without changing the proportions of the isomerides in the residues, whence it is concluded that enolisation takes place in the vapour state. The following figures give the percentages of enolic form (determined by Br titration) present in the equilibrium mixture and obtainable by "slow distillation," respectively, the temp. given in parentheses being the apparent b.p. at 11 mm. during "slow distillation ": Et acetoacetate (I), 7.4, 98—99.5 (42—46°); Et propioacetate [from MgEtI and $CN \cdot CH_2 \cdot CO_2 Et$ (II) in 70% yield], b.p. 84°/15 mm., 6.9, 94-95 (60-62°); Et butyroacetate [from MgPrI and (II) in 55% yield], 8.48, 60-64 (80-82°); Et valeroacetate [from MgBuI and (II) in 25% yield], b.p. 107—108°/15 mm., 11.5, 30—34 (100°/14 mm.); Et hexoylacetate (by hydration and esterification of Δ^{a} -heptinenoic acid in 50% yield), b.p. 115-116°/14 mm., 16.3, —. The preps. of the esters [except (I)] are modified; those prepared from (II) are best purified by way of the Mg derivatives, which are pptd. by aq. $NH_3-NH_4Cl-MgCl_2$, which diminishes the yields by 10-15%. The preps. of the following Et esters are modified : sodioformylacetate (III), α-methylformylacetate (b.p. 154-162°), α-phenylformylacetate (forms, b.p. 144-145°/6 mm. and m.p. 69-71°), benzoylacetate (from BzOEt and EtOAc) (b.p. 140-144°/6 mm., 70% yield). Equilibration of the enolic form of (I) is irregular and catalysed by forces beyond control, although the results of K. Meyer are in the main confirmed. The enolic form of (I) does not react immediately with NH_3 , whilst the equilibrium mixture in ordinary Et_2O at 0° gives with NH3 a cryst. intermediate compound, rapidly decomposed above 0°. It is concluded that reaction takes place by Michael addition to the ketonic form and that the product is Et β -aminocrotonate and not β -iminobutyrate. A trustworthy method of obtaining the form of m.p. 32° is given. (III) and NH₃ under various conditions give only Et₃ trimesate, but the following *Et* esters were prepared from the appropriate acylacetate and base : β -dimethylaminoacrylate, b.p. 97—98°/0.5 mm., cryst. in a freezing mixture (giving with boiling H₂O NHMe₂ and Et₃ trimesate); β-anilinoacrylate, colourless needles, m.p. 114-115°, and yellow plates, m.p. 116°; β-butylaminoacrylate (impure), cryst. (reduced by Na and EtOH to y-benzylaminopropyl alcohol); β-dimethylamino-, b.p. 121°/15 mm., and β -benzylamino- α -methylacrylate, b.p. 146—148°/1 mm.; β-amino-, b.p. 142-149°/0.5 mm. [from Et a-phenylformylacetate and liquid and cryst. forms of (IV), β -methylamino-, b.p. 140—142°/3 mm. [from (IV)], β -dimethylamino-, b.p. 184—185°/16 mm. [from (IV)], and β-benzylamino-α-phenylacrylate, m.p. 64-65° [from (IV)]; β-dimethylamino-, b.p. $135^{\circ}/21$ mm., β-diethylamino-, b.p. $153^{\circ}/20$ mm., β-anilino-, b.p. 142—145°/5 mm., β -benzylamino-, and β -dibenzyl-amino-crotonate, m.p. 110—111°; β -amino-, b.p. 105— 108°/10 mm. (prepared in presence of NH₄NO₃), and β -dimethylamino- Δ^{α} -pentenoate, b.p. 134–135°/21 mm.; β -amino- Δ^{α} -hexenoate, b.p. 105–107°/10 mm. (I) does not condense with NHPhMe or NHPh2. Et a-methylformylacetate with NH₃, Et propioacetate with NH_2 ·CH₂Ph, and Et butyroacetate with $NHMe_2$ give mixtures. Et benzoylacetate and NH_2Me in Et₂O give a cryst. compound, which loses NH₂ when heated, and when kept gives an oil, decomposed by distillation. Attempts to reduce Et β -aminocrotonate, m.p. 32° or 18°, or its Ac derivative, catalytically and with Al amalgam failed. The azine of (I) cannot be reduced, but the phenylhydrazone is reducible by Al amalgam. The best results for (I) and other esters are obtained by reduction of the acetyl- or benzoylhydrazones (not necessarily pure) with Al amalgam, the product being purified by way of the oxalate. The following Et esters were thus prepared : β -amino- α methylpropionate, an oil (chloroplatinate; hydro-chloride, m.p. 130°); β -aminobutyrate, b.p. 68---69°/17 mm. (chloroplatinate; oxalate, m.p. 88-90°; phenylcarbamide, m.p. 110°); β-amino-n-valerate, b.p. 83-84°/17 mm. (chloroplatinate); β-amino-n-hexoate, b.p. 102-104°/25 mm. (chloroplatinate; oxalate, m.p. about 155° after sintering from 130°) (other conditions give 3-n-propyl-5-pyrazolone, m.p. 125°); β-aminon-octoate, b.p. 132-133°/25 mm. (chloroplatinate; phenylcarbamide, m.p. 114°; oxalate). The method failed with Et benzoylacetate, which gives only the pyrazolone. The acetylphenylhydrazones of (I) and Et propioacetate have m.p. 90° and 93°, respectively. The following Et esters were prepared by hydrogenation (PtO₂), best in EtOH, of the unsaturated compounds, although the method failed in many other cases : β -dimethylamino- α -phenylpropionate (impure), b.p. 142-147°/15 mm. (hydrochloride, m.p. 150-151°); β-dimethylamino-, b.p. 81.5°/21 mm. [chloroplatinate ; hydrochloride, m.p. 136-137° (block), 125° (tube)], β -diethylamino-, b.p. 98°/vac. (chloroplatinate, decomp. about 170°; hydrochloride, hygroscopic), β-benzylamino-, b.p. 172-174°/24 mm. (formed

equally easily from the α - and β -forms of β -benzylaminocrotonate) [hydrochloride, m.p. 112-114°; chloroplatinate; slowly hydrolysed by hot H₂O to the corresponding acid, m.p. about 191° (block)], and β-dibenzylamino-butyrate, b.p. 195-200°/5 mm. (chloroplatinate); β-dimethylaminovalerate, b.p. 100°/30 mm. [chloroplatinate; hydrochloride, m.p. 160° (block), 150° after sintering (tube)], hydrolysed by hot H₂O to the corresponding acid, m.p. 90-91°. Alkylation of the saturated primary NH2-esters by alkyl iodides under various conditions led to mixtures; e.g., Et β -aminobutyrate gives, amongst other products, the β-NHMecompound, b.p. 77-81°/20 mm., and then Et crotonate and probably the NMe2-compound (methiodide, cryst.). The following Et esters were prepared in about 60%yield by hydrogenation (PtO₂) of mixtures of the primary base and McCHO in EtOH (Skita's method) : β -ethylaminobutyrate, b.p. 74—75°/12 mm. (hydro-chloride; readily hydrolysed by hot H₂O to the corresponding acid, m.p. $169-170^{\circ}$); β -ethylamino-hexoate, b.p. $110-111^{\circ}/20$ mm. (hydrochloride); β -ethylamino-octoate, b.p. $134-135^{\circ}/20$ mm. (hydrochloride). Attempts to alkylate the sec.-bases by alkyl iodide led to much deamination, whilst Skita's method gives mixtures; the latter method gives slowly a little Et β -ethylbutylaminobutyrate, b.p. 118— 119°/15 mm. (hydrochloride, an oil; chloroplatinate). Reduction of the NH₂-esters by Na and EtOH often leads to unsaturated compounds, depending on the substituents attached to the N and α -C atoms; the following were prepared by this method : y-benzylaminopropyl alcohol (from the acrylate), b.p. 132°/2 mm. (hydrochloride, m.p. 84-85°; hydrochloride of the Bz derivative; phenylcarbamide-phenylurethane, m.p. 107°); y-benzylamino-, b.p. 126°/1 mm. [hydrochloride, m.p. 101°; hydrochloride of the Bz derivative, m.p. 129-130°; phenylcarbamide-phenylurethane, m.p. 126° (block), 119-120° (tube)], and y-dimethylaminoisobutyl alcohol (from the crotonates), b.p. 163-164° (hydrochloride of the Bz derivative); γ-methylamino-, b.p. 125-129°/3 mm. [hydrochloride, m.p. about 80°; hydrochloride of the Bz derivative, m.p. 131-132° (decomp.) (block), softening from 120° to 125° (tube); phenylcarbamide-phenylurethane, m.p. about 150° (block), softening from 138° (tube)], γ -dimethylamino-, b.p. 134°/8 mm., m.p. 35—36° [hydrochloride, an oil; hydrochloride of the Bz derivative, m.p. 172-173° (block)], and γ-benzylamino-β-phenylpropyl alcohol (from the acrylates), m.p. 64° (hydrochloride, m.p. 135—136°; phenylcarbamide, m.p. 135—136°; O-derivatives could not be obtained); the last-named ester was accompanied by some β -benzylamino- α -phenyl-propionic acid, m.p. 225-226° (block), 190-195° (tube); γ -dimethylamino-, b.p. 82-85°/25 mm. (hydrochloride of Bz derivative, hygroscopic), and y-benzylamino-n-butyl alcohol (from the butyrates), b. p. 173-174°/23 mm. (phenylcarbamide, m.p. 110°; no O-derivatives could be obtained); γ -dimethylaminon-amyl alcohol (from the pentenoate), b.p. 79°/20 mm. [hydrochloride, m.p. about 102-103°; hydrochloride of the Bz derivative, m.p. about 117-118° (block), hygroscopic]; γ -methylamino- γ -phenylpropyl alcohol, b.p. 125-130°/2 mm., m.p. 57-58°, hygroscopic (from the cinnamate in poor yield). Et propio- and butyro-acetates with MeCHO and a little NHMe2 at

-10° give Et₂ ethylidenebispropio- and ethylidenebisbutyro-acetate, m.p. 121° and 131°, respectively. In the latter case the yield is better in aq. solution, whence it is concluded that MeCHO reacts in the hydrated form. The yield in this condensation decreases as the length of the C chain increases, and is 0 with Et valeroacetate. Esters containing high proportions of the enolic form give better yields than the equilibrium mixtures. The ethylidene esters do not decolorise Br in EtOH and are, therefore, considered to be diketonic forms, in agreement with previous views. From these results, which are confirmed by experiments with (I), it is concluded that the enolic form of the acylacetic ester condenses with hydrated MeCHO by Michael addition. R. S. C.

Mode of formation of disubstituted malonic ester derivatives. M. S. DUNN, C. E. REDEMANN, and S. LAURITSEN (J. Amer. Chem. Soc., 1932, 54, 4335-4337).—The mol. ratios of Et benzyl- (I) and dibenzyl-malonate formed from equimol. amounts of Na, $CH_2(CO_2Et)_2$, and CH_2PhCl when the reaction is carried out in MeOH (or EtOH) and PhMe are 2:1 and $2\cdot 1$ — $12\cdot 5:1$, respectively; with no solvent the ratio is $1\cdot 2:1$. The results support Leuchs' view that disubstituted malonic esters may be formed directly from the reactants. CH_2PhCl does not react with $CH_2(CO_2Et)_2$ or (I) in boiling PhMe.

H. B.

Cleavage of disubstituted malonic esters by sodium ethoxide. A. C. COPE and S. M. MCELVAIN (J. Amer. Chem. Soc., 1932, 54, 4319-4325).—The following reactions occur when disubstituted malonic esters are heated with dry NaOEt : (i) CR₂(CO₂Et)₂ \rightarrow CHR₂:CO₂Et+CO+CO₂+C₂H₄ etc.; (ii) CR₂(CO₂Et)₂ + NaOEt \rightarrow CO₂Et·CR₂·C(ONa)(OEt)₂ \rightarrow Et₂CO₃ + CR₂:C(ONa)·OEt; the extent of reaction (i) is determined by the yield of CHR₂·CO₂Et and that of (ii) by the wt. of Et₂CO₃. Thus CEt₂(CO₂Et)₂ at 220-230° gives CHEt₂·CO₂Et (67%) and Et₂CO₃ (16%); Et ethylisoamylmalonate similarly affords Et α-ethylisoheptoate (66%) and Et₂CO₃ (12%), whilst Et ethyl-α-methylbutylmalonate yields Et β-methyl-α-ethylhexoate (64%) and Et₂CO₃ (4%); CPhEt(CO₂Et)₂ at 120°/24 mm. furnishes Et αphenylbutyrate (38%) and Et₂CO₃ (58%); Et ethylvinylmalonate gives Et₂CO₃ (38%) and 35% of recovered ester at 100°/14 mm.; CPh₂(CO₂Et)₂ at 100°/20 mm. affords Et₂CO₃ (90%). The following cleavages by EtOH-NaOEt are reported: CPh₆(CO₂Et)₂ to CHPh₂·CO₂Et; CEt₂(CO₂Et)₂ (at 250°) to CHEt₂·CO₂Et; CHEt(CO₂Et)₂ at 250° to PrCO₂Et. 5: 5-Diethylbarbituric acid (65%) is obtained from CEt₂(CO₂Et)₂, CO(NH₂)₂, and dry NaOEt at 170°; CPh₂(CO₂Et)₂ similarly gives (mainly) CHPh₂·CO·NH₂ and some CHPh₂·CO₂H. H. B.

Synthesis of ethylvinylmalonic ester and incidental compounds. A. C. COPE and S. M. MC-ELVAIN (J. Amer. Chem. Soc., 1932, 54, 4311— 4319).—CNaEt(CO₂Et)₂ and CHBr:CHBr in Et₂O give about 25% of *Et ethyl*- β -bromovinylmalonate, b.p. 117—120°/1 mm., reduced catalytically (Adams) to CEt₂(CO₂Et)₂ and by Zn dust and 95% EtOH at 170° to *Et ethylvinylmalonate* (I), b.p. 122—124°/30 mm., also reduced catalytically to $\operatorname{CEt}_2(\operatorname{CO}_2\operatorname{Et})_2$. Other products formed in the above condensation are $\operatorname{Et}_2\operatorname{CO}_3$ (7%) and $\operatorname{Et} \Delta^{\gamma}$ -octene- $\gamma\zeta\zeta$ -tricarboxylate (II) (30.7%), b.p. 150—152°/2 mm., 304—306°/740 mm.; (II) is reduced catalytically (Cu–Cr oxide) to Et octane- $\gamma\zeta\zeta$ -tricarboxylate, b.p. 154—156°/2 mm., which when hydrolysed and then decarboxylated gives $\alpha\alpha'$ -diethyladipic acid. The formation of (II) involves the changes: CHBr:CH·CEt(CO_2Et)_2+ EtOH \longrightarrow Et₂CO₃+CHBr:CH·CHEt·CO_2Et (III); (III) \longrightarrow CH₂Br·CH:CEt·CO_2Et (IV); CNaEt(CO_2Et)_2+ (IV) \longrightarrow

CO, Et CEt. CH CH2 CEt(CO2Et)2; the EtOH is produced by reduction of the original CHEt(CO₂Et)₂ with 23% of the Na used. (I) and EtOH-NaOEt give the unstable Et γ -ethoxy- α -ethylcrotonate, b.p. 96—99°/14 mm., reduced (Cu-Cr oxide catalyst) to CHEt₂·CO₂Et and Et γ -ethoxy- α -ethylbutyrate, b.p. 90—92°/14 mm., which is also prepared by way of Et ethyl-3-ethoxyethylmalonate, b.p. 142-143°/17 mm. [from CHEt(CO₂Et)₂ and OEt·CH₂·CH₂Br], and y-ethoxy-a-ethylbutyric acid, b.p. 138-139°/18 mm. (I) could not be converted into a barbituric acid by $CO(NH_2)_2$ in EtOH-NaOEt; α -ethoxy-crotonamide results by alcoholysis of (I) and subsequent rearrangement of the intermediate ester to CHMe:CEt·CO₂Et, which then reacts with $CO(NH_2)_2$ (or NH₃). Et ethyl- β -bromoethylmalonate (V), b.p. 128—130°/3 mm., when heated, passes into α -carbethoxy- α -ethylbutyrolactone, b.p. 265—267°/740 mm., 135-138°/9 mm. [the Et ethyl-β-hydroxyethylmalonate of Shonle et al. (A., 1930, 1047) is probably this lactonc]. (V) and NMe3 in EtOH at 130° give NMe₄Br and Et ethyl-β-dimethylaminoethylmalonate [hydrochloride, m.p. 147-148° (lit. 154°)]. H. B.

Phenacyl and p-bromophenacyl esters of dibasic organic acids. T. L. KELLY and P. A. KLEFF (J. Amer. Chem. Soc., 1932, 54, 4444—4445).—The following are prepared essentially by Reid's method (A., 1919, i, 157; 1920, i, 480): phenacyl adipate, m.p. 87.6° , pimelate, m.p. 72.4° , subcrate, m.p. 102.4° , azelate, m.p. 69.7° , sebacate, m.p. 80.4° , phthalate, m.p. 154.4° , isophthalate, m.p. 191°, terephthalate, m.p. 192.2° ; p-bromophenacyl glutarate, m.p. 136.8° , adipate, m.p. 154.5° , pimelate, m.p. 130.6° , itaconate, m.p. 117.4° , *l*-malate, m.p. 179°, phthalate, m.p. 152.8° , isophthalate, m.p. 179.1°, terephthalate, m.p. 225° . H. B.

Colour reactions and autoxidation of hydropolyenecarboxylic esters. R. KUHN, P. J. DRUMM, M. HOFFER, and E. F. MÖLLER (Ber., 1932, 65, [B], 1785—1788).—Dihydrocrocetin Me₂ ester in C₅H₆N gives a dark blue colour on addition of 2N-NaOH; the solution becomes orange-red when shaken and gives the crocetin spectrum. In high vac. the blue solution is stable, but addition of O causes immediate production of crocetin Me₂ ester. Methyldihydrobixin similarly affords an emerald-green solution from which β -methylbixin, m.p. 202°, separates on access of air. C₅H₅N can be replaced by quinoline, COMe₂, or COPhMe, but not by EtOH or EtOAc; alkali metal can be used in place of the hydroxide. Et dihydromuconate (I) with cold NaOEt-EtOH or C_5H_5N-2N -NaOH gives a dark red sodio-compound from which (I) can be readily recovered; the colour changes after a time to brownish-yellow. The intensely-coloured compounds are regarded as double enolates. Autoxidation of methyldihydrobixin in presence of amines proceeds to the absorption of 10 O without coming to a definite end; with NaOH rapid absorption of 2 O takes place, followed by a much slower O consumption. The process is accompanied by production of H_2O_2 . H. W.

Plant dyes. XLVI. Constitution of crocetin and bixin. Synthesis of perhydronorbixin. P. KARRER, F. BENZ, R. MORF, H. RAUDNITZ, M. STOLL, and T. TAKAHASHI (Helv. Chim. Acta, 1932, 15, 1399-1419; cf. A., 1932, 1234).-The results of Kuhn et al. (A., 1931, 1067) on the analysis of crocetin (I) and perhydrocrocetin (II) and the quant. CrO₃ oxidation of (I) are confirmed. Formulation of (I) as aexE-tetramethyltetradecaheptaene-aE-dicarboxylic acid and of norbixin (III) as ynun-tetramethyloctadecanonaene-ag-dicarboxylic acid instead of the older unsymmetrical formulæ is supported by the degradative experiments, (a)—(d), and (e) by synthesis of perhydronorbixin (IV). (a) (II), red P, and Br give the $\alpha \alpha'$ -Br₂-acid (not obtained pure), changed by boiling, dil. alkali into the $\alpha\alpha' - (OH)_2$ -acid (not obtained pure), the Me_2 ester, b.p. $165^{\circ}/0.04$ mm. (prepared by CH_2N_2), of which with MgMeI yields the *diglycol*, [OH·CMe_2·CMe(OH)·[CH_2]_3·CHMe·[CH_2]_2·]_2 (cannot be distilled); this with Pb(OAc)_4 in C₆H₆ at 45° gives COMe and β_2 distance to the method parameters of the parameters. COMe₂ and β_0 -diketo- ζ_λ -dimethyl-n-hexadecane, b.p. 132—135°/0.05 mm. (disemicarbazone, m.p. 168°), shown by colour reactions not to be an aldehyde.

(b) (IV) gives similarly the impure $\alpha \alpha' \cdot Br_2$ - and $\alpha \alpha' \cdot (OH)_2 \cdot acid$; the Me_2 ester of the latter, b.p. 213-216°/0·14 mm., gives the diglycol, $[OH \cdot CMe_2 \cdot CH(OH) \cdot CHMe \cdot [CH_2]_2 \cdot CHMe \cdot [CH_2]_2 \cdot]_2$, and thence $\gamma \pi \mu \pi \cdot tetramethyloctadecane \cdot \alpha \sigma \cdot dialdehyde$, b.p. 185°/0·3 mm., which gives colour reactions of aldehydes and is oxidised to the corresponding discrete spin $\alpha = 2\pi i \pi - 2\pi i$ dicarboxylic acid, b.p. 220°/0.1 mm. (amide, m.p. 127°). (c) Na-Hg and bixin in hot EtOH-C₅H₅N with a little H_2O give $\alpha \alpha' \beta \beta'$ -tetrahydro- and (possibly) αα'ββ'γγ'-hexahydro-norbixin, an oily mixture, oxidised by alkaline $KMnO_4$ to succinic acid. (d) The Me₂ ester of (I) gives a similar mixture of tetra- and hexa-hydro-derivatives, oxidised to methylsuccinic acid. (e) The Et₂ ester, b.p. 135°/12 mm., of aa'dimethylpimelic acid, solid, b.p. 208°/12 mm. (obtained in 60% yield from CH₂(CH₂Br)₂ and Et₂ sodiomethylmalonate), yields by reduction βζ-dimethylheptane-an-diol, b.p. 117°/0.45 mm., which with PBr₃ or, better, gaseous HBr gives αη-dibromo-βζdimethylheptane, b.p. 135°/10 mm. This with NaOEt and $CH_2(CO_2Et)_2$ affords $\gamma\eta$ -dimethylnonane- α i-dicarboxylic acid, the Et₂ ester, b.p. 129°/0.2 mm., of which by partial hydrolysis gives the Et ester, b.p. $159^{\circ}/0.2$ mm., electrolysis of which affords Et_2 yn-dimethyldecoate, b.p. about 80°/0.3 mm. (with possibly a little Δ^{θ} -ester), and the Et, ester of (IV). Natural and synthetic (IV) give the same diamide, m.p. 110.5°, and di-tribromoanilide, m.p. 83°. The new formulæ for (I) and (III) necessitate the following constitutions for their derivatives : crocetane, BZAO-

tetramethylhexadecane; bixane, $\delta \theta v_{P}$ -tetramethyleicosane; dibixane, 4:8:13:17:22:26:31:35octamethyloctatriacontane. R. S. C.

d-Galacturonic acid and its methylation products. K. SMOLEŃSKI and M. CICHOCKI (Coll. Czech. Chem. Comm., 1932, 4, 500—503).—d-Galacturonic acid monohydrate (A., 1927, 229), $[\alpha]_{10}^{\infty}$ +77.93° to +52.24° in 24 hr., with 0.25% HCl in McOH at 100° affords the Me ester (I), m.p. 137— 138°, $[\alpha]_{10}^{\infty}$ +124.9° in H₂O, of α -methyl-d-galacturonic acid, m.p. 115—116°, $[\alpha]_{10}^{\infty}$ +138.5°, which is isolated from its Ba salt, $[\alpha]_{10}^{\infty}$ +103.9°, obtained by hydrolysis with Ba(OH)₂. The mother-liquor from (I) affords the impure syrupy Me ester, $[\alpha]_{10}^{\infty}$ -36.92°, of β methyl-d-galacturonic acid, $[\alpha]_{10}^{\infty}$ -32.3° (Ba salt, $[\alpha]_{10}^{\infty}$ -38.6°). J. W. B.

Crystalline *d*-mannuronic acid. K. P. LINK (Science, 1932, 76, 386).—*d*-Mannuronic acid, m.p. 165°, has been obtained [by E. SCHOEFFEL] by decomposing the Ba salt at -10° in presence of EtOH; $[\alpha] -50^{\circ} \longrightarrow -20^{\circ}$ in 2 hr. L. S. T.

isoPropylidenehexuronic acid. L. VON VARGHA (Nature, 1932, 130, 846—847).—When shaken for 24 hr. with COMe₂ in presence of CuSO₄ or when 5% H₂SO₄ is added to its COMe₂ solution, hexuronic acid (I) yields the iso*propylidene* derivative, m.p. 220—222° (decomp.), $[\alpha]^{20} + 20^\circ$, $+15^\circ$, and $+28^\circ$ in H₂O, EtOH, or MeOH, respectively, the corresponding vals. for (I) being $+24^\circ$, $+58^\circ$, and $+50^\circ$. L. S. T.

Action of sodium ethoxide on ethyl *l*- α -benzenesulphonylbutyrate. W. C. ASHLEY and R. L. SHRINER (J. Amer. Chem. Soc., 1932, 54, 4410– 4414).—Et benzenesulphonylacetate (from PhSO₂Na and CH₂Cl·CO₂Et in EtOH) and EtI in EtOH– NaOEt give Et α -benzenesulphonylbutyrate, m.p. 63— 64°; the free acid, m.p. 123—124° (amide, m.p. 169— 170°), is resolved by brucine into 1- α -benzenesulphonylbutyric acid (I), m.p. 105—107° (softens at 60°), a_{10}^{35} —27·3° in EtOH (brucine salt), which is converted through the chloride into the *Et* ester (II), m.p. 44·5—45·5°, a_{20}^{25} —32·48°. Treatment of (II) with EtOH–NaOEt at —10° gives an inactive Na derivative. The half-life periods of (I) and (II) in EtOH at 27° are 1350 and 80 hr., respectively; racemisation is ascribed to the change PhSO₂·CHEt·CO₂R \longrightarrow PhSO₂·CEt:C(OH)(OR). H. B.

Glycidic synthesis of aldehydes. G. DARZENS (Compt. rend., 1932, 195, 884–886).—Hydrolysis of glycidic esters $CR'R''\cdot CR_2'' \cdot CO_2Et$ gives the ketone, CHR'R''·COR''', if R''' is small (cf. A., 1912, i, 627), but when R''' is large, migration occurs with formation of aldehyde, CR'R''R'''·CHO. Et a-chlorolaurate (I), b.p. 132–133°/4 mm., COMe₂, and NaOEt in EtOH at -10° give the glycidic ester, b.p. 162–165°/5 mm., easily hydrolysed by NaOH-EtOH to the glycidic acid, m.p. 22°, b.p. 184–185°/15 mm. When the acid is distilled at atm. pressure, it gives CO₂ and ax-dimethyldodecaldehyde, b.p. 156–160°/16 mm. (semicarbazone, m.p. 59·5°). (I) and cyclohexanone yield similarly the glycidic ester, b.p. 173–176°/5 mm., and 1-n-decyleyclohexan-1-aldehyde, b.p. 166–170°/15 mm. (semicarbazone, m.p. 98.5°), whilst with PhCHO the glycidic ester, b.p. $185-190^{\circ}/5$ mm., and α -phenyl- α -methyl-n-dodecaldehyde, b.p. $178-180^{\circ}$ (pressure not stated), m.p. 49° (semicarbazone, m.p. 195°), are formed. R. S. C.

Polyene compounds. II. Condensation products of crotonaldehyde. Production of alicyclic compounds. K. BERNHAUER and G. NEUBAUER (Biochem. Z., 1932, 251, 173-186; cf. A., 1932, 834). -The condensation product contains two aldehydes (I and II). (I), $C_8H_{10}O$, b.p. $71-73^{\circ}/12$ mm. (p-nitrophenylhydrazone, m.p. 142°; semicarbazone, m.p. 196°; stable H sulphite compound), yields on reduction with H₂ in presence of Pd-CaCO₃ a substance, C₈H₁₂O, m.p. 98-101°, b.p. 75-76/12 mm. (p-nitrophenylhydrazone, m.p. 160-163°), which yields an isomeric aldehyde (p-nitrophenylhydrazone, m.p. 213—214°; semicarbazone, m.p. 171—172°) when boiled at atm. pressure. On oxidation with Ag₂O (I) yields an acid, $C_8H_{10}O_2$ (probably dihydro-o-toluic acid), m.p. 62—63 (Br₂-derivative, unstable, m.p. 134°), which, on dehydrogenation with HBr or Pd-BaSO₄, yields o-toluic acid, m.p. 102°. (I) is probably dihydro-o-tolualdehyde. (II) is less stable. On oxidation with Ag₂O it yields a dibasic unsaturated acid, with one double linking, $C_8H_{12}O_4$, m.p. 124—125°, and an unsaturated monobasic acid, $C_8H_{10}O_3$, b.p. 140—145°/3 mm. Possible mechanisms for the reactions involved in the conversion of unsaturated aliphatic aldehydes into alicyclic and aromatic com-W. McC. pounds are discussed.

Polyene compounds. III. Condensation products of crotonaldehyde. K. BERNHAUER and K. IRRGANG (Biochem. Z., 1932, 254, 434–437).—A fraction of the condensation product, b.p. $81-95^{\circ}/12$ mm., gave on oxidation with Ag₂O-Na₂O₂ p-toluic acid and was probably dihydro-p-tolualdehyde.

P. W. C. Three-carbon series. I. Synthesis of glyceraldehyde and glycerol. II. Chemical and biochemical production of alkyl ethers of dihydroxyacetone. III. Crystalline α-phenylglycerol. Detection of acraldehyde and of methylglyoxal. I. S. NEUBERG (Biochem. Z., 1932, 255, 1–26; cf. A., 1930, 1164).—I. The yield of cryst. glyceraldehyde (I) from fresh 10% acraldehyde and activated Na or Ba chlorate is 14%, but can be increased if the dinitrophenylhydrazone is used for purification. Reduction of (I) yields glycerol in 60% yield. II. The α-Me ether of dihydroxyacetone [2:4-di-

II. The α -Me ether of dihydroxyacetone [2:4-dinitrophenylhydrazone, m.p. 175° (corr.); 2:4-dinitrophenylosazone, m.p. 272—280° (decomp.)] and the α -Et ether [2:4-dinitrophenylhydrazone, m.p. 167° (corr.); 2:4-dinitrophenylosazone, m.p. 265—275° (decomp.)], are obtained as syrups by the action of *Bacterium suboxidans* or (less effectively) of *B.* xylinum or by oxidation with NaOBr. By the biochemical method the yield is $\geq 20\%$ and less by the chemical method.

III. α -Phenylglycerol prepared by the method of Moureu and Gallagher (A., 1922, i, 34) crystallises after 8 months in the dark, m.p. 100.5° (corr.). The 2:4dinitrophenylhydrazones of glyceraldehyde and dihydroxyacetone give 31-44% yields of AcCHO on treatment with hot dil. H_2SO_4 . Acraldehyde-2: 4-dinitrophenylhydrazone, m.p. 166—167°, has very low solubility in aq. liquids. The compound

OH·CMe(SO₃Na)·CH(OH)·SO₃Na is pptd. from aq. solution by EtOH. W. McC.

Colour reaction of ketones. K. TAUFEL and H. THALER (Z. physiol. Chem., 1932, 212, 256—262). —A sensitive colour reaction consists in treating 50 mg. of substance with 0.4 c.c. of pure

o-OH·C₆H₄·CHO, adding 4 c.c. of H₂O, shaking, adding 2 c.c. of conc. H₂SO₄, and again shaking. A red colour in the upper layer usually indicates the presence of the group \cdot CH₂·CO·CH₂·. J. H. B.

Phytochemical reduction of heptan- α -ol- β -one. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1932, 98, 735—738).—dl- α -Chloroheptan- β -ol, b.p. 93°/13 mm., from CH₂Cl·CHO and Mg amyl bromide, is oxidised to α -chloroheptan- β -one, b.p. 80°/13 mm., transformed by HCO₂K in MeOH into α -hydroxyheptan- β -one (I), b.p. 95°/20 mm. (I) is reduced by a fermenting mixture of sugar and yeast to d-heptane- $\alpha\beta$ -diol, b.p. 121— 122°/12 mm., $[\alpha]_{15}^{25}$ +16·81° in EtOH (diphenylurethane, m.p. 111—112°, $[\alpha]_{15}^{25}$ +12·14° in EtOH; α -bromoheptan- β -ol, b.p. 75°/15 mm., $[\alpha]_{15}^{22}$ +2·0°). R. N. C.

Recovery of sugars from their hydrazones. H. COLLATZ and I. S. NEUBERG (Biochem. Z., 1932, 255, 27—37).—Carbohydrates (e.g., glycollaldehyde, glyceraldehyde, dihydroxyacetone, *l*-arabinose, *d*-mannose) can readily be obtained pure (often cryst.) and in good yield by decomposing their phenyl-, diphenyl-, or dinitrophenyl-hydrazones with MeCHO. In some cases other carbonyl compounds of low mol. wt. (e.g., COMe₂) may replace MeCHO and sometimes other substances (e.g., uronic acids) may also be obtained pure in this way. Almost the whole of the MeCHO hydrazone produced may be recovered. Glycollaldehyde-2: 4-dinitrophenylhydrazone has m.p. 155—156° (corr.); glycer-2: 4-dinitrophenylosazone has m.p. 275—277° (corr.). W. McC.

Active reductant of glucose and first steps in its oxidation. J. M. ORT (Proc. Staff. Mtgs. Mayo Clinic, 1932, 7, 203—204).—Activation of glucose proceeds by (1) ionisation as a weak acid, (2) momentary formation of -enediol. Mild oxidising agents attack this, but not normal glucose. At $p_{\rm H}$ 7—10 in absence of air, H is the only reductant accumulating appreciably in slightly alkaline solutions in 1—2 days; at $p_{\rm H}$ 10 the H₂ (pressure 0.01 atm.) can be removed with a pump. When air, H₂O₂, or other oxidants are added, provided these are not able to break the entire -enediol double linking, a glucose oxide and a peroxide are formed. CH. ABS.

Substitution of glucose in position 4. I. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1932, 97, 763—775).—4:6-Benzylidene- β -methylglucoside 2:3-dibenzoate with HCl in COMe₂ gives β -methylglucoside 2:3-dibenzoate (I), $[\alpha]_D^{30} + 92\cdot8^\circ$ in CHCl₃ [Ac_2 derivative, m.p. 131—132° (sinters 123°)], $[\alpha]_D^{30} + 79\cdot8^\circ$ in CHCl₃ (cf. A., 1929, 428)]. Partial benzoylation of (I) gives β -methylglucoside 2:3:6-tribenzoate, m.p. 144.5—145.5°, $[\alpha]_D^{30} + 82\cdot0^\circ$ in CHCl₃ [Ac derivative, m.p. 156—157°, $[\alpha]_D^{30} + 96\cdot0^\circ$ in CHCl₃ (not identical with 6-acetyl- β -methylglucoside 2 : 3 : 4-tribenzoate); 4-p-toluenesulphonate, m.p. 191—192° (decomp.), $[\alpha]_{10}^{20}$ +43.0° in CHCl₃; Me ether (II); $[\alpha]_{10}^{20}$ +58.5° in CHCl₃. β -Methylglucoside 2 : 3 : 6-triacetate (Bz derivative, m.p. 98— 99°, $[\alpha]_{10}^{20}$ —61.0°) (cf. A., 1927,1174), is similarly obtained. (II) on hydrolysis and acetylation gives 4-methyl- β -methylglucoside 2 : 3 : 6-triacetate, m.p. 107—108°, $[\alpha]_{10}^{20}$ —32.8° in CHCl₃, also obtained from the Ac₄ derivative of 4-methylglucose (A., 1925, i, 1242) through the acetobromo-derivative.

A. A. L. Oxidation of β -glucosan. B. HVISTENDAHL (Svensk Kem. Tidskr., 1932, 44, 231—235).—Oxidation of β -glucosan with KMnO₄ gives (CHO)₂ at moderate temp., with org. acids, principally H₂C₂O₄; if a large excess of KMnO₄ be used, and the temp. raised, only H₂C₂O₄ results. No evidence could be obtained of the formation of the diketonic substance mentioned by Pictet (A., 1920, i, 819). Oxidation of glucose and galactose under similar conditions yields only H₂C₂O₄. H. F. H.

Configuration of sedoheptose. V. ETTEL (Coll. Czech. Chem. Comm., 1932, 4, 513–520).—The identity of volemitol with β -d-mannoheptitol (this vol., 47) renders La Forge's configuration for sedoheptose (A., 1917, i, 444; 1920, i, 595) incorrect.

	CH. OH	CH. OH	
	(HO·Ċ·HĨ) ₃	(HO·C·H) ₃	
(I.)	H·C·OH	H-Ç-OH	(II.
1.0	HO·C·H	¢Ο	-mon
	CH-OH	CH. OH	

Consideration of the possible theoretical configurations for this heptose and of known data indicate that β -sedoheptitol is identical with β -l-guloheptitol (I) (Wherry, A., 1920, i, 595) and α -sedoheptitol with d-mannoheptitol, whence sedoheptose is a d-altroketoheptose (II). J. W. B.

Glucosides. IX. Methyl salicylate vicianoside (?violutoside). A. ROBERTSON and R. B. WATERS (J.C.S., 1932, 2770–2771).—The 2:3:4triacetyl- β -glucoside of Me salicylate (A., 1931, 1400) and O-triacetylarabinosidyl bromide in dry C₆H₆ containing Ag₂O afford during 65 min. the O-hexa-acetyl- β -vicianoside of Me salicylate, m.p. 158°, deacetylated by NH₃ in MeOH to Me salicylate β -vicianoside, m.p. 173° after sintering at 168—169°, probably identical with violutoside (A., 1926, 715). J. L. D.

Crystalline Kombé strophanthin. J. S. MEU-LENHOFF (Pharm. Weekblad, 1932, 69, 1161—1173).— The crystals which separate when the solution of the mixed glucosides in a small quantity of H_2O is preserved are extracted with $COMe_2$; Et_2O is added to the dried solution and the fairly pure cryst. ppt. is removed. A pure product is obtained by adding H_2O to an EtOH extract of the crude material; cymarin may be removed by recrystallisation from H_2O or by extraction with CHCl₃. If the EtOH solution is not kept cold, decomp. occurs, and the pure substance can no longer be isolated. The material described by Jacobs contains an appreciable quantity of cymarin. H. F. G.

Microscopical detection of glycogen and galactogen and their separation. F. MAY and F. KORDOWICH (Z. Biol., 1932, 93, 233—238).—Galactogen differs from glycogen in giving no colour reaction with I, but no satisfactory differentiation is at present available. P. G. M.

Mol.wt.and chemical structure of cellulose and starch. I. R. MOROZOV (J. Appl. Chem., Russia, 1932, 5, 211–216).—Formulæ [both $(C_6H_{10}O_5)_{64}$] are proposed for cellulose and starch. CH. ABS.

Highly-polymerised compounds. LXXII. Dependence of the viscosity of cellulose solutions on temperature. H. STAUDINGER (Ber., 1932, 65, [B], 1754—1756).—A reply to Hess and Rabinovitsch (A., 1932, 1117). H. W.

Differentiation of hemicelluloses. L. F. HAW-LEY and A. G. NORMAN (Ind. Eng. Chem., 1932, 24, 1190—1194).—The term hemicellulose is used to include incrusting substances not closely associated with cellulose and generally containing a uronic acid and also substances contained in the Cross and Bevan cellulose fraction which are free from uronic acids. It is suggested that the former class be termed polyuronides and the latter cellulosans. A. G.

Hemicelluloses of wood. (MISS) M. H. O'DWYER (Chem. and Ind., 1932, 968—971).—A review of recent work.

Fission of quaternary ammonium compounds by hydrogenation. XI. Ethylenic and carbonnitrogen linkings. H. EMDE (Helv. Chim. Acta, 1932, 15, 1330—1336; cf. A., 1912, i, 801).—A lecture. The following is new. [With H. KULL.] A C-N linking in quaternary NH₄ salts is broken by hydrogenation (Pd-C or Pd-BaSO₄) in purified AcOH, AcOH-NaOAc, aq. NaOAc, or H₂O. Thus, CH₂Ph·NPhMe₂Cl in AcOH (Pd-BaSO₄) yields PhMe and NPhMe₂. R. S. C.

Synthesis of β -ethoxyamines. I. J. WERNERT and W. R. BRODE (J. Amer. Chem. Soc., 1932, 54, 4365—4369).— β -Ethoxyamines, OEt·CHR·CH₂·NH₂ [accompanied by (OEt·CHR·CH₂)₂NH], are prepared from OEt·CHR·CH₂Br (Boord *et al.*, A., 1930, 1269; 1931, 709; 1932, 361) and MeOH–NH₃ at about 25° or, better, 90—100° under pressure. The following are described: β -ethoxy- β -phenylethylamine, b.p. 107—109°/12 mm.; β -ethoxybutylamine, b.p. 132—135°/ 31 mm.; β -ethoxydibutylamine, b.p. 132—135°/ 31 mm.; β -ethoxyamylamine, b.p. 133·5—134·5°/14 mm.; $\beta\beta'$ -diethoxydiamylamine, b.p. 66—656°/13 mm.; $\beta\beta'$ -diethoxy- γ -methylamylamine, b.p. 68—69°/13 mm.; $\beta\beta'$ -diethoxydibexylamine, b.p. 68—69°/13 mm.; $\beta\beta'$ -diethoxydibexylamine, b.p. 151—154°/12 mm. N- β -Ethoxybutylaniline, from β -ethoxybutyl bromide and NH₂Ph in MeOH, has b.p. 153·5°/21 mm. H. B.

Preparation of diethylisopropylamine. S. CASPE (J. Amer. Chem. Soc., 1932, 54, 4457).— $Pr^{\beta}Br$ heated with NHEt₂ and glycerol [or (CH₂·OH)₂] for 72 hr. gives 60% of *diethylisopropylamine*, b.p. 108°. H. B.

Mode of union of the glucosamine residues in chitin. L. ZECHMEISTER, W. GRASSMANN, G. TÓTH, and R. BENDER (Ber., 1932, 65, [B], 1706-1708).— Chitodextrin, the most sparingly sol. product of the action of superconc. HCl on chitin (cf. A., 1931, 935), is readily hydrolysed by emulsin as shown by the rapid increase of the I val. (Willstätter–Schudel). Increase in acidity is not observed and acetglucosamide is stable towards emulsin. The experiments afford further evidence of the β -glucosidic nature of chitin. H. W.

Reaction of formaldehyde with glycine. E. GUBAREV and A. BYSTRENIN (Biochem. Z., 1932, 255, 92—102).—The extent to which glycine and CH₂O interact and the rate of reaction vary greatly with the proportions of the reactants. Equilibrium is attained in from 1 to more than 30 days. If the medium is alkaline the extent of reaction is increased but the attainment of equilibrium is retarded.

W. McC.

Cupric complexes of glycine and alanine. H. BORSOOK and K. V. THIMANN (J. Biol. Chem., 1932, 98, 671-705).—Absorption spectra indicate the existence of at least four types of complex of both glycine and alanine with Cu, and the absorption spectra of each in the pure state have been determined. The constitution of each has been determined from potentiometric and spectrophotometric data. The no. of H ions set free in the formation of all except the two basic compounds and the orders of magnitude of the instability consts. were determined.

H. G. R.

Aminolysis of aspartic acid. E. BAUR and K. WUNDERLY (Naturwiss., 1932, 20, 873).—Aspartic acid in saturated aq. solution in absence of air, and in contact with C at 40—80°, yields NH_4 lactate, CO_2 , and small amounts of $AcCO_2H$ and MeCHO in addition to NH_4 malate (cf. A., 1924, 847). W. O. K.

Syntheses of peptides of *d*-lysine; *d*-lysyl-*d*glutamic acid and *-l*-histidine. M. BERGMANN, L. ZERVAS, and J. P. GREENSTEIN (Ber., 1932, 65, [*B*], 1692—1696; cf. A., 1932, 935).—*Me* d- $\alpha\epsilon$ -*diaminohexoate dihydrochloride*, m.p. 212° (corr.), is converted through the *dibenzylcarbonato*-compound into *dibenzylcarbonato*-d-*lysinchydrazide* (I). Successive treatment of (I) with NaNO₂ and Et₂ *d*-glutamate affords *Et₂ dibenzylcarbonato*-d-*lysyl*-d-glutamate, m.p. about 105° after softening at 95°, whence the corresponding acid, m.p. about 130° after softening at 96°, and d-lysyl-d-glutamic acid (II),

Optical rotation of *d*-talonamide and of salts of *d*-talonic acid. A. G. RENFREW and L. H. CRETCHER (J. Amer. Chem. Soc., 1932, 54, 4402— 4404).—*d*- γ -Talonolactone (A., 1932, 602) and EtOH– NH₂ give *d*-talonamide (I), m.p. 118—120° (softens at 116°), $[\alpha]_{15}^{25}$ -13·1° in H₂O (hydrate, m.p. 100—102°); NH₄ *d*-talonate, m.p. 148°, $[\alpha]_{15}^{25}$ +2·9° in H₂O, is obtained, using conc. aq. NH₃. Na *d*-talonate has $[\alpha]_{\overline{\mu}}^{-}+2\cdot5^{\circ}$ in H₂O. The lævorotation of (I) is in accordance with Hudson and Komatsu's rule (A., 1919, i, 524). (I) exhibits slow mutarotation probably owing to the formation of the NH₄ salt. H. B.

Applicability of Artmann and Skrabal's iodometric method for ammonia to the determination of carbamide. K. Wölffel (Z. anal. Chem., 1932, 90, 170–181).—Oxidation of $CO(NH_2)_2$ with NaOBr results in 9–14% of the N being converted into CNO', but good results ($\pm 0.5\%$) may be obtained by Artmann and Skrabal's method (A., 1907, ii, 196) if the solution is made acid with HCl, after the first reaction ceases, to convert the CNO' into NH₄⁺, and then again made alkaline so that the regenerated NaOBr oxidises the NH₄⁺. The solution is finally acidified, treated with KI, and the I corresponding with the excess OBr' titrated with Na₂S₂O₃. Addition of Na₂HPO₄ prevents "after-blueing." A. R. P.

Imperfect silver [nitrate]-guanidine complex. M. LESBRE (Compt. rend., 1932, 195, 880–882).— Guanidine (I) and aq. AgNO₃ form a ppt., which redissolves in excess of (I). Electrometric measurements show that the solution contains a complex ion, [Ag(CH₅N₃)]^{*}, which, as the concn. of (I) decreases, is in equilibrium with increasing amounts of [Ag(CH₅N₃)₃]^{*}. k for the former ion is $5\cdot14\times10^{-10}$. Beyond a certain limiting conen. Ag(CH₅N₃)NO₃ is pptd. R. S. C.

Ethylenic nitriles. α -Methyl- Δ^{α} -octenonitriles and α -hexylacrylonitrile. J. VARHULST and C. GLORIEUX (Bull. Soc. chim. Belg., 1932, 41, 501— 509).—Oxidation of methylhexylcarbinol with Cr₂O₃ affords *Me hexyl ketone*, b.p. 173·6—174°/770 mm. [*cyanohydrin*, b.p. 131—132°/11 mm., which with SOCl₂ and then with HCl yields β -chloro- α -methyloctonitrile (I), b.p. 113—114°/10 mm., and α -chloromethyloctonitrile (II), b.p. 121—122°/10 mm.]. (I) with C₅H₅N gives cis- α -methyl- Δ^{α} -octenonitrile, b.p. 201·2— 201·8°/767 mm., and the trans-form, b.p. 219—219·6°/ 767 mm., hydrolysed by cold H₂SO₄ to amides, m.p. 68·2—68·6° (III) and 53·2—53·6°, respectively. (II) with C₅H₅N affords α -hexylacrylonitrile, b.p. 200·6— 201·2°/766 mm., hydrolysed by cold H₂SO₄ to (III). J. L. D.

Applications of thallium compounds in organic chemistry. VIII. Molecular association of dialkylthallium chelate compounds. E. R. WILT-SHIRE and R. C. MENZIES (J.C.S., 1932, 2734-2739; cf. A., 1932, 1269).—Chelate dialkyl Tl compounds formed from β -diketones show an association in freezing C₆H₆ varying approx. between 1 and 2. The effect of the alkyl groups on the association is small, the nature of the diketone being the important factor. Association is probably due to the marked tendency of the Tl atom to increase its outer electronic shell to 12. The following are described: Me (dimethylthalli)-, m.p. 184°; Me (diethylthalli)-acetoacetate, m.p. 127°; Et (dimethylthalli)-, m.p. 133°; Et (diethylthalli)-benzoylacetate, m.p. 95°; (dimethylthalli)-, m.p. 173-175°; (diethylthalli)-dibenzoylmethane, m.p. 112°. J. L. D.

Reactions of $\Delta^{1:3}$ -cyclohexadiene. P. BEDOS and A. RUYER (Compt. rend., 1932, 195, 802-804).

Interaction of $\Delta^{1:3}$ -cyclohexadiene (I) with HOCl affords the monochlorohydrin, C₆H₈Cl·OH, (II), b.p. 98°/18 mm., m.p. 28—29°, small amounts of dichlorohydrin, m.p. 123°, and two dichlorides, b.p. 68—69°/12 mm. and 73—77°/12 mm., respectively. (I) and HOI give an iodohydrin, transformed, as is (II), into the monoxide, C₆H₈O (III), b.p. 45°/22 mm. (III) or a dioxide, b.p. 66°/11 mm., is obtained from (I) and BzO₂H. J. L. D.

Mechanism of nitration of benzene. B. V. TRONOV and L. V. LADYGINA (Ukrain. Chem. J., 1932, 7, [Sci.], 55–63).—The reaction is assumed to be one between double mols. of HNO_3 and C_6H_6 , with the formation of an intermediate residual valency complex. R. T.

Catalytic oxidation of *p*-cymene in the liquid phase. C. E. SENSEMAN and J. J. STUBBS (Ind. Eng. Chem., 1932, 24, 1184—1186).—When O_2 is bubbled through *p*-cymene containing MnO₂ or Mn *p*-toluate the principal product of oxidation is *p*-toluic acid, the max. yield of which is 50% of the *p*-cymene consumed. Cr₂O₃, Co₂O₃, CeO₂, Fe₂O₃, Ni₂O₃, and CuO are less active catalysts. A. G.

Additive products of styrene and aromatic hydrocarbons. A. SPILKER and W. SCHADE (Ber., 1932, 65, [B], 1686—1689).—Addition of 93% H_2SO_4 and styrene to C_6H_6 at 30—35° yields CHPh₂Me, b.p. 148°/15 mm. (oxidised to COPh₂), in about 25% yield. α -Phenyl- α -p-tolyl-, α -phenyl- α -3:4-dimethylphenyl-, α -phenyl- α -2:4-dimethylphenyl-, and α -phenyl- α -2:5-dimethylphenyl-ethane are prepared similarly. $C_{10}H_8$, styrene, and 93% H_2SO_4 in CCl₄ yield α -phenyl- α -2-naphthylethane, b.p. 220—222°/ 15 mm., m.p. 69° (oxidised to Ph β -naphthyl ketone, m.p. 81°), and non-cryst. α -phenyl- α -1-naphthylethane. H. W.

Rearrangements of poly-inenes. II. s-Tetraphenyldiphenylethinylethane. H. E. MUNRO and C. S. MARVEL (J. Amer. Chem. Soc., 1932, 54, 4445-4450).-Na diphenylphenylethinylmethyl (I), prepared by the method of Moureu et al. (A., 1927, 355) or from triphenylpropargyl Me ether and 40% Na-Hg, with $ClCO_2$ Me gives Me aay-triphenyl- Δ^{β} -butinenoate, b.p. 98-105°/2-3 mm., and is converted by CMe2Br CMe2Br in Et2O into the unstable (not isolated) s-tetraphenyldiphenylethinylethane (ayyoozhexaphenyl- $\Delta^{\alpha\epsilon}$ -hexadi-inene) (II). (II) absorbs O_2 rapidly (but does not give a stable peroxide) and is cleaved by 40% Na-Hg to (I). (II) rearranges readily into the hydrocarbon $C_{42}H_{30}$ (III), m.p. 172–173° described by Moureu et al. (loc. cit.; cf. Wieland and Kloss, A., 1929, 1053) as (II). (III) does not absorb O2 and is not cleaved by 40% Na-Hg, but gives a compound, $C_{42}H_{30}Na_2$, which is converted by H_2O into a hydrocarbon, C42H32, m.p. 239-241°, and by $ClCO_2Me$ into an impure ester, $C_{42}H_{30}(CO_2Me)_2$, m.p. H. B.

Proposal to adopt the stem "xen" of A. W. Hofmann's xenyl as basis for nomenclature of diphenyl and its derivatives. W. J. HALE (J. Amer. Chem. Soc., 1932, 54, 4458-4459).—The following nomenclature is suggested : xenene for diphenyl; xenyl for diphenylyl; xenols for hydroxydiphenyls; xenylenediamines for diaminodiphenyls; xenenecarboxylic (or xenoic) acids for diphenylcarboxylic acids; chloroxenenes for chlorodiphenyls.

H. B.

Nitration of 4:4'-dichlorodiphenyl. C. C. VERNON, A. REBERNAK, and H. H. RUWE (J. Amer. Chem. Soc., 1932, 54, 4456-4457).—The results of Shaw and Turner (A., 1932, 259) are confirmed. H. B.

Rearrangements of poly-inenes. III. Synthesis of 1:1'-bis-(1:3-diphenylindenyl). L. F. HALLEY and C. S. MARVEL (J. Amer. Chem. Soc., 1932, 54, 4450—4454).—1-Lithio-1:3-diphenylindene (from 1:3-diphenylindene and LiBu in C_6H_6 and N_2) and CMe₂Br·CMe₂Br give 1:1'-bis-(1:3-diphenylindenyl), ($C_6H_4 < CPh > CH_2$, m.p. 190—191°, which is not identical with the hydrocarbon $C_{42}H_{30}$ (J), m.p. 172—173°, obtained by rearrangement of $\alpha\gamma\gamma\delta\delta\zeta$ hexaphenyl- $\Delta^{\alpha\epsilon}$ -hexadi-inene (this vol., 56). Oxidation of (I) with CrO₃ in AcOH gives o- C_6H_4Bz ·CO₂H, whilst treatment with HCl in boiling AcOH affords a hydrocarbon, m.p. 261—262°, and a small amount of a substance, m.p. 290°. It is improbable that (I) and related compounds (A., 1932, 505) are di-indenyls.

H. B.

Derivatives of 2-ethylnaphthalene. G. LÉVY (Compt. rend., 1932, 195, 801—802).—Nitration of $2 \cdot C_{10}$ H-Et in AcOH at 3—10° affords 1-*nitro*-2-ethylnaphthalene, m.p. 49·5—50°, reduced by Fe in boiling AcOH during 4 hr. to 2-ethyl- α -naphthylamine, m.p. 25—28° (Ac derivative, m.p. 156·2°), decomp. of the diazonium sulphate affording 2-ethyl- α -naphthol (A., 1932, 734). J. L. D.

Chlorination of fluorene. J. BUFFLE (Helv. Chim. Acta, 1932, 15, 1483—1495).—2-Chlorofluorene is best prepared from fluorene and Cl_2 in C_6H_6 or AcOH at 80—90° in presence of I. Some 2:7- Cl_2 -derivative is also formed. Purification is best effected by distillation. R. S. C.

Alkylphenanthrenes. V. 9-Methyl-, 1:9-dimethyl-, and 1:2:8-trimethyl-phenanthrenes. R. D. HAWORTH and C. R. MAVIN (J.C.S., 1932, 2720-2723; cf. following abstract).-1-C10H7Me affords with succinic anhydride, AcCl, and AlCl₃ in PhNO₂, 4-methyl-α-naphthyl Me ketone (picrate, m.p. 101-102°) and β-(4-methyl-1-naphthoyl)propionic acid, m.p. 168-169° [semicarbazone, m.p. 202-203°; Me ester, m.p. $45-47^{\circ}$ (I)]. (I) is reduced by Clemmensen's method and cyclised to 1-keto-9-methyl-1:2:3:4tetrahydrophenanthrene, m.p. 74-75° (semicarbazone, m.p. 255-257°), which, with MgMeI and subsequent dehydrogenation, affords 1:9-dimethylphenanthrene, m.p. 87-88° (picrate, m.p. 160°). 5-Čyano-1-methyl-naphthalene, m.p. 92-93° (from the 5-NH₂-compound), in boiling PhMe with MgMeI during 3 hr. affords 5-methyl-a-naphthyl Me ketone, m.p. 44-46°, the oily ω -Br-compound of which with CMeNa(CO₂Et)₂ in C₆H₆ during 12 hr., followed by alkaline hydrolysis and heating at 160°, affords β -(5-methyl-1-naphthoyl)isobutyric acid, m.p. 160-161°, converted into 1-keto-2:8-dimethyl-1:2:3:4-tetrahydrophenanthrene (II), m.p. 108-109° [semicarbazone, m.p. 256-258° (decomp.)]. Interaction of (II) with MgMeI in Et₂O and

of the product with Se affords 1:2:8-trimethylphenanthrene, identical with methylpimanthrene (A., 1931, 359). J.L. D.

Alkylphenanthrenes. IV. 7-Methyl-1-ethyland 1-ethyl-7-isopropyl-phenanthrenes: constitution of abietic and d-pimaric acids. R. D. HAWORTH (J.C.S., 1932, 2717—2720; cf. A., 1932, 1024).—7-Methyl-1-ethyl- and 1-ethyl-7-isopropylphenanthrene obtained from 4-keto-7-methyl-1-ethyl-(semicarbazone, m.p. 198—200°) and 4-keto-1-ethyl-7isopropyl-1: 2: 3: 4-tetrahydrophenanthrene (semi carbazone, m.p. 225—226°) are identical respectively with methylpimanthrene and methylretene, which arise from abietic and d-pimaric acids (formulæ suggested) probably by a Wagner-Meerwein change (cf. ibid., 949). J. L. D.

Resin acids. II. 1-Methyl-7-isopropylphenanthrene (retene). J. C. BARDHAN and S. C. SENGUFTA (J.C.S., 1932, 2798–2800; cf. A., 1932, 1241).—Reduction of Et γ -isopropylidenepimelate (J.C.S., 1907, 91, 1743) with H₂ affords Et γ -isopropylpimelate, b.p. 170°/27 mm., which with Na in C₆H₆ gives Et 4-isopropylcyclohexan-1-one-2-carboxylate (I), b.p. 130–132°/10 mm. The K derivative of (I) affords, with β -o-tolylethyl bromide in boiling C₆H₆ during 28 hr., Et 4-isopropyl-2-(β -o-tolylethyl)eyclohexan-1-one-2-carboxylate, b.p. 195–197°/2 mm., reduced by Na-Hg to Et 4-isopropyl-2-(β -o-tolylethyl)cyclohexan-1-ol-2-carboxylate, b.p. 200–205°/2 mm., which, when treated successively with P₂O₅ and Se, affords 1-methyl-7-isopropylphenanthrene, identical with retene from abietic acid (A., 1932, 839).

J. L. D. Trihalides of perylene. K. BRASS and E. CLAR (Ber., 1932, 65, [B], 1660—1662).—Treatment of perylene in C_6H_6 with excess of Br in C_6H_6 ppts. a *compound*, $C_{20}H_{12}Br_3$, m.p. 162° (decomp.) after softening at 157°, from which 1 Br is removed in PhNO₂ by Na₂S₂O₃. It appears probable that after removal of 1 Br atom, the residual two add to the perylene mol.

with production of a dibromide. A less stable tri-iodide, partly molten at 190° after softening at 170° (vac.), is obtained from which I is completely removed by Na₂S₂O₃. H. W.

Dissociable organic oxides. Extension of methods of preparation of rubrene. Synthesis of a dichlorodiphenylrubene, $C_{30}H_{18}Cl_2$, and its preparation from dibenzoylmethane. C. DU-FRAISSE and R. BURET (Compt. rend., 1932, **195**, 962—



964).—Ph phenylethinyl ketone and PCl_5 give a compound (I), $C_{30}H_{20}Cl_4$, m.p. 310° (previous decomp.), which when heated loses 2HCl to form 1 : 1'dichloro - 3 : 3' - diphenylrubene (II), garnet-red, m.p. 251°. (I) [and hence (II)] is also formed from CH_2Bz_2 and

PCl₅ (by way of CClPh:CH·COPh) (cf. A., 1932, 616). H. B.

Sulphonation of aromatic amines by the socalled "baking process." W. HUBER (Helv. Chim. Acta, 1932, 15, 1372—1383).—To obtain good yields of sulphonic acid by heating the acid sulphate it is necessary to use pure base, to ensure homogeneity of the salt and avoid excess of H_2SO_4 , and to remove H_2O

(which causes hydrolysis of the acid and consequent further sulphonation) as it is formed. Addition to the melt of substances, e.g., $H_2C_2O_4$, which yield H_2O by decomp. is disadvantageous. Pure H sulphates are not obtained by the methods given in the lit. They are best obtained by adding the liquid base to the theoretical amount of 70% H₂SO₄, or a solution of the base in AcOH to the theoretical amount of conc. H₂SO₄, and drying the product in vac. Salts thus prepared give the following yields of sulphonic acid when heated at 180°/12-15 mm. in a special apparatus; the temp. given in parentheses are the approx. m.p. of the H sulphates : NH_2Ph (160°), 97.9; o-, m-, (I), and p-toluidine (145°, 120°, and 175°, respectively), 96.2-96.3; 1:3:4- and 1:4:2-xylidine (135° and 160°, respectively), 96·0 and 96·4; α - and β -naphthyl-amine (170° and 205°, respectively), 93·3 and 89·0 (β -salt heated at 220—230°); dehydrothio-*p*-toluidine, 92 (heated at 210—220°); 1-aminoanthraquinone, 90.3% (heated at 200°). Small amounts of base were recovered in each case. Contrary to statements in the lit., (I) gives the 6-sulphonic acid, whilst sulphonation of m-nitrotoluene occurs in the 5- (75%) and 6- (25%)positions, and the toluidines and xylidine are sulphonated with oleum at low temp., m- as well as p- to the NH₂ group. R. S. C.

Action of ω -aminoacetophenone and of piperidine on aromatic nitro-compounds. M. GIUA and G. REGGIANI (Atti R. Accad. Sci. Torino, 1932, 67, 51—56; Chem. Zentr., 1932, ii, 875).— ω -Aminoacetophenone hydrochloride in EtOH in presence of NaOAc with 2:4:5-trinitrotoluene causes substitution of 5-NO₂; with chloro-2:4-dinitrobenzene and picryl chloride the phenacylamine residue substitutes the Cl atom. 4:6-Dinitro-N-phenacylm-toluidine, m.p. 194°; 2:4-dinitro-, m.p. 178°, and 2:4:6-trinitro-N-phenacylaniline, m.p. 170°. N-4:6-Dinitro-, m.p. 111°, and 2:6-dinitro-m-tolylpiperidine, m.p. 99.5°. A. A. E.

Rearrangements by the action of nitrous acid on amines of the type CHPhMe·CH₂·NH₂. P. A. LEVENE, R. E. MARKER, and A. ROTHEN (J. Amer. Chem. Soc., 1932, 54, 4463-4464).—Active CHPhMe·CH₂·NH₂ and NOCl give (active) CHPhEtCl (cf. A., 1930, 1287); a similar rearrangement occurs with α -phenyl- α -methylpropylamine (cf. A., 1931, 1413). Dextrorotatory substituted phenylacetic acids are now correlated with lavorotatory substituted β -phenylpropionic acids. H. B.

Desulphurisation of thiocarbamides by bromate and iodate solutions. H. H. CAPPS and W. M. DEHN (J. Amer. Chem. Soc., 1932, 54, 4301-4305).--Arylthiocarbamides, NH₂·CS·NHAr, are readily desulphurised by KBrO₃ or KIO₃ in aq. NaOH to the corresponding cyanamides, whilst the mixed thiocarbamides, NHR·CS·NHAr (except α -phenyl- γ benzylthiocarbamide of those studied), give the corresponding carbamides. The following are new: α -phenyl- γ -2 : 4-, m.p. 168°, and -2 : 5-, m.p. 168°, -dichlorophenyl-, - γ -o-ethoxyphenyl-, m.p. 145°, and - γ -4-hydroxy-2-methylphenyl-, m.p. 177°, -thiocarbamides; anisyl-, m.p. 210°, and 2 : 5-dichlorophenyl-, m.p. 185°, -thiocarbamides; α -o-tolyl- γ -m-4-xylylthiocarbamide, m.p. 162°; α -phenyl- γ -2 : 4-dichlorophenyl-, m.p. 208°, and $-\gamma$ -m-4-xylyl-. m.p. 226°, and α -otolyl- γ -p-chlorophenyl-, m.p. 212°, -carbamides. Thiocarbamides often show varying m.p. owing to decomp.; they are best crystallised from PhMe. H. B.

Rearrangement of o-amino-sulphones. L. A. WARREN and S. SMILES (J.C.S., 1932, 2774–2778; cf. A., 1932, 735).—o-Nitrophenyl-o-aminoarylsulphones rearrange under the influence of alkaline reagents into the corresponding sulphinic acids: NHR·Ar·SO₂·C₆H₄·NO₂ \longrightarrow SO₂H·Ar·NR·C₆H₄·NO₂. A similar rearrangement, leading eventually to the disulphide, is undergone by a similarly substituted sulphoxide [cf. (III) \longrightarrow (VIII) below]. The N-Me derivative (Me₂SO₄ and NaOH), m.p. 84°, of o-nitrobenzenesulpho-p-toluidide, m. p. 116°, is converted by conc. H₂SO₄ at 100° (cf. A., 1915, i, 228) into o-nitrophenyl · 4 - methylamino - m - tolylsulphone, m.p. 122°. This is not demethylated by HBr in AcOH; it is converted slowly by 2N-NaOEt in EtOH and rapidly by 50% aq. KOH at 70–80° into K o-nitrophenylmethylamino-m-tolylsulphinate (I) and a little (II) (below). With MeI in aq. MeOH (I) gives 4-onitrophenylmethylamino-m-tolyl disulphine, m.p. 120°, with SO₂ and a little HI in EtOH it gives 4-o-nitrophenylmethylamino-m-tolyl disulphide, m.p. 132—133°, and with warm AcOH (with loss of HNO₂) 3 : 6-dimethylthiodiphenylamine dioxide (II), m.p. 153°.

o-Nitrophenyl 2-acetamido-1-naphthyl sulphoxide (III), m.p. 198° (decomp.), is obtained from the corresponding sulphide, H₂O₂, and AcOH at 100°; further oxidation at 100° gives the sulphone (IV), m.p. 160°, hydrolysed by EtOH-H₂SO₄ to o-nitrophenyl-2-amino-1-naphthylsulphone (V), m.p. 171°. This is isomerised by N-NaOH in aq. EtOH to 2-o-nitroanilinonaphthyl-1-sulphinic acid (VI), m.p. 210° (decomp.) [methylsulphone (VII), m.p. 125° (MeI and NaOMe in MeOH)]. The Ac derivative of (VI) is similarly formed from (IV), but was not isolated pure, being identified by methylation to 2-o-nitrophenylacetamido-1-naphthylmethylsulphone, m.p. 195°, which is readily hydrolysed to (VII) by NaOH in EtOH, and is converted by HI in AcOH into N-0-nitrophenyl-1-methyl-β-naphthathiazyl periodide, C₁₀H₆ SCMe I₃,m.p.183°. 2-o-Nitroanilino-1-naphthyl disulphide (VIII), m.p. 235° (decomp.), is obtained either from (VI) with HI (d 1.7) in COMe₂ or as a product of rearrangement of (III) by warm 2N-NaOH. (VI) is converted by AcOH at the b.p. into bis-2-o-nitroanilino-1-naphthyl sulphoxide (IX), m.p. 225° (decomp.), and o-nitrophenyl- β -naphthylamine, m.p. 110°; the last-named and H₂S are also formed by reduction of (VIII) or (IX) with HI in AcOH at the b.p. H. A. P.

Bromination of β-naphthylamine. F. BELL (J.C.S., 1932, 2732—2734).—Bromination of ptoluenesulphon-2-naphthalide in CHCl₃ gives the 1:6-Br₂-derivative (I), m.p. 145°, whilst in C₅H₅N the 1:3-Br₂-derivative (II), m.p. 163°, is formed. (II) is also formed by bromination of the 1-Brcompound, m.p. 100° (from 1-bromo-β-naphthylamine and C₆H₄Me·SO₂Cl), in C₅H₅N, in which no further bromination occurs; in CHCl₃, (II) is attacked slowly by Br, some 1:3:6-tribromo-β-naphthylamine being isolated. Further action of Br in CHCl₃ on (I) gives the 1:3:6-Br₃-derivative, m.p. 184°. 1:3-Dibromo- β -naphthylamine, m.p. 119° (Ac derivative, m.p. 201°), is prepared by hydrolysis of (II). 1:6-Dibromo- β -naphthyl Me ether gives with Br in CHCl₃ the 1:4:6-Br₃-compound. Nitration of β -naphthol in AcOH gives the 1:6-(NO₂)₂-derivative; its *m*-nitrobenzenesulphonate, however, gives a mixture of 8-nitro-, m.p. 144—146°, and 5-nitro-, m.p. 166°, -2-naphthyl m-nitrobenzenesulphonates.

H. A. P.

Chemical behaviour of Millon's base. II. A. BERNARDI and M. A. SCHWARZ (Gazzetta, 1932, 62, 905–908).—Millon's base does not react with benzenesulphonic or sulphanilic acids. With naphthionic and naphthylamine-2 : 3-disulphonic acids in EtOH in presence of ZnCl, it gives additive compounds, $3Hg_2O_2$, NH_3 , $C_{10}H_6(NH_2)$ ·SO₃H and

 $5Hg_2O_2,NH_3,C_{10}H_5\cdot NH_2(SO_3H)_2$, respectively, and with G and R acids *compounds*,

 $5Hg_2O_2,NH_3,2C_{10}H_5 \cdot OH(SO_3H)_2,4H_2O$, formed by addition and condensation. All are insol. and unstable in air, but can be kept over CaCl₂ in vac.

E. E. J. M.

Reaction products from hippuryl chloride. P. KARRER and V. ITSCHNER (Helv. Chim. Acta, 1932, 15, 1420).—"NN'-Dibenzoylglycine anhydride" (A., 1913, i, 968) is 1:3-dibenzamido-2:4-dihydrocyclobutadiene, identical with that obtained from Et hippurate and NaOEt (A., 1889, 249) or hippuryl chloride, C_5H_5N , and Cu (A., 1928, 428). R. S. C.

Purification of aromatic amines. A. WEISS-BERGER and E. STRASSER (J. pr. Chem., 1932, [ii], 135, 209—210).—A solution of the amine in dil. HCl is treated with 0.05—0.1 part of SnCl₂ at about 50° and the Sn pptd. with H₂S (this process is repeated if necessary), NaCl is then added, the resultant colourless solution made alkaline (H₂S is removed if necessary with Na₂SO₃), and extracted with Et₂O (if the amine is not pptd.). *m*- and *p*-C₆H₄(NH₂)₂, benzidine, tetramethylbenzidine, 4 : 4'-diaminodiphenic acid, aminoquinol Me₂ ether, *p*-NH₂·C₆H₄·OH, and NHPhEt are readily purified by this process. H. B.

Nitro-dye from *m*-phenylenediaminesulphonic acid and chlorodinitrobenzene. V. G. GULINOV and V. L. BUNITSKI (Ukrain. Chem. J., 1932, 7, [Tech], 9–16).—Na 2:4-di-2':4'-dinitroanilinobenzenesulphonate, a golden-brown dye for wool, is obtained from 1-chloro-2:4-dinitrobenzene and Na 2:4-diaminobenzenesulphonate. R. T.

Spectrochemistry and configuration of azoxybenzenes and stilhenes. K. VON AUWERS (Annalen, 1932, 499, 123—133; cf. A., 1928, 688).—Spectrochemical data are recorded for "normal" and isoazoxybenzenes, -o-, -m-, and -p-azoxytoluenes, -oazoxyanisoles, and -2:2'-dichloroazoxybenzenes, and 2-chloro-2'-bromoazoxybenzene (Müller, A., 1932, 263, 734) in quinoline. The exaltations in refractive power of the iso-forms are usually about half those of the "normal." Müller's conclusion (loc. cit.) that the pairs are cis-trans-isomerides is correct. The "normal" form is designated anti and the isoas syn. The sp. exaltation of trans-stilbene differs from that of isostilbene in the same manner (but more markedly) as with the azoxybenzenes. cisand trans- $\alpha\beta$ -Dimethylstilbenes do not show any appreciable difference in their sp. exaltations. Data for $\beta\gamma$ -diphenylbutadiene and $\beta\gamma$ -diphenylbutane are also given. H. B.

Azo-derivatives of trinitromethane. A. QUILICO (Gazzetta, 1932, 62, 912-927; cf. A., 1915, i, 1011; 1916, i, 609).-Solutions of diazonium salts react with NH, nitroformate in presence of cryst. NaOAc giving benzene-, p-nitro-, p-bromo-, and p-chloro-benzene-, and \$-naphthalene-azotrinitromethanes, R.N.N.C(NO2)3, and 4: 4'-diphenyldisazotrinitromethane; all are yellow and explode on heating or percussion. With SnCl₂ in HCl they give the amine corresponding with the diazonium salt used, CO_2 , and $N\dot{H}_3$. When heated in solution in an inert solvent, e.g., AcOH, or left for several days they lose 2 NO₂, giving the following carbonitrosohydrazines, R·N(NO)·N:CO: phenyl-, m.p. 85°; p-nitro-, m.p. 160°; p-bromo-, m.p. 145°, and p-chloro-phenyl-, m.p. 133°; β -naphthyl-, m.p. 115°, and 4: 4'-diphenylyl-, decomp. about 260°. These are colourless and stable; with SnCl₂ in HCl they give the hydrazines and with hydrolysing agents the diazoimides corresponding with the radical R.

E. E. J. M.

Structure of Para-red and related dyes. F. A. MASON (J. Soc. Dyers and Col., 1932, 48, 293— 295).—Sudan-I (benzeneazo- β -naphthol) readily forms a compound, C₁₀H₁₁ON₂SnCl₃, with SnCl₄ in PhMe at room temp., and also a boroacetate, m.p. 204— 206° (shrinks 198°). Similarly, Para-red (p-nitrobenzeneazo- β -naphthol) forms a compound,

 $C_{16}H_{10}O_3N_3SnCl_3$, and a boroacetate, m.p. 260–265° (decomp.). A chelated structure is therefore assigned to these dyes, and the formation (or otherwise) of Cr lakes by o-hydroxyazo-dyes is ascribed to the degree of stability of the chelate ring.

H. A. P.

Resistance of the linking between the arylazogroup and the nucleus in aminoazo-derivatives. G. B. CRIPPA and P. GALIMBERTI (Gazzetta, 1932, 62, 937-944; cf. A., 1929, 181).-When I-benzeneazo- β -naphthylamine is heated with $H_2C_2O_4$ at 135-180°, fission between the NPh:N group and naphthalene occurs, giving β-naphthyloxamic acid and oxalonaphthalide, with phenol. 4-Benzeneazo-anaphthylamine, o-aminoazobenzene, and chrysoidine condense with $H_2C_2O_4$, giving bis-4-benzeneazo-1-oxalonaphthalide, m.p. 180°, bis-o-benzeneazo-oxanilide, m.p. 279° (I), and dioxalylbis-2 : 4-diamino-1-benzeneazobenzene, m.p. 229°. The relatively weak attachment of the NAr:N group to the naphthalene nucleus when in the ortho position to NH₂ is explained on the theory of covalency. (I) with Fe in boiling AcOH gives 2: 2'-dibenziminazole. E. E. J. M.

Azo-dyes and their intermediate products. XI. peri-Bisazo-dyes. II. P. RUGGLI and A. COURTIN (Helv. Chim. Acta, 1932, 15, 1342—1352; cf. A., 1932, 264).—An azo-group in the α -position in C₁₀H₈ derivatives hinders, but does not prevent, coupling in the peri-position. The bisazo-dyes thus obtained are, if sol., brown to violet-brown dyes for wool. PhN₂Cl and 7-hydroxy- α -naphthylamine (I), m.p. 206—207° (decomp.) [Ac derivative (II), m.p. about 194° (decomp.) (lit. 165°)], in NaOH at -4° give 7-hydroxy-8-benzeneazo-a-naphthylamine (III) [Ac derivative, similarly obtained from (II)], which with SnCl, and HCl in HCO₂H gives some NH₂Ph and 2-hydroxy-1: 8-perimidine (hydrochloride), readily oxidised to I: 8-perimidinequinone, decomp. 200-212°; reduction in AcOH gives the corresponding Me derivatives. Diazotised (III) and β -naphthol in neutral aq. EtOH give the 1:8-bisazo-dye. (II) and diazotised Na sulphanilate at -4° give Na7 - hydroxy-8-benzeneazo-1-acetnaphthalide-4'- sulphon ale, hydrolysed to the NH2-compound [also obtained. from (I) at -10°]. The last-named gives a diazocompound which is stable to H_2O , with hot EtOH and Cu₂O gives Orange II, with boiling 10% H₂SO₄ gives Na 2:8-dihydroxy-1-benzeneazonaphthalene-4'sulphonate, and couples with β -naphthol or resorcinol in EtOH-NaOAc to give peri-bisazo-dyes. R. S. C.

Mechanism of catalytic hydrogenation of phenol under high pressure. II. S. ANDO (J. Soc. Chem. Ind. Japan, 1932, 35, 455–458B; cf. B., 1931, 1085).—The reaction of PhOH with 3 H₂ at 150—250° in an autoclave and in presence of a Ni catalyst gives rise to cyclohexanol. At higher temp. cyclohexane, cyclohexene, and C₆H₆ are formed. cycloHexene can be formed from cyclohexanol in presence of Al₂O₃ as catalyst. E. S. H.

Dielectric constant as a means of organic analysis. A. CHRÉTIEN and P. LAURENT (Compt. rend., 1932, 195, 792—794).—When the dielectric const. of a C_6H_6 solution $(0\cdot1--0\cdot25M)$ of a mixture of an acidic and basic org. substance is plotted against the mol.-% composition of the mixture the curve consists of one straight line if no compound is formed, or of two or more such lines meeting at points denoting the composition of the resulting compounds. In this way the existence is indicated in C_6H_6 solution of equimol. compounds of PhOH with quinoline; C_5H_5N with PhOH, β -naphthol, and pyrole; 2:4dinitrophenol with NH₂Ph; o-NO₂· C_6H_4 ·OH with NHPh·NH₂; of 1 mol. of pyrocatechol or of dimethylglyoxime with 2 mols. of C_5H_5N ; 1 of phloroglucinol with 2 and 3 of C_5H_5N ; and of 2 and 1 of 2:4-dinitrophenol with 1 of phenazine. No compounds are indicated between PhOH and NPhMe₂; o-NO₂· C_6H_4 ·OH and NHPh₂ or NPhMe₂; or β -naphthol and NH₂Ph or C_5H_5N . C. A. S.

Dibromopicric acid. H. WILLSTAEDT and F. REUTER (J. pr. Chem., 1932, [ii], 135, 211-214).- $3:5-C_6H_3Br_2$ ·OH (prepared in 20% yield by decomp. of the diazonium sulphate) and HNO₃ (d 1.52) in AcOH give dibromopicric acid (I), m.p. 165°. Trinitroanisole and Br in presence of Fe afford picric acid. Extraction of the anthocyanin of red cabbage is best accomplished by an aq. solution of (I) (rather than pieric or dichloropicric acids). H. B.

Structure of amber musk. I. tert.-Butyl-mtolyl methyl ether and its nitration products. II. O. A. SEIDE and B. M. DUBININ (J. Gen. Chem. Russ., 1932, 2, 455–471, 472–477).—I. m-Tolyl Me ether and Bu^gCl condense (AlCl₃) to the tert.-Bu compound (I), more easily prepared from mtolyl Me ether, isobutylene, and AlCl₃, b.p. 223°, m.p. 23-24°. The mixture obtained by the nitration of (I) can be separated by vac. distillation into amber musk (II), b.p. 185°/16 mm., m.p. 85°, and 4:6dinitro-*m*-tolyl Me ether (III), b.p. 202-203°/16 mm., m.p. 101°. The lower b.p. of (1) makes Barbier's formula (A., 1928, 291) for it improbable. (II) can be obtained by the nitration of acetyl-tert.-butyl-mtolyl Me ether (IV) (loc. cit.) together with 2:4dinitro-6-acetyl-m-tolyl Me ether, the structure of which is established; the former is produced by the replacement of the Ac and the latter of the tert.-Bu group of (III) by NO₂. The tert.-Bu in (IV) cannot therefore occupy position 6, since this is occupied by the Ac group and the only possible position is 4. It follows that (II) is 2:6-dinitro-4-tert.-butyl-mtolyl Me ether and (I) is 4-tert.-butyl-m-tolyl Me ether. This has been proved as follows: 4-nitro-mtolyl Me ether is reduced to the $4-NH_2$ -compound, b.p. 109°/11 mm. (picrate, decomp. 198-199° with previous darkening), and converted by the Sandmeyer reaction into 4-bromo-m-tolyl Me ether, b.p. 107-109°/11 mm.; the Br is replaced (Grignard) by tert.-Bu, giving (I) nitrated to (II). (IV) must therefore be 6-acetyl-4-tert.-butyl-m-tolyl Me ether.

Nitration of (I) yields, in addition to the products already isolated (loc. cit.), a quinone, m.p. 96°, in the fraction b.p. 135-145°/14 mm., and a mononitroderivative (V), m.p. 81-82°, in the fraction 145-171°/14 mm.; these become the sole products with HNO3 d 1.38-1.42. The quinone is 4-tert.-butyltoluquinone, reduced by NHPh·NH₂ to the quinol, m.p. 122-123°, and forming the *quinhydrone*, violet plates, m.p. 116°, on mixing with the latter. (V) gives (II) on further nitration and must therefore be either the 2- or the 6-NO2-derivative; as some 4:6-dinitro-m-tolyl Me ether is formed at the same time (by displacement of the CMe₃ group), the former possibility is ruled out. The nitration of (I) is accompanied by an intense coloration, due to the formation of an oxonium salt, isolated as the perchlorate (VI), $C_{24}H_{34}O_7NCl, 0.5H_2O$, probably 2: 2'dimethyl-5: 5'-di-tert.-butyl-4:4'-dimethoxydiphenylhydroxylamine-N-oxide perchlorate. (VI) is hydrolysed by dil. H₂SO₄ to the above quinone and accounts for its formation.

II. A repetition of Darzens and Lévy's synthesis of amber musk (A., 1931, 1152) shows that the tert.butyl-m-tolyl Me ether (VII) obtained by their method has b.p. $102-104^{\circ}/8$ mm., m.p. 6°, and is nitrated to an isomeride (VIII) of (II), m.p. 111°, possessing a much weaker musk odour than (II). No coloured oxonium salt is formed during the nitration. A NO_2 -compound m.p. 82-83° (IX), not identical with the 6-NO₂-derivative (cf. above) and devoid of musk odour, is also formed; a compound of m.p. 72° was not isolated. It is suggested that (VII) is 6-tert.-butyl-m-tolyl Me ether, (IX) the 4-NO₂- and (VIII) the 2:4-(NO₂)₂-derivative. The statement (loc. cit.) that the odour of musk is due to two NO₂ groups or the to the OMe is evidently incorrect. G. A. R. K.

Nitro-dye from aminophenolsulphonic acid and chlorodinitrobenzene. V. G. GULINOV (Ukrain. Chem. J., 1932, 7, [Tech.], 5-8).-A

methoxy-1-ethylbenzene (by Clemmensen reduction of isoacetovanillone), m.p. 37-38.5°, b.p. 73-78°/1 mm. [benzoate, m.p. 52°; p-nitrobenzoate, m.p. 67°; Et glycollate, m.p. (anhyd.) 89-92°; carbonate, m.p. 95°]; eugenol (benzoate, m.p. 70°; p-nitrobenzoate, m.p. 80.5°); isoeugenol [benzoate, m.p. 104°; p-nitrobenzoate, m.p. 124°; Et glycollate, m.p. (from H₂O) 86-88°, (anhyd.) 118°; carbonate, m.p. 106°]. All m.p. are corr. R. S. C.

Condensation of phenols with aliphatic aldehydes. W. C. HARDEN and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 4325-4334).—The following are prepared usually from the phenol and Alk-CHO in presence of conc. HCl: (a) from PhOH: 4:4'- (Br_4 derivative, m.p. 226°) and 2:4'-dihydroxydiphenylmethane (Br₄-derivative, m.p. 193°); αα-di-p-hydroxyphenyl-ethane, m.p. 122° $(Br_4$ -derivative, m.p. 140°), -propane, m.p. 129° $(Br_4$ -derivative, m.p. 140°), -butane, m.p. 137° $(Br_4$ -derivative, m.p. 152°), -pent-ane, m.p. 120° $(Br_4$ -derivative diacetate, m.p. 168°), -hexane, m.p. 110.5° (Br4-derivative diacetale, m.p. 129°), and -heptane, m.p. 120° (lit. 103°) (Br_4 -derivative diacetate, m.p. 111°); (b) from o-cresol; 4:4'-dihydroxy-3: 3'-dimethyldiphenylmethane $(Br_2$ -derivative, m.p. 173.5°); $\alpha \alpha$ -di-(4-hydroxy-3-methylphenyl)-ethane, m.p. 100° (Br_2 -derivative, m.p. 77°), -propane, m.p. 94° (Br_2 -derivative, m.p. 111°), -butane, m.p. 135° (Br_2 -derivative, m.p. 104°), -pentane, m.p. 97° (Br2-derivative diacetate, m.p. 150°), -hexane, m.p. 78° (Br2-derivative diacetate, m.p. 121°), and -heptane, m.p. 85° (Br2-derivative di-p-nitrobenzoate, m.p. 215°); (c) from m-cresol: 4:4'-dihydroxy-2:2'-dimethyldiphenylmethane, m.p. 113° (Br_4 -derivative, m.p. 185°); ax-di-(4-hudroxu-2-methylphenyl)ethane, m.p. 128° ax-di-(4-hydroxy-2-methylphenyl)ethane, m.p. 128° (Br_2 -, m.p. 189°, and Br_4 -, m.p. 207°, derivatives), (Br_2^{-} , m.p. 189, and Br_4^{-} , m.p. 207, derivatives), -propane, m.p. 140° [Br_4 -derivative, m.p. 121° (di-acetate, m.p. 81°)], -butane, m.p. 145° (Br_4 -derivative, m.p. 142°), -pentane, m.p. 149° (Br_4 -derivative diacetate, m.p. 78°), -hexane, m.p. 152° [Br_4 -derivative, m.p. 119° (diacetate, m.p. 142°)], and -heptane, m.p. 156° (Br_4 -derivative, m.p. 67°); (d) from resorcinol: 2 · 4 · 2' · 4', tetra hydroxydinhonylmethene (Br_4 -derivative) 2:4:2':4'-tetrahydroxydiphenylmethane (Br_4 -derivative); aa-di-(2: 4-dihydroxyphenyl)-ethane, -propane, -butane, -pentane, -hexane, and -heptane, all of which have m.p. > 300° and give Br_4 -derivatives; (e) from chloral : $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -di-p-hydroxyphenyl-, m.p. 199–200°, - $\alpha\alpha$ -di-(4-hydroxy-3-methyl-phenyl)-, m.p. 121–122°, m.p. (+C₆H₆) 91°, - $\alpha\alpha$ -di-(4-hydroxy-2-methylphenyl)-, m.p. 162–163°, and - $\alpha\alpha$ di-(4-hydroxy-2-methyl-5-isopropylphenyl)-, m.p. 193.5°, -ethanes. Data on the solubility, bactericidal action towards S. aureus, and toxicity towards goldfish and seedlings of Lupinus albus of the above compounds are given. In general, bactericidal action increases with length of the C-chain [except in (c) and (d), where max. activity is with the -butane and -pentane, respectively] and is a function of the lipoid solubility.

H. B. **Tetralin peroxide.** M. HARTMANN and M. SEI-BERTH (Helv. Chim. Acta, 1932, 15, 1390—1392).— Tetralin (I) and air (with or without a catalyst, e.g., Zn turnings) at room temp. or 70—80° gives gradually the peroxide (II), m.p. 53—54°, which is given the formula $C_6H_4 < CH_2 - CH_2$, since it is sol. in NaOH

golden-yellow dye for wool, Na 2:4-dinitroanilinophenol-m-sulphonate, is obtained from 1-chloro-2:4dinitrobenzene and Na p-aminophenol-m-sulphonate. R. T.

Reaction of primary and secondary aminoalcohols and aminophenols with arylsulphonyl chlorides. K. H. SLOTTA and R. BEHNISCH (J. pr. alcohol (I) (1 mol.), obtained in 80% yield from $(CH_2)_2O$ and cold conc. aq. NH_3 , and $p \cdot C_6H_4Me \cdot SO_2CI$ (II) (1 mol.) at 130° give p-toluenesulphon- β -chloroethylamide, m.p. 101°; with 0.5 mol. of (II) at 100°, ptoluenesulphon-\beta-hydroxyethylamide (III), b.p. 250° 10 mm., m.p. 56° (Na and K salts), also prepared from equimol. amounts of (I) and (II) in C_5H_5N , results. Benzenesulphon- β -hydroxyethylamide, b.p. 247—248°/ 10 mm. (Na salt), is obtained from (I) and PhSO₂Cl at 100°. (II) and (III) in boiling C_5H_5N afford β -ptoluenesulphonamidoethylpyridinium p-toluenesulphon-ate, m.p. 193–194° (sinters at 188°) (corresponding picrate, m.p. 165°), also obtainable directly from (I), (II), and C_5H_5N . β -Benzenesulphonamidoethylpyridinium benzenesulphonate, m.p. 180° (corresponding picrate, m.p. 110°), is similarly prepared. β-Methylaminoethyl alcohol and (II) at 100° give p-toluene-sulphon-N-methyl-β-hydroxyethylamide, b.p. 250°/20 mm., 180-185°/3.5 mm. (O-Ac derivative, b.p. 150°/ 0.3 mm., m.p. 58°), also prepared by the Schotten-Baumann method and from $p-C_6H_4Me\cdotSO_2NHMe$, CH₂Cl·CH₂·OH, and EtOH-KOH at 170°. p- $NMe_2 \cdot C_6H_4 \cdot OH$, prepared from *p*-NMe_2 \cdot C_6H_4 \cdot OMe and HBr (d 1.49) in AcOH, and (II) in C₅H₅N afford p-dimethylaminophenyl p-toluenesulphonate, m.p. 130° (hydrochloride, m.p. 188°; picrate, m.p. 146°). Piperazine formation is not observed in the above cases as with NR₂·CH₂·CH₂·OH (A., 1932, 1042). H. B.

Diphenyl sulphide. W. W. HARTMAN, L. A. SMITH, and J. B. DICKEY (Ind. Eng. Chem., 1932, 24, 1317–1318).—The prep. of Ph_2S using C_6H_6 , S_2Cl_2 , and $AlCl_3$ is described and references are given to 22 other methods. On a semi-commercial scale a yield of 83.3% is obtained. S. M.

4-Hydroxy-3-methoxystyrene (4-vinylguaiacol). T. REICHSTEIN (Helv. Chim. Acta, 1932, 15, 1450-1453).—Vanillin and MgMeI (3 mols.) give 4-hydroxy-3-methoxyphenylmethylcarbinol ("apo-4-hydroxy-3-methoxyphenylmethylcarbinol ("apo-cynol," J.C.S., 1908, 93, 1520), b.p. about 180°/12 mm., m.p. 102.5-103°, or, under other conditions, 4-hydroxy-3-methoxystyrene (I), b.p. about 120°/12 mm. [and a (?) dimeric distillation residue] (also obtained from ferulic acid by NaOH at 300° or, better, Cu powder and quinoline at 240°) [benzoate, m.p. 112°; p-nitrobenzoate, m.p. 107°; Et glycollate, m.p. (from H₂O) 85°, (anhyd.) 110°; carbonate, m.p. 104°; phosphate, m.p. 67—70° (uncorr.); Me ether (3: 4-di-methoxystyrene), b.p. 85°/1 mm.]. Fromm's phenol (A., 1927, 968) from coal tar is, therefore, not (I). The following m.p. are recorded : creosol [benzoate, m.p. 76°; p-nitrobenzoate, m.p. 109°; Et glycollate, m.p. (from H₂O) 99-103°, (anhyd.) 117°; carbonate, m.p. 148°; phosphate, m.p. 103°]; 4-hydroxy-3methoxy-1-ethylbenzene [benzoate, m.p. 64°; p-nitrobenzoate, m.p. 100°; Et glycollate, m.p. (from H₂O) 68°, (anhyd.) 86°; carbonate, m.p. 118°]; 3-hydroxy-4and pptd. therefrom by CO_2 or acids, liberates I from HI, oxidises leucomethylene-blue, gives α -tetralol with Zn dust and 50% AcOH, and α -tetralone with aq. FcSO₄. (II) explodes in contact with conc. H₂SO₄ or when strongly heated, and with aq. NaHSO₃ gives the Na salt of a sulphonic acid, which with acids gives dihydronaphthalene. (II) may be isolated as Na salt when (I), which has been kept in air for some time, is shaken with aq. NaOH, or by removing unchanged (I) at 50—70°/2—3 mm. Distillation residues of old specimens of (I) may explode when heated. R. S. C.

Size of ring II in cholesterol. R. CRIEGEE (Ber., 1932, 65, [B], 1770-1772) .- The oxidation of cisglycols with Pb(OAc), proceeds more rapidly than that of trans-compounds and the magnitude of the difference in the rate of reaction depends above all on the magnitude of the ring in which the glycol grouping occurs. The ratio of the rates of oxidation of the isomeric glycols k_{cis} : k_{trans} is recorded for the following compounds, the size of the ring being placed in parentheses: cyclohexane- (6), 23; tetrahydronaphthalene- (6), 21.6; hydrindene- (5), 55,000; acenaphthene- (5), 130,000, -diol: methylmannofuranoside (5) and ethylglucofuranoside carbonate (5), > 90,000; mannono- γ -lactone (5) and arabono- γ -lactone (5), > 20,000. Since the ratio for the cisand trans-glycols of cholesterol is about 36,000, ring II must be five-membered unless the improbable hypotheses be accepted that, unlike other 6-membered rings, its structure is plane and fixed. Oxidation of the glycols shows that the double linking of cholesterol cannot be in the $\alpha\beta$ position to a OH group. H. W.

Ring system of sterols and bile acids. II. O. ROSENHEIM and H. KING (Chem. and Ind., 1932, 954—956).—The views previously expressed (A., 1932, 736, 1131) are supplemented. Deoxycholic, chenodeoxycholic, and hyodeoxycholic acids are now postulated as 3:12-(I), 3:7-, and 3:6-dihydroxycholanic



acids, respectively; cholic acid remains 3:7:12-trihydroxycholanic acid, but its distinctive OH group is now at C_7 instead of C_{12} . The attachment of the side-chain at C_{17} explains the X-ray crystallographic measurements of Bernal (*ibid.*, 327) and unpub-

lished results on *apo*cholic (II) and dihydroxycholenic (III) acids. Since reduction of (III) gives (I), it follows that (II) does not arise by ring formation between position 17 and the sp. OH group of cholic acid (cf. *loc. cit.*). (II) is convertible by HCl into (III); it is suggested that a bridge linking between C_7 and C_9 in (II) gives rise to a double linking between C_8 and C_9 in (III). A similar scheme explains the production of α -ergostenol from ergosterol if the conjugated double linkings of the latter are $C_5:C_6:C_7:C_8$. Migration of the *tert.*-Me group from C_{10} to C_7 would make ring II aromatic and thus explain the production of toluenceteracarboxylic acid from ergosterol, etc. (*ibid.*, 612). The postulation of ring IV as fivemembered (Wieland and Dane, *ibid.*, 1131) is favoured; evidence supporting this view is quoted. The ultraviolet absorption spectrum of the hydrocarbon $C_{18}H_{16}$, obtained by dehydrogenation (Se) of cholesterol and ergosterol, is similar to that of chrysene and is intermediate between that of the latter and octahydrochrysene. H. B.

Tachysterol. A. WINDAUS, F. VON WERDER, and A. LUTTRINGHAUS (Annalen, 1932, 499, 188-200).—Acetylation (Ac_2O) of the adduct formed when irradiated ergosterol is treated with citraconic anhydride (I) (A., 1932, 311) gives the adduct, $C_{15}H_{50}O_5$, m.p. 161–162°, $[\alpha]_{10}^{30} + 75 \cdot 2^{\circ}$ in CHCl₃, of (I) and tachysteryl acetate, which when heated at 165-190°/0.001 mm., regenerates its components. Treatment of the crude irradiation product (freed from ergosterol) (loc. cit.) with 2:6-dinitro-p-toluoyl chloride in C_5H_5N at 70°, gives tachysteryl 2:6-dinitro-p-toluate, m.p. 154—155° (and vitamin- D_2 2:6-dinitro-p-toluate), hydrolysed by 3% MeOH-KOH in N₂ to tachysterol (II), $[\alpha]_{10}^{18}$ —70° in "benzine," which has not been obtained cryst. (II) is isomeric with ergosterol (as shown by analysis of the adduct), consumes 4-5 O when titrated with BzO₂H, is oxidised (O_3) to α -methylisovaleraldehyde, does not give toluenetetracarboxylic acid with HNO3, and undergoes autoxidation (O_2 in MeOH) to a product (III), $C_{28}H_{44}O_7$, decomp. 130° (sinters at 98°). (II) has no antirachitic action, but when irradiated gives vitamin- D_2 and both suprasterols. The following changes occur when ergosterol is irradiated : ergosterol \longrightarrow lumisterol \longrightarrow tachysterol \longrightarrow vitamin- D_2 \rightarrow suprasterols. When (II) is heated at 190°/6 hr. (sealed tube), the dextrorotatory pyrotachysterol (IV), C28H44O, is produced. (IV) is not activated by irradiation and does not give an adduct with (I). Absorption curves are given for (II), (III), (IV), and the mixture obtained when (II) is treated with Na and PrOH.

[By E. FERNHOLZ.] The mother-liquors from the prep. of dihydrovitamin- D_2 allophanate (loc. cit.) contain (after hydrolysis with MeOH-KOH) an alcohol, which gives a 3:5-dinitrobenzoate $C_{35}H_{46(48)}O_6N_2$, m.p. 164—165°, $[\alpha]_{15}^{18} + 138^{\circ}$ in COMe₂. Dihydrovitamin- D_2 3:5-dinitrobenzoate has m.p. 95°, $[\alpha]_{15}^{16} + 32\cdot2^{\circ}$ in CHCl₃. H. B.

Light-absorption and constitution. VI. Lightabsorption of conjugated systems. A. BURAWOY (J. pr. Chem., 1932, [ii], 135, 145–154).—Polemical (cf. Dilthey, A., 1932, 1028). H. A. P.

Alkali-fastness of Patent-blue dyes. G. HEL-LER (Chem.-Ztg., 1932, 56, 902—903).—The fastness to alkalis of CHPh₃ dyes containing a SO_3H group ortho to the central C atom is probably a steric effect, wandering of the OH group from the N atom to this C atom being hindered. C. I.

Nitriles and amides of cinnamic acid. J. GHOSEZ (Bull. Soc. chim. Belg., 1932, 41, 477–500).— Fractional distillation and crystallisation of the mixture of cinnamonitriles (prep. described from PhCHO and cyanoacetic acid) affords a trans-iso-meride, b.p. $263\cdot8^{\circ}/756$ mm., and a cis-isomeride, b.p. $249-249\cdot4^{\circ}/756$ mm. β -Phenylglutaronitrile, m.p. 26° , b.p. $207\cdot5-208\cdot5^{\circ}/12-13$ mm., was also isolated. Hydrolysis of the cis-nitrile with H₂SO₄ affords cis-cinnamamide, m.p. $199-202^{\circ}$. J. L. D. Colour and properties in the cinnamic series. (MME.) RAMART-LUCAS and TRIVÉDI (Compt. rend., 1932, 195, 783—785).—Introduction of an α - or β -methyl group into Ph·CH:CH·COR (R=OH, OEt, NH₂) shifts the absorption bands towards the ultraviolet and diminishes their intensity, and also depresses the reactivity of the group •COR. J. L. D.

8-Bromo- and -iodo-naphthoic acids. H. GOLDSTEIN and P. FRANCEY (Helv. Chim. Acta, 1932, 15, 1362—1366).—Na 8-amino-1-naphthoate (modified prep. from naphthastyril) gives by diazo-reactions 8-bromo-1-naphthoic acid (chloride; anilide, m.p. 151°) and 8-iodo-1-naphthoic acid, m.p. 164.5° [Me and Et esters, from the Ag salts (not by EtOH and acid), m.p. 59° and 64.5°, respectively; chloride; anilide, m.p. 171.5°]. R. S. C.

Transformation products of bromonaphthastyril. H. GOLDSTEIN and P. FRANCEY (Helv. Chim. Acta, 1932, 15, 1366-1372).-Bromonaphthastyril (I) (modified prep.) [N-Ac derivative (II), m.p. 161.5°] and boiling aq. NaOH give 5-bromo-8-amino-1-naphthoic acid (III), which regenerates (I) slowly in vac. and rapidly at 250° or in hot EtOH, and with hot Ac₂O gives (II). (III) with alkaline Me₂SO₄ yields N-methylbromonaphthastyril, m.p. 139.5°, and, when diazotised and heated at 60°, the lactone, m.p. 192°, of 5-bromo-8-hydroxy-1-naphthoic acid, formed by bromination of naphtholactone (cf. A., 1889, 153); the acid regenerates the lactone at 210° and with an excess of alkaline Me₂SO₄ gives Me 5-bromo-8-hydroxy-1-naphthoate, m.p. 124°. (II) affords by diazo-reactions 5:8-dibromo-1-naphthoic acid, m.p. 227.5° (Me and Et esters, m.p. 73° and 74°, respectively; chloride; anilide, m.p. 212°), and 5-bromo-8-iodo-1-naphthoic acid, m.p. 250° (Me, m.p. 122°, and Et, m.p. 89-5°, esters, from Ag salt; chloride; amide, m.p. 230°; anilide, m.p. 190.5°). R. S. C.

Reactivity of peri-substituted naphthalenes. II. Replacement of halogen in 8-halogeno-1naphthoic and o-halogenobenzoic acids. H. G. RULE and A. J. G. BARNETT (J.C.S., 1932, 2728-2732). —The reactivity towards ONa compounds in the presence of Cu-bronze of the 8-halogeno-1-naphthoic acids is in general greater than that of the corresponding o-halogenobenzoic acids, the same type of replacement occurring in the former case with the Br compounds as in the latter with the I compounds. Na o-bromobenzoate is, however, readily converted by NaI and Cu-bronze in PrOH at 80° into the iodobenzoate, whilst attempts to carry out this reaction with the naphthoate resulted in partial dehalogenation; Na o-iodobenzoate, but not the bromonaphthoate, is converted into the NO2-compound by NaNO2. Condensation could not be brought about between the bromonaphthoate and CHNa(CO2Et)2 or CHAcNa·CO₂Et, either dry or in EtOH, and Na 8-chloro-1-naphthoate is inert under the conditions studied. The following are described : 8-n-propoxy-, m.p. 176-177°, 8-n-butoxy-, m.p. 154-155°, 8-1menthoxy-, m.p. 206-207°, 8-phenoxy-, m.p. 139-140°, and 8-benzyloxy-, m.p. 125-126°, -1-naphthoic acids. H. A. P.

Stereochemistry of diphenyls. XXV. Relative interfering effects of the groups F, OMe,

F

Cl, and Br as determined by the relative rates of racemisation of 2'-substituted 2-nitrodiphenyl-6carboxylic acids. R. W. STOUGHTON and R. ADAMS. XXVI. Effect of substitution on rate of racemisation of optically active diphenyls. H. C. YUAN and R. ADAMS (J. Amer. Chem. Soc., 1932, 54, 4426-4434, 4434-4443).—XXV. Me 2bromo-3-nitrobenzoate (I), m.p. $78-78\cdot5^{\circ}$ (by esteri-fication of the acid), $o-C_{\rm c}H_{4}I\cdotOMe$, and Cu-bronze at 240-250° give (after hydrolysis) 2-nitro-2'methoxydiphenyl-6-carboxylic acid, m.p. 196.5-197° (corr.), resolved by brucine into the d-form, m.p. 196—197°, $[\alpha]_{11}^{m}$ +29.5° (initial) in EtOH [brucine salt (+0.5H₂O), m.p. 219—220°, m.p. (anhyd.) 223-224°]. 4-Chloro-3-iodotoluene and (I) similarly give 2:2'-dichloro-5:5'-dimethyldiphenyl, m.p. 85-86°, and 2'-chloro-2-nitro-5'-methyldiphenyl-6-carboxylic acid, m.p. 234-234.5° (corr.), which is resolved into d-, [a]²_D +18.6° in EtOH (brucine salt, m.p. 220-221°), and 1-forms, m.p. 234.5° (slight softening at 180°), $[\alpha]_{11}^{118} - 68.9^{\circ}$ (initial) in AcOH [brucine salt (+0.75H₂O), m.p. (anhyd.) 215-217°]. 4-Bromo-3iodotoluene, b.p. 145-150°/20 mm. (from the 4-NH2compound), and (I) afford 2'-bromo-2-nitro-5'-methyldiphenyl-6-carboxylic acid, m.p. 228-229° (corr)., resolved into d-, m.p. 226.5-228° (softens at 177°), [α]³⁰₁₀ +27.5° in EtOH (brucine salt, m.p. 228-229°), and 1-forms, m.p. 227-228° (softens at 177°), [a]¹¹³ -58.4° (initial) in AcOH [brucine salt (+H₂O), m.p. 203° (softens at 150°), m.p. (anhyd.) 219°]. 3-Iodo-4-fluorotoluene, b.p. 122–125°/30 mm. (from the 4-NH₂-compound), and (I) give 2'-fluoro-2-nitro-5'methyldiphenyl-6-carboxylic acid (II), m.p. 187-188° (corr.) [brucine salt ($+0.25H_2O$), m.p. 213—214.5° (softens at 150°), m.p. (anhyd.) 214—215°, $[\alpha]_{l_1}^n$ +15° (calc.) $\rightarrow -3\cdot4^\circ$ (5 hr.) in CHCl₃; quinine salt (+2H₂O), m.p. 135—140°, m.p. (anhyd.) 138—140°, $[\alpha]_{l_2}^n$ -125° (calc.) $\rightarrow -82\cdot5^\circ$ (5 hr.) in CHCl₃; strychnine salt, m.p. 194—196°, $[\alpha]_{l_2}^n$ -31·2° in CHCl₃], which acould not be obtained in an action form which could not be obtained in an active form. The rates of racemisation of the active acids in various solvents show that the interfering effect of the 2'substituent is Br>Cl>OMe>F. (II) warmed with conc. H₂SO₄ gives 4-fluoro-5-nitro-1-methylfluorenone, m.p. 204-205°.

XXVI. 3-Iodo-4-methoxytoluene, (I) (above), and Cu-bronze at 240-260° give (after hydrolysis) a little 6: 6'-dinitrodiphenic acid (III) and 2-nitro-2'-methoxy-5'-methyldiphenyl-6-carboxylic acid, m.p. 182-183°, resolvable into the l-form, m.p. 180—182°, $[\alpha]_{p}^{ss} - 20^{\circ}$ (initial) in EtOH (brucine salt, m.p. 146-150°). 4-Chloro-2-iodoanisole and (I) similarly give (III), 5:5'-dichloro-2:2'-dimethoxydiphenyl, m.p. 144.5-145.5°, and 5'-chloro-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 174—175°, which is resolvable into the 1-form, m.p. 173—175°, $[\alpha]_{b}^{ij}$ -115° (initial) in EtOH [brucine salt (+H₂O), m.p. 148-153°]. 4-Bromo-2-iodoanisole and (I) afford 5'-bromo-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 186-187° (Me ester, m.p. 148-149°), resolved into the l-form, m.p. 185-187°, [a]²⁶ -84° (initial) in EtOH (brucine salt, m.p. 162-165°), whilst 2-iodo-4-nitroanisole and (I) give 2:5'-dinitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 202-203°, resolvable into the l-form, m.p. 201–202°, $[\alpha]_{\mu}^{285}$ –93° (initial) in EtOH [brucine

salt (+3H₂O), m.p. 179-183°]. The rates of racemisation of the above active acids and of 1-2-nitro-2': 5'-dimethoxydiphenyl-6-carboxylic acid (A., 1932, 945) are compared with that of 2-nitro-2'-methoxydiphenyl-6-carboxylic acid (Part XXV). The halflife periods for the free acids in EtOH at 26° increase in the order : 5'-substituent=H, OMe, Me, Cl, Br, NO2. All the above brucine salts exhibit mutarotation, but the 5'-NO2-acid salt has a much smaller half-life period than the other four salts (which have approx. the same val.). The Na salts racemise less readily in H₂O (but more readily in EtOH) than the acids in org. solvents. The possible causes of the differences in the rates of racemisation of the free acids are discussed; the dipole moments of the *p*-substituted anisoles (*i.e.*, the variable part of the above acids, which are 4-substituted-2-2'-nitro-6'-carboxyphenylanisoles) parallel the rates of racemisation (these decrease with rise in the moment). There appears to be some relation between the rate of racemisation and the polarity of the 5-'group. H. B.

Phenacyl and p-bromophenacyl esters of monosubstituted benzoic acids. T. L. KELLY and H. W. HowARD (J. Amer. Chem. Soc., 1932, 54, 4383-4385).—The following are prepared essentially by Reid's method (A., 1919, i, 157; 1920, i, 480): (a) phenacyl esters: o-, m.p. $83 \cdot 2^{\circ}$, and m-, m.p. 113.4°, -bromobenzoates; o-, m.p. 83° , m-, m.p. 113.4°, -bromobenzoates; o-, m.p. 83° , m-, m.p. 116.4°, and p-, m.p. $87 \cdot 6^{\circ}$, -chlorobenzoates; o-, m.p. 71°, m-, m.p. 115.6°, and p-, m.p. 101° (decomp.), -iodobenzoates; o-, m.p. 124.5°, and m-, m.p. 104.5°, -nitrobenzoates; o-, m.p. 126°, m-, m.p. 146.5°, and p-, m.p. 126°, m-, m.p. 126°, m-, m.p. 106°, m-, m.p. 110.2°, m-, m.p. 126°, -chlorobenzoates; o-, m.p. 110.2°, m-, m.p. 100.6°, m-, m.p. 133.6°, and p-, m.p. 134°, -nitrobenzoates; m-, m.p. 168°, and p-, m.p. 134°, -nitrobenzoates; o-, m.p. 168°, and p-, m.p. 200°, -N-p-bromophenacyl-amidobenzoates are prepared, using an excess of $p-C_6H_4Br-CO-CH_2Br.$

Preparation of stereoisomeric methoxyphenylacetic acids by resolution of the racemic acid. E. BAMANN and J. M. PORTMANN (Arch. Pharm., 1932, 9, 513—519).—Crystallisation of the quinine (I), quinidine, cinchonine, or cinchonidine salts of dl-methoxyphenylacetic acid (modified prep.) gives the salt of the *d*-acid; the morphine (II) or strychnine salt leads to that of the *l*-acid. (I) and (II) (recryst. from H₂O) are most suitable for prep. of the active acids (cf. A., 1932, 269). R. S. C.

Benzylidenepyruvic acid. II. L. MUSAJO (Gazzetta, 1932, 62, 901—905; cf. A., 1889, 990).—The oily benzylidenepyruvic acid obtained by condensing PhCHO with AcCO₂H in presence of gaseous HCl becomes, when dried in vac. at 25—30°, an amorphous solid which cannot be freed from a trace of the acid $C_{27}H_{20}O_6$ (*loc. cit.*). It softens at 80° and on further heating decomposes; mol. wt. determination in AcOH indicates the formula $(C_{10}H_8O_3)_2$. The solid benzylidenepyruvic acid, m.p. $62-63^\circ$, obtained from PhCHO and AcCO₂H in alkali is $C_{10}H_8O_3$. The theory that the two acids are stereoisomerides is not supported. E. E. J. M.

Stereoisomerism of 2: 2'-disubstituted derivatives of diphenyl. II. A. CORBELLINI and M. ANGELETTI (Atti R. Accad. Lincei, 1932, [vi], 15, 968-973; cf. A., 1932, 849).-Crystallisation of the brucine salt of 2-a-hydroxy-a-methylethyldiphenyl-2'-carboxylic acid, m.p. 137° (lactone, m.p. 123°), from EtOH yields (1) a fraction, m.p. 217° , $[\alpha]_{1}^{24}$ $-35\cdot35^{\circ}$ in CHCl₃, and (2) a residue, m.p. 214°, $[\alpha]_{D}^{24}$ -33.49°. In CHCl₃ solution both salts are unstable, $[\alpha]_D$ gradually falling to that of the racemic salt, -1.87° . In the crystallisation of the racemic salt, the equilibrium dextro salt \implies lævo salt is displaced towards the right, owing to the lower solubility of the lawo salt. $2-\alpha$ -Hydroxy- α -ethyl-npropyldiphenyl-2'-carboxylic acid, obtained from Et H diphenate and MgEtI, has m.p. 140-141° (lactone, T. H. P. m.p. 137°; Na salt).

Oxidation products of 1:2:5-trimethylnaphthalene. I. M. HEILBRON and D. G. WILKIN-SON (J.C.S., 1932, 2809—2810).—The Me ester (I), m.p. 71—72°, obtained by action of MeOH-HCl on 3-methylacetophenone-2-carboxylic acid (II) (cf. A., 1931, 484) is the ψ -ester, $C_6H_3Me < \underbrace{CO}_{CMe(OMe)} > O$, and does not react with semicarbazide. (II) or its normal Me ester with NH₂OH gives the oxime anhydride, m.p. 174°. "Me 4-methylacetophenone-2-carboxylate" (A., 1931, 80) proves to be identical with (I); the ester, m.p. 78—79°, described at the same time is Me 3: 4-dimethylacetophenone-2-carboxylate, and the neutral substance, $(C_4H_4O)_n$, m.p. 70—71°, is the lactone of α -hydroxy- α -o-carboxy-

H. A. P.

Lichen substances. XV. Divaricatic acid. Y. ASAHINA and T. HIRAKATA (Ber., 1932, 65, [B], 1665—1668).—Concentration of the ethereal extract of *Evernia mesomorpha f. esoredioso*, Mull. Arg., leads to the isolation of a little *d*-usnic acid and divaricatic acid (I), m.p. 137° (Ac_2 derivative, m.p. 145—146°,

phenylethyl Me ketone (cf. A., 1931, 484).

OMe CO CO CO OH

prepared with Ac_2O containing a trace of CO_2H H_2SO_4 ; *Me* ester, m.p. OH 76°). (I) with excess of CH_2N_2 gives the cor-

responding Me_2 ether of the Me ester, m.p. 85°, hydrolysed by KOH-MeOH to 2:4-dimethoxy-6propylbenzoic acid, m.p. 64°, and Me 4-hydroxy-2methoxy-6-propylbenzoate, m.p. 121° [corresponding acid, m.p. 93° (also $+0.5H_2O$)]. H. W.

Constitution of the bile acids. XLIV. 6-(formerly 13)-hydroxyallocholanic acid. H. WIELAND and E. DANE (Z. physiol. Chem., 1932, 212, 41-49; cf. A., 1932, 1131).—Oxidation of hyodeoxycholic acid with CrO₃ in AcOH gives 3hydroxy-6-ketocholanic acid (I), m.p. 159-160° (from EtOAc), 160-162° (from dil. MeOH), 170-173° (needle clusters from EtOAc). Thermal decomp. of (I) gives 6-keto-3-cholenic acid (II), m.p. 128°.

Catalytic hydrogenation (PtO2) of (II) affords 6hydroxyallocholanic acid (II), m.p. 228° (Me ester, m.p. 95°), which with CrO₃ in AcOH gives 6-keto-cholanic acid, m.p. 151°, and on distillation 6-cholenic acid, m.p. 148—149°. Oxidation of (III) with HNO3 yields a tricarboxylic acid, m.p. 258°, probably allothilobilianic acid, since its anhydride, m.p. 196-199°, gives no depression in m.p. with thilobilianic anhydride. With Na in EtOH the semicarbazone of (I) gives a 3-OH-acid (IV), m.p. 175° (Me ester, m.p. 115-117°, 162° after recryst.), apparently a mixture of isomeric lithocholic acids. The free acid (3-hydroxyallocholanic acid) from the ester with m.p. 162° has m.p. 207-209°. This acid appears identical with a degradation product of chlorocholestane. If identity is established, the OH group of cholesterol in ring A must have the same position as in the bile acids, namely, C_3 not C_4 . (IV) with CrO_3 in AcOH gives 3-ketocholanic acid; distillation yields 3-cholenic acid. By Wieland and Weyland's method, (IV) gives lithobilianic acid. On boiling with aq. KOH, (I) gives an inversion product, m.p. 185-187°. J. H. B.

Hydrogen cyanide. IV. Gattermann's hydrogen cyanide aldehyde synthesis. L. E. HINKEL, E. E. AYLING, and W. H. MORGAN (J.C.S., 1932, 2793—2798).—At its b.p., but not at 40° or below, C_6H_6 interacts with HCN, HCl, and AlCl₃ to give PhCHO (14% of theory calc. on HCN). Apparently the compound AlCl₃,2HCN is stable < 40° (cf. A., 1898, i, 476). Yields of 85—100% of aldehyde are obtained from the simple homologues (PhMe, o-, m-, and p-C₆H₄Me₂, and mesitylene), the highest yields being obtained at 100°, and with AlCl₃ in excess of that needed to form the compound AlCl₃,2HCN. In no case does the yield exceed 100% calc. on the assumption that 2HCN enter into reaction, even with PhOMe or resorcinol, in which case AlCl₃ is unnecessary. This is in accordance with the hypothesis that chloromethyleneformamidine and not iminoformyl chloride is the active agent (cf. A., 1930, 1421); the reaction therefore follows the course : NH:CH-N:CHCl+C₆H₆ \longrightarrow NH:CH-N:CHPh $\xrightarrow{(2H,0)}$

Action of metallic oxides on benzotrichloride and benzylidene chloride. W. DAVIES and J. H. DICK (J.C.S., 1932, 2808—2809).—Interaction of pure ZnO with CPhCl₃ at 100° gives BzCl in 58% yield; technical ZnCl₂ (which contains ZnO), but not pure, also gives BzCl, although this is formed with pure ZnCl₂ in presence of H₂O. A little BzCl is also obtained with CdO or PbO, but not with Fe₂O₃; Al₂O₃ reacts only slightly, and P₂O₅ not at all. ZnF₂ (containing ZnO) gives BzF (65% of theory). With ZnO in C₆H₆ CHPhCl₂ gives PhCHO in 30% yield, but in absence of a diluent tarry products only are formed. H. A. P.

Action of bromine and iodine monochloride on some Schiff's bases. F. B. DAINS and G. A. LEH-MANN (Trans. Kansas Acad. Sci., 1931, 34, 297— 302).—N-Halogenation is effected in CCl_4 , $CHCl_3$, or glacial AcOH. ICl is a good iodinating agent, but contaminates the product with I. CH. ABS.

Colour reaction of thiocarbonyl compounds. H. W. SCHWECHTEN (Ber., 1932, 65, [B], 1734-1737) .- Thiocarbonyl compounds which are themselves coloured in some degree and are to some extent sol. in H₂O or MeOH give colorations with $\begin{array}{l} [Fe^{II}(CN)_5(NH_3)] Na_3. \quad Examples cited are CS(NHAc)_2, \\ CSCl_3, \quad Ph \cdot CS \cdot NH_2, \quad Ph \cdot CS \cdot NHPh, \quad CO_2H \cdot CS \cdot NHPh, \\ (CS \cdot NHPh)_2, \quad (CS \cdot NH \cdot C_6H_4 \cdot SO_3H)_2, \quad MeCS_2H, \quad Ph CS_2H, \\ 4 \cdot thio \cdot 2 : 6 \cdot dimethylpyrone, \quad and \quad CSPhMe. \quad Color- \\ \end{array}$ ations are darker in MeOH than in H₂O. The compounds pass by autoxidation into coloured FeIII derivatives. Dark blue colours are given when H₂S is passed into solutions or suspensions of the following aldehydes in $[Fe(CN)_5(NH_3)]Na_3$, reaction being attributed to the monomeric thioaldehyde : PhCHO, m- and p-C₆H₄Me·CHO, p-C₆H₄Ph·CHO, p-C₆H₄I·CHO, p-C₆H₄Br·CHO, o-, m-, and p-OH·C₆H₄·CHO, p-C₆H₄Me(OH)·CHO, p-OMe·C₆H₄·CHO, p-furfuraldehyde, CHMe:CH·CHO, citral. Lower fatty aldehydes yield no or pale pink colours; heptaldehyde and citronellal give pink and violet-red solutions in H₂O and MeOH, respectively. CH₂Ph·CHO and CH₂Ph·CH₂·CHO yield solutions which ultimately become blue. Ketones do not react. Incidence of the reaction appears to be conditioned by the presence of an ethylenic linking or an aromatic system vicinal to CHO. H. W.

Carbon rings. XX. Unsaturated 16- and 18-membered carbon rings of the type of civet-One. L. RUZICKA, M. STOLL, W. SCHERRER, H. SCHINZ, and C. F. SEIDEL (Helv. Chim. Acta, 1932, 15, 1459-1467; cf. A., 1932, 1134).-Electrolysis of a mixture of Me H adipate and undecenoic acid in MeOH-NaOMe gives Me_2 sebacate, $\Delta^{\alpha r}$ -eicosadiene, m.p. 30–32°, and Δ^{v} -pentadecenoic acid; the Me ester, b.p. 135-140°/0.5 mm., of the last-named acid gives in AcOH the ozonide, decomposed by Zn dust and H_2O to Me μ -aldehydododecane- α -carboxylate, this and 1_2 to be the p-tate-gated activity activity of π^2 , m.p. 101–103°, b.p. 130–150°/0·1 mm., which with $CH_2(CO_2H)_2$ and C_5H_5N at 80° gives Δ^{α} -tetradecene- $\alpha\xi$ -dicarboxylic acid (I), m.p. 122–125°, also obtained in very poor yield from α -bromohexadecane- $\alpha\pi$ -dicarboxylic acid and NPhMe₂. The Ce salt of (I) to 1^{\pm} $1^$ at 450° in vac. gives no cyclic ketone, but, amongst other products, Me dodecyl ketone; the acid is assumed to decompose to AcOH and dodecane-audicarboxylic acid, which further decomposes to give CO₂ and tridecoic acid; the latter with AcOH then gives the ketone. Me2 0-ketopentadecane-ao-dicarboxylate, when hydrogenated (PtO2) in AcOH at room temp., gives the θ -OH-ester, m.p. 55-56°, which with 2-C₁₀H₇·SO₃H (II) at 220° in CO₂ gives Me2 D7-pentadecene-ao-dicarboxylate, m.p. 172-174°/ 0.3 mm. The Y salt of the corresponding acid, m.p. 86-87°, at 350-400° gives, amongst other products, Δ⁸-cyclohexadecen-1-one, m.p. 23°, b.p. 193-195°/19 mm. (semicarbazone, m.p. 180-181°). Δ'-Undecenoic acid and Fe at $240-300^{\circ}$ give $di - \Delta^{\circ}$ -decenyl ketone, b.p. $160^{\circ}/0.2$ mm., m.p. $41-42^{\circ}$, yielding with O₃ in CCl4 1-ketoheptadecane-ar-dicarboxylic acid (20% yield), the Me, ester, m.p. 50-52°, of which is

hydrogenated (PtO₂) in AcOH to Me_2 *i-hydroxy-heptadecene-ax-dicarboxylate*, m.p. 51—53°, b.p. 212—215°/0.05 mm. This with (II) at 210—220° in vac. gives $Me_2 \Delta^{0}$ -heptadecene-ax-dicarboxylate, b.p. 180—190°/0.1 mm. The Y salt of the corresponding acid at 450° in vac. affords, amongst other products, Δ^{9} -cyclooctadecen-1-one, m.p. 37.5—38° (semicarbazone, m.p. 178—180°). R. S. C.

Haloform reaction. VII. Effect of ortho chlorine atoms. R. C. FUSON, J. W. BERTETTI, and W. E. Ross (J. Amer. Chem. Soc., 1932, 54, 4380-4383).-2:4:6-Trichloroacetophenone (I), m.p. $156-157^{\circ}$, from MgMeI and 2:4:6-C₆H₂Cl₃·COCl, and aq. NaOBr give 2:4:6-trichloro-aca-tribromoacetophenone, m.p. $126-127^{\circ}$, converted by 50°_{\circ} NaOH at 90° into 2:4:6-C₆H₂Cl₃·CO₂H. (I) and aq. NaOCl afford α :2:4:6-C₆H₂Cl₃·CO₂H. (I) and aq. NaOCl afford α :2:4:6-C₆H₂Cl₃·CO₂H. (I) and aq. NaOCl afford α :2:4:6-C₆H₂Cl₃·CO₂H. [also produced by prolonged action of NaOCl on (I)]. H. B.

Synthetical experiments in the tetraphenylallene series. E. BERGMANN, H. HOFFMANN, and H. MEYER (J. pr. Chem., 1932, [ii], 135, 245-266).p-Bromophenyl styryl ketone and MgPhBr give p-bromophenyl \$\$-diphenylethyl ketone, m.p. 137-139°. Definite products are not obtained from this or p-bromophenyl β -phenyl- β -p-bromophenylethyl ketone and MgPhBr or from p-bromophenyl p-bromo-styryl ketone, m.p. 185–186°, and $p-C_6H_4Br$ MgBr. Mg ßß-diphenylvinyl bromide (I) and di-p-tolyl ketone give yy-diphenyl-aa-di-p-tolylallyl alcohol, m.p. 149—150°, and $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -butadiene (II). Fluorenone and (I) afford (II) and 9-hydroxy-9-ββdiphenylvinylfluorene, m.p. 118-121° (decomp.), which is dehydrated by AcCl or hot AcOH to aadiphenyl-yy-diphenyleneallene, m.p. 139-140°. 4:4'-Dibromobenzophenone and (I) yield (II) and $\gamma\gamma$ -diphenyl-aa-di-p-bromophenylallyl alcohol, m.p. 91— 92° (meniscus formation), 110° (clear), dehydrated at 130° to aa-diphenyl-yy-di-p-bromophenylallene, m.p. 112-114°. aa-Diphenyl-yy-di-p-chlorophenylallene, m.p. 93-95°, is similarly prepared from yy-diphenylaa-di-p-chlorophenylallyl alcohol, m.p. 85°. β-Phenyl- β -p-bromophenylvinyl bromide does not react with Mg, whilst Mg β -phenyl- β -p-chlorophenylvinyl bromide [from Mg activated with EtBr and the less fusible -vinyl bromide (A., 1932, 506)] and p-chlorobenzophenone give $\alpha\delta$ -diphenyl- $\alpha\delta$ -di-p-chlorophenyl- $\Delta^{\alpha\gamma}$ butadiene, m.p. 230°, and an oil containing some allene derivative (since treatment with AcOH-HCl affords 6-chloro-1: 3-diphenyl-1-p-chlorophenyl- or 1-phenyl-1:3-di-p-chlorophenyl-indene, m.p. 139°). PhF, BzCl, and AlCl₃ give p-fluorobenzophenone (III), b.p. 159– 161°/13 mm., m.p. 45–47° [phenylhydrazone, m.p. 105°; oxime, m.p. 135°, converted by PCl_5 in Et_2O into benz-p-fluoroanilide, m.p. 187° (when prepared from p-C₆H₄F·NH₂ and BzCl)], whilst PhF, CCl₄, and AlCl₃ in CS₂ afford (after hydrolysis with conc. H2SO4) 4:4'-difluorobenzophenone, m.p. 109° (phenylhydrazone, m.p. 146—147°). CH₂Br·CO₂Et, (III), and Zn in C₈H₆ yield Et β -hydroxy- β -phenyl- β -pfluorophenylpropionate (IV), m.p. 86°, dehydrated by 85% HCO_2H at 150° to Et β -p-fluorophenylcinnam-

ate, b.p. 193-194°/11 mm., m.p. 61°, which with MgPhBr affords 6-fluoro-3: 3-diphenyl- or 3-phenyl-3p-fluorophenyl-hydrindone, m.p. 120-122° (the Cl-analogue, m.p. 111-112°, is similarly obtained by way of Et B-hydroxy-B-phenyl-B-p-chlorophenylpropionate, m.p. 69°, and Et β -p-chlorophenylcinnamate, b.p. 210–212°/13 mm.). The following are prepared as (IV): Et β-hydroxy-ββ-di-p-chlorophenyl-, m.p. 102°, -β-phenyl-β-p-bromophenyl-, m.p. 93°, -ββ-di-p-bromo-phenyl-, m.p. 111°, -β-phenyl-β-p-iodophenyl-, m.p. 75°, and $-\beta\beta$ -di-p-tolyl,- m.p. 81—82° [free acid, m.p. 163—164° (decomp.)], -propionates. These are dehydrated by HCO₂H (unless stated otherwise) to Et hydrated by HOO_2H (timess stated otherwise) to D_2 p-chloro- β -p-chlorophenyl-, m.p. 65°, Et β -p-bromo-phenyl-, b.p. 220—222°/12 mm., Et p-bromo- β -p-bromophenyl-, m.p. 80—81°, Et β -p-iodophenyl-, m.p. 100—102°, and Et β -p-tolyl-p-methyl-, b.p. 218°/17 mm. (free acid, m.p. 168-170°), -cinnamates, respectively; the last-named ester is best prepared by dehydration with HCl in EtOH-C₆H₆ in presence of Na₂SO₄. Et β -hydroxy- $\beta\gamma$ -diphenylbutyrate, m.p. 60-62° (from deoxybenzoin, CH2Br•CO2Et, and Zn in C_6H_6), is dehydrated (HCO₂H) to the *Et* ester, b.p. 211°/15 mm., of $\beta\gamma$ -diphenvl- Δ^{β} -butenoic acid. H. B.

Ease of substitution of aromatically bound hydrogen atoms. II. J. VON BRAUN and A. FRIEDSAM (Ber., 1932, 65, [B], 1680-1686; cf. A., 1929, 562).--Experiments on the mode of ring-closure of dibenzylacetyl chlorides differently substituted in the two Ph groups show that the readiness of substitution of the H atom diminishes in the sequence propionyl chloride is converted by AlCl₃ in CS₂ into a mixture of the two possible benzylhydrindones, C₁₆H₁₃OCl, b.p. 178-185°/0.2 mm. (semicarbazone, m.p. 175-192°; oxime, m.p. 80-102°), oxidised by CrO₃ in AcOH to phthalic acid containing a little 3-chlorophthalic acid and m-chlorobenzoic acid containing a little BzOH. Et benzyl-m-bromobenzylmalonate, b.p. 199-202°/0.3 mm., is transformed successively into the acid, m.p. 175°, and a-m-bromobenzyl-β-phenylpropionic acid, b.p. 215-218°/0·3 mm., m.p. 92°; the corresponding chloride gives a ketone mixture, b.p. $193-197^{\circ}/0.5$ mm. (semicarbazone, m.p. $170-182^{\circ}$; oxime, m.p. $99-120^{\circ}$), oxidised to monocarboxylic acids, mainly $C_{6}H_{4}Br \cdot CO_{2}H$, and dicarboxylic acids, preponderatingly C6H3Br(CO2H)2. For comparison, 5-bromo-1-hydrindone is condensed with PhCHO to 5-bromo-2-benzylidene-1-hydrindone, m.p. 194°, hydrogenated in presence of Pd-C to 5-bromo-2-benzyl-1-hydrindone, m.p. 149° (semicarbazone, m.p. 184°). Similarly, 1-hydrindone and $m - C_6H_4Br$ -CHO afford 2 - m - bromobenzylidene - 1hydrindone, m.p. 149°, hydrogenated to 2-m-bromobenzyl-1-hydrindone, b.p. $180-181^{\circ}/0.2$ mm. (semi-carbazone, m.p. 189°). Et m-chlorobenzyl-m-bromo-benzylmalonate, b.p. $222-226^{\circ}/0.7$ mm., from $C_6H_4Cl\cdotCH_2CH(CO_2Et)_2$ and $m\cdot C_0H_4Br\cdot CH_2Br$, yields successively the corresponding acid, m.p. 175°, and a-m-bromobenzyl-3-m-chlorophenylpropionic acid, b.p. 235°/0·3 mm., m.p. 98—100°. Its chloride yields a ketone mixture, b.p. 237—245°/1 mm., m.p. 64—72° (semicarbazone, m.p. 134-160°; oxime, m.p. 92123°), the monocarboxylic acids from which contain about 70% of m-C₆H₄Br·CO₂H and the dicarboxylic acid about 70% of C₆H₃Cl(CO₂H)₂. Et benzyl-mfluorobenzylmalonate, b.p. 214—216°/12 mm., from CH₂Ph·CH(CO₂Et)₂ and m-C₆H₄F·CH₂Br, gives the corresponding acid, m.p. 156—158°, and m-fluorobenzyl-β-phenylpropionic acid, b.p. 208—212°/12 mm., m.p. 83°. The mixture of ketones from the chloride has b.p. 200—206°/7 mm. (semicarbazone, m.p. 152— 170°; oxime, m.p. 82—96°), and yields mixtures of mono- and di-carboxylic acids both containing about equal proportions of fluorinated and unsubstituted acids. Et m-chlorobenzylmalonate and p-C₆H₄Me·CH₂Br afford Et m-chlorobenzyl-p-methylbenzylmalonate, b.p. 199—203°/0·3 mm. (acid, m.p. 140—156°), whence a-m-chlorobenzyl-β-p-tolylpropionic acid, b.p. 190—192°/0·2 mm., m.p. 65°. The mixture of ketones, b.p. 174—178°/0·2 mm. (semicarbazone, m.p. 235—239°; oximo, m.p. 152—159°), is oxidised to a small amount of terephthalic acid, much m-C₆H₄Cl·CO₂H, much trimellitic acid, and little C₆H₃Cl(CO₂H)₂.

2:3-Benzanthrone and 2:3-benzanthranyl acetate. E. DE B. BARNETT and R. A. LOWRY (Ber., 1932, 65, [B], 1649—1650).—2: $3 \cdot C_{10}H_6(CO)_2O$ is converted by C_6H_6 and AlCl₃ at room temp. into 3-benzoyl-2-naphthoic acid, m.p. 210°, reduced by Zn dust, NH₃, aq. NaOH, and a little CuSO₄ to 3benzyl-2-naphthoic acid (I), m.p. 204°. (I) is transformed by ZnCl, at 175° but not by H₂SO₄ into 2:3benzanthrone, m.p. 184°, which, contrary to Fieser (A., 1931, 1064), is converted by Ac₂O and C₅H₅N at 100° into 2: 3-benzanthranyl acetate, m.p. 213°. Tetrahydro-2: 3-benzanthrone, best prepared by reduction of the quinone with Al and conc. H₂SO₄, similarly yields tetrahydro-2: 3-benzanthranyl acetate, m.p. 175° Tetrahydronaphthoylbenzoic acid is obtained in 97% yield by gradual addition of AlCl₃ to $o - C_6 H_4(CO)_2 O$ H. W. and tetrahydronaphthalene in $C_2H_2Cl_4$.

Anionotropic and prototropic changes in 4hydroxycyclopentenones. H. BURTON and C. W. SHOPPEE (Chem. and Ind. 1932; 981).—Acetylation $(Ac_2O-H_2SO_4)$ of 4 - hydroxy - 3 : 4 - diphenyl-5 : 5-dimethyl- Δ^2 -cyclopentenone (I) is considered to give 2-acetoxy - 3: 4 - diphenyl - 5: 5 - dimethyl - Δ^3 - cyclo pentenone (II), m.p. 137° [and not the acetate of (I) as stated by Gray (J.C.S., 1909, 95, 2131, 2138)], as the result of an anionotropic change. The conthe result of an anionotropic change. version of (II) into 2-hydroxy-3: 4-diphenyl-5: 5dimethyl- Δ^2 -cyclopentenone (III) by EtOH-KOH (Gray, loc. cit.) would then involve a prototropic change (concurrent with hydrolysis). Conclusive evidence for these tautomeric changes is furnished by the observation that (II) and 2:4-dinitrophenylhydrazine in EtOH-H₂SO₄ give 2-ethoxy-3: 4-diphenyl - 5 : 5 - dimethyl - Δ^3 - cyclopentenone - 2 : 4 - di nitrophenylhydrazone, m.p. 182° (decomp.), which differs from the 2:4-dinitrophenylhydrazone, m.p. 205°, of the Et ether of (III) and the 2:4-dinitrophenylhydrazone, m.p. 204° (decomp.), of the Et ether of (I) [obtained by ethylating (I) with EtI and "activated" Ag_2O]. The results of Allen and Spanagel (following abstract) are considered to be (partly) inconclusive. H. B.

Reactions of anhydroacetonebenzils with halogen compounds. C. F. H. Allen and E. W. SPANAGEL (J. Amer. Chem. Soc., 1932, 54, 4338-4347).—Anhydroacetonebenzil (4 - hydroxy - 3 : 4 - di phenyl- Δ^2 -cyclopentenone) (I) (Japp et al., J.C.S., 1899, 75, 1017) and AcCl (or SOCl₂, PCl₃, POCl₃, or AlCl₃ in C₆H₆) give 4-chloro-3: 4-diphenyl- Δ^2 -cyclo-pentenone (II), m.p. 121°, converted by KOAc, AgOAc, or Pb(OAc), in MeOH into 4-methoxy-3: 4-diphenyl- Δ^2 cyclopentenone (III), m.p. 126° (oxime, m.p. 173°; $5:5-Br_2$ -derivative, m.p. 175°), which affords two benzylidene derivatives, m.p. 124° and 160°, both of which are converted by Ac₂O-H₂SO₄ into 4-acetoxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone (Gray, J.C.S., 1909, 95, 2131). (III) is reduced by red P and HI to 3:4-diphenyl- Δ^3 -cyclopentenone. The chloride obtained from (I) and HCl by Japp (J.C.S., 1887, **51**, 420) is considered to be 2-chloro-3:4-diphenyl- Δ^4 -cyclopentenone, m.p. 128° (IV) (2:4-dinitrophenylhydrazone, m.p. 217°); the 2-Br-analogue has m.p. 113°. (II) and (IV) are both converted by EtOH-KOH into the compound, $C_{34}H_{24}O_2$ (Japp, loc. cit.), which is also obtained from (I) and PCl₃ in absence of solvent, by reduction of (III) with Sn and HCl, and from (II) and EtOH. (I) and SO₂Cl₂ give mixture of 5-chloro-4-hydroxy-3: 4-diphenyl- Δ^2 cyclopentenone, m.p. 194° [acetate, m.p. 159°, formed together with a compound, $C_{34}H_{22}O_2Cl_2$, m.p. 217° (decomp.), by the action of $Ac_2O-H_2SO_4$], and a compound, probably $\begin{pmatrix} \text{CCl:CPh} \\ \text{CO-CCl}_2 \end{pmatrix} > \text{CPh} \cdot \begin{pmatrix} 2 & 2 & 2 & 4 \\ 2 & 0 & 4 \end{pmatrix}$, m.p. 129°. (I) and Br give (cf. Japp) 5-bromo-4-hydroxy-3:4diphenyl-∆²-cyclopentenone, m.p. 198° [acelate, m.p. 148°, formed together with a compound, C₃₄H₂₂O₂Br₂, m.p. 212° (decomp.), by Ac₂O-H₂SO₄].

ββ-Dimethylanhydroacetonebenzil (4-hydroxy-3:4diphenyl-5:5-dimethyl- Δ^2 -cyclopentenone) (V) and SOCl₂ give 4-chloro-3:4-diphenyl-5:5-dimethyl- Δ^2 cyclopentenone, m.p. 133°, which with KOH, KOAc, or AgOAc in EtOH regenerates (V), with AgOAc in AcOH affords the 4-OAc-derivative (Gray, loc. cit.), and with AgOAc in MeOH gives 4-methoxy-3:4diphenyl-5:5-dimethyl- Δ^2 -cyclopentenone, m.p. 144°. H. B.

Condensations and ring closures in the naphthalene series. III. peri[=3:4]-Succinylacenaphthene. L. F. FIESER and (in part) M. A. PETERS. IV. Synthesis of [8:9-Jacephenanthrene. L. F. FIESER and M. A. PETERS (J. Amer. Chem. Soc., 1932, 54, 4347-4356, 4373-4379).-III. Acenaphthene, succinic anhydride, and AlCl₃ in PhNO₂ at 0° give 78% of β -3-acenaphthoylpropionic acid (I), m.p. 208° (decomp.) [Me ester (II), m.p. 89° (oxime, m.p. 146°)], and 15% of β -1-acenaphthoylpropionic acid (III), m.p. 181° (Me ester, m.p. 126°); at -15° the corresponding % are 87 and 5. Oxidation of (I) with KMnO₄ gives (according to the conditions used) naphthalene-1:4:5-tricarboxylic acid [ahydride (Me ester, m.p. 222°)] or an acid, C₁₅H₁₀O₄, m.p. 259°, or mellophanic acid [also formed by oxidation of (III)]. (II) heated with AlCl₃-NaCl at 150° affords 3:4-succinylacenaphthene (IV), m.p. 180° [dioxime, decomp. when heated (diacetate]], reduced (Wolff-Kishner) to 3:4-tetramethyleneacenaphthene, m.p. 138°, and oxidised (Na₂Cr₂O₇-AcOH) to naphthalene-1:4:5:8-tetracarboxylic acid. Compounds of type (IV) could not be obtained from β -2-methyl-1-



naphthoylpropionic acid, m.p. 168° [Me ester, m.p. 85° (β -Br-derivative, m.p. 81°)], which appears to be identical with the β -6-methyl-2-naphthoylpropionic acid of Haworth et al. (A., 1932, 839), β-2: 7-dimethyl-1-naphthoylpropionic acid, m.p. 130° , and β -2-methoxy-1-naphthoylpropionic acid, m.p. 152° , which are prepared from succinic anhydride and $2 \cdot C_{10}H_7Me$, 2:7- $C_{10}H_6Me_2$, and $\beta \cdot C_{10}H_7$ OMe, respectively. $\beta \cdot 2$ -Hydroxy-1-naphthoylpropionic acid has m.p. 232°. Acenaphthene and glutaric anhydride give a poor viold of an 3-acenaphthoulbuturic acid, m.p. 201° yield of γ -3-acenaphthoylbutyric acid, m.p. 201° (Me ester, m.p. 120°). Me β -bromo- β -3-acenaphthoyl-propionate, m.p. 113°, from (II) and Br in CHCl₃, with NaOAc in AcOH at 100° gives Me β -3-acenaphth-oylacrylate, m.p. 113° (free acid, m.p. 165°, also obtained in poor yield from acenaphthene and maleic anhydride), which with $AlCl_3$ -NaCl at 140° affords about 5% of (probably) the *keto-acid* (V), m.p. 214° (decomp.). Maleic anhydride could not be condensed with $C_{10}H_8$. Anthracene, succinic anhydride, and AlCl₃ in PhNO₂ give (cf. G.P. 376,635) a complex mixture of substances including β-2-anthroylpropionic acid, m.p. 228° (Me ester, m.p. 148°; quinone, m.p. 207°). γ -2-Anthrylbutyric acid has m.p. 197°. IV. Clemmensen reduction of Me β -3-a

β-3-acenaphthoylpropionate gives y-3-acenaphthylbutyric acid, m.p. 148°, the chloride, m.p. 83°, of which with $AlCl_3$ in PhNO₂ at 0° affords 1-keto-1:2:3:4-tetrahydro-8:9-acephenanthrene (VI), m.p. 147° (oxime, m.p. 225°; phenylhydrazone, m.p. 206°; semicarbazone, m.p. 302°). Oxidation of (VI) with dil. HNO₃ at



160° gives phenylglyoxyldicarboxylic acid (oxidised by KMnO4 to hemimellitic acid), whilst reduction (Clemmensen or Wolff-Kishner) affords 1:2:3:4tetrahydro-8: 9-acephenanthrene (VII), m.p. 92.5° (picrate, m.p. 112°). Distillation of (VI) with Zn dust and subsequent dehydrogenation with S gives 8:9-acephenanthrene, m.p. 106° (picrate, m.p. 145°), oxidised by Na₂Cr₂O₇-AcOH to phenanthrene-8:9dicarboxylic anhydride. (VI) and an excess of MgPhBr yield 1-phenyl-3: 4-dihydro-8: 9-acephenanthrene, m.p. 144°; with MgMeI, 1-methyl-, m.p. 159°, or 1-methyl-1:2:3:4-tetrahydro-, m.p. 133° (decomp.), -8: 9-acephenanthrene is obtained, according to the conditions used. Succinic anhydride,

(VII), and AlCl₂ in PhNO₂ give 5-B-carboxypropionyl-1:2:3:4-tetrahydro-8:9-acephenanthrene, m.p. 218° (Me ester, m.p. 146°), reduced (Clemmensen) to the 5-y-carboxypropyl derivative, m.p. 158°, and cyclised (by way of the chloride) to 1-keto-5: 6-tetramethylene-1:2:3:4-tetrahydro-8:9-acephenanthrene, m.p. 172°.

 β -1-Acenaphthoylpropionic acid is reduced (Clemmensen) to γ -1-acenaphthylbutyric acid, m.p. 155°, which is cyclised (by way of the chloride) to 1-keto-1:2:3:4tetrahydro-5: 10-aceanthrene (VIII), m.p. 145°, con-vertible by distillation with Zn dust into aceanthrene, m.p. 113° (picrate, m.p. 120°) (cf. Liebermann and Zsuffa, A., 1911, i, 387). H. B.

Synthesis of 2:3-dimethoxyfluorenone. B. REICHERT (Arch. Pharm., 1932, 9, 551-553).-3:4-Dimethoxybenzophenone and 65% HNO3 at room temp. give the 6-NO2-derivative, m.p. 137°, the constitution of which is proved by conversion into the 6-carboxylic acid, which yields 2:3-dimethoxyanthraquinone. Reduction (H_2, PtO_2) gives the $6-NH_2$ -compound, m.p. 201° (decomp.) (Ac derivative, m.p. 188°), which by diazotisation and boiling yields 2:3-dimethoxyfluorenone, m.p. 164° (cf. A., 1907, i, 142). R. S. C.

Mixed benzoins. IX. meso-Chloro-deriv-atives. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1932, 54, 4359-4365).-Benzoin, 4'-methoxy-, 2-chloro-4'-methoxy-, and 2-chloro-3': 4'-dimethoxybenzoins (for nomenclature see A., 1932, 1034) are converted by PCl_5 in C_6H_6 into Ph aa-dichloro-benzyl ketone, anisyl aa-dichlorobenzyl ketone, m.p. 81° (accompanied by a little p-methoxytolane tetra-chloride, m.p. 153°), anisyl $\alpha \alpha$: 2-trichlorobenzyl ketone, m.p. 109°, and 3: 4-dimethoxyphenyl aa: 2-trichlorobenzyl ketone, m.p. 120°, respectively; the corresponding benzils are intermediates. These ketones are reduced (H2, PtO2, EtOH) to Ph a-chlorobenzyl, m.p. 68°, impure anisyl α -chlorobenzyl, anisyl α : 2-dichlorobenzyl, m.p. 75°, and 3: 4-dimethoxyphenyl α : 2-dichlorobenzyl, m.p. 99°, ketones, respectively (and then to the aryl benzyl ketones), which with EtOH-NaOEt regenerate the original benzoins. Ph aa-dichlorobenzyl ketone and EtOH-NaOEt give BzOEt and PhCHO (from CHPhCl.) $PhCO \cdot CPhCl_2 + EtOH \longrightarrow BzOEt + CHPhCl_2$ side reaction is $PhCO \cdot CPhCl_2 + EtOH + 2NaOEt \longrightarrow CHPh(OEt)_2 + BzOEt + 2NaCl.$ The other dichloro-

benzyl compounds behave similarly. H. B.

Molecular rearrangements of α -glycols. IV. Influence of substituents on the reactivity of a pinacone. Reduction of 4:4'-dimethoxybenzo-phenone. V. Relative electronegativities of p-methoxy- and p-ethoxy-phenyl radicals. M. MIGITA (Bull. Chem. Soc. Japan, 1932, 7, 334-340, 341-345).-IV. Reduction of 4:4'-dimethoxybenzophenone (I) with Zn dust and hot or cold AcOH gives anisyl trianisylmethyl ketone (II), m.p. 140-141° (decomp.), the rearrangement product of stetra-anisylethylene glycol (III), decomp. 176° (slow), 181° (rapid heating) (cf. Bouvet, A., 1915, i, 766), which is prepared by reduction of (I) with EtOH in sunlight. The ready conversion of (III) into (II) by AcCl or warm AcOH is in accordance with the mechanism previously proposed (A., 1929, 448). Dianisylcarbinol and (I) are produced when (III) is heated.

V. Reduction of 4-methoxy-4'-ethoxybenzophenone, m.p. 106—107° (from PhOEt, p-OMe·C₆H₄·COCl, and AlCl₃ in CS₂), with Zn dust and hot AcOH gives anisyl anisyldi-p-ethoxyphenylmethyl ketone, m.p. 160°, also formed by reduction with EtOH in sunlight, thus showing that p-OEt·C₆H₄· is more negative than p-OMe·C₆H₄·. H. B.

Constitution and reactivity. I. Sulphonation of anthraquinone. II. Replacement of the sulphonic acid group in anthraquinone by hydrogen or chlorine. K. LAUER (J. pr. Chem., 1932, [ii], 135, 164-181, 182-192).-I. A kinetic study of the sulphonation of anthraquinone in the β - and, under the influence of Hg salts, in the α -position. From the val. of the velocity coeffs. (k_1, k_2) at different temp. (T_1, T_2) , the value of q and α are calc. by the equations $q = RT_1T_2/(T_1 - T_2) \cdot \log_e k_1/k_2$, and $\log_e k_1 = \log_e \alpha - q/RT_1$. Further evidence is offered of the absence of rank baseline in the second the absence of a-sulphonation in complete absence of Hg and its repression by NaCl; it occurred to a slight extent in the β -monosulphonation studied, the ratio of α : β -SO₃H being unaltered by wide variations in temp. and concn. of SO₃. The extent of 2-sulphonation was determined by measuring the unreacted anthraquinone; the reaction is approx. bimol. Further sulphonation of the 2-SO3H gave only 2:6- and 2:7-disulphonic acids, which were not interconvertible under the conditions used; the proportions formed were measured by mixed-m.p. determinations of the derived dichloroanthraquinones, and the vals. of q calc. on the assumption that α is equal in the two cases.

 α -Sulphonation is approx. bimol., the val. of k depending on the concn. of Hg in the reaction medium; this is higher the less is the SO₃ content, and β sulphonation is almost completely inhibited by HgSO₄ in 5% oleum. The Hg added is effective only as HgSO₄, and if added as metal or as another salt much β -sulphonation occurs in the early stages of the reaction. Further sulphonation in presence of Hg is essentially similar in these respects, and was studied in a similar manner to the β -disulphonation. Marked differences were found in the reaction consts. in the α - and β -series, corresponding with the differences in reaction mechanism.

II. The hydrolysis of anthraquinone-1- and -2sulphonic acids, and -1:5-, -1:6-, -1:7-, and -1:8disulphonic acids by means of aq. H_2SO_4 in presence of $HgSO_4$, and the conversion of these, and also of the -2-mono- and -2:6- and -2:7-disulphonic acids, into the corresponding chloroanthraquinones by the action of Cl₂ on a boiling aq. solution, are studied kinetically. The former reaction leads in the case of the 1-monosulphonic acid to anthraquinone, and with the $\alpha\beta$ -disulphonic acid to anthraquinone-2sulphonic acid. In both reactions similar vals. of α (but varying vals. of q) are observed for the α and β -derivatives, respectively, but in the latter reaction where the β -SO₃H groups are displaced, although much slower than are the α -groups, there is a considerable difference in the vals. of α for the two series. H. A. P.

Constitution and reactivity. III. Replacement of sulpho-groups in anthraquinones by the amino-group. K. LAUER (J. pr. Chem., 1932, [ii], 135, 204—208).—Vals. of $k \times 10^4$, activation energies, and reaction coeffs. (cf. preceding abstract) for the reactions (involving replacement of one SO₃H by NH₂) between 1 mol. of 0·1N-solutions of anthraquinone-1- and -2-sulphonic, and -1: 5-, -1: 8-, -2: 6-, and -2: 7-disulphonic acids and 20% aq. NH₃ (100 mols.) in presence of BaCl₂ (1·5 mols.) and NH₄Cl (10 mols.) at 160—200°, are given. A similar reaction coeff. is found for all the acids containing the 1-SO₃H group; this is much smaller than the coeff. (also similar) for the 2-substituted acids. H. B.

Nitration of 3-methoxyacenaphthenequinone and 2-methoxynaphthalic anhydride. R. I. DAVIES, I. M. HEILBRON, and F. IRVING (J.C.S., 1932, 2715-2717).--3-Methoxyacenaphthenequinone (I) is converted by HNO₃ in H_2SO_4 at 10–30° into its 7-NO₂-derivative, m.p. 264–265°, the orientation of which follows from its oxidation by CrO₃-AcOH to 6-nitro-2-methoxynaphthalic anhydride (II), m.p. 297-298°, which gives 6-nitro-2-naphthyl Me ether (Chem. News, 1896, 74, II, 302) with Cu-bronze and quinoline at the b.p. CrO3-AcOH oxidises (I) to 2-methoxynaphthalic anhydride (III), which with Hg(OAc)₂ gives 8-hydroxymercuri-7-methoxy-1-naphthoic anhydride. This with Br in AcOH gives 8-bromo-7-methoxy-1-naphthoic acid, m.p. 195° (decomp.), and with 3N-HCl at 100° gives 7-methoxy-1-naphthoic acid, which is readily demethylated by conc. HCl. Nitration of (II) in H_2SO_4 gives (II), converted by mercuration and hydrolysis into 3-nitro-7-methoxy-1naphthoic acid, m.p. 240-241°. H. A. P.

Identity of diffractaic acid with the dirhizonic acid of Hess. Y. ASAHINA and F. FUZIKAWA (Ber., 1932, 65, [B], 1668; cf. A., 1932, 396, 613).—Direct comparison of the acids, their Me esters, and the Me esters of the Me ethers establishes identity. It is proposed to retain the name diffractaic acid. H. W.

Tephrosin. II. isoTephrosin. E. P. CLARK and H. V. CLABORN (J. Amer. Chem. Soc., 1932, 54, 4454—4456).—isoTephrosin (I), $C_{23}H_{22}O_7$, m.p. 252°, isomeric with tephrosin (II), has been isolated from Peruvian cubé root. (I) is dehydrated by Ac_2O -NaOAc or EtOH-HCl to dehydrodeguelin and oxidised (KMnO₄ in COMe₂) to isotephrosindicarboxylic acid, $C_{23}H_{22}O_{11}$ (+0.5H₂O), m.p. 187°, which when heated with boiling Ph₂O for 30 sec. gives tephrosinmonocarboxylic acid (A., 1932, 950). (I) and (II) probably differ in the orientation of the OH group. H. B.

Polyterpenes and polyterpenoids. LXXVI. Dihydro- α -elemolic acid and δ -elemic acid and the tetrahydro-derivative of the latter. L. RUZICKA, R. L. WAKEMAN, M. FURTER, and M. W. GOLDBERG. LXXVII. Dehydration of betulin, gypsogenin, and siaresinolic acid. Hydroxysapotalin. L. RUZICKA, H. BRUNGGER, R. EGLI, L. EHMANN, and M. W. GOLDBERG (Helv. Chim. Acta, 1932, 15, 1454—1459, 1496—1506; cf. A., 1932, 1254).—LXXVI. Pure α -elemolic acid (I), m.p. 217—219°, $[\alpha]_p - 27°$ in MeOH, yields, when hydrogenated (PtO₂) in EtOAc at 50—60°, dihydro- α elemolic acid, dimorphic, m.p. about 232°, $[\alpha]_p - 18.7°$ in MeOH, $-14\cdot5^{\circ}$ in CHCl₃ [Me ester, a mixture, m.p. 119–121° after sintering at 100°, $[\alpha]_{\rm b} -6^{\circ}$ in CHCl₃, contains one ethylenic linking (R)], low- and high-(about 258–263°) -melting mixtures. Crude (I) gives dihydro-acids, m.p. 284–287°, $[\alpha]_{\rm b} -53^{\circ}$ in MeOH–CHCl₃, and m.p. 239–241°, $[\alpha]_{\rm b} +39^{\circ}$ in CHCl₃. All these acids are $C_{30}H_{50}O_3$. Previous results (A., 1931, 1067) are thus confirmed and the contentions of Mladenović (A., 1932, 397) refuted. δ -Elemic acid (II), $[\alpha]_{\rm b} +28\cdot6^{\circ}$ in MeOH, is hydrogenated (PtO₂) in EtOAc (1 mol. of H₂ is absorbed at room temp. and 1 at 50°) to tetrahydro-8-elemic acid, $C_{30}H_{50}O_3$, m.p. 236–237°, $[\alpha]_{\rm b}$ about +37° in MeOH, +55° in CHCl₃ [axime, m.p. 233–234°; Me ester, m.p. 110–111° after sintering at 98°, saturated (R) (oxime, m.p. 191–192°)]. (II) is thus a diethylenic, tetracyclic keto-acid.

LXXVII. The low-boiling fraction of the Sedehydrogenation products from betulin (I) contains $1:2:3:4-C_6H_2Me_4$ (II). Gypsogenin and Se at 350° give $2:7-C_{10}H_6Me_2$, sapotalin, an oily (possibly impure) hydrocarbon, $C_{14}H_{16}$ (picrate, m.p. 139–140°; styphnate, m.p. 135—136°), hydroxysapotalin (III), a hydrocarbon, probably C₂₇H₂₈ (possibly a dinaphthyl-ethane), m.p. 117-118° (corr.) (styphnate, m.p. 223-224°; picrate, m.p. 207-209°), and a hydrocarbon (IV), C25H20, m.p. 304° (corr.), 294-295° (uncorr.). Siaresinolic acid gives (II), (III), (IV), and a hydrocarbon (V), $C_{25}H_{24}$ (lit. $C_{27}H_{28}$), m.p. 141—141.5° (uncorr.), 143° (corr.) (lit. 138°) [dipicrate, new m.p. 212° (corr.), distyphnate, m.p. 226° $206.5 - 207.5^{\circ}$ (uncorr.); (corr.); compound with 2C₆H₃(NO₂)₃, m.p. 227° (corr.), 221-222° (uncorr.)]. (III) [Me ether (by Me_2SO_4), m.p. 89.5–90° (compound with $C_6H_3(NO_2)_3$, m.p. 145-146°)] with Zn dust at 400° in N₂ gives $1:2:7-C_{10}H_5Me_3$. It is contended that the OH group of (III) is in position 2 or 13 of the general triterpene formula (VI). The formulæ shown are suggested for (I), (V), and hederagenin (VII). (IV) is possibly a trimethylpicene.



Oxide of carotene.H. VON EULER, P. KARRER,
and O. WALKER (Helv. Chim.
Acta, 1932, 15, 1507—1510).—
β-Carotene (I) and BzO₂H (1 mol.)
in CHCl₃ give a small amount
of a substance, m.p. (impure)
180° (possibly isocarotene), and
a 20% yield of carotene oxide,
m.p. 161°, believed to be (II),

since its absorption (max. at 486, 456, and 427 mµ in

 CS_2 , and 465, 437, 410, 390, 364, and 320 m μ in CHCl₃) closely resembles that of (I). R. S. C.

Neutral products of oxidation of pinene. II. K. SEAWIŃSKI and W. ZACHAREWICZ (Rocz. Chem., 1932, 12, 854-861).-The fraction, b.p. 88-97°/2 mm., of the neutral oxidation products of pinene yields norpinic acid, originating from pinononaldehyde, and a dibromide, $C_{10}H_{14}O_2Br_2$ (A), m.p. 116°, on treatment with NaOBr; with NaOEt the products are pinononic acid and a keto-alcohol, $C_{10}H_{16}O_2$ (B), m.p. 35°, b.p. 98-99°/2 mm. (semicarbazone, m.p. 204°, 1and i-benzylidene derivatives, m.p. 78-79° and 98°), which is also obtained by eliminating Br from (A). Since pinene glycol yields *l*-pinononaldehyde on oxidation with $K_2Cr_2O_7$ it is concluded that the original neutral fraction consists of pinene glycol, l-pinononaldehyde, and (B). R. T.

Derivatives of 4-methylcamphor in relation to its structure. S. NAMETKIN and L. BRÜSSOF (J. pr. Chem., 1932, [ii], 135, 155–163).—4-Methylcamphor (I) is converted by NaNH₂ and amyl nitrite in C₆H₆ into its oximino-derivative, m.p. 174–175°, which is hydrolysed by HCl and CH₂O to 4-methylcamphorquinone, m.p. 199–200°, the hydrazone, m.p. 108–109°, of which is oxidised by yellow HgO in light petroleum to diazo-4-methylcamphor (II), m.p. 87–90°. Distillation of (II) in presence of Cu-bronze gives methylisotricyclenone, m.p. 150–150·6° (semicarbazone, m.p. 251–253°; hydrazone, m.p. 89–

CH-CH CH-CH CH₂-CH CH₂-CHe-CH₂ (III.)

92⁵), which is reduced by the Wolff-Kishner method to 4-methylisotricyclene (III), m.p. 113-114°; this is identical with the product of oxidation of 4-methylcamphorhydrazone with HgO ("methylcyclene," cf. A., 1924, i 1176) thus affording further proof of

i, 1176), thus affording further proof of the position of the Me group in (I).

Attempts to dehalogenate the α -Br-derivative, m.p. 126—128°, of (I) to (III) failed; alcoholic alkali, NaOPh, and semicarbazide in EtOH regenerated (I), and NHPhEt at 150—160° gave an *isomeride*, m.p. 114—116°. H. A. P.

Syntheses in the santene series. G. KOMPPA (Ber., 1932, 65, [B], 1708–1710).—Me₂ β -methyl-glutarate and Me₂C₂O₄ afford Me₂ 4:5-diketo-2-methylcyclopentane-1:3-dicarboxylate, m.p. 103–104° (corresponding Et_2 ester, m.p. 107—108°), transformed by MeI and NaOMe into Me_2 4:5-diketo-2:3-dimethylcyclopentane-1: 3-dicarboxylate (I), m.p. 54-55° [corresponding Et_2 ester, m.p. 53–54°, and its phenylosazone, m.p. 123° (decomp.)], and Me_2 (Et_2) 4-keto-5 - methoxy-2 : 3 - dimethyl- Δ^5 -cyclopentene-1 : 3dicarboxylate. Treatment of (I) with Na-Hg leads to non-cryst. 4: 5-dihydroxy-2: 3 - dimethylcyclopentane-1: 3-dicarboxylic acid, transformed by P and HI into 2: 3-dimethyl - Δ^5 -cyclopentene - 1: 3-dicarboxylic acid (II), m.p. 195-196°. (II) and HBr yield a Br-acid reduced by Zn dust and AcOH to 2: 3-dimethylcyclopentane-1: 3-dicarboxylic acid (π -apocamphoric acid), which with Ac₂O affords an anhydride of m.p. (93°) identical with that of cis-isosantenic anhydride. The prep. of a second dehydro $-\pi$ - apocamphoric acid, m.p. 196-198°, is announced; the mixed m.p. with (II) is 164-170°. Santenic anhydride has been

catalytically reduced to santenecampholide, m.p. 50-51°, and cis- has been converted into trans-santenic acid. H. W.

Sesquiterpene ketones. A. PFAU (Helv. Chim. Acta, 1932, 15, 1481—1483).—Atlas and Himalayan cedar oils contain, as chief constituent, atlantone, $C_{15}H_{22}O$, probably a mixture of (I) and (II). The chief constituent of turmeric oil is a mixture of turmerone, a monocyclic, hydroaromatic ketone, $C_{15}H_{22}O$, probably (III), and dehydroturmerone, a monocyclic, aromatic ketone, $C_{15}H_{20}O$, probably (IV). The natural occurrence of two dicyclic ketones, $C_{15}H_{22}O$, similar to eremophilone (following abstract), is announced.



Constitution of eremophilone and of two related hydroxy-ketones from the wood oil of Eremophila Mitchelli. A. E. BRADFIELD, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1932, 2744-2759) .- From the wood oil of E. Mitchelli, eremophilone (I), $C_{15}H_{22}O$, m.p. 41–42°, b.p. 171°/15 mm., $[\alpha]_{5461}$ -207°, 2-hydroxy- (II), m.p. 66–67°, $[\alpha]_{5461}$ +153°, and 2-hydroxy-1 : 2-dihydro-eremophilone (III), m.p. $102-103^{\circ}$, $[\alpha]_{5461}+94^{\circ}$, have been isolated. (I) forms a semicarbazone, m.p. 202-203° (decomp.), and hydroxymethylene-eremophilone, m.p. 105°, showing the presence of ·CH2·CO·CH:CH. It is reduced catalytically to tetrahydroeremophilone, b.p. 165°/17 mm., d²⁵/₂₅ 0.9641, [α]₅₄₆₁+12.5° [semicarbazone, m.p. 213-214° (decomp.); oxime, m.p. 126-127.5°; 2:4-dinitrophenylhydrazone, m.p. 178-179°], and by Na and EtOH to dihydroeremophilol (IV), b.p. 168-170°/14 mm., [α]₅₄₆₁+68·8° (3 : 5-dinitrobenzoate, m.p. 119-121°), which is oxidised by CrO₃ to dihydroeremophilone [semicarbazone, m.p. 214-215° (decomp.)] and dehydrogenated by Se to eudalene. (IV) yields on ozonolysis CH2O and 6-acetyl-4:9dimethyl-2-decalol (2:4-dinitrophenylhydrazone, m.p. 146-149°), which is oxidised with NaOBr in MeOH to CHBr3 and 4: 9-dimethyl-2-decalol-6-carboxylic acid, m.p. 155°. Oxidation of (I) with H_2O_2 affords eremophilone oxide, m.p. 63-64°, $[\alpha]_{5461}$ -208° (reduced catalytically to dihydroeremophilone oxide, m.p. 53—54°, $[\alpha]_{5461}$ –205°), which is converted by AcOH and NaOAc into (II).

Oxidation of (II) (which is purified through the Bz derivative, m.p. $119-120^{\circ}$, $[\alpha]_{5461}+162^{\circ}$) with O_3 gives COMe₂, a trace of CH₂O, and a mixed anhydride, $C_{19}H_{18}O_5$, m.p. 186–188°, which on hydrolysis with KOH-EtOH affords BzOH and 9-methyl- Δ^2 -decalene-4 : 6-dione-2-carboxylic acid, isolated as the semicarbazone, m.p. 215–216° (decomp.). (II) is oxidised

by H_2O_2 to 2-hydroxyeremophilone oxide, m.p. 150– 151°, $[\alpha]_{5461}$ +196° (Ac derivative, m.p. 122–123°), and a mixture of two stereoisomeric forms of 1methyl-4-(α -hydroxyisopropyl)cyclohexane-1-acetic-2- α lactic acid (α -), m.p. 167–168° (decomp.) [which gives with AcCl the Ac derivative of the lactonic acid, m.p. 192–193 (decomp.)], and (β -), m.p. 198° (decomp.) [which forms with AcCl an anhydride or dilactone, m.p. about 172°)]. Benzoyl-2-hydroxyeremophilone is reduced catalytically to a hydroxy-ketone, isolated as 2-hydroxytetrahydroeremophiloneoxime (β -form), m.p. 146°.

(III) forms a 2:4-dinitrophenylhydrazone, m.p. 239–241° (decomp.), diacetate, m.p. 69–70°, and 3:5-dinitrobenzoate, m.p. 145–146°. Catalytic reduction of (III) yields 2-hydroxytetrahydroeremophilone (VI) (α -form), m.p. 84–85°, [α]₅₄₆₁ +84·2° (oxime,



m.p. 158—160°; 2:4-dinitrophenylm.p. hydrazone, $210 - 220^{\circ}),$ and with Na and EtOH, a glycol is obtained which is dehydrogenated with Se to eudalene. (III) is oxidised with O3 to CH₂O and 6acetyl - 4 : 9 - di methyldecal-2-on-3-ol, obtained as the semicarbazone, m.p. 216-219° (decomp.), and with H₂O₂ to the α-form of (V). Re-CH·OH duction of (VI) with Na-Hgresults in tetrahydroere mophilone, oxid-

ation with H_2O_2 in an oil, and with CrO_3 in a ketone forming 2-hydroxy- ω -dihydroeremophilone-2: 4dinitrophenylhydrazone, m.p. 158—160°. These results are in agreement with the formulæ (I), (II), and (III). F. R. S.

Super-aromatic properties of furan. I. Scission of lead phenyl furyl compounds by hydrogen chloride. H. GILMAN and E. B. TOWNE (Rec. trav. chim., 1932, 51, 1054–1064).—The reaction PbR'₂R''₂ +2HCl=PbR'₂Cl₂+2R''H is used as a criterion of aromatic character, the more aromatic groups being removed first. Furyl, thienyl, and Ph are thus decreasingly aromatic. PbPh₂Cl₂ and Mg furyl iodide [from purified 2-iodofuran (A., 1932, 399)] give Pb Ph₂ di-2-furyl, m.p. 118° (softens 116°), which in CHCl₃ with HCl gives PbPh₂Cl₂, and furan, isolated as **3**: 6-endoxytetrahydrophthalic anhydride. The following are similarly obtained, the scission products being given in parentheses: Pb Ph₂ di-2-thienyl (I), m.p. 185° (softens 184°) (yield 92%) (PbPh₂Cl₂ and thiophen, isolated as **2** - chloromercurithiophen); Pb Ph₃ 2-furyl, m.p. 166–167° (softens 165°) (yield 82%) (PbPh₂Cl₂, PbPh₃Cl, and furan); Pb Ph₃ 2-thienyl, m.p. 206–207° (softens 204–205°) (yield 93·1%) [PbPh₃Cl (64·8%), PbPh₂Cl₂ (32·1%), and

thiophen]. Pb tetra-2-thienyl in C_6H_6 with HCl gives Pb di-2-thienyl dichloride (II), decomp. 202° (sinters 200°) (yield 96%), which with Mg furyl iodide give Pb di-2-furyl di-2-thienyl, m.p. 117—119° (yield 62%). This with HCl gives (II) [converted by MgPhBr into (I)] and furan, but no thiophen. Pb tetra-2-furyl has m.p. 52—53° (softens 50°).

A. A. L.

p-Dimethylaminobenzylidene [derivatives of] ketones. III. Auxochromic groups. H. RUPE, F. PEDRINI, and A. COLLIN (Helv. Chim. Acta, 1932, 15, 1321-1329; cf. A., 1932, 60).-1-p-Dimethylaminostyrylbenziminazole (I) and its derivatives containing quinquevalent N are dyes for cotton, wool, and silk mordanted with tannin. 2-Methylquinoline and p-NMc₂·C₆H₄·CHO (II) give a coloured product, which gives coloured and colourless salts and a colourless methiodide. Ketones are thus not the only substances showing this phenomenon. Some derivatives of dehydracetic acid (III) show similar colour changes. 1-Methylbenziminazole and (II), best with H₃BO₃ at 215°, give (I), yellow, m.p. 256° [*perchlorate*, yellow, m.p. 232° (decomp.); *methiodide*, yellow, m.p. 234° (decomp.); *oxalate*, coloured], hydrogenated (Ni) in EtOH-EtOAc-H2O at 70-74° to β -p-dimethylaminophenylethylbenziminazole, colourless, m.p. 187° (*picrate*, m.p. 198°). (II), (III), and a little piperidine at 100° give 3-p-dimethylaminocinnamoyl-6-methylpyronone,

 $p \cdot \mathrm{NMe}_2 \cdot \mathrm{C}_6\mathrm{H}_4 \cdot \mathrm{CH} \cdot \mathrm{CH} \cdot \mathrm{CO} \cdot \mathrm{CH} \underset{\mathrm{CO}}{\overset{\mathrm{CO} \cdot \mathrm{CH}}{\overset{\mathrm{CH}}{\overset{\mathrm{CO}}}} \hspace{-0.5mm} > \hspace{-0.5mm} \mathrm{CMe}, \quad \mathrm{dark}$

red, m.p. 215° [hydrochloride, pale yellow, decomp. 110°; perchlorate, colourless in absence of atm. H_2O , m.p. 150° (decomp.)], hydrogenated to 3-β-p-dimethylaminophenylpropionyl-6-methylpyronone, yellow, m.p. 115°, the hydrochloride, m.p. 202°, or oxalate (both colourless) of which with warm, conc. aq. NH₃ gives 2: 4-diketo-3- β -p-dimethylaminophenylpropionyl-6methyl-1:2:3:4-tetrahydropyridine (the diketonic form of 2: 4-dihydroxy-3-B-p-dimethylaminophenylpropionyl-6-methylpyridine), colourless, m.p. 191° [oxalate, m.p. 150° (decomp.)]. The Na salt of (III) in presence of a little acid in H₂O is hydrogenated (Ni) at room temp. to 3-acetyl-6-methyldihydropyronone (IV), solid (semicarbazone), and B8-dihydroxyn-heptane (formed in larger amount at 40-50°), b.p. 113°/11 mm. (dibenzoate, b.p. 218-219°/11 mm.). (IV) and (II) with a little piperidine at 100° give 3-p-dimethylaminocinnamoyl-6-methyldihydropyronone, red, m.p. 210° (hydrochloride, colourless, m.p. 168° (decomp.)], hydrogenated (Ni) to 3-B-p-dimethylaminophenylpropionyl-6-methyldihydropyronone, yellow, m.p. 81° (hydrochloride, colourless, m.p. 160°). (III) and MgPhBr (5 mols.) in C_6H_6 give a poor yield of the substance, OH-CPhMe-CH<-CPh(OH) CH, m.p. 201°, and a small amount of a substance, m.p. 184°. R. S. C.

Hydrogenation of heterocyclic compounds. G. M. MACH and V. N. CHADSHINOV (Ukrain. Chem. J., 1932, 7, [Tech.], 32—40).—The products of hydrogenation of diphenylene oxide a 400—470° in presence of MoO₃ are unchanged substrate (45%), C_2H_6 , methylcyclopentane, cyclohexane, dicyclohexyl, CH_4 , C_6H_6 , H_2O , phenols, and higher aromatic hydrocarbons. R. T.

Synthesis of anthocyanins. Synthesis of cyanenin chloride and an indication of the synthesis of cyanin chloride. R. ROBINSON and A. LÉON. Synthesis of malvenin chloride. R. ROBINSON, A. LÉON, and D. SANROMA (Anal. Fís. Quím., 1932, 30, 840—845, 846—848).—Cf. A., 1932, 1038.

Cichoriin and constitution of æsculin and scopolin. K. W. MERZ (Arch. Pharm., 1932, 270. 476–494).—Cichoriin (I), $C_{15}H_{16}O_{9,2}H_{2}O$ (cf. Nietzki, A., 1877, i, 477, who gives $C_{32}H_{34}O_{19,4}\cdot 5H_{2}O$), m.p. 213–215°, $[\alpha]_{19}^{18}$ –104.5° in 50% dioxan $[Ac_5$ derivative (II), m.p. 217-218°; Me ether (III), m.p. 215-217°], is hydrolysed to glucose and cichorigenin (IV), $C_9H_6O_4$, m.p. 268–270° (dibenzoate, m.p. 185–186°; di-p-nitrobenzoate, m.p. 207-208°), which is identical with æsculetin [6:7-dihydroxycoumarin (V)]. Hydrolysis of (III) with dil. H₂SO₄ gives 7-hydroxy-6-methoxycoumarin [scopoletin] [acetate, m.p. 179-180° (lit. 177°)]; (I) is, therefore, 6-hydroxy-7-glucosidoxycoumarin. Acetobromoglucose and (V) in COMe₂-10% KOH give 6-hydroxy-7-tetra-acetylglucosidoxycoumarin, m.p. 194-195°, which is acetylated further to (II) and deacetylated by EtOH-NH₃ to (I). \pm Sculin [Ac₅ derivative, m.p. 166° (lit. 130°)] is 7-hydroxy-6-glucosidoxycoumarin; its Me ether $(+2H_2O)$ (VI), m.p. 231-232°, is hydrolysed to 6-hydroxy-7-methoxycoumarin [formed together with 6:7-dimethoxycoumarin when (IV) is methylated (CH₂N₂)], which with acetobromoglucose gives 7-methoxy-6-tetra-acetylglucosidoxycoumarin, m.p. 176-177°, deacetylated to (VI). 6-Methoxy-7-tetra-acetylglucosidoxycoumarin, m.p. 168-169°, is similarly deacetylated to 6-methoxy-7-glucosidoxycoumarin [scopolin], which is identical with (III). H. B.

Reductions with zinc dust in pyridine. II. Cyanidin. R. KUHN and A. WINTERSTEIN (Ber., 1932, 65, [B], 1742—1743).—The analogy between the



I cyanidin and CHPh₃ dyes is completed by the OH observation that cyanidin chloride is reduced by Zn dust and a few drops of AcOH in C_5H_5N

to leucocyanidin (I), readily autoxidised to cyanidin. H. W.

Constitution of the dye of Robinia pseudacacia. L. SCHMID and F. TADROS (Ber., 1932, 65, [B], 1689— 1691; cf. A., 1931, 738).—The air-dried dye, $C_{15}H_{10}O_7,H_2O$, loses 1 H_2O at 70°/high vac. Reducing action towards Fehling's solution is proper to the dye and not caused by admixed sugars. Cautious alkaline degradation leads only to resorcinol. Treatment in MeOH with $Et_2O-CH_2N_2$ gives the Me_5 derivative, m.p. 149°, converted by KOH-EtOH into fisetol, m.p. 67°, and 3:4:5-trimethoxybenzoic acid, m.p. 172° (Me ester, m.p. 82°). The dye is therefore 3:3':4':5'-tetrahydroxyflavonol. Oxidation with HNO₃ (d 1·4) at 100° affords styphnic acid, m.p. 177°. H. W.

Condensation of aldehydes with β -hydroxynaphthoic acid or its anilide and fission of dinaphthylmethanes. K. BRASS and J. FIEDLER (Ber., 1932, 65, [B], 1654-1660).—Gradual addition of CCl₃·CH(OH)₂ to 2-hydroxy-3-naphthoic acid (I) in conc. H_2SO_4 at room temp. affords 4-trichloromethyl-2:3:5:6-di-1':2':1'':2''-naphthapyran-3':3''-dicarboxylic acid, decomp. above 315° (Et₂ ester, m.p. 193°), in small yield. Condensation of (I) with PhCHO in AcOH containing conc. HCl gives benzylidenedi-2-hydroxy-3-naphthoic acid (II), decomp. above 253° [Ac2 derivative (III), decomp. 285°], converted by Zn dust and NaOH into (I) and hydrobenzoin. The process is therefore essentially hydrolysis instead of reductive fission, leading through 2-hydroxy-1hydroxybenzyl-3-naphthoic acid to (I) and PhCHO, whence benzoin and hydrobenzoin. Heating of (II) or (III) in AcOH containing H_2SO_4 or in PhNO₂ leads to 4 - phenyl - 2 : 3 : 5 : 6 - di - 1' : 2' : 1'' : 2'' - naphtha-pyran-3' : 3''-dicarboxylic acid, decomp. 337° (Et₂ ester, m.p. 182.5—183°), also obtained directly from (I) in conc. H₂SO₄ and PhCHO in AcOH. 2-Hydroxy-3-naphthanilide does not condense with PhCHO under the conditions which lead to (II), whereas in presence of H₂SO₄ and AcOH, 4-phenyl-2:3:5:6di-1': 2': 1'': 2"-naphthapyran-3': 3"-dicarboxylanilide, decomp. 365°, is obtained. H. W.

Constitution of podophyllotoxin and picropodophyllin. E. SPATH, F. WESSELY, and E. NADLER (Ber., 1932, 65, [B], 1773-1777; cf. A., 1932, 1137).-Podophyllotoxin with alkaline KMnO4 at 60-70° yields a small amount of 4 : 5-methylenedioxyphthalic acid (identified as the anhydride and ethylimide) in addition to 3:4:5-trimethoxybenzoic acid. Podophyllomeronic acid with KOH-NaOH at 230° affords 6:7-dihydroxy-3-methylnaphthalene-2-carboxylic acid, m.p. 250° (slight decomp.), transformed by CH_2N_2 into Me 6:7-dimethdimorphous, oxy-3-methylnaphthalene-2-carboxylate, m.p. 129° or m.p. 109-110° and 129° after re-solidification, whence 6:7-dimethoxy-3-methylnaphthalene-2-carboxylic acid (I), m.p. 228°. (I) in conc. H_2SO_4 is transformed by N₃H in CHCl₃ into 6 : 7-dimethoxy-3-methyl- β -naphthylamine, m.p. 204–205° (vac.), oxidised to 4:5-dimethoxyphthalic acid (anhydride, m.p. 178-179°). The constitutions A and B are therefore ascribed to podophyllotoxin and picropodophyllin, respectively.



Derivatives of dioxan. J. BÖESEKEN, F. TELLE-GEN, and P. C. HENRIQUEZ (J. Amer. Chem. Soc., 1932, 54, 4461—4462).—Chlorination of 2:3-dichlorodioxan gives a liquid as-tetrachlorodioxan (cf. Butler and Cretcher, A., 1932, 949), a cryst. hexachlorodioxan, and higher chlorinated derivatives. The naphthodioxans (A., 1931, 1162) and related compounds are being investigated. H. B.

Thiophen derivatives. I. J. RINKES (Rec. trav. chim., 1932, 51, 1134—1142).—Thiophen-2-carboxylic acid in Ac₂O with HNO₃ (*d* 1.51) gives 5- (I), m.p. 158° (*Me* ester, m.p. 76°; gives 2-nitrothiophen when heated $> 200^{\circ}$), and 4-nitrothiophen-2carboxylic acid, m.p. 154° (Me ester, m.p. 99°; gives 3-nitrothiophen, m.p. 68-69°, when heated > 200°), and 2-nitrothiophen by replacement of CO₂H by NO₂. 2-Methylthiophen similarly gives 5-nitro-2-methylthio-phen (II), setting point 27.4° , oxidised to (I). More intense nitration gives (?) 3:5-dinitro-2-methylthio-phen (III), m.p. 99-100°. 2-Methyl-5-acetothienone, new m.p. 23.8° (from 2-methylthiophen and AcCl), with KMnO4 in KOH followed by H2O2 gives 2-methylthiophen-5-carboxylic acid, new m.p. 138-139° (and a little thiophen-2: 5-dicarboxylic acid). Nitration of this at -10° to -5° gives (II), a little (III), and ?)3-nitro-2-methylthiophen-5-carboxylic acid, m.p. 180-181°, which gives 3-nitro-2-methylthiophen, m.p. 44-45°, when decarboxylated. The last-named product gives (III) on further nitration. Orientation in the thiophen series is discussed. A. A. L.

Indigoid dyes. Ethers of leucothioindigotin. M. M. TSCHILIKIN (Ber., 1932, 65, [B], 1651—1653).— Confirmation of the hypothesis that dissolved leucothioindigotin derivatives are an equilibrium mixture, CB(OR) and CO a U (A)

$$C_6H_4 < C_5 > C_6H_4 (A) \Rightarrow$$

 $\begin{bmatrix} C_8H_4 \\ \hline S \\ \hline S$

Action of aromatic nitro-derivatives on magnesium pyrryl and indolyl compounds. M. GIUA and G. RACCIU (Atti R. Accad. Sci. Torino, 1932, 67, 121–124; Chem. Zentr., 1932, ii, 875).— The oxidation of Mg pyrryl compounds affords black dyes (pyrrole-blacks). Mg indolyl compounds are less readily oxidised. Mg indolyl iodide and pirryl chloride afford a red, amorphous substance and the additive compound, $C_8H_7N, C_6H_2Cl(NO_2)_3$, m.p. 126–127°; 1-chloro-2:4:5-trinitrobenzene similarly affords two substances, the latter having n.p. 113°. A. A. E.

Unsaturated diketones of the indole series. G. SANNA (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 29—30; Chem. Zentr., 1932, i, 1784).—Aq. NH₂ at 100° (bomb tube) converts 3-chloroacetyl-2-methylindole (α -methylindacyl chloride) into a yellow powder containing the compounds C₂₂H₁₈O₂N₂, m.p. 162°, C₂₂H₁₈O₂N₂, m.p. 220°, probably the cis-trans-isomeride (Br₂-derivative, m.p. 241°), and C₃₃H₂₇O₃N₃, unchanged by Br. The first two compounds yield only one additive product, m.p. 220°, with aniline.

L. S. T.
Pyridine boron trifluoride. P. A. VAN DER MEULEN and H. A. HELLER (J. Amer. Chem. Soc., 1932, 54, 4404—4406).—Details are given for the prep. of C_5H_5N,BF_3 , b.p. $300\pm5^\circ$, m.p. $45\pm1^\circ$, which is converted by 95% EtOH into C_5H_5N fluoborate. The heat of dissociation in the range 313-356° is 50,600 g.-cal. H. B.

Cleavage of phenacylpyridinium halides by alkali. S. H. BABCOCK, jun., F. I. NAKAMURA, and R. C. FUSON (J. Amer. Chem. Soc., 1932, 54, 4407-4409),— $\alpha\delta$ -Dibromo- $\alpha\delta$ -dibenzovlbutane and C₅H₅N in BzOEt at 120° give the dipyridinium dibromide $(+2H_2O)$, m.p. 212.5° (corr.), which with cold dil. NaOH affords BzOH. *Phenacylpyridinium chloride* (+H₂O), m.p. 109-110°, and dil. NaOH give BzOH; p-bromophenacylpyridinium bromide $(+H_2O)$, m.p. 225-230°, similarly affords $p-C_6H_4Br\cdot CO_2H.$ 2': 4': 6'-Trimethylphenacylpyridinium chloride, m.p. 245-246°, does not undergo cleavage to 2:4:6-C₆H₂Me₃·CO₂H. H. B.

Catalytic synthesis of phenylpyridines. M. COLONNA and S. MUSAJO (Gazzetta, 1932, 62, 894-901; cf. A., 1905, i, 609).—Attempts to prepare phenylethylpyridine from 4-ethylpyridine with MgPhBr or with PhN₂Cl with or without AlCl₃ were unsuccessful. Condensation of 1 mol. of COPhMe and 2 mols. of MeCHO with NH₃ at 400° in presence of Al_2O_3 pptd. on powdered pumice (A., 1931, 630) gives C_5H_5N and 2-phenyl-4-methyl- and 4-phenyl-E. E. J. M. 2-methyl-pyridine.

Stereochemistry of platinum metals and nickel. H. REIHLEN and W. HUHN (Annalen, 1932, 499, 144-157; cf. A., 1931, 1167).-The monoacetate of 3-methyl-4-ethyl-2-aminomethylquinoline (basic and neutral chloropalladoates; basic d-bromocamphor-m-sulphonate) and K2PdCl, in aq. solution, give (first) dichloro-3-methyl-4-ethyl-2-aminomethyl- $\begin{bmatrix} C_{13}H_{14}N \\ NH_2 \end{bmatrix} Pd < \begin{bmatrix} Cl \\ Cl \end{bmatrix}$ and then quinolinepalladium, di-3 - methyl-4 - ethyl-2 - aminomethylquinolinepalladium $\begin{bmatrix} \mathbf{C}_{13}\mathbf{H}_{14}\mathbf{N} \\ \mathbf{N}\mathbf{H}_2 \end{bmatrix} \mathbf{P} \mathbf{d} \mathbf{H}_2 \\ \mathbf{N}\mathbf{C}_{13}\mathbf{H}_{14} \end{bmatrix} \mathbf{C} \mathbf{l}_2 (+4\mathbf{H}_2\mathbf{O}),$ chloride (I), convertible into the corresponding nitrate (II) (+H₂O), chloropalladoate $(+2H_2O)$, and tartrate $(+3H_2O)$, $[M]_{1,1}^{16}$ +123° in H₂O (readily racemised in warm aq. solution). (I) and $NH_4 d-\alpha$ -bromocamphor- π -sulphonate give about 70% of the corresponding d-a-bromocamphor- π -sulphonate (III) (+3H₂O), [M]_b $+524^{\circ}$ in EtOH (whence $[M]_{\rm p}$ -112° is obtained for the ion); the remainder of the material is not isolable in a pure state and probably consists of material formed by interaction of the complex with NH4Cl. (II) [prepared from (I) and NaNO3] and Na d- α -bromocamphor- π -sulphonate also give (III) in practically quant. yield, thus precluding the view that (I) may be a mixture of cis- and trans-forms. (III) is readily decomposed by aq. or EtOH-HCl: $\begin{array}{l} [\mathrm{Pd}(\mathrm{NC}_{13}\mathrm{H}_{14}\cdot\mathrm{NH}_2)_2]\mathrm{X}_2 + 2\mathrm{HCl} \longrightarrow \\ [\mathrm{Cl}_2\mathrm{Pd}\cdot\mathrm{NC}_{13}\mathrm{H}_{14}\cdot\mathrm{NH}_2] + \mathrm{NC}_{13}\mathrm{H}_{14}\cdot\mathrm{NH}_2, 2\mathrm{HX}. \\ 3 \cdot \mathrm{Methyl} \cdot 4 \cdot \mathrm{othyl} \cdot 2 \cdot \mathrm{aminomethyl quinoline} \quad \mathrm{hydro-} \end{array}$

chloride and Ni hydroxide give di-3-methyl-4-ethyl-2aminoethylquinolinenickel chloride (IV), C26H32N4Cl2Ni $(+4H_2O?)$, which with $NH_4 d-\alpha$ -bromocamphor- π -camphorsulphonate (V) affords the *l*-base *d*-acid

salt $(+4H_2O?)$, $[M]_{5463} +573^{\circ}$ in EtOH (whence $[M] -221^{\circ}$ for the ion). (IV) and Na tartrate give the neutral *tartrate*, $[M]_{5463} +484^{\circ}$ in EtOH, which is a non-electrolyte; treatment of the motherliquors with (V) affords the impure d-base d-bromocamphor- π -sulphonate, $[M]_{5463}$ +900° (whence [M]H. B. $+106^{\circ}$ for the ion).

Preparation of 2-phenylquinoline from phenyl o-nitrostyryl ketone. R. J. W. LE FÈVRE and J. PEARSON (J.C.S., 1932, 2807–2808).—Ph o-nitrostyryl ketone is best prepared from $o-NO_2 \cdot C_6 H_4 \cdot CHO$ and COPhMe in presence of HCl; under alkaline conditions indigotin is the principal product (cf. A., 1902, i, 379). It gives 2-phenylquinoline on reduction with Fe and EtOH-HCl. Ph *m*- and *p*nitrostyryl ketones, m.p. 145-146° and 164°, respectively, may be prepared under both alkaline H. A. P. and acid conditions.

Reactivity of groups in substituted acridones. I. Replacement of nitro-groups by piperidyl and piperazyl. H. B. NISBET and (in part) A. B. GOODLET (J.C.S., 1932, 2772-2773).-2-Chloro-, m.p. 260-261°, and 2-bromo-5-nitrodiphenylamine-6'-carboxylic acid, m.p. 252°, prepared from 2-halogen-5nitroaniline, K o-bromobenzoate, and Cu, give with H2SO4, 1-chloro-, m.p. 320°, and 1-bromo-4-nitroacridone, m.p. 305°. The NO2 group in the acridones is replaced by C₅H₁₁N or piperazine to form 1-chloro-, m.p. 110° (hydrochloride, m.p. 168-169°), and 1-bromo-4-piperidino-, m.p. 112° (decomp.) (hydrochloride, m.p. 164-165°), and 1-chloro-4-piperazinoacridone, m.p. 198°. The heterogeneous polarity caused by the o-position of CO and NO, is absent in 2-chloro- and Cl is replaced to yield 2-piperidino-5nitroaniline, m.p. 79-81°. F. R. S.

Molecular compound in veramon. A. KOFLER and R. FISCHER (Arch. Pharm., 1932, 270, 441-449).—Crystallographic data are given for the mol. (1:1) compound (I), m.p. 116-117° (micro-method; A., 1932, 713), of veronal (II) and pyramidone (III) present in veramon. (I) decomposes at or just above the m.p. and some (II) crystallises. Crystals of (I) and (III) are obtained when either veramon or a mixture of (II) (1 mol.) and (III) (2 mols.) is sublimed; (I) (mainly) is similarly obtained from an equimol. mixture of (II) and (III). Pyramidone exists in two modifications. H. B.

Formaldehyde condensations with aliphatic ketones. I. G. T. MORGAN and E. L. HOLMES (J.C.S., 1932, 2667-2673).-COMe₂, aq. CH₂O, and 2N-NaOH condense to γ -ketobutyl alcohol [acetate, b.p. 125—130°/30 mm.; γ -ketobutyl acetate semi-carbazone, m.p. 207° (decomp.)], 3:3- or 3:5-bishydroxymethyltetrahydro- γ -pyrone, b.p. 164—165°/ 20 mm. (oxime, m.p. 134—135°; monobenzoate, m.p. 107—107.5°; phenyl-, m.p. 137°, and 2:4-dinitro-phenyl-hydrazone, m.p. 180°, of the benzoate), and much resin. Similar condensation of COMeEt gives little resin and a mixture of γ -keto- β -methylbutyl alcohol [acetate, b.p. 99–100°/20 mm., and its semi-carbazone, m.p. 134.5°; p-nitrobenzoate, m.p. 54°; 1-(2': 4'-dinitrophenyl)-3: 4-dimethyl-4: 5-dihydro-pyrazole, m.p. 191° (prepared from 2: 4-dinitrophenylhydrazine)], γ -keto- β -hydroxymethyl- β -methylbutyl alcohol, m.p. 60°, b.p. 138°/16 mm. [dibenzoate, m.p. 78—79°; di-p-nitrobenzoate, m.p. 177—178°; diacetate, b.p. 140—145°/10 mm., and its semicarbazone, m.p. 132.5°; 6-phenyl-3-methyl-3-hydroxymethyltetrahydro- γ -pyrone, m.p. 103° (prepared from PhCHO)], and numerous resin intermediates. COEt₂, aq. CH₂O, 2N-NaOH, and MeOH yield γ -keto- β -methyl-n-amyl alcohol, b.p. 191—192°/760 mm. [p-nitrobenzoate, m.p. 50—51°; 1-(2': 4'-dinitrophenyl)-4-methyl-3-ethyl-4: 5-dihydropyrazole, m.p. 149—150°], impure γ -keto- β -methyl- β -hydroxymethyl-n-amyl alcohol [di-p-nitrobenzoate, m.p. 147—148°; possibly 3-acetyl-1-(2': 4'-dinitrophenyl)-4-methyl-4 - bydroxymethyl-4 - hydroxymethyl-4 - bydroxymethyl-4 - hydroxymethyl-4 - bydroxymethyl-4 - hydroxymethyl-4 - for 2: 4'-dinitrophenyl-4-hydroxymethyl-4. 5. dihydropyrazole - 2'': 4''-dinitrophenyl-4-hydroxymethyl-4 - bydroxymethyl-4 - hydroxymethyl-4 - bydroxymethyl-4-hydroxymethyl-4-hydroxymethyl-4 - bydroxymethyl-4-hydroxymethyl-4 - 5-dihydropyrazole - 2'': 4''-dinitrophenyl-4-hydroxymethyl-4-hydro

Compounds of the type amino-acid-(2:5-diketopiperazine) and their behaviour towards acid, alkali, and enzymes. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chim., 1932, 212, 61-71).-The following anhydrides and precursors were obtained: 1-leucyl(glycyl-1-tyrosine anhydride), decomp. at 275°, $[\alpha]_{11}^{\infty}$ +8-6° in aq. NH₃ (Bz₂ derivative, decomp. 155°), from d- α -bromoisohexoylglycyl-1-tyrosine, m.p. 92°, $[\alpha]_{12}^{\infty}$ +48-8° in EtOH, and the tripeptide, m.p. 185°, $[\alpha]_{11}^{\infty}$ +18-3° in H₂O; 1-leucyl(glycyl-1leucine anhydride), m.p. 250°, $[\alpha]_{11}^{\infty}$ +6·7° in MeOH; leucyl(glycylserine anhydride) (final product inactive), m.p. 248-249°, from d- α -bromoisohexoylglycyl-1-serine, m.p. 103°, $[\alpha]_{2}$ +14·3° in EtOH, and the tripeptide, m.p. 241°, $[\alpha]_{21}^{\infty}$ +14·3° in H₂O. The action of dil. NaOH and enzymes indicates that the 2: 5-diketopiperazine ring in the anhydride is labile, the tripeptide being readily formed. J. H. B.

Complex compounds derived from diethylbarbituric acid. J. J. L. ZWIKKER (Pharm. Weekblad, 1932, 69, 1178—1188).—The following compounds are described : $[(C_8H_{11}O_3N_2)_2Co(NH_3)_2]$ (red); $[Co(NH_3)_2](OH)(C_8H_{11}O_3N_3)_2$ (brown) :

blad, 1952, 05, 1173–1183).—The following compounds are described : $[(C_8H_{11}O_3N_2)_2Co(NH_3)_2]$ (red); $[Co(NH_3)_6](OH)(C_8H_{11}O_3N_2)_2$; $[CoCl_2(C_8H_{11}O_3N_2)_2]K_2$, and $[CoCl(OH)C_8H_{11}O_3N_2)_2]K_2$, (blue). The colour (blue or red) of the Co complexes formed under any given conditions is governed, not by the quantity of H₂O present in the reacting mixture, but by the quantity of NH₃; blue compounds result when only a limited amount of NH₃ is present. The compound $[Zn(C_5H_5N)$ barbital₂], analogous to the corresponding Cu derivative, has been prepared, and the Cd derivative appears to exist also. The quinoline derivative $[Cu(C_9H_7N)_2$ barbital₂] is described, but the analogous NH₂Ph and substituted quinoline derivatives could not be prepared. H. F. G.

Quinazolines. IV. Alcoholysis in the quinazoline series and preparation of mixed diethers of quinazoline. N. A. LANGE and F. E. SHEIBLEY (J. Amer. Chem. Soc., 1932, 54, 4305-4310).-2-Chloro-4-methoxyquinazoline and EtOH-NaOEt give 2:4-diethoxyquinazoline, which with MeOH-NaOMe affords 4-methoxy-2-ethoxyquinazoline, m.p. 61-62°. Similarly, 2-chloro-4-ethoxyquinazoline (I) and MeOH-NaOMe give 2:4-dimethoxyquinazoline, converted by EtOH-NaOEt into 2-methoxy-4-ethoxyquinazoline, m.p. 57-58°. Alcoholysis of these mixed ethers can be accomplished; the 4-OAlk group is replaced. 2-Chloro-4-phenoxyquinazoline and EtOH-NaOEt give (I), whilst 2: 4-diphenoxyquinazoline, m.p. 160-161° (from the 2: 4-Cl₂-derivative and molten Na in PhOH), similarly affords 2-phenoxy-4-ethoxyquinazoline (II), m.p. 107-108°, also prepared by addition of (I) to molten Na in PhOH. 2-Phenoxy-4-methoxy-quinazoline (III), m.p. 139.5°, is similarly prepared and is converted by EtOH-NaOEt into (II), whilst (II) and McOH-NaOMe give (III). 2:4-Dichloroquinazoline and $(CH_2 \cdot ONa)_2$ give $2: 4 \cdot di \cdot \beta \cdot hydroxy ethoxyquinazoline, m.p. <math>153-154^\circ$ (Ac₂ derivative, H. B. m.p. 65-66°).

Benzoyl derivatives of indigotin. E. HOPE and D. RICHTER (J.C.S., 1932, 2783-2787).-NN'-Di-benzoylindigotin, m.p. 238°, prepared by Schwartz (J. pr. Chem., 1863, 91, 382) contains Cl and is identical with the "Dessoulavy compound " (I) (G.P. 247,154), $C_{30}H_{17}O_3N_2Cl.$ The violet substance (cf. Posner and Hofmeister, A., 1926, 1156) is also converted into (I) by prolonged treatment with BzCl. Ciba-yellow 3G (II) (modified prep.; Cl-substituted compound, m.p. 306°, obtained from m-C₆H₄Cl·COCl) with 15% aq. NaOH takes up 1 H₂O to give a carboxylic acid (co-ordination compounds with EtOH and MeOH) which is methylated to a monomethyl-carboxylic acid (III) or further to a Me_2 derivative (hydrolysed by aq. NaOH or aq. HI to the mono-acid). (III) loses CO₂ at 280° to form a product, m.p. 168°. (II) and 10% aq. NaOH at 220° afford 3-hydroxy-4-phenylquinoline-2'-carboxylic acid (?), m.p. 220-230°, which when heated gives a lactone, m.p. 215°, anthranilic acid, a pyridone derivative, m.p. above 360°, and a substance, m.p. 228°, isomeric with the lactone. With 15% NaOEt (II) forms a base, m.p. 197°. (I) is converted into (II) by heating alone or in presence of a catalyst. These results are not consistent with the formula of Posner and Hofmeister (loc. cit.) and (II) is suggested for ciba-yellow 3G, and (I) for the Dessoulavy compound.



Reductions with zinc dust in pyridine. I. Reversible hydrogenation and dehydrogenation of cyanine dyes. R. KUHN and A. WINTERSTEIN (Ber., 1932, 65, [B], 1737—1742).—Anhyd. AcOH in dry C_5H_5N does not behave as an acid or react with Zn dust. In presence of a trace of H_2O the mixture develops very strong reducing properties, which appear to depend on the development of H_3O^+ ions and on the passage of Zn into complex Zn- C_5H_5N ions. Reduction can be moderated by substitution of EtOH for H_2O . Indolenine-red (I; n=1) is rapidly and without apparent evolution of H reduced to the

$$C_{6}H_{4} \underbrace{CMe_{2}}_{NMe} \underbrace{C[CH-CH]_{n} \cdot CH-C}_{0} \underbrace{CMe_{2}}_{NMe} \underbrace{C_{6}H_{4}}_{C_{6}H_{4}} \underbrace{CICH-CH]_{n} \cdot CH-C}_{0} \underbrace{CHe_{2}}_{NMe} \underbrace{C_{6}H_{4}}_{C_{6}H_{4}} \underbrace{CMe_{2}}_{0} \underbrace{CICH}_{0} \underbrace{CH:CH}_{0} \underbrace{CHe_{2}}_{0} \underbrace{C_{6}H_{4}}_{0} \underbrace{CHe_{2}}_{0} \underbrace{CCH}_{0} \underbrace{CH:CH}_{0} \underbrace{CHe_{2}}_{0} \underbrace{CCH}_{0} \underbrace{CHe_{2}}_{0} \underbrace{CHe$$

methine leuco-base (cf. II), m.p. 114—116° (decomp.), rapidly oxidised by $K_3Fe(CN)_6$ in acid solution to (I). It differs from the methylene base (III), m.p. 121— 122° (decomp.), obtained by condensation of CH_2O with 1:3:3-trimethyl-2-methyleneindoline, which is not oxidised by $K_3Fe(CN)_6$. Indolenine-yellow (I; n=0) is reduced with difficulty by this method, reduction of the perchlorate with Zn dust and NH_3 -EtOH being preferable. Indolenine-violet (I; n=2) is readily decolorised and the dye is partly re-formed by exposure of the solution to air. Indolenine-blue (I; n=3) is very easily reduced, but reduction appears to proceed beyond the stage of the leuco-base, since it has not been found possible to regenerate the dye. H. W.

Synthesis of tetrazole compounds from nitriles. J. von BRAUN and W. KELLER (Ber., 1932, 65, [B], 1677-1680).-Nitriles appear unable to add N₃H directly. In presence of conc. H₂SO₄ they add the NH: residue of N₃H, yielding carbodi-imides, $R \cdot C:B + NH < \longrightarrow R \cdot C(:NH)N < \longrightarrow NH:C:NR$, which readily add 1N3H, yielding products which form substituted tetrazoles by ring closure, NH:C:NR The following examples are cited : heptonitrile with 2.5 mols. of N₃H in C₆H₆ and conc. H₂SO₄ at 35-40° to 5-amino-1-hexyltetrazole, m.p. 162° (Ac derivative, m.p. 106°), in about 60% yield; 5-amino-1-phenyltetrazole, m.p. 159° (Ac derivative, m.p. 211°), from PhCN; p-toluonitrile to unchanged material (5%), a little p-toluamide, and 5-amino-1-p-tolyltetrazole, m.p. 190°; CH₂Ph·CN to unchanged material (6%), a little phenylacetamide, and 5-amino-1-benzyltetrazole, m.p. 187° (Ac derivative, m.p. 107°); sebaconitrile to a mixture of the ditetrazole, NH2. N4C.[CH2]8. N4C.NH2, m.p. 250°, and 5-amino-1-0cyano-octyltetrazole, hydrolysed by conc. HCl at 120—130° to 5-amino-1-0-carboxyoctyltetrazole, m.p. 152° (Et ester, m.p. 116°). H. W.

[Effect of] hydrogen-ion concentration on degradation of uric acid. F. ROSENTHAL.—See this vol., 33.

4-Nitro-5-(3-pyridyl)pyrazole, a new oxidation product of nicotine. II. Methylation products. H. KING (J.C.S., 1932, 2768—2770).—4-Nitro-5-(3-pyridyl)pyrazole (I) (A., 1932, 68) and MeI-MeOH give 4-nitro-5-(3-pyridylmethiodide)pyrazole, m.p. 257° (decomp.), from which the base, m.p. 287° (decomp.) [methochloride, m.p. 290° (decomp.); picrate, m.p. 212° (decomp.)], is liberated by NaOH. The Ag salt of (I) yields with MeI-McOH a mixture of two monomethyl *methiodides*, m.p. 271-272° and m.p. 224-225°, unchanged by aq. NaOH and corresponding with the tautomeric forms of (I). F. R. S.

Constitution of bile pigment. IX. Synthesis of 5-hydroxy-2 : 4-dimethyl-3-ethylpyrrole and a new synthesis of xanthobilirubic acid or bilirubic acid. H. FISCHER, T. YOSHIOKA, and P. HARTMANN (Z. physiol. Chem., 1932, 212, 146—156 ; cf. A., 1932, 1045).—Oxidation of cryptopyrrole (I) with H₂O₂ in C₅H₅N gives 5-hydroxy-2 : 4-dimethyl-3-ethylpyrrole (II), m.p. 84—84-5° [phenylcarbimido-derivative (obtained at 200°), m.p. 104°], and di-(2 : 4-dimethyl-3ethyl-5)-pyrryl peroxide, m.p. 219°. A N-free by-product giving with picric acid a compound, C₁₈H₁₄O₁₃N₆, m.p. 181°, is formed. C₅H₅N by H₂O₂ oxidation gives 3-hydroxypyridine. Wolff-Kishner reduction of (II) gave no (I) but a small amount of a hydrazine reaction product, C₈H₁₃N₃, m.p. 179°. With (II) SO₂Cl₂ gives a Cl₂-compound (III), m.p. 150—151°, yielding with NH₂Ph a product C₂₀H₂₁N₃, m.p. 244—245°. (III) gave no methylethylmaleinide with HNO₃ or CrO₃. With Br in CCl₄ (II) gives a Br-compound (IV), which with excess of (II) then forms 5-hydroxy-4 : 3' : 5'-trimethyl-3 : 4'-diethylpyrromethene, m.p. 244—245° (not 254° as previously stated). With the Me ester of the crypto-acid, (IV) affords Me xanthobilirubate. J. H. B.

Mechanism of the introduction of iron into porphyrins. A. TREIBS (Z. physiol. Chem., 1932, 212, 26—32).—The Fe-porphyrin complex is reversibly decomposed by strong acids. In AcOH containing NaCl, Fe(OAc)₂ forms the complex on heating, but after cooling it is partly decomposed as shown by the colour change and spectrum. This effect is due, not to the production of HCl, but to the formation of a NaCl-AcOH complex, more strongly acid than AcOH (cf. the effect of salts on the dissociation of acids). Org. acids stronger than AcOH show a similar effect in proportion to their strength. J. H. B.

Ultra-violet absorption of the porphyrins. A. TREIBS (Z. physiol. Chem., 1932, 212, 33-40).— All porphyrins examined show an intense band in the long-wave ultra-violet. Those of the ætioporphyrin group agree, but the uroporphyrins and rhodoporphyrins differ; uroporphyrin and *iso*uroporphyrin show a slight divergence in the position of the max. No gross differences are observed. J. H. B.

Composition and possible constitution of several sulphur dyes. W. N. JONES, jun., and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 4393–4402).—p-Hydroxydiphenylamine (25 g.), Na₂S,9H₂O (90 g.), S (50 g.), and H₂O (70 c.c.) at 145–150°/34 hr. give (after dilution and oxidation with atm. O₂) a red dye, empirical formula, $C_{12}H_7ONS_3$, designated Bordeaux Y; the use of Na₂S₂ affords the keto-

thiodiphenylimide (I) of Bernthsen SH (A., 1885, 259; 1886, 53), whilst O Na₂S₃ gives (probably) a polymeric thiol compound (as II). 4-Hydroxy-4'-methyldiphenylamine (27 g.),

Na₂S,9H₂O (90 g.), S (50 g.), and H₂O (70 c.c.) at $120^{\circ}/34$ hr. afford a red dye (Bordeaux X),

(II.)

C13H9ONS4, whilst 4-amino-4'-hydroxy-3-methyldiphenylamine similarly furnishes the dye Navyblue RL, $C_{13}H_{10}ON_2S_3$; 4-amino-4'-hydroxydiphenyl-amine gives dyes, $C_{12}H_7ON_2S_7$ and $C_{12}H_7ON_2S_9$ (termed Green Z "B" and "Å," respectively) under identical conditions. Reduction of the above dyes with SnCl₂ and conc. HCl in AcOH-H₃PO₄ causes elimination of 1, 2, 1, 4, and 6 atoms of S (as H_2S), respectively (for the above order); H₂S is not formed by similar reduction of (I) and (II). The dyes probably contain S:S, S:S:S, or S:S:S's groups (according to the no. of S atoms present); structural H. B. formulæ (units) are suggested.

Vasicine. T. P. GHOSE, S. KRISHNA, K. S. NARANG, and J. N. RAY (J.C.S., 1932, 2740-2744; cf. A., 1925, i, 958).—Vasicine (I), m.p. 198°, is readily oxidised by aq. $\rm KMnO_4$ at 0° and its hydrobromide decolorises aq. Br to give a substance, m.p. 225°. (I) is easily converted by alkaline reagents

$$\begin{array}{c} C_{6}H_{4} < \stackrel{NH}{\underset{C(OH):N}{\longrightarrow}} CH \cdot CH_{2} \cdot CH : CH_{2} \quad (I.) \\ (II.) \qquad \stackrel{C_{6}H_{4} \cdot N - CH_{2} - CH_{2}}{\underset{OH \cdot CN - CH_{2} \cdot CH_{2}}{\xrightarrow}} CH_{2} \end{array}$$

into isovasicine (II), m.p. 164° (decomp.) [which gives a methiodide, m.p. 191°, identical with that obtained from (I)], and with fused KOH forms anthranilic acid. Oxidation of (I) with KMnO4 yields 4-quinazolone and with H2O2 gives two successive substances, $C_{11}H_{10}ON_2$, ${}_{2}H_2O$, m.p. 168° (decomp.), and $C_{11}H_{10}O_2N_2$, m.p. 214°. Ac₂O and (I) form a substance, $C_{15}H_{11}ON_2$, m.p. 165°. The constitutions of (I) and (II) are suggested for vasicine and isovasicine, respectively. F. R. S.

Alkaloids of Picralima Klaineana, Pierre. II. T. A. HENRY (J.C.S., 1932, 2759-2768; cf. A., 1927, 982).—In addition to akuammine (I), the seeds contain akuammine hydrate (methiodide, m.p. above 300°), akuammicine (II), $C_{18}H_{17}ON_2(OMe)$, m.p. 177.5°, pseudakuammicine, $C_{18}H_{17}ON_2(OMe)$, m.p. 187.5° (hydrochloride, m.p. 216°), akuammenine, C₁₉H₁₉O₃N₂(OMe) (*picrate*, m.p. 216⁺), akuammenine, (II), C₂₀H₂₁O₂N₂(OMe) (*picrate*, m.p. 225[°]), akuammidine (III), C₂₀H₂₁O₂N₂(OMe) (+H₂O), m.p. 248.5[°], [α]]⁶ +21[°], akuammigine (IV), C₂₁H₂₃O₂N₂(OMe) (+H₂O), m.p. 125[°], [α]]²⁰₀ -44.4[°], *pseudakuammigine* (V), C₂₀H₂₀O₂N(OMe)(NMe), m.p. 165[°], [α]²⁰₀ -53.8[°], *akuammiline* (VI), C₂₁H₂₁O₃N₂(OMe), m.p. 160[°], [α]²⁰₀ +47.9[°], NH₃, a trace of an alkylamine, a wax, oil succose and a substance resembling inulin. The oil, sucrose, and a substance resembling inulin. The alkaloids are isolated from the seeds in two groups by light petroleum and by EtOH. (I) forms with HNO₂-HCl nitroakuammine hydrochloride and a Bz derivative, m.p. 245°. (V) gives a hydriodide, m.p. 90° (+H₂O), 238° (anhyd.), perchlorate, m.p. 70° and 110°, picrate, m.p. 215°, *methiodide*, m.p. 195° and 233°, $[\alpha]_{15}^{16}$ +16·3° (*Bz* derivative, m.p. 240°), *Ac*, m.p. 272°, and *Bz* derivatives, m.p. 219°. (VI) is converted into a hydrochloride, m.p. 196°, [a]^m_D -29.6°, hydriodide, m.p. 210°, nitrate, m.p. 204°, and methiodide, m.p. 233°, $[\alpha]_{12}^{20}$, -83·3°. (IV) yields a nitrate, m.p. 261°, picrate, m.p. 240°, and hydrochloride, m.p. 287°, $[\alpha]_{12}^{20}$, -37·8°. Derivatives of (V) are the hydrochloride, m.p. 183° (+H₂O), 218° (ahyd.), $[\alpha]_{D}^{20} = -15.4^{\circ}$, hydriodide, m.p. 215°, $[\alpha]_{D}^{20} = -1.43^{\circ}$,

picrate, m.p. 223°, and methiodide, m.p. 275°. (II) gives a hydrochloride, m.p. 171°, $[\alpha]_{1}^{6}$ -626·2°, sulphate (+4H₂O), m.p. 161°, nitrate, m.p. 182·5°, and methiodide, m.p. 252°. F. R. S.

Cytisine. II. H. R. ING (J.C.S., 1932, 2778– 2780; cf. A., 1931, 1171; 1932, 1146).—Methyl-cytisine is oxidised by $Ba(MnO_4)_2$ to N-methyl- α -, m.p. 214—215°, and N-methyl- β -cytisamide, m.p. 179-180°, which are hydrolysed by KOH and converted by PhSO₂Cl, respectively, into N-benzenesulphonyl-N-methyl-a-, m.p. 152-153°, and -β-cytis-

OTL OT		ÇH,•	CO·
		NMe	NMe
(I.) NH CH	2 11 0	Ċ0.	CH.
CH2 CH	n ₂ čo	(II.)	(III.)

amic acid, m.p. 130-131° (decomp.). The β-acid loses CO₂ at its m.p. to give the benzenesulphonyl base, m.p. 141-142°. These results are explained by assigning formula (I) to cytisine, with (II) and (III) for α - and β -methylcytisamide, respectively. F. R. S.

Reduction of 3:2'-nicotyrine to dihydronicotyrine and to inactive nicotine. Catalytic disproportioning of dihydronicotyrine into nicotine and nicotyrine. J. P. WIBAUT and J. T. HACKMANN (Rec. trav. chim., 1932, 51, 1157– 1165).—3 : 2'-Nicotyrine (I) with Zn and HCl gives nicotine (II) (picrate, m.p. 223–224°) (yield 12%), and a dihydronicotyrine (III), b.p. 244–246° (di-picrate, m.p. 163–164°), which is unaffected by further action of Zn and HCl. (III) with H₂ (Adams) gives (II) (I) and dihydrometanicotine (dipicrate. gives (II), (I), and dihydrometanicotine [dipicrate, m.p. 161-162° (cf. A., 1909, i, 827)]. (III) in AcOH with the Pt catalyst in the absence of H₂ gives (II) and (I), yields being given under varying conditions. A. A. L.

Quinine hydrobromide with chloroform and bromoform of crystallisation. W. SCHNELLBACH and J. ROSIN (J. Amer. Pharm. Assoc., 1932, 21, 1009-1012).-A description of cryst. compounds of quinine hydrobromide with CHCl₃ (2.5 mols) and CHBr₃ (2 mols). E. H. S.

Constitution of pellotine and anhalonidine. E. SPATH [with, in part, J. PASSL] (Ber., 1932, 65, [B], 1778-1785; cf. A., 1922, i, 163, 567, 852).-Pellotine (I) is transformed by diazoethane in anhyd. EtOH at room temp. into the O-Et ether, b.p. 130-140° (bath)/1 mm., oxidised by KMnO₄ to 4:5dimethoxy-3-ethoxyphthalic acid (II) (anhydride, m.p. $108-109^{\circ}$). (I) is therefore A. Since anhalonidine



is obtained by isoquinoline ring closure from βamino-a-3: 4-dimethoxy-5-acetoxyphenylethane, is

OMe² **OMe**

OH

(C)

a sec. base, and gives the same quaternary compound as pellotine NH when methylated under conditions which do not affect the phenolic OH, it must be B, whilst

anhalamine is probably C. The structure of (II)

is elucidated as follows. 1:2:3:5:6:7-Hexa-hydroxyanthraquinone (III) is converted by short treatment with CH_2N_2 in Et₂O-MeOH into 1:5dihydroxy-2:3:6:7-tetramethoxyanthraquinone (IV), m.p. 252-253°, which must have the free OH groups in the position indicated, since it does not give trimethoxyphthalic acid when oxidised and consumes the same relative amount of KMnO₄ as does 5hydroxy-3: 4-dimethoxybenzoic acid. Prolonged treatment of (III) with CH_2N_2 affords a single Me_5 ether (II), m.p. 189–190°, and a Me_6 ether, m.p. 239-240°; the difficulty of methylation is due to the vicinal position of the OH to the CO groups, confirmed by the observation that 2:3-dihydroxyanthraquinone readily passes into its Me2 ether, m.p. 241-242°, without giving the Me1 compound, whereas alizarin gives almost exclusively 1-hydroxy-2-methoxyanthraquinone. Oxidation of (V) with KMnO₄ affords 3:4:5-trimethoxyphthalic acid (anhydride, m.p. 144°), identical with the acid obtained from colchicine. Treatment of (IV) with KOH and EtI in EtOH yields 5-hydroxy-2:3:6:7tetramethoxy-1-ethoxy- (VI), m.p. 175-176°, and 2:3:6:7-tetramethoxy-1:5-diethoxy-, m.p. 237-238°, -anthraquinone. Oxidation of (VI) affords 4:5-dimethoxy-3-ethoxyphthalic acid identical with that derived from pellotine. H. W.

Synthesis of nor-Lupin alkaloids. VII. lupinane. K. WINTERFELD and F. HOLSCHNEIDER (Annalen, 1932, 499, 109-122).-1-Methyl-2-pyrrolidone, Et pyridine-2-carboxylate, and NaOEt in C₆H₆ give 2-pyridyl 3-1-methyl-2-pyrrolidonyl ketone, m.p. 82—84° (slight previous sintering) [picrate, m.p. 137—138°; mercurichloride, $C_{11}H_{12}O_2N_2,HgCl_2,2HCl, m.p. 212-213^{\circ} (decomp.)],$ converted by fuming HCl into 2- γ -methylaminobutyrylpyridine (dihydrochloride, decomp. 183-184°; phenylhydrazone hydrochloride, decomp. $221-222^{\circ}$). The Bz derivative of this is reduced (H₂, PtO₂, AcOH) to the oily N-Bz derivative (I) of 2- δ -methylamino- α hydroxybutylpiperidine. (I) and PBr₅ at $150-160^{\circ}/$ vac. give PhCN, MeBr, and 2- $\alpha\delta$ -dibromobutylpiperidine (admixed with a little unsaturated material); the latter is converted by EtOH-NaOEt into 9bromo-octahydropyridocoline, which is reduced (H₂, Pd-CaCO₃, EtOH-KOH) to (mainly) octahydro-pyridocoline (II), b.p. 92—93°/14·5 mm. [picrate, m.p. 193°; chloroaurate, m.p. 168°; methiodide, m.p. 333—335° (decomp.); hydrobromide, m.p. 265— 266°], and a small fraction, b.p. 110°/14.5 mm. (picrate, m.p. 192—193°). (II) is considered to be identical with norlupinane (cf. Clemo *et al.*, A., 1931, 499; 1932, 178). The bromocyanoamide from (II) and CNBr in C_6H_6 on successive reduction (H₂, Pd-CaCO₃) and hydrolysis (EtOH-HCl) gives 2-nbutylpiperidine, b.p. 191-193°, also prepared by reduction (Adams) of 2-n-butylpyridine, which is obtained by Ziegler and Zeiser's method (A., 1930, 1191). Norlupinane, obtained by soda-lime distillation of lupininic acid and subsequent reduction (H₂, Pd-CaCO₃, EtOH) of the distillate, has b.p. 70-72°/13 mm. (cf. Clemo et al., loc. cit.); the picrate, chloroaurate, and methiodide are identical with those of (II). H. B.

Structure of strychnine and brucine. O. ACH-MATOWICZ (Rocz. Chem., 1932, 12, 862–868).— Neostrychnidine dimethiodide, C₂₃H₃₀ON₂I₂,H₂O, m.p. 295°, prepared from neostrychnidine dimethosulphate and NaI, yields with AgCl the corresponding dimethochloride, identical with Clemo, Perkin, and Robinson's (A., 1927, 888) "methoxymethyldihydrostrychnidine dimethochloride (A), $C_{25}H_{36}O_2N_2Cl_2$," prepared by the successive action of Me_2SO_4 , NaI, and AgCl on methoxymethyldihydroneostrychnidine. The (A)salt undergoes Emde's reaction during methylation, involving the stages of methylation, elimination of MeOH, and reconstruction of the strychnidine ring; the same applies to the (A) salts of methoxymethyltetrahydrostrychnidine, which are in reality dimethosalts of dihydrostrychnidine, and have the composition $C_{23}H_{32}ON_2X_2$, and not, as stated by Clemo et al., $C_{25}H_{38}O_2N_2X_2$; in this case Emde's reaction is catalysed by H₂O. Methoxymethyldihydroncostrychnidine yields neostrychnidine methiodide on treatment successively with Me₂SO₄ and NaI. R. T.

Sinomenine. XXXIV. Dihydrosinomenilone and its Hofmann degradation. K. Goto and K. TAKUBO (Annalen, 1932, 499, 169–174).—1-Bromosinomenilone (I) (A., 1932, 760) is debrominated (H₂, Pd-BaSO₄-PdCl₂, 5% AcOH) to sinomenilone, m.p. 176° (softens at 155°), $[\alpha]_{11}^{16}$ +442·14° (all rotations are in CHCl₃) (oxime, m.p. 238°). Reduction of (I) with Na-Hg and EtOH gives 1-bromodihydrosinomenilone, m.p. 180°; methiodide, m.p. 220° (decomp.)], debrominated (as above) to dihydrosinomenilone (II), m.p. 132°, $[\alpha]_{11}^{16}$ +207·75° [oxime, m.p. 155—156° (decomp.)]. The methiodide, decomp. 220—240°, of



(II) and boiling 16.6% KOH give de - N - methyldihydrosinomenilone (III), m.p. 220° (decomp.), the methiodide of which is similarly degraded to anhydrobis-sinomelone (IV), C₃₂H₃₀O₅, m.p. 266°
NMe (softens at 262°), [a]²/₁₀ - 522.71°, instead of the expected sinomel-

one [(IV) probably arises from this by condensation between a CH₂ of one mol. and a CO group of a second mol.]. Reduction (H₂, Pd-BaSO₄-PdCl₂, 5% AcOH) of (III) affords dihydrode-N-methyldihydrosinomenilone, m:p. 175° (softens at 170°), $[\alpha]_{14}^{24}$ -24·56°, the methiodide of which is degraded to anhydrobisdihydrosinomelone, m.p. 247° (softens at 244°), also prepared by catalytic reduction of (IV). H. B.

p-Arsanilic acid derivatives of N-substituted malonamides. J. KENNEDY (J.C.S., 1932, 2781— 2782).—Condensation of the appropriate bromomalonamide with p-arsanilic acid has given the following: p-arsonoanilinomalon-amide (I), m.p. 226° (decomp.) (lit. m.p. >260°); -bismethyl-, m.p. >295°; -bisethyl- (II), m.p. >300°; -bis-n-propyl-, m.p. >265°; -bis-n-butyl-, m.p. 293° (decomp.); -bisisobutyl-, m.p. >260°; -bis-n-amyl-, m.p. 297° (decomp.) (malonbis-n-amylamide, m.p. 128°; Brderivative, m.p. 98°); and -bisisoamyl-amide, m.p. >260° (malonbisisoamylamide, m.p. 74°; Brderivative, m.p. 110°); and Et p-arsonoanilinomalonate, m.p. 230° (decomp.). Methyl-, m.p. 165°, and ethyl-bromomalonamide, m.p. 160°; ethyl-, m.p. 177°, and ethylbromo-malonbismethylamide, m.p. 130°, are also described. Only (I) and (II) show therapeutic effect. F. R. S.

derivatives Aminomethylene containing arsenic and antimony from hydroxymethylene compounds. E. BENARY (Ber., 1932, 65, [B], 1669-1677).—The following N-substituted p-aminophenylarsinic acids are obtained by addition of a conc. aq. solution of the Na salt of the requisite hydroxymethylene compound to a solution of the arsinic acid (I) containing an equiv. amount of HCl at room temp. : y-keto-∆a-butenyl-, decomp. 172-175° after darkening at 165°, from hydroxymethyleneacetone; γ -keto- β -methyl- Δ^{α} -butenyl-, decomp. about 220°; γ-keto-β-ethyl-Δa-butenyl-, decomp. 225-230° after darkening at 215°; γ -keto- γ -phenyl- Δ^{α} -propenyl-, decomp. about 330°; γ -keto- γ -1-naphthyl- Δ^{α} -propenyl-, decomp. about 280°; methylenecyclohexanone-, decomp. about 217-218°; methylenecamphor- (cf. Rupe, A., 1920, i, 241); methylenementhone-, decomp. 176-178°; β-carbethoxyethenyl-, m.p. about 168° (decomp.) [the corresponding derivative from 2-amino-4-hydroxyphenylarsinic acid (II) is described; the Pra and amyl esters are analogously prepared]; β-cyanoethenyl-, decomp. 210-230°; methylene-5-acetyl-2-methylpyridine-, decomp. about 220° after softening at 175°; methylene-6-methoxy-4acetylquinoline-, decomp. about 265-266° [corresponding derivative from (II), decomp. about 205°]; methylene-4-acetyl-2-phenylquinoline-, decomp. about 185°; di-ββ-carbethoxyethenyl-, decomp. about 270° [from Et ethoxymethylenemalonate and (I) in boiling MeOH]; γ -keto- β -carbethoxy- Δ^{α} -butenyl-, decomp. 270—280° after darkening at 260°; γ -keto- β -acetyl- Δ^{α} -butenyl-, decomp. 245—250° after darkening at 235°; δ -chloro- γ -keto- β -carbethoxy- Δ^{α} -butenyl-, decomp. 235—240° after darkening at 210°. The methyleneacetophenone-, decomp. about 240° after darkening at 235°, and methylenecyclohexanone-, decomp. 230-235° after darkening at 220°, derivatives of (II) are described. Pyrone and (I) yield the compound CO(CH:CH·NH·C₆H₄·AsO₃H₂)₂, decomp. 225—230° after darkening at 200°, whereas δ -hydroxy- $\Delta^{a\nu}$ -butadiene- α -aldehyde yields the substance AsO3H2·C6H4·N:CH·CH:CH·CH:CH·NH·C6H4·AsO3H2,

decomp. about 180°; analogous products from (II) are described. 3:3'-Diamino-4:4'-dihydroxyarsenobenzene with hydroxymethyleneacetone, hydroxymethylenemethyl Et ketone, and Et sodioformylacetate, respectively, gives the compounds $C_{20}H_{20}O_4As_2$, decomp. 225—235° after darkening at 180°, $C_{21}H_{22}O_4N_2As_2$, m.p. about 223° (decomp.) after softening at 180°, and $C_{22}H_{24}O_6N_2As_2$, m.p. about 175°. p- γ -Keto- Δ° -butenylaminophenylstibinic acid and the corresponding compound with Et sodioformylacetate are described. Some of the simpler compounds show marked physiological activity, which diminishes with increase in size of the mol. of the hydroxymethylene compound. H. W.

Derivatives of phenylboric acid, their preparation, and action on bacteria. II. Hydroxyphenylboric acids. F. R. BEAN and J. R. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 4415-4425).—Arylboric acids are best prepared from Mg aryl bromides and Bu^a borate at -75° to -70° ; phenyl-, *p*-tolyl-(I), anisyl- (II), and *p*-bromophenyl- (III), m.p. 286— 289° (corr.) (decomp.), m.p. (block) 301—302°, -boric acids are thus obtained. m-Hydroxyphenylboric acid (IV), m.p. 225° (decomp.) (softens at 219°), m.p. (block) >380°, converted by aq. HgCl₂ into m-hydroxyphenylmercuric chloride, m.p. 240·5—241·5° (corr.), is prepared by the usual method from

m-NH₂·C₆H₄·B(OH)₂, which is best obtained by reduction (H₂, PtO₂, aq. MeOH) of the NO₂-acid. o-Aminophenylboric acid, m.p. 179—180° (corr.) (cf. A., 1931, 502), is prepared by similar reduction of the o-NO₂-acid. (I) and HNO₂-free HNO₃ (d 1·5) at -30° to -28° give 2-nitro-p-tolylboric acid, m.p. 260—264° (corr.) (darkens at 250°), m.p. (block) 264°, reduced (as above) to the 2-NH₂-acid, m.p. 209—212° (corr.) (softens at 200°), m.p. (block) 267—270° (slowly), 285° (instantly) [Ac, m.p. 244—246°, and Bz, m.p. 95—100°, re-solidifying with m.p. 315° (corr.), derivatives], which is converted into 2-hydroxy-ptolylboric acid (V), m.p. 266—268° (corr.) (decomp.), m.p. (block) >380°. (V) and aq.HgCl₂ give 2-hydroxy-p-tolymercuric chloride, m.p. 143·6—144·6° (corr.) with darkening. Nitration of (III) affords 4-bromo-3nitrophenylboric acid, m.p. 300—301° (corr.), m.p. (block) 320°; (II) similarly gives 2 : 4-dinitroanisole. (IV) and (V) have practically no bactericidal action towards S. aureus. The bacteriostatic effects of the above and the nitrophenylboric acids are determined; (III) has the highest action. H. B.

Germanium. XI. Organic compounds of germanium. R. SCHWARZ and W. REINHARDT (Ber., 1932, 65, [B], 1743–1746).—GeCl₄ in Et₂O is converted by the Mg derivative of $\alpha \varepsilon$ -dibromopentane into Ge cyclopentamethylene dichloride,

 $CH_2 < CH_2 CH_2 CH_2 > GeCl_2$, b.p. 55-60°/12 mm., trans-

formed by MgEtBr into 1: 1-diethylgermaniumcyclopentamethylene, b.p. $52^{\circ}/13$ mm. GeCl₄ and K pyrrole in light petroleum, b.p. 60° , afford Ge tetra-1pyrrolyl, m.p. 202°. NaOPh suspended in boiling C₆H₆ and GeCl₄ yield Ge tetraphenoxide, b.p. 210— 220°/0·3 mm. Analogously, or by successive addition of PhSH and GeCl₄ to MgPhBr, Ge tetrathiophenoxide, m.p. 104°, is derived. SnPhCl₃ and Na in C₆H₄Me₂ yield SnPh₄ and Sn. H.W.

Globin. K. FELIX and O. KAHLERT (Z. physiol. Chem., 1932, 212, 157—160).—Natural and denatured globin were esterified with MeOH. The analyses of the ester hydrochlorides of the two forms were identical. From the OMe and Cl content, the CO_2H and basic groups amount to 12.8 and 13.2, respectively, per 100 atoms of N. J. H. B.

Extractives of muscle. XXX. Determination of carnosine. II. Deamination of β -alanine by nitrous acid. XXXI. Determination of carnosine. III. L. BROUDE (Z. physiol. Chem., 1932, 212, 196-204, 205-206; cf. A., 1928, 665).--XXX. A total error of 14% in the determination of carnosine by hydrolysis, deamination of the β alanine to hydracrylic acid by HNO₂, conversion into acrylic acid, and measurement of the Br absorption is probably due in part to production of some acrylic acid in deamination, which then forms β -nitropropionic acid with excess of HNO_2 .

XXXI. The error is avoided by removal of excess of HNO_2 with $NH_2 \cdot SO_3H$. There is an error of 4%inherent in the Br absorption; when this is corrected for the method gives exact results. J. H. B.

Basic amino-acids of livetin. T. H. JUKES and H. D. KAY (J. Biol. Chem., 1932, 98, 783—788).— The arginine-N figure for livetin, determined by the arginase method, is 11.7% as compared with 14.7% for vitellin. The cystine content of livetin by the Sullivan method (cf. A., 1930, 1604) is 2.3%; that of vitellin is 1.1%. Isolation of the basic NH₂-acids of livetin gave a basic N distribution of 10.3% arginine-N, 2.11% histidine-N, and 5.92% lysine-N.

R. N. C.

Clupein. VI. K. FELIX, K. DIRR, and A. HOFF (Z. physiol. Chem., 1932, 212, 50–52; cf. A., 1932, 1269).—Arginase acts on arginine substituted in the NH₂ group by a peptide or protein group as in clupein Me ester hydrochloride, the optimum $p_{\rm H}$ varying with the substituent. This fact may be used to determine whether in a protein a free CO₂H group belongs to arginine. J. H. B.

Sources of error in organic elementary analysis. IX. Metallic copper as substitute for lead peroxide in micro-elementary analysis. J. LINDNER (Ber., 1932, 65, [B], 1696—1706).—Increased accuracy in the determination of H, already attained by the volumetric method and refinement of apparatus in the case of N-free substances, cannot be secured with compounds containing N if PbO₂ is retained. The use of Cu is advocated, N₂ being employed as transport gas and O₂ or air used in the actual combustion. MeOH or HCO_2H is unsuitable for reduction of CuO, which should be effected with H₂. H. W.

Determination of halogens in organic compounds. F. GOVAERT (Compt. rend., 1932, 195, 797-798).—A modification of the method of Vaughn and Nieuwland (A., 1931, 1393) is described.

J. L. D.

Determination of chlorine and bromine in organic compounds. M. DESTERLIN (Angew. Chem., 1932, 45, 673—674).—Vieböck's method is inapplicable to such compounds as alkaloid salts which evolve acid vapours on decomp. In the method described, which is suitable for micro-determinations, the sample (5 mg.) is decomposed with $H_2SO_4-K_2Cr_2O_7$, and the gas evolved is passed through 0.2—0.3 c.c. N_2H_4 , H_2O and then through H_2O . The solution is acidified (Congo-red) with HNO₃, and after addition of 0.2 c.c. of 10% Na nitroprusside solution is titrated with 0.01N-Hg(NO₃)₂. The method is very rapid, and is not influenced by large amounts of NO₃' or NO₂'. H. F. G.

Comparison of the methods of determining salicylic and benzoic acids in presence of each other. B. BRODSKY and J. PERELMANN (Pharm. Zentr., 1932, 73, 721—725, 741—745).—Tests of the various methods of determining NaOBz and Na salicylate (I) show that the most trustworthy is to determine (a) the total Na and (b) (I) bromometrically (A., 1911, ii, 546) in < 0.008N solution. R. S. C. Determination of phenols by bromination. I. M. KOLTHOFF (Pharm. Weekblad, 1932, 69, 1147— 1158).—The method of Autenrieth and Beuttel for the determination of PhOH as tribromophenol yields results 7—8% low, whilst with Walton and O'Brien's iodometric method (A., 1932, 72) even greater errors occur. In one method recommended, 1 g. NaOAc and 20—40 c.c. saturated Br-H₂O are added to 5— 10 c.c. of *M*-PhOH solution; the ppt. is separated after 5—10 min., washed with H₂O, and added to 5—10 e.c. *N*-KI, and after 10 min. the suspension is titrated with 0·1*N*-Na₂S₂O₃. Alternatively, the tribromophenol bromide may be dried over H₂SO₄ and weighed. The error of both these methods is $\geq 2\%$. In a third method the ppt. is removed, 2 g. Hg₂Cl₂ are added to the filtrate to remove excess Br, and the HBr present is titrated with 0·1*N*-NaOH (bromocresol-green); if the ppt. filters with difficulty it may be removed with CCl₄ or CHCl₃. The error is about 1%. H. F. G.

Bromination of salicylic acid. I. M. KOLTHOFF (Pharm. Weekblad, 1932, 69, 1159–1161).—Addition of Br-H₂O to a solution of salicylic acid yields first dibromosalicylic acid and then CO_2 and tribromophenol (I). The reaction may be employed for the determination of salicylic acid, by determining either the (I) formed or the CO_2 evolved; the error in either case is about 2%. H. F. G.

Detection of carbon dioxide during autoxidation of carotenoids. H. H. ESCHER (Helv. Chim. Acta, 1932, 15, 1421—1424).—Carotene and xanthophyll in O_2 or air give CO_2 (0.827—0.848 and 0.642— 0.679 mol., respectively) and a volatile substance (possibly glyoxal) which gives a Ag mirror in the cold. Carotene is thereby changed into an acid. Pure linseed oil gives no CO_2 . Possibly glyoxal is the primary and CO_2 a secondary oxidation product. R. S. C.

Microscopical identification of ephedrine with nitrous acid. F. GRILL (J. Amer. Pharm. Assoc., 1932, 21, 1012—1014).—Ephedrine hydrochloride and HNO₂ give characteristic crystals (NO-compounds ?). E. H. S.

Microchemical identification of alkaloids. F. AMELINK (Pharm. Weekblad, 1932, 69, 1270–1272, 1289–1296). — Pantocaine (butylaminobenzoyldimethylaminoethanol hydrochloride) yields an illdefined ppt. with AuCl₃, but by adding NaBrcharacteristic brown crystals are formed; the sensitivity is 0.1%. K₄Fe(CN)₆, preferably in neutral solution, and K₃Fe(CN)₆ (in neutral solution only) yield characteristic ppts. from 0.2% solutions. PtCl₄, HgCl₂, KOH, and Dragendorff's reagent do not yield cryst. derivatives. With K₂Cr₂O₇ a cryst. ppt. is formed from 0.1% solutions.

HgCl₂, KOH, and Dragendorn's reagent do not yield cryst. derivatives. With $K_2Cr_2O_7$ a cryst. ppt. is formed from 0.1% solutions. α -Eucaine yields a characteristic cryst. ppt. with PtCl₄, AuCl₃, HgCl₂, and KI in neutral solution, and with $K_4Fe(CN)_6$ in acid solution; the limiting conen. of alkaloid is about 0.1% in each case. Psicaine may be identified by the cryst. ppts. obtained with PtCl₄ in neutral solution, after addition of EtOH (limit 0.1%), and with $K_4Fe(CN)_6$ in acid solution (limit 0.2%). With eucodal the PtCl₄ reaction is of little use, but on addition of NaI characteristic crystals separate (limit 0.1%); the ppts. obtained with $AuCl_3$ in neutral solution and with KOH are characteristic also (limits 0.5% and 0.1%). Various other reactions of the three alkaloids are described.

H. F. G.

Microchemical detection of atropine. E. ILIESCU (Rev. farm., 1931, 51, No. 3, 34-39; Chem. Zentr., 1932, ii, 577).—Saturated aq. picric acid detects 0.04 mg.; glycerol+saturated picric acid in 96% EtOH detects 0.02 mg., whilst 5% aq. picric acid rendered alkaline with Na₂CO₃, treated with glucose, and boiled until reddish-brown, detects 0.01 mg. A. A. E.

Biochemistry.

Spectrophotometric studies. I. Spectrophotometric constants for common hæmoglobin derivatives in human, dog, and rabbit blood. D. L. DRABKIN and J. H. AUSTIN (J. Biol. Chem., 1932, 98, 719-733).-The use of solutions of $CuSO_4$ in 2N-aq. NH₃ is suggested as a simple, reproducible, inorg. standard for spectrophotometric technique. Vals. of the mol. extinction coeff. at λ 510-600 mµ for 0.05M- and 0.025M-CuSO₄ solutions did not deviate by > 1.7%; at 610-700 mµ by > 4.1%. Vals. of the absorption const. of various hæmoglobin derivatives from blood of man, dog, and rabbit are presented. Under the same conditions, the absorption consts. do not vary with the species. The components of a mixture of two pigments can be determined by measurement of the absorption consts. of the pure components and of the mixture. The rate of conversion of oxyhæmoglobin into a hæmoglobin derivative on keeping after dilution also can be measured by observing the change in absorption const., but the solution must not be more dil. than 1/100, since oxyhæmoglobin is unstable in very dil. R. N. C. solutions.

Dissociation curve of oxyhæmoerythrin in the cœlomic liquid of Sipunculus. M. FLORKIN (Compt. rend., 1932, 195, 832—833).—The dissociation curve of the respiratory pigment of S. nudus is practically independent of the CO_2 tension, and, as compared with that of human hæmoglobin, indicates greater combination with O_2 at the same O_2 tension. W. O. K.

Comparison of different stimulants of blcodcell regeneration. A. RANSON (Bull. Soc. Chim. biol., 1932, 14, 1218—1221).—Rapid regeneration of hæmoglobin is caused by feeding anæmic rabbits with the following daily doses per animal for 9 days, respectively: (A) Fe peptonate 0.01 g. (128), (B) chlorophyll 0.004 g. and 5 units of carotene (132), (C) liver and spleen extracts 0.02 g. each (117), and (D) a mixture of the above quantities (132), the figures in parentheses indicating their val. by comparison of the hæmoglobin vals. at the end of treatment with untreated controls. Treatments (A) and (C) cause only slight, and (B) a marked, increase in the blood count. The mixture is superior in all respects to any of the single substances. A. C.

Factors in food influencing hæmoglobin regeneration. II. Liver in comparison with whole wheat and prepared bran. M. S. ROSE and L. KUNG (J. Biol. Chem., 1932, 98, 417-437).--Rats, rendered anæmic by restriction to a milk diet, were fed with diets of milk supplemented by whole wheat (I), bran (II), dried liver (III), or a modified Osborne-Mendel diet (IV). During the period of return to a normal blood condition no differences occurred in the production of hamoglobin expressed in terms of blood vol. Rats on (II) attained a normal level most rapidly, whereas greatest growth occurred with (III) and (IV). The gain in hamoglobin per g. body-wt. was 20-60% greater in females than in males, a phenomenon also occurring after extensive bleeding, a process which reduced the Fe content of the body (minus digestive tract) to $0.0021\pm0.00003\%$ for both sexes. F. O. H.

Differences in chemical behaviour of blood of various animal species. K. BINGOLD (Z. klin. Med., 1932, 120, 503—509; Chem. Zentr., 1932, ii, 395).—Hæmatin, present in human blood only in pernicious anæmia and yellow atrophy of the liver, is frequently present in dog's, and always present in avian, blood. *Pneumococcus* and Fraenkel's bacillus convert hæmoglobin into hæmatin. At various high temp. decomp. of H_2O_2 by the blood is prevented by chemical decomp. of the pigment. Certain bacteria cause profound decomp. of hæmoglobin, such that porphyrins, urobilin, or bilirubin cannot be detected. A. A. E.

Glass electrode for testing the $p_{\rm H}$ of blood. D. DuBois (Science, 1932, 76, 441-443).—An apparatus requiring 0.25 c.e. or less of blood and eliminating serious drift is described. L. S. T.

Applicability of Winterstein's microelectrode for the determination of blood- $p_{\rm H}$. H. WINTER-STEIN (Arch. exp. Path. Pharm., 1932, 168, 305— 306).—A reply to Laubender (A., 1932, 635).

W. O. K.

Determination of potassium in blood-plasma. A. D. MARENZI and R. GERSCHMANN (Bull. Biol. Pharm., 1932, 18, 315–316).—K is pptd. as cobaltinitrite, and the Co determined colorimetrically. The method is accurate to $\pm 2\%$. The K content of dog plasma is 19.07 mg. per 100 c.c. A. L.

Ether-soluble acids of the blood. S. L. ØRSKOV (Skand. Arch. Physiol., 1932, 63, 255—276; Chem. Zentr., 1932, ii, 554—555).—The acids (0—3·3, average $1\cdot22$, $\times 10^{-3}N$) extracted, like lactic acid, with Et₂O are largely sol. in PhMe. The volatile acids ($0\cdot1\times10^{-3}N$) include HCO₂H ($<0\cdot25$ mg. per 100 c.c.) and AcOH ($<0\cdot5$ mg. per 100 c.c.). Minute quantities of coupled glycuronic and bile acids are also present. A. A. E.

Lactic and total ether-soluble acids in the blood of dogs on various diets. S. L. ØRSKOV (Skand. Arch. Physiol., 1932, 63, 213-239; Chem. Zentr., 1932, ii, 555).-Glucose, galactose, sucrose, and particularly fructose increase the blood-lactic acid. Fat following meat, but not following carbohydrate, also causes an increase. Lean meat following carbohydrate diminishes the blood-lactic acid. The other Et_2O -sol. acids are unaffected. A. A. E.

Determination of blood-sugar A. J. L. TERWEN (Med. Tijdschr. Geneesk., 1932, **76**, 2487—2492; Chem. Zentr., 1932, ii, 577).—K₃Fe(CN)₆ is reduced to K₄Fe(CN)₆, which reacts with Fe^{III}, the Prussianblue being retained in solution with $H_4P_2O_7$ and compared colorimetrically with that obtained using 0·1% glucose solution. A. A. E.

[Determination of] blood-sugar. R. RAZA-FIMAHERY (Ann. Chim. Analyt., 1932, [ii], 14, 488— 493).—A discussion of the merits of the Hagedorn-Jensen method of determination and a modification in which $CCl_3 \cdot CO_2H$ replaces $Zn(OH)_2$ as protein precipitant. P. G. M.

Relation of sugar to cholesterol in the blood. H. O. MOSENTHAL (Arch. Int. Med., 1932, 50, 684— 689).—After administration of 100 g. of glucose to adults, the plasma-cholesterol may rise, fall, or remain const. W. O. K.

Nature and stability of protein-lipin linkings in blood-serum. Extraction of lipins by ether in presence of alcohol. M. A. MACHEBŒUF and G. SANDOR (Bull. Soc. Chim. biol., 1932, 14, 1168-1190).-The amount of lipin extracted from horseserum in 6 hr. by an equal vol. of Et₂O rises sharply to a max. of 50% of the lipin content as the added EtOH is increased to 10% of the serum-vol., and falls rapidly as the EtOH is increased further to 20%. Moderate variation of the vol. of, or renewing, the Et₂O has little influence on the amount of lipin extracted. Following an initial period of slow extraction, which increases as the added EtOH is reduced, and is 1 hr. in the case of optimum concn. of EtOH, extraction of lipin proceeds rapidly. After extraction, the globulin and albumin can be isolated in the native state, and the latter is associated with the lipin fraction which resists extraction. Similar results are obtained with human, rabbit, and sheep sera. The hydrophilic groups of protein, and its possible linking with lipin through common groups, are considered in explaining the results. A. C.

Modifications of serum-proteins and myxoprotein isolated by the acetone method. A. BONOT (Compt. rend., 1932, 195, 1046—1048).— Protein is pptd. from dog-serum by COMe₂ and dried in vac. from filter (I), or centrifuge (II). Aq. solutions of (I) and (II) give with 0.1N-HCl or CO₂ to $p_{\rm H}$ 5.5 protein fractions incompletely sol. in 0.1M-NaCl. The denaturation is partly reversed by storage at 0°. The serum, and a protein solution prepared from it as (II), but under anhyd. conditions, give ppts. of native globulin at $p_{\rm H}$ 5.5 and do not change with age at 0°. Myxoprotein is a mixture of almost native globulins rich in pseudoglobulins and denatured protein.

Factors involved in the use of organic solvents as precipitating and drying agents of immune sera. M. H. MERRILL and M. S. FLEISHER (J. Gen. Physiol., 1932, 16, 243-256).—Concns. of 70-75% of MeOH, EtOH, PrOH, and COMe₂ completely ppt. serum-proteins and produce max. loss of solubility.

A. C.

With agglutinating sera the loss of agglutinin is approx. parallel to the loss of solubility. Concns. >75% produce complete pptn., but a decreased loss of solubility; at concns. >87% the ppts. are completely sol. in saline. Rise of temp. or prolonged exposure to the solvent increases the degree of denaturation. At 5° no denaturation occurs. A max. ppt. is obtained at $p_{\rm R}$ 6.0, whilst a greater proportion of protein is pptd. from a more conc. serum. Dry immune sera are prepared by pptn. with abs. EtOH or COMe₂.

F. O. H.

Immunisation with lecithin from human urine. F. PLANT and H. RUDY (Z. Immunität., 1932, 73, 385—391; Chem. Zentr., 1932, ii, 555— 556).—The lecithin (C 65·79, H 10·55, P 3·80, N 1·73%; NH₂-N 0·8%) did not give a Molisch reaction for cerebroside. Lecithin antisera (rabbit) could not be prepared by combination of this lecithin with pig serum or by addition of pure cholesterol. The antigenic activity of commercial lecithin is due to the presence of egg-yolk. A. A. E.

Serological reactions with simple chemical compounds (precipitin reactions). K. LAND-STEINER and J. VAN DER SCHEER (J. Exp. Med., 1932, 56, 399-409).—Azo-dyes are pptd. by immune sera prepared by injection of azoproteins containing the same azo-component. Hence antibodies combine specifically with substances of small mol. wt. The colloidal state of the solution and the composition of the substance determine the tendency to separate from the liquid on combination with antibody. The following were prepared : p-nitro-malon-, m.p. 157° (decomp.); -succin-, m.p. 194—195°; -glutar-, m.p. 170—171°; -adip-, m.p. 174—175°; -pimel-, m.p. 147—148°; -suber-, m.p. 158—159°, -anilic acids; p-NH₂-derivatives, m.p. 175—176° (decomp.), 183—184°, 186—187°, 165—166°, 178—179°, and 162—163°, respectively. CH. ABS.

Preparation of hæmolytic and precipitating sera. H. J. STAFSETH (Science, 1932, 76, 444).— An immune serum prepared by using clear serum as antigen can function as a hæmolytic serum, and a hæmolytic serum prepared by washing red bloodcells as antigen can act as a precipitating serum. Hæmolytic and precipitating sera have been obtained, using the clear saline solution in which blood-cells have been washed as antigen. L. S. T.

Hæmolytic action of fatty acids. M. BODANSKY (J. Cell. Comp. Physiol., 1932, 1, 429–434).—The hæmolytic action of fatty acids is discussed in relation to permeability, lipin solubility, and Traube's rule of attraction pressure. A. G. P.

Extractives of the embryo of Acanthias vulgaris. F. KUTSCHER, E. MÜLLER, and W. SPAHR (Z. Biol., 1932, 93, 239-240).—Betaine and choline were isolated, but no NMe₃:O was detected.

P. G. M.

Physiology of plant and animal membranes. E. WERTHEIMER (Kolloid-Z., 1932, 61, 181-198).-A review. E. S. H.

Digestive enzymes of the Colorado potato beetle and the influence of arsenicals on their activity. D. E. FINK (J. Agric. Res., 1932, 45, 471—482).—Amylase, lactase, invertase, lipase, and proteolytic enzymes exist only in the mid-gut of the beetle and in regurgitated liquids. As fed on sprayed foliage did not appreciably affect the activity of the digestive enzymes. Direct injection of As into the mouth inhibited the action of proteolytic enzymes. A, G, P.

[Composition of] ovaries of various animals and of commercial ovary powders. J. VINTI-LESCO and J. BIBESCO (J. Pharm. Chim., 1932, [viii], 16, 369—375).—Detailed analyses are given of fresh dried (105°) ovaries of the ewe, cow, and sow, and of four commercial ovary powders. These powders, if unadulterated, should contain H_2O 8, Et_2O -sol. material 8—12, non-saponifiable material 2—3·5, cholesterol (total) 3·5—3·2, and glycogen 16—20%, and have sap. val. 180—205, and I val. 80—90. Fresh, but not dried, ovaries contain 0·21—0·33% of glutathione. Dried ovaries have only peroxidase action, probably due to traces of hæmoglobin. R. S. C.

Intracellular fatty substances in various tissues cultivated in vitro. Z. SZANTROCH (Atti R. Accad. Lincei, 1932, [vi], 15, 904—907).—The fats appearing in embryonic tissue (hen) cultures are examined. T. H. P.

Surface resistance of human enamel to acid decalcification. E. C. DOBBS (J. Dental Res., 1932, 12, 581—584).—The org. protective membrane is lost on tryptic digestion. CH. ABS.

Detection of elements in tissues. I. Lead. WALTHER GERLACH and WERNER GERLACH (Arch. Gewerbepath. Gewerbehyg., 1931, 2, 7—10; Chem. Zentr., 1932, i, 2871).—Cu and Pb are detected spectroscopically (cf. A., 1931, 328). A. A. E.

Determination of oxygen and hydrogen potential in the muscle tissue of the frog. J. W. LANGELAAN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 440-441).—Two characteristic potentials at +0.37 to +0.32 and at -0.32 to -0.28 volt were observed, the exact val. depending on the $p_{\rm H}$ of the phosphate solution in which the tissue was placed.

H. J. E.

Demonstration of organic phosphorus compounds and of a phosphatase in the mammary gland. W. BORST (Z. physiol. Chem., 1932, 212, 126—134).—Mammary gland tissue contains org. P compounds. The amount is highest in the virginal gland and successively lower in the gravid organism, during lactation, and in the senile gland. Between lactation periods org. P is stored. From inactive tissue adenosinephosphoric acid was isolated. In mammary tissue and in many other organs an enzyme is present capable of eliminating P from adenylic acid. J. H. B.

Decomposition and synthesis of organic phosphate in the mammary gland. W. BRENNER (Z. physiol. Chem., 1932, 212, 135–145).—In surviving mammary gland tissue, inorg. P increases by autolysis faster than lactacidogen is destroyed. The decomp. of lactacidogen is complete in 2 hr.; the production of inorg. P lasts 6 hr. F' and citrate ions do not cause synthesis of H_3PO_4 esters, but they inhibit

hydrolysis. Oxalate and lactate ions accelerate the hydrolysis. Ageing of the tissue changes the inhibition by fluoride only in respect of concn.; hexosediphosphatase is not injured by ageing. Ca strongly accelerates hydrolysis. From the acid hydrolysis curve it is concluded that the mammary gland contains no $H_4P_2O_7$. J. H. B.

Milk from amputated cow udders. I. Quantity. II. Composition. W. W. SWETT, F. W. MILLER, and R. R. GRAVES (J. Agric. Res., 1932, 45, 385-400, 401-419).—I. The average yield post mortem from cows killed by a blow was $61\cdot1\%$ of that obtained during life, the udders being allowed to get cold, whilst in a group killed by shooting the yield was $75\cdot32\%$ when the udders were kept at blood-temp.

II. The butter-fat content in the first post-mortem milking was only 50% of that in ante-mortem, the % of total solids being also lower. The ash content of a second sample of post-mortem milk was > that of the first. The fat : protein ratio in post-mortem was < in ante-mortem milk. P. G. M.

Transference of drugs to mother's milk. O. TONN (Pharm. Zentr., 1932, 73, 727).—Nicotine (I) in human milk can be detected by acidification, removal of the fat, addition of excess of NaOH, steamdistillation, and extraction of the distillate with Et_2O . The residue from the Et_2O gives ppts. characteristic of (I). Milk from a mother who smoked heavily contained (I) and caused nicotine-poisoning in her child. R. S. C.

Flavour in milk. I. R. H. LEITCH (Scot. J. Agric., 1932, 15, 167—173).—Effects of physiological and pathological conditions and of food materials on milk flavour are recorded. A. G. P.

Variations in fat content of milk following the change from stall to pasturage. K. L. CHRZASZCZ (Milchwirts. Forsch., 1932, 13, 339— 362).—Transition from stall feeding to pasturage decreased the milk secretion, but increased the % of fat in the milk. The extent of the change was influenced by temp. and the composition of the herbage. A. G. P.

Influence of the marsh horsetail (Equisetum palustre) on the composition of milk and butterfat. A. MEETZ (Milchwirts. Forsch., 1932, 13, 405-430).—The feeding to milch cows of silage containing horsetail caused a reduction in the acidity and the sp. gr. of the milk. Effects on the fat, fatfree dry matter, and protein contents varied considerably in individual cows. The proportion of lactose was slightly, and that of Cl' more markedly, increased. In general ash contents were slightly increased, there being a tendency towards lower P and higher Ca contents. The Ca and P of the blood increased. A. G. P.

Effect of work in harness on the secretion and composition of cow's milk. J. TAUFER, A. KARAKOZ, and S. KOLAČEK (Věstn. Českoslov. Akad. Zem., 1932, 8, 194—198; Chem. Zentr., 1932, ii, 459).—The lactose and protein fall correspondingly with the fall in milk production, but the fat production is increased, so that the fall in total solids is smaller. The yield of good milkers is specially affected, but is usually normal after 32 hr.

A. A. E.

Iodine content of the colostrum of cows. M. MIETHKE and H. COURTH (Milchwirts. Forsch., 1932, 13, 394—404).—The colostrum contains high proportions of I for a few milkings after calving, but vals. return to normal after 2 days. The max. I content attained increases with the length of the preceding dry period, during which there is an apparent accumulation of I in the milk glands.

A. G. P. Thread-forming property of physiological liquids and the methods of measurement. J. Jochums (Kolloid-Z., 1932, 61, 250-256).—A review.

E. S. H.

Thread-forming property of the vitreous humour of animal and human eyes. F. P. FISCHER (Kolloid-Z., 1932, 61, 265-268).—Photoultramicrographs reveal the existence of threadlike particles in the vitreous humour. E. S. H.

Glucose and phosphate concentrations in blood-plasma, glomerular fluid, aqueous humour, cerebrospinal fluid, and lymph. A. M. WALKER, E. H. ELLINWOOD, and J. A. REISINGER (Amer. J. Med. Sci., 1932, 184, 145–146).—In 61 experiments the mean glomerular urine of the frog and necturus contained 97% as much sugar and 100% as much PO₄ as the plasma. In 12 experiments the sugar and PO₄ of the lymph obtained from the frog's web were nearly identical with plasma vals. Cerebrospinal fluid of the frog contained 66%as much sugar and 39% as much PO₄ as the plasma. Aqueous humour contained 63% as much sugar and 42% as much PO₄ as the plasma. Cff. ABS.

Influence of plasma-protein on chloride content of cerebrospinal fluid. H. I. COOMBS and K. W. THOMPSON (J. Exp. Med., 1932, 56, 449-453).—When the plasma-protein of dogs is lowered by plasmaphoresis the concess. of Cl' and Na' in the plasma and cerebrospinal fluids tend to become equal. This accords with the theory that the cerebrospinal fluid is a dialysate, with the choroid plexus acting as a simple dialysing membrane. CH. ABS.

Ammonia and urea content of human saliva. J. MAUPETIT (Bull. Biol. Pharm., 1932, 18, 303– 304).—In normal and in several pathological salivas collected in aq. $CCl_3 \cdot CO_2 H$ to prevent fermentation, the sum of NH_3 -N and urea-N is almost equal to the N evolved by NaOBr. Normally the lastnamed val. varies from 150 to 200 mg. per litre.

A. L.

Relationship between internal secretions and sodium chloride content of bile. K. SASAKI (J. Chosen Med. Assoc., 1931, 21, 41-66).—Continuous feeding of thyroid increases the NaCl content of the fistula bile in a rabbit. Intravenous injection of thyroxine produces a less pronounced change. When adrenaline is given, biliary NaCl is decreased. Insulin also increases NaCl excretion by stimulation of bile flow. CH. ABS.

Synthesis of bile acids. V. Cortinellus shiitake and the secretion of bile acids. S.

HIGASHI (Arb. Med. Okayama, 1932, 3, 22—30).— C. shiitake fed to dogs increases the production of bile acids; the effect is due to the presence of ergosterol. CH. ABS.

Stomach. I. Normal secretion of the Pavlov stomach. I. SUGISHIMA (Japan. J. Exp. Med., 1932, 10, 177—201).—Changes in acidity, [Cl'], and peptic strength were followed. CH. ABS.

Significance and origin of lactic acid in the gastric contents. I. MURRAY and A. B. ROBERTSON (Brit. Med. J., 1932, I, 607—609).—Test meals from 37 out of 50 cases, pathological and normal, showed the presence of lactic acid (I), which is more frequent in hyposecretion than in hypersecretion, but is of no clinical significance. The formation of (I) is probably due to *B. acidi lactici*, which was identified in the normal stomach. L. S. T.

Natural pigments of raw silk fibre. III. M.p. of cocoon xanthophyll. M. OKU (J. Agric. Chem. Soc. Japan, 1932, 8, 655-658).—The purified xanthophyll has m.p. 193° (corr.), which is that of Kuhn's lutein. CH. ABS.

Purification of snake venoms. A. HANSEN (Compt. rend. Soc. Biol., 1932, 106, 322–324; Chem. Zentr., 1932, ii, 555).—Adsorption on Al_2O_3 is being tried. Proteolysis is not thereby affected.

A. A. E.

Nitrogen and carbon of organic acids of human urine. Distribution of urinary carbon. M. LAFARGUE (Bull. Soc. Chim. biol., 1932, 14, 1191— 1201, and Bull. Biol. Pharm., 1932, 18, 297— 299).—The micro-method of determining urinary org. acids (A., 1931, 1082) has been modified to remove phenols and pigments before Et_2O -extraction of the acids. The N and C contents of the org. acids represent 2.5 and 16.8—19.8%, respectively, of the total urinary N and C. Urinary C is distributed as (a) N compounds 64.87%, (b) org. acids 18.45%, and (c) undetermined C 16.68%. A. C.

Organic acids of human urine. Index of acidosis. Index of acido-carbonuria. M. LAFAR-GUE (Bull. Soc. Chim. biol., 1932, 14, 1202—1209).— The normal urinary excretion of carboxylic acids as determined by the author's micro-method (A., 1931, 1082) is closely parallel to that of the combined N of NH₃ and urea. The ratio of the former (in c.c. 0.1N-acid) to the latter (in g.) is termed the index of acidosis, which has a normal val. of 20—25. This index may be artificially increased, without true acidosis, by low excretion of urea caused by a proteinpoor diet. The "index of acido-carbonuria," the ratio org.-acid-C: total urinary C, offers a more trustworthy guide to acidosis. The normal val. is 15-20%. A. C.

Excretion of inorganic sulphates. J. M. HAY-MAN, jun., and S. M. JOHNSTON (J. Clin. Invest., 1932, 11, 607—619).—Inorg. SO_4 is less conc. than creatinine or urea by the human kidney. After intravenous injection of SO_4 its concn. ratio approaches that of creatinine. CH. Abs.

Determination of enzymes in duodenal juice and fæces. L. RACZ (Deut. med. Woch., 1932, 58, 814-815; Chem. Zentr., 1932, ii, 577).-Diastase is extracted from fæces by means of Willstätter's PO_4 -NH₃ solution of p_n 8. For the determination of trypsin in fæces 1 c.c. of the emulsion is allowed to act on 25 c.c. of 2% gelatin, the fission being measured by CH₂O titration. A. A. E.

Constituents of the blood in health and disease. J. S. HEPBURN (Hahnemannian Monthly, 1932, 67, 618-626).—A summary. CH. Abs.

Copper and non-hæmoglobinous iron contents of the blood-serum in disease. A. LOCKE, E. R. MAIN, and D. O. ROSBASH (J. Clin. Invest., 1932, 11, 527—542).—Vals. ($\times 10^{-6}$ g. per c.c.) for Fe in hæmoglobin-free serum were : young men 1.0, young women 0.77, infants, adults with mild bilirubinæmia and cirrhosis of the liver, 1.4. Carcinoma, pregnaney, hypo- and hyper-thyroidism, and lues had no effect; barbital poisoning, nephritis, pituitary and ovarian dysfunction, leucæmia, tuberculosis, and diabetes gave low vals. Serum-Cu vals. were : young men 0.8, young women 0.92; vals. above 2.0 were found in pregnancy and advanced carcinoma. CH. ABS.

Chemical changes in the blood in Addison's disease. R. F. LOEB (Science, 1932, 76, 420-421). —Data for three cases are recorded. Loss of inorg. base appears to be an important factor. The Na content of blood-serum decreases, whilst that of K tends to increase. Administration of NaCl results in marked clinical improvement. L. S. T.

Phosphatase test in cases of arthritis and osteitis. J. RACE (Arch. Med. Hydrology, 1932, 10, 1798; Chem. Zentr., 1932, i, 1798).—A modification of Kay's process is described. L. S. T.

Fœtal blood. III. Chemical nature of asphyxia neonatorum. N. J. EASTMAN (Bull. Johns Hopkins Hosp., 1932, 50, 39—50).—The primary change is an extreme fall in the fœtal blood-O₂. CH. ABS.

Effects of excessive intake of magnesium by the rat. Production of renal calculi. E. WAT-CHORN (J. Hyg., 1932, 32, 156–170).—Excess of MgCO₃ in the diet caused the development of urinary calculi in rats; addition of excess of CaCO₃ prevented calculus formation. The blood-Ca, -Mg, and -P were not significantly altered. Extra Mg or Ca, or Na₂CO₃ lowered urinary PO₄. Mg and Ca had little mutual effect on the amount excreted in the urine. CH. ABS.

Cancer problem from the physico-chemical viewpoint. V. COFMAN (Bull. Biol. Pharm., 1932, 3, 281-292).--A discussion.

Lubricating oils and cancer. H. R. HIRST and A. T. KING (Nature, 1932, 130, 810; cf. A., 1932, 1277).—Crude shale oils give rise to insol. compounds which are removed from wool fibres only with difficulty by solvents and not at all by soaps. The ionisation process of Hayes-Gratze gives products of reduced surface tension and high H_2O -emulsifiable nature when applied to oils, especially those of a vegetable origin. Ionised oil also has marked curative properties in cases of dermatitis. L. S. T.

Coal-tar constituents and cancer. J. W. COOK, C. HEWETT, and I. HIEGER (Nature, 1932, 130, 926).—An active carcinogenic hydrocarbon possessing a typical fluorescence spectrum has been isolated from active fractions of coal-tar pitch. It is probably identical with 1:2-benzpyrene, which has now been synthesised. The synthetic and natural materials are equally active in producing cancer of the skin in mice, and much more active than 1:2:5:6-dibenzanthracene. Perylene and 4:5-benzpyrene have also been isolated from coal-tar pitch, and I:2-benzanthracene from the chrysene fraction of coal tar. L. S. T.

Physico-chemical change of the blood in gynæcological diseases. I. Uterine cancer. A. Colloid stability of the blood-plasma and serumprotein. B. Cholesterol in the blood-serum. M. IKEDA (Japan. J. Obstet., 1931, 14, 296—301, 302—306).—In uterine cancer the total protein is unchanged, but the colloidal stability much reduced except during menstruation. Pathological and normal vals. were, respectively: serum-albumin : globulin 0.51—1.82, 1.58—3.50; euglobulin, 0.30—1.10, 0.12— 0.41; plasma-fibrinogen 0.31—0.89, 0.11—0.13; total cholesterol 105—201, 106—201; directly extractable cholesterol 33.0—68.5, 49.5—85.4 mg. per 100 c.e. CH. ABS.

Glutathione in organs in presence of experimental tumours. N. B. MEDVEDEV (Zhur. Med. Tsiklu, 1932, 2, 93—103).—The glutathione content of the thyroid, adrenals, kidneys, brain, spleen, lungs, heart, muscles, submaxillary glands, pancreas, liver, testes, and ovaries is greater in normal rats and mice than in those infected with experimental sarcoma and carcinoma. During the growth of the tumour the tissue-glutathione decreases, particularly in the thyroid. Ch. Abs.

Glutathione in normal blood and in cancer. F. F. ULIBARRI (An. vías digest. sangre nutrit., 1930, 2, 242).—Blood-glutathione is normally 40 mg. per 100 c.c.; in cancer it is less. CH. Abs.

Cholesterol in dermatoses. S. ROSNER (Rev. Argentine dermat., 1931, 15, 11).—Hypercholesterolæmia accompanies syphilitic, cancerous, or infectious skin affections. CH. Abs.

Distribution of sugar in the blood of diabetic and non-diabetic Indians. J. P. BOSE (Indian Mcd. Gaz., 1932, 67, 415-435).—In normal persons the plasma-sugar (I) is slightly < the whole bloodsugar (II) and slightly > the corpuscular sugar (III), whereas in diabetes (1) is significantly > (II) and (III) to an extent depending on the severity of the disease. Hence the ratio (III): (I) is a criterion of the gravity of diabetes. Administration of glucose and of insulin gives vals. for (I), (II), and (III) which indicate that the hormone increases the permeability of the corpuscles to sugar and facilitates its storage and utilisation. F. O. H.

Glycæmia in diphtheria. H. D. GONZÁLEZ (Semana Méd., 1932, I, 1949—1961).—No relation between the gravity of the case and the blood-sugar could be found. CII. ABS.

Parathyroid physiology. III. Effect of phosphate ingestion in clinical hyperparathyroidism. F. AlbRIGHT, W. BAUER, D. CLAFLIN, and J. R. COCKRILL (J. Clin. Invest., 1932, 11, 411–435).— The serum-P and $-Ca \times P$ were increased and the serum-Ca and urinary Ca were decreased; the threshold for P excretion was lowered. CH. Abs.

Liver function in hyperthyroidism. S. S. LICHTMAN (Arch. Int. Med., 1932, 50, 721-729).-In 16 out of 20 cases of uncomplicated hyperthyroidism there was an impairment in the ability to oxidise einchophen, indicating diminished liver function, but little or no sign of impaired hepatic function was obtained from the galactose tolerance test, or from studies on the icteric index, bilirubinæmia, urobilinuria, and urobilinogenuria. W. O. K.

Metabolism of sodium *dl*-lactate. I. Response of normal human subjects to the intravenous injection of sodium *dl*-lactate. II. Subjects with acidosis. III. Subjects with liver damage, disturbed water and mineral balance, and renal insufficiency. A. F. HARTMANN and M. J. E. SENN (J. Clin. Invest., 1932, 11, 327-335, 337-344, 345-355).—I. The lactate was apparently converted into glucose; Na appeared in body-fluids as NaHCO₃.

II. The Na lactate was metabolised normally.

III. In acute catarrhal jaundice there was slight delay. CH. Abs.

Modifications in the changes of blood-sugar produced by pharmacodynamic substances as a proof of altered equilibrium of the vegetative nervous system in experimental nephritis. R. MESSINA (Arch. Farm. sperim., 1932, 54, 262–284). —The blood-sugar level of normal rabbits is raised by morphine and pilocarpine and lowered by ergotamine, probably by stimulation or depression, respectively, of the sympathetic nervous system. In nephritis produced by subcutaneous injection of $UO_2(NO_3)_2$, the blood-sugar level is lowered; morphine then lowers it slightly, pilocarpine produces a rise less marked than before, and the hypoglycæmic action of ergotamine is intensified. In nephritis there is vagotonia due to renal insufficiency, and the alteration in the effects of the alkaloids is due to this disturbance of the sympathetic-vagus equilibrium.

R. K. C.

Excretion of xylose as an index of damaged renal function. E. H. FISHBERG and L. FRIEDFELD (J. Clin. Invest., 1932, 11, 501—512).—After ingestion of xylose (50 g.) the intact kidney excretes 25% in 24 hr. Blood-vol. can be determined by the use of xylose. CH. ABS.

Blood in high intestinal obstruction. I. Distribution of phosphorus and intracellular changes. G. M. GUEST and W. DEW. ANDRUS. II. Relation between "toxæmia "and chemical changes. W. DEW. ANDRUS, G. M. GUEST, R. F. GATES, and A. ASHLEY (J. Clin. Invest., 1932, 11, 455-473, 475-488).—I. In experimental pyloric and mid-duodenal obstruction in dogs the ester-P increased; the increase was prevented by parenteral administration of NaCl.

II. Repeated small injections of histamine into dogs with pyloric obstruction hastened blood changes usually regarded as the cause of death. CH. ABS. Blood in normal pregnancy and eclamptogenic toxæmia. S. KAPLAN (Amer. J. Obstet. Gyn., 1932, 23, 673-678).—Non-protein-N increased and sugar decreased from the third to the ninth month; uric acid increased slightly during the ninth month. In pre-eclamptic toxæmia the non-protein-N, urea-N, and uric acid increased slightly; eclampsia and, particularly, nephritic toxæmia were accompanied by larger increases. CH. ABS.

Blood and urinary amylase in pregnancy and its late toxæmias. A. N. ARNESON and K. C. MORRIN (Amer. J. Obstet. Gyn., 1932, 23, 664— 672).—In long and difficult parturition blood-amylase rises slightly above the normal (and pregnancy) val. (4—7 units per c.c.). Subnormal vals. were found in 35% of cases of toxæmia of pregnancy with hypertension. Urinary vals. show wide variations.

CH. ABS.

Biochemical pregnancy test. Hormonal hypercholesterolæmia. R. L. MASCIOTTRA and R. M. DE Hoz (Semana Méd., 1932, II, 53-55).--Urine of pregnancy or the anterior pituitary hormone, but not normal female urine, when injected into guinea-pigs, increases the blood-cholesterol (e.g., by 30-50% within 24 hr.). CH. ABS.

Calcium and inorganic phosphorus content of prenatal and *post-partum* serum. J. W. MULL and A. H. BILL (Amer. J. Obstet. Gyn., 1932, 23, 807-814).—The cord-serum contained 11.7 mg. Ca per 100 c.c. In women the normal val. is 10.4; at onset of labour it was 9.8, and on the 7th and 12th—14th day *post partum* it was respectively 10.3 and 10.5. The inorg. P was max. (5.1 mg.) at delivery; the val. declined slightly and then recovered to a slightly higher level. Six weeks *post partum* the val. was 3.7—3.9. The val. for cord-blood was 5.8. CH. ABS.

Relation of calcium and phosphorus to growth and rachitic leg weakness in chickens. R. T. PARKHURST and M. R. MCMURRAY (J. Agric. Sci., 1932, 22, 874—882).—Low-Ca rations (0.26% Ca and Ca : P=0.44 : 1) and also a high-Ca ration (3% Ca and Ca : P=4.4 : 1) resulted in retarded growth and poor bone development. A. G. P.

Fixation of strontium in experimental rickets. G. MOURIQUAND, A. LEULIER, and NOGIER (Compt. rend. Soc. Biol., 1931, 106, 18–19; Chem. Zentr., 1932, ii, 240).—Administration of Sr appears to intensify the rickets. Only then is Sr present (detected spectroscopically) in the ash of the epiphysis, and this ash is smaller in wt. in animals so treated than in normal animals. A. A. E.

Calcium and phosphorus content of the brain in experimental rickets and tetany. A. F. HESS, J. GOSS, M. WEINSTOCK, and F. S. BERLINER (J. Biol. Chem., 1932, 98, 625-635).—Total Ca and inorg. P of the brain are decreased in the rachitic rat in spite of high-Ca diets. There is no relation between the concn. of Ca in blood and in brain. In rickets the total Ca is unchanged in blood and diminished in brain; in parathyroid tetany it is low in the blood and undiminished in the brain. H. G. R. Metabolism in tetany. S. MORRIS (Biochem. J., 1932, 26, 1606-1608).—A reply to Greenwald (A., 1932, 1159).

Intravenous injections. Composition of the blood during continuous intestinal trauma when no fluid is injected and when fluid is injected continuously. J. W. BEARD and A. BLALOCK (J. Clin. Invest., 1932, 11, 249-265). CH. ABS.

Intravenous injections. Effects on composition of blood of injection of various fluids into dogs with normal and with low blood-pressure. A. BLALOCK, J. W. BEARD, and C. THUSS (J. Clin. Invest., 1932, 11, 267—290). CH. ABS.

Effects of hæmorrhage, trauma, histamine, and spinal anæsthesia on composition of blood when no fluids are injected and when fluids are introduced intravenously. J. W. BEARD, H. WILSON, B. M. WEINSTEIN, and A. BLALOCK (J. Clin. Invest., 1932, 11, 291-309). CH. ABS.

Effects on composition of blood of subcutaneous injection of normal salt solution into normal dogs and into dogs subjected to intestinal trauma, graded hæmorrhages, and histamine injection. A. BLALOCK and J. W. BEARD (J. Clin. Invest., 1932, 11, 311-325). CH. ABS.

Cholesterol in tuberculosis. G. SAYAGO and I. DEL VILLAR (Prensa med. Arg., 1932, 18, No. 27). —Subnormal vals. (*i.e.*, <0.1456%) are observed only in malignant cases. CH. Abs.

Oxygen tension-oxygen consumption curves of fertilised arbacia eggs. P. TANG and R. W. GERARD (J. Cell. Comp. Physiol., 1932, 1, 503—513). —Earlier work (Biol. Bull., 1931, 60, 242) is extended. A. G. P.

Manometric analysis of the metabolism in avian ontogenesis. I. Normal respiratory quotient of blastoderm, embryo, and yolk-sac during the first week of development. II. Effects of fluoride, iodoacetate, and other reagents on the respiration of blastoderm, embryo, and yolk-sac. J. NEEDHAM (Proc. Roy. Soc., 1932, B, 112, 98-113, 114-138; cf. A., 1930, 1312).--I. Embryos (I) of 2½-6 days' development have a R.Q. of nearly 1. That of the yolk-sac (II) falls from 0.9 at 2½ days to approx. 0.6 at 8 days. Absence of the area pellucida (IV) from the blastoderm (III) results in low vals. of R.Q. Up to 2½ days of development (III) has a R.Q. varying between 0.85 and a little above 1.

II. Iodoacetate inhibits the respiration of (I), (II), and (III), the action with (I) being reversible (by addition of lactate) and with (II) irreversible. F' inhibits the respiration of (I), (II), and (III), high concess. being necessary for total inhibition of that of (I), whilst only with (III) is there a lowering of the R.Q. Phenylurethane partly inhibits the respiration of (III) without affecting the R.Q. Malachitegreen inhibits the respiration and considerably lowers the R.Q. of (I) and (III). KCN strongly inhibits the respiration of (III). F. O. H.

Excretion and re-absorption in the small intestine, with special reference to sterols. R. SCHONHEIMER and L. HRDINA (Z. physiol. Chem., 1932, 212, 161—172).—By means of a sterile intestinal cyst in a dog, endogenous metabolic products not capable of resorption were allowed to accumulate for several months. Dihydrocholesterol was obtained in quantity. The secretions of the stomach and pancreas contained practically no sterols. J. H. B.

Heart function. II. Influence on the function of extirpated toad heart of the skeletal muscle extract and potassium exposed to ultra-violet rays, Röntgen rays, and radium emanation, and the characteristics of the active substance contained in the alcohol extract of the skeletal muscle. III. Controls. M. OANA (Japan. J. Exp. Med., 1932, 10, 123-155, 157-175).-Skeletal muscle extract contains a thermostable substance (neither sensitised nor destroyed by irradiation), neither fat nor lipin, which stimulates the function of the extirpated heart of the toad. The ash of the extract also produced stimulation, the min. stimulating concn. being approx. the same as that of K. The active substance is present chiefly in heart-muscle. CH. ABS.

Anaërobic fatigue of cardiac muscle and the effect of temperature, cyanide, and adrenaline on its development. J. T. EDSDALL, H. B. HUNT, W. P. READ, and A. C. REDFIELD (J. Cell. Comp. Physiol., 1932, 1, 475—501).—Relationships between stresses developed in successive beats, the duration of activity, and the lactic acid accumulation in muscle are discussed mathematically, and the different effects of cyanide and adrenaline on these factors are examined. A. G. P.

Growth-stimulating substance in fatigued muscle. H. M. Fox and G. P. SMITH (Nature, 1932, 130, 774).—Blow-fly larvæ fed on fatigued frog muscle grow larger than those fed on resting muscle. L. S. T.

Metabolic changes involving phosphorus and carbohydrate in the autolysing gastrocnemius and cardiac muscles of normal, thyroxinised, and adrenalectomised animals. M. V. BUELL, M. B. STRAUSS, and E. C. ANDRUS (J. Biol. Chem., 1932, 98, 645-669).—In gastrocnemius decomp. of phosphocreatine (I) and adenylpyrophosphate takes place rapidly and soon ceases, whereas lactic acid (II) production continues at its initial rate throughout the experimental period. Formation of equimol. quantities of (II) and inorg. P suggests that the precursor of most of the (II) is hexosediphosphate. In thyroxinised animals, formation of (II) is inhibited in gastrocnemius and the glycogen and total acid-sol. P decreased, but with no significant change in the relative distribution of P. Heart-muscle contains the normal acid-sol. P and lower glycogen, otherwise the autolysis curves are indistinguishable. In adrenalectomised animals, formation of (II) is inhibited, the total and inorg. P low, and the pyrophosphate > normal. It is suggested that characteristics of hyperthyroidism and Addison's disease may be associated with the inability of the muscles to produce (II) normally, limiting the resynthesis of (I). H. G. R.

Disappearance of lactic acid, arising from muscular activity, in the dehepatised animal. E. AUBEL, R. GAYET, and Y. KHOUVINE (Ann. Physiol. Physicochim. biol., 1931, 7, 302–309; Chem. Zentr., 1932, ii, 399).—The blood-lactic acid (I) of dogs of which the liver was excluded from the circulation rose until death supervened; muscular contraction led to an immediate rise in (I), which then further rose until death occurred. Simultancously the blood-sugar falls. Addition of glucose to the blood results in a fall in (I). A. A. E.

Exchange of materials between muscle, blood, and liver during work. L. WACKER (Biochem. Z., 1932, 255, 222-229).-In so far as it is not oxidised the lactic acid (I) produced in muscle during work passes out as alkali lactate, causing an average increase of 658.8% in the resting lactate content of the blood-serum. In the liver that lactate combines with CO₂ from the blood, carbohydrate and NaHCO₃ being regenerated. Since the amount of alkali in muscle is insufficient for neutralisation of the (I) liberated, it follows that NaHCO₃ from the blood passes into the muscle and a corresponding amount of Na lactate passes in the opposite direction. An explanation is thus provided for biochemical changes which occur W. McC. during muscular contraction.

Lactic acid transformability of muscle and liver. S. L. ØRSKOV (Skand. Arch. Physiol., 1932, 63, 240—254; Chem. Zentr., 1932, ii, 557).—Rabbit's liver and muscle can cause the transformation of large quantities (equal per unit wt.) of lactic acid. After exercise the cells of a living animal transform twice as much as those of perfused muscle or liver. The quantity of Et_2O -sol. acids is unaffected by perfusion. A. A. E.

Significance of bile acids in carbohydrate metabolism. XXI. Production of glycogen in liver and muscle by bile acid and adenylic acid. K. WATANABE (Biochem. Z., 1932, 255, 155—159).— In rabbits administration of adenylic acid (I) reinforces the action of cholic acid (II) in promoting the production of glycogen in the liver, but in muscle this effect of the (II) is diminished by giving (I). It follows that there is a close relation between the effect of (II) on glycogen production and its effect on nucleic acid metabolism. W. McC.

Influence of sex and age on liver- and muscleglycogen, and alkali reserve in fasting rats. R. STÖHR (Z. physiol. Chem., 1932, 212, 121—125). —The liver-glycogen of fasting rats varies with age and sex. In females the alkali reserve and muscleglycogen are somewhat lower than in males.

J. H. B.

Hypoglycæmia following glucose ingestion. W. S. McClellan and H. S. H. WARDLAW (J. Clin. Invest., 1932, 11, 513—526).—The causes of hypoglycæmia are reviewed. Hypoglycæmia following ingestion of glucose and due to excessive oxidation or excessive storage is recorded. CH. Abs.

Physiological behaviour of the trioses and related compounds. III. Muscle-glycogen and blood-sugar after feeding methylglyoxal and glyceraldehyde. IV. Alkali reserve after feeding methylglyoxal, glyceraldehyde, dihydroxyacetone, and glucose, and its relation to liverglycogen. Alimentary hyperglycæmia. R. STÖHR (Z. physiol. Chem., 1932, 212, 85—98, 98— 106; cf. A., 1932, 645).—III. AcCHO (I) and glyceraldehyde (II) fed to fasting rats do not increase the glycogen content of the muscle. They increase liverglycogen, but to a smaller extent than dihydroxyacetone (III). In relation to the amount resorbed (II) is little inferior to (III) in glycogen-forming power. (I) causes a greater rise in blood-sugar than (II). The max. production of liver-glycogen by (II) is reached in 1 hr., by (I) not even in 3 hr.

is reached in 1 hr., by (I) not even in 3 hr. IV. (I) and (II) decrease the alkali reserve of the blood, (I) more strongly; (III) has no effect. (I), (II), and glucose are probably transformed into glycogen by way of an acid intermediate product (OH·CHMe·CO₂H). J. H. B.

Behaviour of liver-glycogen, alkali reserve, and blood-sugar after acetol feeding. R. STÖHR and R. MÜLLER (Z. physiol. Chem., 1932, 212, 107— 110).—Acetol fed to fasting rats did not produce any marked change in liver-glycogen, alkali reserve, or blood-sugar. Acetol was present in the blood in high conen.; it does not appear to be converted into AcCHO. J. H. B.

Action of methylglyoxal on acetoacetic acid. IV. Muscle-glycogen, alkali reserve, and blood-sugar after ketol feeding. R. STÖHR and M. HENZE (Z. physiol. Chem., 1932, 212, 111—120; cf. A., 1932, 645).—The ketol does not affect muscleglycogen, but depresses the alkali reserve; a transitory increase in blood-sugar is probably due to formation of AcCHO and can be almost suppressed by correct dosage. The increase of liver-glycogen by the ketol is confirmed. The behaviour shown strongly resembles that observed with AcCHO administration. J. H. B.

 β -Oxidation. V. Effect of insulin and acetoacetic acid on the production of glycuronic acid. A. J. QUICK and M. A. COOPER (J. Biol. Chem., 1932, 98, 537—541).—By measuring the amount of glycuronic acid monobenzoate excreted after administration of BzOH as a measure of the glycuronic acid synthesised by dogs, insulin is shown to stimulate, and acetoacetic, lactic, and glycollic acids to decrease, the output. A. L.

Utilisation of melezitose by bees. E. F. PHILLIPS (Z. Unters. Lebensm., 1932, 64, 383—389).— Various methods are compared and criticised (cf. A., 1931, 1327). Bees or larvæ fed with melezitose survived the starved controls. J. G.

Digestibility of raw starch. E. POZERSKI (Ann. Physiol. Physicochem. biol., 1931, 7, 220—224; Chem. Zentr., 1932, ii, 398).—Starch of rye, buckwheat, or potato fed to fowls is almost completely digested, but when fed with caseinogen or gluten it is largely undigested. Starch of undamaged grain is digested better than that of milled grain. A. A. E.

Metamorphosis of insects. VIII. Rôle of the hæmolymph in the metabolism of butterfly pupæ. J. HELLER (Biochem. Z., 1932, 255, 205-221; cf. A., 1930, 809).—The compositions of the blood and of the remainder of the pupæ of *Deilephila euphorbiæ* which have hibernated and the changes in these compositions which occur during development indicate that the blood, which also serves as a H_2O depôt, supplies about 70% of the material needed for energy requirements. During the first half of the pupal period the rôles of the various constituents in the energy exchanges which occur resemble those assumed during pupation, whilst in the second half of the period they resemble those assumed in the butterfly. W. McC.

Yeast ingestion and the composition of the urine and fæces. H. B. PIERCE, D. D. Posson, V. DU VIGNEAUD, C. A. MORRISON, Z. DU VIGNEAUD, and M. S. PEARCE (J. Biol. Chem., 1932, 98, 509-535).—Administration of live yeast has a laxative effect more marked on a carbohydrate-rich than on a protein-rich diet. With the ingestion of yeast elimination of inorg. SO4 decreases, that of ethereal SO₄ increases. Total phenol, indican, and indole excretion rises, but the increase is not so great as would be expected were the yeast-tryptophan subject to the same degree of putrefaction as the protein in the control diet. Acidity of the urine falls, but urinary NH₃, and NH₃ and volatile acids in the fæces, increase. Most of the yeast-N is retained, and the excretion of uric acid decreases or remains unchanged. A. L.

Relation of the dicarboxylic amino-acids to nutrition. R. R. ST. JULIAN and W. C. ROSE (J. Biol. Chem., 1932, 98, 439–443).—Aspartic, glutamic, and hydroxyglutamic acids are not indispensable constituents of the diet of rats. F. O. H.

Proline and hydroxyproline in nutrition. R. R. ST. JULIAN and W. C. ROSE (J. Biol. Chem., 1932, 98, 445-455).—The mixtures of NH_2 -acids obtained by acid hydrolysis of caseinogen, lactalbumin, and edestin were repeatedly extracted with abs. EtOH. The residues, used in diets as a source of N and supplemented by essential NH_2 -acids not present in the original protein, promoted normal growth in rats. Hence proline and possibly hydroxyproline are not essential dietary constituents. F. O. H.

Possible interchangeability in nutrition of certain 5-carbon amino-acids. R. R. ST. JULIAN and W. C. ROSE (J. Biol. Chem., 1932, 98, 457–463).— The use of hydrolysed caseinogen, from which arginine, dibasic $\rm NH_2$ -acids, and the prolines have been removed, as a source of N in otherwise adequate diets results in deficient growth in rats even when tryptophan, cystine, and histidine are added. Subsequent addition of arginine, aspartic acid, glutamic acid, and proline does not improve growth. Hence ornithine, glutamic and hydroxyptoline are not interchangeable from a nutritive point of view. F. O. H.

Metabolism of cystine and methionine. Availability of methionine in supplementing a diet deficient in cystine. R. W. JACKSON and R. J. BLOCK (J. Biol. Chem., 1932, 98, 465-477).—Experimental data and discussion of the replaceability of cystine by methionine in the diet of the rat are given (see A., 1932, 83). F. O. H.

Metabolism of sulphur. XIX. Distribution of urinary sulphur in the dog after oral administration of bromobenzene as influenced by the

character of the dietary protein and by the feeding of *l*-cystine and *dl*-methionine. A. WHITE and H. B. LEWIS (J. Biol. Chem., 1932, 98, 607— 624).—The org. S fraction of urine after oral administration of PhBr is higher when a protein rich in cystine is fed. On low-cystine diets the extra ethereal sulphate-S excretion is greater after PhBr is administered. The addition of either *l*-cystine or *dl*-methionine to the low-cystine diet prevents the increased excretion of N which occurs after the administration of PhBr; the S distribution is similar to that with high-cystine diet. No increase in org. S was observed after feeding p-C₆H₁Br·OH with a low-cystine diet. H. G. R.

Growth-promoting properties of *d*- and *l*cystine. V. DU VIGNEAUD, R. DORFMANN, and H. S. LORING (J. Biol. Chem., 1932, 98, 577–589).— A method of resolving *dl*-cystine using the strychnine salt of the formyl derivative is described; *d*-, unlike *l*-cystine, is not active in producing growth. A. L.

Availability of d-tryptophan and acetyl-d-tryptophan to the animal body. V. DU VIGNEAUD, R. R. SEALOCK, and C. VAN ETTEN (J. Biol. Chem., 1932, 98, 565—575).—The growth resulting from the feeding of d- and l-tryptophan to rats is the same for both isomerides, whilst the feeding and subcutaneous injection of acetyl-d- and -l-tryptophan shows the former to be inactive and the latter quite active in producing growth. It is suggested that the oxidation of tryptophan, in contrast to the hydrolysis of the Ac derivative, is not an enzymic reaction, and that it takes place through the keto-acid, the next step in the case of the unnatural isomeride being the synthesis of the natural one. A. L.

Chemistry of mitogenetic radiation. III. Decomposition of creatinephosphoric acid as a source of the radiation. A. E. BRAUNSTEIN and B. A. SEVERIN (Biochem. Z., 1932, 255, 38–43; cf. Å., 1932, 966).—Mitogenetic radiation (λ 2000— 2150 Å.) is emitted by Ca creatinephosphate during hydrolysis (at room temp. and at 40°) with 0.5N-H₂SO₄. The spectrum of the reaction is very similar to that of the reaction which occurs during the metabolic changes in nerves following stimulation. W. McC.

Feeding tests with bran and linseed cake. J. A. CRICHTON and W. M. ALLCROFT (Scot. J. Agric., 1932, 15, 63—66).—The feeding val. of bran for cattle is probably nearer to the Scandinavian standard found in feeding trials than to Kellner's val. based on analysis. A. G. P.

Comparison between the reconstructive food values of certain vegetables and of grain. V. FAMIANI and V. ZAGAMI (Atti R. Accad. Lincei, 1932, [vi], 16, 57—61).—After fasting, pigeons gain wt. more rapidly on a diet of *Ervum lens*, *Lathyrus sativa*, and *L. cicera* than on one of *Triticum vulgare*; moreover, a certain loss in wt. is recovered on a smaller amount of the former diet. T. H. P.

Thyroid problem and iodine metabolism. A. SCHITTENHELM (Deut. med. Woch., 1932, 58, 803-806; Chem. Zentr., 1932, ii, 393).—Factors regulating the I metabolism are discussed. The thyroid is not the centre of the total I metabolism. The central nervous system plays a leading part. A. A. E.

Inorganic salts in nutrition. IV. Changes induced in the blood by a ration deficient in inorganic constituents. V. Progressive changes in the blood of rats maintained on a ration poor in inorganic salts. P. P. SWANSON and A. H. SMITH (J. Biol. Chem., 1932, 98, 479-498, 499-507).—A diet of low ash content (0.94% of the total diet) produced in rats a polycythæmia accompanied by a reduction in the size and abs. hæmoglobin content of the erythrocytes.

F. O. H.

Minerals and vitamin in the nutrition of the hen. MÜLLER-LENHARTZ and VON WENDT (Z. Fleisch- Milch-hyg., 1932, 42, 364—366; Chem. Zentr., 1932, ii, 890).

Calcium and phosphorus metabolism. XIV. Relation of acid-base balance to phosphate balance after ingestion of phosphates. W. T. SALTER, R. F. FARQUHARSON, and D. W. TIBBETTS (J. Clin. Invest., 1932, 11, 391-410).-25% of the ingested PO₄ (NaH₂PO₄ and Na₂HPO₄) was stored. 25% of the excess PO₄ excretion was faecal as Na₂HPO₄. Acid phosphate caused increased excretion of urinary inorg. base equiv. to the amount of base necessary to neutralise excess PO₄ excretion. CH. ABS.

Effect of the calcium-phosphorus relationship on growth, calcification, and blood composition of the rat. R. M. BETHKE, C. H. KICK, and W. WILDER (J. Biol. Chem., 1932, 98, 389-403).—An increase of the Ca: P ratio from 1.0 to 5.0 produces a decrease in growth (I), bone-ash (II), and seruminorg. P, that in (I) and (II) being most marked when vitamin-D is absent from the diet. High concess. of Ca and P favour increased vals. of (I) and (II), but the Ca: P ratio is of greater importance. The optimum ratio for (I) and (II) is between 2.0 and 1.0, at which val. vitamin-D requirements are at a min. F. O. H.

Strontium and the physiological function of calcium. O. LOEW (Münch. med. Woch., 1932, 79, 718; Chem. Zentr., 1932, ii, 558).—Although Sr salts have a coagulating effect on milk and blood similar to that of Ca salts, Sr cannot replace Ca physiologically, *e.g.*, in bone formation. A. A. E.

Influence of sex on size and composition of tibiæ of growing chicks. A. D. HOLMES, M. G. PIGOTT, and W. B. MOORE (Poultry Sci., 1932, 11, 243—249).—Variations in Ca and P are recorded. CH. ABS.

Induced and photochemical oxidations and their importance in biological phenomena. C. C. PALIT (J. Physical Chem., 1932, 36, 2504-2514).— The oxidation of fats is retarded by carbohydrates and proteins, and that of proteins by fats and carbohydrates. Oxidation of insulin causes oxidation of glucose. Fe, preferably colloidal, accelerates food oxidation. Oxidation of foods is increased by alkali. ZnO, U(NO₃)₂, and Fe(NO₃)₃ act as sensitisers in org. photochemical oxidations. Org. substances are oxidised in sun and air to CO₂. Peroxides are formed

in passing air through aq. suspensions of food oils and some carbohydrates. Irradiated and aërated olive oil is next to sunlight in its curative properties for deficiency diseases. I. J. P. (c)

[Therapeutical] adsorbing and neutralising substances. H. VOLLMER (Arch. exp. Path. Pharm., 1932, 168, 379—399).—Experiments have been carried out to determine the power of charcoal, magnesia usta, and various commercial preps. used in dyspepsia, to adsorb colchicine salicylate, strychnine nitrate, and pepsin, as well as, in certain cases, their power to neutralise acids. Administration of Ca silicate to rabbits or man in sufficient quantity results in adsorption of Ca and increase of serum-Ca. W. O. K.

Excretion of thymol, carvacrol, eugenol, and guaiacol and the distribution of these substances in the organism. V. SCHRÖDER and H. VOLLMER (Arch. exp. Path. Pharm., 1932, 168, 331—353).—The above substances administered to animals by mouth undergo 25—95% absorption from the intestinal tract in 24 hr. and soon appear in the urine. In the blood, lung, kidney, and liver significant amounts are found only during the first hr., whilst at most only traces are excreted through the lungs. Administration to guinca-pigs of thymol and K guaiacolsulphonate (I), but not of the other compounds, increases the H₂O content of the lungs, and thymol, carvacrol, eugenol, and (I) increase that of the liver. W. O. K.

Eye of the white mouse as pharmacological test object. I. Determination of very small quantities of atropine and other mydriatics. P. PULEWKA (Arch. exp. Path. Pharm., 1932, 168, 307-318). W. O. K.

Leech preparations. Detection of acetylcholine in presence of other pharmacologically active substances of tissue origin. B. MINZ (Arch. exp. Path. Pharm., 1932, 168, 292—304).—The leechmuscle eserine test (cf. A., 1932, 966) is not materially affected by the presence of choline, histamine, peptone, adrenaline, adenylic acid, or thyroxine. W. O. K.

Effect of histamine on the arterial oxygencombining curve and on the arterial oxygen pressure. Action of histamine on the lung vessels. C. TANG (Arch. exp. Path. Pharm., 1932, 168, 274—286).—The administration of histamine to man lowers the degree of saturation of the arterial blood as a result of inhibition of the attainment of equilibrium between the alveolar air and the lungblood. The O₂-combining curve of the blood is usually modified in the sense that rather more complete saturation is obtained at any given O₂ pressure. Together these two effects result in a reduction of the O₂ pressure of the arterial blood. The clinical bearings are discussed. W. O. K.

Uric acid excretion through the intestine and the effect of drugs thereon. H. SCHROEDER and B. B. RAGINSKY (Arch. exp. Path. Pharm., 1932, 168, 413-423).—Uric acid administered intravenously to cats in partly excreted into the intestinal tract, the rate being increased by substances which stimulate the normal intestinal secretions as well as by heat. Atropine has an inhibiting, and atophan, histamine, and pilocarpine have no action. Colchicine increases the rate of secretion through the ileum. W. O. K.

Nicotine content of tobacco smoke. E. WASER and M. STAHLI (Z. Unters. Lebensm., 1932, 64, 470-485).—Cigarettes were "smoked" artificially by the method of Pfyl and Schmitt (A., 1927, 955) and the degree of denicotinisation of the smoke was shown to increase with the H_2O content of the tobacco; the smoke from tobacco containing enough H₂O to render it almost unsmokable contained 15% < that from the same dry tobacco. Bonicot's fluid removed 12% of the nicotine and was the most effective of the denicotising agents tested. On shaking 500 c.c. of a 0.5% solution of nicotine with < 37.5 g. of active C, or re-activated C, or with ≤ 50 g. of SiO₂ gel for 15 min., 80-94, 25-55, and 95% of the nicotine was removed, respectively. Pfyl and Schmitt's method of determination of nicotine (loc. cit.) gives results slightly > a modification of Rasmussen's method, themax. deviation being 0.03%. J. G.

Absorption of nicotine from cigarette smoke. C. PYRIKI (Z. Unters. Lebensm., 1932, 64, 163— 171).—Nicotine absorption in the mouth is very small, but considerable on inhalation. Tolerance to nicotine is developed in heavy smokers and absorption lessened. E. B. H.

Activity of p- and m-sympatol. H. FLECKEN (Arch. exp. Path. Pharm., 1932, 168, 400-412). m-Sympatol, m-OH·C₆H₄·CH(OH)·CH₂·NHMe, has a marked action on the blood-vessels, raises the bloodpressure, and decreases the heart-rate, whilst the p-isomeride has little effect on blood-pressure or pulse-rate but increases the heart-beat vol.

W. O. K.

Local anæsthetics, pantocaine and larocaine, as compared with novocaine. O. GESSNER, J. KLENKE, and F. R. WURBS (Arch. exp. Path. Pharm., 1932, 168, 447-472).—The toxicities and anæsthetic activities are in the order pantocaine>larocaine> novocaine. W. O. K.

Poisoning by veronal. E. LABORDE and P. DUQUENOIS (J. Pharm. Chim., 1932, [viii], 16, 479–483).—The method of Fabre and Fredet (A., 1925, i, 1505) is recommended for the extraction of drugs of the barbituric acid series. Sublimation (330°) was employed as a confirmatory test. Veronal was found in the brain, but not in the liver, spleen, heart, or lungs. T. MCL.

Salvarsan and blood-bilirubin. O. SATKE and K. THUMS (Z. klin. Med., 1932, 120, 386—399; Chem. Zentr., 1932, ii, 395).—Injection of salvarsan affects (25% increases; 75% decreases) the serum-bilirubin independently of the amount present. Variation in the dose of salvarsan, or disturbance of liver function, was without influence. A. A. E.

Classification of different ions in natural chemical groups by their vasomotor action in trans-cerebral dielectrolysis. G. BOURGUIGNON and S. ELIOPOULOS (Compt. rend., 1932, 195, 976-978).—Study of the trans-cerebral dielectrolysis (socalled "ionisation") of 24 different ions shows that in the production of change of the oscillometric index of the arm opposite to the hemisphere treated the inactive and active ions fall into groups identical with those in the periodic classification and that within an active group the activity increases with at. wt.

R. K. C.

The Hofmeister series in muscle [irritation]. E. GELLHORN (Protoplasma, 1932, 16, 369–377).— The effects of Na salts in maintaining and restoring irritability in muscle preps. were in the order citrate < SO₄"<Cl' \leq Br'<SCN'. A. G. P.

Action of carbon dioxide on marine infusoria. M. A. GALADSHIEV and E. N. MALM (Bull. Acad. Sci. U.R.S.S., 1932, No. 1, 109—115).—CO₂ is toxic to oxybiotic infusoria; the tolerance of infusoria to CO₂ increases with their tolerance to H_2S and to deprivation of O₂. R. T.

Effect of heavy metals on ctenophores. O. V. HYKES (Compt. rend. Soc. Biol., 1932, 106, 328— 329; Chem. Zentr., 1932, ii, 558).—The order of decreasing toxicity is: Hg>Cu>Ag>Pb, Pt>Zn> U>Mn. A. A. E.

[Administration of] copper. II. C. G. SAN-TESSON (Skand. Arch. Physiol., 1931, 63, 101–116, 117–118; Chem. Zentr., 1932, ii, 399).—Small (2.4 mg.) subcutaneous doses of $CuSO_4$ can be gradually increased beyond the toxic dose (7 mg.) for rabbits. Occasionally CuS is found in the intestines and large hepatic and renal veins. A. A. E.

Solubility of metallic sulphides in minced organs. C. G. SANTESSON (Skand. Arch. Physiol., 1931, 63, 119—123; Chem. Zentr., 1932, ii, 558).— Injection of suspensions of insol. sulphides causes toxic symptoms in rabbits. HgS, Bi_2S_3 , and CuS were dialysed with minced liver or serum at 37° in presence of 5% CO₂ for 1.5 weeks. The dialysate gave reactions for Cu>Hg>Bi. A. A. E.

Arsenic content of hair. L. VAN ITALLIE (Pharm. Weekblad, 1932, 69, 1134—1145).—Existing data regarding the As content of human hair from cases of As poisoning are tabulated and discussed. In the method recommended for the determination, the sample is washed with EtOH and Et_2O , dried, and warmed with a mixture of H_2SO_4 (5 c.c.) and HNO_3 (5 c.c.) until carbonisation begins, and finally heated until free from HNO_3 ; As is then determined by Cribier's colorimetric method. The As content of the hair of normal persons rarely exceeds 0.03 mg. per 100 g. H. F. G.

Arsenic content of [finger and toe] nails. L. VAN ITALLIE (Pharm. Weekblad, 1932, 69, 1145— 1147).—The contents of As in finger and toe nails differ considerably, and vary between wide limits. H. F. G.

Poisoning by wine containing cadmium. P. FORTNER (Pharm. Zentr., 1932, 73, 769-774).—The wine contained Cd, derived from the plating of filters through which it had passed. W. O. K.

Alteration of bones by experimental chronic sodium fluoride poisoning. W. DITTRICH (Arch. exp. Path. Pharm., 1932, 168, 319-330).—The bones of guinea-pigs, rabbits, and young rats poisoned by the oral administration of small doses of NaF exhibit macroscopic and microscopic abnormalities consisting in the inhibition of normal growth and marked resorption of the normal bone. Repair takes place if sufficient Ca is administered after ceasing the administration of NaF. W. O. K.

Poisoning by sodium fluosilicate. J. A. LABAT (Bull. Soc. Chim. biol., 1932, 14, 1222—1227).—The deaths of four people were caused by ingestion of cake containing approx. $2\cdot1\%$ of Na₂SiF₆. F was found *post mortem* in the urine, blood, and several organs. A. C.

Hydrocyanic and thiocyanic acids in the living organism. J. A. KLAASEN (Pharm. Weekblad, 1932, 69, 1311—1314).—In cases of HCN poisoning CN' is converted into CNS' in organs containing the highest concn. of labile S (glutathione etc.). Any dislocation of S metabolism (as in injury to liver) brings about decrease in CNS' formation. Similar results are observed in P poisoning. S. C.

Mechanism of enzyme action. A. FODOR (Ergebn. Enzymforsch., 1932, 1, 39-76; Chem. Zentr., 1932, i, 1793).—A summary of the author's views, which are opposed to Willstätter's. L. S. T.

Activation of plant enzymes. K. SUESSENGUTH (Ergebn. Enzymforsch., 1932, 1, 364—369; Chem. Zentr., 1932, ii, 1796).—The question whether a certain effect is due to new enzymes or to the activation of enzymes is discussed. The saccharification of starch and the hydrolysis of maltose are considered.

A. A. E. Organic catalysts. VI. Preparation of and kinetics of [the catalytic decomposition of aketo-acids by] derivatives of 3-amino-oxindole. W. LANGENBECK, R. JUTTEMANN, and F. HELBRUNG (Annalen, 1932, 499, 201-212).-The following are prepared by reduction of the appropriate isatin-3-oxime with SnCl, and conc. HCl in AcOH except where stated otherwise : 5-bromo- (hydrochloride) and 5:7-dibromo- (hydrochloride) -3-amino-oxindoles; 3amino-1-methyl- (picrate) and -1-phenyl- (picrate) -oxindoles; 3-amino-4: 5-benzo-oxindole (hydrochloride); 3-amino-6: 7-benzo-oxindole (I) (hydrochloride); 3amino-oxindole-6-carboxylic acid [prepared by reduction (H₂, PtO₂, MeOH) of isatin-3-oxime-6-carboxylic acid (II), m.p. $>290^{\circ}$]; 3-amino-6: 7-2': 3'-pyridino-oxindole [obtained by reduction (H₂, Pd-C, AcOH) of 6:7-2':3'-pyridinoisatin-3-oxime (perchlorate)]; 3amino-7: 6-2': 3'-pyridino-oxindole (dihydrochloride) [prepared by reduction (H2, Pd-C, AcOH) of 6 : 7-2': 3'pyridinoisatin-3-oxime, m.p. about 265° (decomp.) (darkens at about 250°)]. Oxindole-6-carboxylic acid and p-NO·C6H4·NMe2 in EtOH give isatin-3-p-dimethylaminoanil-6-carboxylic acid, m.p. >290°, converted by an excess of NH₂OH into (II). 5-Aminoquinoline and CO(CO₂Et)₂ in AcOH afford Et 3-hydroxy-6.7 2': 2' aminopulation of the state of the s 6:7-2': 3'-pyridino-oxindole-3-carboxylate, decomp. about 200° without melting, which when dissolved in 5% NaOH, oxidised with atm. O2, and then neutralised (HCl) gives 6:7-2':3'-pyridinoisatin (hydrochloride). 7:6-2':3'-Pyridinoisatin is similarly prepared by way of Et 3-hydroxy-7: 6-2': 3'-pyridinooxindole-3-carboxylate, decomp. about 200° without melting, from 8-aminoquinoline. Of the above aminooxindoles, (I) is the best catalyst for the decomp. of BzCO₂H to PhCHO and CO₂ (cf. A., 1930, 714; 1931, 495). The kinetics of the catalytic decomp. of α -keto-acids are discussed briefly. H. B.

Organic catalysts. VII. Catalytic actions of iminazole-hæmins. W. LANGENBECK, R. HUT-SCHENREUTER, and W. ROTTIG (Ber., 1932, 65, [B], 1750—1754).—Investigation has been made of the influence of 2-methyl-1-ethyl- (I), 2:4:5-trimethyl-, 2-methyl-, 4(5)-cyanomethyl-, 4(5)-methyl-iminazole, iminazole, 4(5)-phenyliminazolesulphonic acid, not molten below 300°, pilocarpine, and C_5H_5N on the catalase activity of hæmin, its peroxidase action towards pyrogallol, and its oxidising action towards cysteine. Na 4(5)-phenyliminazolesulphonate has no effect on the catalase action of hæmin, but increases the peroxidase action 14-fold. Iminazole increases catalase and peroxidase actions 4- and 12:5-fold. The oxidative actions of iminazole- and phenyliminazolesulphonic acid-hæmin show no characteristic differences. (I) strongly restricts catalase but enhances oxidase activity. H. W.

Catalase. IV. Optical behaviour. K. G. STERN (Z. physiol. Chem., 1932, 212, 207—214; cf. A., 1932, 1062).—Purified catalase solutions were subjected to ultra-violet spectral analysis, luminescence analysis, and other optical tests. The colloidal carrier of the enzyme is probably responsible for the effects observed. J. H. B.

Tryptophanase. K. KURONO, H. KATSUME, and H. OKI (J. Agric. Chem. Soc. Japan, 1932, 8, 82— 94).—Koji and sake yeast contain tryptophanase, which is also present in commercial pepsin, trypsin, and papain. The optimum $p_{\rm H}$ is 6·2, and the optimum temp. 20°. Its action is arrested at 100°. It does not liberate NH₃ or produce melanin from tryptophan; the products give only weak reactions for indolecarboxylic and -acetic acid. CH. ABS.

Tyrosinase. II. Colloid-chemical behaviour of the tyrosinase reaction. D. OKUYAMA (Fukuoka-Ikwad. Zasshi, 1931, 24, 29—32).—The conversion of the red dye into melanin is not accelerated by univalent cations, but is accelerated by Pb>Al, La, Ce >Ca>Ba>Mg. The transformation is electrolytic and is not due to the enzyme. In the action of tyrosinase on *p*-cresol the velocity does not increase parallel with the cresol concn.; the temp. coeff. is 1.2. The velocity is max. when *p*-cresol and glycine are present in equal quantities. The glycine reaction occurs only in an alkaline medium. CH. ABS.

Specificity and mechanism of action of carbohydrases. R. WEIDENHAGEN (Ergebn. Enzymforsch., 1932, 1, 168—208; Chem. Zentr., 1932, i, 1793).—Views contrary to the theories of Kuhn and Leibowitz are based on the observation that the same α -glucosidase accomplishes the fission of sucrose and maltose. A new classification of carbohydrases is given. L. S. T.

Specificity of amylases. II. Enzymic analysis of starch and glycogen. G. A. VAN KLINKENBERG (Z. physiol. Chem., 1932, 212, 173— 195; cf. A., 1932, 1062).—On sol. potato-starch malt-β-amylase produces 64% of the possible amount of maltose. The initial velocity of hydrolysis is proportional to enzyme concn.; at low concns. the velocity is const. With increasing amounts of α -amylase there is strong inhibition after 36% of the theoretical amount of maltose has been formed. The initial velocity is proportional to enzyme concn. The enzyme is activated by heating to 70°; it then rapidly produces 36% of maltose and more slowly up to 78%. Glutathione has no effect on the hydrolysis by either enzyme.

Starch (potato, wheat, buckwheat, arrowroot) is regarded as a mixture of two mutameric forms, α and β -starch, present in the ratio 36:64. Only α starch gives a colour with iodine. β -Amylase is associated only with green plants; in the animal body and colourless plants only α -amylases and hence α -starch occur. Glycogen consists almost exclusively of α -starch. J. H. B.

Influence of certain ions on the extraction of malt-amylase from alumina gel. M. L. CALD-WELL and S. E. DOEBBELING (J. Biol. Chem., 1932, 98, 553-563).—The effectiveness of ions in the elution of malt-amylase from Al_2O_3 gel is $Cl' < AcO' < oxalate < SO_4'' < tartrate < citrate < PO_4'''$. The close similarity of this series to that of the order of penetration of anions suggests that the mechanism involves an exchange of active enzyme from the Al ion complex for anions of the electrolyte. A. L.

Effects of certain variations in preparation of a starch substrate in amylase viscosimetry. C. H. WIES and S. M. MCGARVEY (J. Gen. Physiol., 1932, 16, 221-227).—The effect of dilution on the viscosity and amylase digestivity of a standard starch substrate (A., 1931, 1331) and the comparison of various commercial sol. starch preps. were investigated in order to establish a reproducible standard.

F. O. H.

Reproducible standard substrate in starchamylase viscosimetry. W. R. THOMPSON, S. M. McGARVEY, and C. H. WIES (J. Gen. Physiol., 1932, 16, 229-231).—A fairly satisfactory reproduction of the standard (cf. preceding abstract) is prepared by admixture of two starches, which yield solutions of viscosity respectively > and < the standard, in proportions to give a relative viscosity comparable with that of the standard under certain definite conditions. F. O. H.

Similarity of the kinetics of invertase action in vivo and in vitro. II. B. G. WILKES and E. T. PALMER (J. Gen. Physiol., 1932, 16, 233-242).— Under identical external conditions the $p_{\rm H}$ -activity curves for the hydrolysis of sucrose by the living cells of Saccharomyces cerevisiæ and by invertase preps. from this yeast are identical. Thus the intracellular site of invertase action changes its $p_{\rm H}$ to coincide with that of the surrounding medium and is therefore probably situated at the outer region of the cell. With living cells at $p_{\rm H}$ 6.9 no hydrolysis due to an α -glucosidase occurs. F. O. H.

Oxynitrilese of emulsin. I. Synthetic action of emulsin. H. ALBERS and K. HAMANN (Biochem. Z., 1932, 255, 44-65; cf. Rosenthaler, A., 1909, i, 74).—The non-enzymic synthesis of mandelonitrile from PhCHO and HCN in aq. EtOH is a two-stage bimol. reaction (cf. Lapworth, J.C.S., 1904, 85, 1206) consisting of a slow addition of CN ions to the aldehyde mols. followed by a rapid addition of H to the hydroxynitrile ions thus produced. The velocity of the reaction is determined by the first stage and the velocity coeff. is independent of the [H']. The asymmetric synthesis induced by the "oxynitrilese" of emulsin proceeds independently of the accompanying non-enzymic synthesis, the production of the *d*-hydroxynitrile being accelerated by the enzyme which likewise accelerates the hydrolysis to the same extent. W. McC.

Biochemical synthesis of $\alpha\gamma$ -butylene glycol- β glucoside. J. VINTILESCO and N. IOANID (Bull. Soc. Chim. biol., 1932, 14, 1228—1234).—In the presence of emulsin, glucose reacts with 10—95% aq. solutions of $\alpha\gamma$ -butylene glycol. The optimal concn. of the latter is 70%, when 69% of glucose is converted in several weeks. A mixture of 450 g. of optically inactive glycol, 193 g. H₂O, 190 g. glucose, and 5 g. emulsin yielded in 2.5 months 135 g. of non-cryst. $\alpha\gamma$ -butylene glycol- β -glucoside, $[\alpha]_{0}$ —33.96°. The synthesis is not asymmetrical, since both the unchanged glycol and that produced by hydrolysis of the glucoside are inactive. A. C.

Production of lactic acid by tissues. W. HAARMANN (Biochem. Z., 1932, 255, 103-124).— The anaërobic production of lactic acid from preformed and added carbohydrate (glycogen, hexosediphosphate, glucose, fructose) by tissues (muscle, heart, liver, kidney, spleen, pancreas, brain, lung, thyroid, and suprarenal glands of rabbit, dog, cat, frog) and the factors which influence this production have been measured and examined. In the dog the power of the thyroid gland to decompose glycogen varies greatly with the time of year, there being max. production of lactic acid in March and October.

W. McC.

Production of lactic acid from methylglyoxal; influence of carbohydrates. W. HAARMANN (Biochem. Z., 1932, 255, 125—135).—AcCHO is converted (to the extent of 80—90%) into lactic acid by muscle, liver, kidney, or brain (rabbit, dog), but some of it is otherwise changed. When carbohydrate (glucose, fructose, glycogen, hexosediphosphate) is added the amount of lactic acid obtained is sometimes < the sum of the amounts to be expected from the substances together. W. McC.

Production of lactic acid from pyruvic acid. W. HAARMANN (Biochem. Z., 1932, 255, 136—137).— Surviving tissue from liver, heart, muscle, brain, kidney (dog, rabbit, cat, pigeon, goose) produces lactic acid from AcCO₂H anacrobically. The same organ from different animals varies greatly in activity. W. McC.

Combined action of carbohydrates in production of lactic acid. W. HAARMANN (Biochem. Z., 1932, 255, 138-141).—The production of lactic acid by tissues from muscle, heart, or kidney (rabbit, dog, pigeon, goose) is in some cases unaffected, in some increased, and in others decreased by addition of single carbohydrates or pairs of carbohydrates (glucose, fructose, hexosediphosphate, glycogen).

W. McC.

Degradation of glycogen and glucose in tissues. W. HAARMANN (Biochem. Z., 1932, 255, 142—150).— Skeletal muscle (dog, rabbit, pigeon) converts glycogen approx. quantitatively into lactic acid, but with other organs (heart, spleen, tongue) the amount of the acid produced does not correspond with that of glycogen degraded. It follows that in these cases the reducing intermediate carbohydrates produced are not further degraded to lactic acid. W. McC.

Production of lactic acid from products of enzymic hydrolysis of glycogen. W. HAARMANN (Biochem. Z., 1932, 255, 151—154).—The products of degradation (carbohydrates) obtained from glycogen by the action of organs (other than liver) are further degraded to lactic acid by such organs only as can also produce the acid from glycogen itself (e.g., striped muscle). Liver converts glycogen into a carbohydrate the further degradation of which resembles that of added glucose. W. McC.

Proteolytic enzymes of the animal and vegetable kingdoms. W. GRASSMANN (Ergebn. Enzymforsch., 1932, 1, 129—167; Chem. Zentr., 1932, i, 1795).—A summary. L. S. T.

Action of rennet. H. HOLTER (Biochem. Z., 1932, 255, 160-188; cf. A., 1931, 766) .- A viscosimetric method for the determination of the time of coagulation of caseinogen (I) solutions treated with rennet is described. The coagulation consists of a chemical change [(I) to casein] followed by a colloidal change (flocculation). Sometimes at least proteolytic hydrolysis accompanies the changes, but it may be caused by impurities. There is a close relation between coagulation and Ca content. The product of time of coagulation and concn. of enzyme is not const. and depends on experimental conditions, but a factor, calc. in a manner described, may be substituted for this product and used as a basis for a unit for measuring the action of rennet. On the assumption that (I) is an unstable complex consisting of at least three substances (cf. Linderstrøm-Lang, A., 1928, 1043), one, which is easily attacked by rennet, is supposed to act as a protective colloid for the others. The active agent of rennet is not identical with pepsin. W. McC.

Kinetics and structural chemistry of the enzymic hydrolysis of proteins. M. BERGMANN (Collegium, 1932, 751—761).—The rate of dissolution of gelatin by trypsin is proportional to the concn. of the latter. The degree of hydrolysis x is expressed by $x=kt_{\sqrt{F}}$, where F is the concn. of the enzyme and t the time of reaction. Gelatin strips were treated with pancreatin solutions, then thoroughly washed, and placed in H₂O at 28°. The gelatin was decomposed in all the tests, so that some of the pancreatin must have combined with the gelatin in the preliminary treatment. The rate and amount of hydrolysis of the washed strips were independent of the time of exposure to, and the concn. of, the pancreatin employed in the pretreatment. The action of the combined enzyme gradually diminished. Putrefaction in raw skins cannot be checked by washing, owing to the formation of such proteinenzyme compounds. The effect of the structure of

dipeptides on their hydrolysis by different enzymes is discussed. D. W.

Proteolytic enzymes. II. Mode of union of proline in gelatin. M. BERGMANN, L. ZERVAS, and H. SCHLEICH (Ber., 1932, 65, [B], 1747—1750).— Hydrolysis of gelatin by trypsin containing mainly active proteinase and carboxypolypeptidase with little dipeptidase and scarcely any aminopolypeptidase proceeds with production of equiv. amounts of NH₂ and CO₂H groups, thus involving the exclusive fission of normal ·CO·NH· linkings. Further hydrolysis by erepsin occurs with preponderating liberation of CO₂H in comparison with NH₂ groups. It appears, therefore, that in gelatin the ·NH· group of proline (and also hydroxyproline) is concerned in the structure of the peptide chains and that the linking is ruptured by ereptic fermentation. H. W.

Proteolytic enzymes: behaviour of proline peptides. M. BERGMANN, L. ZERVAS, H. SCHLEICH, and F. LEINERT (Z. physiol. Chem., 1932, 212, 72-84).-The following dipeptides were synthesised by condensation of carbobenzyloxy-glycine or -alanine with the appropriate NH,-acid and catalytic hydrogenation of the product, whereby the carbobenzyloxygroup is eliminated as PhMe and CO_2 : glycyl-l-proline (I), m.p. 185° (corr.), $[\alpha]_D^m -113.8^\circ$ in H₂O, from the N-carbobenzyloxy-derivative, m.p. 156° (corr.); d-alanyl-l-proline (II), m.p. 178° (corr.), $[\alpha]_{D}^{35}$ -114.4°, from carbobenzyloxy-d-alanyl chloride, m.p. about 35°, glycylsarcosine (III), m.p. 220° (corr.), from the carbobenzyloxy-derivative, m.p. 102° (corr.). (I) is not hydrolysed by pancreatic proteinase or polypeptidase. (I) and (II) are attacked by aminopolypeptidase or a similar enzyme, but not by dipeptidase of yeast. The latter also fails to hydrolyse (III). For the action of dipeptidase, NH at the peptide linking appears to be essential. J. H. B.

Crystalline trypsin. I. Isolation and tests of purity. II. Properties. III. Methods of measuring activity. J. H. NORTHROP and M. KUNITZ. IV. Reversibility of inactivation and denaturation by heat. V. Kinetics of digestion of proteins with crude and crystalline trypsin. J. H. NORTHROP (J. Gen. Physiol., 1932, 16, 267-294, 295-311, 313-321, 323-337, 339-348). I. Cryst. trypsin (A., 1931, 655) is not a pure protein, but probably a solid solution. It is stable in dil. HCl, its behaviour in this medium indicating the presence of an inactive protein denatured by heat and an active protein not denatured by heat. This leads to an improved method of prep. using a pre-liminary pptn. with acid and yielding a P-free cryst. material of twice the activity of the original cryst. prep. Fractionation is accompanied by a considerable loss of milk-clotting activity and the final material is free from amylase and resembles trypsin-kinase in not hydrolysing dipeptides (A., 1929, 1338). Fractionation and solubility data indicate that the recryst. product is neither a mixture nor an adsorption complex. In hot acid solution the degree of denaturation is parallel to the loss of activity. Loss of activity accompanies peptic digestion or keeping in slightly alkaline media.

II. The enzyme hydrolyses caseinogen (I), gelatin

(II), edestin (III), denatured (but not native) hæmoglobin (IV), and peptones prepared by peptic digestion of (I), (II), and (III). It accelerates the coagulation of blood but not the clotting of milk. The extent of the digestion of (II) by cryst. trypsin equals that due to pepsin. Enterokinase does not increase the activity. The following data were obtained : mol. wt., 34,000; mol. radius, 2.6×10^{-7} cm.; isoelectric point, $p_{\rm H}$ 7.0—8.0; optimum $p_{\rm H}$ for hydrolysis of (I), 8.0—9.0; optimum stability at $p_{\rm H}$ 1.8.

III. Evaluation was determined by changes in the viscosity of (I) and (II), in the sol. N of (I), and in the formol titre of (I) and (II).

IV. The degrees of protein denaturation and of tryptic activity for various temp. and salt concns. indicate that between native and denatured trypsin there is an equilibrium the extent of which is determined by the temp. Evidence for the proteolytic activity being an intrinsic property of the native protein mol. is also forthcoming.

V. The rate of hydrolysis of (I), (II), and (IV) increases approx. in proportion to the concn. of protein. Hydrolysis of (I) by crude trypsin is a unimol. reaction, whilst with purified trypsin the velocity coeff. decreases as the reaction proceeds. With (IV) the unimol. velocity coeff. decreases with both purified and crude enzyme. The effect of various substrate concns. disappears in viscosity determinations and a unimol. reaction is indicated. The abnormalities are probably due to the occurrence of several consecutive reactions and not to the formation of a substrate-enzyme complex.

F. O. H.

Digestion and inactivation of crystalline urease by pepsin and papain. J. B. SUMNER, J. S. KIRK, and S. F. HOWELL (J. Biol. Chem., 1932, 98, 543— 552).—The rapid inactivation of cryst. urease by pepsin and papain-H₂S corresponds with the proteolysis. Below $p_{\rm H}$ 4.3 the rate of inactivation is increased, whilst above $p_{\rm H}$ 4.3 and at 0° it is much slower. The inactivation of urease by acid follows the unimol. law. The evidence in support of the identity of the enzyme proper and cryst. urease questioned by other workers is discussed. A. L.

Activation of urease. W. A. PERLZWEIG (Science, 1932, 76, 435-436).—The SH group is partly responsible for urease activity. L. S. T.

Alcoholic fermentation. Initial stages of fermentation. Fermentation in the yeast cell. A. HARDEN (Ergebn. Enzymforsch., 1932, 1, 113-128; Chem. Zentr., 1932, i, 1799). L. S. T.

Lactic acid dehydrogenase in yeast. A. HAHN, E. FISCHBACH, and H. NIEMER (Z. Biol., 1932, 93, 121-122).—An extract of fresh yeast will decolorise methylene-blue in a vac. in presence of lactic, but not of succinic, malic, citric, or hexosediphosphoric, acid. Lactic acid is oxidised to AcCO₂H.

P. G. M.

Yeast co-zymase. K. MYRBĀCK, H. VON EULER, and H. HELLSTRÖM (Z. physiol. Chem., 1932, 212, 7-25).—Yeast adenylic acid (I) is chemically closely related to muscle adenylic acid (II). The ultraviolet adsorption of co-zymase was compared with that of other adenylic acids, inosic acid, and guanosine. Co-zymase and other adenine derivatives show an ultra-violet adsorption max. at 258-260 mu, indicating that the adenylic acid group is responsible and similar in (I) and (II). Phosphatase has no action on co-zymase. Co-zymase is inactivated after I hr. at 100° at $p_{\rm H}$ 3, but only 4.5% of the P is eliminated. The diffusion coeffs. of the active and inactivated solutions are similar, but the optical rotations differ. The titration curve of (II) also differs from that of co-zymase. The inactivation of co-zymase by heating is closely paralleled by the increase in NaOH required during neutralisation. The final val., however, is practically the same in both active and inactive material, indicating that no new acidic groups are unmasked. J. H. B.

Cytochrome and yeast-iron. T. B. COOLIDGE (J. Biol. Chem., 1932, 98, 755—764).—The oxidationreduction potential of cytochrome has been determined in artificially prepared solutions and in the yeast cell; in each case $E_h=0.260$ volt. Yeast extracts contain, besides cytochrome, a colourless Fe compound the apparent mid-point potential of which in presence of protein is about 0.020 volt. This compound is an Fe-protein complex, and its potential is the same as that of any similar Feprotein complex artificially prepared. A P compound is associated with the complex. The potential of the Fe compound is lowered considerably by deproteinisation of the yeast extract. The purest preps. of cytochrome so far obtained contain at least 2/3 of their Fe in the form of this compound, and the cytochrome-Fe forms 0.3% or less of the total yeast-Fe. R. N. C.

Sensitisation of yeasts to X-rays by dyes. A. A. IMSCHENETSKI (Bull. Acad. Sci. U.S.S.R., 1932, No. 2, 225—240).—The toxicity of dyes to yeasts increases in the order trypan-blue <Congored <eosin < cresol-blue < Bismarck-brown < neutralred; the toxic action of X-rays in the presence of dyes is > that of the sum of these factors taken separately. R. T.

Influence of nitrogenous nutrition on spore formation in six yeasts. W. OCHMANN (Zentr. Bakt. Par., 1932, II, 86, 458-465).-Combined N is not always essential to spore formation. Sporulation is favoured by the presence of nitrates and by K salts to a greater extent than by Ca salts. NH₄ salts accelerate spore formation, the effect varying with the salt used and with the nature of the yeast. Amides have a favourable effect on Saccharomyces (I), but an inhibitory action on Schizomyces (II). NH2-acids accelerate sporing of (I). NH2-monocarboxylic acids favour and NH2-dicarboxylic acids repress sporulation of (II). Cyanates had a favourable effect on (I) and retarding action on (II), whereas thiocyanates were less favourable to the former and less injurious to the latter type of organism. A. G. P.

Staining of the spores of the Schizosaccharomyces. W. OCHMANN (Woch. Brau., 1932, 49, 381—382).—The spores may be identified by treatment with methylene-blue followed by Bismarckbrown. The spores are stained grey to bluish-green and the vegetative cells brown. C. R. Thermodynamics of cell reactions. E. I. FULMER (Ergebn. Enzymforsch., 1932, 1, 1-20; Chem. Zentr., 1932, i, 1792).—Theoretical. A thermodynamic treatment of cell reactions with special consideration of the decrease in free energy in the chemical action of micro-organisms. L. S. T.

Effect of temperature, salts, and [H'] on the rupture of the plasma-gel sheet, rate of locomotion, and gel/sol ratio in Amæba proteus. S. O. MAST and C. L. PROSSER (J. Cell. Comp. Physiol., 1932, 1, 333—354).—Frequency of rupture is increased by a rise in temp. and by lowered concn. of salts and H', which reduce the thickness of the gel layer. Relationships between the gel/sol ratio and salt concn. are of a similar nature for the chlorides of Na, Mg, and Ca, but a higher concn. of NaCl than of MgCl₂ or CaCl₂ is necessary to produce a given ratio. The rate of locomotion of the organism increases with salt concn. to a max. val. and subsequently declines to zero. Each salt possesses a sp. concn. giving max. locomotion.

A. G. P.

Energy of growth of Aspergillus niger. E. F. TERROINE and R. WURMSER (Bull. Soc. Chim. biol., 1932, 14, 1163—1167).—Polemical against Algera (Rec. Trav. bot. néerland., 1932, 29, 48). The energy yield is reduced by half by the increased respiration caused by the growth of the culture. The energy content of the mycelium arises from incomplete oxidation of glucose. A. C.

Assimilation of molecular nitrogen by Aspergillus. M. ROBERG (Zentr. Bakt. Par., 1932, II, 86, 466–479).—Aspergillus failed to utilise free N₂. A. G. P.

Production of fructose from steamed glutinous rice by moulds. N. YAMAZAKI and K. NOGUCHI (J. Agric. Chem. Soc. Japan, 1931, 7, 539–546).— *Rhizopus, Aspergillus*, and *Mucor* were employed with a 50% aq. solution at 30° for 90 hr. CH. ABS.

Preparation of citric acid by moulds. II. Penicillium. K. SAKAGUCHI (J. Agric. Chem. Soc. Japan, 1932, 8, 172—176).—The production of citric acid from a solution containing glucose 10, peptone 0.3, NH₄NO₃ 0.2, K₂HPO₄ 0.015, KH₂PO₄ 0.015, MgSO₄,7H₂O 0.01 g., NaCl and FeCl₃ trace, in 100 c.c. H₂O, by 17 species of *Citromyces*, 4 species of "bridge forms," and 4 species of *Penicillium* has been compared. CH. ABS.

Energy and chemical mechanism of nitrogen fixation by Azotobacter. D. BURK (Proc. 2nd Internat. Cong. Soil Sci., 1932, 3, 67-71).—A supply of Ca considerably in excess of that required for metabolic processes is essential for N fixation by Azotobacter. Sr, but no other element, may replace Ca for this purpose (cf. A., 1930, 1068). A. G. P.

Utilisation of various hemicelluloses as sources of energy for nitrogen-fixing bacteria. R. A. DIEHM (Proc. 2nd Internat. Cong. Soil Sci., 1932, 3, 151-157).—Mannan, galactan, and xylan act as energy sources for *Azotobacter vinelandii*. Hemicellulose cannot be utilised (cf. A., 1931, 1192). A. G. P.

Production of phthalic acid by Azotobacter. K. Aso, M. MIGITA, and M. TOMODA (Proc. 2nd Internat. Cong. Soil Sci., 1932, 3, 40-41).—In culture solutions Azotobacter produced HCO₂H, AcOH, and o-phthalic acid. A. G. P.

Injury and recovery of respiration and catalase activity in Azotobacter. D. BURK, C. K. HORNER, and H. LINEWEAVER (J. Cell. Comp. Physiol., 1932, 435-449).—Respiratory activity of Azotobacter is a reversible function of $p_{\rm H}$, with an optimum val. at $p_{\rm H}$ 7·2 and range limits of $p_{\rm H}$ 5-9. Respiration permanently ceases at $p_{\rm H}$ 4·6. Catalase activity of Azotobacter reaches an optimum at neutrality, but is still apparent at $p_{\rm H}$ 3-4. Complete lack of O₂ or carbohydrate does not destroy permanently the capacity for growth or N fixation by the organism. A. G. P.

Physiological characteristics of *B. fluorescens* as a denitrifier. E. V. RUNOV (Proc. 2nd Internat. Cong. Soil Sci., 1932, 3, 160—163).—The denitrification process under aërobic conditions differs considerably from that under anaërobic conditions. Considerable reaction changes in the medium are involved. At the same $p_{\rm H}$, temp. has little effect on the quantity of N lost. The extent of the denitrification increases with the amount of NO₃' present. A. G. P.

Growth of *B. radicicola* under reduced oxygen pressure. C. BARTHEL (Proc. 2nd Internat. Cong. Soil Sci., 1932, 3, 72—73).—Growth in an atm. containing 0.5% O₂ (in N₂ or H₂) was approx. 25% of that under normal aerobic conditions. A. G. P.

Micro-organisms in oil waters and rocks and their biochemical processes. T. GINSBURG-KARAGICHEV (Proc. 2nd Internat. Cong. Soil Sci., 1932, 3, 297—298).—Micro-organisms from depth samples of oilfields are able to reduce SO_4'' , yielding H_2S and FeS, and also to decompose S-containing proteins with the production of H_2S and NH_3 . Nitrates are reduced and cellulose is decomposed to yield CH_4 , H_2 , CO_2 , and lactic and acetic acids. Organisms develop in media containing 18% NaCl, but max. H_2S formation occurs with 1—7% NaCl. A. G. P.

Acetic fermentation. A. BERTHO (Ergebn. Enzymforsch., 1932, 1, 231—269; Chem. Zentr., 1932, i, 1798—1799).—In both the stages $EtOH \longrightarrow MeCHO$ $\longrightarrow AcOH$ the same dehydrase is active. The AcOH bacteria also show a mutase, apparently different from the dehydrase, catalase, cytochrome, and indophenoloxidase, as well as a complete zymase system. L. S. T.

Biological decomposition of *n*-butyric acid. I. Formation and transition of butyric acid in natural fermentative processes. G. BREDEMANN (Zentr. Bakt. Par., 1932, II, 86, 353-381).---Pr°CO₂H is produced from sugars by soil bacteria, but is subsequently decomposed by other organisms for which its salts serve as sources of C. In artificial culture the fermentation of $(PrCO_2)_2Ca$ without gas production results in the separation of crystals of CaCO₃. The production of volatile acids of lower mol. wt. as intermediate products is indicated.

A. G. P.

Effects of hormones and certain other substances on cell (luminous bacteria) respiration. G. W. TAYLOR (J. Cell. Comp. Physiol., 1932, 1, 297-331).—Among numerous hormones examined, only adrenaline (I) showed a definite effect on luminescence, which it invariably decreased. This action is attributable to the ability of (I) to act as a H acceptor in cell oxidative processes. The intensity of luminescence is to some extent influenced by respiratory activity. Luminous bacteria are able to detoxicate cresol. A. G. P.

Pigments of Sarcina lutea. E. CHARGAFF and J. DIERYCK (Naturwiss., 1932, 20, 872-873).—The organism contains two carotenoids: (1) a hydrocarbon sarcinin, with two strong absorption bands in $C_{g}H_{g}$ solution at 469 and 440 mµ and a weaker band at 415 mµ; (2) a xanthophyll-like compound, with absorption bands at 469 and 440 mµ.

W. O. K. Reversible reduction in two stages of pyocyanine and α -hydroxyphenazine. L. MICHAELIS, E. S. HILL, and M. P. SCHUBERT (Biochem. Z., 1932, 255, 66—81; cf. A., 1932, 809).—The theory of oxido-reduction in two stages is applied experimentally to pyocyanine and α -hydroxyphenazine. It is shown how the three partial normal potentials which can be distinguished in the two-stage system are related to each other and to the $p_{\rm H}$ and to what extent the ordinary one-stage reduction of quinonoid dyes is a limiting case of the two-stage process. W. McC.

Decomposition of fats by micro-organisms. G. SELIBER (Proc. 2nd Internat. Cong. Soil Sci., 1932, 3, 142–150).—A review. A. G. P.

Lipins of tubercle bacilli. XXVIII. Phthioic acid. Isolation of a lævorotatory acid from the phthioic fraction of the human tubercle bacillus. R. J. ANDERSON (J. Biol. Chem., 1932, 97, 639– 650).—Fractionation of Me phthioate (A., 1930, 252) at < 0.0001 mm., followed by freezing of the COMe₂ solution, gave Me phthioate, hydrolysed to the acid, C₂₆H₅₂O₂, $[\alpha]_{b}^{0}$ +11.96°, and the *Me* ester of an acid, C₃₀H₆₀O₂, m.p. 48–60°, $[\alpha]_{b}^{20}$ -6.16°. A. A. L.

Specific agglutination and precipitation. II. Velocity of reactions. H. EAGLE (J. Immunol., 1932, 23, 153-186). CH. Abs.

B. pestis antigens. I. Antigens and immunity reactions of B. pestis. II. Antigenic relationship of B. pestis and B. pseudotuberculosis rodentium. III. Prophylactic value of the envelope and somatic antigens of B. pestis. H. SCHÜTZE (Brit. J. Exp. Path., 1932, 13, 284-288, 289-293, 293-298). CH. ABS.

Production of toxin by C. diphtheriæ. I. Energy sources. II. Effects produced by additions of iron and copper to the medium. C. G. POPE (Brit. J. Exp. Path., 1932, 13, 207-217, 218-223). CH. Abs.

Loss of immune substances from the body. III. Diphtheria antitoxin in human sweat. J. M. NEILL, E. L. GASPARI, R. A. MOSLEY, and J. Y. SUGG (J. Immunol., 1931, 21, 101—102).—Diphtheria antitoxin was found in the sweat of men having large amounts in the blood. CH. ABS.

Purification and concentration of the virus of poliomyelitis. A. B. SABIN (J. Exp. Med., 1932, 56, 307-317).—Adsorption and inactivation of the virus on Al_2O_3 gel C is reversible by changing the

 $p_{\rm H}$, whereby the virus also undergoes considerable purification. The purified virus gave negative biuret, xanthoproteic, and ninhydrin reactions. CH. ABS.

Intestinal antisepsis : observations on mice. J. G. GRAHAM (J. Pharm. Exp. Ther., 1932, 46, 273— 283).—The administration to mice, by mouth, of various antiseptic compounds, including anil and styryl derivatives of quinoline, Na argentothioglycerolsulphonate, hexylresorcinol, and certain dyes, failed to sterilise the intestinal tract. At most only some reduction of bacterial content was effected.

W. O. K.

Is calcium a necessary element for microorganisms? A. RIPPEL and U. STOESS (Arch. Mikrobiol., 1932, **3**, 492—506).—Apart from the neutralising action of $CaCO_3$, the presence of Ca accelerated the growth of a no. of fungi and bacteria. In some cases (e.g., Aspergillus niger) no definite effect was observed except in media abnormally high in Mg. The function of Ca depends partly on the phenomenon of ion antagonism and partly on ecological and physiological factors. Ca may be partly replaced by Sr or by tannin. A. G. P.

Colorimetric determination of peptones in nutrient media. E. GUBAREV and E. SERGEJEVA (Biochem. Z., 1932, 255, 88—91).—After removal of proteins (if necessary) peptones are determined colorimetrically in the media by means of the biuret reaction. A const. ratio must be maintained between the amounts of CuSO₄ and peptone. The average error is -3.85%. W. McC.

Determination of hormones. (MISS) K. CUL-HANE and S. W. F. UNDERHILL (Analyst, 1932, 57, 684—698).—Physiological tests are described. Adrenaline, especially synthetic, may show an $[\alpha]_{D}$ of -49° to -53° and yet display only 64—88% of activity. Thyroxine is best determined by chemical methods. T. McL.

Influence of adrenaline on nitrogen metabolism and blood-sugar in hypophysial insufficiency. B. BRAIER (Rev. soc. argentina biol., 1931, 7, 283-301).—Intravenous injection of adrenaline (I) reduces urinary N in normal and hypophysectomised fasting dogs; creatinine falls and bloodurea rises. Blood-sugar rises less in operated than in control animals. In non-fasting animals (I) produces greater hyperglycæmia in operated dogs than in the controls. CH. ÅBS.

Relation of creatinuria to muscle-glycogen in man. C. BRENTANO (Z. klin. Med., 1932, 120, 249— 271; Chem. Zentr., 1932, ii, 557).—Injection of adrenaline (I) is followed by increase in blood-lactic acid (II) ($10-36\cdot5$ mg. per 100 c.c.), but in creatinuria the increase is zero or much < 10 mg. The behaviour of (II) after injection of (I) is apparently related to the muscle-glycogen; hence creatinuria probably indicates a disappearance of glycogen from skeletal muscle. A. A. E.

Blood-coagulating influence of parathyroid injections. G. F. BUME and E. WERBER (Klin. Woch., 1932, 11, 988—989; Chem. Zentr., 1932, ii, 554).—The decrease in blood-coagulation time following injection of parathormone is due to increase in thrombokinase and not to the increase in blood-Ca. A. A. E.

Effect of parathyroid extract on blood-magnesium. D. M. GREENBERG and M. A. MACKEY (J. Biol. Chem., 1932, 98, 765—768).—Subcutaneous injection of parathormone in the dog produced a small increase in blood-Mg, which appeared between the 2nd and 6th hr. after injection, and fell quickly to the normal val. The average rise was 0.6 mg. Mg per 100 c.c. plasma. The Mg increase appeared to be independent of the extent of the subsequent increase in blood-Ca. R. N. C.

Activation of insulin. H. P. HIMSWORTH (Lancet, 1932, 223, 935—936).—Variation in the efficiency of insulin (I) in diabetes is discussed. Experiments with normal subjects showed that by altering the composition of the diet the efficiency of (I) in depressing blood-sugar could be varied at will, and that there is a definite latent period after injection during which (I) exerted no measurable action. (I) as known and as secreted by the pancreas is an inactive material which requires activation by an unknown substance, called insulin-kinase, which is probably produced in the liver. L. S. T.

Effect of lecithin on the action of insulin. E. SKOUGE and A. SCHRUMPF (Z. klin. Med., 1932, 120, 754-767; Chem. Zentr., 1932, ii, 890).—Lecithin alone has no action on the blood-sugar, but when given with insulin it delays the action. A. A. E.

Hypoglycæmic action of callicrein (padutin). E. K. FREY, H. KRAUT, and E. WERLE (Klin. Woch., 1932, 11, 846—849; Chem. Zentr., 1932, ii, 394).—In diabetes, or in the depancreatised dog, but not in normal man or animals, the blood-sugar is markedly lowered, but the effect gradually diminished on repeated dosage. The activity is partly regained after administration of insulin. The hypoglycæmic and pressor components are destroyed by boiling. The prep. contains only a small quantity of P, chiefly inorg.; the amount of adenylphosphoric acid is too minute to have pharmacological action. A. A. E.

Hormone of the pituitary pars intermedia. II. Intermedin in the organism. B. ZONDEK and H. KROHN (Klin. Woch., 1932, 11, 849-853; Chem. Zentr., 1932, ii, 392; cf. A., 1932, 432).—The intermedin (I) contents of the pituitary of various animals are : minnow 7, frog 10, hen 75, rabbit 200-300, ox 5000-6000, man 4000-7000 phoxin units; the content per g. is : ox 3300, man 10,000. (I) is produced in the pars intermedia and diffuses into the other portions of the gland. Low vals. were obtained in pernicious anaemia and high vals. in uræmia, carcinoma of the liver, and eunuchoid adiposity. In the brain, (I) exists only in the wall of the third ventricle. A. A. E.

Effect of the growth-promoting hormone on the mouse. F. WADEHN (Biochem. Z., 1932, 255, 189-199).—A method for obtaining from the anterior lobe of the pituitary gland stable preps. containing growth-promoting hormone and for testing them on the mouse is described. Greatly increased growth, only partly due to accumulation of H_2O and accompanied by decrease in fat content and in ash content of the skeleton, follows injection of the preps. The ash content of the rest of the mouse and Ca and PO₄ remain unchanged, but in the skeletal ash Ca is reduced. Apart from the spleen, the wt. of which is increased by about 50%, there is no increase in the relative wt. of the organs. W. McC.

Effects of combinations of potassium iodide with anterior pituitary and with thyroid on basal metabolism in guinea-pigs. W. J. SIEBERT and E. W. THURSTON (J. Pharm. Exp. Ther., 1932, 46, 293—301).—The intraperitoneal administration to guinea-pigs of acid extracts of the anterior lobe of ox pituitary raised the basal metabolic rate and caused a decrease in wt., but these changes were inhibited when a daily dose of 0.05 g. KI was given. The administration by mouth of Armour's anterior pituitary tablets, or of thyroid gland, to guinea-pigs also caused a rise in basal metabolic rate and a loss of wt., but in both cases simultaneous administration of KI had no inhibitory effect. W. O. K.

Preparation of extracts of anterior pituitarylike substances of urine of pregnancy. P. A. KATZMAN and E. A. DOISY (J. Biol. Chem., 1932, 98, 739—754).—Active extracts of the anterior pituitarylike substance from urine of pregnancy have been obtained by the two following methods: (1) acidification of the urine to $p_{\rm II}$ 5 with AcOH, adsorption on norit, elution with 90% PhOH, pptn. with 95% EtOH, and extraction with H₂O; (2) acidification with AcOH, adsorption on B2OH, elution by dissolving BZOH in COMe₂, and extraction with H₂O. Extracts prepared by the BzOH method had a potency of 1250 mouse units per mg. By fractional pptn. with COMe₂ the extract was purified to a potency of more than 3000 mouse units per mg. The extract gave positive biuret and Millon reactions, and was shown by bio-assay to be free from œstrogenic hormones. The immature mouse and rat units are defined.

R. N. C.

Mucification of the vaginal epithelium of mice as a test for pregnancy-maintaining potency of extract of corpora lutea. R. G. HARRIS (Science, 1932, 76, 408).—A reply to criticism (A., 1932, 423). L. S. T.

New crystalline sex hormone. A. GIRARD, G. SANDULESCO, A. FRIDENSON, and J. J. RUTGERS (Compt. rend., 1932, 195, 981—983; cf. A., 1932, 433, 547).—The mother-liquors of the hormone from urine from pregnant marcs yield a substance of greater acidity, equilenin, $C_{18}H_{18}O_2$, m.p. 258—259° (decomp.), $[\alpha]_{11}^{m}$ +87° in dioxan (crystallographic description) (Bz, m.p. 222—223°, and Ac, m.p. 156—157°, derivatives; oxime, m.p. 249—250°). Bromination yields $C_{18}H_{17}O_2Br$, m.p. 225—227° (decomp.). (All m.p. are corr.) The æstrogenic activity is $\frac{1}{12}$ to $\frac{1}{20}$ that of æstrin. R. K. C.

Vitamins aid reduction of lost time in industry. A. D. HOLMES, M. G. PIGOTT, W. A. SAWYER, and L. COMSTOCK (Ind. Eng. Chem., 1932, 24, 1058— 1060).—The beneficial effects of cod-liver oil are demonstrated. E. H. S. Vitamin-A, B_1 , C, and B_2 content of Concord grapes. E. P. DANIEL and H. E. MUNSELL (J. Agric. Res., 1932, 45, 445—448).—The pulp and juice are a poor source of vitamins-A and $-B_1$, whilst vitamins-C and $-B_2$ are entirely lacking. The vitamins may be conc. in the skins. P. G. M.

Halibut-liver oil. I. Vitamin potency, physical constants, and tolerance. A. D. EMMETT, O. D. BIRD, C. NIELSEN, and H. J. CANNON (Ind. Eng. Chem., 1932, 24, 1073—1077).—Halibut-liver oils $(d^{25} 0.927 - 0.928$, sap. val. 179—193, I val. 118—126, unsaponifiable matter 7.44 - 7.9%) were about 100 (75-125) times as vitamin-A-potent as was cod-liver oil. The colour in the Carr-Price test, however, is bluish-green, the dominant band being at $\lambda 622$. The vitamin-D potency of the oil is also very high. Massive doses produced no abnormality in the test-animals.

E. L.

Quantitative variations in vitamin-A content of butter-fat. G. S. FRAPS and R. TREICHLER (Ind. Eng. Chem., 1932, 24, 1079-1081).-Cows fed on cottonseed meal and hulls yielded butter-fats containing about 2 units of vitamin-A per g. (modified Sherman-Munsell bio-assay; cf. Fraps, A., 1932, 433). Cows receiving in addition (a) sorghum silage and (b) silage and pasture grass gave a higher daily yield of butter-fat containing, respectively, 2-12 and about 33 units of vitamin-A per g. (cf. butter-fats from local farm animals reared on grain and pasture containing 17-50 units per g. according to season). Only a small proportion of the vitamin-A content of the food was accounted for by the vitamin in the butter-fat in cases (a) or (b). E. L.

Does vitamin-A possess vitamin-D-sparing properties when fed to growing chicks? J. E. HUNTER, R. A. DUTCHER, and H. C. KNANDEL (Poultry Sci., 1932, 11, 239-240).—No sparing effect, so far as the ossifying properties of vitamin-D are concerned, was observed. CH. Abs.

Vaginal smear method of determining vitamin-A. C. A. BAUMANN and H. STEENBOCK (Science, 1932, 76, 417—420).—The growth, ophthalmic, and vaginal smear methods have been compared in rats, using carotene as the source of vitamin-A. The smear method can be used to determine this vitamin. L. S. T.

Antimony trichloride test for vitamin-A. A. F. McCARLEY (Analyst, 1932, 57, 709).—Certain oil-sol. aniline dyes give intense carmine to violet colours with SbCl₃ and the possibility of their presence must be considered. T. McL.

Ferrous iodide and linoleic acid in vitamin-A deficiency. F. E. CHIDESTER (Science, 1932, 76, 436-437).—A reply to criticism (A., 1932, 1293). L. S. T.

Do the B-vitamins influence the utilisation of lipins? R. LECOQ (Compt. rend., 1932, 195, 827-829).—The replacement, in a diet which produces polyneuritic symptoms in pigeons, of carbohydrate by lipins furnishing an equal quantity of energy, does not abolish its polyneuritic action. When yeast is also administered to pigeons on such

a diet of high lipin content the polyneuritic symptoms disappear. W. O. K.

Antineuritic vitamin. IV. Preparation of a highly potent concentrate. R. J. BLOCK and G. R. COWGILL (J. Biol. Chem., 1932, 98, 637— 643).—Assuming vitamin- B_1 to be an org. base, extraction from aq. alkaline solution by org. solvents should be possible. By this technique concentrates approximating in potency to those of Jansen and Donath (A., 1926, 644) can be obtained directly from rice polishings or yeast. H. G. R.

Potency of vitamin- B_1 preparations. H. W. KINNERSLEY, J. R. P. O'BRIEN, and R. A. PETERS (Nature, 1932, 130, 774).—Comparative tests on pigeons show that cryst. vitamin- B_1 from baker's yeast is more potent that the prep. of Windaus *et al.* (A., 1932, 310). L. S. T.

Ultra-violet absorption spectrum and chemical structure of vitamin- B_1 . F. F. HEYROTH and J. R. LOOFBOUROW (Nature, 1932, 130, 773; cf. A., 1932, 1175).—Absorption curves for ten different vitamin- B_1 concentrates have been determined. Correlation of biological activity and absorption, which shows a max. at or near 2600 Å., indicates that vitamin- B_1 is characterised by a band at 2600 Å. This type of absorption resembles most closely that of compounds containing a pyrimidine ring or of the type of ergothioneine. The curve of Windaus' prep. (*ibid.*, 310) is similar to that of uracil. L. S. T.

Ultra-violet absorption spectrum and chemical structure of vitamin- B_1 . F. P. BOWDEN and C. P. SNOW (Nature, 1932, 130, 774).—A reply to criticism. L. S. T.

Effect of heat at varying hydrogen-ion concentrations on vitamin- B_1 in protein-free milk. N. HALLIDAY (J. Biol. Chem., 1932, 98, 707-717).— The vitamin- B_1 potency of protein-free milk has been studied at $p_{\rm II}$ 4·3, 7, and 10, the milk being supplied to rats on the Sherman-Chase diet. Storage in the cold of solutions at $p_{\rm II}$ 4·3 and 7 caused practically no loss of activity, but nearly complete loss at $p_{\rm II}$ 10. Heating for 1 hr. at 97° destroyed 10% at $p_{\rm II}$ 4·3, 30% at $p_{\rm II}$ 7, and 75-90% at $p_{\rm II}$ 10; heating for 4 hr. destroyed 15% at $p_{\rm II}$ 4·3, 40-50% at $p_{\rm II}$ 7, and 75-90% at $p_{\rm II}$ 10. The results show close similarity with those reported for vitamin- B_2 under the same conditions. Addition of whole wheat to the diet prevented cessation of growth after 5-6 weeks which normally occurs in rats on this diet. It is suggested that the wheat contains a third factor necessary for the growth of the rat, which is thought to be identical with vitamin- B_4 . R. N. C.

Effects of parboiling and milling on the antineuritic vitamin (B_1) and phosphate content of rice. W. R. ARKROYD (J. Hyg., 1932, 32, 184—192).—Highly milled parboiled rice was rich in vitamin- B_1 , whilst roughly milled raw rice was deficient. Polishings from raw rice contained less B_1 than those from parboiled rice. Parboiled rice contained more P_2O_5 than raw rice when milled to the same degree. Parboiling probably causes vitamin- B_1 and phosphate to diffuse through the endosperm. CH. ABS.

Vitamin-C. J. TILLMANS (Z. Unters. Lebensm., 1932, 64, 11–20).—A review. E. B. H.

Hexuronic acid as the antiscorbutic factor. E. G. Cox, E. L. HIRST, and R. J. W. REYNOLDS (Nature, 1932, 130, 888) .- The taking-up of 2 I by aq. solutions of hexuronic acid is due to oxidation at a double linking. H₂O is essential and the product (I), which is not a di-iodide, can be reduced to hexuronic acid by evaporation in presence of HI. The biological activity of the acid is probably due to this double function of oxidation and reduction. I is further oxidised by NaOI; O is absorbed, two new CO₂H groups are formed, and 1 mol. of H₂C₂O₄ is produced quantitatively. Acid KMnO4 and hexuronic acid form a trihydroxybutyric acid (possibly d-threonic acid), whilst HCl gives furfuraldehyde quantitatively on heating. Hexuronic acid is monobasic and not a lactone; a suggested structure is CO.H.[CO]. CH. CH(OH) CH. OH. It forms a diphenylhydrazone, a hydrated di-(p-bromophenylhydrazone), and yields a condensation product with o-tolylencdiamine at 15° . The Na or Ca salt gives a violet colour with FeCl₃, and the Na salt a deep blue colour with Na nitroprusside. Acid and salts show an intense absorption band with a head at approx. 265 m μ . At 175° the acid loses CO₂ without darkening or melting, but when heated rapidly the pure acid melts at 192°. In H_2O $[\alpha]_{5780} + 24°$ and the slow change $[\alpha]_{5780} + 24°$ to +31° is due to partial neutralisation by the alkali from the glass. Mutarotation does not occur. The Na salt has $[\alpha]_{5780}$ +105° in H₂O, +135° in 0·1N-alkali. Alkaline solutions of the acid are stable in the absence of O_2 . The absorption spectrum of decitrated lemon juice shows the hexuronic acid content to correspond with the recorded antiscorbutic activity of the isolated acid. L. S. T.

Vitamin-C, adrenaline, and adrenals. A. VON SZENT-GYÖRGYI (Deut. med. Woch., 1932, 58, 852– 854; Chem. Zentr., 1932, ii, 392–393).—Animals receiving 1 mg. daily of hexuronic acid (from adrenals) showed normal growth and were not scorbutic. Hexuronic acid is probably related to Swingle's cortin. "Novadrenin" from the adrenal medulla is 15 times as active as adrenaline and is probably the true hormone of the adrenal medulla. It appears to be readily convertible into adrenaline. A. A. E.

Reducing value of plant-juices containing vitamin-C as determined by 2:6-dichlorophenolindophenol. H. H. MOTTERN, E. M. NELSON, and R. WALKER (J. Assoc. Off. Agric. Chem., 1932, 15, 614-616).—This indicator is more sp. than I for vitamin-C, although it is reduced by many compounds having no vitamin-C activity. The titration val. of cabbage-juice decreases by almost 50% after 5 min. in air, owing to the presence of active hexoxidase, but if this is destroyed by steaming the original cabbage, the results are more consistent with the biological response (cf. A., 1932, 658). J. G.

Indirect determination of the vitamin-C state of students in Upsala in autumn and spring by measurement of the strength of skin capillaries. K. O. GEDDA (Skand. Arch. Physiol., 1932, 63, 306-311; Chem. Zentr., 1932, ii, 556).—Lack of vitamin-C during the winter was indicated; normal conditions were re-established very slowly.

A. A. E.

Determination of vitamin-D. L. L. LACHAT, H. A. HALVORSON, and L. S. PALMER (J. ASSOC. Off. Agric. Chem., 1932, **15**, 660—675).—The use of chickens enables results to be obtained in a short time, and since the vitamin-D requirement of the chick is high, the results are correspondingly trustworthy. Of 13 rickets-producing rations a mixture of 59 parts of yellow maize, 25 of wheat-flour middlings, 12 of crude casein, and 1 each of pptd. CaCO₃, Ca₃(PO₄)₂, NaCl, and dry baker's yeast gives the best growth rate and uniformly low bone-ash vals. at 4—5 weeks of age (viz., 30—34% for negative control groups, and 45—48% for a satisfactory supply of vitamin-D). J. G.

Plasticity of calcified tissues. II. Results of minor variations in the calcium-phosphorusvitamin-D complex. W. G. Downs, jun. (J. Dental Res., 1932, 12, 363-373).—Marked alterations in dietary Ca: P produced decaloification of the teeth and jaws of rats. Addition of vitamin-D emphasised the histological changes when the P content of the diet was low, but aided the tissues to prevent the changes when Ca was low. CH. ABS.

Growth and calcification catalysts in animals. F. BILEK (Věstn. Českoslov. Akad. Zem., 1932, 8, 363—367; Chem. Zentr., 1932, ii, 397).—Vitamin-D promotes calcification, but growth only to a small extent, whilst carotene in large doses markedly accelerates growth. A. A. E.

Photochemical reaction in photosynthesis. R. EMERSON and W. ARNOLD (J. Gen. Physiol., 1932, **16**, 191-205; cf. A., 1932, 548).—Cells of *Chlorella* pyrenoidosa of varying chlorophyll content were exposed to continuous and intermittent light of high intensity. With an intensity approaching that necessary for max. photosynthesis, 2480 mols. of chlorophyll are present for each mol. of CO_2 reduced for a single flash of light. The duration of a complete cycle of photochemical and Blackman (recovery) reactions is 0.02 sec. at 25°. The rate of photochemical reaction is given by R = AIN, where R = velocity coeff., I = light intensity, and N =no. of units available for photochemical reaction, a unit being the mechanism capable of reducing 1 mol. of CO_2 . F. O. H.

Mol. wt. of phycocyan and of phycoerythrin. III. T. SVEDBERG and I. ERIKSSON (J. Amer. Chem. Soc., 1932, 54, 3998—4010; cf. A., 1930, 233).—The sedimentation const. of c-phycocyan (I) determined in fresh extracts of Aphanizomenon flos aquæ is identical with the val, for (I) purified by crystallisation with $(NH_4)_2SO_4$. (I) therefore probably exists in the cells of the algæ with the same mol. wt., 208,000, as in the purified product. The sedimentation const. of r-phycoerythrin (II) in fresh extracts of *Ceramium rubrum* is identical with the val. for (II) purified with $(NH_4)_2SO_4$; native (II) is therefore probably identical with the purified product with regard to mol. wt. Phycoerythrin (III) (from *Polysiphonia urceolata*) is not quite homogeneous

but the sedimentation const., 12.4×10^{-13} , mol. wt., 196,000, and $p_{\rm H}$ stability range are of the same order of magnitude as for normal (II). The sedimentation const. of the modifications of (III) from the algæ Bornetia secundiflora (IV), Griffithsia furcellata (V), and Sebdenia monardiana (VI) are determined; that from (VI) shows the same val. as (II) (11.3×10^{-13}) , whilst the consts. for (IV) and (V) are slightly higher $(12 \cdot 1 \times 10^{-13})$. This deviation is probably due to inhomogeneity. The $p_{\rm H}$ stability range is the same as for (II). The light absorption of the modification from (IV) is identical with that of (II), that of (V) resembles closely (III), but that of (VI) differs considerably from that of the other modifications. A semi-quant. study of the fluorescence of the modifications did not reveal any marked difference in the wave-length of the fluorescence light but showed that the intensity is considerably lower for that from (V). From p_{μ} 2.5 to 5.0 the sedimentation const. of (II) is 11.3×10^{-13} , and the mol. wt. is 209,000. On both the alkaline and acid sides of this normal region, which includes the isoelectric point $(p_{\rm H} 4.85)$, there is a region where the sedimentation const. is $5.8-5.9 \times 10^{-13}$ and the mol. wt. half the normal val. These regions are connected to the normal by transition regions where the solution contains mols. of the normal and of half the normal wt. at the same time. In solutions of $p_{\rm H} < 1.5$ or > 8.0, the phycocyan mol. begins to decompose and form systems heterogeneous with regard to mol. wt.

C. J. W. (b)

VI. Energy transformations at surfaces. Carbon dioxide assimilation. I. H. KAUTSKY, A. HIRSCH, and F. DAVIDSHÖFER (Ber., 1932, 65, [B], 1762-1770).-Irradiation of a green leaf which has been kept in the dark with ultra-violet or visible light causes (i) a rapid increase of fluorescence to a max., (ii) a steady decline reaching within a few min. (iii) a level which remains const. under fixed conditions. The course of alteration in the intensity of fluorescence can be repeated at will if the leaf is kept in the dark for a period corresponding with that of its irradiation. The initial, almost extinguished fluorescence of chlorophyll in (i) is ascribed to the trans-ference of the absorbed light energy to a particular type of mol. of the assimilation system. The rapid decline is due to the rapid decrease of possibility of transference of energy, since the already excited mols. pass into a condition in which for the time being they cannot absorb energy from the fluorescing pigment. This phase is not appreciably influenced by lowering of temp. or by the presence of HCN. The phase (ii) is characterised by the gradual incidence of a catalyticchemical reaction of assimilation which is restricted or abolished by lowering of temp. or the presence of HCN. Two changes are therefore involved, the chemical process coupled with the liberation of O and the increasing transference of absorbed light energy from the chlorophyll to a definite mol. type of the assimilation system which becomes increasingly available. Phase (iii) represents the steady state of normal assimilation under the given conditions. On the assumption that the total light energy necessary for assimilation is absorbed by the chlorophyll and transferred to the system and that this transference

involves a more or less pronounced diminution of the fluorescence of chlorophyll, it is shown that O is the only type of mol. of the system to which the energy is transferred. O is therefore the collector and carrier of the energy of assimilation. H. W.

Life of plants in a closed atmosphere. J. BEAUVERIE and S. MONCHAL (Compt. rend., 1932, 195, 897—899).—Various plants sealed in glass jars with H_2O and soil survive sometimes for 4 years. Gas pressure may rise at night by $\frac{1}{15}$ atm. and fall $\frac{1}{10}$ atm. in the day. H. D.

Effect of amino-acids on the oxygen consumption of submerged plants. G. SCHWABE (Protoplasma, 1932, 16, 397-451).-Natural, optically active NH2-acids increase O2 consumption, but no relationship between this effect and the constitution of the acid was observed. The action of NH₂-acids (I) is more marked in plants of high physiological activity and having adequate nutrients. The effect of (I) is sp. and does not depend on $p_{\rm H}$ changes. Treatment of plants with (I) does not alter the R.Q. The inhibitory action of HCN on the activity of (I) resembles that on normal respiration. (I) do not affect peroxidase activity. The respiratory changes examined are ascribed partly to the actual oxidation of the (I) and partly to the action of the latter as O_2 carriers. A. G. P.

New aspects of plant nutrition. R. W. THAT-CHER (Science, 1932, 76, 281—285).—Evidence is discussed for the view that in plant nutrition there is a series of phenomena (the action of small amounts of elements such as Cu, Mn, B, and Zn) and principles which are comparable with the vitamin function in animal nutrition. L. S. T.

Plant nutrition. B. V. NATH (Soc. Biol. Chem. India. Reprint, 1932, 39 pp.).—The nutritive processes in plants are discussed and their general similarity to the corresponding processes in animals is emphasised. A. G. P.

Relation of mineral nutrition to transpiration in plants. A. H. K. PETRIE (J. Counc. Sci. Ind. Res. Australia, 1932, 5, 177–180).—The effect of NO_3' treatment in reducing the transpiration ratio of *Atriplex semibaccatum* cannot be explained in terms of reduction of the osmotic pressure of the cell sap. Other possible interpretations are discussed.

W. G. E.

Relationship between transpiration and resorption of ions [in plants]. M. GRAČANIN (Compt. rend., 1932, 195, 899—901).—Comparison of the quantities of HPO_4 " resorbed and the intensity of transpiration of plants maintained in pure solutions of CaHPO₄ and subjected to varying degrees of illumination shows no correlation between the two processes. H. D.

Amounts and distribution of some phosphorus and nitrogen compounds in wheat during growth. F. KNOWLES and J. E. WATKIN (J. Agric. Sci., 1932, 22, 755—766).— The phytin-(I), lipin-(II), and inorg. P, and the protein-(III) and non-protein-N contents of the root straw and ear of wheat throughout the growing season are recorded and discussed. Variations in the (II) and (III) constituents were similar. (I) and (III) rose and fell concurrently. A. G. P.

Growth and differentiation. III. Distribution of calcium and phosphate in tissues of *Kleinia articulata* and some other plants. D. THODAY and H. EVANS (Ann. Bot., 1932, 46, 781— 806).—Ca occurs in the stems of *K. articulata* in solution in the sap, in pith, and in patches in the inner cortex in areas sharply defined from adjoining Ca-free tissue. $PO_4^{\prime\prime\prime}$ accumulation is mainly in the bundle zone. Acidity is low in the pith and high in the bundle zone. Complementary localisation of Ca and P was observed in several plants and in *Mesembryanthemum* sol. Ca and sol. oxalate occurred in separate cells. A. G. P.

Effect of $[H^*]$ on growth and geotropism. S. STRUGGER (Ber. deut. bot. Ges., 1932, 50, 77–92). —The rate of growth of both the intact and decapitate germinal roots of *Helianthus annuus* is increased on acidification within the limits $p_{\rm H}$ 7–3. By immersion in suitable buffers curvature of the hypocotyls, indicating active membrane growth and of non-osmotic nature, can be produced. This phenomenon is reversible only in the early stages. P. G. M.

Potash requirements of the tobacco crop. P. J. ANDERSON, T. R. SWANBACK, and O. E. STREET (Connecticut [New Haven] Agric. Exp. Sta. Bull., 1932, No. 334, 137—217).—The K content of tobacco leaves is inversely related to the proportions of Ca and Mg, is increased in proportion to the amount of K applied, and is usually higher in dry than in wet seasons. Liberation of relatively unavailable K in soils is accelerated to some extent by treatment with CaSO₄, S, NaNO₃, acid fertilisers, and by the ploughing-in of cover crops. In lysimeter tests losses of K in drainage were considerable. These were increased by applications of $(NH_4)_2SO_4$ and decreased by NaNO₃. Org. manures had no action in this respect. The period of max. rate of intake of K by plants corresponded with the max. intake of N and max. increase in dry wt. produced. Reduced applications of K affect the quality of the leaf more than the actual yield. A. G. P.

Test on plant material for diagnosing phosphorus deficiencies. S. F. THORNTON (Indiana Agric. Exp. Sta. Bull., 1932, No. 355, 20 pp.).— Samples of stems or leaf petioles are taken from or near actively growing points of plants. 1—1.5 g. of the crushed material are treated with 10 c.c. of a reagent containing 4 g. of NH₄ molybdate dissolved in 500 c.c. of H₂O, to which are added 63 c.c. of conc. HCl and 437 c.c. of H₂O. After vigorous shaking with the reagent a small crystal of SnCl₂ is added. The blue coloration indicates the inorg. P in the stems.

A. G. P.

Determination of the atomic weight of potassium separated from peas. V. G. CHLOPIN and M. A. PASVIK-CHLOPIN (Bull. Acad. Sci. U.S.S.R., 1932, 381-390).—Determinations of the KCl: AgCl ratio with K from peas give for the at. wt. of K $39.09\pm$ 0.018, so that no accumulation of the heavy, radioactive isotope of K occurs in peas. That separation of the isotopes in living organisms does not occur is not, however, considered to be finally proved (cf. Loring and Druce, Chem. News, 1930, **140**, 34; Druce, *ibid.*, 1931, **142**, 33; Lowry, A., 1931, 141). T. H. P.

Effect of plane-polarised light on the formation of carbohydrate in leaves. R. H. DASTUR and R. D. ASANA (Ann. Bot., 1932, 46, 879-891).— In the plants examined no significant differences were apparent in the carbohydrate content of leaves grown in polarised and in non-polarised light.

A. G. P. Role of reserve substances of the vine in the setting of fruit and in the ripening of the grapes. L. MOREAU and E. VINET (Ann. Agron., 1932, 3, 363— 374).—The development of fruit buds is largely influenced by the accumulation of sugars in the sap. Ripening is associated with a rapid initial rise in the sugar content of the grapes, followed by a further but slower increase to the period of full maturity. The rapid accumulation of sugars is derived to a large extent from the carbohydrate reserves of the main stem. A. G. P.

Seasonal changes in the composition of Stayman apple trees. I. Carbohydrates. H. R. KRAYBILI, J. T. SULLIVAN, and L. P. MILLER (Proc. Amer. Soc. Hort. Sci., 1931, 27, 206).—Starch is max. in November; subsequently it is hydrolysed, synthesised between February and April, and again hydrolysed in April and May. CH. Abs.

Nitrogen and carbohydrate metabolism of young apple trees as affected by excessive applications of sodium nitrate. N. W. STUART (New Hampshire Agric. Exp. Sta. Tech. Bull., 1932, No. 50, 26 pp.).—In leaves from trees receiving heavy dressings of nitrates the general level of N metabolism was much higher than in those from unfertilised controls. Differences were associated with the lipinand residual N fractions. The carbohydrate content of leaves was lower in unfertilised trees. Differences in carbohydrate metabolism were shown in the nature of the insol. reserve produced. The carbohydrate : N ratio was narrower in fertilised trees. A relationship between leaf injury and the presence of NO_3' in the leaves is suggested. A. G. P.

Exculus changes during the breaking of buds of **Exculus hippocastanum.** G. KLEIN and H. LINSER (Planta [Z. wiss. Biol.], 1932, 17, 641-643; cf. A., 1932, 436).—Earlier work is confirmed in older trees and further details of variations in æsculin content of buds and bud scales are recorded.

A. G. P.

Biosynthesis. IX. Plant materials. H. EMDE (Ber. Sächs. Ges. Wiss., math.-physikal. Kl., 1931, 83, 219–237; Chem. Zentr., 1932, i, 2963).—The biochemical synthesis of cinchonine and the *Coca* alkaloids, and the plant physiological role of quinic, shikimic, protocatechuic, gallic, salicylic, and benzoic acids, are discussed. It is postulated that these alkaloids are synthesised in the plant primarily from sugars or their transformation products, and only secondarily from NH₂-acids arising from hexoses. The relation between alkaloids and essential oils as plant products is also considered. A. A. E. Effect of manuring with blood on the colour of flowers of *Primula auricula*. A. MUSSACK (Ber. Deut. bot. Ges., 1932, 50, 391–392).—Addition of blood manures to soil provides a stimulant to the production of carotene in flowers. A. S. P.

Physiological processes causing the loss of winter cereals under the ice crust. A. A. RICHTER and A. I. GRETSCHUSCHNIKOV (Bull. Acad. Sci. U.S.S.R., 1932, 391–408).—The formation of an ice crust results in anaërobic conditions and increases the hot-bed effect, a rise in temp. occurring under the ice layer at the expense of the sunlight traversing it. Anaërobic processes, leading to development of CO_2 and accumulation of EtOH in the tissues, proceed to a greater or smaller extent in different cereals and in their different parts, and the plant undergoes alcoholic auto-poisoning. T. H. P.

Utilisation of atmospheric nitrogen by germinating seeds of leguminous plants. III. N. VITA and R. SANDRINELLI (Biochem. Z., 1932, 255, 82-87; cf. A., 1932, 1180).—The amount of N absorbed by germinating seeds (peas, lupin) is usually increased by addition of dil. solutions of salts (Fe, Mn, Mg, K sulphates), but the extent of the increases varies greatly with the concn. of salt and of O_2 in the atm., the duration of the action, and the degree of illumination. It is possible that the observations give the results of several concurrent processes of different kinds. W. McC.

Oxidising power of the chondriosome and cytoplasmic sexualisation of fungi. P. JOYET-LAVERGNE (Compt. rend., 1932, 195, 894—896).— The oxidising power of the filaments of *Pythium* is manifested by the coloration of the leuco-derivatives of methylene-, Nile-, cresyl-, and methyl-blue. In the male gamete the mitochondria have a higher oxidising power than in the female, demonstrating the sexualisation of the cytoplasm. H. D.

Bioelectric potentials in Valonia. Effect of substituting potassium chloride for sodium chloride in artificial sea-water. E. B. DAMON (J. Gen. Physiol., 1932, 16, 375–395; cf. A., 1930, 965).—The p.d. across the protoplasm of V. macrophysa is decreased by lowering and increased by raising the conen. of KCl in the external solution. Changes of p.d. with changes of $p_{\rm H}$ of the medium indicate that K enters the cell more rapidly from alkaline than from acidified KCl-rich sea-H₂O. F. O. H.

Biology of the potato. XIII. Water cultures of potato. W. SCHROPP. XIV. Determination of the degree of decomposition of tubers by electrometric measurements. A. HEY. XV. Catalase of potato tubers. M. KLINKOWSKI (Arb. biol. Reichsanst. Land- u. Forstwirts., 1932, 20, 49— 77, 79—90, 91—99).—XIII. The effects of various nutrient solutions on the growth and nutrient intake of potatoes are recorded. Nutrients containing high proportions of Cl' produce plants of higher H_2O content than do those having a predominance of $SO_4^{\prime\prime}$. The sensitivity of plants in high Cl' nutrients to the addition of $(NH_4)_2SO_4$ is associated with the markedly increased Cl intake produced.

XIV. Relations between the reduction-oxidation

potential of tubers and the degenerative process are examined.

XV. Sound potatoes in storage show a smaller decrease in catalase activity than do those undergoing decomp. In the vegetative period no relationship exists between the health condition of the plant and its catalase activity. A. G. P.

Effect of carbon dioxide content of storage atmosphere on carbohydrate transformation in certain fruits and vegetables. E. V. MILLER and C. BROOKS (J. Agric. Res., 1932, 45, 449–459).— Storage in an atm. containing 35-47% CO₂ at $>85^{\circ}$ did not result in appreciable carbohydrate transformation in sour or sweet cherries or peaches. Under similar conditions the transition of sugars in peas and sweet corn was retarded. Limiting conditions of temp., [CO₂], and period of exposure necessary to avoid changes in flavour of various materials are examined. A. G. P.

Hormone and growth-promoting substance of pollen. F. LAIBACH (Ber. Deut. bot. Ges., 1932, 50, 383-390).—Pollen hormone present in H_2O extracts of pollen from certain orchids and *Hibiscus* and the growth-promoting substance are very similar if not identical substances. A. G. P.

Chlorophyll mutants of barley. H. von EULER, D. BURSTRÖM, H. HELLSTRÖM, and B. VON KÖHLER (Z. physiol. Chem., 1932, 212, 53—60; cf. A., 1932, 785).—Further chlorophyll-normal and -defective mutants of barley show similar absorption curves in the ultra-violet. The chlorophyll ratio in defective and normal shoots is not paralleled by their absorption. Tyrosine, tryptophan, and Mg were determined, but marked differences were not observed. J. H. B.

Constituents of the northern mistletoe, Viscum album, L. J. A. MÜLLER (Arch. Pharm., 1932, 270, 449—476).—Details are given for the isolation of AcOH, Mg dl-lactate, d-mannitol, choline, propionylcholine (I) ("reineckate"), and acetylcholine (?) from the expressed juice. (I) is responsible for the depressor action of the juice. H. B.

Rhatany catechin. M. NIERENSTEIN (J.C.S., 1932, 2809).—The presence of d- and dl-gambircatechin in "rhatany root" is proved by extraction with CHCl₃, fractionation by Et₂O and aq. AcOH, and conversion into Ac₅ derivatives. H. A. P.

Colouring matter of acacia wood. K. BRASS and H. KRANZ (Annalen, 1932, 499, 175-187).-Extraction of the wood of Gleditschia monosperma with $COMe_2$ gives 5'-hydroxyfisetin [7:3':4':5'tetrahydroxyflavonol] (I), which is obtained anhyd. (green) and +1 (bronze), 1.5 (brick-red), and $2H_2O$ (yellow); the hydrochloride, Ac_5 derivative, m.p. 224°, and Me_5 ether (II), m.p. 148°, are prepared. KOH fusion of (I) affords $m - C_6 H_4(OH)_2$ and β resorcylic acid, whilst (II) is degraded by MeOH-KOH in N₂ to 3:4:5-(OMe)₃ C_6H_2 ·CO₂H and 2hydroxy- ω : 4-dimethoxyacetophenone. 3-Oximino-7:3':4':5'-tetramethoxyflavanone (Dean and Nierenstein, A., 1925, i, 951) and 10% H₂SO₄ in AcOH give 7:3':4':5'-tetramethoxyflavonol, m.p. 194°, methylated (Me₂SO₄) to (II). The COMe₂ extract of the wood of Robinia pseudacacia contains (probably)

a glucoside of (I) (cf. Schmid and Pietsch, A., 1931, 738) (acetylation gives the above penta-acetate) and a substance, decomp. 230—240° (acetate, m.p. 141°). H. B.

Globulins of some Cucurbitaceæ seeds. R. HIROHATA (Z. physiol. Chem., 1932, 212, 1-6).-Cryst. globulins were isolated from species representing seven genera. The preps. showed great similarity in chemical properties, but by means of the precipitin reaction differences were observed. The genera Benincasa, Citrullus, Cucumis, Lagenaria, and Cucurbita are very similar. Trichosanthes and Luffa differ from these and from one another. Momordica gave no cryst. globulin. Citrullus globulin has a high feeding val. J. H. B.

Chemical examination of the seeds of Abrus precatorius, L. I. N. GHATAK and R. KAUL (J. Indian Chem. Soc., 1932, 9, 383–387).—Extraction of the powdered kernels (scarlet variety of seeds) with light petroleum gives an oil, $[\alpha]_{15}^{35}$ +0·39°, d^{25} 0·9139, n^{25} 1·4662, acid val. 2·44, sap. val. 191·7, Hehner val. 88·06, Ac val. 0, I val. 95·1, unsaponifable matter 1·68%. Further extraction with EtOH gives *abrine*, C₁₂H₁₄O₂N₂, m.p. 295°, and *abralin*, C₁₃H₁₄O₇, amorphous, m.p. 105°, $[\alpha]_{15}^{35}$ -27·37° in H₂O, in addition to a considerable amount of reducing sugars. H. B.

Presence of sucrose in the branches and leaves of *Euonymus europœus*. F. D. BATON (Compt. rend., 1932, 195, 823-825).—The branches "and leaves contain sucrose and dulcitol. W. O. K.

Alcohol and sugar contents of olive presswater. II. A. MANGINI (Annali Chim. Appl., 1932, 22, 658—662; cf. A., 1931, 1199).—Atm. pptn. and *Mosca olearia* have no influence on the sugar content of olives and hence on the sugar and EtOH contents of the H_2O expressed with the oil, but the presence of mannitol in the olives has some effect in this connexion. T. H. P.

Determination of sugar in plant extracts (including glucoside sugars). G. KERSTAN (Planta [Z. wiss. Biol.], 1932, 17, 491-492).--Glucosides (I) and maltose are removed from plant extracts by adsorption on charcoal, and hexoses are determined in the filtrate. In another portion of extract (I) are hydrolysed by emulsin and after treatment with charcoal glucoside sugars are recorded by the increased reducing power of the filtrate. If large proportions of charcoal are used, other sugars (glucose, sucrose) may be partly adsorbed. Adsorbed maltose, but not (I), can be removed from charcoal by washing with Et₂O (cf. Lehmann, B., 1931, 1038). A. G. P.

Determination of pentosans in vegetable materials by Tollens' method. A. P. ZAKOSH-CHIKOV, V. T. IVANOVA, and A. KURENNOVA (J. Appl. Chem., Russia, 1932, 5, 235-245).—The method is untrustworthy. CH. Abs.

Simple sugars and polysaccharides in hemp stems. E. PARISI (Annali Chim. Appl., 1932, 22, 555-560).—From the powdered material first extracted with warm H₂O, then treated with sulphite solution (4.35% SO₂ and 0.62% CaO), and finally boiled with 6% aq. NaOH, were obtained glucose,

fructose, and hemicelluloses which on hydrolysis produce xylose, glucose, and a xylan. From the residue cellulose was obtained. O. F. L.

Nature and composition of the mucilage of the seed of white mustard (Brassica alba). K. BAILEY and F. W. NORRIS (Biochem. J., 1932, 26, 1609—1623).—The mucilage is a complex of cellulose and acid polysaccharides. The former can be readily separated by warming with dil. H_2SO_4 . The addition of aq. $Ba(OH)_2$ to the mucilage solution forms a gel and also a sol. fraction composed of rhamnose, arabinose, galactose, and galacturonic acid. By the action of 4% NaOH the gel is further separated into cellulose and a fraction composed of arabinose, galactose, galacturonic acid, and glycuronic acid. The acid polysaccharides contain OMe groups in ether linking. Aldobionic acids, probably rhamnose- and galactosegalacturonic acids are present in the mucilage. A peroxidase system is present in the cells close to the mucilage-secreting cells. S. S. Z.

Biochemical properties and difference in fermentation of various kinds of molasses. W. BRAUN and M. KOTSCHOPOULOS (Biochem. Z., 1932, 254, 398-409).-The view that differences in fermentability of molasses are due to differences in protein content is not upheld, the inability to ferment being much more the result of the presence of inhibitors than lack of fermentable material. Pptn. by Fe(OH)₂ does not differentiate between proteins, but CCl₃·CO₂H ppts. only a particular protein group and this group is qualitatively very different for different samples of molasses. The greater the melanin-N, the poorer is the fermentation of the molasses. In a well-fermenting mash, the protein pptd. by CCl_a·CO₂H decreases and almost disappears, whereas in a feebly fermenting mash it tends to P. W. C. increase.

Analysis of Cicer arietinum, var. album and fuscum. A. RIUS Y MIRÓ and F. DE BUSTINZA (Anal. Fís. Quím., 1932, 30, 673—678).—The results accord generally with those in the literature, but the phytin content is high (0.88% for album, 0.995% for fuscum). H. F. G.

H. F. G. Organic acids in the fruits of Ceylon olives (*Eleocarpus serratus*, Lin.). R. YAMAMOTO, Y. OSIMA, and T. GOMA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1932, 19, 132–133).—The pulp of the Ceylon olive contains H_2O S5·73%, total acid (as citric acid) 4·37%, reducing sugar (as glucose) 1·93%, non-reducing sugar (as sucrose) 0·98%, ash 0·62%, crude fibre 1·8%, crude fat 0·23%, and N 0·05%. Citric, mucic, and tartaric (a trace) acids were identified. The fresh juice gives Bezsonoff's vitamin-*C* reaction and 4 c.c. are equiv. to 3 c.c. of lemon juice when fed to guinea-pigs. R. S. C.

Wax-like coating of apples. K. S. MARKLEY, S. B. HENDRICKS, and C. E. SANDO (J. Biol. Chem., 1932, 98, 103—107).—The petroleum extract of apple cuticle does not contain a ketone in isolable amounts (cf. A., 1923, i, 990), the principal hydrocarbon being *n*-nonacosane, m.p. 65·1°, whilst the sec. alcohol present is nonacosan- κ -ol (A., 1932, 203) and not heptacosan- ξ -ol. F. O. H. Determination of the sterol contents of cereals and legumes. E. KEDING (Biochem. Z., 1932, 254, 374—380).—A table summarises the sterol contents of a no. of cercals before and after hydrolysis. Pretreatment with alkali considerably increases the yield of sterol. P. W. C.

Alkaloid content of various organs of Atropa belladonna. A. TORRICELLI (Pharm. Acta Helv., 1932, 7, 20—24; Chem. Zentr., 1932, i, 3452).—The leaves and unripe berries have the highest alkaloid content (0.97—0.89%), but the stem, even when completely lignified, contains noteworthy quantities. A. A. E.

Alkaloids of fumaraceous plants. I. Dicentra canadensis, Walp. II. Dicentra cucullaria (L.), Bernh. R. H. F. MANSKE (Canad. J. Res., 1932, 7, 258—264, 265—268).—I. The tubers of D. canadensis contain protopine, bulbocapnine, corydine [methiodide, decomp. 228—230° (corr.) after sintering at 220°], isocorydine, at least one other alkaloid, and an orange substance, $C_{32}H_{29}O_5(OMe)_3(NCO)_2$, m.p. 237—238° (corr.). Dicentrine is absent. The separation of the phenolic bases is modified. The genetic significance of the results is discussed.

II. The tubers of *D. cucullaria* contain sucrose (34.8%), protopine, cryptopine, and two phenolic alkaloids, α -, $C_{20}H_{17}O_6N$ (OMe absent), m.p. 177° (corr.), and β -, $C_{20}H_{23}O_6N$, $C_{20}H_{23}O_7N$, or $C_{19}H_{22}O_5N$, m.p. 215° (corr.). R. S. C.

New active principle in Bryonia dioica. J. CHAZE (Compt. rend., 1932, 195, 825—827).—An alkaloid-like principle has been detected in the superficial cells of various parts of *B. dioica*. It is located in the cell vacuoles. W. O. K.

Microchemical reactions in plant fibres. V. M. GLEZIN (Farm. Zhur., 1932, 65–67).—Colour reactions of colchicine, aconitine, hyoscyamine, strychnine, and certain glucosides with H_2SO_4 , vanillin, HNO₃, and furfuraldehyde are tabulated. CH. ABS.

Feulgen's nucleal reaction with plants. F. Boas and O. BIECHELE (Biochem. Z., 1932, 254, 467-474).—The nucleal reaction with many plants proves very suitable for staining cell nuclei and chromosomes. P. W. C.

The carboxylase system in green plants. K. WETZEL (Planta [Z. wiss. Biol.], 1932, 17, 1—14). —The reduced carboxylase activity of finely-powdered leaves is not due to carboxylase deficiency in the green tissue (Kobel and Scheuer, A., 1930, 258), but to the injurious effects of grinding on the cozymase and co-carboxylase or on the carboxylase itself. Addition of yeast extract increases CO_2 production both from hexosediphosphate and K pyruvate, its action being to favour the normal alcoholic rather than the lactic fermentation. A. G. P.

Enzymes of the coffee plant. E. HERNDLHOFER (Biochem. Z., 1932, 255, 230—246).—The enzyme (lipase, protease, amylase, catalase, peroxidase, oxygenase) content of the coffee plant and of its parts at various stages of development (seed to 30-years-old trees) has been examined. The enzymes are absent from or present only in small amounts in the resting seeds, but increase in amount, often greatly, during germination. In the young plants there are great variations in the presence (or absence) and distribution of the various enzymes throughout the various parts of the plant, the functions of both enzyme and part of plant being factors involved. At all stages the leaves have alow content of the enzymes, some of which are never found in them. In old plants the young branches have high enzyme content, but the young fruit is poor in enzymes. W. McC.

Localisation of tyrosinase in the sugar beet. E. W. SCHMIDT (Z. Ver. deut. Zucker-Ind., 1932, 82, 564-569).—The method consists in treating the parts of the plant with a dil. solution of tyrosine (e.g., 0.1%), and observing the colour change. J. P. O.

Isolation of glutamine from an enzymic digest of gliadin. M. DAMODARAN, G. JAABACK, and A. C. CHIBNALL (Biochem. J., 1932, 26, 1704— 1713).—Gliadin was digested in succession with pepsin, trypsin, and yeast-dipeptidase and glutamine obtained in successive crops of crystals from the decomposed phosphotungstic acid ppt. of the digest. Glutamine is unstable in aq. solution. S. S. Z.

Hydrocyanic acid in Glyceria aquatica, Wahlb. (G. spectabilis, M. and K.). P. GUÉRIN (Compt. rend., 1932, 195, 1036—1037).—In April the leaves, creeping stem, and fine roots contain 1.053, >0.2, and 0.162 g. of glucosidic HCN per kg., respectively. The leaf figure falls to 0.6 in May and 0.348 in June, when the spikelets of the panicle contain 0.66 g. per kg. The HCN content of September shoots is 0.35 g. per kg. A. C.

Calcium content of cabbage. S. J. COWELL (Biochem. J., 1932, 26, 1422—1423).—The Ca content of the outermost leaves in summer may be from 20 to 30 times as great as that of the inner leaves. S. S. Z.

Occurrence of calcium tartrate. J. GICKLHORN (Biochem. Z., 1932, 254, 459—466).—The mucous sap obtained at old internodal cross-sections of the stem of *Tradescentia zebrina*, Lont., on drying yields crystals of Ca tartrate. The occurrence is sp., and of the types examined only the above and *T. purpurea* gave these crystals. The cell press-juices of the medullary, cortical, and epidermal cells do not give the crystals. P. W. C.

Silicic acid content of bread. R. BERG (Biochem. Z., 1932, 254, 329-331).—Tables summarise the contents of sol. silicic acid in rye grain and meal and in various samples of rye bread. P. W. C.

Boron as a physiologically critical element. T. SCHMUCKER (Naturwiss., 1932, 20, 839).—The development of the pollen grains of the tropical water-lily does not occur in artificial medium in the absence of small quantities of H_3BO_3 . 0.01 mg. per 1 c.e. of medium was highly active, whilst 0.0005 mg. had a marked effect. W. O. K.

Twisted trees—real and mineral. M. COPISA-ROW (Nature, 1932, 130, 541—542).—The genetic role of mineral matter and its substitution is discussed in relation to tree-twisting. This appears to be due primarily to local soil peculiarities which in the course of time modify the structural constituents of plants.

L. S. T.

Zinc in fungi. M. MOUSSERON and P. FAUROUX (Bull. Soc. Chim. biol., 1932, 14, 1235—1239).—The Zn contents of several species of fungus determined by the micro-method (A., 1931, 1260) are recorded. These increase with the nucleolytic power as measured by determining the $PO_4^{\prime\prime\prime}$ liberated from Na nucleinate by the fungus extract. With the exception of *Hygrophorus conicus*, which contains an agglutinin, fungi containing >100 mg. of Zn per kg. (dry) are hæmolytic. The fungus extracts also hydrolyse Na α -glycerophosphate and phytin. A. C.

Microcolorimetric determination of iron in small amounts of plant ash. W. SCHOLZ (Z. Pflanz. Düng., 1932, 26A, 212—216).—The NH₄CNS reaction is utilised for quantities of approx. 0.01 mg. Fe in 1 c.c. A. G. P.

Determination of the inorganic nitrogen in the maize plant by the expressed sap method. R. W. GERDEL (Plant Physiol., 1932, 7, 517—526).—The total inorg. N in the sap can be determined satisfactorily by the method of Sessions and Shive (A., 1929, 960). Sap samples may be preserved for a time by addition of PhMe or by storage at -20° . A. G. P.

Antigen-antibody reactions in plants. O. MORITZ (Ber. Deut. bot. Ges., 1932, 50, 100—106).— Vicia faba plants grown in sand and watered with 2—3% ovalbumin solution for 2 days before an experiment are able to produce typical anaphylactic reactions with the isolated uterus of a guinea-pig previously sensitised to ovalbumin. The general principles of immunity reactions applied to plants are

discussed. P. G. M. Effect on the geotropic reaction of roots of Zea mais of pretreatment with fluorescein dyes and salts. D. MILDEBRATH (Bot. Archiv, 1932, 34, 161—215).—The geotropic reaction period of seedling maize roots was increased and the extent of the reaction decreased by dipping in solutions of the dyes. Growth rates were not, however, retarded. Comparative effects of fluorescein, eosin, erythrosin, and their salts and of various inorg. salts indicate

a sp. action. A. G. P. Photodynamic action of eosin on the root tips of Vicia faba. W. PRESCHER (Planta [Z. wiss. Biol.], 1932, 17, 461-488).—The inhibitory action of eosin on root elongation increases with the concn. of the dye used, with the period of action and light intensity. A. G. P.

that cations, anions, and mol. compounds have each

Influence of narcotics, mechanical agents, and light on the permeability of protoplasm. W. W. LEPESCHKIN (Amer. J. Bot., 1932, 19, 568— 580).—Narcotics (e.g., CHCl₃) increase or decrease the permeability of protoplasm to H₂O-sol. substances according to whether the solubility of these substances in the narcotic is > or < that in H₂O. A. G. P.

Toxic action. IV. Relative toxicities of isomeric alcohols of the aliphatic series. W. STILES and M. L. L. STIRK, V. Toxicity of aliphatic aldehydes towards potato tuber. K. W. DENT (Protoplasma, 1932, 16, 79—101, 357—368).— IV. The toxicity of isomeric alcohols, as determined by the rate of exosmosis of electrolytes from cells of potato tubers, was in the order: normal>other primary>sec.>tert. alcohols. In general the change in toxicity resulting from the substitution of Me for H in aliphatic alcohols depends on the relative positions of the substituted and the OH group; higher toxicity is associated with substitution furthest removed from the OH group and vice versa.

V. Using the exosmosis method (Stiles and Stirk, A., 1932, 206) the relative toxicity of aldehydes is shown to be: CH_2O , 1; MeCHO, 0.64; EtCHO, 1.28; PrCHO, 1.54; valeraldehyde, 7.37. Pr²CHO and *iso*valeraldehyde are more toxic than the corresponding normal isomerides. CH_2O is much more toxic than MeOH. A. G. P.

Plant tumours. I. Nitrogen balance. II. [H^{*}]. G. KLEIN and E. KEYSSNER. III. Catalase content of normal and tumour tissue. G. KLEIN and W. ZIESE (Biochem. Z., 1932, 254, 251-255, 256-263, 264-285).—I. In all the plants investigated, the protein-N of the tumour tissue produced by *Bacterium tumefaciens* is many times that of normal tissue and the sol. inorg. and org. N in tumour tissue is higher in balsam, geranium, and tomato, but lower in beet, than in normal tissue.

II. The p_{Π} , acid, and ash contents of normal and tumour tissues are recorded. The results show that tumour tissue is more alkaline than normal tissue.

III. The catalase content of the tumour tissue of various types of beetroot is much higher than of normal tissue. The increased activity is not due to the presence of a non-enzymic activator. The catalase content is not directly related to the particular strain of organisms used. P. W. C.

Use of an extract of the seeds of *Echinocystis* lobata for the detection of citric acid. T. BROMAN (Skand. Arch. Physiol., 1932, 64, 171–176; Chem. Zentr., 1932, ii, 412).—The seeds can replace those of *Cucumis sativa*. The reaction is also given by hexosediphosphoric and adenosinetriphosphoric acids. A. A. E.

Diphenylbenzidine as a test for nitrates and nitrites. H. STROMBERG.—See A., 1932, 1221.

Spectrographic microanalysis. Histological detection of certain elements. A. MOREL and A. POLICARD (Bull. Soc. chim., 1932, [iv], 51, 1125— 1131).—A method is described for the direct spectrographic detection of elements in microscopic pieces of tissue, preliminary ignition of the material being unnecessary. D. R. D.

Determination of iodine according to Kuhn and Loeser. G. BARKAN and G. KINGISEPP (Arch. exp. Path. Pharm., 1932, 168, 228—231).—The method of Kuhn and Loeser (cf. A., 1928, 1064) is not always trustworthy for the determination of organically combined I and the empirical factor introduced by them in calculating the results is unnecessary.

W. O. K.