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# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JULY, 1933.



### General, Physical, and Inorganic Chemistry.

**Effect of helium on the continuous and secondary spectra of hydrogen.** A. S. ROY (Proc. Nat. Acad. Sci., 1933, 19, 441—444).—The lines of the triplet system were, in general, increased in intensity relative to the lines of the singlet system, and the continuous spectrum was very much stronger. This is attributed to the limitation of electron velocities by the He, which would increase the probability of exciting the triplet states of H. N. M. B.

**Characteristic structure of the hydrogen resonance line  $\lambda$  1216 Å.** M. KULP and H. E. BINKELE (Physikal. Z., 1933, 34, 420—423). A. J. M.

**Spectra emitted by high-frequency and direct-current discharges in helium.** J. E. KEYSTON (Phil. Mag., 1933, [vii], 15, 1162—1173).—The light emitted by He discharges in the visible and ultra-violet regions has been investigated spectroscopically. The results are discussed with reference to the theory of Townsend (A., 1932, 440). J. W. S.

**Laboratory excitation of nebular lines  $N_1$  and  $N_2$ .** H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1933, 9, 146—148; cf. A., 1932, 552).—Using a modification of the disruptive discharge method described previously the nebular lines 5006.8 and 4958.97 Å. have been reproduced in the laboratory. J. W. S.

**Opposite asymmetry of the widening of different lines of a series.** C. FUCHTBAUER and F. GÖSSLER (Naturwiss., 1933, 21, 315).—The widening of the three principal series lines of Cs in different gases was studied. There is a marked change in the widening in the transition between second and third series members. In Ne and  $N_2$ , the first and second lines (8521.1 and 4555.3 Å.) were widened a little towards the red, whilst the third (3876.7 Å.) was widened considerably towards the violet. A. J. M.

**Infra-red spectra of neon, argon, and krypton.** W. F. MEGGERS and C. J. HUMPHREYS (Bur. Stand. J. Res., 1933, 10, 427—448).—About 200 infra-red lines between 7600 and 12,200 Å. were photographed for each of the gases Ne, Ar, and Kr. New H-like terms from  $f$ -type electrons were found, and missing  $3d$  terms in the Ar I and Kr I spectra identified. New infra-red wave-length standards are suggested. H. J. E.

**Continuous spectrum of sodium.** H. HAMADA (Sci. Rep. Tôhoku, 1933, 22, 31—54).—The spectrum is described and discussed. It can be explained in the same way as those of Hg, Cd, Zn, and Mg. A. J. M.

**Excitation of resonance series in sodium vapour by illumination with the  $D$ -line.** W. G. BROWN and P. PRINGSHEIM (Z. Physik, 1933, 82, 584—588). A. B. D. C.

**Excitation potential of the argon atom.** R. G. LOYARTE (Physikal. Z., 1933, 34, 416—420).—A no. of new potentials are recorded, especially in the range  $1s_2-2p_{10}$ . A. J. M.

**Electrodeless ring discharge through potassium vapour.** B. ARAKATSU and Y. UEMURA (Mem. Fac. Sci. Agric. Taihoku, 1932, 5, 159—161).—With the electrodeless ring discharge in K vapour at low pressure a dark bluish-violet after-glow is observed. The spectrum of the glow shows no arc lines, but intense spark lines. The glow is attributed to the positive ions of atoms expelled from the discharge region by the electrostatic field set up at the instant of the excitations of the ring discharge. J. W. S.

**Absorption of the  $1s-3d$  lines by potassium.** T. OKUDA (Sci. Rep. Tôhoku, 1933, 22, 9—12).—Forbidden lines of the  $1s-3d$  series were observed in the absorption spectrum of K. The effect of admixture of  $H_2$  and  $N_2$  with the Na vapour was investigated. A. J. M.

**Absolute value of the terms of As.** W. M. HICKS (Phil. Mag., 1933, [vii], 15, 1080—1085).—Theoretical. The Ounmultiple law is applied to recent data. J. W. S.

**Spectrum of selenium. II.** Se III. J. S. BADAMI and K. R. RAO (Proc. Roy. Soc., 1933, A, 140, 387—398).—The spectrum of doubly-ionised Se has been studied with the aid of data obtained from the analysis of the spectra of Se IV and Se V (A., 1931, 664). The largest term,  $4p^3P_0 = 274,924 \text{ cm}^{-1}$ , leads to a val. of 33.9 volts for the third ionisation potential of Se. A special feature of the analysis is the discovery of multiplets involving a transition of one of the inner electrons. L. L. B.

**Multiplets in the spectra of Nb III and Mo IV.** A. Y. ELIASON (Physical Rev., 1933, [ii], 43, 745—748).—Term vals. for the multiplets in Nb III and Mo IV are obtained by an application of the Moseley law and the irregular doublet law to the corresponding multiplets in Y I and Zr II. N. M. B.

**Extension of the Pd I-like isoelectronic sequence to antimony VI and tellurium VII.** G. K. SCHOEFFLE (Physical Rev., 1933, [ii], 43, 742—744).—Wave-lengths, frequencies, and term vals. for the region 784—1331 Å. are tabulated. N. M. B.



**Fine structure of the resonance Ag I lines.** W. E. WILLIAMS and A. MIDDLETON (Nature, 1933, 131, 692).—The structure previously observed (A., 1931, 993) is due to self-reversal. L. S. T.

**Structure of the lines of the arc spectrum of silver.** D. A. JACKSON (Nature, 1933, 131, 691—692).—All the more important lines are simple (cf. preceding abstract). L. S. T.

**Change of optical absorption of iodine on being bound.** J. H. DE BOER and J. F. H. CUSTERS (Z. physikal. Chem., 1933, B, 21, 208—224; cf. A., 1931, 1226).—The absorption curve of  $I_2$  mols. adsorbed on a vac.-sublimed  $CaF_2$  film is displaced considerably towards the violet, compared with that of gaseous  $I_2$ . The curve is the more sharply defined the smaller is the amount of  $I_2$  adsorbed,  $m$ . When  $m$  is small, the absorption curve has max. at 342 and 283  $m\mu$ , but as  $m$  increases, there are superimposed on this curve the curves for the less active centres, which lie nearer the red. The absorptive power of the  $I_2$  first adsorbed is more than 100 times  $>$  than that of  $I_2$  taken up when the surface is already partly occupied, and 10,000 times that of  $I_2$  dissolved in  $H_2O$ . The possible interpretations of the absorption curves are examined with the aid of potential curves and surfaces. R. C.

**Temperature dependence of the absorption of excited mercury vapour.** O. MASAKI (J. Sci. Hiroshima Univ., 1933, 3, 187—192; cf. A., 1931, 276).—The absorption of light by excited Hg vapour in presence of excess Ne corresponding with the transitions  $2^3P_{0,1,2}$ — $3^3D_{1,2,3}$  shows great variation with temp. Other transitions and intercombination lines show little variation. J. S. A.

**Spectra of Pb II, Hg I, Sb I, Cl II, and I II.** K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 20, 285—297).—Terms are classified with the aid of hyperfine structure. Lines of Cl II and I II are classified. Nuclear moments are  $Sb^{121}$   $5/2$ ,  $Sb^{123}$   $7/2$ , I  $5/2$ . N. M. B.

**Effect of moisture on the spark potential in air.** C. DEI (Nuovo Cim., 1932, 9, 150—155; Chem. Zentr., 1933, i, 23—24).—A method for studying the effect of moderate humidities, where vals. decrease with decreasing  $H_2O$  tension, is described. A. A. E.

**Contour of spectral lines excited by electron collision.** W. HEITLER (Z. Physik, 1933, 82, 146—150).—A spectral line excited by monochromatic electrons has a contour which falls off towards the red more slowly than the natural line. A. B. D. C.

**Solar ultra-violet radiometry.** W. D. FLEMING (Philippine J. Sci., 1933, 50, 279—299).—The application of thermopiles to the determination of the intensities of the spectral bands 290—310, 310—370, 370—400, and 400—460  $m\mu$  in sunlight is described. C. W. G.

**High-frequency discharge in argon in presence of mercury.** R. ZOUCKERMANN (Compt. rend., 1933, 196, 1478—1480; cf. A., 1928, 214; 1931, 403). C. A. S.

**Activation of air by the electrodeless ring discharge.** B. ARAKATSU and K. KIMURA (Mem. Fac. Sci. Agric. Taihoku, 1932, 5, 143—157).—Three

distinct types of after-glow have been observed with air after passage at low pressure through the electrodeless discharge, viz., green at 1—0.07 mm. pressure, sky-blue at 0.07—0.05, and orange below 0.05 mm. The possible chemical reactions causing these different phenomena are discussed. J. W. S.

**Conditions for striking low-voltage arcs and grid-directed low-voltage arcs.** F. KLAIBER (Physikal. Z., 1933, 34, 441—447). A. J. M.

**Experimental investigation of grating ghosts.** W. RUDOLPH (Z. Physik, 1933, 82, 372—396).—Ghosts due to several Rowland gratings were determined. A. B. D. C.

**Determination of reflexion capacity of metals in the visible and ultra-violet.** K. VON FRAGSTEIN (Ann. Physik, 1933, [v], 17, 1—21).—The reflexion capacity of steels of various composition was determined by a spectrophotometric method in the visible, whilst in the ultra-violet several other substances were examined as well. A. J. M.

**Structure of K-rays of light elements.** A. HAUTOT (J. Phys. Radium, 1933, [vii], 4, 236—245).—An amplified account of work already published (this vol., 108, 201, 440).

**Dependence of K lines of elements from Cu to Ti on chemical combination.** S. YOSHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 20, 298—310).—Using the method of cold excitation with X-rays, no effects of chemical combination on  $K\alpha_1\alpha_2$  and  $K\alpha_{3,4}$  were detected.  $K\beta'$  and  $K\beta_1$  are distinctly separated in strongly paramagnetic compounds; slight displacements of  $K\beta_5$  were observed for Mn, Cr, and Ti. A new line  $K'\beta_5$  was always observed for substances which show a sharp absorption line on the long wave-length side of the absorption edge. N. M. B.

**K series spectrum of tungsten.** J. C. HUDSON and H. G. VOGT (Proc. Nat. Acad. Sci., 1933, 19, 444—448).—The  $\beta$  and  $\gamma$  doublets were resolved and photographed together with the  $\delta$  line. Using the vals. 0.21341 and 0.20860 for the  $\alpha_2$  and  $\alpha_1$  line, respectively, the wave-lengths were calc. as  $\beta_2$  0.18477,  $\beta_1$  0.18397,  $\gamma_2$  0.17917,  $\gamma_1$  0.17899,  $\delta$  0.17803 Å. The averaged vals. for the  $\beta$  and  $\gamma$  doublets on the basis that the shorter wave-length line has twice the intensity of the longer component are 0.18423 and 0.17905 Å., respectively. N. M. B.

**Analysis of secondary radiation from aluminium, nickel, silver, and gold at the entrance and exit of X-rays.** H. SCHENCK (Ann. Physik, 1933, [v], 17, 146—168).—The dependence of the electron emission from Al, Ni, Ag, and Au on the hardness of the X-rays employed and on the thickness of the irradiated element was investigated for both entrance and exit of the rays. The total emission was analysed into (a) characteristic secondary radiation, (b) electron emission due to primary radiation, and (c) electrons of the third kind, which are set free by the re-absorption by the metal of the characteristic radiation. The emission of secondary scattered radiation is negligible. The asymmetry of the electrons set free by primary radiation is const. with



respect to hardness of rays for Au. It increases as at. no. decreases. A. J. M.

**X-Ray emission spectra of gaseous elements: K spectrum of krypton.** (MLLE.) Y. CAUCHOIS and H. HULUBER (Compt. rend., 1933, 196, 1590—1592; cf. this vol., 248, 450).—The authors' method, with Se, Br, and Rb as reference elements, gives for Kr  $K\alpha_2$  982.1,  $K\alpha_1$  978.1,  $K\beta_{1,3}$  876.7, and  $K\beta_2$  864.3 X (cf. A., 1931, 4). C. A. S.

**Relation between line and continuous X-ray spectra.** W. W. HANSEN and K. B. STODDARD (Physical Rev., 1933, [ii], 43, 701—706).—For Pd up to 180 kv. there is a const. ratio between the probability of ejection of a K electron and the probability of emission of a quantum of continuous radiation when an electron collides with a Pd atom. The val. 2 is found for the ratio, for a thick target, of the amount of  $K\alpha$  radiation resulting from ionisation by collision and that from fluorescence. N. M. B.

**Excitation potentials of light metals. II. Beryllium.** H. W. B. SKINNER (Proc. Roy. Soc., 1933, A, 140, 277—301; cf. A., 1932, 316).—Measurements have been made of the "excitation curve" ( $\Delta i/\Delta V$  plotted against  $V$ ) for Be, using both W and dull-emitter filaments, and it is found that the "break potentials" (vals. of  $V$  for which abrupt changes in  $\Delta i/\Delta V$  occur) are displaced correspondingly with the change of filament. When a correction for the work function of the filament is applied, the break potentials are consistent. Excitation starts at 8.5 volts, rises continuously up to 92 volts, when large and abrupt changes in  $\Delta i/\Delta V$  occur and persist up to 125 volts. There is an appreciable difference between the min. K-excitation potentials of Be in the form of metal and of a polar compound. An approx. model for the excited state of the metal, based on the state of the corresponding at. system, is proposed. L. L. B.

**Ionisation of argon, neon, and helium by A, Ne, and He atoms.** C. J. BRASEFIELD (Physical Rev., 1933, [ii], 43, 785—787; cf. A., 1932, 1185).—Using a method eliminating errors due to secondary electrons, ionisation of each gas, bombarded by its own atoms, set in at approx. 100 equiv. volts. Bombardment of any of the gases by atoms of either of the other two caused no detectable ionisation. N. M. B.

**Energy distribution of photo-electrons.** L. A. DU BRIDGE (Physical Rev., 1933, [ii], 43, 727—741).—Expressions are derived for the form of the normal and total energy distribution and current-voltage curves in the vicinity of the apparent max. energy, which cannot be sharply defined, owing to the thermal energies of the electrons. Results are in agreement with experimental data for Mo. N. M. B.

**Relations between the combination coefficients of atmospheric ions.** F. J. W. WHIPPLE (Proc. Physical Soc., 1933, 45, 367—380).—Experimental evidence and possible applications of a formula dealing with the combination coeffs. for large and small ions are discussed. W. R. A.

**Scattering of rapid protons by light elements on close approximation to the nucleus.** G. SCHNEIDER (Naturwiss., 1933, 21, 349).—The scatter-

ing at C and B of protons of 75—300 kv. is considered. The scattering curve, drawn between the proton velocity and the no. of particles possessing a given velocity shows a max. for B, but not for C.

A. J. M.

**Action of mercury metastable atoms on a tungsten surface.** S. SONKIN (Physical Rev., 1933, [ii], 43, 788—803).—Factors and conditions effecting the sensitivity of a metal surface to electron emission were investigated. Heating and outgassing produced a const. normal sensitivity. For a W surface the deposition of Hg atoms was essential for the formation of a surface sensitive to Hg metastable atoms. Residual  $O_2$  resulted in the establishment of a stable complex arrangement of Hg and O atoms on the W. Transient sensitivities 50—100 times the normal val. were found at a certain stage at which the formation of a monat. film was possible. For the normal surface not more than 1 or 2% of metastable atoms cause electron emission. N. M. B.

**Influence of condensation nuclei and dust particles on atmospheric ionisation.** P. J. NOLAN (Proc. Roy. Irish Acad., 1933, A, 41, 61—69).—Available data on the relation between the rate of disappearance of small ions in a closed vessel and the concn. of nuclei and dust agree with the deduction that small ions combine with dust particles as well as with condensation nuclei. Respective combination coeffs. are deduced. The square-root law of recombination is explained in the experimental indications that at high concns. the disappearance rate is proportional to the square of the concn., and is a coagulation process, and at low concns. is proportional to the concn., and is a diffusion process. N. M. B.

**Secondary emission of electrons from molybdenum.** P. L. COPELAND (J. Franklin Inst., 1933, 215, 593—598).—The ratio of the no. of secondary to primary electrons of various energies incident on a Mo plate, previously heat-treated, gives results agreeing more closely with those of Hyatt (cf. A., 1929, 229) than of Petry (cf. A., 1925, ii, 1017). N. M. B.

**Diffraction of electrons in amorphous and in crystalline antimony.** J. A. PRINS (Nature, 1933, 131, 760—761).—Electron diffraction patterns of Sb obtained by evaporation in a vac. show that the structure is amorphous and remains so indefinitely when the films are very thin. Films of medium thickness soon develop cryst. spots and become wholly cryst. in 2 hr.; thick deposits are always cryst. L. S. T.

**Diffraction of electrons by metal surfaces.** L. H. GERMER (Physical Rev., 1933, [ii], 43, 724—726).—Fast electrons scattered from polished metal surfaces do not form diffraction patterns. A strong Debye-Scherrer pattern is produced by electrons scattered by a roughened surface through the irregularities of which electrons can pass. Results indicate that there is no considerable amorphous layer on a polished metal surface, and that Debye-Scherrer patterns are formed only by transmitted electrons. Fast electrons scattered at a small glancing angle from an etched polycryst. surface form a diffraction pattern only if the surface is rough. N. M. B.



**Electron diffraction and photo-electric effect for alkali metal surfaces.** W. KLUGE and E. RUPP (*Z. Physik*, 1933, 82, 568—583).—Previous results are confirmed (A., 1932, 893). At  $-170^\circ$  max. appear as the energy of the electrons is increased, but not when decreased; similarly, several edges in the reflexion curves appear at higher energies with increasing energy and at lower energies with decreasing energy of the beam. The first phenomenon may be due to adsorbed electrons. A. B. D. C.

**Dependence of electron-ray concentration on the type of gas.** E. F. RICHTER (*Physikal. Z.*, 1933, 34, 457—458).—Beams of electrons in various gases were investigated. The pressure range in which a "thread" ray (*i.e.*, a beam which, after passing through a relatively strong, non-homogeneous magnetic field, does not become diffuse) exists varies in different gases, changing from  $10^{-1}$  to  $10^{-3}$  mm. from He to Xe. The results were compared with the efficiencies of ionisation derived by Tate and Smith (A., 1932, 321) for the gases and electron velocities used in the experiment. A. J. M.

**Electron diffraction by vapours.** H. DE LASZLO (*Nature*, 1933, 131, 803).—Preliminary photographs of the electron diffraction of the vapour of org. compounds have been taken. L. S. T.

**Elastic electron scattering in gases.** S. WERNER (*Nature*, 1933, 131, 726—727).—Anomalies discovered in the velocity scattering curves for Ne and Ar are discussed. L. S. T.

**Diffraction of electrons in mercury vapour.** II. F. L. ARNOT (*Proc. Roy. Soc.*, 1933, A, 140, 334—344).—An extension of previous work (A., 1931, 542, 1347) to larger angles and to lower electron energies. L. L. B.

**Diffraction of electrons at some gaseous halides ( $\text{OsF}_8$ ,  $\text{HgI}_2$ ,  $\text{HgBr}_2$ ,  $\text{HgCl}_2$ ).** H. BRAUNE and S. KNOKE (*Naturwiss.*, 1933, 21, 349—350).—Owing to the ease of decomp. of  $\text{OsF}_8$ , it is not possible to decide the arrangement of the F atoms. The distance Os—F is almost the same for the two models put forward for this substance—dice model and Archimedean antiprism. The distance Hg—I in  $\text{HgI}_2$  is 2.55; Hg—Br in  $\text{HgBr}_2$  2.40; and Hg—Cl in  $\text{HgCl}_2$  2.17 Å. A. J. M.

**Electron diffraction by gaseous sulphur, selenium, and tellurium hexafluorides.** H. BRAUNE and S. KNOKE (*Z. physikal. Chem.*, 1933, B, 21, 297—309).—The results agree with an octahedral structure in which the distances between F and the central atom are  $\text{SF}_6$ , 1.56;  $\text{SeF}_6$ , 1.67;  $\text{TeF}_6$ , 1.82 Å. R. C.

**Determination of crystal lattice constants by electron diffraction.** G. I. FINCH and A. G. QUARRELL (*Nature*, 1933, 131, 842).—An accurate comparison method for the determination of crystal lattice const. by electron diffraction is described. L. S. T.

**Interference pattern obtained by irradiation of single brucite crystals with rapid electrons.** G. AMNOFF (*Arkiv Kemi, Min. Geol.*, 1933, 11 B, No. 10, 4 pp.).—The pattern is described. A. J. M.

**Transition of electrons to the region of negative energy values.** S. SZCZENIEWSKI (*Bull. Acad. Polonaise*, 1933, A, 21—39).—The tunnel effect is investigated for one dimension using Dirac's wave equation. A. B. D. C.

**Free positive electrons resulting from the impact on atomic nuclei of the photons from thorium-C''.** C. D. ANDERSON (*Science*, 1933, 77, 432).—Free positive electrons are ejected from Pb by the  $\gamma$ -radiation of Th-C'', showing that when absorbed by nuclei, photons eject both positive and negative electrons, as is the case with cosmic rays (*cf.* A., 1932, 76, 238; this vol., 441). L. S. T.

**Origin of positive electrons.** (MME.) I. CURIE and F. JOLIOU (*Compt. rend.*, 1933, 196, 1581—1583; *cf.* this vol., 549).—The emission of both positive and negative electrons when radiation from Po+Be falls on Pb is reduced by 40% by the interposition of 2 cm. Pb; with a radiator of  $\text{UO}_2$  the emission is slightly increased, with one of Cu greatly diminished. The max. energy of negative and positive electrons is respectively 4.7 and  $2.2 \times 10^6$  ev. Trajectories of both kinds of electron sometimes appear to start from the same point, and the proportion of positive electrons increases with the at. wt. of the radiator. It is concluded that both positive and negative electrons are due to nuclear absorption of  $\gamma$ -radiation. This view is supported by examination of the electrons produced by the action on Pb of  $\gamma$ -rays from Th-C'' and the deductions therefrom as to the energies of the electrons and  $\gamma$ -rays concerned. C. A. S.

**Possible property of the positive electron.** W. ELSASSER (*Nature*, 1933, 131, 764).—Theoretical. If the proton consists of a neutron and a positive electron, the latter should obey Bose statistics and have an integral spin momentum (0 or 1). L. S. T.

**Electrolytic isolation of the heavier hydrogen isotope by the method of G. N. Lewis.** M. POLANYI (*Naturwiss.*, 1933, 21, 316—317).—The causes of the large difference in overvoltage of the two H isotopes, which has been suggested by Lewis (this vol., 442) as providing a suitable method for effecting their separation, and the nature of the phenomenon, are discussed on the basis of quantum mechanics. The overvoltage seems to be due to an energy barrier over which the proton has to rise in order to reach the surface of the electrode. A. J. M.

**Isotope separation by the method of Hertz.** H. HARMSSEN (*Z. Physik*, 1933, 82, 589—609).—The method is developed to give almost complete separation of  $\text{Ne}^{20}$  and  $\text{Ne}^{22}$ . A. B. D. C.

**Calcium isotope with mass 41 and the radioactive half-period of potassium.** J. KENDALL, W. W. SMITH, and T. TAIT (*Nature*, 1933, 131, 688—689).—Ca extracted from a felspar ( $10^9$  years old) from Rhiconich, Sutherlandshire, gave an at. wt. of  $40.092 \pm 0.0006$ , whilst that from a pegmatite ( $6 \times 10^8$  years old) from Portsoy, Banffshire, gave  $40.089 \pm 0.0004$ . Ca derived from recent marine sources, sea-shells, and Bermuda limestone, gave 40.076 and 40.077, respectively. The calc. radioactive half-period of  $\text{K}^{41}$  is of the order  $1 \times 10^{12}$  years in both cases (*cf.* A., 1930, 1496). L. S. T.



**Revision of at. wt. of selenium. Synthesis of silver selenide.** O. HÖNIGSCHMID and W. KAPFENBERGER (Z. anorg. Chem., 1933, 212, 198—208).—By direct combination of Ag with Se vapour at 400°, the val.  $2\text{Ag} : \text{Ag}_2\text{Se} = 0.732081$  has been obtained, whence  $\text{Se} = 78.962 \pm 0.002$ , in agreement with Aston's figure.

J. S. A.

**At. wt. of lead from Katanga pitchblende.** G. P. BAXTER and C. M. ALTER (Science, 1933, 77, 431—432).—The at. wt. of Pb obtained by extraction with HCl of the yellow portion of Katanga pitchblende (I) is 205.97, whilst that obtained from the remaining black portion is 206.00; average 205.99 for the whole (I). Vals. for common Pb from Cœur d'Alene and for Pb from Bedford cyrtolite simultaneously determined are 207.22 and 205.94, respectively. Assuming Aston's isotopic composition for Katanga Pb, the results give the low val. of 205.90—205.93 for  $\text{Pb}^{206}$ . The difference in at. wts. of Pb from the yellow and black portions of (I) is discussed.

L. S. T.

**Revision of the at. wt. of arsenic. Comparison of arsenic trichloride with iodine pentoxide.** G. P. BAXTER and W. E. SHAEFER (J. Amer. Chem. Soc., 1933, 55, 1957—1963; cf. this vol., 442).—The at. wt. of As is 74.91 from determinations of the ratio  $6\text{AsCl}_3 : \text{I}_2\text{O}_5$ , and the data show that  $\text{I}_2\text{O}_5$  has the normal composition (cf. A., 1931, 543). J. G. A. G.

**Revision of the at. wt. of indium.** G. P. BAXTER and C. M. ALTER (J. Amer. Chem. Soc., 1933, 55, 1943—1946).—The at. wt. of In is 114.76 from determinations of the ratios  $\text{InCl}_3 : 3\text{Ag}$  and  $\text{InBr}_3 : 3\text{Ag}$ .

J. G. A. G.

**Interpretation of Aston's data.** W. SWIENTO-SLAWSKI (Compt. rend., 1933, 196, 1600—1602).—From the differences in the masses of the nuclei of various pairs of isotopes the average mass of a neutron is deduced as 0.9997, and that of a demihelion,  $D_h = (A_n - 0.9997x)/n$ , where  $A_n$  is the mass of the at. nucleus of element no  $n$ , and  $x$  the no. of neutrons.  $D_h$  diminishes from 2.00053 for He to 1.9974 for Kr, and then rises to 1.9998 for Pb and (by extrapolation) to 2.00032 for U. Deducing from this the mass of the at. nucleus of U, the loss of mass consequent on the radioactive transformation of U into Pb is 0.033, which agrees fairly with that (0.041) calc. from the heat emitted.

C. A. S.

**$\alpha$ -Ionisation in pressure chambers.** J. C. JACOBSEN and C. B. MADSEN (Naturwiss., 1933, 21, 350).— $\alpha$ -Particle ionisation falls rapidly with increasing pressure.

A. J. M.

**Direct measurement of intensities of fine structure of  $\alpha$ -particles.** S. ROSENBLUM and P. CHEVALLIER (Compt. rend., 1933, 196, 1484—1486).—An arrangement in which a Geiger counter replaces the photographic plate is described whereby individual  $\alpha$ -particles can be recorded. Applied to determining the fine structure of  $\alpha$ -particles from Th-C, it gives results in close agreement with those obtained photographically.

C. A. S.

**Radiation excited by  $\alpha$ -particles in fluorine.** P. SAVEL (Compt. rend., 1933, 196, 1482—1484).—Using an ionisation chamber containing A or  $\text{H}_2$  under

30 atm. pressure, the radiation emitted by F (as  $\text{CaF}_2$ ) under the action of  $\alpha$ -particles from Po is composed of homogeneous  $\gamma$ -rays of mass absorption coeff.  $\mu/\rho = 0.058$  and energy  $1.3 \times 10^6$  ev. and consisting mainly of photons, and of very penetrating neutrons half absorbed by 5.5 cm. of Pb. The min. energies of the  $\alpha$ -particles which excite  $\gamma$ -rays and neutrons are respectively 0.9—1.2 and 2.5—2.7 ev. These results, with those of Chadwick and Constable (cf. A., 1932, 318), imply that there are at least two sources of  $\gamma$ -rays, possibly excited with and without capture of the  $\alpha$ -particle as suggested for Li (cf. this vol., 334).

C. A. S.

**Fine structure of the magnetic spectrum of  $\alpha$ -particles from radioactinium and its derivatives.** (MME.) P. CURIE and S. ROSENBLUM (Compt. rend., 1933, 196, 1598—1600; cf. A., 1932, 555).—Revised and additional data are given for intensities and energies of 11 lines of Rd-Ac, 3 of Ac-X, and 3 of An (cf. A., 1932, 671). Close agreement between twelve energy differences of Rd-Ac and two of An with the energies of corresponding  $\gamma$ -rays is demonstrated.

C. A. S.

**Absolute velocities of principal groups of  $\alpha$ -particles.** S. ROSENBLUM and G. DUPOUY (J. Phys. Radium, 1933, [vii], 4, 262—268).—A detailed account of work already noted (A., 1932, 671).

**Anomalous absorption of  $\gamma$ -rays. Possibility of the quantum jump of the rest-mass of an electron.** B. ARAKATSU (Mem. Fac. Sci. Agric. Taihoku, 1932, 5, 163—168).—Theoretical.

J. W. S.

**Emission of slightly penetrating radiation by some metals.** J. REBOUL (Compt. rend., 1933, 196, 1596—1598; cf. A., 1896, ii, 601).—The impression produced by Zn on a photographic plate thought to be due to emission of vapour of Zn is stated to be due to a radiation emitted by the Zn capable of exciting the air or other substance intervening between the Zn and the plate.

C. A. S.

**Atomic disintegration with neutron emission.** G. KIRSCH (Naturwiss., 1933, 21, 332).—At. disintegration of C, N, Mg, Al, S, Fe, Ni, Cu, Zn, Mo, Pd, As, Sn, W, Pt, Au, and Pb can be brought about with Po  $\alpha$ -rays, neutrons being emitted. The elements already examined, Li, Be, and B, give greater effects than the above.

A. J. M.

**Chemical proof of artificial transmutation of elements.** F. PANETH and P. L. GÜNTHER (Naturwiss., 1933, 21, 367—368).—The sensitivity of chemical methods of proving that transmutation has taken place is discussed.

A. J. M.

**Interaction of neutrons and protons.** J. SOLOMON (J. Phys. Radium, 1933, [viii], 4, 210—220).—Mathematical. Models for taking account of proton-neutron interaction are reviewed. Assuming a similar nature for the neutron-proton binding in the  $\text{H}^2$  isotope and the forces involved in neutron-proton collisions, a relation between the effective section for collisions and the mass defect of  $\text{H}_2$  is established.

N. M. B.

**Proof of the wave nature of molecular radiation by scattering in mercury vapour.** F. KNAUER



(Naturwiss., 1933, 21, 366—367).—Results on the scattering of mol. radiation from He and H<sub>2</sub> by Hg vapour cannot be reconciled with the classical theory, but are in agreement with wave mechanics. A. J. M.

**Significance of recent measurements of cosmic rays.** A. H. COMPTON (Science, 1933, 77, 480—482).—Recent experiments favour the view that cosmic rays are electrified particles and the data are in accord with Lemaitre's theory of their origin. L. S. T.

**Mass of the neutron.** J. J. PLACINTEANU (Compt. rend., 1933, 196, 1474—1476).—To explain the fact that the mass of the neutron,  $m_n$ , is < the sum of the masses of the proton,  $m_p$ , and electron  $m_e$ , of which it is regarded as constituted, it is suggested that it consists of a proton and Dirac's electron of negative energy (cf. A., 1930, 271). This gives results for mass ( $m_p - m_e$ ) and energy radiated in agreement with experiment. C. A. S.

**Electron spin and theory of the neutron.** W. WESSEL (Z. Physik, 1933, 82, 415—444).—Completion of Dirac's equation by addition of a spin potential leaves H fine structure unchanged, but gives proper functions of very high energy vals., and these may be identified with neutrons. A. B. D. C.

**Masses of atoms and the structure of atomic nuclei.** K. T. BAINBRIDGE (J. Franklin Inst., 1933, 215, 509—534).—A general survey. N. M. B.

**Theory of atomic nuclei. III.** E. N. GAPON (Z. Physik, 1933, 82, 404—407; cf. this vol., 443).—Anomalous absorption of  $\gamma$ -rays is explained, and the no. of free neutrons in at. nuclei determined. A. B. D. C.

**Relativistic treatment of the Fermi atom.** H. JENSEN (Z. Physik, 1933, 82, 794—802).

**Theory of the nucleus.** E. MAJORANA (Z. Physik, 1933, 82, 137—145).—A statistical method is developed for the nucleus from Heisenberg's theory (this vol., 335). A. B. D. C.

**Application of the phase integral method to the hydrogen molecule ion.** E. M. VAN ENGERS and H. A. KRAMERS (Z. Physik, 1933, 82, 328—336).—The phase integral method gives results in agreement with earlier calculations. A. B. D. C.

**Constitution of metallic sodium.** E. WIGNER and F. SEITZ (Physical Rev., 1933, [ii], 43, 804—810).—Mathematical. The chemical properties are investigated using the free electron concept. The lattice const., binding energy, and compressibility are calc. by wave mechanics. N. M. B.

**Thermodynamic functions of radiation.** F. G. DONNAN (J. Indian Chem. Soc., 1933, Rây No., 61—64).—Theoretical. H. J. E.

**Degrees of freedom and the constant  $M/m$ .** V. V. NARLIKER (J. Indian Chem. Soc., 1933, Rây No., 141—142).—Theoretical. H. J. E.

**General chemical equation.** W. HARRISON (Chem. and Ind., 1933, 370).—If the elements are represented by formulæ of the type  $A_xN_y$ , where  $x$  is the at. wt. and  $y$  the at. no., radioactive changes and the transmutations of light elements may be represented by equations which resemble ordinary chemical

equations, e.g.,  $\text{Li} + \text{H} = 2\text{He}$  becomes  $A_7N_3 + A_1N_1 = 2A_4N_2$ . D. R. D.

**Band spectrum of potassium hydride.** T. HORI (Mem. Ryojun Coll. Eng., 1933, 6, 1—33).—KH shows an extensive band spectrum in the region 4090—6610 Å., corresponding with a  $^1\Sigma \rightarrow ^1\Sigma$  combination. The spectrum is classified into 62 bands and 5  $v'$ -band systems. The intensity distribution is in agreement with the unusually large change in the moment of inertia ( $I_c'' = 8.12 \times 10^{-40}$ ;  $I_c' = 21.20 \times 10^{-40}$ ) and with the wide Franck-Condon parabola. Decomp. of the mols. yields K and H atoms in the ground state. J. W. S.

**Ultra-violet absorption bands of ammonia.** J. K. DIXON (Physical Rev., 1933, [ii], 43, 711—715).—Frequencies and classifications for a no. of intense double-headed bands in the region 2400—1900 Å. are tabulated. The doublet separation is 70 cm.<sup>-1</sup> Fundamental frequencies in the upper state are at 890 and 2720 cm.<sup>-1</sup> The double-headed bands at 46,140 and 47,030 cm.<sup>-1</sup>, on heating to 150° or 300°, shift to the red and become triple-headed. Predissociation in the excited state is discussed and explained. N. M. B.

**Fine structure of absorption bands of sulphur dioxide in the ultra-violet.** A. IONESCU (Compt. rend., 1933, 196, 1476—1478).—The absorption band spectrum of SO<sub>2</sub> has been analysed with reference to the three possible moments of inertia of the mol. by application of the asymmetric top theory. C. A. S.

**Atmospheric transmission in the water vapour bands  $\rho$  and  $\phi$  according to spectrographic measurements made in Tunisia in 1926—1927.** W. GORCZYŃSKI and E. STENZ (Bull. Acad. Polonaise, 1933, A, 53—64). A. B. D. C.

**Ultra-violet bands of oxide of phosphorus.** P. N. GHOSH and A. K. SEN-GUPTA (Nature, 1933, 131, 841).—Mol. const. have been obtained for the spectrum attributed to PO. L. S. T.

**Extension of the visible absorption system of NO<sub>2</sub> to longer wave-lengths.** J. CURRY and G. HERZBERG (Nature, 1933, 131, 842).—A series of bands starting at approx. 8900 Å. and extending to shorter wave-lengths has been observed. L. S. T.

**Interpretation of ultra-violet absorption bands of alkali halides.** W. KLEMM (Z. Physik, 1933, 82, 529—537).—Absorption may occur within the crystal if asymmetrical polarisation of the ions is taken into account (cf. Born, this vol., 5). A. B. D. C.

**Optical investigation of uranium compounds.** F. EPHRAÏM (J. Indian Chem. Soc., 1933, Rây No., 243—250).—Absorption spectra of UF<sub>4</sub>, UCl<sub>4</sub>, and UBr<sub>4</sub> at 18° and -180° were measured. They resemble those of the rare earths, and are attributed to similar abnormalities of electron arrangement (cf. A., 1927, 121). H. J. E.

**Relation of emission and absorption spectra of salts of rare earths in the solid state. I. Phosphorescence due to impurities.** R. TOMASCHKE and O. DEUTSCHBEIN (Z. Physik, 1933, 82, 309—327).—Emission and absorption spectra due to ions of the rare earths were investigated between 4000



and 9000 Å. Emission may coincide with absorption in the long-wave but not in the short-wave region.

A. B. D. C.

**Displacement of absorption bands of rare-earth salts.** Y. UZUMASA (J. Fac. Sci. Hokkaido, 1933, 1, 383—393; cf. A., 1932, 557).—The influence of the solvent and of the anion on the position of the absorption max. has been studied for salts of Pr, Nd, Sm, and Er. For Er the influence of added salts with a common anion has also been studied. F. L. U.

**Absorption of ultra-violet light by some organic substances.** XXVIII. W. GABRYELSKI and L. MARCHLEWSKI. XXIX. L. MARCHLEWSKI and T. SURZYCKI (Bull. Acad. Polonaise, 1933, A, 87—94, 95—98).—XXVIII. Absorption due to cellobiose, raffinose, cellobiose acetate, lactobiose  $\beta$ -acetate, sucrose acetate, and maltose acetate was investigated between 2200 and 3600 Å.

XXIX. Pyridine-2-, -3-, and -4-carboxyldiethylamide were investigated between 2200 and 3000 Å.

A. B. D. C.

**Purification and ultra-violet transmission of ethyl alcohol.** L. HARRIS (J. Amer. Chem. Soc., 1933, 55, 1940—1942; cf. A., 1931, 1110).—Commercial abs. EtOH is purified by means of Zn. Physical consts. and absorption coeffs. between 2450 and 2120 Å. are recorded. J. G. A. G.

**Continuous absorption spectrum of polyatomic molecules.** II. Y. HUKUMOTO (Sci. Rep. Tôhoku, 1933, 22, 13—30; cf. this vol., 336).—The effect of foreign gases (air,  $H_2$ ,  $N_2$ ,  $O_2$ ) on the absorption spectra of the vapours of alkyl halides was found to be negligible. The absorption spectrum of  $(CHCl)_2$  is affected by temp., which may be due to the existence of two stereoisomeric forms. The mechanism of the photo-dissociation is discussed. A. J. M.

**Spectroscopic investigation of the explosion zones of methane and other hydrocarbons.** F. J. LAUER (Z. Physik, 1933, 82, 179—191).—Flames of  $CH_4$ ,  $C_2H_2$ , and  $C_6H_6$  in  $O_2$  were investigated spectroscopically between 6200 and 2200 Å. The active explosion zone of  $CH_4$  gave the CH band at 3142 Å., and in addition to the known bands due to OH, CH, and  $C_2$ , a band due to  $CH_2$  was observed at 3672 Å. Reaction mechanisms are discussed.

A. B. D. C.

**Band spectra and molecular structure.** I. W. WEIZEL (Physikal. Z., 1933, 34, 425—440).—A review.

**Spectroscopy in the service of chemistry.** M. N. SAHA (J. Indian Chem. Soc., 1933, Ray No., 293—307).—A review. H. J. E.

**Water vapour absorption in the infra-red part of the solar spectrum according to spectrographic measurements made at the Mediterranean coast during 1931—1932.** E. STENZ (Bull. Acad. Polonaise, 1933, A, 65—76).—Infra-red absorption gives a more accurate estimate of  $H_2O$  vapour content than ordinary methods, and shows that before rainfall and cloudy periods atm. absorption increases.

A. B. D. C.

**Infra-red spectrum of carbon dioxide.** I. A. ADEL and D. M. DENNISON (Physical Rev., 1933,

[ii], 43, 716—723; cf. A., 1932, 982).—Mathematical. Previous work is extended by introducing a second-order perturbation. N. M. B.

**Infra-red absorption measurements of organic substances. I. Apparatus and absorption of some solvents and organic dyes.** G. BUSS. II. Absorption of some organic liquids below  $2.7 \mu$ . O. EICHMANN (Z. Physik, 1933, 82, 445—460, 461—472).—I. Absorption between 0.8 and  $2.4 \mu$  was determined for  $C_6H_6$ ,  $H_2O$ , EtOH, glycerol, and azo-, phthalein,  $CHPh_3$ , and acridine dyes.

II.  $CH_3PhCl$ , Me salicylate, EtOBz, anethole, paraldehyde, *l*- and *d*-pinene,  $C_5H_{11}OH$ ,  $C_5H_{11}O \cdot NO$ ,  $EtCO_2H$ , and  $Et_2C_2O_4$  were investigated. A. B. D. C.

**Fine structure of residual rays.** M. BORN and M. BLACKMAN (Z. Physik, 1933, 82, 551—558).—Anharmonic coupling of normal vibrations of a lattice gives various overtones in the infra-red spectrum, and from this are deduced the positions of subsidiary max. A. B. D. C.

**Raman spectrum of rock-salt.** M. BLACKMAN (Naturwiss., 1933, 21, 367).—The Raman spectrum of rock-salt shows more intensity max. than indicated by the simple theory. An explanation is discussed. A. J. M.

**Raman effect.** XXV. Raman spectrum of monobasic organic acids. K. W. F. KOHLRAUSCH, F. KÖPPL, and A. PONGRATZ (Z. physikal. Chem., 1933, B, 21, 242—255).—The Raman spectra of sixteen fatty acids, the chloroacetic acids, and  $BzOH$  have been determined. From the variation in intensity of the lines with the length of the chain, it is concluded that the characteristic frequencies of the normal acids  $\Delta\nu=1650$ , 1410, and  $1110 \text{ cm}^{-1}$  correspond with the vibrations of groups which occur only once in the mol., whilst the frequencies 1300 and  $1450 \text{ cm}^{-1}$  belong to groups the no. of which in the mol. is proportional to the length of the chain. With increasing branching of the chain in the  $\alpha$  position there is a slight depression of the CO frequency  $1650 \text{ cm}^{-1}$ . R. C.

**Raman effect and depolarisation factor.** O. SPECCHIA (Nuovo Cim., 1932, 9, 133—137; Chem. Zentr., 1933, i, 17).—Two methods for determining the depolarisation factor of Raman bands are described, and used for  $H_2O$  bands. Results are compared with those of Ramaswamy. A. A. E.

**Halochromism of ketones in acids.** L. C. ANDERSON (J. Amer. Chem. Soc., 1933, 55, 2094—2098).—The absorption curves of benzoquinone in  $Et_2O$  and  $HClO_4$  and of anthraquinone,  $COPh_2$ , and xanthone in  $Et_2O$  and conc.  $H_2SO_4$  indicate that the colours produced in acid are concerned with the reactivity of the CO group. In some cases, quinonoidation may be also responsible. H. B.

**Thermo-luminescence spectrum of calcite.** S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 20, 274—284).—The spectrum of calcite containing traces of the rare earths and of Th showed a continuous single band in the range  $670\text{--}535 \text{ m}\mu$ , coinciding with the spectra of cathodo- and photo-luminescence. A close agreement with the combustion spectrum of Ca in  $O_2$  indicates the explanation as the chemo-luminescence due to the combustion of free  $O_2$



and colloidal Ca which causes the coloration of the crystal. The theory of the mechanism of luminescence in fluorite is developed to apply to the present case.

N. M. B.

**Fluorescence of pure salts of the rare earths.** R. TOMASCHEK and O. DEUTSCHBEIN (*Physikal. Z.*, 1933, **34**, 374—376; cf. this vol., 446).—The spectra, especially at low temp., are very sharp. Some emission lines coincide with absorption lines. The fluorescence spectra of solutions of salts of the rare earths are also examined.

A. J. M.

**Fluorescence of "special salt."** S. OKA and S. YAGI (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 143—144B).—NaCl and KCl crystals from solutions containing Mn, Sn, or Pb are fluorescent. Luminescence and transparency run parallel.

J. S. A.

**Blue rock-salt.** E. REXER (*Naturwiss.*, 1933, **21**, 332).—When a specimen of blue rock-salt is placed in a beam of X-rays which ordinarily produce a yellow colour in the salt, the yellow colouring of the previously colourless regions is considerably more intense than that where the blue colour was, and shows the normal absorption bands. By photo-electric colouring there is a complete reversal of the form of the coloured part.

A. J. M.

**Efficiency of anti-Stokes fluorescence in dyes.** A. JABLOŃSKI (*Nature*, 1933, **131**, 839—840).—Theoretical.

L. S. T.

**Transparent crystals of potassium halides.** S. OKA (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 141—143B).—The presence of Sb, Bi, Pb, and Sn ions markedly alters the crystal habit of KCl and KBr. With Pb and Sn present, perfectly transparent octahedral crystals which fluoresce in ultra-violet light are formed.

J. S. A.

**Internal photo-electric effect in liquid dielectrics.** G. LIANDRAT (*Compt. rend.*, 1933, **196**, 1385—1386; cf. A., 1930, 398).—The initial conductivity,  $10^{-15}$  ohm $^{-1}$  per cm., of the CCl $_4$  used, which after exposure for 1 hr. to a Hg arc rose to  $10^{-14}$ , and regained its initial val. in 2 hr. after removal of the arc, was so high and irregular as to indicate that the CCl $_4$  was insufficiently pure to permit a decision as to its photoconductivity.

C. A. S.

**New type of photo-electric effect in cuprous oxide in a magnetic field.** I. KIKOIN and M. NOSKOV (*Nature*, 1933, **131**, 725—726).—When a plate immersed in liquid air and placed in a magnetic field parallel to its plane is illuminated by a beam of white light perpendicular to this plane, an e.m.f. is developed between the ends of the plate at right angles to the light and the magnetic field. The direction of supposed flow of negative electrons appears to coincide with that of the light. The effect disappears when red light is used, and is not observed at room temp. A peculiar Hall effect of the moving photo-electrons produced at the entrance of the light into the plate appears to be involved.

L. S. T.

**Thermo-electric force and voltaic potential of cuprous oxide.** G. MONCH (*Naturwiss.*, 1933, **21**, 367).—A thermo-element made up of metal-Cu $_2$ O-metal has a comparatively large thermo-electric force due to the different electron concn. in the semi-

conducting Cu $_2$ O. The same potential should be obtained at the ends of a polycryst. rod of Cu $_2$ O maintained at a temp. difference. Such an arrangement gave 0.4—0.5 volt, for 100° temp. difference. Part of this is due to the voltaic potential of the free Cu $_2$ O surface which varies with temp., amounting to about 0.15 volt for 100° temp. difference.

A. J. M.

**Photo-electric effect in specially active layers of a carborundum crystal.** O. V. LOSSEV (*Physikal. Z.*, 1933, **34**, 397—403).—Rectification by a carborundum crystal may be due to the presence of an active layer at the surface, the thickness of which can be measured with a microscope. The electrical conductivity of the layer at various depths was found for small c.d., and the potential distribution inside the layer was determined. The photo-electric effect can take place in the active layer, but the source of the photo-electrons is the boundary between the active layer and the crystal itself. In many respects the SiC crystal behaves similarly to the Cu $_2$ O "sperrschicht" cell. The presence of active layers on galena crystals, and on single crystals of Si containing Al, Cu, and Fe, is reported.

A. J. M.

**Mechanism of action of light on electrodes photosensitised with copper salts.** R. AUDUBERT (*Compt. rend.*, 1933, **196**, 1588—1590).—Measurements of the photopotential of electrodes of Cu coated with Cu $_2$ O, CuO, CuI, or CuCl in aq. CuSO $_4$  of varying concn. agree with the results calc. on the theory that a positive photopotential is connected with oxidation, negative with reduction, i.e., that the photo-voltaic behaviour in such electrodes is due to the photolysis of H $_2$ O (cf. A., 1931, 999).

C. A. S.

**Photo-electric properties of magnesium.** G. DÉJARDIN and (Mlle.) R. SCHWÉGLER (*Compt. rend.*, 1933, **196**, 1585—1587; cf. A., 1932, 789).—Photo-electric cells with Mg were prepared (a) by condensing Mg vapour on the glass wall, (b) by cathodic sputtering, and (c) by partial volatilisation of a Mg-Ba (70—75:30—25) alloy. (a) showed a threshold at 3400—3500 Å., and emission (in  $10^{-5}$  amp. watt) of 0.4—1.0 for 3130 Å., and 4.0—7.9 for 2537 Å.; with (b) and (c) if volatilisation occurred at  $\geq 900^\circ$ , results were similar, but with volatilisation at a higher temp. (c) gave results indicating presence of Ba, the threshold being at 5000—5500 Å.

C. A. S.

**Photo-electric sensitivity of magnesium.** R. J. CASHMAN and W. S. HUXFORD (*Physical Rev.*, 1933, [ii], **43**, 811—818).—The photo-electric sensitivity of gas-free surfaces of Mg deposited on glass was determined in the visible region of the spectrum; the long-wave limit for all such surfaces deposited in vac. is approx. 5100 Å. Traces of air, or O $_2$ , or N $_2$  activated by glow discharge sensitise the surface to light of longer wave-lengths. Further oxidation of the surface shifts the threshold into the ultra-violet.

N. M. B.

**Determination of photo-electric wave-length limit for rhenium.** A. ENGELMANN (*Ann. Physik*, 1933, [v], **17**, 185—208).—The photo-electric wave-length limit for Re at various stages of outgassing was determined; for complete outgassing it was about 250 m $\mu$ . The presence of vapours of hydrocarbons causes a considerable displacement of the red limit



towards the longer waves. The results agree with the theory of Fowler on the analysis of spectral distribution curves at various temp. A. J. M.

[Electrical] conductivity of mixtures of gases. S. P. MCCALLUM and L. KLATZOW (Nature, 1933, 131, 841).—Curves for He, A, and He + 0.025% A are given and discussed. A large no. of new ions, attributed to direct collisions of electrons with A atoms, are formed in the He-A mixture when the potential between the parallel plates increases from 9 to 18 volts.

L. S. T.

Piezoelectric and dielectric properties of Rochelle salt. E. SCHWARTZ (Elek. Nach. Tech., 1932, 9, 481—495). CH. ABS.

Ionic polarisation in crystals. J. ERRERA and H. BRASSEUR (Physikal. Z., 1933, 34, 368—373).—The dielectric const. of crystals along their principal axes is measured, and from this the ionic polarisation is derived. A. J. M.

Dielectric polarisation in solids. S. O. MORGAN, W. A. YAGER, and A. H. WHITE (J. Amer. Chem. Soc., 1933, 55, 2171—2172).—A transition in the solid state accompanied by changes of heat capacity and dielectric const. occurs in *d*-camphor between  $-37^\circ$  and  $-32^\circ$ , in *dl*-camphor between  $-70^\circ$  and  $-80^\circ$ , and in borneol and isborneol at  $70-80^\circ$  and  $25-45^\circ$ , respectively. The data are discussed with reference to at. polarisation or group rotation which depends on temp. J. G. A. G.

Dipole rotation and the transitions in the crystalline hydrogen halides. C. P. SMYTH and C. S. HIRCHCOCK (J. Amer. Chem. Soc., 1933, 55, 1830—1840).—Dielectric consts. and sp. conductances have been determined between  $-37^\circ$  and  $-189^\circ$  at frequencies between 300 and 60,000, and the data confirm the transition points revealed by sp. heat determinations. For some distance below the m.p. the mols. in the cryst. solids orient in the externally applied electric field to almost the same extent as in the liquid, and in general, the polarisations vary inversely as the abs. temp. between the transitions. Below  $-174.6^\circ$ , the dielectric const.,  $\epsilon$ , of HCl falls to very low vals., indicating negligible rotatory oscillation of the mols. Vals. of  $\epsilon$  for HI increase rapidly with fall of temp. below  $-147.5^\circ$  owing to an increasing no. of mols. passing from states of complete rotation to rotatory oscillation as the temp. falls. For HBr,  $\epsilon$  has a strong sharp max. between  $-183^\circ$  and  $-185^\circ$ . The results are discussed with reference to Pauling's theory. J. G. A. G.

Electric moments of nitrogen dioxide and nitrogen tetroxide. C. T. ZAHN (Physikal. Z., 1933, 34, 461—462).—The dielectric consts. of the equilibrium mixture  $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  were determined between  $296^\circ$  and  $397^\circ$  abs., and at pressures between 0 and 1 atm. It is very probable that both  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  have definite dipole moments, that of  $\text{N}_2\text{O}_4$  being the greater. The vals. given as upper limits are  $0.55 \times 10^{-18}$  and  $0.39 \times 10^{-18}$ , respectively. A. J. M.

Refractivities of liquid compounds of phosphorus. W. J. JONES, W. C. DAVIES, and W. J. C. DYKE (J. Physical Chem., 1933, 37, 583—596).—Vals. of the density,  $n$ , and mol. refractivities of 84 liquid

P compounds are tabulated. At. and group refractivities are tabulated, and their relation to mol. structure is discussed. H. J. E.

Molecular refraction of alums. K. WENDEKAMM (Z. Krist., 1933, 85, 169—198).—Density, mol. vol., and mol. refraction of the alums  $\text{XY}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , where  $\text{X}=\text{K}, \text{Rb}, \text{Cs}, \text{Ti}^{\text{II}}, \text{NH}_4, \text{NH}_3\text{Me}$ , and  $\text{NH}_3\text{OH}$ ,  $\text{Y}=\text{Al}, \text{Cr}$ , and also the corresponding double Al selenates, have been determined and compared *inter se* and with V and Fe alums by plotting the vals. of these properties for the other series against those of the Al alum series. In almost every case the relation is linear, as also in the case of the double sulphates  $\text{M}^{\text{II}}\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .  $\text{Ti}^{\text{II}}$  derivatives show the greatest deviation. C. A. S.

Refractive dispersion of eugenol and iso-eugenol. G. THOMPSON (J.C.S., 1933, 557; cf. *ibid.*, 1923, 1594).—Vals. of  $n$  for the two isomerides at  $20^\circ$  are tabulated (cf. Eykman, A., 1890, 748).

H. J. E.

Dispersion of electric birefringence in ethyl ether. M. SCHWOB (Compt. rend., 1933, 196, 1383—1384; cf. A., 1925, ii, 755).—The electric birefringence of  $\text{Et}_2\text{O}$  at  $17^\circ$  for  $\lambda$  5780, 5460, and 4360 is 20.1, 20.9, and 27.6, respectively (that of  $\text{CS}_2$  being 100), giving dispersions  $\beta_{4360}/\beta_{5780}=1.37$ , and  $\beta_{4360}/\beta_{5460}=1.31$ , as compared with 1.33 and 1.25 by Havelock's formula.

C. A. S.

Variation with temperature of magnetic birefringence of liquid oxygen. P. LAINE (Compt. rend., 1933, 196, 1594—1596; cf. this vol., 556).—Langevin's theory as regards the temp. variation of magnetic birefringence (I) of paramagnetic substances gives the correct ratio between (I) of liquid  $\text{O}_2$  at  $77.9^\circ$  and  $90.1^\circ$  abs., whereas his theory, based on the same fundamental ideas, for the variation of the magnetic susceptibility gives a result double experimental (cf. A., 1910, ii, 578). Weiss attributes this to the mol. field, which, however, should affect (I) similarly. For (I) the result is explicable if the effect of the mol. field is exactly counterbalanced by change with temp. of the optical anisotropy as in the case of  $\text{HCO}_2\text{H}$  and  $\text{AcOH}$ . C. A. S.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. VI. Magneto-optical dispersion of acetic acid and *n*-propyl acetate. W. J. LEWIS and G. E. JONES (Phil. Mag., 1933, [vii], 13, 1065—1079; cf. A., 1931, 24).—Data are tabulated for the magneto-optical dispersion of these compounds in the region  $0.46-0.27 \mu$ , and for the natural dispersion in the region  $0.6678-0.2766 \mu$ . Expressions are deduced which accord with these data. The absorption bands in the Schumann-Lyman region are at  $0.1042 \mu$  and  $0.1077 \mu$ , and the calc. vals. of  $e/m$  are  $0.916 \times 10^7$  and  $1.01 \times 10^7$  e.m.u., respectively. J. W. S.

Theory of the Kerr effect of diatomic molecules. G. NEUGEBAUER (Z. Physik, 1933, 82, 660—673).—Quantum theory leads to classical results.

A. B. D. C.

Kerr's law at high field strengths. J. A. HOOTMAN (Physical Rev., 1933, [ii], 43, 749—755).—In pure non-polar  $\text{CS}_2$  Kerr's law held for all fields; in polar



liquids,  $\text{Et}_2\text{O}$  and  $\text{CHCl}_3$ , deviations were found. Curves for the variation of the Kerr const. with electric field strength are given for  $\text{Et}_2\text{O}$  at  $-78.5^\circ$  and  $\text{CHCl}_3$  at  $-22.5^\circ$ . N. M. B.

**Stereomagnetism. I. Significance of atomic interaction for magnetism. II. Problem of perminvar.** O. VON AUWERS and H. KÜHLEWEIN (Ann. Physik, 1933, [v], 17, 107—120, 121—145).—I. The effect of at. coupling and cryst. superstructure on the magnetic properties of substances in general is discussed.

II. The properties of Fe-Co-Ni alloys which after heating and subsequent slow cooling possess const. permeability are discussed in connexion with the theory previously put forward. A special model is used to investigate the action of the coupling field in a mixed crystal lattice with ferromagnetic components with superstructure, from which an explanation of the behaviour of perminvar is obtained. A. J. M.

**Susceptibilities of paramagnetic solutions.** C. J. GORTER (Physikal. Z., 1933, 34, 462—464; cf. A., 1932, 900).—Polemical against Fahlenbrach (this vol., 340). A. J. M.

**Diamagnetism of carbon tetrachloride, benzene, and toluene at different temperatures.** G. F. BOEKER (Physical Rev., 1933, [ii], 43, 756—760; cf. this vol., 212).—Experimental data are tabulated and plotted. The mass susceptibilities show a decrease  $< 1\%$  with rise of temp. N. M. B.

**Temperature and diamagnetism.** S. S. BHATTAGAR (J. Indian Chem. Soc., 1933, Spec. No., 171—176).—Change of temp. generally changes the diamagnetism more in aromatic than in aliphatic compounds. H. J. E.

**Magne-crystallic action. II. Paramagnetics.** K. S. KRISHNAN, N. C. CHAKRAVORTY, and S. BANERJEE (Phil. Trans., 1933, A, 232, 99—115).—The principal magnetic susceptibilities of the hydrated sulphates of  $\text{Fe}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ , and  $\text{Cu}^{++}$ , their double sulphates with K and  $\text{NH}_4$ ,  $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot \text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{FeCO}_3$  have been measured by methods already described (A., 1927, 192; this vol., 340). Errors in Jackson's method of calculation (cf. A., 1928, 1081) are corrected. D. R. D.

**Magnetic structure of an iron alum in strong fields.** J. FORREST (Phil. Mag., 1933, [vii], 15, 1153—1162; cf. A., 1927, 299; 1931, 154).—The magnetic anisotropic character of crystals of  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  has been confirmed. J. W. S.

**Influence of light on paramagnetic susceptibility.** P. W. SELWOOD (Nature, 1933, 131, 762).—Solutions of  $\text{FeCl}_3$ ,  $\text{CrCl}_3$ , and  $\text{Nd}(\text{NO}_3)_3$  show a slow decrease in paramagnetic susceptibility on exposure to light (cf. A., 1932, 900). L. S. T.

**Structure of basic salts of bivalent metals.** W. FEITKNECHT (Helv. Chim. Acta, 1933, 16, 427—454; cf. A., 1930, 436).—X-Ray examination of basic Zn salts  $\text{ZnX}_2 \cdot 4\text{Zn}(\text{OH})_2$  and  $\text{ZnY} \cdot 3\text{Zn}(\text{OH})_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{NO}_3$ ;  $\text{Y} = \text{SO}_4$ ,  $\text{CO}_3$ ) shows that normal salt and hydroxide occur in alternate layers in the lattice. Corresponding salts (excluding bromides and iodides) of Co, Ni,  $\text{Mn}^{II}$ , Cd,  $\text{Fe}^{II}$ , and Mg show similar struc-

ture.  $\text{H}_2\text{O}$  of crystallisation is held between the layers. On dehydration the distance between the latter decreases, the lattice remaining intact. Basic Zn salts readily take part in topochemical changes, in which the action takes place along the plane of the layers. Two kinds of mixed basic salts have been prepared, in one of which only the cation of the normal salt component is replaceable, whilst in the other the cation of the hydroxide component is also replaceable. Werner's conception of basic salts as "hexol salts" is incorrect. F. L. U.

**Electronic structure of ethylenic carbon.** G. ALLARD (Compt. rend., 1933, 196, 1500—1502).—One of the linkings in C:C is represented by  $1/\sqrt{3}s + \sqrt{3}p_x$ ,  $1/\sqrt{3}s - 1/\sqrt{6}p_x + 1/\sqrt{2}p_y$ , or  $1/\sqrt{3}s - 1/\sqrt{6}p_x - 1/\sqrt{2}p_y$ , whilst the other (which has a small energy and restricts free rotation) is represented by  $p_z$ . The first three functions represent three valencies situated in the same plane at angles of  $120^\circ$ ; the fourth is normal to the plane of the other three. H. B.

**Structure of hypophosphoric acid.** P. NYLÉN and O. STELLING (Z. anorg. Chem., 1933, 212, 169—181).—Cryoscopic measurements on aq. solutions of the acid and its Na salt support the double formula  $\text{H}_4\text{P}_2\text{O}_6$ . X-Ray examination of the Na and Ba salt shows only one K absorption edge, corresponding with that expected for the structure  $\text{R}_4(\text{O}_3\text{P} \cdot \text{PO}_3)$ . J. S. A.

**Structure of pyrophosphoric acid.** P. NYLÉN (Z. anorg. Chem., 1933, 212, 182—186).—Treatment of  $\text{NaPO}(\text{OEt})_2$  with I or with  $\text{POCl}(\text{OEt})_2$ , air oxidation of  $\text{Et}_4\text{P}_2\text{O}_6$ , and action of  $\text{EtI}$  on  $\text{Ag}_4\text{P}_2\text{O}_7$ , lead to formation of  $\text{Et}_4\text{P}_2\text{O}_7$ . This, when shaken with  $\text{BaCO}_3$  and  $\text{H}_2\text{O}$ , forms  $\text{Ba}(\text{Et}_2\text{PO}_4)_2$ . The symmetrical formula  $\text{R}_4(\text{O}_3\text{P} \cdot \text{O} \cdot \text{PO}_3)$  is therefore indicated for  $\text{R}_4\text{P}_2\text{O}_7$ . J. S. A.

**Formulæ of antimonie acid and the antimonates.** L. PAULING (J. Amer. Chem. Soc., 1933, 55, 1895—1900).—From the ratios of ionic radii and geometrical considerations, formulæ are assigned to the oxy-acids of many elements in their highest valency states. Evidence is adduced in favour of the formula  $\text{HSb}(\text{OH})_6$  for antimonie acid. The change from an ortho- to a meta-acid (or salt), e.g.,  $\text{H}_3\text{BO}_3$  to  $(\text{HBO}_2)_x$ ,  $\text{HSb}(\text{OH})_6$  to  $(\text{HSbO}_3)_y$ , generally involves polymerisation rather than a change in co-ordination no. J. G. A. G.

**Constitution of molecular compounds.** P. R. RÂY (J. Indian Chem. Soc., 1933, Rây No., 161—169).—A review. H. J. E.

**Quantum mechanics and the benzene problem. I, II.** G. ELSEN (Chem. Weekblad, 1933, 30, 310—317, 322—328).—A review of recent work. H. F. G.

**Quantum mechanics of chemical valency.** H. HELLMANN (Z. Physik, 1933, 82, 192—223).—The method of Heitler, Rumer, and Weyl is generalised semi-empirically. Coulomb are separated from exchange forces, and evaluations of each from known data for simple mols. are used to predict structures of more complex mols. Thus, exchange and Coulomb (including polarisation) terms are evaluated for the at. pairs H-H, H-N, N-N, C-H, C-C, and C-H, and



are used to discuss the mols.  $N_2H_4$ ,  $N_3H$  (linear),  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$ . A. B. D. C.

Calculation of intramolecular atomic distances from dissociation constants of dibasic acids. II. Acidity of dicarboxylic acids and polymethylenediammonium ions in aqueous alcohol. III. Acidity of substituted malonic acids in aqueous alcohol. G. SCHWARZENBACH (Helv. Chim. Acta, 1933, 16, 522—528, 529—533; cf. this vol., 25).—II. The empirical relation  $\phi = k/D^a$  ( $\phi$  = work done in removing the second  $H^+$  from the univalent ion of a dicarboxylic acid,  $D$  = dielectric const. of medium) is valid for the acids  $CO_2H \cdot [CH_2]_n \cdot CO_2H$  ( $n=1, 2, 3$ , and 6), which have been examined in 0, 20, 40, 60, and 80% aq. EtOH. The same relation (with changed sign) applies to the removal of the first  $H^+$  from the ion  $NH_3^+ \cdot [CH_2]_n \cdot NH_3^+$  ( $n=2, 3, 4, 5$ , and 8). The val. of  $a$  increases with the length of the C chain, but is always  $< 1$ .

III. Similar experiments with alkyl-substituted malonic acids show that  $a$  is smaller than for malonic acid, the effect increasing with the size of the substituent group. F. L. U.

Quantitative crystal analysis by X-rays. M. E. NAHMIAS (Z. Krist., 1933, 85, 319—321; cf. this vol., 44).—Further details of the method are given.

C. A. S.

Production of single crystals with prescribed axial orientation. P. A. PALIBIN and A. I. FROIMAN (Z. Krist., 1933, 85, 322—325).—A method for obtaining crystals of, e.g., Zn or Cd with the hexagonal axis parallel to their length is described. C. A. S.

Laue reflexion photographs with oscillating quartz rod. E. BLECHSCHMIDT and W. BOAS (Z. Krist., 1933, 85, 329; cf. A., 1932, 363; this vol., 213).—A quartz rod with sides parallel and perpendicular to a digonal and parallel to the hexagonal axis, respectively, oscillating in the direction of its length, had no effect on reflexion Laue photographs.

C. A. S.

Reflexion and refraction of X-rays by perfect crystals. G. W. BRINDLEY (Proc. Roy. Soc., 1933, A, 140, 301—313; cf. A., 1932, 903). L. L. B.

Effects of mechanical strain in the intensity of X-rays reflected by a crystal. E. FUKUSIMA (J. Sci. Hiroshima Univ., 1933, 3, 177—186).—Local mechanical strain increases the reflecting power by eliminating internal extinctions. The effect is greater with perfect crystals (e.g., quartz) than with imperfect (e.g., rock-salt). J. S. A.

New representation of geometrical crystallography. B. DELAUNAY (Z. Krist., 1933, 85, 332; cf. this vol., 213).—A correction. C. A. S.

Total reflexion of X-rays by thin layers. A. I. ALICHANOV and L. A. ARZIMOVIC (Z. Physik, 1933, 82, 489—506).—Total reflexion was observed with Ag and W layers on glass, Ag layers on Al, Al on Ag, and Ag on Pt and W. A. B. D. C.

Formation of crystal nuclei in piperonal and *all*cinnamic acid. E. BILLMANN and A. KLIT (Kgl. Danske Vidensk. Selskab, 1933, 12, No. 4, 3—51).—The no. of nuclei formed in melts of piperonal on cooling decreases as the temp. of the melt is raised and

with duration of the heating. In under-cooled melts the no. of nuclei decreases with time, indicating that there is no essential difference in the liquid phase above and below the m.p. Reproducible results can be obtained under const. conditions when the glass tubes used have been used previously. Fresh glass surfaces may provide crystallisation centres. When the melting conditions are const. the no. of nuclei formed increases with the degree of cooling, if the lowest temp. reached is not too far below the m.p. Formation and disappearance of the nuclei are not reversible. The observations are explained by supposing that crystallisation centres are formed by dust particles of colloidal dimensions, which acquire a sheath of oriented mols. of the melt. This view is supported by the fact that the nuclei can be centrifuged. Similar phenomena are observed in melts of the three modifications of *all*ocinnamic acid. The results suggest that these modifications are polymorphic. E. S. H.

Needle-shaped crystals of sodium chloride. W. S. HINEGARDNER (J. Amer. Chem. Soc., 1933, 55, 1461—1462; cf. A., 1932, 797).—Fine needles of NaCl appeared after unwashed  $SiO_2$  gel from Na silicate and HCl had dried sufficiently to fracture.

J. G. A. G.

Crystalline state of thin sputtered films of platinum. G. P. THOMSON, N. STUART, and C. A. MURISON (Proc. Physical Soc., 1933, 45, 381—388).—Films of Pt sputtered in various gases have been examined by electron diffraction. They show patterns indicating that the small crystals are oriented with one face parallel to the surface of the specimen, the crystals being otherwise at random. The width of the rings formed by diffraction shows that in many cases the crystals are very small, of the order of  $5 \times 10^{-7}$  cm. Some films of  $PtO_2$  showed crystals of the order of  $2 \times 10^{-7}$  cm. W. R. A.

Crystal structure of  $\alpha$ -( $\beta$ )-tungsten. M. C. NEUBURGER (Z. Krist., 85, 232—238; cf. A., 1931, 805, 1377).—As the new modification is stable only below  $650^\circ$ , the designations  $\beta$  and  $\alpha$  have been interchanged. The unit cell has  $a$  5.038 and contains 8 W, space-group  $T_1^2 O \cdot O_h^3$ , the lattice being of a new type. The at. vol. is 9.70, that of ordinary ( $\beta$ -)W being 9.547. C. A. S.

Lattice constant of beryllium. M. C. NEUBURGER (Z. Krist., 1933, 85, 325—328; cf. A., 1923, ii, 766).—Specially pure Be has  $a$  2.2679,  $c$  3.5942 Å., with 2 mols. in the unit cell;  $d^{20}$  1.85, at. radius 1.112 Å.

C. A. S.

Anomalous scattering of X-rays by copper. A. A. RUSTERHOLZ (Z. Physik, 1933, 82, 538—550).—The atom factor for the (220) face of Cu was determined for different wave-lengths. A. B. D. C.

Transformation of cobalt single crystals. U. DEHLINGER, E. OSSWALD, and H. BUMM (Z. Metallk., 1933, 25, 62—63).—Single crystals of Co have been obtained by very slow cooling of the metal from  $1480^\circ$  in an induction furnace. The hexagonal crystals during transformation to the cubic form behave similarly to the Ti crystals previously examined (A., 1932, 1193); they can be converted into the



cubic form and back into the hexagonal many times without breaking down into several crystals. A theoretical explanation is given. A. R. P.

**Crystal structure of indium.** F. P. DWYER and D. P. MELLOR (J. Proc. Roy. Soc. New South Wales, 1933, 66, 234—239).—There are four atoms per unit cell;  $a_0$ ,  $4.588 \pm 0.002$ ,  $b_0$ ,  $4.946 \pm 0.002$  Å.,  $a : c = 1.078 \pm 0.002$ . C. W. G.

**Crystal structure and lattice constants of mercury.** M. C. NEUBURGER (Z. anorg. Chem., 1933, 212, 40—44).—X-Ray diffraction lines attributed by Alsén and Aminoff to Hg (A., 1924, ii, 554) are shown to be due to solid CO<sub>2</sub>. The lattice of solid Hg is rhombohedral, and not hexagonal. H. J. E.

**Diffuse scattering of X-rays from sylvine. III. Scattering at the temperature of liquid air.** G. G. HARVEY (Physical Rev., 1933, [ii], 43, 707—710).—An extension of previous work (cf. this vol., 549). A general expression for the intensity of scattering over the full temp. range is found. N. M. B.

**Crystal structure of potassium thiocyanate.** H. P. KLUG (Z. Krist., 1933, 85, 214—222).—KCNS is orthorhombic with  $a$  6.66,  $b$  7.58,  $c$  6.635 Å., and 2 mols. in the unit cell, space-group probably  $V_h^1$ . C, N, and S in CNS' are in a straight line; the structure is similar to that of KCNO (cf. A., 1926, 113). C. A. S.

**Crystal form of dinitrocobaltamines.** W. M. McNABB and H. A. ALSERTZER, jun. (Z. Krist., 1933, 85, 297—304).—1:6-Dinitrotetramminocobaltic iodide and chromate, and 1:2-dinitrotetramminocobaltic chromate and dichromate are respectively: hexagonal,  $a : c = 1 : 0.6757$ ; hemihedral tetragonal,  $a : c = 1 : 1.4901$ ; tetragonal,  $a : c =$  (from H<sub>2</sub>O) 1:1.5034, from aq. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 1:1.2957; and monoclinic,  $a : b : c = 1.2023 : 1 : 1.7388$ ,  $\beta$  115° 1'. C. A. S.

**Cobaltinitrites of ammonium, potassium, rubidium, caesium, and thallium.** A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1933, [vi], 17, 390—398; cf. A., 1932, 483).—The following vals. of  $a$  (Å.) and  $d$ , respectively, were obtained for the compounds of the general formula  $M_3[\text{Co}(\text{NO}_2)_6]$ , where M = metal atom or NH<sub>4</sub>: NH<sub>4</sub>,  $10.81 \pm 0.02$ , 2.00; K,  $10.44 \pm 0.02$ , 2.64; Rb,  $10.73 \pm 0.01$ , 3.18; Cs,  $11.15 \pm 0.01$ , 3.51; Tl,  $10.72 \pm 0.02$ , 5.10. The unit cell contains 4 mols. in every case. The NH<sub>4</sub> compound may contain 1.5H<sub>2</sub>O and the Rb and Cs compounds 1H<sub>2</sub>O. Pb<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]<sub>2</sub> is anhyd. and isomorphous with K<sub>6</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]<sub>2</sub>. O. J. W.

**X-Ray and thermal characterisation of lattice formation of zinc oxide.** R. FRICKE and P. ACKERMANN (Naturwiss., 1933, 21, 366).—By varying the temp. of heating Zn(OH)<sub>2</sub> to produce ZnO the latter can be made in varying degrees of energy content as indicated by the mol. heat of dissolution. X-Ray photographs of the oxides showed a diminution of the abs. line intensity and a stronger decrease in the intensities of higher-order spectra with increase in energy content. The larger energy of the oxides prepared at lower temp. is due to incomplete lattice formation. A. J. M.

**Crystalline structure of calcium-nitrogen compounds.** H. H. FRANCK, M. A. BREDIG, and G. HOFFMANN (Naturwiss., 1933, 21, 330—331).—There are three Ca nitrides differing in structure: black ( $a$ ) formed between 650° and 750°, brown ( $b$ ) between 750° and 1150°, and yellow ( $c$ ) at 1150—1200°.  $b$  is space-centred cubic, resembling Mg<sub>3</sub>N<sub>2</sub>.  $a$  is either hexagonal or simple tetragonal. When H<sub>2</sub> is passed over Ca<sub>3</sub>N<sub>2</sub> a yellowish-green compound, containing H, probably CaNH, and having a cryst. structure similar to CaO, is formed. A. J. M.

**Crystal orientation in spherulites.** W. JANSEN (Z. Krist., 1933, 85, 239—270).—X-Ray examination of ten spherulitic minerals shows that the axis of the constituent fibres always coincides with a crystallographic axis, with but very slight distortion. The precise axis depends on the direction of most rapid growth and is in accordance with the Gross-Möller selection principles. Wavellite, 4AlPO<sub>4</sub>·2Al(OH)<sub>3</sub>·9H<sub>2</sub>O, rhombic, has  $a$  7.27,  $b$  14.41,  $c$  10.80 Å., with 2 mols. in the unit cell. Salol, rhombic, has  $a$  11.24,  $b$  11.62,  $c$  8.08 Å. C. A. S.

**X-Ray study of opals, silica glass, and silica gel.** I. LEVIN and E. OTT (Z. Krist., 1933, 85, 305—318; cf. A., 1925, ii, 638; 1932, 451). C. A. S.

**Macromolecular lattice of polyethylene oxide.** E. SAUTER (Z. physikal. Chem., 1933, B, 21, 161—185).—X-Ray examination of polyethylene oxide fractions of mol. wt. 2400—100,000 has shown them all to have the same macromol. lattice. The eucolloidal oxide of mol. wt. 100,000 gives a fibre diagram when stretched. The macromol. lattice has  $b$  19.5,  $a$  9.5,  $c$  12.0 Å.,  $\beta$  101°, the unit cell is simple primitive, and the probable space-group  $C_{2h}^1$ . There are 36 primary mols. in the basal cell. The polyethylene oxide principal valency chain in the cryst. state has the "meander" form deduced from viscosity data; a model is suggested. R. C.

**Model of principal valency chain in macromolecular lattice of polyoxymethylenes.** E. SAUTER (Z. physikal. Chem., 1933, B, 21, 186—197).—The model has been deduced from a consideration of the arrangement of the primary mols. in the principal valency chains of polyethylene oxides (cf. preceding abstract). It accounts qualitatively for the intensity relations of the X-ray diagram and for the conversion of trioxy- into polyoxy-methylene. R. C.

**Crystal structure of phenyldiphenyl.** E. HERTEL and G. H. RÖMER (Z. physikal. Chem., 1933, B, 21, 292—296).—The space-group is  $C_{2h}^2$ , and the unit cell, which contains 2 mols., has  $I_a$  8.14,  $I_b$  5.64,  $I_c$  14.1 Å.,  $\beta$  105°. In the mol. the three C<sub>6</sub> nuclei are coplanar and lie in a straight line in the direction of the  $c$  axis. R. C.

**X-Ray fibre diagram as a quantitative measure of change in structural units of cellulose fibre caused by chemical processes.** K. HESS and C. TROGUS (Z. physikal. Chem., 1933, B, 21, 349—352; cf. A., 1932, 234).—Polemical against Schramek (this vol., 452). X-Ray fibre diagrams cannot be used for the above purpose. R. C.



**Law of discontinuous distribution of Curie points.** II. R. FORRER (J. Phys. Radium, 1933, [vii], 4, 186—209; cf. A., 1932, 449, 452; this vol., 556).—Application of the law to a large no. of ferromagnetics of known crystal lattice enables their electronic orientation lattice to be determined, and in certain cases, the direction for optimum magnetisation. Vals. of the function  $\Theta$  for the limiting range of alloys as solid solutions, and the relation to efficacious contacts of the grouping of Curie points, are considered; their relation to the significance of solid solution is discussed. N. M. B.

**Magnetism and crystal distortions. X-Ray investigations of  $\alpha$ -iron.** F. REGLER (Z. Physik, 1933, 82, 337—354).—Changes in the crystal lattice due to magnetisation were observed; they vary with the intensity of the magnetic field and the state of strain of the crystal. A. B. D. C.

**Magnetic properties of metals at low temperatures.** W. J. DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 263—270; cf. this vol., 14).—In general, the susceptibility of diamagnetic metals increases as temp. is lowered, but, excepting Cd, shows little change between 20.4° and 14.2° abs., whereas with paramagnetic metals a marked change occurs in this region. F. L. U.

**Change of resistance of metals in a magnetic field at low temperatures.** W. J. DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 253—262; cf. this vol., 14).—The resistance of pure metals and alloys in a magnetic field has been measured at 14—77° abs. The effect of impurities on change of resistance is greater at low temp. than at high. F. L. U.

**Selective lattice distortion in wires under torsion.** W. A. WOOD (Nature, 1933, 131, 842).—Lattice distortion has been detected in Cu and Ni wires under torsion, by X-ray diffraction. L. S. T.

**Plasticity in single crystals.** H. SCHLECHTWEG (Physikal. Z., 1933, 34, 404—407).—The classical method of calculating plasticity fails when considering single crystals. The phenomenon of plastic slipping in a single crystal can be explained without assuming a mosaic structure by means of a combination of the Polanyi theory and the Prandtl model of a solid body based on the kinetic theory. A. J. M.

**Stretching of tin crystals.** J. OBINATA and E. SCHMID (Z. Physik, 1933, 82, 224—234).—A redetermination of the translation system of white Sn confirmed earlier results (Polanyi and Schmid, A., 1925, ii, 752). No simple relation was observed between rigidity and translation, and at higher temp. behaviour of the crystal indicated no transition point. A. B. D. C.

**Tensile strength of mica and the problem of technical strength.** E. OROWAN (Z. Physik, 1933, 82, 235—266).—The discrepancy between the technical and theoretical tensile strengths of mica is shown to be due not to internal flaws, but to fissures on the boundaries of the crystals; eliminating these gave a tensile strength of 32,000 kg. per sq. cm. A. B. D. C.

**Breakdown strength of the thinnest Ta<sub>2</sub>O<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub> layers in relation to layer thickness.** H. BETZ (Z. Physik, 1933, 82, 644—649).—An extension of Just's work (cf. this vol., 555) using Cu, Al, Zn, Mg, W, and Ta as electrodes. A. B. D. C.

**Diffraction of light by ultra-sound waves.** R. BÄR and F. MEYER (Physikal. Z., 1933, 34, 393—396).—Demonstration experiments are described. A method for determining the wave-length of ultrasonic waves in liquids, making use of a wire grating in a way similar to an ordinary diffraction grating, is given. The results are in good agreement with those obtained by an optical method. A. J. M.

**Mechanism of superconductivity.** C. BENEDICKS (Ann. Physik, 1933, [v], 17, 169—184).—The "phoretic" theory of electrical conductivity in metals is developed to provide an explanation of the facts of superconductivity. Previous objections to the theory are removed. A model illustrating the mechanism of superconductivity and the effect on it of crit. current strength and a magnetic field is constructed. A. J. M.

**Specific heat, m.p., and latent heat of fusion of hydrogen fluoride.** J. DAHMLOS and G. JUNG (Z. physikal. Chem., 1933, B, 21, 317—322).—Sp. heats of solid and liquid HF have been measured at 98—273° abs. The latent heat of fusion of 20 g. of HF is 1094 g.-cal. R. C.

**Exact measurement of specific heats at higher temperatures. XI. Variability of specific heats of fused and solidified silver.** F. M. JAEGER, E. ROSENBOHM, and W. A. VEENSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 291—298; cf. this vol., 343).—Anomalies in the sp. heat of Ag have been traced to the presence of O. The measurements show that O<sub>2</sub> absorbed by the liquid metal is not completely given off on solidification. True vals. of  $C_p$  and  $C_v$  from 0° to 800° are given. F. L. U.

**Determination of the specific heat, specific heat ratio, or the equation of state of a gas from the velocity of sound. Velocity of sound in gaseous helium at the temperature of liquid hydrogen.** A. VAN IJTERBEEK and W. H. KEESOM (Comm. phys. Lab. Leiden, 1932, No. 209, 19—31; Chem. Zentr., 1933, i, 29).

**Estimation of latent heats of vaporisation.** J. H. ARNOLD (Ind. Eng. Chem., 1933, 25, 659—661).—A review of available calorimetric data shows that the Dieterici equation  $M\lambda = P(V_2 - V_1) + CRT \times \log_e (V_2/V_1)$  is trustworthy to within 5% from room temp. to the crit. point;  $M$  is the mol. wt.,  $\lambda$  the total latent heat, and  $V_2$  and  $V_1$  are the molal vols. of the vapour and liquid, respectively.  $C$  is always near to 1.70 at low temp., but varies from 1.66 to 1.86 at higher temp. A. G.

**Purification and physical properties of organic compounds. I. Interpretation of time-temperature curves in f.-p. determinations and as a criterion of purity.** E. L. SKAU (Proc. Amer. Acad. Arts Sci., 1933, 67, 551—576).—An apparatus which permits manipulation of the sample in vac. is described. The interpretation of the curves is dis-



cussed and the relative merits of comparative and non-comparative criteria are examined. CH. ABS.

**Purification and physical properties of organic compounds. II.** F.p. of thermometer calibration standards for low temperatures. E. L. SKAU (J. Physical Chem., 1933, 37, 609—614; cf. preceding abstract).—The vals. were:  $\text{CCl}_4$   $-22.8_5^\circ$ ,  $\text{PhCl}$   $-45.2_0^\circ$ ,  $\text{CHCl}_3$   $-63.4_5^\circ$ ,  $\text{EtOAc}$   $-83.6_0^\circ$ ,  $\text{CS}_2$   $-111.8_5^\circ$ ,  $\text{Et}_2\text{O}$  (stable)  $-116.3^\circ$ ,  $\text{Et}_2\text{O}$  (unstable)  $-123.3^\circ$ , methylcyclohexane  $-126.3_5^\circ$ . H. J. E.

**Joule-Thomson effect and heat capacity at constant pressure for ammonia.** K. C. SU and T. C. HUANG (J. Chinese Chem. Soc., 1933, 1, 1—9).—A modification of the Scatchard equation (A., 1931, 295) is developed, expressing  $\mu C_p$  and  $C_p$  as functions of  $p$  and  $T$  ( $\mu$ , Joule-Thomson coeff.;  $C_p$ , heat capacity at const.  $p$ ). Vals. for  $\mu$  and  $C_p$  calc. for  $\text{NH}_3$  between 0 and 20 atm. and  $0^\circ$  and  $150^\circ$  agree with experimental vals. for  $\mu$  above  $30^\circ$  and for  $C_p$  above  $100^\circ$ . H. J. E.

**Equation of state of unimolecular films.** J. GUASTALLA (Compt. rend., 1933, 196, 1376—1378).—Superficial pressure,  $P$ , is regarded as the resultant of the kinetic pressure of the mols. of the film,  $RT/Nl^2$  ( $N$  is Avogadro's no., and  $l$  the distance between adjacent mols.); of pressure caused by interaction of the mols. of the film due to their dipolarity,  $=6.3m^2/l^5$ , where  $m$  is the electric moment; and of that due to change in capillary tension of the  $\text{H}_2\text{O}$  below the film caused by its electric field, which may be represented by  $-B/l^3$ . The equation of state takes the form  $P=Al^{-5}-Bl^{-3}+Cl^{-2}$ . C. A. S.

**Influence of intensive desiccation on certain physical properties of benzene.** A. W. C. MENZIES and D. A. LACOSS (Proc. Nat. Acad. Sci., 1933, 19, 393—396).—Using an improved isotenoscope the v.p. near  $80^\circ$  of superdried  $\text{C}_6\text{H}_6$  in absence of dust was markedly lower after drying at room temp., and slightly raised after drying above  $80^\circ$ . The max. const. rise after 20 months' drying was  $2.2^\circ$ . The v.p. reverted to normal on admission of air. In the sealed apparatus no reversion was shown on keeping at room temp. Samples the b.p. of which had been raised  $0.4^\circ$  by drying at room temp. reverted after heating at  $78^\circ$  out of contact with  $\text{P}_2\text{O}_5$ ; a sample similarly raised  $2.2^\circ$  showed no reversion after heating at  $150^\circ$  for 9 days. N. M. B.

**Vapour pressure of caesium.** J. H. DE BOER and C. J. DIPPEL (Z. physikal. Chem., 1933, B, 21, 273—277).—The various published equations for the v.p. of Cs are critically reviewed. R. C.

**Vapour pressure of cadmium oxide.** W. B. HINCKE (J. Amer. Chem. Soc., 1933, 55, 1751—1753).—The v.p. of  $\text{CdO}$  in the range  $1140$ — $1311^\circ$  abs. is given by  $\log_{10} p_{\text{mm.}} = 9.59 - 12,150/T$ , from which the mol. heat of vaporisation is  $55,600$  g.-cal. The normal sublimation point is  $1813^\circ$ . J. G. A. G.

**Vapour pressure of corrosive substances.** K. ARII (Sci. Rep. Tôhoku, 1933, 22, 182—199).—The v.p. of  $\text{POCl}_3$ ,  $\text{TiCl}_4$ , and  $\text{SOCl}_2$  have been determined by means of a glass spring manometer at temp. from  $20^\circ$  to their respective b.p. Results show that these are normal liquids. A. J. M.

**Physical constants of organic liquids at low temperatures.** T. TONOMURA (Sci. Rep. Tôhoku, 1933, 22, 104—130).—The densities of  $\text{Pr}^n\text{OH}$ ,  $\text{Bu}^n\text{OH}$ ,  $\text{C}_3\text{H}_5\text{OH}$ ,  $\text{PhMe}$ , and  $\text{COMeEt}$ , and the viscosities of  $\text{Et}_2\text{O}$ ,  $\text{COMe}_2$ ,  $\text{EtOH}$ ,  $\text{Pr}^n\text{OH}$ ,  $\text{Pr}^i\text{OH}$ ,  $\text{Bu}^n\text{OH}$ , and  $\text{Bu}^i\text{OH}$ , were determined over the temp. range  $0^\circ$  to  $-100^\circ$ . The surface tensions of  $\text{Et}_2\text{O}$ ,  $\text{COMe}_2$ ,  $\text{MeOH}$ , and  $\text{PhMe}$ , determined by the method of capillary rise at temp. between  $0^\circ$  and  $-100^\circ$ , obeyed the Eötvös law satisfactorily with the exception of  $\text{MeOH}$ , for which an empirical relationship is put forward. A. J. M.

**Application of the law of mathematical probability to the behaviour of gases in their pressure-volume-temperature relations.** G. A. LINHART (J. Physical Chem., 1933, 37, 645—653). H. J. E.

**Viscosity of gases and other problems on the kinetic theory.** N. GERASIMOV (Physikal. Z., 1933, 34, 387—388).—Mathematical. A. J. M.

**Viscosity anomalies of self-separating systems. II. Structure viscosity of mesomorphic fusions.** W. OSTWALD and H. MALSS (Kolloid-Z., 1933, 63, 192—203; cf. this vol., 456).—Cholesteryl acetate, propionate, and butyrate exhibit at temp. above their respective clearing points a normal viscosity coeff. independent of rate of shear. When cooled to the temp. at which the liquids become anisotropic there is a sudden rise in the val. of the coeff., and at  $1$ — $2^\circ$  lower a sudden fall. The viscosity-temp. curve then resumes a normal course. At temp. between the clearing and m.p. the viscosity varies with the rate of shear. Et  $p$ -azoxybenzoate may become rigid in the region in which the others show variable viscosity, but its behaviour is complicated by hysteresis effects. The phenomena closely resemble those observed with binary liquid mixtures near their crit. unmixing temp. F. L. U.

**Viscosity of gases at high temperatures.** P. BRÉMOND (Compt. rend., 1933, 196, 1472—1474).—The coeffs. of viscosity of air and  $\text{CO}_2$  determined experimentally for temp.  $0$ — $1134^\circ$  by application of Poiseuille's law agree with those deduced from Breitenbach's vals. for Sutherland's const. (cf. A., 1899, ii, 403), the average differences being  $1.16$  and  $1.39\%$  respectively. C. A. S.

**Viscous damping of vibrating metal bars.** K. SEZAWA (Nature, 1933, 131, 803).—The coeff. of solid viscosity in c.g.s. units is  $7.5$ — $8.0 \times 10^6$  for duralumin,  $5.9$ — $6.8 \times 10^6$  for Al,  $9.3$ — $11.6 \times 10^6$  for Cu, and  $12.7$ — $15.0 \times 10^6$  for brass. The coeff. varies with amplitude of vibration. L. S. T.

**Effect of water vapour on the diffusion coefficients of ions in nitrogen and oxygen.** J. J. NOLAN and A. C. GALVIN (Proc. Roy. Soc., 1933, A, 140, 452—456; cf. A., 1930, 658).—The vals. for the diffusion coeffs. of ions in  $\text{N}_2$  containing various amounts of  $\text{H}_2\text{O}$  vapour do not show the type of oscillation previously found with air (*loc. cit.*). When observations are made in  $\text{O}_2$  the oscillations reappear. The effects in air and  $\text{O}_2$  are attributed to the formation of  $\text{O}_3$  and oxides of N by the action of the  $\alpha$ -particles. L. L. B.



**Liquid-vapour composition curves of acetic acid and water at sub-atmospheric pressures.** D. B. KEYES (Ind. Eng. Chem., 1933, 25, 569).—For mixtures which contain > 50 mol.-% H<sub>2</sub>O the composition of the vapour phase at reduced pressures is nearer that of the liquid phase than at atm. pressure.

A. G.

**Application of Henglein's equation to solutions and mixtures.** V. KIREJEV (Z. Elektrochem., 1933, 39, 268—269; cf. A., 1920, ii, 732).—The equation  $\log T_1 = a \log T_2 + b$  is shown to apply to the b.p. of solutions and mixtures. The b.p. of H<sub>2</sub>O-COMe<sub>2</sub> mixtures are recorded.

H. J. E.

**Specific heats of aqueous solutions of potassium *n*-octoate at 15°.** D. G. DAVIES (J.C.S., 1933, 551—552; cf. A., 1932, 1091).—Sp. heats have been measured at 13.5—16.5° at concns. up to 20%. There is a break in the sp. heat-concn. graph between 6 and 8%, which is the crit. concn. for micelle formation according to *d*, f.p., and dew-point data.

H. J. E.

**Influence of small amounts of acids on the refractive index of liquid mixtures.** T. TOMONARI (Angew. Chem., 1933, 46, 269—271).—The *n* of MeOH-COMe<sub>2</sub> and MeOH-cyclohexanone mixtures increases with the addition of small amounts of HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, or AcOH. The increase is linear up to about 0.3% HNO<sub>3</sub>, after which little further change occurs. The position of the break in the curve is independent of the composition of the mixture, except with AcOH, in which it is not so well defined. No break is observed when these acids are replaced by NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub>, or Ca(NO<sub>3</sub>)<sub>2</sub>, but the behaviour of AgNO<sub>3</sub>, when kept for some days under the influence of light, is similar to that of HNO<sub>3</sub>. A similar effect is obtained with a by-product of the nitration of cellulose.

E. S. H.

**Validity of Raoult's law in molten solutions of lead chloride and lead bromide.** J. SHRAWDER, jun. (J. Amer. Chem. Soc., 1933, 55, 1975—1976; cf. A., 1931, 309).—Polemical against Jelinek and Golubovski (A., 1930, 849).

J. G. A. G.

**Determination of the vapour pressures of amalgams by a dynamic method.** J. S. PEDDER and S. BARRATT (J.C.S., 1933, 537—546; cf. A., 1930, 4).—The partial pressure of Hg over Cd amalgams (16.88—84.93 mol.-% Hg) at 283.5°, over Zn amalgams (43.5—83.7 mol.-% Hg) at 284°, over K amalgams (4.3—42.8 mol.-% K) at 300°, and that of K and Hg over K amalgams (41.1—72 mol.-% K) at 387.5° were measured by a flow method. From the abnormal slope of the K partial pressure-composition graph at 387.5°, the formation of a compound, probably KHg, in the vapour phase is inferred.

H. J. E.

**Diffusion in crystals.** G. VON HEVESY (Naturwiss., 1933, 21, 357—362).—A summary.

A. J. M.

**Self-diffusion in solid lead.** W. SEITH and A. KEIL (Z. Metallk., 1933, 25, 104—106).—By two different methods using Th-B as radioactive indicator the rate of self-diffusion in Pb at 106° and 324° has been calc. to be  $1.45 \times 10^{-11}$  and  $4.58 \times 10^{-5}$  sq. cm. per day. The temp. coeff. is given by  $D = 5.76 \times$

$10^5 \cdot e^{-14,025/T}$ ; from this it follows that the heat of loosening of the Pb lattice is 27,870 g.-cal. The self-diffusion appears to be independent of the crystal structure of the specimen.

A. R. P.

**Grain boundary effects as a factor in heterogeneous equilibrium of alloy systems.** A. PHILLIPS and R. M. BRICK (J. Franklin Inst., 1933, 215, 557—577).—X-Ray observations on Cu-Al alloys show that for fine- and coarse-grained wires and powder the lattice const. of a single crystal is larger than that of a polycryst. aggregate. The time for complete pptn. in the single crystal is much longer than in polycryst. alloys of the same composition (cf. Wiest, A., 1932, 330).

N. M. B.

**Relation between mean atomic volume and composition in silver-zinc alloys.** E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1933, A, 140, 344—358).—Ag-Zn alloys in the  $\alpha$ -phase region were prepared by the process of interdiffusion, and the mean at. vols. of the different phases at 380° studied by means of the X-ray precision camera. As in the Cu-Zn system, the mean at. vol. at a const. temp. changes almost linearly with composition, decreasing with increasing Zn content in the  $\alpha$ -,  $\gamma$ -, and  $\delta$ -regions. That of both phases in the mixed regions, however, remains const. The results form the basis of the determination of the positions of phase boundaries.

L. L. B.

**Thermoelectric properties of platinum-rhodium alloys.** F. R. CALDWELL (Bur. Stand. J. Res., 1933, 10, 373—380).—The thermal e.m.f. and thermoelectric powers of Rh and Pt-Rh alloys against pure Pt have been determined between 0° and 1200°. The results are compared with published data.

J. W. S.

**Röntgen analysis of the systems iron-boron, cobalt-boron, and nickel-boron.** T. BJURSTRÖM (Arkiv Kemi, Min., Geol., 1933, 11 A, No. 5, 1—12).—X-Ray analysis of the systems containing 0—20% B indicates the existence of Fe<sub>2</sub>B, FeB, Co<sub>2</sub>B, CoB, and Ni<sub>2</sub>B. Fe<sub>2</sub>B, Co<sub>2</sub>B, and Ni<sub>2</sub>B form space-centred tetragonal crystals with space-group  $D_{2h}^{18}$  and 4 mols. in the unit cell; *a* and *c* (in Å.) are: 5.099, 4.240 for Fe<sub>2</sub>B; 5.006, 4.212 for Co<sub>2</sub>B; 4.980, 4.236 for Ni<sub>2</sub>B. FeB and CoB are rhombic, with space-group  $V_6^{16}$  and 4 mols. per unit cell; *a*, *b*, and *c* are 4.053, 5.495, and 2.946 Å. for FeB, and 3.948, 5.243, and 3.037 Å. for CoB. Detailed structures are deduced.

D. R. D.

**Influence of nickel and silicon on the miscibility gap of the system Fe-Cu in the solid state (20°).** F. ROLL (Z. anorg. Chem., 1933, 212, 61—64).—The solubility of Cu in Fe is increased more by Ni than by Si. The alloys contained 0.8—2% of C. Sections of the ternary diagrams are given.

H. J. E.

**Influence of a third metal on the constitution of brasses.** V. Manganese. O. BAUER and M. HANSEN (Z. Metallk., 1933, 25, 17—22).—The system Mn-Zn-Cu in the range 70—50% Cu and 0—6% Mn has been investigated by thermal methods and micrographic examination. The solidus is similar to that of binary Zn-Cu alloys. The peritectic reaction  $\alpha + \text{liq.} \rightleftharpoons \beta$ , which occurs at 905° in the



Zn-Cu system, takes place at slightly lower temp. on addition of Mn, the max. lowering being  $45^\circ$  with 5.5–7% Mn according to the Cu content. Mn displaces the  $(\alpha + \beta)$ -boundary further from the Cu side, and in alloys containing  $\beta$  causes the separation of a Mn-rich phase below  $375^\circ$  when the Mn is  $> 4$ –4.7%, since Mn is much less sol. in  $\beta$ -brass than in  $\alpha$  and its solubility in  $\beta$  decreases rapidly with fall in temp. A. R. P.

**Fluidity of ternary alloys.** A. PORTEVIN and P. BASTIEN (Compt. rend., 1933, 196, 1396–1398; cf. B., 1933, 24).—For a difference of  $100^\circ$  between the temp. of pouring and that of the commencement of primary crystallisation, the flowability of Sn-Bi, Bi-Pb, and Pb-Sn alloys follows the laws previously enunciated. The data for the ternary alloys Sn-Bi-Pb show that the flowability is a max. for the ternary eutectic. The limits of solid solution have been revised (cf. A., 1903, ii, 77). C. A. S.

**Ternary system aluminium-antimony-magnesium.** W. GUERTLER and A. BERGMANN (Z. Metallk., 1933, 25, 81–84, 111–116).—In the binary Al-Sb system the solidus rises slowly to a max. at 82% Sb corresponding with the formation of AlSb, which, however, appears to dissociate at the m.p., since free Al occurs as minute particles in air-cooled alloys containing  $> 82\%$  Sb. AlSb is rapidly decomposed by moisture, becoming first brown and then falling to a grey powder; it forms an ill-defined eutectic with Al at  $657^\circ$  and  $< 2\%$  Sb and a well-defined eutectic with Sb at  $623^\circ$  and  $< 1\%$  Al. In the ternary system Al-Mg-Sb no ternary compound is formed and the following quasi-binary systems exist: (A)  $\text{Al}_3\text{Mg}_4\text{-Mg}_3\text{Sb}_2$ , (B)  $\text{Al}_3\text{Mg}_2\text{-Mg}_3\text{Sb}_2$ , (C)  $\text{Mg}_3\text{Sb}_2\text{-AlSb}$ , (D)  $\text{Al-Mg}_3\text{Sb}_2$ . In D there is a miscibility gap extending from 9 to 98%  $\text{Mg}_3\text{Sb}_2$  and in the ternary system this extends to 41% Mg in the Mg corner and to 73% Sb in the Sb corner. Binary eutectics occur in all the quasi-binary systems and ternary eutectics in the quasi-ternary systems:  $\text{Al}_3\text{Mg}_4\text{-Mg}_3\text{Sb}_2\text{-Mg}$ ,  $\text{Al}_3\text{Mg}_2\text{-Al}_3\text{Mg}_2\text{-Mg}_3\text{Sb}_2$ ,  $\text{Al-AlSb-Mg}_3\text{Sb}_2$ , and  $\text{AlSb-Sb-Mg}_3\text{Sb}_2$ , but not in  $\text{Al}_3\text{Mg}_2\text{-Al-Mg}_3\text{Sb}_2$ . A. R. P.

**Ternary system cobalt-chromium-tungsten.** W. KÖSTER (Z. Metallk., 1933, 25, 22–27).—The system contains a ternary eutectic between the  $\alpha$ ,  $\gamma$ , and  $\delta$  phases at  $1380^\circ$  (Cr, 25, W 25.5, Co 49.5%); in the eutectic the  $\alpha$  phase is a solid solution containing Cr 32, W 33, Co 35%, and the  $\gamma$  phase a solid solution containing Cr 24, W 18, Co 58%. The temp. at which  $\alpha$  separates in the Co-Cr system is raised by addition of W from  $1271^\circ$  to  $1330^\circ$ . At  $1330^\circ$  the ternary peritectic reaction  $\alpha + \gamma + \delta = \eta$  occurs, the  $\eta$  phase containing Cr 27, W 36, Co 37%. The reactions in the solid state are very complex; equilibrium diagrams for const. W contents of 0, 5, 15, 20, 30, and 40% W and a space model of the ternary system are shown. Alloys in the  $\gamma + \delta$  field can be age-hardened by quenching from  $1300^\circ$  and ageing at  $800$ – $900^\circ$ ; a max. Brinell hardness of 600 is obtained in this way with alloys containing 5% W and 45% Cr or 30% W and 10% Cr. A. R. P.

**Equilibrium in liquid systems of three components.** W. T. REDBURN and W. N. SHEARER

(J. Amer. Chem. Soc., 1933, 55, 1774–1779).—Miscibility data, chiefly at  $25^\circ$ , are recorded for the ternary systems  $\text{H}_2\text{O}$ -halogen acid-org. liquid. The mutual solubility of  $\text{H}_2\text{O}$  with isoamyl alcohol,  $\text{Bu}^n\text{OH}$ , and cyclohexanone is increased by  $\text{HCl} < \text{HBr} < \text{HI}$  and the results agree qualitatively with Harkins' theory of miscibility. J. G. A. G.

**Rate of dissolution of oxygen in alcoholic solutions of anhydrous stannous chloride.** S. MIYAMOTO and E. UTUNOMIYA (J. Sci. Hiroshima Univ., 1933, 3, 193–208; cf. this vol., 233).—The rate of absorption is better explained on the author's theory than on the diffusion layer theory. At low concns. the rate of dissolution is independent of the  $\text{SnCl}_2$  concn. At high concns., the rate of absorption decreases with increase of the concn. J. S. A.

**Solubility of barium nitrate in water.** J. N. FRIEND and W. N. WHEAT (J.C.S., 1933, 501–502).—Data are recorded between  $0^\circ$  and  $95^\circ$ . No evidence for a dihydrate has been obtained (cf. Hirzel, Z. Pharm., 1854, 49). H. J. E.

**Effect of glycine and alanine on the insoluble salts of silver and lead.** H. M. MAPARA and A. M. PATEL (Kolloid-Z., 1933, 63, 291–295).—In the pptn. of the chlorides, bromides, iodides, and chromates of Ag and Pb by addition of a sol. K salt, the amount of glycine or alanine required to prevent pptn. increases with the concn. of the Ag or Pb salt solution, when the amount of the pptg. solution is const. Alanine is the more effective inhibitor. The amount of non-electrolyte required is independent of the vol. of the system. The non-electrolyte does not exert a peptising influence and forms no simple compound with any of the cations present, but a complex compound is probably formed. E. S. H.

**Medium effect of various solvents on silver bromate at  $25^\circ$ .** B. B. OWEN (J. Amer. Chem. Soc., 1933, 55, 1922–1928).—The solubility of  $\text{AgBrO}_3$  in binary mixtures of  $\text{H}_2\text{O}$  with  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{Pr}^n\text{OH}$ ,  $\text{COMe}_2$ , glycol, glycerol, mannitol, and glycine is a linear function of the dielectric const., with a characteristic slope for each alcohol (cf. this vol., 19). The medium effects are characteristic of the non-electrolyte as well as of the dielectric const. and thus Born's simple theory is inadequate. J. G. A. G.

**Solvation of molecules of glucose penta-acetate and cellobiose octa-acetate in organic liquids.** I. SAKURADA and M. TANIGUCHI (Kolloid-Z., 1933, 63, 169–175; cf. B., 1929, 713).—The solubility of the acetates in a series of liquids has been determined, and is seen in most cases to increase with the val. of  $\mu/V$  or  $\mu^2/\epsilon$  ( $\mu$ =dipole moment,  $\epsilon$ =dielectric const.).  $\text{H}_2\text{O}$  and alcohols are exceptions. The viscosity of the solutions at concns.  $> 2\%$  follows Einstein's law. Solvation, calc. from viscosity data, varies from 0 to 0.3 c.c. of solvent per c.c. of acetate. No solvation is observed in non-polar solvents. F. L. U.

**Kinetic proof of the law of Berthelot and Jungfleisch concerning the partition of a substance between two immiscible solvents.** A. SCONZO (Gazzetta, 1933, 63, 186–189).—The simple partition law is derived from the kinetic theory. O. J. W.



**A phenomenon of surface chemistry.** R. DUBRISAY and (MLLE.) P. DROUOT (Compt. rend., 1933, 196, 1392—1394; cf. A., 1932, 460).—When solutions containing NaOH, KOH, or  $N(C_2H_4\cdot OH)_3$  and lauric acid are shaken, the ratio of base to acid in the foam is reduced in comparison with the ratio in the solutions. If a mixture of the acid with two bases is similarly treated, the stronger base accumulates in the foam. C. A. S.

**Determination of dynamic activity of adsorbents.** S. URAZOVSKI and N. SENJUTA (Ukrain. Chem. J., 1932, 7, [Sci.], 228—240).—When air containing  $C_6H_6$  or  $Cl_2$  is passed through a tube filled with adsorbent, the time necessary for attainment of const. wt. is proportional to the dynamic activity of the adsorbent and to the length of the tube. R. T.

**Significance of Freundlich's adsorption isotherm.** B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1933, 8, 120—125).—Theoretical. The isotherm is derived from Gibbs' equation and a two-dimensional equation of state, and the physical meaning of the const. is discussed. F. L. U.

**Adsorption of caesium on calcium fluoride films.** J. H. DE BOER and C. J. DIPPEL [with J. A. OTTEN] (Z. physikal. Chem., 1933, B, 21, 278—291).—The isotherms for the adsorption of Cs vapour on vac.-sublimed  $CaF_2$  at  $20^\circ$  consist of two parts intersecting at an angle. It appears that the formation of a monat. film, in which the most active points of the surface are occupied first, is accompanied by the formation of a polyat. film, varying in thickness from point to point. Ultimately the interlamellar spaces in the  $CaF_2$  fill up, and the second part of the adsorption isotherm corresponds with adsorption on the remaining surface. Reaction between Cs and glass, with formation of  $H_2$  and  $Cs_2O$ , is perceptible at  $100^\circ$  and rapid above  $200^\circ$ . R. C.

**Factors affecting the ratio of adsorption of radium-B and -C on metal.** J. A. CRANSTON and C. BENSON (J. Roy. Tech. Coll., 1933, 3, 52—56).—The ratio of Ra-C to Ra-B adsorbed on Ni from a solution containing these elements increases progressively with decreasing  $p_H$  and is little affected by the electrode potential between the Ni and the solution. The potential of Ni in 0.001N-HCl falls with the time of contact, rapidly at first and then more slowly, reaching an approx. const. val. after 1 hr. A. R. P.

**Adsorption in solutions and physical properties of the solvent. II. Complete adsorption isotherms of binary liquid mixtures.** E. HEYMANN and E. BOYE (Kolloid-Z., 1933, 63, 154—165; cf. A., 1930, 408, 1364; 1932, 639).—Changes in the composition of pairs of miscible liquids caused by adsorption on C have been measured interferometrically. When the apparent adsorption of one component is plotted against the mole fraction, a curve passing through a max. and then descending asymptotically to the composition axis is obtained for mixtures in which one component is much more adsorbable than the other, and in which the heats of wetting of the components differ markedly. When these properties are nearly the same for the two com-

ponents, a curve is obtained which passes through a max., cuts the composition axis, and then passes through a min. In mixtures of  $CCl_4$  with  $C_nH_{2n+1}\cdot OH$  Traube's rule is reversed. F. L. U.

**Interface equilibria and inner equilibria in heterogeneous systems. I. Exchange and charging processes on surfaces of heteropolar crystals. II. Theory of fractional crystallisation.** L. IMRE (Z. physikal. Chem., 1933, 164, 343—363, 364—376).—I. Measurements of the adsorption of Th-B ( $Pb^{++}$ ) on  $PbSO_4$  and  $PbI_2$  at various temp. have been used to calculate the heat of adsorption,  $Q$ ; on  $PbSO_4$  this is approx. half and on  $PbI_2$  one third of the negative heat of dissolution,  $S$ . Theory indicates that for the adsorption of the ions of a heteropolar salt with  $n$  ions  $Q=S/n$ . Extension of this interpretation of  $Q$  to cases where larger amounts of ions are adsorbed, and the surface consequently acquires a charge, permits the calculation of the consts. of the adsorption isotherm in simple systems; the results for  $AgI-Ag^+$  and  $AgI-I^-$  agree with experiment. In these systems the incorporation of the adsorbed ion into the inner layers of the adsorbent may be characterised by the same heat effect as the surface adsorption.

II. The separation of an ion present in small amount with a heteropolar salt with which it forms mixed crystals has been investigated under conditions favourable to rapid crystallisation. If the adsorabilities of the constituents of the mixed crystal are regarded as characterised by their heats of adsorption, the experimental data for partition coeffs. for fractional crystallisation in the systems  $Ra^{++}-BaSO_4$  and  $Pb^{++}-BaSO_4$  are accounted for. If the lattice structures of the salts composing the mixed crystals are very similar, the energy effects for the addition of the various components to the mixed crystals seem to be the same as for addition to the lattices of the pure components. R. C.

**Exchange adsorption and its influence on the solubility of precipitates with ionic lattices in electrolyte solutions.** I. M. KOLTHOFF and E. B. SANDELL (J. Amer. Chem. Soc., 1933, 55, 2170—2171; cf. this vol., 346).—Pptd.  $CaC_2O_4\cdot H_2O$  adsorbs the anions from aq. solutions of alkali iodates, sulphates, and NaOH, and the cations from solutions of  $BaCl_2$  and  $MnCl_2$ . The solubility of the oxalate in the electrolyte solutions is a function of the total surface exposed by the solid. J. G. A. G.

**Adsorption and solution volume. II. Dependence of ionic exchange on dilution.** E. IVANOVA and A. RABINERSON (Kolloid-Z., 1933, 63, 165—169; cf. A., 1929, 999).—Using 10 g. of chernozem soil and solutions containing respectively 100 milliequiv. of NaCl and 10 and 1 of  $Na_2CO_3$ , the exchange adsorption ( $Na^+$  in,  $Ca^{++}$  out) varies with the dilution ( $v$ ) according to  $X=Kv^{-1/n}$ . A dilution effect is absent in the system 1.17 g. Na-kaolin + 2 milliequiv.  $BaCl_2$ . In general, factors which increase adsorption diminish the dilution effect. F. L. U.

**Surface tension of oils.** E. CANALS and RAMAHENNA-RANAIVO (J. Pharm. Chim., 1933, [viii], 17, 505—508).—The surface tensions of sweet almond



oil, olive oil, and cod-liver oil vary linearly with temp., and at the same rate. J. S. A.

**Measurements of the surface tension of solutions of the sodium and potassium salts of higher fatty acids by the ring method.** I. A. LOTTERMOSER and E. SCHLADITZ (*Kolloid-Z.*, 1933, 63, 295—304).—The surface tension-concn. curves for several Na soaps have been determined at temp. between 5° and 90°. The results at temp. below the m.p. of the corresponding fatty acid are not readily reproducible. Comparison of data obtained at the m.p. of the respective fatty acids shows that the surface tension is at a min. when the concn. is about  $10^{-3}$  to  $10^{-4}$  g. per c.c., but the breadth of the min. increases throughout the series palmitate—laurate. As the no. of C atoms increases the min. is reached at a lower concn. of soap. With solutions of K soaps, the results are reproducible at temp.  $10-20^\circ$  < the m.p. of the corresponding fatty acids.

E. S. H.

**Spreading of water on asphalt bitumen and tar.** F. J. NELLENSTEYN and N. M. ROODENBURG (*Kolloid-Z.*, 1933, 63, 339—347).—Measurements of surface tension in the system bitumen- $H_2O$  at different temp. confirm the validity of Antonow's rule. From these data the contact angle of  $H_2O$  against different bitumens is calc. for temp. between 0° and 100°.

E. S. H.

**Wetting of hydrophilic and hydrophobic powders in a system of two non-miscible liquids. II. Adsorption and wetting phenomena with lead glance and zinc blende powders.** E. BERL, B. SCHMITT, and H. SCHULZ (*Kolloid-Z.*, 1933, 63, 327—338; cf. A., 1932, 1200).—Powdered PbS and ZnS become converted partly into sulphates when kept in the air. Cations are adsorbed at the sulphidic portions of the particle, and anions at the parts covered by  $SO_4^{2-}$ . Thus, the S :  $SO_4$  ratio determines the adsorption of flotation agents and the wetting by  $C_6H_6$ . Adsorption of anions leads to the formation of readily sol. adsorption compounds and improvement of the conditions for adsorption of the flotation agent. The conditions are also improved by adsorption of the  $CO_3^{2-}$  of ordinary  $H_2O$  and the sol. components of ZnS powder at the parts covered by  $SO_4^{2-}$ . NaCN,  $Na_2S$ , and  $Na_2CO_3$  reduce the wettability of partly oxidised ZnS and improve that of PbS.

E. S. H.

**Theory of unimolecular adsorbed film.** N. FUCHS (*Z. physikal. Chem.*, 1933, B, 21, 235—241).—From Langmuir's adsorption theory and consideration of the intermol. forces in a unimol. adsorbed film, Langmuir's isotherm has been statistically deduced for linear adsorption. The theory excludes the possibility of a two-dimensional condensation in the adsorbed film.

R. C.

**Structure of unimolecular films. II. Surface films of proteins.** R. J. FOSBINDER and (Miss) A. E. LESSIG (*J. Franklin Inst.*, 1933, 215, 579—591).—For isodisperse proteins having a particle mass > 34,500, spontaneous spreading to form a homogeneous film does not occur if the  $[H^+]$  of the substrate is within the  $[H^+]$  stability range of the

protein. The tryptic digestion of casein and albumin films has been investigated. The  $\alpha$ -keratin type of structure is the probable form of the protein micelles in a close-packed film.

N. M. B.

**Interaction between soot films and oil.** J. H. COSTE (*Nature*, 1933, 131, 691).—The patterns formed when certain oils or substances such as  $CHCl_3$ ,  $PhNO_2$ ,  $NH_2Ph$ , etc. are allowed to fall on a smoked glass surface are described.

L. S. T.

**Sintering phenomena in vacuum-sublimed films of salts.** J. H. DE BOER and C. J. DIPPEL (*Z. physikal. Chem.*, 1933, B, 21, 198—207).—On heating vac.-sublimed films of  $CaF_2$ ,  $BaF_2$ , and  $BaCl_2$ , the lamellar structure sinters together and the total surface area decreases (cf. A., 1931, 1226). The I adsorption isotherms show that the active centres suffer most in this change, which is most marked with  $BaCl_2$  and least with  $CaF_2$ . The sintering increases with rise in temp., but at a given temp. soon ceases. If adsorbed I is already present, it is included. At higher temp. recrystallisation may occur, probably under the influence of  $H_2O$  released from the glass; with sol. films moist air at room temp. causes recrystallisation.

R. C.

**Two-dimensional reactions. I.** S. E. BRESLER, W. W. DRUSCHININ, and D. L. TALMUD (*Z. physikal. Chem.*, 1933, 164, 389—392).—A preliminary qual. investigation of the formation of the ester from cetyl alcohol and myristic acid and of the acetal from cetyl alcohol and palmitaldehyde in the unimol. film at an air- $H_2O$  interface at room temp. is described. The reactions are followed by change in the two-dimensional surface pressure.

R. C.

**Determination of distribution of pores according to their size in filters and ultra-filters.** F. ERBE (*Kolloid-Z.*, 1933, 63, 277—285).—A discussion of the calculation of results obtained by the existing methods.

E. S. H.

**Capillary systems. XIV (2). Dynamics of plasmolysis. I. Mathematical treatment of semipermeable protoplasts.** E. MANEGOLD and C. STÜBER (*Kolloid-Z.*, 1933, 63, 316—323).

E. S. H.

**Capillary systems. XII (2). Calculation of material content of homogeneous filter structures. I. Sphere planes and sphere layers as structural elements of homogeneous sphere lattices.** W. NOWACKI (*Kolloid-Z.*, 1933, 63, 352—353). E. MANEGOLD and W. VON ENGELHARDT (*ibid.*, 353—354).—A criticism on crystallographic grounds (cf. this vol., 458) and a reply.

E. S. H.

**Capillary systems. XII (4). Calculation of material content of heterogeneous structures. I. Material content of regular binary sphere-aggregates of type AB.** E. MANEGOLD and W. VON ENGELHARDT (*Kolloid-Z.*, 1933, 63, 149—154; cf. A., 1931, 1123).

F. L. U.

**Pore statistics and sieve action in ultra-filters and animal membranes.** M. PISA (*Kolloid-Z.*, 1933, 63, 139—148).—The distribution of pore size in natural and artificial membranes has been studied by measuring the rate of flow of liquids at a series of



pressures, in conjunction with determinations of the size of pore groups by the max. bubble pressure method. In "cellafilters" the sieve action cannot be deduced merely from the flow characteristics of the membrane, since the size distribution varies from place to place. The permeability of collodion filters for hæmoglobin increases with the age of the solution used in their prep. Pores of 58  $\mu$  diam., and probably those of 40  $\mu$ , are completely permeable to hæmoglobin. The pore characteristics of amnion and chorion membranes from sheep are little changed by ageing, although in the former they may vary considerably in different pieces of the same membrane.

F. L. U.

**Permeability. Passage of substances through lipin membranes.** J. SIVADJIAN (J. Pharm. Chim., 1933, [viii], 17, 457—461).—Aq. acetates of Zn (I), Pb, Mn, and U (II), at concns. corresponding with max. stability (A., 1887, 767), have been dialysed in collodion-castor oil sacs against  $H_2O$ . Whilst control solutions remain perfectly clear, ppts. form in the sac [greatest with (II), least with (I)] and AcOH is present in the external fluid. In addition to hydrolysis, double decomp. of mixtures such as  $ZnCl_2 + NaOAc$  or the hydrochloride of a local anaesthetic +  $NaOAc$  is also accelerated by the membrane.  $NH_3$  diffuses from a saturated solution of  $AgCl$  in aq.  $NH_3$  and  $AgCl$  separates as crystals  $> 2$  mm. in length.

F. O. H.

**Multiphase equilibria in systems subdivided by membranes.** R. EISENSCHITZ (Z. physikal. Chem., 1933, 164, 393).—The theoretical methods used in a previous paper (*ibid.*, 1932, 162, 216) are compared with those of other authors.

R. C.

**Osmotic systems in which non-diffusing substances may occur.** IV. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 285—291; cf. this vol., 122).—Mathematical.

F. L. U.

**Relative impermeability of plastic sediments for rain-water, spring water, and alkaline solutions.** P. URBAIN (Compt. rend., 1933, 196, 1036—1038).—The observed rates of filtration of (1) rain-water,  $p_H$  5.5; (2) spring water,  $p_H$  7.2, containing 2.1 g. solids (mainly  $CaSO_4$ ) per litre; (3) aq.  $NaOH$ ,  $p_H$  7.2; and (4) aq.  $NaOH$ ,  $p_H$  9.3, through a layer of marl are in the ratio 1 : 28 : 1.6 : 330. The slowness with (1) and (3) is due to adsorption of  $H_2O$  by, and consequent swelling of, the particles of halloysite, which is counteracted more or less by the ions in (2) and (4).

C. A. S.

**Cryoscopic determination of hydration of ions of sodium chloride.** F. BOURION and (MLLE.) O. HUN (Compt. rend., 1933, 196, 1489—1491; cf. this vol., 566).—The hydration of the ions in  $M$ - and  $0.5M$ - $NaCl$  is represented by  $NaCl \cdot 13.2H_2O$  and  $NaCl \cdot 15.6H_2O$ , respectively.

C. A. S.

**Distribution of particle diameters in disperse liquid phases.** C. ROSSI (Gazzetta, 1933, 63, 190—199).—The dispersion of one liquid phase in another is discussed, and is shown to be influenced to a greater extent by the mechanical dispersion process employed than by the physico-chemical factors which characterise the emulsion already formed. Assuming that

the interfacial tension affects the dispersion process and not the stability of the emulsion, then the distribution of the size of the particles should not be uniform, but should follow some statistical law. Using the Boltzmann expression, a formula for the distribution of particle size is derived, which is used to define the degree of dispersion.

O. J. W.

**Indefinite concepts in colloid science.** V. COFMAN (Protoplasma, 1933, 18, 141—152).—Reports of a series of lectures.

A. G. P.

**Preparation of colloidal solutions of the alkali metals.** M. I. GEN, I. L. ZELMANOV, and A. I. SCHALNIKOV (Kolloid-Z., 1933, 63, 263—268).—When the vapours of Na and an org. liquid impinge together on a surface cooled by liquid air a Na organosol is formed. A technical process is also described, in which the vapour of the metal condenses directly in the liquid dispersion medium. By this means sols of Na in xylene and butadiene can be prepared; these may reach a concn. of 0.3% and are stable for several weeks.

E. S. H.

**Colloidal silicic acid.** II. W. D. TREADWELL and W. KÖNIG (Helv. Chim. Acta, 1933, 16, 468—478; cf. this vol., 348).—In the prep. of colloidal silicic acid by electrolysis of Na silicate with a Hg cathode, the  $p_H$  falls continuously, with a step at 11.3 corresponding with the formation of  $Na_2Si_2O_5$ , and finally reaching 3.2 in 0.5M solution. At this stage the product contains no detectable Cl or Na. The time of gelatinisation of a 0.5M solution is a min. (1 hr.) at  $p_H$  5.8. The acidity of all solutions decreases with time, the total decrease (after 260 days) being proportional to the initial acidity. Pptn. of albumin is a min. with solutions containing mainly  $Na_2Si_2O_5$ , and increases rapidly with decreasing  $p_H$ . A curve showing the potentiometric titration of completely desalted silicic acid with  $NaOH$  is given.

F. L. U.

**Relations between the different viscosity formulæ for lyophilic colloids.** I. SAKURADA (Kolloid-Z., 1933, 63, 311—315).—Mathematical.

E. S. H.

**Highly-polymerised compounds.** LXXXII. Viscosities of solutions of derivatives of higher paraffins with branched chains. H. STAUDINGER and R. C. BAUER (Helv. Chim. Acta, 1933, 16, 418—426; cf. this vol., 370).—Measurements have been made with  $C_6H_6$  and  $CCl_4$  solutions of alcohols, acids, esters, and ketones derived from isoparaffins. The sp. viscosity of a 1.4% solution is in all cases proportional to the no. of C atoms in the chain, counting O atoms as C if in the main chain, and is not affected by the presence of a double linking. Temp. coeffs. are also given.

F. L. U.

**Viscosimetric behaviour of heavy-metal ferrocyanides precipitated in dilute solution.** W. D. TREADWELL, W. KÖNIG, and B. ADAM (Helv. Chim. Acta, 1933, 16, 375—382).—Viscosities of 0.01M solutions of various heavy-metal salts, when increasing quantities of 0.01M-alkali ferrocyanide are added, exhibit max. corresponding approx. with stoichiometric proportions of the reacting ions. A time effect may be present owing to the permutite-like character of the ppts. The results are interpreted



on the assumption of growing chains of primary particles giving rise to a network in which liquid is enmeshed.  
F. L. U.

**Viscosity anomalies of self-separating systems. III. Structure viscosity and flow elasticity of sulphur melts and other disperse systems.** WO. OSTWALD and H. MALSS (Kolloid-Z., 1933, 63, 305—310; cf. this vol., 668).—Molten S at 120—150° (below the viscosity max.) exhibits structure viscosity and elastic properties. These effects continue to increase up to 160°, although the abs. viscosity decreases at that temp. Structure viscosity has also been observed in foams of K stearate. These results confirm the colloid nature of such systems.  
E. S. H.

**Effect of slipping on the viscosity of suspensions.** R. EISENSCHITZ (Physikal. Z., 1933, 34, 411—415).—The supposition that a viscous liquid is completely arrested when it comes into contact with a small particle in the liquid is probably not true. If there is complete slip at the liquid-particle interface, the viscosity will be independent of the thickness of the particle, assumed, for purposes of calculation, to be rod-like.  
A. J. M.

**Surface tension of colloidal solutions, and the action of light on soap solutions.** P. L. DU NOTY (Nature, 1933, 131, 689; cf. A., 1932, 333).—The fall in surface tension of colloidal solutions is due to adsorption; in the case of soaps light increases the magnitude of the effect.  
L. S. T.

**Coagulation of colloids from the viewpoint of Smoluchowski's theory. IV. Variation of surface tension during coagulation of manganese dioxide sol.** S. S. JOSHI and A. N. LAL (J. Indian Chem. Soc., 1933, 10, 61—70).—Coagulation of  $\text{MnO}_2$  sol (A., 1921, ii, 642) by  $\text{KCl}$  and  $\text{BaCl}_2$  results in a continuous diminution of  $\gamma$  (except when Na oleate is added). Sucrose has no appreciable effect on the progress of coagulation. The reasons for the discrepancies between calc. vals. and the results of Mukherjee and Mazumdar (A., 1924, ii, 395) are discussed.  
J. L. D.

**Range of orienting forces and the stability of foams and emulsions.** S. E. BRESLER and D. T. TALMUD (Kolloid-Z., 1933, 63, 323—327).—The orientation by surface forces of the quasi-cryst. complexes in liquids, leading to the formation of a quasi-mono-cryst. film, is considered as a factor determining the stability of foams and emulsions. Data for the stability (as a function of time) of (a)  $\text{H}_2\text{O}$  in  $\text{C}_6\text{H}_6$ , (b)  $\text{C}_6\text{H}_6$  in  $\text{H}_2\text{O}$  emulsions in presence of electrolytes and non-electrolytes are given.  
E. S. H.

**Radial precipitation of strontium carbonate.** (MLLE.) S. VEIL (Compt. rend., 1933, 196, 1491—1492; cf. A., 1931, 301).—The Liesegang rings formed by a drop of aq.  $\text{SrCl}_2$  on gelatin impregnated with  $\text{K}_2\text{CO}_3$  are described. They are made up of a series of separate spots, the inner ones connected by radial lines.  
C. A. S.

**Viscosimetric effect in the pasting of starches.** I. W. SECK, F. DITTMAR, and H. BLUME (Kolloid-Z., 1933, 63, 347—352).—Sufficiently conc. pastes

undergo a decrease in viscosity on heating. The effect is more pronounced in potato- than in maize-starch, and is accelerated by stirring. The crit. concn., above which the effect is observed, depends on the kind of starch and on its grain size. The change is not due to mechanical rupture, but to partial conversion into a sol.  
E. S. H.

**Relation of concentration to action of gelatinising agents on starch.** C. E. MANGELS and C. H. BAILEY (J. Amer. Chem. Soc., 1933, 55, 1981—1988).—The effect of aq. solutions of various reagents has been studied by changes in the viscosity at 30° (cf. Ostwald and Frenkel, A., 1928, 122). In general, increased concn. causes an increase in their swelling power. The lyotropic effect of Na salts leads to the series  $\text{Cl} < \text{Br} < \text{I} < \text{CNS} < \text{salicylate} < \text{OH}$ ;  $\text{Cl}^-$  has no measurable effect at any concn.  $\text{NaOH}$  is more effective than  $\text{KOH}$  at concns.  $< 0.3M$ ; there is little difference at  $0.3$ — $0.5M$ , whilst at  $0.75M$ ,  $\text{KOH}$  is the more effective. For the thiocyanates:  $\text{NH}_4 < \text{Na} < \text{K}$  at  $1.4$ — $2M$ ,  $\text{NH}_4 < \text{K} < \text{Na}$  at  $2.2$ — $4M$ , and  $\text{K} < \text{NH}_4 < \text{Na}$  at higher concns. Iodides show  $\text{Na} < \text{K}$  at concns. up to  $2.4M$  and  $\text{K} < \text{Na}$  above this. Microscopical examination indicates that increase in viscosity at the lower concns. is due to the friction between swollen granules; with increased concn., the granules burst and the amylopectin is dispersed (forming a true colloidal system).  
H. B.

**Diffusion coefficient of crystalline trypsin.** H. W. SCHERP (J. Gen. Physiol., 1933, 16, 795—800).—The diffusion coeff. in half-saturated  $\text{MgSO}_4$  at 5° is  $0.020 \pm 0.001$  sq. cm. per day, corresponding with a mol. radius of  $2.6 \times 10^{-7}$  cm. The rate of diffusion of the proteolytic activity is the same as that of the protein-N.  
H. G. R.

**Dielectric constants of aqueous solutions of amino-acids and polypeptides.** M. FRANKENTHAL (Z. physikal. Chem., 1933, B, 21, 310—316).—The results previously reported (this vol., 125) are corr. and compared with those of Devoto (this vol., 447).  
R. C.

**Isoelectric point of proteins.** I. K. O. PEDERSEN (Kolloid-Z., 1933, 63, 268—277).—Electrophoretic measurements with the respiratory proteins of the blood of lower animals show that, contrary to the conclusions of Svedberg and Eriksson (this vol., 171), these substances have different properties. The isoelectric points of 12 proteins are given. The solubility is a min. at the isoelectric point.  
E. S. H.

**Formation of spiral rings in drying gels.** S. GHOSH and S. PRAKASH (Kolloid-Z., 1933, 63, 315).—Spiral structures have been observed at the surface of drying gels of  $\text{Fe}^{III}$  phosphate and arsenate.  
E. S. H.

**Effect of pressure on equilibrium in the system  $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{EtOH}$ .** A. H. LOVELESS and W. WRIGHT (J. Roy. Tech. Coll., 1933, 3, 65—75).—High-pressure apparatus for studying the reaction between  $\text{C}_2\text{H}_4$  and  $\text{H}_2\text{O}$  at high temp. in the presence of a catalyst is described in detail. With an active C catalyst an exothermic reaction occurs at 60 atm. and 200° with the formation of  $\text{COME}_2$ ,  $\text{HCO}_2\text{H}$ , and  $\text{EtOH}$ ; with  $\text{Al}_2\text{O}_3$  catalyst  $\text{MeCHO}$ ,



EtOH, and AcOH are formed. The thermodynamics of the action are discussed. A. R. P.

**Theory of the calculation of dissociation constants from the electrometric titration of acids.** E. SÖDERBÄCK (Arkiv Kemi, Min., Geol., 1933, 11 A, No. 8, 1—48).—The formulæ applicable to an  $n$ -basic acid are deduced on the lines suggested by Auerbach and Smolezyk (A., 1925, ii, 118), avoiding the approximations made by these authors. D. R. D.

**Second dissociation constant of phosphoric acid from 20° to 50°.** L. F. NIMS (J. Amer. Chem. Soc., 1933, 55, 1946—1951).—From e.m.f. measurements of cells of the type

$\text{H}_2|\text{NaH}_2\text{PO}_4(m_1), \text{Na}_2\text{HPO}_4(m_2), \text{NaCl}(m_3)|\text{AgCl}|\text{Ag}$   
 $K_2$  is found to have a max. at 43°. J. G. A. G.

**Amino-nitrogen of proteins. I. Dissociation constants of asparagine.** M. GIORDANI (Annali Chim. Appl., 1933, 23, 159—168).—For  $l$ - $\beta$ -asparagine at 25° the vals. of  $K_A$  and  $K_N$  are found to be  $0.16 \times 10^{-1}$  and  $0.17 \times 10^{-8}$ , respectively. T. H. P.

**Acid strength and its dependence on the nature of the solvent.** W. F. K. WYNN-JONES (Proc. Roy. Soc., 1933, A, 140, 440—451).—Theoretical. The existing data for acids in  $\text{H}_2\text{O}$ , MeOH, and EtOH are in accord with the relation  $\Delta \log K_r \propto \Delta(1/D)$ , where  $K_r$  is the relative strength of an acid and  $D$  the dielectric const. of the solvent. It is suggested that the "intrinsic" strength of an acid is its relative strength in a solvent of infinite  $D$ . On this basis vals. for the intrinsic strengths of several acids are derived by extrapolation. L. L. B.

**Indicator studies of acids and bases in benzene.** V. K. LA MER and H. C. DOWNES (J. Amer. Chem. Soc., 1933, 55, 1840—1864; cf. A., 1931, 584).—An improved technique for the electrometric titration of acids and bases in  $\text{C}_6\text{H}_6$  is described. The vals. of e.m.f. are nearly double those predicted by the Nernst equation (cf. *ibid.*, 1015). Relative strengths of acids and bases in  $\text{C}_6\text{H}_6$  have been determined quantitatively by a colorimetric method, and 16 acid-base systems, including 7 indicators, have been investigated. Whilst the uncharged acids retain the same numerical differences of  $p_K$  in  $\text{C}_6\text{H}_6$  as in  $\text{H}_2\text{O}$ , the indicators exhibit marked changes and their colours show strong salt effects. The extent of salt formation has been determined and it is shown that the action of  $\text{NH}_4\text{Et}_2$  and piperidine in dil. solution is not a sp. indication of the strength of an acid. The indicator properties of Me-red in  $\text{C}_6\text{H}_6$  are anomalous. J. G. A. G.

**Activity coefficients of nitric acid.** F. HARTMANN and P. ROSENFELD (Z. physikal. Chem., 1933, 164, 377—385).—Activity coeffs. have been calc. from f.-p. measurements with solutions containing 0.03—6.6 mols. per 1000 g.  $\text{H}_2\text{O}$ . R. C.

**Properties of electrolytes in the solvent sulphuric acid.** L. P. HAMMETT and A. J. DEYRUP (J. Amer. Chem. Soc., 1933, 55, 1900—1909; cf. this vol., 26).—F.-p. data for  $\text{H}_2\text{SO}_4$  containing  $\text{H}_2\text{O}$ ,  $\text{KHSO}_4$ ,  $\text{NaHSO}_4$ , and  $\text{BaH}_2(\text{SO}_4)_2$  are consistent with the large degree of dissociation of the  $\text{H}_2\text{SO}_4$ . Ionic activity coeffs. are const. over a wide range of concn.,

and the solubility product principle is applicable to the effect of  $\text{H}_2\text{O}$  on the solubility of  $\text{BaSO}_4$  in  $\text{H}_2\text{SO}_4$ . The van 't Hoff factor,  $i$ , for 15 org. bases in pure  $\text{H}_2\text{SO}_4$  has been determined. J. G. A. G.

**Equilibria, complex ions, and electrometric titrations. I. Iodine or bromine in hydrochloric acid.** J. H. FAULL, jun., and G. S. FORBES. II. Iodine, bromine, and hydrobromic acid. Iodine tribromide. G. S. FORBES and J. H. FAULL, jun. (J. Amer. Chem. Soc., 1933, 55, 1809—1820, 1820—1830).—I. From the e.m.f. of cells of the type  $\text{Hg}, \text{Hg}_2\text{Cl}_2|4N\text{-HCl}|4N\text{-HCl} + \text{Br}_2(\text{or I})|\text{Pt-Ir}$  at 25°, vals. of  $K = [\text{I}']^2[\text{Cl}_2]/[\text{I}_2][\text{Cl}']^2$  at high dilution were found to be  $1.67 \times 10^{-27}$  and  $1.05 \times 10^{-27}$  in 4*N*- and 6*N*-HCl, respectively, after correcting for the formation of complex halogen ions and interhalogen compounds. In the presence of  $\text{O}_2$ , the potential of I in HCl is much > the predicted val. owing to ICl formation. If  $\text{O}_2$  is excluded and loss of halogen avoided, the electrometric titration of < 0.1*M*-I with  $\text{Cl}_2$  is accurate to within 0.02% in 2—6*N*-HCl. The anomalous variation of e.m.f. with  $[\text{Br}_2]$  in HCl (cf. A., 1927, 209) is in quant. agreement with calculations in which allowance is made for complex ion and interhalogen compound formation. Electrometric titration of  $\text{Br}_2$  with  $\text{Cl}_2$  is impracticable especially in the presence of ICl. ICl,  $\text{I}_2$  and  $\text{BrCl}_3$  do not exist under the conditions.

II. From e.m.f. data, the  $M$ -potential of  $\text{Br}_2$  is 1.0548 and 0.8706 over a wide range of concn., and vals. of  $K = [\text{Br}_2][\text{I}]^2/[\text{I}_2][\text{Br}]^2$  are  $5 \times 10^{-17}$  and  $8 \times 10^{-18}$ , in 0.974 and 4.72*N*-HBr, respectively, when corr. for complex formation. The corresponding dissociation consts. of IBr (uncorr. for complex formation) are  $2 \times 10^{-8}$  and  $3 \times 10^{-8}$ . Electrometric titrations through the I and IBr points are within 0.01% of stoichiometric and the existence of  $\text{IBr}_3$  (or  $\text{IBr}_4'$ , dissociation const.  $0.3 \pm 0.2$ ) is demonstrated. J. G. A. G.

**Complex ions formed by iodine cyanide with cyanide and iodide ions. Vapour pressure, free energy, and dissociation of iodine cyanide.** D. M. YOST and W. E. STONE (J. Amer. Chem. Soc., 1933, 55, 1889—1895).—From the distribution of ICN between  $\text{CCl}_4$  and  $\text{H}_2\text{O}$ , aq. KI, and aq. KCN the following equilibrium consts. at 25° have been calc.:  $[\text{I}_2\text{CN}']/[\text{ICN}][\text{I}'] = 1.17$ ,  $[\text{I}(\text{CN})_2']/[\text{ICN}][\text{CN}'] = 2.5$ . The v.p. of solid ICN between 25° and 101° is given by  $\log_{10} p_{\text{mm}} = 10.225 - 13.940/2.3026RT$ , and the free energy of formation of gaseous ICN is  $\Delta F^\circ_{298} = 45,940 \pm 1500$  g.-cal. Gaseous  $\text{I}_2$  and  $(\text{CN})_2$  do not react appreciably to form ICN; this agrees with calculations based on the third law of thermodynamics. J. G. A. G.

**Reduction potential of vanadic acid to vanadyl ion in hydrochloric acid solutions.** C. D. CORVELL and D. M. YOST (J. Amer. Chem. Soc., 1933, 55, 1909—1915).—From the e.m.f. of the cell  $\text{Pt}|\text{VOCl}_2(c_1) + \text{HVO}_3(c_2) + \text{HCl}(c_3)|\text{HCl}(c_3)|\text{HgCl}(s), \text{Hg}(l)$ , the reduction potential,  $E$ , of vanadic acid to vanadyl ion in  $M$ -HCl at 25° is  $-1.0216$  volt with reference to the  $M$ - $\text{H}_2$  electrode.  $E$  varies greatly with concn. of HCl, since the activity coeff. of  $\text{HVO}_3$  decreases with the increased solubility of  $\text{V}_2\text{O}_5$  in conc. HCl.



From the temp. coeff. of the e.m.f. between 25° and 33.9°, the change in heat content,  $\Delta H$ , accompanying the reaction  $\text{VO}^{2+} + 2\text{H}_2\text{O}(l) = \text{HVO}_3$  (in  $M\text{-HCl}$ ) +  $3\text{H}^+ + 0.5\text{H}_2$  (1 atm.) is 29,350 g.-cal. J. G. A. G.

**Binary systems : nitrates of metals of group II and water.** II.  $\text{Be}(\text{NO}_3)_2\text{-H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2\text{-H}_2\text{O}$ , and  $\text{Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ . A. SIEVERTS and W. PETZOLD (Z. anorg. Chem., 1933, 212, 49—60; cf. A., 1932, 573).—Solubility data are recorded. The respective eutectic temp. are  $< -90^\circ$ ,  $-32.0^\circ$ , and  $-16^\circ$ .  $\text{Be}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  has a congruent m.p. at  $61.0^\circ$ .  $\text{Zn}(\text{NO}_3)_2\cdot 9\text{H}_2\text{O}$  is stable below  $-17.6^\circ$ ; above  $-17.6^\circ$   $\text{Zn}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ ,  $4\text{H}_2\text{O}$ ,  $2\text{H}_2\text{O}$ , and  $1\text{H}_2\text{O}$  are successively stable. The compounds with 6, 4, and 2 mols.  $\text{H}_2\text{O}$  have congruent m.p. at  $36.4^\circ$ ,  $45.5^\circ$ , and  $54.1\text{--}54.2^\circ$ , respectively. The anhyd. salt has not been observed.  $\text{Cd}(\text{NO}_3)_2\cdot 9\text{H}_2\text{O}$  is stable below  $3.5^\circ$ .  $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  has a congruent m.p. at  $59.5^\circ$ , and  $\text{Cd}(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$  an incongruent m.p. at  $56.8^\circ$ . Above  $56.8^\circ$  the solution is in equilibrium with anhyd. salt. This has not been isolated. H. J. E.

**Crystalline form in the formation of solid solutions.** IX. Thermal analysis of the anhydrous systems  $\text{CoCl}_2\text{-SnCl}_2$  and  $\text{FeCl}_2\text{-SnCl}_2$ . X. Thermal analysis of the anhydrous systems  $\text{CoCl}_2\text{-PbCl}_2$  and  $\text{FeCl}_2\text{-PbCl}_2$ . A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1933, [vi], 17, 312—317, 473—475; cf. A., 1931, 901).—IX. In both systems eutectics occur at about  $240^\circ$  containing 4 mol.-%  $\text{CoCl}_2$  and 2 mol.-%  $\text{FeCl}_2$ , respectively.

X. Eutectics occur at  $424^\circ$  (23.5 mol.-%  $\text{CoCl}_2$ ) and  $421^\circ$  (28.5 mol.-%  $\text{FeCl}_2$ ), respectively. O. J. W.

**Thermal analysis of system  $\text{BCl}_3\text{-Cl}_2$ .** W. GRAFF (Compt. rend., 1933, 196, 1390—1392).—The thermal diagram shows a eutectic at  $-135.4^\circ \pm 0.3$ , and 65.5%  $\text{BCl}_3$ ; there is no evidence of any compound containing more Cl than  $\text{BCl}_3$ . M.p. of  $\text{Cl}_2$   $-103^\circ \pm 0.3^\circ$ ; of  $\text{BCl}_3$   $-108.7^\circ \pm 0.3^\circ$ . C. A. S.

**Active oxides.** LXIV. Alteration in magnetic and X-ray spectroscopic properties during the transformation of a mixture of magnesium oxide and iron oxide into spinel. H. KITTEL, G. F. HÜTTIG, and Z. HERMANN (Z. anorg. Chem., 1933, 212, 209—213; cf. this vol., 560).—Mixtures of  $\text{MgO}$  and  $\text{Fe}_2\text{O}_3$  showed no change of magnetic susceptibility (I) when heated together below  $500^\circ$ . At  $500\text{--}550^\circ$ , (I) increased, but ferromagnetism did not appear below  $600^\circ$ , indicating no spinel formation below this temp. X-Ray examination of crystal structure affords similar results. J. S. A.

**System  $\text{MgSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ .** R. ARDITTI (Compt. rend., 1933, 196, 1388—1390).—Data for  $0^\circ$ ,  $19^\circ$ , and  $35.5^\circ$  show the existence of  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ ;  $\text{MgSO}_4\cdot \text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$ ;  $\text{MgSO}_4\cdot \text{H}_2\text{SO}_4$ ;  $3\text{MgSO}_4\cdot 2\text{H}_2\text{SO}_4$ ; and  $3\text{MgSO}_4\cdot \text{H}_2\text{SO}_4$ , all of which were obtained in cryst. form. C. A. S.

**Thermodynamic studies on potassium and sodium sulphates.** F. L. E. SHIBATA, S. ODA, and S. FURUKAWA (J. Sci. Hiroshima Univ., 1933, 3, 227—242; cf. A., 1932, 573).—For  $2\text{K} + \text{S}$  (rhombic) +  $2\text{O}_2 = \text{K}_2\text{SO}_4$ ,  $\Delta F = -313,524$  g.-cal.;  $\Delta H = -339,662$  g.-cal.; entropy of  $\text{K}_2\text{SO}_4 = 51.5$ . For  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O} =$

$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ ,  $\Delta F = 1612$  g.-cal.;  $\Delta H = -22,290$  g.-cal. For  $2\text{Na} + \text{S}$  (rhombic) +  $2\text{O}_2 = \text{Na}_2\text{SO}_4$ ,  $\Delta F = -301,672$  g.-cal.;  $\Delta H = -330,103$  g.-cal.; entropy of  $\text{Na}_2\text{SO}_4 = 35.0$ . J. S. A.

**Heat of combustion, entropy, and free energy of cyanogen gas.** J. McMORRIS and R. M. BADGER (J. Amer. Chem. Soc., 1933, 55, 1952—1957).—The directly determined heat of combustion of  $(\text{CN})_2$  gas is  $251,400 \pm 1200$  g.-cal. ( $15^\circ$ ), from which the heat of formation is  $H_{298.2} = 62,900$  g.-cal. The entropy of the gas at  $298.2^\circ$  abs. and 1 atm. is  $57.8 \pm 2.0$  e.u. and the free energy,  $F_{298.2} = 60,000$  g.-cal. J. G. A. G.

**Heat of combustion of cyanogen.** H. VON WARTENBERG and H. SCHÜTZ (Z. physikal. Chem., 1933, 164, 386—388).—The heat of combustion at const. pressure is  $261.3 \pm 0.2$  kg.-cal. R. C.

**Heat of formation of compounds between praseodymium and magnesium and between praseodymium and aluminium.** G. CANNERI and A. ROSSI (Gazzetta, 1933, 63, 182—185; cf. A., 1932, 575).—The heats of dissolution of Pr,  $\text{PrMg}$ ,  $\text{PrMg}_3$ , and  $\text{PrAl}_4$  in  $\text{HCl}$  (1 mol./8.808 mols.  $\text{H}_2\text{O}$ ) are 166.7, 271.3, 494.1, and 616.17 kg.-cal. per mol., respectively. The calc. vals. of the heat of formation of the three compounds are 8.2, 11.0, and 52.1 kg.-cal. per mol., respectively. O. J. W.

**Standard states for bomb calorimetry.** E. W. WASHBURN (Bur. Stand. J. Res., 1933, 10, 525—558).—Standard vals. for the temp. and pressure of the reactants and products are suggested. Methods for correcting observed vals. and for calculating the intrinsic energy change for the reaction defined by these standard states are described. H. J. E.

**Conductance of electrolytes.** V. Redetermination of the conductance of standard potassium chloride solutions in absolute units. G. JONES and B. C. BRADSHAW (J. Amer. Chem. Soc., 1933, 55, 1780—1800).—Full details are given for determining the abs. sp. conductance of solutions in cells for which the consts. are determined by resistance measurements when the cells are filled with Hg. The data refer to  $0^\circ$ ,  $18^\circ$ , and  $25^\circ$  and  $\text{KCl}$  solutions containing 71.1352, 7.41913, and 0.745263 g.  $\text{KCl}$  per 1000 g. of solution (in vac.). Vals. of the conductivity are  $0.02\text{--}0.12\%$  > those recorded by Parker (A., 1924, ii, 304). J. G. A. G.

**Electrical conductivity of mixtures of acetic acid with amines.** N. A. PUSHIN and P. S. TUTUNDZIO (Z. Elektrochem., 1933, 39, 305—308; cf. A., 1932, 1197, 1204).—Conductivities of mixtures of  $\text{AcOH}$  with  $\text{C}_5\text{H}_5\text{N}$ ,  $\alpha$ -picoline, 2:4-dimethylpyridine, quinoline, and  $\text{NPhEt}\cdot\text{CH}_2\text{Ph}$  have been measured. All show max. vals. between 80 and 95 mol.-%  $\text{AcOH}$ , decreasing in the above order. Compound formation does not seem to be indicated. H. J. E.

**Simultaneous conduction by electrolytes during the measurement of the resistance of palladium wire containing hydrogen.** C. A. KNORR and E. SCHWARTZ (Z. Elektrochem., 1933, 39, 281—283).—The resistance of a Pd wire charged with  $\text{H}_2$  and immersed in aq.  $\text{H}_2\text{SO}_4$  is at first too low, due to conduction by the electrolyte. The latter quickly



polarises, and the resistance of the wire rises to its true val. Pd uncharged with  $H_2$  does not show the effect. H. J. E.

**Weston standard cells with buffered electrolytes.** R. J. PRIEPKE and W. C. VOSBURGH (J. Amer. Chem. Soc., 1933, 55, 1801—1809; cf. A., 1931, 1129).—The e.m.f. of Weston standard cells with electrolytes at  $p_H$  4.1—4.8 buffered with  $Cd(OAc)_2$  and  $AcOH$  is const. over long periods, and hysteresis due to temp. change is small at  $p_H$  4.1 and  $p_H$  8.1. If  $Hg_2SO_4$  is replaced by basic  $Hg_2SO_4$ , the e.m.f. decreases with decreasing  $H^+$  activity, and an approx. val. of  $p_H$  can be calc. at which basic and normal  $Hg_2SO_4$  exist in equilibrium with saturated  $CdSO_4$ . Cells with a mixture of the normal and basic salts at the  $Hg$  electrode have high e.m.f. if the  $p_H$  is above, but the e.m.f. is normal if the  $p_H$  is below, the transition point. When the layer of  $Hg_2SO_4$  is thin (1—2 mm.) the e.m.f. is variable if the  $p_H$  is below the transition point. The interpretation of these phenomena is discussed. J. G. A. G.

**Cadmium iodide and zinc iodide cells.** A. E. SALZAR (Anal. Univ. Chile, Santiago, 1933, 5—15).—A preliminary report of determinations of the e.m.f. of the cells  $M|aq. MI_2|I$  (where  $M$  is  $Cd$  or  $Zn$ ) at 20—30°. E. S. H.

**Potential [at metallic electrodes] in electrolytes with foreign ions.** V. The halogen electrode. A. SCHMID and P. VÖGELE. VI. Development of potential. A. SCHMID, W. WINKELMANN, and P. VÖGELE (Helv. Chim. Acta, 1933, 16, 366—375, 398—403; cf. this vol., 354).—V. The efficiency of a "diffusion" electrode when used with  $Cl_2$  or  $Br$  varies with the porosity of the material, and the concn. of halogen in the electrolyte is indefinite. Satisfactory measurements are possible when an externally prepared halogen-electrolyte solution is caused to flow at const. speed over a  $Pt$  anode. Experiments with a  $Zn-Br(Pt)$  cell are described, in which the concn. of  $Br$  and electrolyte was const. and other factors were varied. The observed variation of efficiency of the anode with the nature of the electrolyte supports the authors' views on the influence of the oppositely charged ions.

VI. Theoretical. The classical laws governing electrochemical potential are valid only in limiting cases. It is necessary also to recognise the occurrence of a process involving the electromotively active substance and ions of opposite charge, these latter being essential for the development of the max. e.m.f. F. L. U.

**Conductivity and potential measurements with salts of higher alkylsulphuric acids.** A. LOTTER-MOSER and F. PÜSCHEL (Kolloid-Z., 1933, 63, 175—192).—Conductivities of aq. solutions of  $Na$  salts of alkylsulphuric acids containing 12, 14, 16, and 18  $C$  atoms have been determined. The  $\Lambda$ - $c$  curves pass through a max. at high and a min. at intermediate concns., the min. being displaced towards smaller concns. with increasing mol. wt. The free acids behave similarly. Activities of  $Ag^+$  in solutions of the  $Ag$  salts ( $Ag$  salts with  $C_{16}$  and  $C_{18}$ ) show a similar relation to concn. The general behaviour

closely resembles that of  $Na$  or  $K$  soaps, but there is practically no hydrolysis. Salts with bivalent cations are more strongly aggregated than those with univalent. The min. in the surface tension curves (this vol., 458) occurs at concns. at which formation of neutral micelle begins to be marked. F. L. U.

**Free energy of lactic acid oxidation. Scale for biological oxidation-reduction potentials.** A. SZENT-GYÖRGYI.—See this vol., 748.

**Oxidation-reduction potential of ascorbic acid.** K. LAKI.—See this vol., 756.

**Thermoelectric investigations on solid electrolytes.** H. REINHOLD and A. BLACHNY (Z. Elektrochem., 1933, 39, 290—305; cf. A., 1928, 846; 1931, 312).—The thermal e.m.f. of the following chains has been measured:  $Ag|Ag_2S|Ag$ ,  $Ag|Ag_2Se|Ag$ ,  $Ag|Ag_2Te|Ag$ ,  $Cu|CuCl|Cu$ ,  $Cu|CuBr|Cu$ ,  $Cu|CuI|Cu$ ,  $Cu|Cu_2S|Cu$ ,  $Pb|PbBr_2|Pb$ ,  $Pb|PbI_2|Pb$ ,  $Br|PbBr_2|Br$ ,  $Ag|AgCl|PbCl_2|AgCl|Ag$ ,  $Pb|PbCl_2|AgCl|PbCl_2|Pb$ ,  $Pb|PbCl_2|PbBr_2|Pb$ ,  $Ag|AgBr|AgI|Ag$ . Except for chains with  $Ag_2S$ ,  $Ag_2Se$ ,  $Ag_2Te$ , and  $CuS$ , the observed e.m.f. is determined largely by a homogeneous effect, and not by the temp. coeff. of the phase boundary potentials. H. J. E.

**Hydrogen effect.** H. VON HALBAN and G. KORTUM (Z. Elektrochem., 1933, 39, 288—289).—Wolf's experimental results (A., 1932, 1207) are not confirmed. H. J. E.

**Electrolysis of water under pressure.** H. CASSEL and J. VOIGT (Naturwiss., 1933, 21, 331).—The  $H$  overvoltage at a  $Ni$  electrode in the electrolysis of  $N$  solutions of  $H_2SO_4$ ,  $HCl$ , and  $KOH$  with c.d. of 1—10 ma. has been determined at pressures of 1—25 atm. Increase in pressure results in a parallel displacement of the current-potential curve in the direction of decreasing overvoltage. This is in agreement with the theory of Erdey-Gruz and Volmer (cf. A., 1932, 24). A. J. M.

**Structure of electrodeposited alloys. II. Effect of current density and temperature of deposition on the structure of silver-cadmium deposits.** C. W. STILLWELL and H. I. FEINBERG (J. Amer. Chem. Soc., 1933, 55, 1864—1870; cf. A., 1932, 989).—The % of  $Cd$  in the deposit rises with increase of c.d. from 0.1 to 1000 amp. per sq. dm., but decreases with rise of temp. from 27° to 90°. An alloy deposited at low c.d. is more homogeneous than one of the same composition deposited at high c.d., and in the former, the crystals are oriented with respect to the cathode. High c.d. and high temp. favour the formation of (1) non-adherent deposits which contain  $Cd(OH)_2$  and (2) traces of the metastable  $\beta'$ -phase. J. G. A. G.

**Thermal decomposition of ozone.** A. GLISSMANN and H. J. SCHUMACHER (Z. physikal. Chem., 1933, B, 21, 323—348).—The decomp. has been investigated at 70—110° with  $O_3$  at 20—400 mm. and in presence of  $O_2$  at 3—600 mm. The effect of the wall is in general < 10% of the total reaction. A slight decomp. of  $O_3$  starts on the wall, and some reaction chains are also broken there. In absence of  $O_2$  the decomp. is essentially a homogeneous bimol. reaction.  $O_2$  has an accelerating action, which



causes the velocity coeff. to rise as reaction proceeds, and also a retarding action. In explanation of the kinetics of the decomp. it is suggested that there are two independent reactions: (1)  $O_3 + O_3 = 3O_2^*$ , (2)  $O_2 + O_3 = 2O_2 + O$ . (2) is followed by  $O + O_3 = 2O_2^*$ ,  $O + O_2 + M = O_3 + M$ ,  $O_2^* + O_3 = 2O_2 + O$ ,  $O_2^* + O_3 = O_2 + O_3$ ,  $O_2^* + O_2 = 2O_2$ . Insertion in the resulting velocity equation of vals. for consts. derived from data for the photochemical decomp. and for the thermal decomp. under limiting conditions indicates that the above scheme is fundamentally correct. The  $O_2^*$  mols. formed by reaction (1) are capable of secondary activation of further  $O_3$  mols., but this effect is of moment only at high pressures and  $O_3$  concns. He,  $N_2$ , and  $CO_2$  have an accelerating effect which increases in this order, and can be qualitatively interpreted. R. C.

**Mechanism of flame movement. III. Speed of flame in currents of mixtures of methane and air.** H. F. COWARD and E. H. M. GEORGESON (J.C.S., 1933, 546—551).—The effect of current speed on the speed of flame in  $CH_4$ -air mixtures is approx. additive, the increase being slightly  $>$  the mean speed of current but  $<$  the axial speed. J. S. A.

**Ignition temperatures of ammonia-air mixtures.** P. LAFFITTE and H. PICARD (Compt. rend., 1933, 196, 1486—1488; cf. A., 1930, 38).—The temp. decrease from  $960^\circ$  to a min. of  $917^\circ$  to rise to  $1002^\circ$  for mixtures containing respectively 8.9, 23.3, and 57.4%  $NH_3$ . Presence of  $H_2O$  has no effect, but addition of even 1%  $H_2$  lowers the temp. substantially (cf. A., 1913, ii, 478). C. A. S.

**Upper limit in explosive chain reactions.** H. W. MELVILLE and H. L. ROXBURGH (Nature, 1933, 131, 690—691).—Experiments with  $PH_3$ - $O_2$  mixtures show that in the region above the upper limit there is a gradual decrease in the length of the reaction chains as the  $O_2$  pressure is increased (cf. this vol., 355). L. S. T.

**Slow combustion of ethane at high pressures.** D. M. NEWITT and A. M. BLOCH (Proc. Roy. Soc., 1933, A, 140, 426—439).—In the slow combustion of 85—90%  $C_2H_6$  : 15—10%  $O_2$  mixtures at pressures up to 100 atm. each of the six possible "hydroxylation" steps may be represented by one or more of the intermediate products isolated. At 100 atm.  $>$  60% of the C burnt survived as condensable and  $H_2O$ -sol. intermediate products, with EtOH and/or AcOH predominating. The influence of an increase in the reaction pressure is favourable to the survival of products (EtOH, MeCHO, and AcOH) of which the formation does not involve any rupture of the  $C_2H_6$  mol.; a lowering of the pressure favours the formation of MeOH,  $CH_2O$ , and  $HCO_2H$ . L. L. B.

**Decomposition of ozone in aqueous solution.** K. SENNEWALD (Z. physikal. Chem., 1933, 164, 305—317).—The decomp. at  $0^\circ$  in buffer solutions of  $p_H$  5.3—8, in pure  $H_2O$ , and in 0.01—0.5M- $K_2SO_4$  follows the bimol. law. The velocity coeff., the logarithm of which in absence of salts increases linearly with the  $p_H$ , is increased by the presence of a salt by an amount approx. proportional to the salt activity, suggesting that the salt brings about a second bimol.

reaction independent of  $[H^+]$ . Ozonised  $O_2$  on passage through buffer solutions undergoes appreciable decomp. only above  $p_H$  10, but at  $p_H$  14 decomp. is very rapid. Borate promotes the decomp., perhaps owing to the intermediate formation of perborate. R. C.

**Kinetics of the carbon dioxide-carbonic acid reaction.** R. BRINKMAN, R. MARGARIA, and F. J. W. ROUGHTON (Phil. Trans., 1933, A, 232, 65—97).—Manometric and photo-electric methods are described for the measurement of the velocity of the reaction  $CO_2 + H_2O \rightleftharpoons H_2CO_3$ . The change in the nature of the reaction with  $p_H$  (A., 1925, ii, 295) is confirmed, but the velocity coeffs. are considerably  $>$  those observed by Faurholt (e.g.,  $k$  1.70,  $k'$  0.0026,  $k_{CO_2-OH}$  840 at  $0^\circ$ ;  $k$  11.1,  $k'$  0.24,  $k_{CO_2-OH}$  2050 at  $18^\circ$ ). It is calc. that  $H^+ + CO_3^{''} = HCO_3' + 3750$  g.-cal. at room temp. D. R. D.

**Reaction velocity and the "equi-valence-change principle."** P. A. SHAFFER (J. Amer. Chem. Soc., 1933, 55, 2169—2170).—It is suggested, irrespective of activity or free energy decrease, that an oxidation-reduction reaction will not occur as a bimol. reaction if the no. of electrons which may be lost or shared by the reductant is not the same as required by the oxidant. The inactivity of  $Tl_2SO_4$  towards  $Ce(SO_4)_2$  is attributed to the fact that the oxidation of  $Tl^+$  requires the loss of two electrons whilst  $Ce^{+++}$  can accept only one, to give known valency states. The catalysis of this reaction by  $MnSO_4$  is consistent with the theory. J. G. A. G.

**Supersaturation of liquids with gases.** T. N. RICHARDSON and K. C. BAILEY (Nature, 1933, 131, 762).—The velocity coeffs. obtained for the oxidation of  $N_2H_4$  by  $K_3Fe(CN)_6$  are much  $>$  those found by Gilbert (A., 1932, 348) owing to an increase in the rate of evolution of  $N_2$  with rate of stirring up to approx. 1000 r.p.m. This is due to supersaturation of the solution by gas, and the amount of  $N_2$  which may accumulate in the unstirred solution is 7—8 times the normal solubility. Supersaturation may thus invalidate quant. work on chemical kinetics. L. S. T.

**Kinetics of the iodine-oxalate reaction.** N. R. DHAR, A. K. BHATTACHARYA, and B. L. MUKERJI (Nature, 1933, 131, 840—841).—For  $N$ - $K_2C_2O_4$  and  $N/850$ -I the relation between velocity and light intensity varies approx. from  $1/3$  to  $5/4$  for wavelengths between 3500 and 8750 Å. The addition of  $N/277$ -KI decreases the velocity and  $k^{32}/k^{22}$  is 8.84 in the dark. L. S. T.

**Kinetics of the action of iodine on potassium oxalate.** A. BERTHOUD (Helv. Chim. Acta, 1933, 16, 393—398; cf. A., 1931, 1135).—The velocity of the "dark" reaction  $I_2 + K_2C_2O_4 \rightarrow 2KI + 2CO_2$  is approx. given by  $K[C_2O_4^{''}][\Sigma I_2]^{1/2}/[I]^{1/2}$ ,  $\Sigma I_2$  denoting total titratable I. The velocity of the corresponding photochemical change differs only in being  $\propto 1/[I]$ . Possible mechanisms are discussed. F. L. U.

**Velocity of splitting off of chlorine from monochloroacetate.** S. MATUURA (Bull. Chem. Soc. Japan, 1933, 8, 113—120).—In the early stages the hydrolysis of the K or Na salt is unimol. Measurements at 20—35° are recorded. The velocity coeff. is



greatly increased by the addition of KOH or NaOH, and diminished by addition of a neutral salt with a common cation. F. L. U.

**Velocities of hydrolysis of methoxydiphenylketimines.** J. D. CULBERTSON and A. L. BRESSON (Proc. Iowa Acad. Sci., 1931, 38, 169—170).—Velocities of hydrolysis to the corresponding ketones are in the order: 3->4->2-methoxydiphenylketimine HCl, all < diphenylketimine HCl. CH. ABS.

**Velocities of hydrolysis of mono- and polyhydroxydiphenylketimines.** J. B. CULBERTSON and J. L. NAUMAN (Proc. Iowa Acad. Sci., 1931, 38, 170).—The phenolic group in 2- and 4-hydroxydiphenylketimine retards hydrolysis, and in the 3-isomeride facilitates it. CH. ABS.

**Reaction velocity-temperature constant of yeast invertase in supercooled solutions.** Z. I. KERTESZ (Z. physiol. Chem., 1933, 216, 229—232).—The velocity of inversion of sucrose by yeast decreases only slowly below 0°. The Arrhenius const.  $A$  falls rapidly from 11,800 at 0° to 6300 at -3.75° and 1400 at -6.25°. J. H. B.

**Rate of absorption of gases by liquids.** R. C. BRIMLEY (Chem. and Ind., 1933, 472—473).—The rate of dissolution of CO<sub>2</sub> in H<sub>2</sub>O or aq. NaOH is controlled by the low rate of diffusion of CO<sub>2</sub> through the surface layer of the liquid and varies with the age of the surface. The same conclusion can be reached from the data of Dirken and Mook (A., 1930, 799). D. R. D.

**Kinetics of surface processes in crystal lattices. II. Elementary processes in formation of a boundary layer consisting of several components.** L. LIRE (Z. physikal. Chem., 1933, 164, 327—342; cf. A., 1931, 421).—Investigation of the rates of adsorption of Ac from aq. solution on BaSO<sub>4</sub>, PbSO<sub>4</sub>, and BaIO<sub>3</sub> has led to some modification of the theory previously advanced. The supposed "second stage" in the adsorption involves the embodiment of the adsorbate ion in the solid surface layer of the adsorbent. In this process the dehydration equilibrium of the adsorbate ion is established immeasurably rapidly even if the adsorption compound is readily sol. The gradual incorporation of the ion into the lattice is explicable by the theory of crystal growth. R. C.

**Theory of metallic corrosion in the light of quantitative measurements. VI. Distribution of corrosion.** G. D. BENGOUGH and F. WORMWELL (Proc. Roy. Soc., 1933, A, 140, 399—425).—An attempt has been made to estimate the limits, if any, within which the differential aëration principle of corrosion holds. Three of the most important methods of producing differential aëration sufficient to affect corrosion distribution have been used, viz., partial immersion, deposits of corrosion products and neutral bodies, and crevices. Corrosion distribution, on Zn and mild steel in stagnant conditions, is not determined by the rate of O<sub>2</sub> supply but by the distribution of protective films which cause the metal to be locally cathodic to bare, or less completely protected, metal. When the films are widespread, corrosion may be

sufficiently localised to be called "pitting"; when the films are restricted, corrosion may finally cover the whole metallic surface. Factors influencing the character, distribution, and continued adherence of films in the solutions and conditions studied are: alkali distribution (affected by sites of depolarisation by O<sub>2</sub>, creep tendency, and neutralisation by metallic salts or atm. gases), surface tension factors, presence of specially reactive areas at the metal surface, gravity, movement of liquid, alternate wet and dry conditions, presence of certain foreign bodies, and nature of the solution. The average rate of corrosion is often determined by the total rate of O<sub>2</sub> supply to the total surface of both protected and attacked areas, but the intensity of corrosion at any given part is determined by the film distribution. L. L. B.

**Rate of oxidation of monolayers of unsaturated fatty acids.** A. H. HUGHES and E. K. RIDEAL (Proc. Roy. Soc., 1933, A, 140, 253—269).—The rate of oxidation of unimol. films of oleic, Δ<sup>α</sup>-isoleic, cis-petroselic, and chaulmoogric acids by dil. KMnO<sub>4</sub> in 0.01N-H<sub>2</sub>SO<sub>4</sub> has been studied by measurements of the change of surface potentials with time. The reaction velocity decreases with the compression of the film, and depends on the accessibility of the double linking to the oxidising agent. It is also affected by the position of the double linking in relation to the polar CO<sub>2</sub>H head group. α- and β-Elæostearic acids exhibit autoxidation, and the effect of quinol as an antioxygen to this reaction has been examined. L. L. B.

**Rate of dissolution of marble in dilute acids.** C. V. KING and CHENG LING LIU (J. Amer. Chem. Soc., 1933, 55, 1928—1940).—The rate of dissolution,  $R$ , of cylinders of marble in 0.002—0.04M-HCl and AcOH between 15° and 35° tends to a max. with increasing speed of rotation. The temp. coeff. per 10° varies from 1.32 to 1.94. In general, the initial  $R$  is parallel to the ionisation consts. of the 10 acids used. Added NaCl increases  $R$  in HCl, and whilst it has no effect at low [AcOH], at higher [AcOH],  $R$  has a max. at a particular [NaCl]. Depression of  $p_H$  by adding salts of weak acids to the corresponding acids decreases  $R$  markedly, but in a manner which indicates some attack of the marble by mols. of undissociated acid. With increasing concn. of HCl, the effect of adding AcOH becomes smaller owing to suppression of ionisation. The results are compared with those obtained with metals (cf. A., 1931, 1373). The data are consistent with the diffusion theory when allowance is made for the fact that H<sub>2</sub>CO<sub>3</sub> is not negligibly weak, that freshly liberated H<sub>2</sub>CO<sub>3</sub> is a stronger acid than the usual equilibrium mixture of H<sub>2</sub>CO<sub>3</sub> and CO<sub>2</sub>, and that the dehydration of H<sub>2</sub>CO<sub>3</sub> is sufficiently slow to influence  $R$  considerably. J. G. A. G.

**Relation between dehydration and hydrolysis of magnesium chloride on heating the crystalline salt.** J. G. SCHTSCHERBAKOV and A. K. RASPOPIA (Kali, Russia, 1932, No. 10, 16—19).—On gradual heating of MgCl<sub>2</sub>·6H<sub>2</sub>O to 300—350° and then to the m.p., the % H<sub>2</sub>O ( $y$ ) and MgO ( $x$ ) are related by  $-dy/dx = ky^2$ . CH. ABS.



**Initial act in auto-oxidation.** H. N. STEPHENS (J. Physical Chem., 1933, 37, 655).—Polemical.

H. J. E.

**Collision activation and homogeneous catalysis of decomposition of nitrous oxide in foreign gases.** M. VOLMER and M. BOGDAN (Z. physikal. Chem., 1933, B, 21, 257—272; cf. this vol., 30).—The heat of activation, variation of reaction velocity with pressure of foreign gas, and comparison of the velocity coeff. with  $k_{\infty}$  show that Hg, Br, and I catalyse the decomp.; with I and Br the catalyst is the halogen atom.  $H_2$  reduces  $N_2O$  directly. In presence of  $H_2$ , Ne, A, Kr, and Xe the reaction is unimol. and the relative probability of activation by collision of  $N_2O$  with the foreign gas mol. has been calc. It decreases with increasing mol. wt. of the foreign gas.

R. C.

**Catalytic oxidation of organic compounds in the vapour state.** G. CHARLOT (Compt. rend., 1933, 196, 1224—1226; cf. A., 1932, 235).—The extent of complete oxidation as measured by  $CO_2$  production has been determined for several hydrocarbons in the presence of  $MgO$ ,  $NiO$ ,  $MoO_3$ , and  $WO_3$  as catalysts at different temp. Each catalyst has a sp. action causing, at a given temp., an approx. const. rate of  $CO_2$  production, independent, within limits, of the nature, concn., or rate of flow of the vapour oxidised.

A. C.

**Ozone as an oxidising catalyst.** V. OZONATION OF sodium sulphite; influence of dilution of ozone and concentration of hydrogen ions. E. BRINER and H. BIEDERMANN (Helv. Chim. Acta, 1933, 16, 548—555; cf. this vol., 234).—Oxidation of aq.  $Na_2SO_3$  induced by  $O_3$  increases markedly on dilution of the latter with  $O_2$ , or on acidifying the liquid. The results are discussed.

F. L. U.

**Influence of sodium borate on the reaction between alkali cyanides and reducing sugars.** J. BOUGAULT, Z. HARDY, and A. PINGUET (J. Pharm. Chim., 1933, [viii], 17, 462—469).—The presence of  $Na_2B_4O_7$  accelerates the reaction between  $CN'$  and reducing sugars (cf. A., 1920, ii, 452). The reaction, however, is not rendered more applicable to sugar determinations owing to increased instability of  $CN'$ .

F. O. H.

**Reduction of methylene-blue by products of the alkaline fission of sugars.** H. VON EULER and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 13, 6 pp.).—Decolorisation of methylene-blue (I) by a mixture of 2% glucose (II) (and other sugars) (1 c.c.) and 0.01N-NaOH (1 c.c.) under anaërobic conditions is accelerated by KCN (1 mg.). The times of decolorisation by (II) and fructose (III) increase with diminished concn. of NaOH, but the ratio time (II) : time (III) remains almost const. Reduction is accelerated by  $NH_2$ -acids. The results with dil. NaOH+ $PO_4'''$  differ from those of Blix (A., 1928, 250). (I) is reduced more readily by an extract of the cortex than of the medulla of the suprarenal gland; heating the extracts at  $80^\circ$  in  $N_2$  causes a loss in reducing power.

H. B.

**Catalysis of air oxidations by iron salts, phosphates, and pyrophosphates.** E. J. THERIAULT,

C. T. BUTTERFIELD, and P. D. MCNAMEE (J. Amer. Chem. Soc., 1933, 55, 2012—2024).—Fe pyrophosphates (I) do not catalyse the oxidation of glucose by air at  $20$ — $50^\circ$  at  $p_H$  vals. within the physiological range provided bacteria are excluded from the solutions. Doubt is cast on the validity of the claims made by Spoehr (A., 1924, i, 836; cf. A., 1926, 385) and by Degering and Upson (A., 1932, 147) regarding the activity of their pyrophosphate complexes at  $38^\circ$  and  $48^\circ$ . Numerous varieties of bacteria exist which are indifferent to (I) and it appears that (I) does not catalyse the oxidations accomplished by bacteria alone or by symbiotic growths of bacteria and plankton (*Colpidium*). The assumption of the presence of a highly specialised intracellular catalyst in biological oxidations appears to be unnecessary.

H. B.

**Heterogeneous catalysis of para-hydrogen transformation.** K. F. BONHOEFFER, A. FARKAS, and K. W. RUMMEL (Z. physikal. Chem., 1933, B, 21, 225—234).—The reaction has been investigated on various catalysts, the order being between 0 and 1. At low temp. transformation occurs principally by the unimol. conversion of an isolated adsorbed  $H_2$  mol. from one form into the other, whilst at high temp. it depends on at. adsorption. The low-temp. mechanism is responsible for the negative temp. coeff. of the catalysis; the high-temp. mechanism has a positive temp. coeff. Mol. adsorbed  $O_2$  greatly accelerates the reaction on C at low temp., probably by virtue of its paramagnetism, but poisons other catalysts.

R. C.

**Preparation of oxide catalysts for the carbon monoxide oxidation.** C. M. LOANE (J. Physical Chem., 1933, 37, 615—622).—Active oxides of Ni, Co, Fe, Mn, and Cu were made by the regulated oxidation of pyrophoric metals made (1) by preparing the Hg amalgam and distilling off the Hg in vac., (2) by reduction of a metal salt by Na in  $NH_3$  solution. The activity of these oxides in the  $CO-O_2$  reaction is comparable with that of pptd. oxides.

H. J. E.

**Energetics of catalysis. I. Energetic homogeneity of a platinum surface.** E. B. MAXTED and G. J. LEWIS (J.C.S., 1933, 502—504).—The catalytic activity of Pt-black towards the decomp. of  $H_2O_2$  in presence of small concns. of poison ( $HgCl_2$ ) varies linearly with the concn. of poison. The energy of activation is const. and independent of the concn. of poison, implying energetic homogeneity of the surface.

J. S. A.

**Various classes of hydrogenation catalysts.** O. SCHMIDT (Naturwiss., 1933, 21, 351).—The metals are classified according to their capacity for bringing about the hydrogenation of  $C_2H_4$  between  $0^\circ$  and  $200^\circ$ , at atm. pressure. The first class contains Cs, Ca, Sr, and Ba, which possess large at. vol., small electron expulsion work, and form stable hydrides in which H functions as a negative ion. The second contains Cu, Cr, Mn, Re, Fe, Co, Ni, Pd, Pt, which have small at. vol., large electron expulsion work, are transition elements, and form unstable hydrides, or take up  $H_2$  in solid solution, in which the H acts as a positive ion. Usually the mechanism of H activation is quite different in the two classes. Whilst in the first class the formation of negative H ions at the surface, through



the ease of formation of free electrons and the electronic affinity of H atoms, is favoured, a similar process is not possible in the second class owing to the high electron affinity of the surfaces of these metals. In this case there is formation of positive H ions in the lattice spaces in the interior of the metal. A. J. M.

**Benzene synthesis from carbon monoxide and hydrogen at atmospheric pressure.** XIII, XIV. Nickel catalysts. K. FUJIMURA and S. TSUNEOKA. —See B., 1933, 452.

**Suppression of aminolysis at a carbon contact.** K. WUNDERLY (Helv. Chim. Acta, 1933, 16, 515—521; cf. A., 1932, 836).—Aminolysis of aq. *dl*-aspartic acid at a surface of animal C is unaffected by treatment of the latter with HCN or H<sub>2</sub>S, either of which abolishes its O-carrying capacity, or with capillary-active compounds. Between  $p_H$  4 and 9 aminolysis increases with acidity. F. L. U.

**Active oxides.** LXI. Catalytic activity of zinc oxide, treated at different high pressures. O. KOSTELITZ and G. F. HÜTTIG (Z. Elektrochem., 1933, 39, 362—368; cf. this vol., 348).—ZnO pellets, prepared by crushing basic Zn carbonate (I) or ZnC<sub>2</sub>O<sub>4</sub> at 50—10,000 atm. and heating at 300—400°, catalyse the decomp. of MeOH at 300° and of EtOH at 320°. About 70—80% of the MeOH is decomposed into H<sub>2</sub> and CO, the remaining products being CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>2</sub>O, and HCO<sub>2</sub>Me. The main products produced from EtOH are H<sub>2</sub> and MeCHO. The course of the catalysis varies somewhat with the conditions of prep. of the ZnO. The catalytic activity per unit wt. of catalyst decreases with increase of the pressure originally applied, but at the same time the activity per unit vol. increases. The magnetic susceptibility of the compressed undecomposed (I) decreases with increasing pressure.

E. S. H.

**Active oxides.** LXII. Chromic oxide as catalyst for the decomposition of methyl alcohol. G. F. HÜTTIG and K. STRIAL [with H. KITTEL] (Z. Elektrochem., 1933, 39, 368—373; cf. preceding abstract).—Cr<sub>2</sub>O<sub>3</sub> has been prepared in 22 different ways, and the efficiency of the products in catalysing the reaction MeOH → CO + 2H<sub>2</sub> determined. The results vary considerably among the individual preps. and no generalisation is clear. The catalytic activity of the preps. is compared with the magnetic susceptibility and the adsorbent power for dyes.

E. S. H.

**Thermal dissociation of gypsum in presence of catalysts.** I. E. ADADUROV, L. GALAMEOVA, and D. V. GERNET (J. Appl. Chem., Russia, 1932, 5, 736—743).—Up to 430° dissociation is due to increase in mobility of the lattice. The change of  $\alpha$ -silicic acid to tridymite at 900—1200° is a secondary reaction. Anomalies observed in presence of Fe<sub>2</sub>O<sub>3</sub> are attributed to formation of silicates of the type FeO, SiO<sub>2</sub> + CaO, SiO<sub>2</sub>, or 3FeO, SiO<sub>2</sub> + CaO, SiO<sub>2</sub>.

CH. ABS.

**Theory of ammonia catalysis.** W. FRANKENBURGER (Z. Elektrochem., 1933, 39, 269—281).—A comprehensive review.

H. J. E.

**Electrolysis of metal salts in liquid ammonia (Faraday's law).** M. C. DEL BOCA (Helv. Chim.

Acta, 1933, 16, 565—571).—Anodic dissolution of Zn, Cd, Sb, or Al in solutions of their respective hexamino-nitrates or -iodides in liquid NH<sub>3</sub> is 44—100% in excess of that required by Faraday's law. Mg does not dissolve under these conditions. If the Pt cathode is enclosed in a canvas bag a part of the metal is deposited on the latter. F. L. U.

**Influence of anions on the electrolytic deposition and dissolution of cadmium and zinc.** E. MÜLLER and H. BARCHMANN (Z. Elektrochem., 1933, 39, 341—352).—The c.d.-p.d. curves for the deposition and dissolution of Cd and Zn are influenced strongly by the nature of the anion present. The steepness of the curves increases in the order ClO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, suggesting a relation with the radius of the anion. At higher temp. the variations are less pronounced, but in the same order. In the deposition of Cd from several electrolyte solutions the current efficiency at medium c.d. is 94—99% and increases with rising temp. Increase in the concn. of the anion, the Cd<sup>2+</sup> ion remaining const., has a depolarising effect. Thick coatings of Cd can be deposited from Cd(ClO<sub>4</sub>)<sub>2</sub> solution, especially in presence of excess of NaClO<sub>4</sub>. Addition of gelatin raises the p.d., especially in solutions containing large anions. Thick layers of Cd can be deposited from CdSO<sub>4</sub> solutions when gelatin is added. The anion also has an influence on the structure of the deposited metal. In general, the grain is refined by rising temp., increased concn., stirring, and the presence of gelatin, and is rendered coarser by increase of c.d.

E. S. H.

**Electrolytic deposition of metallic niobium and its separation from tantalum.** N. ISGARISCHEV and A. F. PREDE (Z. Elektrochem., 1933, 39, 283—288).—The separation of Ta<sub>2</sub>O<sub>5</sub>-Nb<sub>2</sub>O<sub>5</sub> mixtures from minerals is described. The oxide mixture was then fused with K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, and the melt (I) extracted with H<sub>2</sub>O, then with 40% aq. KOH. Electrolysis of the KOH extract + 1—1.5% dextrin with a Pt anode and a Cu cathode yielded pure Nb. Alternatively (I) was extracted with aq. (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or with aq. citric acid and electrolysed at > 80°. Nb was deposited quantitatively. Ta was recovered as Ta<sub>2</sub>O<sub>5</sub> on acidifying the residual electrolyte with H<sub>2</sub>SO<sub>4</sub>. Nb deposits were resistant to corrosion by mineral acids. Electrolysis in acid solution may be used for electro-analysis of Nb-Ta mixtures.

H. J. E.

**Amino-acids and related compounds.** I. **Electrolytic oxidation of glutamic acid.** Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1933, 8, 125—133).—Oxidation of *d*-glutamic acid dissolved in N-H<sub>2</sub>SO<sub>4</sub> at a PbO<sub>2</sub> anode yielded NH<sub>3</sub>, AcOH, succinic and succinamic acids. A mechanism is suggested.

F. L. U.

**Polarographic studies with the dropping mercury cathode.** XXXII. **Activation of hydrogen in the thiol group of some thio-acids in cobalt salt solutions.** R. BRDIČKA (Coll. Czech. Chem. Comm., 1933, 5, 148—164).—The catalysed electrolytic deposition of H<sub>2</sub> at the Hg dropping cathode in the presence of thioglycollic acid (I), cysteine (II), cysteylglycine (III), and glutathione (IV) (in both



$S_2$  and SH forms) in ammoniacal solutions of  $CoCl_2$  in  $NH_4Cl$  was studied by polarographic methods. Since the reduction of cystine (2e per mol.) occurs at a more positive cathode than that at which the catalytic wave appears, the catalytic effect is due to (II). Since similar catalytic effects are observed with (I), (III), and (IV) it is due to the SH group, and its absence in solutions containing hexamminocobaltic chloride shows the necessity of  $Co^{++}$  ions. The effect of  $[NH_3]$  and  $[NH_4^+]$  was also studied and on the basis of the results it is suggested that the co-ordinate linking between the SH group in the  $Co^{++}$  complexes increases the distance between the  $H^+$  and the positive S nucleus in the dipole  $-(S-H)^+$ , which is transported with  $Co^{++}$  ions to the negatively-charged interface between Hg and  $H_2O$  where the increasing potential gradient deforms the dipole so that  $S'$  and  $H^+$  become separated, the H atom removed by discharge being replaced by the reaction  $-S' + H_2O \rightleftharpoons -SH + OH^-$ . Hence  $OH^-$  ions must be removed from the cathode interface by  $NH_4^+$  ions or by buffering. The catalytic effect is very sensitive and can be employed for the determination of thio-acids. J. W. B.

**Heterogeneous reactions in the silent electric discharge.** V. S. MIYAMOTO (J. Sci. Hiroshima Univ., 1933, 3, 209—226; cf. this vol., 33).—The following solid substances were reduced by gaseous  $H_2$  in the silent discharge:  $Li_2SO_4$ ,  $Na_2SO_4$ ,  $Ti(SO_4)_2$ , K Fe alum,  $(NH_4)_2SO_4$ ,  $CoSO_4 \cdot 6H_2O$ ,  $CdCl_2$ ,  $Ca(NO_3)_2$ ,  $Sr(NO_3)_2$ ,  $Ba(NO_3)_2$ ,  $NaNO_3$ ,  $NaNO_2$ , and  $AgNO_3$ . Details of reaction products are given. J. S. A.

**Electrochemical properties of photosensitive electrodes in copper salts.** R. AUDUBERT (Compt. rend., 1933, 196, 1386—1387).—From the fact that a Cu plate covered with a photosensitive substance, when functioning as an electrode in aq.  $CuSO_4$ , behaves as one of pure Cu, it is inferred that within  $p_H$  limits for which the photovoltaic e.m.f. is reproducible and the photosensitive substance is unaltered the electrode potential depends solely on an oxidation-reduction process. C. A. S.

**Photolysis of solutions of alkali metals in liquid ammonia.** R. A. OGG, jun., P. A. LEIGHTON, and F. W. BERGSTROM (J. Amer. Chem. Soc., 1933, 55, 1754—1766).—Pure liquid  $NH_3$  is not decomposed, but 0.002—0.1N solutions of Na, K, and Cs in liquid  $NH_3$  afford  $H_2$  and the metallic amide in light of wave-lengths 2144—2550 Å. The quantum efficiency increases, with increasing concn. of metal, to 0.25, has a max. at about 2300 Å. and a long wave-length threshold. Liquid  $NH_3$  absorbs light of wave-length < 2500 Å., whilst the solutions of metals and their amides exhibit continuous absorption throughout the ultra-violet. The mechanism of the reaction is discussed in relation to the photo-decomp. of gaseous  $NH_3$ . The Na- $NH_2$  linking is probably ionic. J. G. A. G.

**Photo-reduction of alcoholic solutions of ferric chloride in light.** M. PRASAD and P. S. LIMAYE (J. Indian Chem. Soc., 1933, 10, 91—99; cf. A., 1931, 1378).—Photo-reduction proceeds in two stages, both zero-mol., although the first is faster than the second. A striking change occurs in the solution at a certain stage (as shown by measurements of extinction

coeffs.), probably owing to the formation of a complex containing  $Fe^{III}$ . Colloidal  $Fe(OH)_3$  inhibits the reaction, the extent of inhibition increasing with the progress of the reduction, although the course of the reaction from the first to the second stage is unchanged. J. L. D.

**Quantum efficiency of the photo-reduction of alcoholic solutions of ferric chloride.** M. PRASAD and P. S. LIMAYE (J. Indian Chem. Soc., 1933, 10, 101—105; cf. preceding abstract).—The quantum efficiency (0.6—4) in dil. is < that in more conc. solutions; in any solution the quantum efficiency is greater in light of lower  $\lambda$ , and increases with rise in temp. The primary effect of light absorption is the breaking up of the  $FeCl_3$  into  $FeCl_2$  and  $Cl^+$ . No other side reaction is detected. J. L. D.

**Photolysis of aliphatic aldehydes. II. Acetaldehyde.** P. A. LEIGHTON and F. E. BLACET (J. Amer. Chem. Soc., 1933, 55, 1766—1774; cf. A., 1932, 1006).—The quantum efficiency,  $\gamma$ , of the polymerisation and decomp. of  $MeCHO$  in homogeneous light of wave-lengths between 2537 and 3342 Å. has been determined. In general,  $\gamma$  is independent of light intensity, but the polymerisation ( $\gamma_p$  0.08—0.64) decreases and the decomp. ( $\gamma_d$  0.2—0.95) increases as wave-length is decreased. The vapour fluoresces in light absorbed in the regions of distinct and diffuse bands but not in the region of continuous absorption. The data are explained in terms of the absorption spectrum, which is interpreted as consisting of bands with a background of continuous absorption. J. G. A. G.

**Germ and pro-germ formation in relation to the developable centres of the exposed homogeneous silver bromide grain.** L. HAMBURGER (Phot. J., 1933, 73, 95—105; cf. this vol., 350, 359).—Theoretical. Available data are shown to be quantitatively compatible with the author's theory that the crit. developable size of a Ag (or  $Ag_2S$  etc.) germ (nucleus) is 3 atoms; smaller centres are named pro-germs. The distribution of germs and pro-germs on Ag grains and its relation to exposure are considered mathematically. Larger or smaller crit. germ sizes are shown to be erroneous. J. L.

**Relationship between reciprocity law failure and the intermittency effect in photographic exposure.** J. H. WEBB (J. Opt. Soc. Amer., 1933, 23, 157—169).—Identical photographic effects are obtained with an intermittent exposure of average intensity  $I$  and with a continuous exposure of abs. intensity  $I$ , provided that the frequency of the former is that at which only one quantum per flash is incident on the receptive area of a photographic grain. C. W. G.

**Photographic reversal by desensitising dyes.** B. H. CARROLL and C. M. KRETCHMAN (Bur. Stand. J. Res., 1933, 10, 449—464).—The latent image on an exposed plate, which has been bathed in a solution of a desensitising dye, may be destroyed by a second exposure to light of the proper wave-length. The dyes used were pinakryptol-green and -yellow, pararosaniline, safranin (I), and tolusafraanine. The reversal corresponds with the energy absorption by the dyed AgBr between 3500 and 8000 Å. The



effects of bromide and dye concn. were examined. (I) may produce either reversal or normal sensitisation, depending on  $[\text{Br}^-]$ . The reversal process is an oxidation, and is chemically and photographically the reverse of ordinary sensitisation. H. J. E.

**Concentration of the heavy hydrogen isotope.** I. L. NEWELL and J. B. FICKLEN (J. Amer. Chem. Soc., 1933, 55, 2167).—Determinations of  $d$  of  $\text{H}_2\text{O}$  from Cr-plating baths which have been operated for three years indicate the presence of about 0.6% of  $\text{H}_2\text{O}$  containing the heavier H isotope. J. G. A. G.

**Increase of concentration of  $\text{H}^1\text{H}^2$  by fractional evaporation and rectification.** W. H. KEESOM, H. VAN DIJK, and J. HAANTJES (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 248—252).—By the fractional evaporation of 40 litres of liquid  $\text{H}_2$  and rectification of the resulting 500 c.c. at a temp. near the triple point, 2 litres of gas were obtained, the  $d$  of which showed it to contain 3 vol.-% of  $\text{H}^1\text{H}^2$ . F. L. U.

**Thermal decomposition of magnesium silicides.** G. GIRE (Compt. rend., 1933, 196, 1404—1406; cf. A., 1908, ii, 184; 1926, 368).—Finely powdered Mg (20 parts) and Si (6 parts) react in vac. at  $450^\circ$ . On removing excess of Mg by  $\text{EtI} + \text{Et}_2\text{O}$ ,  $\text{SiMg}_2$  remains. At  $550^\circ$  this loses 25% of its Mg, leaving  $\text{Si}_2\text{Mg}_3$  as a dark grey powder which does not evolve spontaneously inflammable H silicide on treatment with HCl, and begins to decompose at  $650^\circ$ . C. A. S.

**Soluble anhydrite as a desiccating agent.** I. Preparation and general characteristics. W. A. HAMMOND and J. R. WITHROW (Ind. Eng. Chem., 1933, 25, 653—659).—Sol. anhydrite, prepared by heating  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  or  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  (I) at  $170$ — $300^\circ$ , is an efficient desiccating agent. The v.p. of (I) is 0.005 mm. and thus  $<$  that obtained over  $\text{CaCl}_2$  or  $\text{H}_2\text{SO}_4$ . The anhyd. material can be repeatedly regenerated by heating and its physical properties are good. It may be used for HCl,  $\text{SO}_2$ ,  $\text{Cl}_2$ , or most org. liquids. A. G.

**Alkaline-earth metal hydrides.** P. REMY-GENETÉ (Ann. Chim., 1933, [x], 19, 353—426; cf. this vol., 569).—Partly a more detailed account of work previously reviewed (A., 1930, 1262; 1932, 1217). The following is new. Ca which has been kept in  $\text{CO}_2$  or obtained (in a finely divided state) by decomp. of  $\text{CaN}_6$  does not adsorb  $\text{H}_2$  at  $20^\circ$  during about 3.5 months or 40 days, respectively; adsorption occurs readily with redistilled Ca (I) (kept out of contact with air). Slow but definite adsorption of  $\text{H}_2$  by (I) occurs at  $-80^\circ$ . Similar results are found for Sr (finely divided Sr, obtained by decomp. of  $\text{SrN}_6$ , is, however, active) and Li; the rates of adsorption vary. Adsorption of  $\text{N}_2$  by (I) occurs slowly during 9 days at  $20^\circ$  and then ceases; the resultant product adsorbs  $\text{H}_2$ . Freshly distilled Sr is attacked superficially when kept in dry  $\text{CO}_2$ :  $5\text{Sr} + 2\text{CO}_2 \rightarrow \text{SrC}_2 + 4\text{SrO}$ . Ba adsorbs  $\text{H}_2$  at  $20^\circ$  irrespective of its method of prep. (cf. *loc. cit.*). H. B.

**Action of white phosphorus on copper salts, and of copper on white phosphorus, in presence of water.** H. PÉLABON (Bull. Soc. chim., 1933, [iv],

53, 260—264).—P immersed in aq.  $\text{CuSO}_4$  causes the formation of a black deposit of  $\text{Cu}_5\text{P}$ , leaving  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_3\text{PO}_3$  in solution. From dil. solutions, or by immersing  $\text{Cu} + \text{P}$  in acidified  $\text{H}_2\text{O}$ , large Cu crystals may be obtained. The presence of  $\text{O}_2$  is necessary. Ag salts behave similarly. J. S. A.

**Carbon with metallic lustre; new form of carbon?** U. HOFMANN (Z. Krist., 1933, 85, 330; cf. this vol., 12).—The previous deduction of similar results is pointed out (cf. B., 1927, 802; A., 1928, 464; 1932, 217, 903, 1078). C. A. S.

**Formation of phosgene in thermal decomposition of carbon tetrachloride.** A. HAMILTON (Ind. Eng. Chem., 1933, 25, 539—541).—Evidence is summarised to show that when fires in enclosed spaces are extinguished with  $\text{CCl}_4$  there is some risk of poisoning by  $\text{COCl}_2$  formed from it. A. G.

[Formation of phosgene in thermal decomposition of carbon tetrachloride.] J. C. OLSEN (Ind. Eng. Chem., 1933, 25, 541—542).—It is claimed that the danger of  $\text{COCl}_2$  poisoning (see preceding abstract) is negligible. A. G.

**Mechanism of the formation of acid oxides at carbon surfaces.** B. BRUNS, M. MAXIMOVA, and E. POS (Kolloid-Z., 1933, 63, 286—291).—The surface oxides produced by direct oxidation of C with  $\text{O}_2$  are not reduced at room temp. by  $\text{H}_2$  in presence of Pt and are not removed by shaking with  $\text{H}_2\text{O}$ . The formation of acid oxides, especially at lower temp., depends on the treatment of the C; activated C gives smaller amounts than non-activated C, possibly because of the smaller content of org. impurities. The presence of Pt reduces the amount of acid oxides formed. Weakly oxidised C adsorbs both cations and anions from solutions of neutral salts. E. S. H.

**Nitrogen compounds of germanium. IV. Action of ammonia and amines on germanium tetraiodide.** W. C. JOHNSON and A. E. SIDWELL (J. Amer. Chem. Soc., 1933, 55, 1884—1889; cf. this vol., 38).—The reaction of  $\text{GeI}_4$  with  $\text{NH}_3$  and  $\text{NH}_2\text{Et}$  at  $-33.5^\circ$  and in  $\text{CCl}_4$  at room temp. is represented by  $\text{GeI}_4 + 6\text{RNH}_2 = \text{Ge}(\text{NR})_2 + 4\text{RNH}_2\text{I}$ . Aminolysis is also effected by  $\text{NH}_2\text{Et}$ , whilst  $\text{N}(\text{Et})_3$  forms the additive compound  $\text{GeI}_4 \cdot 5\text{N}(\text{Et})_3$  (cf. A., 1932, 132). J. G. A. G.

**Peroxidation of cerium.** A. FOUCHET (Bull. Soc. chim., 1933, [iv], 53, 218—221).—A criticism (cf. Lortie, A., 1931, 182). J. S. A.

**Anhydrous hydrazine. VI. Hydrazine tri-nitride monohydrazinate,  $\text{N}_2\text{H}_5\text{N}_3 \cdot \text{N}_2\text{H}_4$ .** A. L. DRESSER and A. W. BROWNE [with C. W. MASON] (J. Amer. Chem. Soc., 1933, 55, 1963—1967).—F.p. data for the system  $\text{N}_2\text{H}_4 - \text{N}_2\text{H}_5\text{N}_3$  (m.p.  $75.4^\circ$ ) have been determined. Hydrazine azide monohydrazinate, m.p.  $66.4^\circ$ , has been isolated. Crystallographic data are recorded. J. G. A. G.

**Behaviour of hydronitrogens and their derivatives in liquid ammonia. VII. Formation of hydrazine by thermal action of incandescent filaments immersed in liquid ammonia.** D. H. HOWARD, jun., and A. W. BROWNE (J. Amer. Chem.



Soc., 1933, 55, 1968—1974).—W filaments gave the highest yields of  $N_2H_4$  (max. 0.25% of  $NH_3$  decomposed) and these are (1) independent of the temp. of the liquid  $NH_3$ , (2) doubled by increasing the filament temp. from 2000—2400° to 2500—3400°, (3) increased by decreasing the diameter of the filament. The mechanism of the reaction is discussed and it is inferred that thermionic emission from the filament is not an important factor. J. G. A. G.

**Complex acids. X. Precipitation of metallic vanadates, with a note on Moser and Brandl's method of determining vanadium.** H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1933, 512—517; cf. this vol., 580).—Solutions of Na ortho-, meta-, and pyro-vanadate give with  $AgNO_3$  the corresponding Ag vanadate; from "unboiled" solutions pptn. was delayed. Pptn. of vanadate from solutions of Mg, Be, Zn, Zr, and Hg begins at the same  $p_H$  as for the hydroxide, basic salt separating. With Pb and Ag pptn. occurs at a lower  $p_H$  than for the hydroxide. Pptn. of  $Ag_3VO_4$  in presence of NaOAc and  $NH_3$  by Moser and Brandl's method gives low and variable results. J. S. A.

**Precipitation of antimonious iodide and its hydrolysis.** F. FRANÇOIS (Compt. rend., 1933, 196, 1398—1400; cf. A., 1920, ii, 197).—If KI is added to a  $M/30$ - $SbCl_3 + 3M$ - $H_2SO_4$  solution pure bright red  $SbI_3$  is pptd.; the  $H_2SO_4$  acts as a dehydrator and can be replaced only by conc.  $H_3PO_4$ . With less conc.  $H_2SO_4$  an orange oxyiodide is pptd. Examination of the interaction of variable amounts of  $SbI_3$  with a fixed vol. of  $H_2O$  or 0.1—0.6N-HI demonstrates the existence of only  $2Sb_2O_3 \cdot SbI_3$ , but with indications also of a solid tending towards  $SbOI$ , and a liquid in which  $SbI_3$  and HI are present in the ratio 3 : 8. C. A. S.

**Preparation of oxygen by means of ammoniacal cobalt salt solutions.** W. GLUUD, K. KELLER, and H. NORDT (Ber. Ges. Kohlentechn., 1933, 4, 210—254).—Compounds of the type  $[Co(NH_3)_6]X_2$  readily absorb  $O_2$  with loss of  $NH_3$  producing peroxides  $[(NH_3)_5Co]_2O_2X_2$  and these give up their O when heated. A small part of the O is used each time in oxidising  $Co^{++}$  to  $Co^{+++}$ , and this must be reduced again. The process is not economic owing to the cost of Co and  $NH_3$  and the necessary electrolytic reduction of  $Co^{+++}$ . A detailed study of the reaction under varying conditions is given, and many other Co complexes were studied. The oxidation loss was greatly minimised by addition of  $AlCl_3$  or to a smaller degree by  $MgCl_2$ , although these additions reduce the absorption capacity of the solution. C. I.

**Higher homologues of sulphur hexafluoride.** K. G. DENBIGH and R. WHYTLOW-GRAY (Nature, 1933, 131, 763).—Fractional sublimation of  $SF_6$  at low temp. yields probably  $S_2F_{10}$ , b.p. near 0°, which is not readily hydrolysed. A volatile oil has been obtained which is immiscible with and not attacked by  $H_2O$ , and may be a still higher homologue. L. S. T.

**Action of nitric acid on hydrogen sulphide and on certain sulphides in presence of hydrazone.** A. KESANS [KESCHAN] (Latvij. Univ. Raksti, 1933, 2, 311—320; cf. A., 1931, 1134).—PbS, CdS,

$SnS_2$ ,  $SnS$ ,  $Sb_2S_3$ , and  $As_2S_3$  react with  $HNO_3$  (6—10N) with production of  $H_2S$ , the solubility of the sulphides diminishing in the order given;  $N_2H_4$  inhibits the reaction to an extent proportional to its concn., and inversely proportional to the solubility of the sulphide, to the temp., and to the concn. of  $HNO_3$ .  $CuS$ ,  $Bi_2S_3$ , and  $Ag_2S$  do not react with  $H^+$  but with  $NO_3^-$ , and  $N_2H_4$  very strongly inhibits this reaction. Inhibition is ascribed to oxidation of  $S^{++}$  by  $HNO_3$ , as a result of which the cation concn. rises, but  $[S^{++}]$  falls; in view of the constancy of the solubility product dissolution of sulphide and oxidation by  $NO_3^-$  cease. At the same time  $HNO_3$ , which acts on undissolved sulphide, is removed by  $N_2H_4$ , with formation of  $HN_3$ ,  $N_2O$ ,  $N_2$ , etc. R. T.

**Lead chamber process. IV. Spectrographic measurements.** E. BERL and K. WINNACKER (Z. anorg. Chem., 1933, 212, 113—133; cf. A., 1932, 1219).—Spectrophotometric study of the "violet acid"  $SO_5NH_2$  and of blue  $H_2SO_4$  solutions of  $HSO_5N$  shows their nature to be entirely different, and the colour of the latter to be due to its hydrolysis products ( $HNO_2$ ). In agreement with this, the transparency max. coincides with that of  $N_2O_3$  at low temp. and in  $H_2O$  under pressure. J. S. A.

**Theory of the lead chamber reaction.** W. J. MÜLLER (Z. Elektrochem., 1933, 39, 309; cf. this vol., 241).—The unstable intermediate  $HNO$ , formed in the reaction  $H_2SO_3 + HNO_2 = H_2SO_4 + HNO$ , decomposes to form  $NO$  and not  $N_2O$  or  $N_2$  (cf. Abel, this vol., 233). H. J. E.

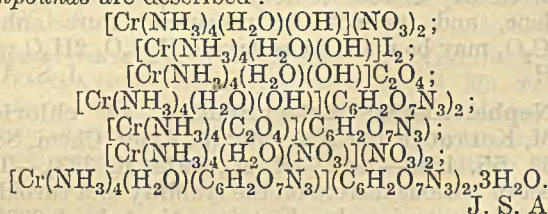
**Action of sulphuryl chloride on metal oxides.** H. DANNEEL and W. HESSE (Z. anorg. Chem., 1933, 212, 214—224).—The action of  $SO_2Cl_2$  on oxides of Cd, Zn, Ag, Cu, Fe, Cr, Mg, Pb, and Hg gives mixtures of the chloride and sulphate in varying proportions, depending on the metal, the conditions of experiment, and the presence of impurities. Dissociation need not precede reaction, since  $Fe_2O_3$  reacts with  $SO_2Cl_2$  at room temp., but with  $Cl_2$  only at 500°. J. S. A.

**Decomposition of thiosulphates with sulphuric acid.** W. GLUUD, W. KLEMPF, and H. HILL (Ber. Ges. Kohlentechn., 1933, 4, 203—209).—The stages are (1)  $(NH_4)_2S_2O_3 + H_2SO_4 = (NH_4)_2SO_4 + H_2S_2O_3$ , (2)  $H_2S_2O_3 = SO_2 + H_2O + S$ . These proceed to the extent of  $\frac{1}{3}$  conversion followed by (3)  $2(NH_4)_2S_2O_3 + SO_2 = 2(NH_4)_2SO_4 + 3S$ . For the complete disappearance of  $(NH_4)_2S_2O_3$  and  $SO_2$  a 3—5% excess of  $H_2SO_4$  is necessary. The above reactions proceed only if  $SO_2$  is destroyed or removed as formed. With rising acid concn. side reactions leading to polythionates occur and the decomp. of these gives an increased free acid concn. which was actually observed. The decomp. of  $H_2S_2O_3$  is not completely represented by (2). C. I.

**Ammines. VIII. Dihydroxotetramminochromic hydroxide and its derivatives.** H. J. S. KING (J.C.S., 1933, 520—523).—Trituration of  $[Cr(NH_3)_4(H_2O)Cl]Cl_2$  with  $Ag_2O$  yields  $[Cr(NH_3)_4(OH)_2]OH$ , as is shown by conductivity measurements. Salts of this series are not isolable but exist in solution. By the action of 2 equivs. of acid, hydroxo-aqua-tetramminochromic salts, and with 3 equivs. of acid, aquo-aqua-tetramminochromic salts,



are obtained. The following mobilities at 0° are calc.:  $[\text{Cr}(\text{NH}_3)_4(\text{OH})_2]^+$  30.4;  $[\text{Cr}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^+$  30.6;  $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OH})]^{++}$  60.5 mhos. The following compounds are described:



J. S. A.

**Luminous reduction of selenium dioxide.** H. J. EMBLEUS and H. L. RILEY (Proc. Roy. Soc., 1933, A, 140, 378—387).— $\text{SeO}_2$  vapour reacts with  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{PrOH}$ ,  $\text{COMe}_2$ ,  $\text{MeCHO}$ ,  $\text{Et}_2\text{O}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{CS}_2$  at about 400°, giving bright blue flames. All the flames have the same spectrum, the bands being attributed to the  $\text{Se}_2$  mol. and possibly also to  $\text{SeO}_2$ . The same bands occur in the flame of Se burning in  $\text{O}_2$ . A phosphorescent flame is obtained by heating  $\text{SeO}_2$  in an  $\text{NH}_3$  stream at 100—300°.

L. L. B.

**Metallic tungstates.** A. KARL (Compt. rend., 1933, 196, 1403—1404).—Molten  $\text{NaCl}$  dissolves up to 0.5  $\text{WO}_3$ , thus:  $4\text{NaCl} + 2\text{WO}_3 + \text{O}_2 = 2\text{Na}_2\text{WO}_4 + 2\text{Cl}_2$ .  $\text{NaBr}$ ,  $\text{KCl}$ ,  $\text{KBr}$ , and  $\text{LiCl}$  behave similarly. If the calc. amount of a metallic oxide or carbonate be added to the mixture  $\text{NaCl} + \text{WO}_3$ , the corresponding tungstate is formed. Well-cryst.  $\text{Cd}$ ,  $\text{Zn}$ ,  $\text{Mn}$ ,  $\text{Fe}$ ,  $\text{Ca}$ ,  $\text{Ba}$ , and  $\text{Sr}$  tungstates and artificial wolframite and hubnerite have been thus prepared.

C. A. S.

**Action of hydrogen peroxide on permanganate.** P. DUBOIS (Compt. rend., 1933, 196, 1401—1403; cf. A., 1890, 1062; 1932, 823).—The variation in the composition of the oxide  $\text{MnO}_n$ , formed by this action when the concn. of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  and  $p_{\text{H}}$  are varied, is shown by plotting  $n$  against concn. or  $p_{\text{H}}$ . In no case has  $n$  a definite val., although it appears to have the vals. 1.58 and 1.88 fairly const. over certain intervals.

C. A. S.

**Rhenium.** I. Potassium rhenichloride and organic derivatives of quadrivalent rhenium. H. SCHMID (Z. anorg. Chem., 1933, 212, 187—197).—Solutions of  $\text{K}_2\text{ReCl}_6$ , which may be conveniently prepared by electrolytic reduction of  $\text{KReO}_4$ , using a  $\text{Hg}$  cathode, undergo hydrolysis to  $\text{ReO}_2 \cdot 2\text{H}_2\text{O}$ , and consequently do not obey Beer's law. The following compounds, obtainable also from  $\text{ReCl}_4$ , are described:  $\text{ReCl}_4 \cdot \text{X}_2 \cdot 2\text{HCl}$ , where  $\text{X} = \text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ ,  $\text{C}_6\text{H}_7\text{N}$ , or  $\text{C}_5\text{H}_5\text{N}$ .

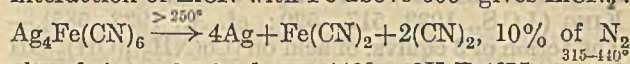
J. S. A.

**Induced reactions and the higher oxides of iron.** W. MANCHOT (J. Physical Chem., 1933, 37, 655—656).—A criticism (cf. Hale, A., 1930, 41).

H. J. E.

**Thermal degradation of complex cyanides of iron.** A. PERRET and A. GISLON (Bull. Soc. chim., 1933, [iv], 53, 283—293).—The progressive thermal decomp. of various ferri- and ferro-cyanides in vac. at temp. up to 650° was studied quantitatively and, on the basis of the observations, the following schemes are adduced:  $\text{Na}[\text{K}]_4\text{Fe}(\text{CN})_6 \xrightarrow{>450^\circ} 4\text{Na}[\text{K}]\text{CN} + \text{Fe} + 2\text{C} +$

$\text{N}_2$ , a similar scheme applying to the  $\text{Li}$  salt but here interaction of  $\text{LiCN}$  with  $\text{Fe}$  above 600° gives  $\text{LiCN}_2$ :



also being obtained at 440°:  $2\text{K}_3\text{Fe}(\text{CN})_6 \xrightarrow{315-440^\circ} \text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6] + \text{K}_4\text{Fe}(\text{CN})_6 + (\text{CN})_2 (57\%) + (\text{CN})_x$ , and at  $>450^\circ$  further decomp. of the complex cyanides into  $\text{KCN}$ ,  $\text{Fe}$ ,  $\text{C}$ , and  $\text{N}_2$  occurs. Decomp. of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$  begins at 200° and at  $<450^\circ \rightarrow \text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6] + \text{Na}_4\text{Fe}(\text{CN})_6 + 3\text{NO} + 1.5(\text{CN})_2$ , the solid residue being a mixture and not  $\text{Na}_2\text{Fe}(\text{CN})_4$  as stated by Etard and Bémont (A., 1885, 233); at  $>450^\circ$  further decomp. of the ferrocyanides gives  $\text{N}_2$ .  $\text{Be}_2\text{Fe}(\text{CN})_6 \cdot 6.8\text{H}_2\text{O}$  [prep. from  $\text{Be}(\text{OH})_2$  and  $\text{H}_4\text{Fe}(\text{CN})_6$  described] decomposes above 200° to give  $\text{Be}_3\text{N}_2$ ,  $\text{Fe}$ ,  $\text{C}$ , and  $\text{N}_2$ , hydrolysis of the intermediate  $\text{Be}(\text{CN})_2$  by remaining  $\text{H}_2\text{O}$  giving some  $\text{HCN}$  and

$(\text{NH}_4)_2\text{CO}_3$ . Similarly  $\text{Mg}_2\text{Fe}(\text{CN})_6 \xrightarrow{>200^\circ} \text{Mg}(\text{CN})_2 \text{ (I)} + \text{Fe}(\text{CN})_2 \text{ (II)}$ , followed by  $6\text{(I)} \rightarrow 6\text{MgCN}_2 + 6\text{C} \rightarrow 2\text{Mg}_3\text{N}_2 + 6\text{C} + 4\text{N}_2$ , and  $\text{(II)} \rightarrow \text{Fe} + 2\text{C} + \text{N}_2$ , a little  $\text{HCN}$  and  $\text{H}_2\text{O}$  also being evolved; above 450° pure

$\text{N}_2$  is obtained. The decomp.  $\text{Ca}_2\text{Fe}(\text{CN})_6 \xrightarrow{650^\circ} 2\text{CaCN}_2 (75\% \text{ yield}) + \text{Fe} + \text{N}_2 + (\text{CN})_2$  (with some  $\text{HCN}$  and its products of hydrolysis  $>500^\circ$ ) confirms the earlier work of Pincass (A., 1922, i, 532), the  $\text{Sr}$  and  $\text{Ba}$  salts decomposing similarly although only 20%

of  $\text{BaCN}_2$  is obtained. Decomp. of  $\text{Zn}_2\text{Fe}(\text{CN})_6 \xrightarrow{>300^\circ} 2\text{Zn}(\text{CN})_2 \text{ (III)} + \text{N}[\text{Fe}(\text{CN})_2] \text{ (IV)}$  followed by  $\text{(III)} \xrightarrow{550^\circ} 2\text{ZnCN}_2 + 2\text{C} \rightarrow 2\text{Zn} + 4\text{C} + 2\text{N}_2$  and  $\text{(IV)} \xrightarrow{>440^\circ} \text{Fe} + 2\text{C} + \text{N}_2$ , a similar scheme applying to  $\text{Cd}_2\text{Fe}(\text{CN})_6$ .

J. W. B.

**Metal carbonyls.** XIX. Iron carbonyl hydride. W. HIEBER and H. VETTER (Z. anorg. Chem., 1933, 212, 145—168; cf. this vol., 476).—Pure  $\text{Fe}(\text{CO})_4\text{H}_2$  has been isolated by fractionation of the product of the action of  $\text{H}_2\text{SO}_4$  on  $\text{Fe}(\text{CO})_5$  treated with  $\text{NaOH}$ . It has m.p.  $-70^\circ$ ; v.p. from  $-10^\circ$  to  $-50^\circ$  is given by  $6.122-1337/T$ , mol. heat of evaporation 6.11 kg.-cal.  $\text{Fe}(\text{CO})_4\text{H}_2$  does not react with dry  $\text{HCl}$  or  $\text{HI}$ ; with  $\text{I}$ ,  $\text{Fe}(\text{CO})_4\text{I}_2$  is formed. Methylene-blue is quantitatively reduced, and the active  $\text{H}$  may be so determined.  $\text{C}_6\text{H}_5\text{N}$  and *o*-phenanthroline yield the stable compounds  $\text{Fe}(\text{CO})_4\text{H}_2 \cdot (\text{C}_6\text{H}_5\text{N})_x$ ,  $\text{Fe}(\text{CO})_4\text{H}_2 \cdot 2\text{C}_{12}\text{H}_8\text{N}_2$ ; the  $\text{H}$  in the latter compound no longer reduces methylene-blue.

J. S. A.

**Decomposition products of potassium thio-nitroprusside.** G. SCAGLIARINI and F. GENTILE (Atti R. Accad. Lincei, 1933, [vi], 17, 398—401; cf. A., 1928, 160).—An aq. solution of  $\text{K}_4[\text{Fe}(\text{CN})_5\text{NOS}]$  when kept for 10 days decomposes giving  $\text{KNO}_2$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{S}$ ,  $\text{Fe}(\text{OH})_2$ , and  $\text{Fe}(\text{OH})_3$ , whilst considerable quantities of  $\text{N}_2$  and  $\text{NO}$  are evolved. The  $\text{NOS}$  group is probably loosened from the complex and reacts thus:  $4(\text{NOS})' = \text{N}_2 + 2\text{NO}_2' + 4\text{S}$ , whilst the resulting aquopentacyanide is transformed into ferrocyanide and  $\text{Fe}(\text{OH})_2$ . These reactions and the behaviour with finely divided  $\text{Ag} (\rightarrow \text{Ag}_2\text{S}$ ,  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{4-}$ , and  $\text{NO}_2'$ ) agree with the proposed

structure,  $\text{K}_4 \left[ \text{Fe}^{\text{II}}(\text{CN})_5 \text{N} \begin{smallmatrix} \text{O} \\ \text{S} \end{smallmatrix} \right]$ .

O. J. W.



**Ammines. VII. Action of acids on dihydroxotetramminocobaltic hydroxide.** H. J. S. KING (J.C.S., 1933, 517—520; cf. A., 1932, 585).—The action of 3 eqivs. of acid on  $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]\text{OH}$  introduces an acid group into the complex. With  $o\text{-C}_6\text{H}_4(\text{OH})\cdot\text{CO}_2\text{H}$  and  $\text{HI}$ , however,  $[\text{Co}\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}_3]\text{X}_6$  ( $\text{X}=\text{NO}_3$ ,  $\text{I}$ ) were obtained.  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]\text{NO}_3$  was shown by conductivity measurement to be hydrolysed in aq. solution, but not  $[\text{Co}(\text{NH}_3)_4\text{X}^{\text{II}}]\text{NO}_3$ , where  $\text{X}^{\text{II}}=\text{C}_2\text{O}_4$ ,  $\text{CH}_2(\text{CO}_2)_2$ . Mobilities of the last two cations at  $0^\circ$  are, respectively, 19.1 and 26.0 mhos. The following compounds were prepared:  $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]\text{NO}_3\cdot\text{H}_2\text{O}$ ;  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}](\text{C}_6\text{H}_5\text{O}_7\text{N}_3)_2\cdot 2\text{H}_2\text{O}$ ;  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{C}_6\text{H}_5\text{O}_7\text{N}_3)](\text{C}_6\text{H}_5\text{O}_7\text{N}_3)_2\cdot 4\text{H}_2\text{O}$ ;  $[\text{Co}\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}_3]\text{I}_6\cdot 3\text{H}_2\text{O}$ . J. S. A.

**Nickel carbonyl. Mechanism of its formation from nickel sulphide and carbon monoxide.** M. M. WINDSOR and A. A. BLANCHARD (J. Amer. Chem. Soc., 1933, 55, 1877—1883).—At room temp., the optimal yield of  $\text{Ni}(\text{CO})_4$  is obtained by shaking  $\text{CO}$  with a liquid originally containing  $M\text{-NaOH}$ ,  $0.1M\text{-Na}_2\text{S}$ , and  $0.5M\text{-NiSO}_4$  (cf. A., 1929, 526). It is suggested that the tendency of  $\text{NiS}$  to dissociate into its atoms is such as to permit the formation of  $\text{Ni}(\text{CO})_4$  in the presence of S-removing reagents.  $\text{NiSe}$  under similar conditions yields  $\text{Ni}(\text{CO})_4$ . The reaction  $\text{CO}+\text{H}_2\text{O}\longrightarrow\text{H}_2+\text{CO}_2$  occurs to a small extent in the presence of  $\text{OH}^-$  ions under the catalytic influence of  $\text{Ni}(\text{CO})_4$ . J. G. A. G.

**From the ponderable to the imponderable.** O. HAHN (Science, 1933, 77, 397—403).—A review of the limits of qual. and quant. detection of substances. L. S. T.

**Consideration of the "rare" elements in mineral analysis.** V. M. GOLDSCHMIDT, H. HAUPTMANN, and C. PETERS (Naturwiss., 1933, 21, 362—365).—It is considered that insufficient attention is paid to the occurrence of rare metals in silicate minerals, and methods are suggested for their determination. A. J. M.

**Indirect volumetric determinations.** J. EISENBRAND (Arch. Pharm., 1933, 271, 315—316).—The theoretical reasoning of Bordeianu (this vol., 582) is incorrect. R. S. C.

**Use of salicylic acid as an acidimetric standard.** S. ŠKRAMOVSKÝ (Coll. Czech. Chem. Comm., 1933, 5, 143—147).—Salicylic acid purified by sublimation can be used in aq.  $\text{EtOH}$  instead of  $\text{H}_2\text{C}_2\text{O}_4$  or  $\text{BzOH}$  as a standard in acidimetry. With  $N\text{-KOH}$  the factors are identical, and with  $0.1N\text{-KOH}$  only  $0.10\% <$  those obtained using these two acids. J. W. B.

**Colorimetric  $p_H$  determination with the simplified original Tödt drop apparatus.** G. GOLLNOW (Chem.-Ztg., 1933, 57, 374—375). E. C. S.

**Determination of the alkalinity of boiler water.** J. LEICK.—See B., 1933, 495.

**Photometric micro-analysis of drinking and service water. IV. Determination of phosphorus.** C. URBACH.—See B., 1933, 494.

**Determination of water of crystallisation.** V. CERCHEZ and C. PANAITESCU (Bull. Soc. chim., 1933, [iv], 53, 243—248).— $\text{H}_2\text{O}$  of crystallisation evolved at  $< 135^\circ$  is removed by refluxing with xylene, and its vol. is measured. Pure anhyd.  $\text{H}_2\text{C}_2\text{O}_4$  may be made by refluxing  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  with  $\text{C}_6\text{H}_6$ . J. S. A.

**Nephelometric determination of chloride.** I. M. KOLTHOFF and H. YUTZY (J. Amer. Chem. Soc., 1933, 55, 1915—1922; cf. A., 1922, ii, 383).—The effect of various factors on the stability and turbidity of  $\text{AgCl}$  suspensions has been investigated.  $0.0008\text{—}0.42\text{ mg. Cl}^-$  in 10 c.c. is determined to within 2% by adding the solution rapidly, with shaking, to 25 c.c. of  $\text{EtOH}$  containing 1 c.c. of  $0.5N\text{-AgNO}_3$  and 5 c.c. of  $0.5N\text{-HNO}_3$  and comparing nephelometrically after 1 hr. with simultaneously prepared standards.  $\text{SO}_4^{--}$  interferes. J. G. A. G.

**Determination of chloride in presence of bromide and iodide.** M. STSCHIGOL (Z. anal. Chem., 1933, 92, 420—425).—To 10 c.c. of the solution are added 35—40 c.c. of 2% aq.  $\text{NH}_3$  and sufficient  $\text{AgNO}_3$  solution to react with all the halide present; 50 c.c. of the filtrate, which contains all the  $\text{Cl}^-$  as  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ , are treated with 3—4 g. of  $\text{Na}_2\text{CO}_3$  and 15—20 c.c. of  $\text{Na}_3\text{AsO}_3$  solution (8 g. of  $\text{As}_2\text{O}_3$  and 21 g. of  $\text{Na}_2\text{CO}_3$  per 100 g.), and the whole is boiled until the pptd.  $\text{Ag}_3\text{AsO}_3$  is reduced. The  $\text{Ag}$  is collected, dissolved in  $\text{HNO}_3$ , and titrated with  $\text{NH}_4\text{CNS}$ . Reduction of the  $\text{AgCl}$  in presence of  $\text{AgBr}$  and  $\text{AgCl}$  yields high results. H. F. G.

**Micro-determination of bromine in presence of chlorine and iodine.** S. H. BERTRAM (Biochem. Z., 1933, 261, 202—206).—By oxidising with  $\text{KMnO}_4$  in a solution maintained suitably acid with  $\text{KHSO}_4$  and  $\text{K}_2\text{SO}_4$  ionised halogens can be separated ( $\text{Cl}^-$  is not oxidised;  $\text{I}^-$  is converted into  $\text{HIO}_3$ ) and  $0.01\text{—}0.005\text{ mg. of Br}^-$  can be determined in material containing  $\geq 0.3\text{ g. of Cl}^-$  and  $0.0025\text{ g. of I}^-$ .  $N$  compounds and metals (other than alkali metals) must be absent. The  $\text{Br}$  is twice distilled into a solution of  $\text{KI}$  and  $\text{KHSO}_4$  and the liberated  $\text{I}$  titrated with  $0.001N\text{-Na}_2\text{S}_2\text{O}_3$ . W. McC.

**Determination of bromide in mixtures of silver chloride and bromide.** D. H. P. VOLLER (Chem. Weekblad, 1933, 30, 331—332).—The mixture is distilled with a solution of  $\text{NaCl}$  and  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$  being added gradually through a side tube, and the  $\text{Cl}_2$  and  $\text{Br}$  evolved are passed into cold  $N\text{-NaOH}$ . The  $\text{NaBr}$  and  $\text{NaOBr}$  formed are oxidised (by the  $\text{NaOCl}$  present) by adding  $\text{Na}_2\text{SO}_4$  and  $\text{H}_3\text{BO}_3$  and heating to  $85\text{—}90^\circ$ ; after cooling,  $\text{H}_2\text{O}_2$  is added, and the excess is removed by boiling the slightly alkaline solution.  $\text{NaBrO}_2$  is then determined by adding  $\text{KI}$  and  $\text{HCl}$ , with a trace of molybdic acid, and titrating with  $\text{Na}_2\text{S}_2\text{O}_3$ . The reagents must be free from  $\text{NO}_3^-$ . H. F. G.

**Determination of fluorine by Carnot's method.** H. HERLEMONT and J. DELABRE (Compt. rend., 1933, 196, 1502—1504; cf. A., 1892, 911).—The low result obtained by this method is due to loss of  $\text{F}$  as  $\text{HF}$ ; it is completely avoided (even if the substance analysed contains  $\text{SiO}_2$ ) by adding about 2 g. of  $\text{Fe-Si}$  (75%  $\text{Si}$ )



for each (approx.) 0.1 g. F, drying thoroughly, and then adding  $\text{H}_2\text{SO}_4$  and heating at  $140^\circ$  etc. as usual. An accurate result is equally obtained if the gases evolved in the ordinary method are passed over Fe-Si before absorption.  
C. A. S.

**Determination of sulphates.** V. NJEGOVAN and V. MARJANOVIĆ (Arh. Hemiju, 1933, 7, 36—41).—Berlin porcelain filter-crucibles are unsuitable for the determination of  $\text{SO}_4^{2-}$  as  $\text{BaSO}_4$ , owing to adsorption of sol. salts from the reaction mixture; these may, in the absence of  $\text{SO}_4^{2-}$ , amount to  $> 50$  mg. after 40 determinations. Ordinary Gooch crucibles should be used.  
R. T.

**Colour reaction for sulphur dioxide.** Z. RUDNITSKI (Ukrain. Chem. J., 1932, 7, [Sci.], 226—227).— $\text{SO}_3^{2-}$  gives characteristic colorations with various tanning extracts in the presence of  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , or  $\text{CrO}_4^{2-}$ . Oak-bark extract is the most suitable for the purpose, giving an intense reddish-violet colour. Should  $\text{NH}_3$  be present, the reaction should be performed in slightly acid solution.  
R. T.

**Reactions for detection of sulphites and thio-sulphates, and the sensitivity of reactions for sulphides and sulphates.** N. S. SCHUB (Ukrain. Chem. J., 1932, 7, [Sci.], 189—202).— $\text{SO}_3^{2-}$  ( $\leq 0.04$  mg.) instantly decolorises 2 c.c. of 0.035% fuchsin; the optimal  $p_{\text{H}}$  is 8.2.  $\text{S}^{2-}$ , if present, should first be pptd. as  $\text{PbS}$  by adding an alkaline solution of  $\text{PbCO}_3$ .  $\text{S}_2\text{O}_3^{2-}$  ( $\leq 11$  mg. per c.c.) is detected by boiling with aq.  $\text{HCl}$ , when turbidity due to separation of  $\text{S}$  appears;  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{AsO}_3^{3-}$ ,  $\text{S}^{2-}$ , and  $\text{SO}_3^{2-}$  should first be pptd. as  $\text{Zn}$  salts.  $\text{SO}_4^{2-}$  ( $\leq 1$  mg. per c.c.) gives a ppt. or turbidity with 10%  $\text{BaCl}_2$  in 2N- $\text{HCl}$ ;  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{AsO}_3^{3-}$ ,  $\text{S}^{2-}$ , and  $\text{SO}_3^{2-}$  should be removed.  $\text{S}^{2-}$  ( $\leq 0.0017$  mg. per c.c.) gives a brown coloration with aq.  $\text{Na}_2\text{PbO}_2$ .  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{CNS}^-$ ,  $\text{NO}_3^-$ ,  $\text{AcO}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{C}_2\text{O}_4^{2-}$  do not interfere with the above reactions.  
R. T.

**Colorimetric determination of hydrogen sulphide in water by means of phosphotungstic acid.** L. N. LAPIN and W. O. HEIN.—See B., 1933, 526.

**Separation of sulphur bases from sulphur acids, and detection of the elements in group II.** C. CANDEA and L. I. SAUCIUO (Bul. Soc. Chim. România, 1933, 14, 179—181).—The separation of group II elements by the solubility of As, Sb, and Sn sulphides in aq.  $\text{NaOH}$  is described.  
F. R. S.

**Assay of nitrogen monoxide.** J. C. KRANTZ, jun., W. F. REINDOLLAR, and C. J. CARR.—See B., 1933, 505.

**Detection of nitrites and their determination by means of the step-photometer.** L. JENDRASIK and E. FALCSIK-SZABÓ (Biochem. Z., 1933, 261, 110—115).—For the determination of  $\text{NO}_2^-$  in concn. equiv. to 0.2—35.0 mg. per litre by means of the step-photometer a mixture of  $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$  (I) and a derivative (II) of  $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$  (e.g., novocaine) is used. (II) is diazotised and coupled with (I) producing a stable sol. dye. The error, when the concn. is 1—15 mg. per litre, is  $\pm 0.6\%$  and outside these limits  $\pm 2.5\%$ . The procedure may also

be applied colorimetrically using hæmatoxylin as standard colour.  
W. McC.

**Detection of nitrites in water by peroxide reagents.** G. CARPENTIER.—See B., 1933, 494.

**Volumetric determination of phosphoric acid and of potassium by the use of a new method of washing.** T. KHOI (Ann. Falsif., 1933, 26, 217—222).—A circular piece of filter-paper is cut to fit the bottom of a Gooch crucible, and replaces the usual asbestos. The filtration of the  $\text{NH}_4$  phosphomolybdate ppt. and of the  $\text{K}_3\text{Co}(\text{NO}_2)_6$  ppt. is satisfactory, and the method facilitates washing. The results obtained are trustworthy.  
E. B. H.

**Gravimetric determination of phosphate ion, and the solubility product of magnesium ammonium phosphate.** N. A. TANANAIEV and P. S. SAVTSCHENKO (Ukrain. Chem. J., 1932, 7, [Sci.], 203—225).—The solubility  $S$  of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (I) in  $\text{H}_2\text{O}$  at  $25^\circ$  is 0.0987 g. per litre, and the solubility product is  $7.88 \times 10^{-14}$ .  $S$  is slightly lowered by  $< 0.02N\text{-NH}_4\text{Cl}$ , but is greatly augmented at higher concn., whilst aq.  $\text{NH}_3$  lowers  $S$  at all concns. These results are ascribed to the acid reaction of aq.  $\text{NH}_4\text{Cl}$  and to reversal of ionisation due to excess of  $\text{NH}_4^+$ . It is concluded that the concn. of  $\text{NH}_4\text{Cl}$  in solutions from which (I) is to be pptd. should not exceed 0.02N.  
R. T.

**Modification of Bettendorff's arsenic test, with adaptation for mercury determination.** W. B. KING and F. E. BROWN (Ind. Eng. Chem. [Anal.], 1933, 5, 168—171).—The sensitivity of Bettendorff's test for As is increased 10—100 times by the presence of 0.00001M- $\text{HgCl}_2$ ; the coloration also appears more rapidly and the test can be made in a lower concn. of  $\text{HCl}$ . At this dilution  $\text{HgCl}_2$  does not form a turbidity with  $\text{SnCl}_2$ . The rate of formation of the coloration is a function of the concn. of  $\text{HgCl}_2$ . By comparing the rate with that in presence of known concns. of  $\text{HgCl}_2$  the test may also be used to determine  $\text{HgCl}_2$  at concns.  $\leq 0.00000002M$ .  
E. S. H.

**Detection of traces of carbon monoxide in air.** H. HARTRIDGE.—See B., 1933, 525.

**Accuracy of the rapid semi-micro-determination of carbon dioxide in air.** L. W. WINKLER.—See B., 1933, 493.

**Colorimetric determination of oxalic acid.** C. A. MITCHELL (Analyst, 1933, 58, 279).—The orange-red colour produced on adding 5 c.c. of 1%  $\text{NaVO}_3$  solution and 3 c.c. of  $\text{H}_2\text{O}_2$  to 5 c.c. of 0.1%  $\text{H}_2\text{C}_2\text{O}_4$  is matched against that from a standard (sensitiveness 3 in  $10^4$ ). Tartaric acid gives a similar reaction (sensitiveness 12 in  $10^4$ ), citric acid a yellow colour, and succinic and malic acids transient red colours. Mineral acids produce a pervanadic acid of similar colour, and must be absent.  
J. G.

**Determination of silica in silicates by the difference method.** G. T. GALFAJAN and W. M. TARAJAN (Z. anal. Chem., 1933, 92, 417—420).— $\text{H}_2\text{C}_2\text{O}_4$  cannot be used for the quant. conversion of fluorides into carbonates, and the method of Tananaev and Pertschik (A., 1932, 922) is therefore not satis-



factory. Sulphates are, however, quantitatively converted into orthophosphates by  $\text{NaPO}_3$ . In the method recommended, the powdered sample (0.5–1 g.) is heated with 1 : 1  $\text{H}_2\text{SO}_4$  and 5–7 c.c. of  $\text{HF}$ , and after a second evaporation with  $\text{H}_2\text{SO}_4$ , 3–4 g. of  $\text{NaPO}_3$  are added and the whole is ignited to const. wt. The method is rapid (5–6 hr.), and the results are accurate to within 0.1%, even in presence of 29% of  $\text{Al}_2\text{O}_3$ . H. F. G.

**Determination of potassium by sodium cobaltinitrite.** J. E. SCHUELER and R. P. THOMAS (Ind. Eng. Chem. [Anal.], 1933, 5, 163–165).—Variations of standard procedure are described with respect to the temp. of pptn., the pptg. medium, the time of pptn., washing of the ppt., and the titration. The method is very accurate for 3–10 mg. K and may be used for < 1 to > 50 mg.  $\text{NH}_4$  salts interfere and org. matter should not be present. E. S. H.

**Gravimetric and polarographic determination of total alkali.** V. MAJER (Z. anal. Chem., 1933, 92, 401–405).—If total alkali (K+Na) is determined by weighing as sulphate and calculating as  $\text{K}_2\text{O}$  ( $\text{Na}_2\text{O}$ ), the error does not exceed 0.20% if  $\geq 1\%$  of  $\text{Na}_2\text{O}$  ( $\text{K}_2\text{O}$ ) is present. Weighing as chloride or as sulphate gives practically the same result if the mixture contains  $\geq 5\%$  of one alkali, whilst the gravimetric and polarographic methods agree closely if  $\geq 10\%$  of one alkali is present. H. F. G.

**Preparation of sodium hydroxide solutions of low carbonate content by centrifugation.** N. ALLEN and G. W. LOW, jun. (Ind. Eng. Chem. [Anal.], 1933, 5, 192).—Conc. aq. solutions of  $\text{NaOH}$  (1 : 1) are freed from undissolved  $\text{Na}_2\text{CO}_3$  by centrifuging. E. S. H.

**Reagent for lithium in presence of other alkalis; separation of lithium and magnesium; determination of lithium; separation of arsenites and arsenates.** T. GASPAR Y ARNAL (Ann. Chim. Analyt., 1933, [ii], 15, 193–194).— $\text{Na}_3\text{AsO}_4$  in alkaline  $\text{EtOH}$  solution gives with  $\text{Li}^+$  a pale pink ppt. which may be used for the determination of  $\text{Li}$ .  $\text{Mg}$ , but not  $\text{Li}$ , is pptd. by  $\text{Na}_3\text{AsO}_4$ . Hence,  $\text{AsO}_4^{4-}$  may be pptd. by  $\text{Li}^+$  + aq.  $\text{NH}_3$  +  $\text{EtOH}$ ;  $\text{AsO}_4^{4-}$  in the filtrate may be pptd. by  $\text{Mg}$ . J. S. A.

**Detection of silver in bismuth salts.** J. F. REITH.—See B., 1933, 505.

**Gravimetric determination of beryllium and thorium using selenous acid, and its application to their separation from certain elements.** J. KOT'Á (Chem. Listy, 1933, 27, 79–84, 100–105, 150–154, 194–197).— $\text{Be}^{II}$  ( $\leq 0.5$  mg.-%  $\text{BeO}$ ) is quantitatively pptd. from alkaline solution as basic selenite by  $\text{H}_2\text{SeO}_3$ ;  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Li}^+$  do not interfere with the reaction. The  $\text{BeO}$  obtained by ignition of the ppt. is readily sol. in  $\text{HNO}_3$  or  $\text{HCl}$ .  $\text{Zr}^{IV}$  and  $\text{Bi}$  are quantitatively pptd. by  $\text{H}_2\text{SeO}_3$  from acid solutions (0.2N- $\text{HCl}$  and 0.4N- $\text{HNO}_3$ , respectively);  $\text{Be}$ , if also present, can be pptd. from the filtrate by adding aq.  $\text{NH}_3$  and  $\text{H}_2\text{SeO}_3$ .  $\text{Al}$ ,  $\text{Mn}$ ,  $\text{U}$ ,  $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Ce}^{III}$ ,  $\text{La}$ , and  $\text{Y}$  do not interfere with the determination of  $\text{Zr}$  by this method.  $\text{Ti}$  is pptd. from acid solution, and  $\text{Th}^{IV}$  from neutral solution in

presence of  $\text{NH}_4\text{OAc}$ . Should considerable quantities of  $\text{Be}$  be present, the pptn. of  $\text{Th}$  should be repeated. R. T.

**Quantitative separation of small amounts of zinc from material rich in iron.** F. G. HILLS (Ind. Eng. Chem. [Anal.], 1933, 5, 201).—The solution in  $\text{HCl}$  is almost neutralised with aq.  $\text{NH}_3$ , excess of  $\text{Na}$  citrate is added, the solution is diluted, and  $\text{H}_2\text{S}$  is passed until the  $\text{ZnS}$  ppt. coagulates. The ppt. is filtered, dissolved in dil.  $\text{HNO}_3$ , evaporated to dryness, redissolved in  $\text{HCl}$  with addition of  $\text{NH}_4\text{Cl}$ , and  $\text{Zn}$  is determined in the solution by the usual methods. E. S. H.

**Colorimetric determination of thallium [in rodenticides].** P. A. SHAW.—See B., 1933, 494.

**Quantitative separation of aluminium from iron.** J. HASLAM (Analyst, 1933, 58, 270–272).— $\text{Fe}$  was pptd. at the b.p. with  $\text{H}_2\text{S}$  in the presence of tartaric acid followed by an excess of aq.  $\text{NH}_3$ , and the filtrate, after removal of the  $\text{FeS}$ , acidified with  $\text{HCl}$ , neutralised with aq.  $\text{NH}_3$  to Me-orange, and 2.5 c.c. of  $\text{NH}_3$  added in excess.  $\text{Al}$  was then pptd. by slow addition of hydroxyquinoline sulphate solution (5 c.c. in excess), coagulated at  $90^\circ$ , and filtered after 4 hr. (cf. A., 1927, 848). The max. recorded error on 0.0048–0.0289 g. of  $\text{Al}$  in the presence of 0.1 g. of  $\text{Fe}^{III}$  is 0.1 mg. J. G.

**Detection and determination of iron in drinking water.** J. PRESCHER.—See B., 1933, 526.

**Conductivity titrations of basic chromium sulphate solutions.** E. R. THEIS, A. W. GOETZ, and R. G. SNYDER.—See B., 1933, 505.

**Potentiometric determination of molybdenum in steel.** P. DICKENS and R. BRENNCKE.—See B., 1933, 510.

**Molybdenum and tungsten content of minerals.** G. VON HEVESY and R. HOBBIÉ (Z. anorg. Chem., 1933, 212, 134–144).—The mineral is fused with  $\text{NaOH}$ , the melt acidified with  $\text{HCl}$ , and  $\text{Mo}$  and  $\text{W}$  oxidised with  $\text{H}_2\text{O}_2$ . Excess of  $\text{BaCl}_2$  is added, and then  $\text{NaOH}$ . The ppt. is immediately filtered, dried by means of  $\text{CO}_2$ , and heated in  $\text{Cl}_2$  at  $600^\circ$ . The sublimate is dissolved in acid, and  $\text{MoS}_2$  pptd. in presence of  $\text{Cu}$ . The  $\text{MoS}_2$  is dissolved in acid,  $\text{Cu}$  removed electrolytically, and  $\text{Mo}$  determined colorimetrically by the method of Montignie (A., 1930, 313).  $\text{W}$  is determined X-ray spectrographically in the filtrate from the  $\text{MoS}_2$  pptn. The mean  $\text{Mo}$  content of igneous rocks is  $1.5 \times 10^{-5}$ ; that of  $\text{W}$   $6.9 \times 10^{-5}$ . J. S. A.

**Volumetric determination of uranium with potassium dichromate as reagent and the application of the method to the indirect titration of minute quantities of sodium.** I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Chem. Soc., 1933, 55, 1871–1876).— $\leq 6$  mg. of  $\text{U}^{IV}$  in 100 c.c. is determined to within 1% by titration with  $\text{K}_2\text{Cr}_2\text{O}_7$  in the presence of  $\text{H}_3\text{PO}_4$  with  $\text{Ba}$  diphenylaminesulphonate and  $\text{FeCl}_3$  as indicator (cf. A., 1926, 40; 1931, 1026). 0.08–0.8 mg. of  $\text{Na}$  is determined to within 5% by pptn. as  $\text{Na}$  uranyl  $\text{Zn}$  acetate (A., 1928, 859) which is reduced in  $\text{H}_2\text{SO}_4$  solution (*loc. cit.*) and the  $\text{U}^{IV}$  titrated with  $\text{K}_2\text{Cr}_2\text{O}_7$  as above. J. G. A. G.



**Determination of small amounts of antimony in copper.** B. PARK and E. J. LEWIS (Ind. Eng. Chem. [Anal.], 1933, 5, 182—183).—Addition of  $\text{KMnO}_4$  and  $\text{MnSO}_4$  to the acid solution of Cu ppts.  $\text{MnO}_2$  and carries down the Sb. The ppt. is dissolved in  $\text{HCl}$ , reprecipitated as  $\text{Sb}_2\text{S}_3$ , again dissolved in  $\text{HCl}$  and evaporated, and a measured amount (0.1 c.c.) is transferred to a hollow bored in the top of a pure graphite electrode. Sb is then determined spectrographically. 1 part of Sb in  $5 \times 10^6$  parts of Cu can be determined. E. S. H.

**Electrical resistance thermometers as applied to human calorimetry.** G. F. SODERSTROM (Rev. Sci. Instr., 1933, [ii], 4, 285—288).—Constructional details are given. C. W. G.

**Temporary depression of zero point of sensitive mercury thermometers.** F. HÖPPLER (Chem.-Ztg., 1933, 57, 394).—By comparison of two specially prepared thermometers, it is shown that the depression of zero point by previous heating for 5 min. in boiling  $\text{H}_2\text{O}$  disappears only after about 1 week. F. R. S.

**U-type mercury thermoregulator.** J. B. RAMSEY (Ind. Eng. Chem. [Anal.], 1933, 5, 218—219).—A method of maintaining a supply of  $\text{H}_2$  at the Hg contact is described. E. S. H.

**Cryostat for low and very low temperatures.** P. WOOG, J. GIVAUDON, and F. DAYAN (Bull. Soc. chim., 1933, [iv], 53, 240—243).—A thermostat for the range  $0^\circ$  to  $-60^\circ$  is described. J. S. A.

**Thermostat for lower temperatures.** T. J. B. STIER and W. J. CROZIER (J. Gen. Physiol., 1933, 16, 757—766).—The thermostats maintain precise temp. ( $\pm 0.001^\circ$ ) down to  $0^\circ$ , and the temp. may be rapidly adjusted. H. G. R.

**Determination of absolute thermal coefficients of expansion of liquids.** J. ZAHRADNÍČEK (Physikal. Z., 1933, 34, 386).—A modified Dulong and Petit apparatus is described in which two U-tubes, connected together, are used. A. J. M.

**Absorption trough for use with the Bürker universal spectroscope.** W. SIERADZKI (Z. physiol. Chem., 1933, 216, 138). J. H. B.

**New type of spectrographic slit.** G. FASSIN (J. Opt. Soc. Amer., 1933, 23, 186—188).—A satisfactory bilateral slit which can be made without specialised labour is described. C. W. G.

**Focus of a concave grating spectrograph.** D. L. MACADAM (J. Opt. Soc. Amer., 1933, 23, 178—181).—A method for mounting a 21-ft. concave grating and slit so that the focus will lie on a previously determined track is based on a precise knowledge of the nature of the general focal curve. C. W. G.

**Moving film cameras in X-ray analysis.** B. W. ROBINSON (J. Sci. Instr., 1933, 10, 165—169).—In one type the film is wrapped around a cylinder which rotates at the same speed as the crystal about an axis perpendicular to the X-ray beam and to the axis of rotation of the crystal. In the other a cylindrical film moves parallel to its own axis, which is also the axis of rotation of the crystal. C. W. G.

**Exact focussing X-ray spectrometer.** T. JOHANSSON (Z. Physik, 1933, 82, 507—528). A. B. D. C.

**Concave grating spectrograph.** J. E. MACK and J. R. STEHN (J. Opt. Soc. Amer., 1933, 23, 184—185; cf. *ibid.*, 1932, 22, 245).—A graph from which the optimum width of a concave grating may be found for any practical case is given. C. W. G.

**Uranium as a source of continuous ultra-violet radiation.** S. J. LEWIS (Chem. and Ind., 1933, 464—465).—A spark between U electrodes provides a continuous spectrum down to 2100 Å. The advantage of this over a line spectrum (W steel) in absorption spectrum work is illustrated by means of photographs of the spectrum of  $\text{C}_6\text{H}_6$  in  $\text{C}_6\text{H}_{14}$ . D. R. D.

**Preparation of test plates for the microscope.** L. C. MARTIN (J. Sci. Instr., 1933, 10, 187—188).—Directions for obtaining a uniform film of realgar on glass are given. C. W. G.

**Thiel's method of absolute colorimetry.** E. LANDT (Z. Elektrochem., 1933, 39, 310—312; cf. A., 1932, 1225).—The grey solutions described by Thiel have an extinction coeff.  $< 0.5$  for red light. The solutions lack the stability and freedom from sensitivity to light which were claimed. H. J. E.

**Absolute colorimetry with grey solutions.** A. THIEL (Z. Elektrochem., 1933, 39, 312—316).—A reply (cf. preceding abstract). Further details of technique are given. A new and more stable solution is described. H. J. E.

**Crystalline quartz double monochromator.** W. E. FORSYTHE and B. T. BARNES (Rev. Sci. Instr., 1933, [ii], 4, 289—294).—Settings on a spectral line can be repeated to 0.1 Å. at 3000 Å. C. W. G.

**Durable glass electrode.** D. A. MACINNES and D. BELCHER (Ind. Eng. Chem. [Anal.], 1933, 5, 199—200).—The electrode and liquid junction device described give results for  $p_{\text{H}}$  which are in good agreement with accepted vals. E. S. H.

**Technique of the glass electrode.** T. F. G. HEBURN (J. Soc. Leather Trades Chem., 1933, 17, 268—270).—The apparatus can be made efficient only in the absence of  $\text{H}_2\text{O}$ , low temp., and electrical disturbances. The results are affected by the proximity of other metallic apparatus. Other necessary precautions are detailed. D. W.

**One-valve amplifier for  $p_{\text{H}}$  determinations with glass electrode.** R. NORDBØ (Tidsskr. Kjemi, 1933, 13, 62—66).—An amplifier of simple construction has been devised, based on the work of Dubois and Stadie (A., 1929, 1262; 1931, 58), which can be employed in potentiometric measurements in conjunction with either a glass or a quinhydrone electrode. H. F. H.

**High-capacity hydrogen electrodes.** A. EUCKEN and K. BRATZLER (Ber. Ges. Kohlentechn., 1933, 4, 290—304).—Measurements of H electrode potential using a Pt net against suitable Hg electrodes in acid and alkaline solutions of varying concns. and for varying c.d. are recorded and compared with those calc. It is shown that in both acid and alkaline solution up



to a c.d. of 1.25 amp. per sq. dm. the current strength is determined by the rate of diffusion of  $H^+$ . The alkaline solution is only slightly inferior to the acid in current yield so that cheaper electrode materials than Pt are possible. With a platinised C cylinder, the alkaline solution was markedly inferior. In neither case did stirring make much difference. The C electrode deteriorated with use probably through adsorption except in strongly acid solution. C. I.

**Radioactive contamination of ionisation chamber materials.** J. A. BEARDEN (Rev. Sci. Instr., 1933, 4, [ii], 271—275).—Cold-rolled steel was least contaminated, followed, in order, by amber, brass, and Cu. Surfaces once cleaned should be kept in an atm. of MeBr,  $CO_2$ , or  $N_2$ . C. W. G.

**Micro-fractionating column for liquids having low heat of vaporisation.** P. E. WESTON (Ind. Eng. Chem. [Anal.], 1933, 5, 179—180).—The apparatus may be used with 10—15 c.c. of liquid. Total condensation occurs at the head of the column and all the vapour must flow past the bulb of the thermometer. E. S. H.

**Head for laboratory fractionating columns.** E. C. WAGNER and J. K. SIMONS (Ind. Eng. Chem. [Anal.], 1933, 5, 183—184).—An all-glass apparatus is described. E. S. H.

**Apparatus and methods for precise fractional-distillation analysis. IV. Standardisation of low-temperature fractionation-analysis apparatus and method of using automatic recording and control.** W. J. PODBIELNIAK (Ind. Eng. Chem. [Anal.], 1933, 5, 171—178; cf. A., 1931, 704).—The apparatus formerly described has been improved by using an automatic recording and control mechanism, with further development and standardisation of the fractionating unit. E. S. H.

**Determination of osmotic pressures by isothermal distillation. II.** M. ULMANN (Z. physikal. Chem., 1933, 164, 318—326).—The apparatus previously described (A., 1931, 1367) has been modified so as to make it suitable for use with solutions in AcOH. Measurements with dil. solutions of maltose octa-acetate and glucose penta-acetate (I) have shown the apparatus to be satisfactory. With (I) there is appreciable association even in 0.2% solution. R. C.

**Continuous extractor of large capacity.** C. M. McCAY (Ind. Eng. Chem. [Anal.], 1933, 5, 213).—The apparatus takes a 10—45 kg. charge of material. E. S. H.

**Device for removing "frozen" glass stoppers from reagent bottles.** C. WIRTH (Ind. Eng. Chem. [Anal.], 1933, 5, 217). E. S. H.

**Burette with greaseless stopcock.** W. A. LANDE, jun. (Rev. Sci. Instr., 1933, [ii], 4, 296).—

The liquid contained in the burette acts as a lubricant for a plunger ground at the lower end and actuated by a screw. C. W. G.

**Micro-burette.** M. MALMY (J. Pharm. Chim., 1933, [viii], 17, 469—474).—The attachment of a fine glass tip to the jet of a micro-burette allows very small drops to be delivered. F. O. H.

**Laboratory screw clamp.** W. A. SPERRY (Ind. Eng. Chem. [Anal.], 1933, 5, 188). E. S. H.

**Air pressure for blast lamps.** G. W. THIESSEN and J. E. WERTZ (Ind. Eng. Chem. [Anal.], 1933, 5, 201).—A vac. cleaner may be adapted. E. S. H.

**Windshield for Saybolt viscosimeter.** F. J. VITOVEC, jun. (Ind. Eng. Chem. [Anal.], 1933, 5, 212).—A glass screen is described. E. S. H.

**Use of the slide rule in calculating hydrogen-ion concentration and  $p_H$  values.** M. C. SANZ (Ind. Eng. Chem. [Anal.], 1933, 5, 218). E. S. H.

**Collodion membrane filters. I, II.** I. ASHESHOV (J. Bact., 1933, 25, 323—337, 339—357).—The prep. and uses of graduated membrane filters are described. A. G. P.

**Regulating the air supply of microburners.** C. A. DALY (Science, 1933, 77, 413).—Details of a satisfactory method are described. L. S. T.

**Buchner filters with heating jackets.** W. GURR (Chem. Fabr., 1933, 6, 248—249).—(1) A Buchner filter may have a simple steam jacket; (2) the filter and jacket may be double the usual depth; (3) the steam may also be led through the filter plate by passages, so reducing the filtration area. The last arrangement allows the temp. in the cake to be raised from 70° to 90° and in many cases the more rapid filtration more than compensates for the loss of filtration area. C. I.

**Bar rider for accurate weighing.** L. RAMBERG (Arkiv Kemi, Min., Geol., 1933, 11 A, No. 7, 24 pp.).—In order to attain an accuracy of 0.001 mg. in weighings made on a microbalance, the position of the rider on the notch of the beam must be reproducible to 0.007 mm., and its angle of inclination from the vertical should not exceed 0.2°. A special rider, consisting of a short rod of quartz glass, permits much greater accuracy than the usual form. It is placed horizontally in the notches of the beam by means of a special transporter. The importance of calibrating the beam of a microbalance before employing a rider is also emphasised. H. F. H.

**Priestley as a practical chemist.** T. S. PATTERSON (Nature, 1933, 131, 690).—A criticism. L. S. T.

**Priestley as a practical chemist.** A. N. MELDRUM (Nature, 1933, 131, 801).—A reply (cf. preceding abstract). L. S. T.

## Geochemistry.

**Formaldehyde in dew.** N. R. DHAR and A. RAM (Nature, 1933, 131, 800; cf. A., 1932, 1106).—Dew from Allahabad contains approx. 0.0015 g. of

$CH_2O$  (I) per litre. It appears to be obtained from air in contact with grass, leaves, and soil. The origin of (I) is discussed. L. S. T.



**Oceanography and geochemistry.** V. J. VERNADSKY (Tsch. Min. Petr. Mitt., 1933, 44, 168—192).—A lecture. L. J. S.

**Boric acid in sea-water and its effect on the carbon dioxide equilibrium.** K. BUCH (Nature, 1933, 131, 688).—Ocean-H<sub>2</sub>O contains 15 g. B<sub>2</sub>O<sub>3</sub> per cu.m. as against 0.7 usually quoted. The ratio B:Cl is 0.237—0.248 × 10<sup>-3</sup>. The effect of H<sub>3</sub>BO<sub>3</sub> on the CO<sub>2</sub> equilibrium of sea-H<sub>2</sub>O is discussed. L. S. T.

**Temperature and salinity of the deeper waters of the Bay of Bengal and Andaman Sea.** R. B. S. SEWELL (Mem. Asiatic Soc. Bengal, 1932, 9, 357—423). CH. ABS.

**Chloride as indicator in detecting the inflowing into an inland-water lake of underground water possessing special physico-chemical properties.** S. YOSHIMURA (Proc. Imp. Acad. Tokyo, 1933, 9, 156—158).—Variation of Cl' content with depth in lake H<sub>2</sub>O is the best indicator of the inflow of underground H<sub>2</sub>O with special physico-chemical properties. J. W. S.

**Algal sediments of Andros Island, Bahamas.** M. BLACK (Phil. Trans., 1933, B, 222, 165—192).—Algal deposits of characteristic structure, consisting of CaCO<sub>3</sub> sediment mechanically entrapped, are described. The structure is best developed in regions of lower salinity than that of open ocean. J. S. A.

**Mineral springs of Chechnya (Caucasus).** G. A. MAXIMOVICH (J. Appl. Chem., Russia, 1932, 5, 1066—1077).—Results of analyses are recorded. CH. ABS.

**Activity of non-pathogenic bacteria utilising mineral matter in the thermal water of Aix-les-Bains and Aix-Burtscheid.** I. A. SCHLOEMER (Z. Unters. Lebensm., 1933, 65, 470—476).—The content of Fe is 1000 times, of Ca and SiO<sub>2</sub> many times, higher in the slimy sediment of the Kaiserbad spring at Aix than in the H<sub>2</sub>O. This is due to the action of Fe-, Ca-, and Brussoff's SiO<sub>2</sub>-bacteria. The sediment is also richer in Al, which was not found by Feder (*ibid.*, 1923, 46, 339) in the H<sub>2</sub>O, but is now shown to be present. E. C. S.

**Corrections and additions to the diagram for the determination of feldspars by Fedorov's method.** V. V. NIKITIN (Tsch. Min. Petr. Mitt., 1933, 44, 117—167).—The crystallographic directions of a series of feldspars are plotted on a stereographic projection with reference to the axes of the optical ellipsoid, and the results given by extinction angles on certain faces and section planes are tabulated. Several new chemical analyses are given of feldspars of which the optical data are determined. L. J. S.

**Position of the cotectic line between potash feldspar and plagioclase and their relations.** H. L. ALLING (Amer. J. Sci., 1933, [v], 25, 471—576).—A discussion of the views of Doggett (J. Geol., 1929, 37, 712), Vogt (Norsk. Videnskaps Akad., 1926, 58; 1931, 225), and Harker ("Natural History of Igneous Rocks," 1909, 250). C. W. G.

**Intrusive igneous rocks of the Muswellbrook-Singleton district. II. Savoy Sill.** H. G. RAG-

GATT and H. F. WHITWORTH (J. Proc. Roy. Soc. New South Wales, 1933, 66, 194—233).—The Savoy intrusion is partly of the simple sill type and partly phacoidal, and is of tertiary age. Analyses of the constituent dolerite and syenite are given. C. W. G.

**Composition and structure of artificial spherulites.** H. W. MORSE, J. D. H. DONNAY, and E. OTT (Amer. J. Sci., 1933, [v], 25, 494—498).—Each spherulite fibre is probably an aggregate of variously oriented crystals, each 10<sup>-3</sup> to 10<sup>-5</sup> cm. (cf. A., 1932, 564). C. W. G.

**Occurrence of sulphur, organic matter, nitrogen, and water in phosphate rock.** W. L. HILL, H. L. MARSHALL, and K. D. JACOB (J. Assoc. Off. Agric. Chem., 1933, 16, 260—276).—The determination of org. C by the dry combustion of rocks has been employed as a standard, and the results obtained have been compared with those by other methods. Colorimetric methods with sugar give high results and those obtained by comparison with tannic acid are probably high, although they agree fairly well for certain types of rock with those obtained by the combustion of actual org. matter extracted from the rock. Colorimetric methods are unsatisfactory for rocks such as Tennessee brown or blue rock, or Idaho phosphate. Results obtained by the direct ignition of the rock are affected by the oxidation of sulphides and org. S, whilst some of the S is expelled. Results are given for the org. C, N, S, and H<sub>2</sub>O contents of 29 samples of natural phosphates. T. McL.

**Granulite containing riebeckite and a calcareous detrital rock in the Niari basin (French Congo).** R. C. SABOT (Compt. rend., 1933, 196, 1517—1519).—Riebeckite, largely transformed into antigorite, occurs in a granulite that forms slabs in the river Bamaga near Bendé. C. A. S.

**Eruptive massif of Cavallo (Constantine).** L. GLANGEAUD (Compt. rend., 1933, 196, 1515—1517).—The tertiary eruptive rock in the neighbourhood of Cavallo (west of Jijelli, Algeria) consists, to the N.E., of microgranodiorites and quartziferous microdiorites containing phenocrysts of plagioclase (30—54% anorthite) and 5—23% of quartz; that in the centre of dacites and dacitoids containing colourless augite, with breccias of various materials. Both also contain green polychroic hornblende, and (especially the microgranodiorites) are traversed by veins of Ag- and Au-containing Cu, Pb, Zn, and Fe minerals, the rock in the neighbourhood of the veins being damouritised, kaolinised, or propylitised to considerable distances. Chlorites also abound. C. A. S.

**β-Cristobalite in Australian opals.** F. P. DWYER and D. P. MELLOR (J. Proc. Roy. Soc. New South Wales, 1933, 66, 378—382).—X-Ray evidence is adduced. C. W. G.

**Age of a Canadian cyrtolite.** O. B. MUENCH (Amer. J. Sci., 1933, [v], 25, 487—493).—Average contents are U 0.529, Pb 0.04308, Th 0.0799%, whence the age is calc. to be 571 × 10<sup>6</sup> years. C. W. G.

**Gypsum deposits of the Stopini-Salaspils-Nāvessala districts.** E. ROSENSTEIN (Latvij. Univ.



Raksti, 1933, 2, 241—288).—Dolomite inclusions (I) occur in deposits of cryst. but not of fibrous gypsum (II). Clay, if present, occurs only in (I), whilst bitumen is found in both (I) and (II). (I) is often intercalated with micro-crystals of (II). R. T.

**Fibre structure and optical properties of chalcedony.** C. W. CORRENS and G. NAGELSCHMIDT (Z. Krist., 1933, 85, 199—213; cf. A., 1922, ii, 304).—Chalcedony consists of quartz, which is capable of fibre-like growth in two crystallographic directions. The double refraction,  $n_D$ , 1.532 along, and 1.538 across, the direction of the fibres, is distinctly < that of quartz, which is attributed to the fibre aggregate possessing a double refraction of form of opposite sense to that of quartz. Density and H<sub>2</sub>O content indicate opal as the cementing material, with free H<sub>2</sub>O in one case. C. A. S.

**Antimony tetroxide and antimonates.** G. NATTA and M. BACCAREDDA (Z. Krist., 1933, 85, 271—296; cf. A., 1932, 450).—Pb<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>, Ca<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>, Sb<sub>2</sub>O<sub>4</sub>, and the corresponding minerals roemeite, bindheimite, and stibiconite are all cubic, space-group  $O_h^1$ , with  $a$  10.44, 10.25, 10.24, 10.25, 10.37—10.43, and 10.26 Å., and 8, 8, 16, 8, 8, and 16 mols. in the unit cell, respectively. Sb<sub>2</sub>O<sub>4</sub> is best written Sb<sup>III</sup><sub>2</sub>Sb<sup>V</sup><sub>2</sub>O<sub>8</sub>, the positions of Sb<sup>III</sup> and Sb<sup>V</sup> being distinguishable in the lattice; the position of one O remains unoccupied in the pyroantimonates. The H<sub>2</sub>O in stibiconite (Sb<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O) has no influence on the structure; this also holds for that in the CaO-containing group of Sb ochres, CaO.Sb<sub>2</sub>O<sub>5</sub>.3H<sub>2</sub>O and 3CaO.2Sb<sub>2</sub>O<sub>5</sub>.8H<sub>2</sub>O, which have the same structure as roemeite, and are designated hydroromeites. Similarly the PbCO<sub>3</sub> often present in bindheimite is an impurity removable by acid, and without effect on the structure. Analyses of hydroromeite (2), stibiconite, cervantite, and bindheimite (2) are given. C. A. S.

**Molybdenite at Azegur (Morocco).** R. E. GROSCLAUDE (Arch. Sci. phys. nat., 1933, [v], 15, 93—126).—Molybdenite occurs at Azegur 80 km. south of Marrakesh, as lamellae 0.5—3 cm. across, disseminated through a garnet hornfels (containing in places diopside, duparcite, and idocrase), which forms lenses in cryst. Cambrian limestone and schists, and is strongly metamorphosed by intrusive granite. This has mineralised the hornfels to distances dependent on the volatility of the mineral, molybdenite occurring nearest, then chalcopyrite, and furthest blende, with hematite, pyrite, pyrrhotite, galena, and mispickel as accessories. Analyses of 12 associated rocks are given. The molybdenite is best separated by pulverising to pass through a no. 200 sieve, and flotation with cresol, a little H<sub>2</sub>SO<sub>4</sub> being added. The concentrates contain 2.1—3% MoS<sub>2</sub>. In places the molybdenite is oxidised to molybdate. C. A. S.

**Mineralogy of Volhynian topaz deposits.** L. L. IVANOV (Bull. Acad. Sci. U.S.S.R., 1933, 421—444).—Topaz occurs in association with orthoclase, biotite, muscovite, smoky quartz, amethyst, and beryl in pegmatite veins of red Korosten granite, and in the products of their weathering. R. T.

**Formation of syngenite.** J. CHLOUPEK (Chem. Listy, 1933, 27, 197—199).—Syngenite is pptd. as

follows:  $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O} + 2\text{K}_2\text{SO}_4 = \text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O} + 2\text{KIO}_3 + 5\text{H}_2\text{O}$ . R. T.

**Plagioclase in the trachydolerite of Pauliberg, Burgenland.** H. WIESENER (Tsch. Min. Petr. Mitt., 1933, 44, 199—204).—The plagioclase of this extrusive igneous rock shows frequent twinning on (001), which is ascribed to the alkali content of the rock. L. J. S.

**Petrography of the Čistá-Jechnitz granite massif, Bohemia.** A. ORLOV (Tsch. Min. Petr. Mitt., 1933, 44, 205—210).—The acid granite and oligoclase-granodiorite forming this mass were derived by crystallisation-differentiation from the same magma. Chemical analyses of the rocks are given. L. J. S.

**Composition and genesis of the alkali-rocks of South Africa.** S. J. SHAND (Tsch. Min. Petr. Mitt., 1933, 44, 211—216).—Occurrences of alkali-rocks in the Bushveld, Transvaal, give support to Daly's hypothesis of the origin of such rocks. A granitic magma has assimilated the limestone into which it was intruded, and the heavier lime silicates have separated, leaving alkalis in excess of the ratio  $\text{R}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 = 1 : 1 : 6$ . L. J. S.

**Genesis of colloidal pyrrhotite and other minerals in the Bottino mine.** C. L. SAGUI and A. JOURDAN (Compt. rend., 1933, 196, 1424—1426).—In the narrower parts of the vein in the Bottino mine (near Florence), where cooling would be more rapid, galena is replaced by pyrites and pyrrhotite. In the light of Stevens' results (cf. Econ. Geol., 1933, 28, 1) this is explicable and due to the increased proportion of Na in the later solidifying portions of the magma, giving rise to Na sulphides, which in turn would convert PbS into the more fusible Na<sub>2</sub>S.PbS (cf. A., 1926, 494), causing it to be carried on more readily past a cooler place, and at the same time convert Fe into pyrrhotite. This on removal of the Na sulphide by H<sub>2</sub>O would be deposited in colloidal form, and be converted into pyrites by excess of S. C. A. S.

**Alkali metals in minerals.** R. BOSSUET (Compt. rend., 1933, 196, 1381—1383; cf. this vol., 363).—The method previously described shows the presence of Li, Na, K, Rb, and Cs in 17, 29, 27, 21, and 14, respectively, of the 29 alkali-containing minerals examined. Rb and Li occur in both orthose and microcline (cf. A., 1911, ii, 122); Rb and Cs chiefly in minerals containing K. C. A. S.

**Beryllium and helium.** (LORD) RAYLEIGH (Nature, 1933, 131, 724).—The richest of about 40 different beryls contains 29.2 cu. mm. of He per g. of beryl, i.e., 1 He to  $2.41 \times 10^4$  Be. Beryls from the younger rocks contain little He, whilst those from older rocks contain a relatively large amount, supporting the view that the He has accumulated as the result of at. disintegration of Be. Using the He-rich mineral a possible  $\alpha$ -activity of beryl was estimated at  $> 1.47 \times 10^7$   $\alpha$ -particles per g. per annum requiring  $5.43 \times 10^{10}$  years for the observed He to accumulate. Be-Al foil gave an activity of  $1.55 \times 10^8$   $\alpha$ -particles per g. per annum requiring a period of  $1.05 \times 10^{11}$  years; both of these periods are too long, and hence the He in beryl cannot be related to existing emission of  $\alpha$ -



particles. The  $\alpha$ -ray activity of Be found by Lange and Raitt (Physical Rev., 1933, [ii], 43, 585) also will not account for the He in beryl. L. S. T.

**James coal of New Zealand.** W. PENSELER (Fuel, 1933, 12, 166—181).—Geologically the James coal marks a transition stage from fresh-H<sub>2</sub>O to marine beds. It is black, dull, hard, and tough, has a conchoidal fracture, and is resistant to weathering. Its composition (H<sub>2</sub>O 6.0, volatile matter 51.5, fixed C 38.0, ash 4.5, S 4.5%) approaches that of a cannel coal. Microscopical examination of thin sections (illustrated) shows that the coal contains an abnormal amount of resistant plant entities, mainly cuticle and suberised tissue, but the absence of spore material distinguishes it from ordinary cannel coal. The evidence suggests that the coal has been formed from forest offal which had drifted into brackish H<sub>2</sub>O in a sheltered region of an estuary. A. B. M.

**Lignin theory of the origin of coal.** P. FISCHER. —See B., 1933, 496.

**Refractive index of agriculturally important compounds and changes under the influence of potassium chloride.** J. H. HELLMERS and R. KÖHLER (Z. Pflanz. Düng., 1933, 29, A, 309—320).—Changes in  $n$  of Al(OH)<sub>3</sub>, Fe(OH)<sub>3</sub>, kaolin, humic

material, etc. after treatment with KCl are recorded and the utilisation of optical methods in the examination of the course of weathering of minerals is discussed. A. G. P.

**Investigation and classification of soils on physicochemical lines.** P. VAGELER and F. ALTEN (Ernähr. Pflanze, 1933, 29, 121—132).—The authors' views on, and methods of examining, the nutrient balance of soils are summarised. A. G. P.

**Soil zones of Australia.** J. A. PRESCOTT (Soil Res., 1933, 3, 133—145).—A general survey. A. G. P.

**Red soils of the Tripolitanian plateau.** A. COMEL (Soil Res., 1933, 3, 126—132).—Chemical and mineralogical data are presented and the formation of these soils is discussed. A. G. P.

**Principles and scheme of a general soil system.** A. A. J. DE 'SIGMOND (Soil Res., 1933, 3, 103—126).—Modifications of existing systems are proposed. A. G. P.

**Soil survey of the Nyah, Tresco, West, Kangaroo Lake (Vic.), and Goodnight (N.S.W.) settlements.** J. TAYLOR, F. PENMAN, T. J. MARSHALL, and G. W. LEEPER (Comm. Australia, Counc. Sci. Ind. Res., Bull. No. 73, 1933, 47 pp.).

## Organic Chemistry.

**Relation between physical properties of organic molecules and their constitution and configuration.** J. TIMMERMANS (Inst. int. Chim. Solvay, Conseil Chim., 1931, 4, 191—237; Chem. Zentr., 1933, i, 201—203).

**Free radicals.** W. SCHLENK (Inst. int. Chim. Solvay, Conseil Chim., 1931, 4, 503—515; Chem. Zentr., 1933, i, 203).

**Catalytic oxidation of organic compounds in the vapour state.** G. CHARLOT.—See this vol., 680.

**Thermal decomposition of isobutane into primary products.** L. F. MAREK and M. NEUHAUS (Ind. Eng. Chem., 1933, 25, 516—519).—Expressed as mols. per 100 mols. of isobutane decomposed in a SiO<sub>2</sub> vessel, the proportions of products at 571° were H<sub>2</sub> and butylene 63.0, CH<sub>4</sub> and propylene 34.5, and C<sub>2</sub>H<sub>6</sub> 2.5; at 617° the corresponding figures were 63.0, 36.0, and 1.5. As calc. by Rice the ratio of CH<sub>4</sub> to H<sub>2</sub> should be 0.91 at 600° instead of 0.56 found. A. G.

**Configurative relationship of hydrocarbons.** V. Optical rotations of hydrocarbons of the isopropyl series. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1933, 100, 769—773; cf. A., 1931, 709).—1- $\alpha$ -Dimethyldecane, b.p. 112°/20 mm.,  $[M]_D^{25}$  —0.51°, is prepared by the action of MeI in dry Et<sub>2</sub>O on Et *d*-methylheptylacetate followed by dehydration with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and subsequent catalytic hydrogenation. 1- $\beta$ -isopropylpentane, b.p. 113—114°/760 mm.,  $[M]_D^{25}$  —1.05°, is prepared in a similar manner from CHMePr<sup>a</sup>-CO<sub>2</sub>H. In the series R·CHMePr<sup>s</sup> the direction of rotation is independent of the weight of R. A. L.

**Causes of the simultaneous production of  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -butene by catalytic dehydration of butyl alcohol by alumina.** C. MATIGNON, H. MOUREAU, and M. DODÉ (Compt. rend., 1933, 196, 973—977).—Dehydration of BuOH with an Al<sub>2</sub>O<sub>3</sub> catalyst (I) at 330—380° affords 85% of  $\Delta^{\alpha}$ - (II) and 15% of  $\Delta^{\beta}$ -butene (III) if (I) is pptd. and washed with dil. alkali. Preps. of (I) containing traces of acidic substances cause isomerisation of (II) to (III), and yield 90% of the latter. After being heated to 650° such catalysts again give (II). A. C.

**Condensation of isoprene.** H. VON EULER and L. AHLSTRÖM (Arkiv Kemi, Min. Geol., 1932, 11 A, No. 2, 18 pp.).—Isoprene (I) and AlCl<sub>3</sub> in CHCl<sub>3</sub> give an amorphous complex, C<sub>10</sub>H<sub>16</sub>.2SbCl<sub>3</sub>, m.p. > 300°, from which (I) could not be regenerated [showing rapid condensation of (I)]. Dipentene similarly gives a complex, C<sub>10</sub>H<sub>16</sub>.3SbCl<sub>3</sub>.7SbOCl. (I) is polymerised by varying amounts of SbCl<sub>3</sub> at 110°; removal of Sb from the resultant products by hot dil. HCl gives amorphous substances. Polymerisation of (I) is retarded by (NPh)<sub>3</sub>, carotene, quinol, AcCl, or Cu wire; little retardation occurs with (NPh)<sub>3</sub>+amyl nitrate (II). The variable rate (due to unknown impurities) of self-polymerisation of (I) is not compensated by a definite amount of a catalyst such as (II). The product from (I) and CO(NH<sub>2</sub>)<sub>2</sub> at 110° is N-free. Coloured and gummy products are formed from (I) and keten (III) at 60—70° and 75—105°. *p*-Benzoquinone and (III) in Et<sub>2</sub>O give the dilactone

$$\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH}:\text{CH} \\ \diagdown \text{CH}:\text{CH} \diagup \end{array} \text{C} \begin{array}{c} \text{CH}_2 \\ \diagup \text{O} \diagdown \end{array} \text{CO}, \text{ decomp. from } 121^\circ \text{ and molten at } 156^\circ.$$

H. B.



**Direct oxidation of acetylene by air.** P. MONDAIN-MONVAL and R. WELLARD (Compt. rend., 1933, 196, 1226—1228).—The concn. zones of mixtures of air and  $C_2H_2$  at atm. pressure which will undergo inflammation at a mean temp. of  $310^\circ$  when heated at const. vol. narrows from 17—85% of  $C_2H_2$  by vol. at a heating rate of  $40^\circ$  per min. to 35—70% at  $25^\circ$  per min. Outside this zone, a faint green luminescence and lowering of pressure, not due to polymerisation of  $C_2H_2$ , are observed. An oil is formed which responds to Schiff's reagent and is similar to that obtained from saturated hydrocarbons (A., 1930, 167). Similar phenomena with mixtures at an initial pressure of 4 atm. are described. A. C.

**Polymerisation and rupture of hydrocarbons under the influence of electric discharge.** R. V. DE SAINT-AUNAY (Chim. et Ind., 1933, 29, 1011—1025).—Hydrocarbons are submitted to a high-frequency silent electric discharge so that the primary products are rapidly removed and condensed, and thus the effect of temp. and p.d. are studied. Three main types of reaction are observed: (a) polymerisation due to activation of the C-H linking, (b) dehydrogenation due to a greater degree of activation of this linking which becomes more important the more saturated is the initial hydrocarbon, and (c) the rupture of C-C linkings and subsequent union of the radicals to more complex compounds. With  $C_2H_2$  only (a) occurs, rapid condensation affording gaseous products (4% of the condensed  $C_2H_2$ ),  $H_2$ ,  $C_2H_4$ , and  $C_2H_6$ , the yields of which increase to a max. and then diminish to 0 as the time of reaction is prolonged. The liquid products, b.p.  $10^\circ/23$  mm., contain  $(C_2H_2)_3$  (partly crystallises at  $-60^\circ$ ; Ag derivative  $C_6H_4Ag_2 \cdot 2AgNO_3$  in which  $CHMe(C:CH)_2$ ,  $(CH_2C:CH)_2$ , and  $(C:CH:CH_2)_2$  are present, since cold 5%  $KMnO_4$  affords  $HCO_2H$ ,  $EtCO_2H$ , and  $H_2CO_3$ , and  $O_3$  gives  $(CH_2CO_2H)_2$ ,  $CH_2O$ , and  $HCO_2H$ , but no  $MeCHO$  or  $AcOH$ ). With  $C_3H_4$  the gaseous products consist of  $H_2$  and  $C_2H_2$  (b) from which  $C_2H_6$ ,  $C_4H_8$ , and  $C_6H_{14}$  are obtained, and fractionation of the liquid products affords  $\Delta^a$ -butene and  $\Delta^a$ -hexene (a).  $C_2H_6$  affords (a)  $C_2H_4$ ,  $C_2H_2$ , and  $H_2$ , and by hydrogenation of these or by (c),  $CH_4$  and higher saturated hydrocarbons.  $CH_4$  gives  $H_2$ ,  $C_2H_6$ ,  $C_2H_4$ , and a little  $C_2H_2$ . With  $C_6H_6$  the gaseous product (produced regularly throughout) contains  $H_2$  52,  $C_2H_2$  32.8,  $C_2H_4$  7.2,  $C_2H_6$  7.2, higher ethylenic hydrocarbons 0.8%. In the liquid products, b.p.  $105$ — $145^\circ/14$  mm., (a) gives dihydrodiphenyl whence by (b)  $Ph_2$  and  $H_2$  are obtained,  $Ph_2$  alone being formed with a more intense discharge. The gaseous products from  $PhMe$  are  $H_2$  58,  $C_2H_2$  etc. 10,  $C_2H_4$  8,  $C_2H_6$  4,  $CH_4$  14, higher olefins 3%, the liquid products, b.p.  $110$ — $145^\circ/18$  mm., containing dihydrotolyls, b.p.  $130$ — $136^\circ/17$  mm., and  $(CH_2Ph)_2$  (crystallises at  $-30^\circ$ ).  $C_6H_{14}$  gives  $H_2$  43,  $C_2H_6$  6,  $C_2H_4$  21,  $CH_4$  12,  $C_3H_8$  11,  $C_3H_6$  6% ( $C_3H_8 \rightarrow CH_4 + C_2H_2$ ;  $C_3H_8 \rightarrow CH_4 + C_2H_4$ ), the liquid products, b.p.  $45$ — $120^\circ/15$  mm., containing  $\Delta^a$ -hexene and saturated hydrocarbons  $>C_9$ . J. W. B.

**Action of gaseous hydrogen iodide on iodo-derivatives of hydrocarbons. Preparation of ethylidene and vinyl iodides and  $\alpha\alpha\alpha$ -tri-iodo-**

**ethane.** G. EMSCHWILLER (Compt. rend., 1933, 196, 1028—1030).—Cold gaseous HI has no action on alkyl iodides,  $CH_2I_2$ ,  $CHMeI_2$  (I),  $CHI_3$ ,  $CMeI_3$  (II), or  $C_2H_4I_2$ .  $CI_4$  is reduced to  $CHI_3$ , and  $(CH_2I)_2$  to (I). Vinyl iodide (III) adds HI yielding (I), but no reaction occurs with conc. aq. HI. The primary product from  $(CHI_2)_2$  and HI (1 mol.) is  $\alpha\alpha\beta$ -tri-iodoethane (IV), but a mixture of this with (I), (III), and I is obtained. The yield of (III) is 70% if (IV) is heated. The sole product from 2 mols. HI is (I).  $(CI_2)_2$  and HI yield (II), probably through the intermediate  $CHI_2 \cdot CI_3$ . A. C.

**Conjugated systems. XII. Addition of bromine, hydrogen bromide, and hypobromous acid to  $\alpha$ -bromobutadiene.** I. E. MUSKAT and L. B. GRIMSLEY (J. Amer. Chem. Soc., 1933, 55, 2140—2145).— $\alpha$ -Bromobutadiene (I) and Br (1 mol.) in light petroleum,  $CHCl_3$ , or  $AcOH$  at  $-20^\circ$  to about  $50^\circ$  give  $\alpha\alpha\delta$ -tribromo- $\Delta^b$ -butene, b.p.  $94^\circ/8$  mm., oxidised by  $O_3$  to  $CH_2Br \cdot CO_2H$ ,  $H_2C_2O_4$ , and  $CHO \cdot CO_2H$  (qual. test), and by  $KMnO_4 \cdot CMe_2$  to  $CH_2Br \cdot CO_2H$ . (I) and dry HBr afford  $\alpha\alpha$ -dibromo- $\Delta^b$ -butene, b.p.  $71$ — $72^\circ/24$  mm. (ozonolysis products,  $AcOH$  and  $H_2C_2O_4$ ), which with Br in  $CHCl_3$  gives  $\alpha\alpha\beta\gamma$ -tetrabromobutane, b.p.  $148$ — $150^\circ/25$  mm. These results are contrary to those of Ingold and Smith (A., 1931, 1391), who state that  $\gamma\delta$ -addition of Br and HBr to (I) occurs, but agree with the principles previously developed (A., 1930, 1553). (I) absorbs 1 mol. of HOBr to give  $\alpha\delta$ -dibromo- $\alpha$ -hydroxy- $\Delta^b$ -butene (ozonolysis products,  $CH_2Br \cdot CO_2H$  and  $H_2C_2O_4$ ). H. B.

**Direct iodination of monosubstituted acetylenes.** T. H. VAUGHN and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1933, 55, 2150—2153).— $CI:CR$  are prepared from  $CH:CR$  and I in liquid  $NH_3$ . When  $R=Ph$ , tolyl, or vinyl, iodination occurs rapidly at  $-34^\circ$  and the yields are almost quant., but when  $R=alkyl$ , reaction is slow and incomplete at  $-34^\circ$  [but at  $25^\circ$  (in an autoclave), the yields are 15—50%; the reaction,  $3I_2 + 8NH_3 \rightarrow 6NH_4I + N_2$ , also occurs].  $CNa:CR$  reacts instantaneously with I in liquid  $NH_3$ . The following are prepared:  $\alpha$ -iodo- $\Delta^a$ -butinene, b.p.  $83$ — $85^\circ/156$  mm., -hexinene, b.p.  $52.5^\circ/6$  mm.,  $75^\circ/20$  mm., -heptinene, b.p.  $93^\circ/21$  mm., m.p.  $-37^\circ$  to  $-35^\circ$  (also prepared using I in  $Et_2O \cdot NH_3$ ), and -noninene, b.p.  $105$ — $107^\circ/4$  mm.;  $\alpha$ -iodo- $\beta$ -phenyl-, decomp. when heated, and -tolyl-, b.p.  $135$ — $141^\circ/16$  mm., -acetylenes. H. B.

**Acetylene polymerides and their derivatives. XI.  $\beta\gamma$ -Dichloro- and  $\alpha\beta\gamma$ -trichloro- $\Delta^{\alpha\gamma}$ -butadienes.** G. J. BERCHE and W. H. CAROTHERS. XIII. Action of chlorine on divinylacetylene. D. D. COFFMAN and W. H. CAROTHERS. XIV. Dihydrochloride of divinylacetylene. D. D. COFFMAN, J. A. NIEUWLAND, and W. H. CAROTHERS (J. Amer. Chem. Soc., 1933, 55, 2004—2008, 2040—2047, 2048—2051).—XI.  $\beta\gamma\delta$ -Trichloro- $\Delta^a$ -butene or  $\alpha\beta\gamma\delta$ -tetrachlorobutane and  $MeOH \cdot KOH$  give  $\beta\gamma$ -dichloro- $\Delta^{\alpha\gamma}$ -butadiene (I), b.p.  $39$ — $41^\circ/80$  mm.,  $98^\circ/760$  mm., whilst  $\alpha\beta\gamma\delta$ -pentachlorobutane and  $MeOH \cdot KOH$  afford  $\alpha\beta\gamma$ -trichloro- $\Delta^{\alpha\gamma}$ -butadiene (II), b.p.  $33$ — $34^\circ/7$  mm., and  $\alpha\beta\gamma$ -tetrachloro- $\Delta^a$ -butene, b.p.  $41$ — $42^\circ/7$  mm. (oxidised by aq.  $KMnO_4$  to  $\alpha\alpha\beta$ -



trichloropropionic acid). Condensation products of (I) with naphthaquinone or maleic anhydride could not be prepared. (I) polymerises much more readily than chloroprene ( $\beta$ -chloro- $\Delta^{\alpha\gamma}$ -butadiene) (III); the polymeride is an opaque, non-plastic, hard mass which is almost entirely devoid of rubber-like properties. The ease of spontaneous polymerisation of the various chlorobutadienes is (I)  $\gg$  (III)  $\gg$  (II)  $>$   $\alpha$ -chloro- $\Delta^{\alpha\gamma}$ -butadiene  $\gg$   $\alpha\beta\gamma\delta$ -tetrachloro- $\Delta^{\alpha\gamma}$ -butadiene.

XIII. Divinylacetylene (I) and  $\text{Cl}_2$  (1.22 mols.) in  $\text{CCl}_4$  at  $-50^\circ$  give 25% of  $\alpha\delta$ -dichloro- $\Delta^{\beta\gamma\epsilon}$ -hexatriene (II), b.p.  $38^\circ/1$  mm.,  $45\text{--}46^\circ/3$  mm., also formed in small yield from (I) and aq.  $\text{HOCl}$ , which is oxidised (aq.  $\text{KMnO}_4$ ) to  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ , is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOAc}$ ) to *n*-hexane, contains 1 active Cl (aq.  $\text{Na}_2\text{CO}_3$ ), and with  $\text{Cl}_2$  (1.18 mols.) in  $\text{CCl}_4$  at  $5\text{--}10^\circ$  affords  $\alpha\gamma\delta\zeta$ -tetrachloro- $\Delta^{\beta\epsilon}$ -hexadiene (III), b.p.  $84\text{--}89^\circ/2$  mm. (oxidation product,  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ ). (II) and  $\text{MeOH}\text{--KOH}$  or  $\text{--NaOMe}$  yield  $\gamma$ -chloro- $\Delta^{\alpha\gamma\delta\epsilon}$ -hexatetraene, b.p.  $55^\circ/54$  mm.,  $82^\circ/163$  mm. [reduced (as above) to *n*-hexane; oxidation product,  $\text{H}_2\text{C}_2\text{O}_4$ ], whilst (II),  $\text{HCl}$  (*d* 1.18), and  $\text{CuCl}$  at  $27^\circ$  afford  $\alpha\delta\delta$ -trichloro- $\Delta^{\beta\epsilon}$ -hexadiene, b.p.  $100\text{--}103^\circ/4$  mm. (oxidation product,  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ ). (I) and  $\text{Cl}_2$  (1.6 mols.) at  $-50^\circ$  to  $-40^\circ$  give (III), which is chlorinated further to  $\alpha\beta\gamma\delta\zeta$ -hexachloro- $\Delta^{\gamma}$ -butene (IV), b.p.  $110\text{--}112^\circ/2$  mm., m.p.  $58\text{--}59^\circ$ , and is converted by  $\text{MeOH}\text{--KOH}$  into  $\alpha\gamma\delta$ -trichloro- $\Delta^{\beta\epsilon}$ -hexatriene, b.p.  $50^\circ/1$  mm., and  $\gamma\delta$ -dichloro- $\Delta^{\alpha\beta\delta\epsilon}$ -hexatetraene (V), b.p.  $38\text{--}40^\circ/3$  mm. Saturation (apparent) of (I) with  $\text{Cl}_2$  in  $\text{CCl}_4$  gives about 10% of (IV) and (mainly) a viscous syrup (*M* 360–370) of the composition  $\text{C}_6\text{H}_6\text{Cl}_6$ . (IV) is not attacked by  $\text{O}_3$  and hot  $\text{HNO}_3$  but is completely destroyed by alkaline  $\text{KMnO}_4$ . Of the above Cl-derivatives, (V) only shows any marked tendency to polymerise spontaneously and gives a dark brown brittle resin. (II) polymerises slowly when kept to a viscous syrup; the polymerisation is greatly accelerated by pressure.

XIV. Divinylacetylene, 12*N*- $\text{HCl}$ , and  $\text{CuCl}$  at  $0^\circ$  or room temp. give 53% of (probably)  $\alpha\gamma$ -dichloro- $\Delta^{\beta\delta}$ -hexadiene, b.p.  $80\text{--}82^\circ/17$  mm. (oxidation products,  $\text{AcOH}$  and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ ), converted by  $\text{MeOH}\text{--KOH}$  and  $\text{NaOAc}\text{--AcOH}$  into  $\gamma$ -chloro- $\alpha$ -methoxy-, b.p.  $88\text{--}92^\circ/30$  mm., and  $\gamma$ -chloro- $\alpha$ -acetoxy-, b.p.  $84\text{--}85^\circ/3$  mm.,  $\Delta^{\beta\delta}$ -hexadiene, respectively; the use of  $\text{CaCl}_2$  for  $\text{CuCl}$  reduces the yield to 6.8%. The (intermediate) monohydrochloride is produced in poor yield and has not yet been obtained pure.

H. B.

#### Acetylene polymerides and their derivatives.

XII. Addition of *p*-thiocresol to divinylacetylene. W. H. CAROTHERS (J. Amer. Chem. Soc., 1933, 55, 2008–2012).—Divinylacetylene (I) (1 mol.) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SH}$  (2 mols.) give (after 10 days at room temp. or in 5 hr. when irradiated by light from a mercury arc) about 80% of  $\alpha\zeta$ -di-*p*-tolylthiol- $\Delta^{\gamma}$ -hexinene, m.p.  $74.5\text{--}75.5^\circ$  ( $\gamma\delta$ -dibromide, m.p.  $46\text{--}47.5^\circ$ ), which is oxidised by  $\text{KMnO}_4$  in  $\text{COMe}_2$  to  $\beta$ -*p*-toluenesulphonylpropionic acid, by  $\text{KMnO}_4$  and dil.  $\text{H}_2\text{SO}_4$  in cold  $\text{CCl}_4$  to  $\alpha\zeta$ -di-*p*-toluenesulphonylhexane- $\gamma\delta$ -dione, m.p.  $200\text{--}201^\circ$  (softens at  $197\text{--}200^\circ$ ), and by  $\text{KMnO}_4$  and dil.  $\text{H}_2\text{SO}_4$  in cold  $\text{CHCl}_3$  to  $\alpha\zeta$ -di-*p*-toluenesulphonyl- $\Delta^{\gamma}$ -hexinene (II), m.p.  $157\text{--}$

$158^\circ$  ( $\gamma\delta$ -dibromide, m.p.  $172.5\text{--}173.5^\circ$ ). (II) and conc.  $\text{H}_2\text{SO}_4$  afford  $\alpha\zeta$ -di-*p*-toluenesulphonylhexan- $\gamma$ -one, m.p.  $134\text{--}135^\circ$ . The above reactions confirm the structure of (I).

H. B.

Chromic oxide as a catalyst for the decomposition of methyl alcohol. G. F. HÜTTIG and K. STRIAL [with H. KITTEL].—See this vol., 681.

Catalytic activity of zinc oxide [in the decomposition of methyl alcohol. O. KOSTELITZ and G. F. HÜTTIG.—See this vol., 681.

Reactions and properties of boron fluoride in methyl alcohol. L. A. O'LEARY and H. H. WENZKE (J. Amer. Chem. Soc., 1933, 55, 2117–2121).—The v.-p. curve of the system  $\text{BF}_3\text{--MeOH}$  indicates that the equilibrium,  $\text{BF}_3 + \text{MeOH} \rightleftharpoons \text{MeOH}\cdot\text{BF}_3$  (I), exists. The conductivity curve indicates that on dilution (I) decomposes to  $\text{OMe}\cdot\text{BF}_2$  and  $\text{HF}$ . *Hg methoxyfluoborate* (II),  $\text{Hg}(\text{OMe}\cdot\text{BF}_3)_2$ , is prepared from (I) and  $\text{HgO}$ ; (I) and  $\text{NH}_3$  give the compound,  $\text{BF}_3\cdot\text{NH}_3$ . The existence of (II) probably explains the rôle of  $\text{HgO}$  in catalysing acetal formation, for which a possible mechanism (cf. Nieuwland *et al.*, A., 1930, 745, 1160; 1931, 1404) is suggested. The acid characteristics of org. compounds containing a donor atom and an ionisable H are greatly increased by addition of  $\text{BF}_3$ .

H. B.

Dehydration of tertiary alcohols by anhydrous copper sulphate. A. MEYER and M. TUOT (Compt. rend., 1933, 196, 1231–1233).— $\beta\delta$ -Dimethylhexan-8-ol,  $\beta\epsilon$ -dimethylhexan-8-ol,  $\beta\delta$ -dimethylheptan-8-ol,  $\beta\epsilon$ -dimethylheptan-8-ol,  $\beta\delta\zeta$ -trimethylheptan-8-ol,  $\beta\gamma\epsilon$ -trimethylhexan- $\gamma$ -ol, b.p.  $72^\circ/21$  mm.,  $\beta\delta$ -dimethyloctan-8-ol, b.p.  $97^\circ/27$  mm., and  $\beta\delta\eta$ -trimethyloctan-8-ol, b.p.  $100^\circ/17$  mm., are dehydrated by anhyd.  $\text{CuSO}_4$  yielding  $\beta\delta$ -dimethyl- $\Delta^8$ -heptene (?),  $\beta\epsilon$ -dimethyl- $\Delta^8$ -hexene,  $\beta\delta$ -dimethyl- $\Delta^8$ -heptene,  $\beta\epsilon$ -dimethyl- $\Delta^8$ -heptene,  $\beta\delta\zeta$ -trimethyl- $\Delta^7$ -heptene,  $\beta\gamma\epsilon$ -trimethyl- $\Delta^8$ -hexene,  $\beta\delta$ -dimethyl- $\Delta^8$ -octene, and  $\beta\delta\eta$ -trimethyl- $\Delta^8$ -octene, respectively.

A. C.

Action of phosphorus pentachloride on ethers. F. C. WHITMORE and D. P. LANGLOIS (J. Amer. Chem. Soc., 1933, 55, 1518–1520).—The action of  $\text{PCl}_5$  on ethers (various types) and acetals,  $\text{CH}_2(\text{OR})_2$ , is studied. Diisopropyl ether (1 mol.) and  $\text{PCl}_5$  (1 mol.) at  $100^\circ$  (bath) give  $\text{HCl}$  (approx. 0.5 mol.), liquid products, b.p.  $50\text{--}168^\circ$ , but no isopropyl chloride;  $\text{Pr}^i_2\text{O}$  (1 mol.) and  $\text{PCl}_5$  (2 mols.) at  $110^\circ$  afford  $\text{Pr}^i\text{Cl}$  (24%), much  $\text{HCl}$ , and material, b.p.  $36\text{--}130^\circ$ ; dibenzyl ether boiled with  $\text{PCl}_5$  yields  $\text{CH}_2\text{PhCl}$  (I),  $\text{CHPhCl}_2$  (II),  $\text{CPhCl}_3$  (III), and (probably) a benzyl phosphate;  $\text{CH}_2\text{Ph}\cdot\text{OBu}$  similarly furnishes  $\text{BuCl}$  (19%), (probably) impure  $\text{CHPrCl}_2$ , and traces of (I), (II), and (III); benzyl amyl ether gives *n*-amyl chloride (18%), (I), and (II); benzyl *sec*-amyl ether affords impure  $\beta$ -chloropentane (39%); diphenylene oxide yields a chlorodiphenylene oxide, m.p.  $94\text{--}96^\circ$  (80%);  $\text{CH}_2(\text{OBu})_2$  furnishes  $\text{BuCl}$  (23%),  $\text{CH}_2\text{Cl}\cdot\text{OBu}$  (?), and *Bu* chlorobutyl ether (?); formaldehyde di-*neopentyl* acetal, b.p.  $176\text{--}177.5^\circ/737$  mm. (cf. Conant *et al.*, A., 1929, 680) gives traces of amyl (mainly *tert.*) chlorides.

H. B.

Cyclic acetals. II. Formation of cyclic acetals of  $\delta\epsilon$ -dihydroxy- $\Delta^{\beta\gamma}$ -octadiene. C. P. BURT, D. R.



CORCORAN, and I. V. KOERBER (J. Amer. Chem. Soc., 1933, 55, 2068—2070; cf. A., 1930, 319).—The following ethers of  $\delta\epsilon$ -dihydroxy- $\Delta^8$ -octadiene (I) are prepared from (I) and the requisite aldehyde or ketone at about 70° using a little 40%  $\text{H}_2\text{SO}_4$  as the catalyst: isobutylidene, b.p. 101°/14 mm. (86% yield), amyliidene, b.p. 110—111°/5 mm. (65%), isoamyliidene, b.p. 106°/4 mm. (77%),  $\beta$ -phenylpropylidene, b.p. 160—161°/4 mm. (79%), and diethylmethylene, b.p. 100—101°/4.5 mm. (57%). Ethers could not be obtained from (I) and Me hexyl ketone, COMeBu<sup>v</sup>, methylheptenone, citral, CPhMe, CPh<sub>2</sub>, Ph styryl and styryl Me ketones, *p*-tolylbenzophenone, *o*-C<sub>6</sub>H<sub>4</sub>Cl·CHO, *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO, and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO. H. B.

**Decomposition of glycol diacetate by alcohol in feebly alkaline medium.** E. M. BELLET (Compt. rend., 1933, 196, 1506—1508).—Glycol diacetate (I) (0.1 mol.), EtOH (100 c.c.), and *N*-EtOH-KOH (II) (6 c.c.) heated at 100° (bath)/3 hr. gives EtOAc = decomp. of 32% of (I). Addition of (II) in 6 portions of 1 c.c. at intervals of 1 hr. under the same conditions gives EtOAc = 55% of (I), indicating that decomp. is not solely a function of the amount of (II) used, but is a function of the time during which alkalinity persists. H. B.

**Action of periodic acid on  $\alpha$ - and  $\beta$ -glycerophosphoric acids.** P. FLEURY and R. PARIS (Compt. rend., 1933, 196, 1416—1418).— $\alpha$ -Glycerophosphoric acid (I) is oxidised rapidly (10 min. at 20—22°) to CH<sub>2</sub>O (1 mol.) and (probably) CHO·CH<sub>2</sub>·O·PO<sub>3</sub>H<sub>2</sub> (Ba salt), whilst the  $\beta$ -isomeride (II) is practically unaffected during 24 hr. The amount of (I) in mixtures of (I) and (II) can thus be determined. H. B.

**Chlorides of alkylsulphurous acids.** P. CARRÉ and D. LIBERMANN (Compt. rend., 1933, 196, 1419—1421).—The following reactions occur between CH<sub>2</sub>R·OH and SOCl<sub>2</sub>: (i) CH<sub>2</sub>R·OH + SOCl<sub>2</sub> → CH<sub>2</sub>R·O·SOCl + HCl; (ii) CH<sub>2</sub>R·O·SOCl + CH<sub>2</sub>R·OH → SO(O·CH<sub>2</sub>R)<sub>2</sub> + HCl; (iii) SO(O·CH<sub>2</sub>R)<sub>2</sub> + SOCl<sub>2</sub> → 2CH<sub>2</sub>R·O·SOCl; (iii) is the slowest reaction. Addition of 1 mol. of EtOH to 1.15 mols. of SOCl<sub>2</sub> gives (after 48 hr. at room temp.) 95% of EtO·SOCl; the following are similarly prepared: Me, Pr<sup>a</sup>, Bu<sup>β</sup>, isoamyl, Bu<sup>a</sup>, b.p. 88°/45 mm.,  $\beta$ -chloroethyl, b.p. 100—101°/300 mm., *n*-heptyl (I), and *n*-decyl (II) chlorosulphites. (I) and (II) decompose on distillation and are converted into Pr<sup>a</sup> heptyl, b.p. 148—150°/18 mm., and Et *n*-decyl, b.p. 188—190°/30 mm., sulphite, respectively. Chlorosulphites could not be prepared from SOCl<sub>2</sub> and *sec*- or *tert*-alcohols. Contrary to Voss and Blanke (A., 1931, 462), Pr<sup>β</sup>OH and SOCl<sub>2</sub> give Pr<sup>β</sup>Cl, C<sub>3</sub>H<sub>7</sub> (partly polymerised), and a little SO(OPr<sup>β</sup>)<sub>2</sub>. Pr<sup>β</sup>, b.p. 71—73°/75 mm., *sec*-Bu, b.p. 75—77°/60 mm., and cyclohexyl, decomp. when distilled, chlorosulphites are prepared from SO(OR)<sub>2</sub> and SOCl<sub>2</sub>. Treatment of SO(OR)(OR') with SOCl<sub>2</sub> gives RO·SOCl and R'O·SOCl; allyl, b.p. 32°/40 mm., benzyl, not distillable, and Bu<sup>v</sup>, unstable, chlorosulphites are thus prepared. cycloHexyl Pr<sup>a</sup>, b.p. 175—178°/60 mm., benzyl Me, b.p. 137—138°/18 mm., and Pr<sup>a</sup> Bu<sup>v</sup>, b.p. 99—100°/30 mm., sulphites are described. H. B.

**Reaction of mercaptans with carbon tetrachloride.** H. J. BACKER and P. L. STEDEHOUDER (Rec. trav. chim., 1933, 52, 437—453).—Mercaptans, CCl<sub>4</sub>, and NaOEt in EtOH give, not substances, C(SR)<sub>4</sub> (A., 1877, 294), but mixtures of disulphides and trithio-orthoformic esters. In this way are prepared Me<sub>3</sub>, Et<sub>3</sub>, Pr<sup>a</sup><sub>3</sub>, b.p. 158—160°/12 mm., Bu<sup>a</sup><sub>3</sub> (I), b.p. 188—189°/12 mm., Bu<sup>v</sup><sub>3</sub> (II), m.p. 64.5°, b.p. 115—117°/4 mm. [previously (A., 1932, 830) believed to be C(SBu<sup>v</sup>)<sub>4</sub>], and (CH<sub>2</sub>Ph)<sub>3</sub> trithio-orthoformate, and the corresponding disulphides. SHBu<sup>v</sup>, however, gives also O-Et S-Bu<sup>v</sup><sub>2</sub> dithio-orthoformate (III), b.p. 118—120°/12 mm., oxidised by HNO<sub>3</sub> to Bu<sup>v</sup>SO<sub>3</sub>H (see below) and by acid KMnO<sub>4</sub> to ethoxy-methylenedi(tert.-butylsulphone), OEt·CH(SO<sub>2</sub>Bu<sup>v</sup>)<sub>2</sub>, m.p. 85°, and decomposed by alkali. Oxidation of the trithio-esters by H<sub>2</sub>O<sub>2</sub> and AcOH gives the sulphonic acids, but acid KMnO<sub>4</sub> gives the following methylenedi(alkylsulphones), CH<sub>2</sub>(SO<sub>2</sub>R)<sub>2</sub>: Me<sub>2</sub>, Et<sub>2</sub>, Pr<sup>a</sup><sub>2</sub> (IV), m.p. 90° (Br<sub>2</sub>-derivative, m.p. 88°), Bu<sup>v</sup><sub>2</sub> (V), m.p. 156—156.5°. Di-(*n*-propylthiol)methane, b.p. 94—95°/13 mm., prepared from SHPr<sup>a</sup>, NaOEt, and CH<sub>2</sub>Cl<sub>2</sub> in EtOH, with acid KMnO<sub>4</sub> gives (IV). Di(tert.-butylthiol)methane, b.p. 99—101°/13 mm., m.p. -4° (HgI<sub>2</sub> complex, decomp. > 120°), similarly prepared, gives (V). (I) and acid KMnO<sub>4</sub> gives anomalously tri-*n*-butylsulphonylmethane, m.p. 229—230°, unaffected by Br. CS(NH<sub>2</sub>)<sub>2</sub>, Bu<sup>v</sup>Br, and H<sub>2</sub>O give tert.-butylthiocarbamide, cryst. BuCl gives in one operation an excellent yield of Bu<sup>v</sup>SH, which with boiling HCO<sub>2</sub>H, HCO<sub>2</sub>Et, and dry HCl, or CHCl<sub>3</sub> and NaOEt in EtOH, gives (II), some (III) being also formed by the last method. Na *n*-butylsulphonate, +H<sub>2</sub>O, and tert.-butylsulphonic acid, m.p. (anhyd.) about 97—100°, (+H<sub>2</sub>O) 114—116°, (+2H<sub>2</sub>O) about 99° after softening at 78° (Na, +1.5H<sub>2</sub>O, K, +H<sub>2</sub>O, Tl, Ba, anhyd. and +H<sub>2</sub>O, Pb, +3H<sub>2</sub>O, Cu, +6H<sub>2</sub>O, and brucine salts), are described. Dibenzyl disulphide and MeI at 100° give after several hr. SME<sub>3</sub>I. The CCl<sub>4</sub> condensation with allyl mercaptan gives diallyl disulphide and polymerised mercaptan, and with  $\alpha\gamma$ -dithiolpropane a spongy mass, oxidised by HNO<sub>3</sub> to Na trimethylenedisulphonate. R. S. C.

**Behaviour of trimethylene sulphide in heptane and naphtha.** R. W. BOST and M. W. CONN (Ind. Eng. Chem., 1933, 25, 526—528).—The following products were obtained from trimethylene sulphide, (C<sub>3</sub>H<sub>6</sub>S)<sub>x</sub>, in heptane and naphtha: C<sub>3</sub>H<sub>6</sub>S<sub>2</sub>HgCl<sub>2</sub>, m.p. 92—95°, C<sub>3</sub>H<sub>6</sub>S<sub>2</sub>MeI, m.p. 98—100°, C<sub>3</sub>H<sub>6</sub>SBr<sub>2</sub>. Oxidation with KMnO<sub>4</sub> or H<sub>2</sub>O<sub>2</sub> yields the sulphone, C<sub>3</sub>H<sub>6</sub>SO<sub>2</sub>, m.p. 75°. No stable compound was obtained with HgI<sub>2</sub>, and HNO<sub>3</sub> and HCl cause polymerisation. The behaviour of Et<sub>2</sub>S is contrasted. A. G.

**Oxidation of disulphides to sulphonic acids with hydrogen peroxide. Synthesis of taurine.** A. SCHÖBERL (Z. physiol. Chem., 1933, 216, 193—202).—Oxidation of dithiodiacetic acid with H<sub>2</sub>O<sub>2</sub> gives sulphoacetic acid. Cystine (I) with H<sub>2</sub>O<sub>2</sub> affords cysteic acid, cystamine (II) yields taurine (III) [phenylcarbamido-derivative, decomp. 195°, and its Ba salt (+H<sub>2</sub>O)]. The oxidation of (I) to (III) *in vivo* probably occurs by way of (II). J. H. B.

**Cholesterol as a microchemical reagent for fatty acids.** G. DENIGÈS (Compt. rend., 1933, 196,



1504—1506).—Cholesterol hydrate (I) (< 1 mg.) is moistened with the acid (e.g., AcOH) (aq. or EtOH solutions of  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  and  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  are used) and the crystals formed (e.g.,  $\text{C}_{27}\text{H}_{46}\text{O}\cdot\text{AcOH}$ ) are examined microscopically; if (I) dissolves in the acid, the solution is first evaporated.  $\text{HCO}_2\text{H}$  does not give defined crystals.  $\text{PrCO}_2\text{H}$  can be distinguished from  $\text{Pr}^{\beta}\text{CO}_2\text{H}$ . H. B.

**Catalytic decomposition in the gaseous phase of esters of fatty acids by pumice and sulphuric acid.** J. B. SENDERENS (Compt. rend., 1933, 196, 979—982).—Decomp. of  $\text{EtCO}_2\text{H}$  vapour by pumice- $\text{H}_2\text{SO}_4$  does not occur below 195°. Esters of fatty acids are catalytically decomposed at 160—170° into acid (I), which is recovered, and alcohol which is converted into the ethylenic hydrocarbon (II). The gaseous product consists of 90% of (II) with small proportions of CO and  $\text{CO}_2$ . At higher temp. the formation of (II) is accompanied by decomp. of (I) with increasing production of CO and  $\text{CO}_2$ .  $\text{EtCO}_2\text{Pr}$  gives at 210° a gas containing CO 41,  $\text{CO}_2$  34.5, and  $\text{C}_3\text{H}_6$  24.5%. Similar results are recorded for  $\text{PrOAc}$  and  $\text{Et isobutyrate}$ . A. C.

**Ether-like compounds. X. Rate of reaction of aliphatic acid halides.** M. H. PALOMAA and R. LEMU (Ber., 1933, 66, [B], 813—815; cf. this vol., 491).—The rates of reaction of  $\text{AcCl}$  (I),  $\text{EtCOCl}$  (II),  $\text{Pr}^{\alpha}\text{COCl}$  (III),  $\text{ClCOCl}$  (IV),  $\text{CH}_2\text{Cl}\cdot\text{COCl}$  (V),  $\text{OEt}\cdot\text{COCl}$  (VI),  $\text{OEt}\cdot\text{CH}_2\cdot\text{COCl}$  (VII), and  $\text{AcBr}$  (VIII) with  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$  in dioxan have been measured at 5°, 15°, 25°, and 35°. For (I)—(III) the rate is in agreement with the avidities of the acids, but differs from the sequence of acid hydrolysis of the esters. In the series (I)—(III)  $\rightarrow$  (V)  $\rightarrow$  (IV) the rate increases greatly, whereas great retardation is observed in the sequence (I)—(III)  $\rightarrow$  (VII)  $\rightarrow$  (VI), Cl and OEt having therefore marked opposed influences. H. W.

**Alkamine esters of aliphatic acids. Novocaine analogues. IV.** H. C. BRILL and T. A. BULOW (J. Amer. Chem. Soc., 1933, 55, 2059—2061).—The following  $\beta$ -diethylaminoethyl ester hydrochlorides are prepared: butyrate, m.p. 115°, valerate, m.p. 118°, isovalerate, m.p. 92°, hexoate, m.p. 127°, heptoate, m.p. 123°, nonoate (I), m.p. 131°, laurate, m.p. 107°, myristate, m.p. 110°, palmitate, m.p. 111°, and stearate, m.p. 133°. The narcotic effect (on goldfish) increases up to (I); above (I), the esters are very toxic. H. B.

**$\alpha\beta$ -Dimethylvaleric acid.** A. E. TSCHITSCHIBABIN and M. M. KATZNELSON (Bull. Acad. Sci. U.S.S.R., 1933, 267—271).—Et sodiumethylmalonate and *sec.*-BuBr in EtOH give *Et methyl-sec.-butylmalonate*, b.p. 236.5—238.5°/748 mm., hydrolysed to the acid, m.p. 118—119°, converted on heating into  $\alpha\beta$ -dimethylvaleric acid, b.p. 210.5—210.8°/750 mm. (*Me* ester, b.p. 155—158°/743 mm.; *chloride*, b.p. 110—113°/193 mm.; *amide*, m.p. 101—103°; *anilide*, m.p. 71—72°; *p-bromoanilide*, m.p. 115—117°). The occurrence of the theoretically possible stereoisomerides was not observed. G. A. R. K.

**Highly polymerised compounds. LXXX. Polyacrylic acids. IV.** Mol. wt. of polyacrylic

acids and esters. H. STAUDINGER and E. TROMMSDORFF (Annalen, 1933, 502, 201—223).—Polymerisation of Et acrylate by heating a solution in BuOAc at 100—200° for 4—25 days gives esters of mol. wt. 2200—41,000 (calc. from viscosity measurements). The lower members ( $M$  2200—7800) dissolve in  $\text{C}_6\text{H}_6$  to slightly viscous solutions which obey the Hagen-Poiseuille law, are difficult to purify, and are hydrolysed by EtOH-NaOH (without alteration in chain-length). Solutions of the resulting acids ( $M$  up to 12,000) in EtOH-NaOH do not undergo any appreciable change when shaken for 5 days, since the sp. viscosities remain almost const. The sp. viscosities of the acids in 2*N*-NaOH are the same as in 2*N*-NaOH containing 20% of NaCl. The sp. viscosities (1.4%) of the acids in 2*N*-NaOH are about 1.5 as great as those of the corresponding esters in BuOAc or  $\text{C}_6\text{H}_6$  (the same relationship is found for an impure Et polyacrylate prepared from the Ag salt of the acid and EtI in  $\text{Et}_2\text{O}$ ). The high vals. for the acids are considered to be due to co-ordinatively bound  $\text{H}_2\text{O}$  (2 mols. per 1 mol. of acrylic acid); if this is taken into account, almost identical vals. are obtained for the acids in 2*N*-NaOH and the esters in BuOAc. The viscosity of a solution of a heteropolar "mol. colloid" in excess of NaOH is solely a function of chain-length as in the case of a homopolar "mol. colloid" in org. solvents. H. B.

**Salts of lævulic acid.** A. PROSKOURIAKOFF (J. Amer. Chem. Soc., 1933, 55, 2132—2134).—The *Ca*, *Mg*, *Cd*, *Ni*, and *Mn* salts are described. H. B.

**Course of alkylation of enolates.** F. ADICKES, G. VON HESSLING, and S. VON MÜLLENHEIM (Ber., 1933, 66, [B], 826—828).—Alkylation of the Na derivative of  $\text{CH}_2(\text{CO}_2\text{Et})_2$  with MeI or of that of  $\text{CH}_2(\text{CO}_2\text{Me})_2$  with EtI followed by hydrolysis does not afford MeOH or EtOH, respectively, thus indicating the improbability of the intermediate production of  $\text{CO}_2\text{R}\cdot\text{CH}\cdot\text{C}(\text{OMe})\cdot\text{OEt}$ . Similar observations are made with  $\text{CH}(\text{CO}_2\text{Et})_2$  and MeI. H. W.

**Action of ammonia on ethyl malonate and ethyl malonamate.** K. C. BAILEY (Proc. Roy. Irish Acad., 1933, 41 B, 161—167; cf. A., 1931, 315).—*K* (calc. for a third-order reaction) for reaction between  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and  $\text{NH}_3$  in EtOH- $\text{H}_2\text{O}$  decreases with increasing EtOH concn. and varies when the concns. of reactants are varied, although when  $\text{CH}_2(\text{CO}_2\text{Et})_2$  is in large excess, after an initial period of high *K* (1), a fairly good second-order coeff. is obtained. (I) is increased by alkali and diminished by acid, which also retards the reaction as a whole; *o*- and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  exert a more powerful effect than  $\text{H}_2\text{SO}_4$  or AcOH, indicating that the uncombined acid has a sp. retarding influence. Interaction of  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$  and  $\text{NH}_3$  in  $\text{H}_2\text{O}$ -EtOH is accompanied by an initial rapid reaction due to the catalytic effect of OH' on hydrolysis; acids retard the reaction. J. L. D.

**Methylation of ethyl  $\alpha\beta$ -dimethylglutaconate.** J. PACKER and J. D. SARGENT (J.C.S., 1933, 556—557).—"Labile"  $\text{Et}_2\alpha\beta$ -dimethylglutaconate is not methylated under Thorpe and Wood's conditions (*ibid.*, 1913, 103, 1759), but with MeI and Na powder



in hot  $\text{Et}_2\text{O}$  gives  $\text{Et}$ ,  $\alpha\beta$ -trimethylglutaconate, hydrolysed by acid or alkali to a mixture of *cis*- and *trans*-acids. R. S. C.

**Fehling's solution and isomerism of tartaric acids.** H. SOBOTKA (J. Amer. Chem. Soc., 1933, 55, 2164).—The oxidising power of Fehling's solution towards glucose is the same whether Na K *d*- or meso-tartrate is used in its prep. H. B.

**Nature of racemates.** V. N. BELOV (J. Gen. Chem. Russ., 1933, 3, 7—12).—Theoretical. The phenomenon of racemisation is interpreted on the assumption of the formation of "homochemical" compounds (A., 1921, ii, 324). This involves the approach of three like groups when optical antipodes form such a complex, whilst only two like groups can approach one another in the case of identical asymmetric mols.; this explains the greater stability of the racemic compound. In some cases both forms of complex exist and are at equilibrium under certain conditions (e.g., Na  $\text{NH}_4$  tartrate at 27°). It is suggested that racemates should possess a higher viscosity than their single constituents. G. A. R. K.

**Constitution of ascorbic acid.** W. N. HAWORTH (Chem. and Ind., 1933, 482—485).—A lecture.

H. W.

**Constitution of vitamin-C.** IV. F. MICHEEL and K. KRAFT (Z. physiol. Chem., 1933, 216, 233—238; cf. this vol., 489).—Ascorbic acid (I) with  $\text{CH}_2\text{N}_2$  gives cryst. *Me methylascorbate* (II), m.p. 63°,  $[\alpha]_D^{25} +38^\circ$  in EtOH. Hydrolysis of the ozonisation product (III) (*loc. cit.*) gives *l*-threonic acid,  $[\alpha]_D^{25} +17.2^\circ$  in  $\text{H}_2\text{O}$  (phenylhydrazide, m.p. 157—158°,  $[\alpha]_D^{25} +30^\circ$  in  $\text{H}_2\text{O}$ ). *Me dinitrobenzoyl-l*-threonate, m.p. 137°, is obtained by partial hydrolysis of (III). From the similarity of the absorption curves of (I) and (II), (I) exists in EtOH solution chiefly in the enol form. J. H. B.

**Constitution of dehydroascorbic acid.** P. KARRER, H. SALOMON, and K. SCHÖPP (Nature, 1933, 131, 800).—Dehydroascorbic acid (I) is probably an inner peroxide (this vol., 490). The view that oxidation of ascorbic acid to (I) should lead to the formation of a new OH group (this vol., 489) is erroneous. L. S. T.

**Vitamin-C and related substances.** H. VON EULER and M. MALM.—See this vol., 756.

**Vitamin-C.** P. KARRER, H. VON EULER, and H. HELLSTRÖM.—See this vol., 756.

**Derivatives of glycuronic acid.** II. Acetylation of glycuron. W. F. GOEBEL and F. H. BABERS (J. Biol. Chem., 1933, 100, 743—748).— $\alpha$ -Triacetylglucuron, m.p. 194—195°,  $[\alpha]_D^{25} +84.1^\circ$  in  $\text{CHCl}_3$ , and  $\beta$ -triacetylglucuron, m.p. 110—112°,  $[\alpha]_D^{25} +203.6^\circ$  in  $\text{CHCl}_3$ , are prepared by acetylation with  $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  and also with  $\text{Ac}_2\text{O}$  and  $\text{ZnCl}_2$ , separation being accomplished by crystallisation from EtOH and AcOH. Results of a crystallographic study of the two isomerides are included. A. L.

**Chemical nature of heparin.** II. Preparation of pure heparin. III. Constitution of heparin. A. SCHMITZ and A. FISCHER (Z. physiol. Chem., 1933, 216, 264—273, 274—280; cf. A., 1932, 1054).—II.

Heparin (I),  $\text{C}_{18}\text{H}_{32}\text{O}_{17} \cdot 6\text{H}_2\text{O}$ , decomp. 250° [cryst. *brucine* salt  $\text{C}_{18}\text{H}_{32}\text{O}_{17} \cdot (\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2) \cdot 4\text{H}_2\text{O}$ , m.p. 255° (decomp.)]; Na and Ba salts], was obtained pure after a long fractionation.

III. (I) is a monobasic acid,  $K=2.0 \times 10^{-4}$ , probably a carbohydrate derivative. It has  $[\alpha]_D^{25} +41.6^\circ$  in aq. HCl [bromophenylosazone (?), m.p. 300—310°]. The acid group carrier is probably a uronic acid. The fission products are laevorotatory. (I) absorbs light only in the extreme ultra-violet. J. H. B.

**Thioketonic esters.** II. S. M. MITRA. III. Alkylation of ethyl thioacetate. P. C. RAY, S. K. MITRA, and N. N. GHOSH (J. Indian Chem. Soc., 1933, 10, 71—74, 75—79).—II.  $\text{CH}_3\text{Ac} \cdot \text{CO}_2\text{Et}$  in EtOH saturated with HCl at 0° affords with  $\text{H}_2\text{S}$  during several hr. Et thioacetate (A., 1931, 1398) free from a by-product, now identified as *Et*  $\beta$ -thiodicronate, b.p. 155°/15 mm. Similarly,  $\text{CO}(\text{CH}_2\text{CO}_2\text{Et})_2$  affords *Et* thioacetonedicarboxylate (I), b.p. 128°/15 mm. (decomp.). The Na derivative of (I) in boiling  $\text{C}_6\text{H}_6$ -EtOH with PrI or EtBr during 4 hr. affords, respectively, *Et n*-propyl-, b.p. 220°/30 mm., and *Et ethyl*-thioacetonedicarboxylate, b.p. 175°/17 mm.

III. The following *S*-alkyl derivatives of Et  $\beta$ -thiolcrotonate are prepared: *Et*, b.p. 114—117°/15 mm., hydrolysed by cold 12% EtOH-KOH to  $\beta$ -ethylthiolcrotonic acid, m.p. 86° (and by boiling dil.  $\text{H}_2\text{SO}_4$  to  $\text{COMe}_2$ ,  $\text{CO}_2$ , and  $\text{Et}_2\text{S}_2$ ), which may be a mixture of the *cis*- and *trans*-forms, m.p. 112° and 92°, respectively; *n*-Pr, b.p. 117—120°/15 mm. ( $\beta$ -*n*-propylthiolcrotonic acid, m.p. 70°); *n*-amyl, b.p. 126—128°/15 mm.; *benzyl*, m.p. 68° ( $\beta$ -benzylthiolcrotonic acid, m.p. 134°); *benzoylmethyl*, m.p. 85°. When boiled with  $\text{NHPH} \cdot \text{NH}_2$ , these compounds afford a *dehydro-pyrazolone*, m.p. 330° (decomp.). J. L. D.

**Photolysis of acetaldehyde.** P. A. LEIGHTON and F. E. BLACET.—See this vol., 682.

**Determination of methylglyoxal.** T. TAKAHASHI (J. Biochem. Japan, 1933, 17, 299—305).—The methods of Fischler and Boettner (A., 1928, 870), of Friedemann (A., 1927, 648), and of Neuberg and Kobel (A., 1929, 354) are the most trustworthy, whilst those of Ariyama (A., 1928, 796) and of Barrenscheen and Dreguss (A., 1931, 825) also give accurate results. Improvements in technique are suggested for some of the above methods. F. O. H.

**Generalisation of the method of condensation of ketones by mixed amino-magnesium derivatives.** J. COLONGE (Compt. rend., 1933, 196, 1414—1416).—The formation of hydroxy-ketones by the action of  $\text{NHPH} \cdot \text{MgBr}$  or  $\text{NPhMe} \cdot \text{MgBr}$  (I) on aliphatic ketones (cf. A., 1932, 499) occurs only when there are  $\leq 3$  H atoms in the immediate neighbourhood of the CO group. Thus,  $\gamma$ -methyl- $\gamma$ -ethylpentan- $\beta$ -one (II) and  $\delta$ -methylhexan- $\gamma$ -one condense readily, whilst  $\beta\beta$ - and  $\beta\delta$ -dimethylpentan- $\gamma$ -one give traces of condensation products. The following are prepared as previously described (*loc. cit.*):  $\kappa$ -methyl-heneicosan- $\kappa$ -ol- $\mu$ -one, m.p. 23°, in 70% yield from Me nonyl ketone;  $\gamma\delta\eta$ -trimethyl- $\gamma\eta$ -diethylnonan-8-ol- $\zeta$ -one (61%), b.p. 135—136°/6 mm., from (II); 1-hydroxy-1-2'-ketocyclopentylcyclopentane (40%), b.p.



98—99°/3 mm., m.p. 31°, and some dicyclopentylidene-cyclopentanone (*oxime*, m.p. 78°) from cyclopentanone; 1-hydroxy-1-2'-ketocyclohexylcyclohexane (50%), b.p. 116—119°/5 mm., m.p. 56° (*oxime*, m.p. 113°), from cyclohexanone;  $\beta$ -diphenylbutan- $\beta$ -ol- $\delta$ -one, m.p. 63°, from COPhMe. Treatment of the product from COPh<sub>2</sub> and (I) with COMeBu<sup>7</sup> gives 35% of  $\alpha$ -diphenyl- $\delta$ -dimethylpentan- $\alpha$ -ol- $\gamma$ -one, m.p. 102°.

H. B.

**Copper-iodometric reagents for sugar determination.** P. A. SHAFER and M. SOMOGYI (J. Biol. Chem., 1933, 100, 695—713).—In iodometric Cu reagents for sugar determination, the lower is the ratio Na<sub>2</sub>CO<sub>3</sub>:NaHCO<sub>3</sub>, the slower is the rate of sugar oxidation, but the higher the amount of Cu reduced. A comparison of the rates of reduction of various sugars by several reagents indicates that no single reagent is best for all sugars. The influence of I<sup>-</sup> and IO<sub>3</sub><sup>-</sup> is considered.

A. L.

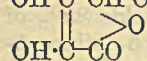
**Reduction by sugar derivatives.** H. VON EULER and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 8, 6 pp.).—When aldo- and keto-sugars are warmed with moderately dil. alkali (hydroxide) or Ba(OH)<sub>2</sub>, substances are produced (in 1.4—8% yield) which, like vitamin-C (Szent-Györgyi, A., 1929, 98), reduce phenolindophenol and KMnO<sub>4</sub>, Fe<sup>+++</sup> salts, and Cu salts in acid solution.

H. B.

**Highly reducing intermediates (reductones) in the alkaline rearrangement of simple sugars.** H. VON EULER and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 12, 6 pp.).—2% glucose (20 c.c.) warmed with 2N-NaOH (2 c.c.) at 77° for 10 min. gives a solution which reduces phenolindophenol and methylene-blue (I) (in N<sub>2</sub>); the reducing power disappears when the solution is kept. (I) is similarly reduced by CO(CH<sub>2</sub>·OH)<sub>2</sub> and AcCHO in alkaline solution.

H. B.

**Glucoreductone.** H. VON EULER and C. MARTIUS (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 14, 4 pp.).—Details are given (cf. this vol., 596) for the isolation of glucoreductone (I), (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)<sub>2</sub>, chars 200—220° (mono-Me derivative, m.p. 67°, by the action of CH<sub>2</sub>N<sub>2</sub>; carbamide derivative, decomp. 200—220°), which has many of the reducing properties of ascorbic acid (II), reduces 2:6-dichlorophenolindophenol to a greater extent than (II), is a weak acid, and with NHPH·NH<sub>2</sub> in AcOH gives the di- and tri-phenylhydrazones of CO(CHO)<sub>2</sub>. (I) is considered to be OH·CH<sub>2</sub>·C(OH)·CHO, i.e., the enol form of OH·CH<sub>2</sub>·CO·CHO or OH·CH(CHO)<sub>2</sub>. The properties of (II) are best explained by the structure



H. B.

**Reduction of methylene-blue by products of the alkaline fission of sugars.** H. VON EULER and E. KLUSMANN.—See this vol., 680.

**Action of oxygen on reducing sugars.** (MME.) N. MAYER-REICH (Compt. rend., 1933, 196, 1337—1339).—30% solutions of glucose, xylose, and fructose in 0.1N-NaOH, buffered by phosphates, absorb O<sub>2</sub> (pure or from air) and evolve CO<sub>2</sub> faster in alkaline than in acid solutions. Heavy metals catalyse the

reaction, since KCN and K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> reduce the velocity by forming complexes with the catalyst. It is believed that the catalyst acts by activating (a) the O<sub>2</sub> and (b) the "mobile" H atom of the sugar.

R. S. C.

**Influence of sodium borate on the reaction between alkali cyanides and reducing sugars.** J. BOUGAULT, Z. HARDY, and A. PINGUET.—See this vol., 680.

**Oxidation of  $\alpha$ - and  $\beta$ -glucose, and isomeric forms of the sugar in solution.** H. S. ISBELL and W. PIGMAN (Bur. Stand. J. Res., 1933, 10, 337—356).—Oxidation of  $\alpha$ - or  $\beta$ -glucose with excess of aq. Br in presence of BaCO<sub>3</sub> and CO<sub>2</sub> gives  $\delta$ -gluconolactone directly, without intermediate formation of the acid (cf. Irvine and McGlynn, A., 1932, 255). The oxidation of the  $\beta$ -form is approx. 35 times as great as that of the  $\alpha$ -form (53 if mutarotation is allowed for), and in an equilibrium mixture of  $\alpha$ - and  $\beta$ -forms the latter oxidises first, and a sudden change in the rate of oxidation then occurs, the results indicating the composition 64% of  $\beta$ - and 36% of  $\alpha$ -forms.

H. A. P.

**Calcium chloride modifications of mannose and gulose.** H. S. ISBELL (J. Amer. Chem. Soc., 1933, 55, 2166—2167).—Oxidation of the compound, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>·CaCl<sub>2</sub>·4H<sub>2</sub>O (I), from *d*-mannose (Dale, A., 1929, 1280) with cold Br-H<sub>2</sub>O in presence of BaCO<sub>3</sub> gives largely  $\gamma$ -mannonolactone, indicating that (I) contains a 1:4-ring. More prolonged oxidation affords a considerable amount of  $\delta$ -mannonolactone, which probably arises from  $\alpha$ -*d*-mannose [formed from (I) by the mutarotation reaction]. The mutarotation of the compound, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>·CaCl<sub>2</sub>·H<sub>2</sub>O, of  $\alpha$ -*d*-gulose is probably more complex than the reversible interconversion of two isomerides. A new compound, (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)<sub>2</sub>·CaCl<sub>2</sub>, obtained from gulose, has  $[\alpha]_D^{20}$  (in H<sub>2</sub>O) +34° (1.4 min. after dissolution)  $\rightarrow$  -167° (const.).

H. B.

**Preparation of crystalline  $\beta$ -*l*-allose, a new aldohexose, from *l*-ribose by the cyanohydrin reaction.** W. C. AUSTIN and F. L. HUMOLLER (J. Amer. Chem. Soc., 1933, 55, 2167—2168).—*l*-Ribose is converted (cf. Levene and Jacobs, A., 1911, i, 14) into *l*-altronic acid (as Ca salt) and *l*-allonolactone (I), m.p. 130°,  $[\alpha]_D^{20}$  +6.3° in H<sub>2</sub>O. Reduction (Na-Hg) of (I) gives  $\beta$ -*l*-allose, m.p. 128—129°,  $[\alpha]_D^{20}$  (in H<sub>2</sub>O) -2.88° (4 min. after dissolution)  $\rightarrow$  -8.13° (34 min.)  $\rightarrow$  -13.88° (const.).

H. B.

**Crystalline 6- $\beta$ -*d*-galactosido-*d*-glucose.** B. HELFERICH and G. SPARMBERG (Ber., 1933, 66, [B], 806—807; cf. A., 1926, 386).—Improvements in technique lead to the isolation of cryst. 6- $\beta$ -*d*-galactosido-*d*-glucose, m.p. 174—176° (decomp.),  $[\alpha]_D^{18}$  +30.7° (final) in H<sub>2</sub>O [*phenylosazone*, m.p. 188—189° (decomp.),  $[\alpha]_D^{18}$  -74.5° (initial) in C<sub>6</sub>H<sub>5</sub>N], which in many respects resembles allolactose (Polonovski et al., A., 1932, 406, 1031).

H. W.

[Determination of] structure of heterosides by their absorption spectra. (MME.) RAMART-LUCAS and RABATÉ (Compt. rend., 1933, 196, 1493—1495).—Sugars in neutral solution are transparent to light of  $> 2200 \text{ \AA}$ ., whether alone or combined to form a



heteroside, provided that the prosthetic group is aliphatic or attached through an aliphatic group; thus the absorption spectrum of phenylethyl- $\beta$ -glucoside is identical with that of  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$ , but if the sugar is attached directly to an aryl nucleus the spectra are different. Thus esterification of a phenol by a sugar shifts the absorption spectrum towards the ultra-violet. C. A. S.

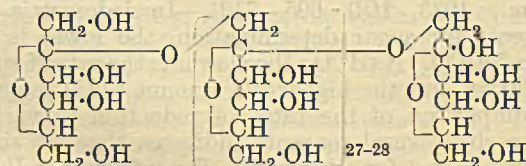
**Digitalis glucosides. VII. Isomeric dihydrogitoxigenins.** W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1933, 100, 671—683).—Gitoxigenin when rapidly hydrogenated in aq. EtOH gives 70%  $\alpha$ -dihydrogitoxigenin (I),  $\text{C}_{23}\text{H}_{36}\text{O}_5$ , m.p. 212—213°,  $[\alpha]_D^{25} +42^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , and on slow hydrogenation,  $\beta$ -dihydrogitoxigenin (II),  $\text{C}_{23}\text{H}_{36}\text{O}_5$ , m.p. 242—244°,  $[\alpha]_D -57^\circ$  in MeOH, both substances showing mutarotation to give the same equilibrium mixture. (I) and (II) give on hydrolysis the same dihydrogitoxigeninic acid,  $\text{C}_{23}\text{H}_{38}\text{O}_6$ , m.p. 170° and after resolidifying 235°,  $[\alpha]_D +22^\circ$  in EtOH, whereas  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$  gives  $\alpha$ -dihydrogitoxigenin dibenzoate,  $\text{C}_{37}\text{H}_{44}\text{O}_7$ , m.p. 250°,  $[\alpha]_D^{25} +52^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , and  $\beta$ -dihydrogitoxigenin dibenzoate,  $\text{C}_{37}\text{H}_{44}\text{O}_7$ , m.p. 233°,  $[\alpha]_D^{25} -45^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , respectively.  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  gives with (II) the usual diacetate, but with (I) only  $\alpha$ -dihydrogitoxigenin monoacetate,  $\text{C}_{25}\text{H}_{38}\text{O}_6$  (III), m.p. 213° (softens at 206—208°),  $[\alpha]_D^{25} +35^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , is formed. (III) could be isomerised with  $\beta$ -dihydrogitoxigenin monoacetate,  $\text{C}_{25}\text{H}_{38}\text{O}_6$ , m.p. 224—226°,  $[\alpha]_D^{25} -82^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . (I) and (II) with  $\text{Ac}_2\text{O}$  and  $\text{ZnCl}_2$  yield respectively anhydro- $\alpha$ - (IV),  $\text{C}_{27}\text{H}_{38}\text{O}_6$ , m.p. 208°,  $[\alpha]_D^{25} +82^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , and anhydro- $\beta$ -dihydrogitoxigenin diacetate (V),  $\text{C}_{27}\text{H}_{38}\text{O}_6$ , m.p. 157°,  $[\alpha]_D^{25} -34^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . Attempts to hydrogenate the double linking of (IV) and (V) were unsuccessful. (II) with  $\text{CrO}_3$  in AcOH, unlike the  $\alpha$ -derivative, does not give  $\alpha$ -oxodihydrogitoxigenin as the main yield, but the compound  $\text{C}_{23}\text{H}_{32}\text{O}_6$  previously obtained, and a new substance,  $\text{C}_{23}\text{H}_{34}\text{O}_5$ , m.p. 228°,  $[\alpha]_D^{25} -42^\circ$  in  $\text{COMe}_2$ . It is suggested that the unsaturated lactonic group of gitoxigenin is attached through an intermediate C atom having a  $\text{OH}\cdot\text{CH}_2$  branched chain.

A. L.

**Modifications of F. Schardinger's  $\alpha$ -dextrin.** K. HESS, C. TROGUS, and M. ULMANN (Z. physikal. Chem., 1933, B, 21, 1—6; cf. A., 1932, 604).—X-Ray investigation shows the existence of at least 10 modification, but whether these are structural isomerides or merely polymorphic modifications is undecided. Their formation depends on the nature of the solvent, whether reaction is homogeneous or heterogeneous, and the temp. of separation. The conditions of interconversion are stated. R. C.

**Methylation and constitution of inulin.** (SR) J. C. IRVINE and T. N. MONTGOMERY (J. Amer. Chem. Soc., 1933, 55, 1988—1994).—Trimethylinulin (improved prep. given; cf. J.C.S., 1920, 117, 1474; 1922, 121, 1060) is hydrolysed by aq. EtOH- $\text{H}_2\text{C}_2\text{O}_4$  (cf. Haworth and Learner, A., 1928, 510) to 3:4:6-trimethyl- $\gamma$ -fructose (I) (87—88.5%), tetramethyl- $\gamma$ -fructose (II) (1.7—2.7%), trimethylanhydro- $\gamma$ -fructose (III) (4.5—4.6%), b.p. 180—190° (bath)/0.06 mm.,  $[\alpha]_D +45.1^\circ$  in  $\text{CHCl}_3$ , trimethylglucose (IV) (1—3.3%), and  $\omega$ -methoxy-5-methylfurfuraldehyde (V) (1.5—

2.5%). The uniformity of (I) is proved by the nature of its condensation product with  $\text{COMe}_2$ . The production of (IV) is due to a secondary reaction involving the transformation (I)  $\rightarrow$  (IV); it is shown that small amounts of (IV), (V), and an anhydro-derivative, b.p. 170—180°/0.04 mm.,  $[\alpha]_D +62.7^\circ$  in  $\text{CHCl}_3$  [similar to (III)], are formed from (I) and aq. EtOH- $\text{H}_2\text{C}_2\text{O}_4$ . The ideal yields of (I) and (II) are considered to be 95 and 4%, respectively; the following constitution is suggested (from these results) for inulin.



H. B.

**Methylene esters of cellulose and their acetates.** P. SCHORIGIN and J. RYMASCHEVSKAJA (Cellulosechem., 1933, 14, 81—83).—Viscose silk is partly acetylated and partly methylenated by  $\text{Ac}_2\text{O}$ ,  $\text{AcOH}$ , and  $\text{CH}_2(\text{OMe})_2$  (I) at 100°. Cellulose, pretreated with  $\text{AcOH-H}_2\text{SO}_4$  (7.5%), and then with (I) and  $\text{Ac}_2\text{O}$  at 40°, gives a product which probably contains chains of  $\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}(\text{OH})(\text{OAc})(\text{O}\cdot\text{CH}_2\cdot\text{OH})\cdot\text{O}$  groupings. If the  $\text{Ac}_2\text{O}$  is omitted, the product contains up to 4.25%  $\text{CH}_2\text{O}_2$ . Cellulose, mercerised by 33% NaOH, with warm (I) gives products containing up to 3.95% of  $\text{CH}_2\text{O}_2$ .  $\text{CH}_2\text{I}_2$  and alkali-cellulose give very slightly methylenated or decomposed products.

R. S. C.

**Preparation of amines by catalytic hydrogenation of derivatives of aldehydes and ketones.** C. F. WINANS and H. ADKINS (J. Amer. Chem. Soc., 1933, 55, 2051—2058).—Good yields of  $\text{NH}_2\text{R}$  are often obtained by reduction of oximes with  $\text{H}_2$  and a Ni-kieselguhr catalyst in  $\text{Et}_2\text{O}$ , EtOH, or methylcyclohexane, usually at 100—125°/100—150 atm.; there is, however, considerable variation in the yields and proportions of  $\text{NH}_2\text{R}$  and  $\text{NHR}_2$  according to the structure of the original aldehyde or ketone. Thus,  $\text{CMe}_2\text{N}\cdot\text{OH}$  gives  $\text{NH}_2\text{Pr}^i$  (67%) and  $\text{NHR}^i$  (10%); *n*-valeraldoxime affords *n*-amylamine (62%) (*p*-bromobenzenesulphonyl derivative, m.p. 60—61°) and di-*n*-amylamine (27%) (hydrochloride); *n*-heptaldoxime yields *n*-heptylamine (61%) and di-*n*-heptylamine (20%) (hydrochloride); cinnamaldoxime furnishes  $\gamma$ -phenylpropylamine (32%) and di- $\gamma$ -phenylpropylamine (12%), also obtained in 48 and 43% yield, respectively, from  $\gamma$ -phenylpropaldoxime;  $\text{CPh}_2\text{N}\cdot\text{OH}$  gives 95% of  $\text{CHPh}_2\text{N}\cdot\text{H}_2$ ; camphoroxime affords 94% of bornylamine; *p*- $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  yields 85% of *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ ; benzoinoxime furnishes  $\beta$ -amino- $\alpha$ -diphenylethyl alcohol (64%) and tetraphenylpyrazine (I) (20%); *syn*-benzildioxime gives ( $\cdot\text{CHPh}\cdot\text{NH}_2$ )<sub>2</sub> (44.5%) and (I) (51%);  $\alpha$ - $\text{CHPh}\cdot\text{N}\cdot\text{OH}$  affords  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$  (73—77%) and  $\text{NH}(\text{CH}_2\text{Ph})_2$  (19—20%). Reduction of various phenylhydrazones, azines, azo-compounds, hydroamides, dihydroglyoxalines, and aldimines is effected by the above method. Thus,  $(\text{NPh})_2$  gives 95% of  $\text{NH}_2\text{Ph}$  at 90° and  $\text{NH}_2\text{Ph}$  (21%), cyclohexylamine (22%) (benzenesulphonyl derivative, m.p. 88—89°), and dicyclohexylamine (48%) at 200°;



CHPr:N·NHPh affords  $\text{NH}_2\text{Ph}$  (95%),  $\text{NH}_2\text{Bu}$  (57%), and  $\text{NHBu}_2$  (40%), showing that fission of the N·N linking must have preceded reduction of the C:N linking; benzaldazine yields  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$  (68%),  $\text{NH}(\text{CH}_2\text{Ph})_2$  (26%), and  $\text{N}(\text{CH}_2\text{Ph})_3$  (2%) (this is the only *tert.*-amine isolated during the investigation); trifurfurylidenediamine (hydrofuranamide) furnishes tetrahydrofurfurylamine (88%) (*phenylcarbamyl* derivative, m.p. 147–147.5°) and ditetrahydrofurfurylamine (90%) (*picrate*, m.p. 104–105°); tri(trimethyl-ethylidene)diamine (hydropinalamide) gives *tert.*-butylcarbinylamine (79%) and *di-tert.*-butylcarbinylamine (62%) (*p*-bromobenzenesulphonyl derivative, m.p. 128–129°); triheptylidenediamine (hydroheptamide) affords *n*-heptylamine (43%) and *di-n*-heptylamine (49%); polymeric hexahydrobenzaldimine yields hexahydrobenzylamine (61%) and dihexahydrobenzylamine (33%) (*hydrochloride*, m.p. 298–299°); polymeric CHPr<sup>β</sup>:NH furnishes  $\text{NH}_2\text{Bu}^\beta$  (70%) and  $\text{NHBu}_2^\beta$  (24%);  $\text{OH}\cdot\text{CHPr}\cdot\text{NH}_2$  (as hydrate) gives  $\text{NH}_2\text{Bu}$  (32%),  $\text{NHBu}_2$  (13%), and 3:5-diethyl-2-*n*-propylpyridine (II) (26%); heptaldehyde-ammonia affords *n*-heptylamine (32%) and *di-n*-heptylamine (12%);  $\text{PrCHO} + \text{EtOH}\cdot\text{NH}_3$  yields  $\text{NH}_2\text{Bu}$  (32%),  $\text{NHBu}_2$  (21%), and (II) (26%); triacetoneamine yields 4-hydroxy-2:2:6:6-tetramethylpiperidine (81%); 2:4:5-triphenyl-4:5-dihydroglyoxaline furnishes the 2:4:5-tricyclohexyl derivative; 2:4:5-trifuryl-4:5-dihydroglyoxaline (furfurin) gives 2:4:5-tritetrahydrofuryl-4:5-dihydroglyoxaline (*picrate*, m.p. 202–203°); 2:4:5-tristyryl-4:5-dihydroglyoxaline affords 2:4:5-tri- $\beta$ -phenylethyl-4:5-dihydroglyoxaline (*picrate*, m.p. 130–132°).

H. B.

**Influence of poles and polar linkings on the course of elimination reactions.** XV. Dynamics of the elimination of olefines from quaternary ammonium compounds. E. D. HUGHES and C. K. INGOLD. XVI. Mechanism of the thermal decomposition of quaternary ammonium compounds. E. D. HUGHES, C. K. INGOLD, and C. S. PATEL. XVII. Thermal decomposition of phosphonium ethoxides. L. HEY and C. K. INGOLD. XVIII. Thermal decomposition of sulphonium hydroxides. C. K. INGOLD, J. A. JESSOP, K. I. KURIYAN, and (in part) A. M. M. MANDOUR (J.C.S., 1933, 523–526, 526–530, 531–533, 533–537; cf. this vol., 262).—XV. The decomp. of  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$  [iodide, m.p. about 225° (decomp.)] is bimol. and proportional to the concn. of each ion. The decomp. of  $\beta$ -*p*-nitrophenylethyl-trimethylammonium iodide (I), m.p. 199° (decomp.) [corresponding *picrate*, m.p. 147° (decomp.)], and of the *bromide*, m.p. 222°, is unimol., and independent of the halide concn., both reactions having the same *k*; the corresponding hydroxide in  $\text{H}_2\text{O}$  at room temp. gives  $\text{NMe}_3$  and *p*-nitrostyrene, whilst (I) gives  $\text{NMe}_3$  and a glassy polymeride of *p*-nitrostyrene. Reaction is retarded by acids and accelerated by bases, and is slower in  $\text{Pr}^\text{OH}$  than in  $\text{H}_2\text{O}$ .

XVI. Theoretical. Recognition of the fact that both modes of decomp. of quaternary ammonium compounds (to give olefines or alcohols) may be either uni- or bi-mol. explains previous anomalies. Von Braun's conception of the decomp. is criticised.

XVII. Decomp. of  $\text{PMe}_3\cdot\text{OEt}$  at 100–140° gives  $\text{C}_3\text{H}_8$  and  $\text{PMe}_3\text{O}$  only.  $\text{PEt}_4\cdot\text{OEt}$  gives *n*- $\text{C}_4\text{H}_{10}$  and  $\text{PEt}_3\text{O}$  only.  $\beta$ -Phenylethyltriethylphosphonium ethoxide gives 90% of *n*-butylbenzene and  $\text{PEt}_3\text{O}$ , with a little  $\text{CHPh}\cdot\text{CH}_2$  and  $\text{PEt}_3$ . Triphenyl- $\beta$ -diphenylethylphosphonium ethoxide (from the corresponding chloride) gives 5% of  $\alpha$ -diphenyl-*n*-butane, b.p. about 170–175°/15 mm., and  $\text{PEt}_3\text{O}$ , and 95% of  $\text{PEt}_3$  and  $\text{CH}_2\cdot\text{CPh}_2$ . The close similarity in the modes of decomp. of corresponding ethoxides and hydroxides is unexpected and its theoretical aspect is discussed.

XVIII. The following were prepared from mercaptans and sulphides: *dimethyl-ethyl-* (I), m.p. about 110° (decomp.), hygroscopic, *-n-propyl-* (II), *cryst.*, hygroscopic, *-n-butyl-* (III), m.p. 82° (decomp.), *-isobutyl-* (IV), m.p. 88–90° (decomp.), and *-isopropyl-* (V), *cryst.*, hygroscopic, *-sulphonium iodide*.  $\text{SEtPr}^\text{a}$ , b.p. 115–117°, and  $\text{MeI}$  in cold  $\text{MeNO}_2$  led to *methylethylisobutylsulphonium iodide* (VII).  $\text{SEt}[\text{CH}_2]_2\cdot\text{Ph}$ , b.p. 113–115°/10 mm. (from  $\text{SEtNa}$  and  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Cl}$ ), gives  $\beta$ -phenylethylmethylethylsulphonium iodide (VIII), m.p. 84–85°.  $\text{SEtPr}^\text{a}$ , b.p. 102–104° (from  $\text{SEtNa}$  and  $\text{Pr}^\text{a}\text{I}$  in  $\text{EtOH}$ ), led to *methylethylisopropylsulphonium picrate* (IX), m.p. 173–175°.  $\text{SHPr}^\text{a}$ , b.p. 57–60°, gives  $\text{SMePr}^\text{a}$ , b.p. 93–95°, which with  $\text{Bu}^\text{a}\text{I}$  and  $\text{Ag}_2\text{SO}_4$  in  $\text{MeNO}_2$  at 80–90° led to *methyloisopropylisobutylsulphonium picrate* (X), m.p. 49–50°. The corresponding hydroxides at 120–130° give the following yields of olefines: (I) 27; (II) 7.7; (III) 3.8; (IV) 1.5; (V) 63%. Decomp. of the hydroxides corresponding with (VI), (VII), and (VIII) gives mixtures of olefines containing 80, 93, and 3% of  $\text{C}_2\text{H}_4$ , respectively, whilst that of (IX) and (X) gives mixtures of olefines containing 75 and 94% of propylene, respectively. The regularities and irregularities of these results exactly parallel those in the ammonium series (except that elimination of  $\text{MeOH}$  is more facile from the S bases) and justify the application of the same reaction mechanism to both reactions. The non-formation of paraffins is probably due to the instability of the S atom with a deficit of electrons (except when, as in the sulphones, some of the linkings are semi-polar).

R. S. C.

**Organic bromine compounds of therapeutic value, and hexamethylenetetramine hydrobromide.** G. AURISICCHIO (L'Ind. Chimica, 1933, 8, 442–444).—When  $(\text{CH}_2)_6\text{N}_4\cdot\text{HBr}$  is prepared directly from the base and the acid, some hydrolysis takes place, and  $\text{MgO}$  is therefore added, the resulting  $\text{MgBr}_2$  remaining in the product, which gives solutions of  $p_\text{H}$  8 or even higher. Methods are suggested of obtaining a product as free as possible from  $\text{MgBr}_2$ .

Condensation of  $\alpha\gamma$ -dibromohydrin with  $\text{NMe}_3$ ,  $\text{NH}_2\text{Et}$ , and  $\text{NH}_2\text{Et}$ , respectively, yields  $\alpha\gamma$ -di(diethylamino)propan- $\beta$ -ol dimethobromide,  $\alpha\gamma$ -di(diethylamino)propan- $\beta$ -ol dihydrobromide, and  $\alpha\gamma$ -di(ethylamino)propan- $\beta$ -ol dihydrobromide.

T. H. P.

**Synthesis of 2-thiolhistidine; experiments towards the synthesis of ergothioneine.** C. R. HARRINGTON and J. OVERHOFF (Biochem. J., 1933, 27, 338–344).—Certain proposed routes to ergothioneine have proved impracticable.  $\text{Et } \alpha$ -chloro- $\beta$ -glyoxaline-4(or 5)-propionate cannot be benzoylated. Treat-



ment of 2-thiol-4(or 5)-aminomethylglyoxaline with I in order to obtain the disulphide yields a complex product. 2-Thiol-4(or 5)-phenoxyglyoxaline (synthesis outlined) cannot be converted into the 4(or 5)-OH- or -Br-compounds. Condensation of phthalimidohalogenoacetones with Et sodiochloromalonate yields resins.

*Acetylaspatic acid* (I), m.p. 142—143°,  $[\alpha]_{D}^{20} +5.9^\circ$  in  $H_2O$ , is obtained from aspartic acid (II) with  $Ac_2O$  and aq. NaOH or with keten in aq. NaOH. Boiling  $Ac_2O$  converts (I) or (II) into the *azlactone* (III), m.p. 145—146°, to which Bergmann *et al.* (A., 1926, 1236) assigned the structure of acetamidossuccinic anhydride (IV). A product, m.p. 175°, probably (IV), is obtained from moist (I) and  $Ac_2O$  at 95°. (III) and  $PCl_5$  in  $AcCl$  yields the *acid chloride*, which, treated with  $CH_2N_2$ , followed by HCl and EtOH, yields *Et*  $\delta$ -chloro- $\alpha$ -acetamido- $\gamma$ -ketovalerate, m.p. 128°, converted into the  $\delta$ -phthalimido-compound (V), m.p. 175°, which yields with 20% HCl under reflux  $\alpha$ -diamino- $\gamma$ -ketovaleric acid monohydrochloride, yellows at 175°, blackens at 210°, which is converted by NaCNS into dl-2-thiolhistidine [2HCl, m.p. 204—206° (decomp.)], oxidised by  $Fe_2(SO_4)_3$  to dl-histidine.  $\alpha$ -Amino- $\alpha$ -phthalimido- $\gamma$ -ketovaleric acid (VI), m.p. 165—166° (decomp.), is obtained from (V) by refluxing with  $N-HCl$ ; it cannot be methylated, but yields only  $NMe_3$  and an unsaturated acid. Treatment of (VI) in  $3N-H_2SO_4$  with KBr and  $NaNO_2$  yields the  $\alpha$ -bromo-compound, m.p. 185—186° (decomp.), hydrolysis of which yields a non-basic oil. R. K. C.

**Electrolytic oxidation of glutamic acid.** Y. TAKAYAMA.—See this vol., 681.

**Acyl derivatives of aminomethanesulphonic acids.** H. J. BACKER and H. MULDER (Rec. trav. chim., 1933, 52, 454—468).—The constitution of Reinking's aminomethanesulphonic acid (I) (A., 1905, i, 261) is confirmed by its transformation by  $NOCl$  into chloromethanesulphonic acid. Differentiation of sulphonic acids from alkyl sulphites by cleavage by KCN, supposed to be typical of the latter, is invalid, since some sulphonic acids, e.g., (I) and its  $SO_2Ph$  derivative (II), are thus cleaved, whereas acylation by other acids and  $N$ -nitration or -nitrosation of (II) gives stable substances. In the cases marked \* below the free acid was not isolated. (I),  $Ac_2O$ , and aq. NaOH give *acetamidomethanesulphonic acid*,  $+H_2O$  ( $Na$  and  $K$  salts; *nitrate*,  $+H_2O$ );  $Na_2CO_3$  and the chloroformate give the *carbomethoxy-* and *carbethoxy-* derivatives\* of (I) ( $Na$  salts), and KCN the *carbamyl* derivative (carbamidomethanesulphonic acid),  $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot SO_3H$  ( $K$  salt).  $CH_2O$ , aq.  $NaHSO_3$ , and the appropriate amine give *N-methyl-*\* ( $Na$ , decomp. 80°, and  $K$  salts; *nitrate* of  $K$  salt;  $K$  salt of  $Ac$  derivative), *tert.-butyl-*\* [ $Na$  salt,  $+H_2O$  (*nitrate*)], *dimethylamino-*\* ( $Na$  salt) and *phenyl-aminomethanesulphonic acid* [ $Na$  salt,  $+H_2O$ ;  $Na$  salt (III) of the  $Ac$  derivative;  $Na$  salt of the  $N-NO$ -derivative].  $NH_2Bz$  gives similarly *benzamidomethanesulphonic acid* ( $K$ ,  $+H_2O$ , and  $Na$ ,  $+2H_2O$ , salts). The last and also the following derivatives\* of (I) are prepared by the Schotten-Baumann method:  $SO_2Ph-$  ( $Na$  salt), *o-* ( $Na$  salt), and *p-toluenesulphonyl-* [ $K$  salt;  $K$  salts of  $NO$ - and  $NO_2$ - (IV)-derivatives]. The action

of KCN on the salt of the appropriate acid gives *tert.-butylamino-*, b.p. 83—88°/14 mm., *dimethylamino-*, *benzenesulphonamido-*, m.p. 77°, and *o-toluenesulphonamido-* (V), m.p. 63.5°, *-acetonitrile*. (V) with  $H_2O_2$  and NaOH in EtOH at 50° gives  $o-C_6H_4Me \cdot SO_2 \cdot NH_2$ , and with EtOH and dry HCl in cold  $Et_2O$  gives the *hydrochloride* of the *imino-ether*,  $o-C_6H_4Me \cdot SO_2 \cdot NH \cdot CH_2 \cdot C(OEt) \cdot NH \cdot HCl$ , which with  $H_2O$  affords *Et o-toluenesulphonylglycine*, an oil. (IV) with conc. aq.  $NH_3$  at 100° gives  $p-C_6H_4Me \cdot SO_2 \cdot NH_2$ . R. S. C.

**Thiocarbamyl chloride.** M. BATTEGAY and E. HÉGAZI (Compt. rend., 1933, 196, 1030—1032).—The action of dry HCl (I) on HCNS (II) in  $Et_2O$  yields *thiocarbamyl chloride* (65%), decomp. 75—80°.  $H_2O$  decomposes it into (I) and (II), alcohols into thiourethanes,  $NH_2 \cdot CS \cdot OR$ . A. C.

**Organic compounds of boron.** T. THOMSON and T. S. STEVENS (J.C.S., 1933, 556).—Attempts to prepare compounds of the type  $[BR_4]M$  by heating  $BMe_3$  or  $BPh_3$  with LiEt, LiPh, NaMe, NaEt, or  $Na \cdot CH_2Ph$  in a neutral solvent failed. LiEt or NaEt in ligroin at 120° gives a solid which on hydrolysis yields  $H_2$ , corresponding with 50% of LiH. R. S. C.

**Action of arsines with halogenoarsines.** W. STEINKOPF (J. Amer. Chem. Soc., 1933, 55, 2165; cf. Blicke and Powers, A., 1932, 1049).—The results of Steinkopf and Smie (Ber., 1926, 59, B, 1459) have been shown to be incorrect by Steinkopf and Dudek (A., 1929, 1471). H. B.

**Action of arsines with halogenoarsines.** F. F. Blicke and L. D. POWERS (J. Amer. Chem. Soc., 1933, 55, 2165—2166).—A reply to Steinkopf (preceding abstract). H. B.

**Existence of metal ketyls in the aliphatic series.** A. E. FAVORSKY and J. N. NAZAROW (Compt. rend., 1933, 196, 1229—1231).—Na with  $CO(CMe_3)_2$  (I) produces a deep red solution which is decolorised on exposure to air with the appearance of reactions for  $H_2O_2$ . In  $Et_2O$  slow association of the metal ketyl produces the pinacol alcoholate  $[ONa \cdot C(CMe_3)_2]_2$ , decomposed by  $H_2O$  into *tetratert.-butylethylene glycol*, m.p. 85—86°, b.p. 156°/13 mm., which with cold conc.  $H_2SO_4$  affords  $\beta\beta\epsilon\epsilon$ -*tetramethyl- $\delta\delta$ -ditert.-butylhexan- $\gamma$ -one*, b.p. 135—136°/20 mm., which gives a violet colour with Na.  $CMe_3 \cdot COPr^s$  reacts with Na similarly to (I). Pinacolin does not give a coloration with Na. Treatment of the reaction product with  $H_2O$  leads to the isolation of  $\beta\gamma$ -*ditert.-butyl- $\Delta^2$ -buten- $\gamma$ -ol*, b.p. 105—107°/15 mm. (II), and  $\beta\beta\delta$ -*trimethyl- $\delta$ -tert.-butylpentan- $\gamma$ -one*, b.p. 200—202°, reduced to the corresponding *alcohol*, b.p. 99°/15 mm. (*benzoate*, m.p. 48—49°). (II) is dehydrated by anhyd.  $H_2C_2O_4$  to  $\beta\gamma$ -*ditert.-butylbutadiene*, b.p. 168—170°, which gives, with maleic anhydride, a *ditert.-butyltetrahydrophthalic anhydride*, m.p. 128—129°. A. C.

**Reaction of monobromoamine with Grignard reagents.** G. H. COLEMAN, H. SOROOS, and C. B. YAGER (J. Amer. Chem. Soc., 1933, 55, 2075—2080).— $NH_2Br$  (method of prep. given; cf. Moldenhauer and Burger, A., 1929, 897) treated with  $MgRX$  ( $R=$



Bu<sup>a</sup>, Bu<sup>γ</sup>, *sec.*-Bu, ·CH<sub>2</sub>Ph, ·C<sub>2</sub>H<sub>4</sub>Ph, and Ph; X = Cl, Br, I) in Et<sub>2</sub>O at -5° to 0° gives N<sub>2</sub> (5–15%), NH<sub>3</sub> (22–89%), and NH<sub>2</sub>R (3–63%). The yield of NH<sub>2</sub>R is greatest with MgRCl and smallest with MgRI; smaller yields are obtained than with NH<sub>2</sub>Cl (A., 1928, 622; 1929, 431). H. B.

**Thermal decomposition of cyclohexane and cyclohexene in presence of silica gel.** A. MAILHE (Chim. et Ind., 1933, 29, 759–765; cf. A., 1932, 729).—Thermal decomp. of cyclohexene (I) in presence of SiO<sub>2</sub> commenced at about 500°, was slight below 600°, whereas at 600–700° increasing quantities of C<sub>6</sub>H<sub>6</sub> were formed with varying amounts of C<sub>2</sub>H<sub>4</sub> and its homologues (C<sub>2</sub>H<sub>6</sub> in general preponderating). Above 700°, PhMe, C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>, C<sub>10</sub>H<sub>8</sub>, and anthracene were formed (in addition to C<sub>6</sub>H<sub>6</sub>). cycloHexane began to decompose at about 600°; the primary reaction at this and higher temp. was apparently simple dehydrogenation to (I), the reaction products being the same as were obtained with the latter. A. B. M.

**Preparation of hydrocarbons with a hemicyclic double linking.** N. K. ALEXANDROVITSCH (J. Gen. Chem. Russ., 1933, 3, 48–51).—cycloHexylcarbinol is converted by Na and CS<sub>2</sub> in Et<sub>2</sub>O into *Me* cyclohexyl xanthate, m.p. 165° (*amide*, m.p. 75–76°), pyrolysed above 200° to methylenecyclohexane. 4-Methylcyclohexylcarbinol similarly affords *Me* 4-methylcyclohexyl xanthate (*amide*, m.p. 104–105°), pyrolysed to methylene-4-methylcyclohexane. G. A. R. K.

**Carotenoids. IV. Degradation of carotene and β-ionone with ozone.** R. PUMMERER and L. REBMANN (Ber., 1932, 66, [B], 798–801; cf. A., 1931, 491).—Ozonisation of β-ionone followed by fission with warm H<sub>2</sub>O and separation of the products with steam gives a 15.2% yield of neutral oil and a 23.8% yield of non-volatile acids, among which ε-keto-αα-dimethylheptic and αα-dimethyladipic acids were identified. Geronaldehyde is accompanied by an unidentified trimethylcyclohexanone (*semicarbazone*, m.p. 206°). The *p*-nitrophenylhydrazones of β- and α-ionone have m.p. 173° and 113°, respectively. H. W.

**Oxidation of β-carotene.** P. KARRER, H. VON EULER, H. HELLSTRÖM, and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1932, 11 B, No. 3, 5 pp.).—Oxidation of β-carotene (I) occurs slowly when a colloidal aq. solution is kept in vac. or (more rapidly) in air at 39°; oxidation with H<sub>2</sub>O<sub>2</sub> (large excess) proceeds much more rapidly to completion in a similar manner. Carotene oxide, m.p. 161°, from (I) and BzO<sub>2</sub>H in CHCl<sub>3</sub>, has an absorption spectrum which differs from that of (I), β-hydroxycarotene (Kuhn and Brockmann, A., 1932, 749), and β-carotene (*loc. cit.*); it exhibits marked growth-promoting properties towards rats. H. B.

**Apparent anomalous lability of the 2-nitro-group in 2:3-dinitrotoluene. Example of the reversed-field effect.** H. H. HODGSON and E. W. SMITH (J.C.S., 1933, 500–501).—3-Nitro-*o*-toluidine (modified prep.) and K<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub>-EtOH-H<sub>2</sub>O give 3:3'-dinitro-2:2'-azoxytoluene, m.p. 121°, oxidised by HNO<sub>3</sub> (*d* 1.5) at < 20° to 2:3-dinitrotoluene. This with NaOH gives 3-nitro-*o*-cresol, with Na<sub>2</sub>S in

aq. COMe<sub>2</sub> 3:3'-dinitro-2:2'-ditolyl sulphide, m.p. 152° (lit. 150°) [oxidised (without isolation) by K<sub>3</sub>Fe(CN)<sub>6</sub> to 3:3'-dinitro-2:2'-ditolyl disulphide, m.p. 145°], and with Na<sub>2</sub>S<sub>2</sub> in aq. COMe<sub>2</sub> to 3:3'-diamino-2:2'-ditolyl disulphide, m.p. 123° (Ac<sub>2</sub> derivative, m.p. 167°; *dipicrate*, m.p. 158°). The above and similar replacement reactions of the 2-NO<sub>2</sub>-group are examples of the reversed-field effect. R. S. C.

**Relative stability of penta-arylethanes. I. Preparation of penta-arylethanes.** W. E. BACHMANN (J. Amer. Chem. Soc., 1933, 55, 2135–2139).—The following are prepared from CPh<sub>3</sub>MgBr and the appropriate CHAr<sub>2</sub>Br in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> and N<sub>2</sub>: penta-phenyl-, m.p. 182–185° (in N<sub>2</sub>); the m.p. quoted in N<sub>2</sub> are all with decomp. and are > in air, probably owing to oxidation taking place in the latter case), ααα-triphenyl-β-diphenylene-, m.p. 248–256° (in N<sub>2</sub>), αααβ-tetraphenyl-β-*p*-tolyl-, m.p. 183–185° (in N<sub>2</sub>), ααα-triphenyl-ββ-di-*p*-tolyl-, m.p. 170–180° (in N<sub>2</sub>), αααβ-tetraphenyl-β-*anisyl*-, m.p. 172–176° (in N<sub>2</sub>), ααα-triphenyl-ββ-dianisyl-, m.p. 168–176° (in N<sub>2</sub>), αααβ-tetraphenyl-β-*p*-diphenyl-, m.p. 166–175° (in N<sub>2</sub>), ααα-triphenyl-ββ-di-*p*-diphenyl-, m.p. 180–190° (in N<sub>2</sub>), and αααβ-tetraphenyl-β-*α'*-naphthyl-, m.p. 194–196° (in N<sub>2</sub>), -ethane. The CHAr<sub>2</sub>Br used are prepared from CHAr<sub>2</sub>·OH, HBr, and AcBr in AcOH; the 4:4'-dimethyl-, m.p. 48.5–49°, and *p*-phenyl- (I), m.p. 104°, -benzhydryl bromides are new. (I) is also prepared from *p*-phenyldiphenylmethane and Br at 185°. *p*-Methoxybenzhydryl chloride, m.p. 64° (the bromide could not be prepared), is obtained from the hydrol and dry HCl in C<sub>6</sub>H<sub>6</sub>+CaCl<sub>2</sub>.

9-Bromo-9-phenylfluorene and CPh<sub>3</sub>MgBr give (·CPh<sub>3</sub>)<sub>2</sub> and αβ-diphenyl-αβ-di(diphenylene)ethane (II), m.p. 254° (in N<sub>2</sub>). 9-Chloro-9-phenylfluorene and MgPhBr afford a mixture of 9:9-diphenylfluorene and (II) (cf. A., 1930, 1279, and Schmidt-Nickels, A., 1929, 695). H. B.

**Dissociation into free radicals of tetradiphenylylditert.-butylethane.** J. B. CONANT and R. F. SCHULTZ (J. Amer. Chem. Soc., 1933, 55, 2098–2104).—Li *p*-diphenyl (I) (from Li and *p*-bromodiphenyl in Et<sub>2</sub>O and N<sub>2</sub>) and CMe<sub>3</sub>·CO<sub>2</sub>Et in Et<sub>2</sub>O give *di-p*-diphenylyltert.-butylcarbinol, m.p. 129–130°, which with SOCl<sub>2</sub> at -15° (and then at room temp.) affords the *chloride* (II), m.p. 105–106°. Crystallisation of (II) from hot C<sub>6</sub>H<sub>6</sub> gives a considerable amount of an isomeric *chloride*, m.p. 181°, also formed in appreciable amount from the carbinol and SOCl<sub>2</sub> at 25°. (II) and 40% Na-Hg in Et<sub>2</sub>O yield Na *di-p*-diphenylyltert.-butylmethyl (III), converted by CO<sub>2</sub> into *di-p*-diphenylyltert.-butylacetic acid, m.p. 178–181°, and by moist Et<sub>2</sub>O into *di-p*-diphenylyltert.-butylmethane, m.p. 178–179°. (III) and *s*-C<sub>2</sub>Me<sub>4</sub>Br<sub>2</sub> give *s*-tetra-*p*-diphenylylditert.-butylethane (IV), light orange, m.p. (in N<sub>2</sub>) 136–137° (becoming red; the colour fades at 145–150°), resolidifying with m.p. 160–175°, which absorbs O<sub>2</sub> instantaneously in PhBr giving *di-p*-diphenyl ketone, and is cleaved by 40% Na-Hg to (III). Solutions of (IV) in PhMe are orange-red at room temp. and the intensity of the colour is diminished by cooling; at 80°, disproportionation occurs. The *Me* ether, m.p. 141.5–142.5°, of cyclohexyldi-*p*-diphenylylcarbinol, m.p. 126–



127° [from (I) and Me hexahydrobenzoate], and 40% Na-Hg in Et<sub>2</sub>O give a violet Na derivative, which with *s*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> yields an orange-coloured solution of *s*-dicyclohexyltetra-*p*-diphenylethane (not isolable owing to rapid disproportionation). H. B.

[4 : 4'-Derivatives of diphenyldidiphenyl and didiphenyl.] R. PUMMERER (Ber., 1933, 66, [B], 802; cf. A., 1931, 1406).—An acknowledgment of the work of Kuhn (A., 1929, 1435). H. W.

Preparation of chloromethylnaphthalenes and 1 : 5-dimethylnaphthalene. A. R. ANDERSON and W. F. SHORT (J.C.S., 1933, 485).—1-C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>Cl (I) (modified prep.) and alkaline Na<sub>2</sub>SO<sub>3</sub> give 1-C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>·SO<sub>3</sub>Na, which gives a very little 1-C<sub>10</sub>H<sub>7</sub>Me (II) when distilled with NaOH. (I) with Na and EtOH gives a mixture of (II) and its reduction products, dehydrogenated by S at 220°, and with Zn needles and dry HCl in EtOH at 0° a 68% yield of (II). (I) and NH<sub>2</sub>Ph at 100° give 1-naphthylmethylamine (77% yield) (NO-derivative, m.p. 57°), oxidised by KMnO<sub>4</sub> in COMe<sub>2</sub> at 0° to naphthylidene-aniline (poor yield) and smoothly hydrolysed to C<sub>10</sub>H<sub>7</sub>·CHO, obtained in 60% yield from (II) and (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> in EtOH. (I), paraform, ZnCl<sub>2</sub>, and dry HCl in ligroin at 60–65° give a mixture of C<sub>10</sub>H<sub>6</sub>(CH<sub>2</sub>Cl)<sub>2</sub>, oxidised by K<sub>3</sub>Fe(CN)<sub>6</sub> to 1 : 5-C<sub>10</sub>H<sub>6</sub>(CO<sub>2</sub>H)<sub>2</sub>, and reduced by Zn and HCl-EtOH to a mixture of C<sub>10</sub>H<sub>6</sub>Me<sub>2</sub> (crude picrate, m.p. 139–140°), containing some of the 1 : 5-isomeride (picrate, m.p. 138–139°). R. S. C.

Reaction between naphthalene-2-sulphonyl chloride and some thiol compounds. B. C. SAUNDERS (Biochem. J., 1933, 27, 397–402).—Both glutathione (I) and its oxidation product (presumably the disulphide) reduce 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>2</sub>Cl (II) to 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>2</sub>H. Since (I) reduces 1·5 mols. of (II), it appears that glutathione disulphoxide is formed, but a pure product could not be isolated. No *N*-sulphonyl derivative of glutathione is formed. Analogously, cysteine yields di(naphthalene-2-sulphonyl)-cysteine (*Na* derivative, decomp. 214°, isolated at *p*<sub>H</sub> 8·8) and 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>2</sub>H. *S*-Benzylcysteine, however, yields *N*-naphthalene-2-sulphonyl-*S*-benzylcysteine, m.p. 132°, without formation of 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>2</sub>H. Thiolacetic acid yields dithioglycolic acid and 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>2</sub>H. R. K. C.

Stereochemistry of dicyclic ring systems. VIII. Δ<sup>1:9</sup>-Octahydronaphthalene. W. HÜCKEL and H. NAAB (Annalen, 1933, 502, 136–155).—Successive treatment of the Na derivative of *trans*-decahydro-α-naphthol, m.p. 63°, with CS<sub>2</sub> and MeI in Et<sub>2</sub>O affords the Me xanthate, which decomposes at 180–210°/vac. to give 30–40% of a mixture (A) of Δ<sup>1:9</sup>-octahydronaphthalene (I) (about 80%), b.p. 196·5–198·5° [bimol. nitrosochloride, colourless, m.p. 127°; nitrolpiperidide, m.p. 179° (decomp.)], and *trans*-Δ<sup>1:2</sup>-octahydronaphthalene (II) (about 20%). Oxidation (O<sub>3</sub>, AcOH) of (A) gives (mainly) γ-2-ketocyclohexylbutyric acid (III), m.p. 60–61° (semicarbazone, m.p. 189°; oxime, m.p. 101–103°), which is oxidised (alkaline KMnO<sub>4</sub>) further to δ-ketosebacic acid; (III) arises from (I). Oxidation (KMnO<sub>4</sub>) of (A) affords (III), δ-ketosebacic, *trans*-β-2-carboxy-

cyclohexylpropionic, succinic, and liquid acids, and a trace of non-cryst. glycols. The Me xanthate, m.p. 86°, from *cis*-decahydro-α-naphthol (IV), m.p. 93°, similarly decomposes to (mainly) *cis*-Δ<sup>1:2</sup>-octahydronaphthalene (V) and a little (I) [(III) is not isolated on ozonolysis], whilst the *p*-toluenesulphonate of (IV) and Na<sub>2</sub>CO<sub>3</sub> in boiling MeOH afford (I) (about 80%), (V) (about 20%), and a trace of Δ<sup>9:10</sup>-octahydronaphthalene (VI). The *p*-toluenesulphonate of *trans*-decahydro-α-naphthol, m.p. 49°, similarly gives (I) (about 80%), (II) (about 20%), and a trace of (VI). (I) is largely isomerised to (VI) by *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H in MeOH. The *N*-Me derivative, b.p. 119–122°/22 mm., of *trans*-decahydro-α-naphthylamine, m.p. –1°, MeI, and MeOH-KOH give *trans*-decahydro-α-naphthyltrimethylammonium iodide, decomp. partly from 180°; thermal decomp. of the hydroxide affords almost 100% of (II), which is oxidised by BzO<sub>2</sub>H to a glycol (VII), C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>, m.p. 184–186°, and by KMnO<sub>4</sub> to *trans*-β-2-carboxycyclohexylpropionic acid. The mol. heats of combustion of (I) and (VI) are 1452–1454 and 1455–1456 kg.-cal., respectively, and are approx. the same as that of *trans*-Δ<sup>2</sup>-octahydronaphthalene (VIII) (A., 1930, 76), thus indicating the absence of strain in (I).

[With E. BAERTICH and (in part) A. GERCKE.] Oxidation (BzO<sub>2</sub>H) of a specimen of (VIII) which contains about 10% of *trans*-Δ<sup>1</sup>-octahydronaphthalene gives the oxide, b.p. 91–92°/10 mm., hydrated to a mixture of a glycol (IX), m.p. 163°, and a little (VII). (IX) is the sole product when (VIII) is first regenerated from its dibromide, m.p. 85° (during the prep. of which an isomeride, m.p. 49–50°, is also formed), with Mg; about 50% of decahydronaphthalene is produced during this treatment. *Di-trans*-decahydro-β-naphthyl ethers, m.p. 52–54° and 62–65°, are by-products in the prep. of (VIII) from *trans*-decahydro-β-naphthol, m.p. 75° (cf. *loc. cit.*).

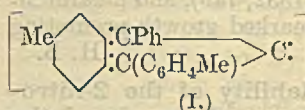
[With A. GERCKE and A. GROSS.] Oxidation (CrO<sub>3</sub>, AcOH) of (VI) gives *trans*-9 : 10-dihydroxydecahydronaphthalene, m.p. 96° (cf. *loc. cit.*) (monoacetate, m.p. 132°), and 1-keto-Δ<sup>9:10</sup>-octahydronaphthalene, b.p. 123–130°/12 mm. (semicarbazone, m.p. 243°); the latter is reduced (H<sub>2</sub>, Pd-C, MeOH) to 1-ketodecahydronaphthalene. H. B.

Dissociable organic oxides. The dissociable oxide of 1 : 1'-di-*p*-tolyl-3 : 3'-diphenyl-5 : 5-dimethylrubene. C. DUFRAISSE and J.-A. MONIER (Compt. rend., 1933, 196, 1327–1329).—Et phenylpropionate and *p*-C<sub>6</sub>H<sub>4</sub>Me·MgBr yield γ-phenyl-α-di-*p*-tolylpropinen-α-ol, m.p. 87–88° (giving a Me ether, m.p. 75–76°, and phenyl β-di-*p*-tolylvinyl ketone, m.p. 107–108°). This affords 1 : 1'-di-*p*-tolyl-3 : 3'-

diphenyl-5 : 5'-dimethylrubene (I), m.p. (anhyd.) 242° (+0·33BuOAc 194°), giving the peroxide, C<sub>46</sub>H<sub>36</sub>O<sub>4</sub>, m.p. 210° (anhyd.), which decomposes quantitatively at 170°.

R. S. C.

Nitration of alkyl oxanilates. G. TIERIE (Rec. trav. chim., 1933, 52, 420–424).—Et oxanilate affords good yields of the *p*-NO<sub>2</sub>- (by HNO<sub>3</sub>, *d* 1·45, at 0°), 2 : 4-di-, m.p. 143° (by abs. HNO<sub>3</sub> at 0°), and





2 : 4 : 6-*trinitro*-, m.p. 105° (by abs.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  at < 35°), -derivatives. Me oxanilate gives similarly the *p*-, m.p. 232° (also obtained from *p*-nitroaniline and  $\text{Me}_2\text{C}_2\text{O}_4$  at 100°), 2 : 4-*di*-, m.p. 181°, and 2 : 4 : 6-*trinitro*-, m.p. 132—134°, -derivatives. R. S. C.

**Nitrosation of methylaniline.** J. C. EARR and N. F. B. HALL (J.C.S., 1933, 510—512).—Interaction of  $\text{NPhMe}$ ,  $\text{HCl}$  and  $\text{HNO}_2$  in  $\text{MeOH}$  studied in a dilatometer (A., 1932, 1125) shows that at 8° vol. contraction occurs during the initiatory period (I) followed by a sudden expansion (II) and then contraction to const. vol. (II) is due to a sudden rise in temp. of about 1°. Reaction probably occurs as a result of the formation of  $\text{NPhMe}^+$  followed by an accumulation of  $\text{H}^+$  which catalyses the reaction. This explanation finds strong support in conductivity measurements on the reaction mixture, and in the fact that the greater is the acid concn. the shorter is (I). J. L. D.

**Influence of the nitroso-group on the formation of [complex salts of] amines.** R. RĂSCANU (Ann. Sci. Univ. Jassy, 1933, 17, 130—148).—The following salts are prepared: (a)  $[\text{UO}_2\text{B}]\text{X}_2$ ; B = *p*- $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$  and *p*- $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2$ ; X =  $\text{NO}_3$ ,  $\text{OAc}$ , and  $0\cdot5\text{C}_2\text{O}_4$ ; (b)  $[\text{UO}_2\text{B}_2]\text{X}_2$ ; B as above; X =  $\text{NO}_3$ ,  $\text{Cl}$ ,  $\text{Br}$ , and  $0\cdot5\text{SO}_4$ . They are stable in air, decomposed by dil. acids, and give reactions for  $\text{UO}_2$ .  $\text{NPhMe}_2$  and  $\text{NPhEt}_2$  do not form such salts. The NO-group is thus probably responsible for complex formation, and its position appears to influence the readiness with which it takes place. However, antipyrine forms a salt, and the NO-derivative gives a salt containing 3 mols. of base. R. S. C.

**Reductions with lead-sodium [alloys].** F. FICHTER and H. STENZL (Helv. Chim. Acta, 1933, 16, 571—573; cf. A., 1932, 49).—An aq. solution of  $\text{NPhMe}_3\cdot\text{SO}_4\text{Me}$  is reduced by 30% Na-Pb alloy to  $\text{NMe}_3$  and  $\text{C}_6\text{H}_6$ ; the alloy behaves qualitatively and quantitatively like a Pb cathode. Na-Hg is without action. F. L. U.

**Alkylanilines with tertiary alkyl groups.** W. J. HICKINBOTTOM (Nature, 1933, 131, 762—763).—Pure *tert*-.butyl- (I), -amyl- (II), and -hexyl-aniline (III) have been obtained by a modification of Nef's method. The *tert*-.alkyl group is removed by heating the amines with dil. mineral acid, and this type of fission occurs more readily with the arylsulphonyl derivatives. With hot, dil.  $\text{H}_2\text{SO}_4$  the readiness with which the alkyl group is eliminated is in the order (I) < (II) < (III). The free amines do not readily react with  $\text{Ac}_2\text{O}$  or arylsulphonyl chlorides.  $\text{MeI}$  readily reacts with (I). L. S. T.

**Aromatic compounds of fluorine.** XIV. Reaction of *p*-fluorophenylhydrazine; *N*-alkylated fluoroanilines. G. SCHIEMANN and W. WINKELMÜLLER (Ber., 1933, 66, [B], 727—732; cf. A., 1932, 1247).—Diazotisation of *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$  in  $\text{HCl}$  followed by reduction with  $\text{NaHSO}_3$  gives *p*-fluorophenylhydrazine (I), b.p. 129·2°/21 mm., m.p. 39°, in 74% yield (cf. Rinkes, A., 1914, i, 679, 1200). The hydrochloride volatilises with decomp. without melting. (I) smoothly yields *salicylaldehyde-p*-fluorophenylhydrazone, m.p. 166·5°, *glucose-p*-fluorophenylosazone,

decomp. 187—188°, and *benzoylacetyl-p*-fluorophenylhydrazone, m.p. 179·5°. (I) and  $\text{COMe}_2$  in presence of  $\text{ZnCl}_2$  at 100° afford 5-fluoro-2-methylindole, m.p. 102°. Treatment of (I) with  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$  in boiling 50%  $\text{AcOH}$  leads to impure 1-*p*-fluorophenyl-3-methylpyrazol-5-one, transformed by boiling  $\text{COMe}_2$  into a mixture of 4 : 4'-isopropylidenedi-1-*p*-fluorophenyl-3-methylpyrazol-5-one (II), m.p. 141·5°, and 1-*p*-fluorophenyl-3-methyl-4-isopropylidenepyrazol-5-one (III), m.p. 136°. (II) is partly transformed into (III) in boiling  $\text{COMe}_2$ .

[With R. PILLARSKY.] *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$  is diazotised and converted into the *diazonium fluoborate*, decomp. 151°, which when heated with sand gives *p*-fluorodimethylaniline, b.p. 78—79·5°/16 mm., m.p. 25° (hygroscopic hydrochloride, m.p. 118°; picrate, m.p. 151·5°), in 17·2% yield. Similarly, *p*-diethylaminophenyldiazonium fluoborate, decomp. 113°, gives *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NEt}_2$ , b.p. 92·5°/12 mm. (picrate, m.p. 150·6°), in 20% yield. H. W.

**Action of heat on  $\beta$ -naphthylisopropylamine hydrochloride.** T. HEAP (J.C.S., 1933, 495—496).— $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ , and  $\text{Pr}^i\text{Br}$  in a sealed tube at 180° during 6 hr. afford  $\text{NHPr}^i\cdot\text{C}_{10}\text{H}_7\cdot\beta$  (*Bz* derivative, m.p. 96—98°; *p*-toluenesulphonamide, m.p. 119—120°; hydrochloride, m.p. 209—210°), which when heated under pressure at 300—320° for 6 hr. decomposes completely into propylene and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ . At 200—220° some  $\text{NH}(\text{C}_{10}\text{H}_7\cdot\beta)_2$  (I) is formed, the amount depending on the time of heating. (I) is formed similarly from  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2\cdot\text{HCl}$  (cf. A., 1885, 990). J. L. D.

**Heteropolarity.** XXI. *NN'*-Diphenyl-*p*-phenylenediamine and triphenylmethyl chloride. W. DILTHEY and G. ESCHERICH (Ber., 1933, 66, [B], 782—783; cf. A., 1932, 263).—The increase in the intensity of colour developed by the gradual addition of  $\text{Br}_2$  in  $\text{AcOH}$  to the "blue" chloride confirms the constitution  $[\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}]^+\text{Cl}\cdot\text{C}_{18}\text{H}_{18}\text{N}_2$  previously assigned. *NN'*-Diphenyl-*p*-phenylene-diamine and -imine do not appear to yield a chemical compound comparable with a quinhydrone. H. W.

**Ditolyl series.** V. Resolution into optical antipodes of *dl*-2-iodo-2'-amino-6 : 6'-dimethyldiphenyl. A. ANGELETTI (Gazzetta, 1933, 63, 145—151).—The  $\text{NO}_2$ -compound (A., 1932, 152) is reduced ( $\text{SnCl}_2$ ) to *dl*-2-iodo-2'-amino-6 : 6'-dimethyldiphenyl, m.p. 46—47° (I) (hydrochloride, m.p. 203—204°), from which the *d*-bromocamphorsulphonates, m.p. 167—168° (decomp.),  $[\alpha]_D^{20} + 48\cdot0^\circ$ , and m.p. 125° (decomp.),  $[\alpha]_D^{20} + 39\cdot33^\circ$ , respectively, of the *d*- and *l*-isomerides yield the hydrochlorides, each of m.p. 202—203°,  $[\alpha]_D^{20} + 2\cdot33^\circ$ , and  $-2^\circ$ , respectively. From (I), or from 2 : 2'-diamino-6 : 6'-dimethyldiphenyl, 2 : 2'-*di*-iodo-6 : 6'-dimethyldiphenyl, m.p. 92—93°, is obtained, with an insol. product. E. W. W.

**Action of bromine on nitrobenzeneazoacetates and related compounds.** F. D. CHATTAWAY and D. R. ASHWORTH (J.C.S., 1933, 475—479; cf. A., 1932, 1125).—*p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  (I) and cold  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$  afford *Et p*-nitrobenzeneazoacetate (II), m.p. 127°. *Et* 2-bromo-4-nitro-, m.p.



130°; *Et* 2:6-dibromo-4-nitro-, m.p. 135°; *Et* o-nitro-, m.p. 93°, and *Et* m-nitro-benzeneazoacetate, m.p. 128°, are similarly prepared. (I) with  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$  in aq. NaOAc at 0° affords  $\alpha$ -ketopropaldehyde-p-nitrophenylhydrazone (III), m.p. 217°.  $\alpha$ -Ketopropaldehyde-2-bromo-4-nitro-, m.p. 187°; -2:6-dibromo-4-nitro-, m.p. 151°; -o-nitro-, m.p. 128°; -m-nitro-, m.p. 152°, and -4-bromo-2-nitro-phenylhydrazone, m.p. 176°, are similarly prepared. (II) (1 mol.) and Br (1 mol.) in AcOH containing excess of NaOAc in the cold afford *Et*  $\alpha$ -bromoglyoxylate-p-nitrophenylhydrazone, m.p. 203°, which with  $\text{NH}_3\cdot\text{EtOH}$  affords *Et*  $\alpha$ -aminoglyoxylate-p-nitrophenylhydrazone, m.p. 181°. The following are prepared similarly: *Et*  $\alpha$ -bromoglyoxylate-2-bromo-4-nitro-, m.p. 126° ( $\alpha$ -amino-compound, m.p. 124.5°); -2:6-dibromo-4-nitro-, m.p. 144° ( $\alpha$ -amino-compound, m.p. 191°); -o-nitro-, m.p. 137° ( $\alpha$ -amino-compound, m.p. 123°); -m-nitro-phenylhydrazone, m.p. 149°. (I) with  $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  in aq. EtOH-NaOAc during 6 hr., or Br (1 mol.) and (II) (1 mol.) in hot AcOH, affords *Et* p-nitro-benzeneazo- $\gamma$ -bromoacetate (IV), m.p. 163°. The following are prepared similarly: *Et* 2-bromo-4-nitro-, m.p. 138°; *Et* 2:6-dibromo-4-nitro-, m.p. 118°; *Et* o-nitro-, m.p. 145°; *Et* m-nitro-benzeneazo- $\gamma$ -bromoacetate, m.p. 122°. (II) (1 mol.) with Br (2 mols.) in boiling AcOH affords *Et* p-nitrobenzeneazo- $\gamma\gamma$ -dibromoacetate (V), m.p. 134°. The following are prepared similarly: *Et* 2-bromo-4-nitro-, m.p. 167°; *Et* 2:6-dibromo-4-nitro-, m.p. 153°; *Et* o-nitro-, m.p. 116°; *Et* m-nitro-benzeneazo- $\gamma\gamma$ -dibromoacetate, m.p. 117°. (II) (1 mol.) with Br (3 mols.) in boiling AcOH affords  $\beta\beta\omega$ -tribromo- $\alpha$ -ketopropaldehyde-p-nitrophenylhydrazone, m.p. 194°. The following are prepared similarly: -2-bromo-4-nitro-, m.p. 186°; -2:6-dibromo-4-nitro-, m.p. 128°; -m-nitro-, m.p. 158°; -o-nitro-, m.p. 145.5°; -4-bromo-2-nitro-phenylhydrazone, m.p. 160°. (III) (1 mol.) with Br (1 mol.) in cold AcOH in 1 hr. affords  $\omega$ -bromo- $\alpha$ -ketopropaldehyde-p-nitrophenylhydrazone, m.p. 233°, which with saturated EtOH- $\text{NH}_3$  affords the  $\omega$ -amino-compound, m.p. 240° (decomp.);  $\omega$ -anilino-compound, m.p. 167°. The following are prepared similarly: -2-bromo-4-nitro-, m.p. 162°; -2:6-dibromo-4-nitro-, m.p. 156°; -o-nitro-, m.p. 185°; -m-nitro-phenylhydrazone, m.p. 214°. (III) with Br (2 mols.) in AcOH at 90° affords  $\beta\omega$ -dibromo- $\alpha$ -ketopropaldehyde-p-nitrophenylhydrazone, m.p. 228°, and similarly are prepared the -2-bromo-4-nitro-, m.p. 177°; -2:6-dibromo-4-nitro-, m.p. 136°, and -o-nitro-phenylhydrazone, m.p. 175° ( $\omega$ -amino-compound, m.p. 174°;  $\omega$ -anilino-compound, m.p. 140°). (III) with excess of Br affords the nitrophenylhydrazino-derivatives of  $\beta\beta\gamma$ -tribromo- $\alpha$ -ketopropaldehyde. (IV) in boiling EtOH with KOAc affords 4-hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole, m.p. 220° (*Ac* derivative, m.p. 167°), brominated in boiling AcOH to 5-bromo-4-hydroxy-3-carbethoxy-1-(4'-nitrophenyl)pyrazole, m.p. 163° (*Ac* derivative, m.p. 126°), also obtained by the interaction of KOAc in boiling EtOH with (V). The following are prepared similarly: 4-hydroxy-3-carbethoxy-1-(2'-bromo-4'-nitrophenyl)pyrazole, m.p. 189° [*Ac* derivative, m.p. 138.5°]; 5-*Br*-derivative, m.p. 218° (*Ac* derivative, m.p. 108°); -1-(2':6'-dibromo-4'-nitrophenyl)pyrazole, m.p. 170° [*Ac* derivative,

m.p. 148°; *Bz* derivative, m.p. 143°; 5-*Br*-derivative, m.p. 209.5° (*Ac* derivative, m.p. 126°)]; -1-(2'-nitrophenyl)pyrazole, m.p. 153° [*Ac* derivative, m.p. 115°]; 5-*Br*-derivative, m.p. 161° (*Ac* derivative, m.p. 111°)]; -1-(3'-nitrophenyl)pyrazole, m.p. 199° (*Ac* derivative, m.p. 140.5°]; 5-*Br*-derivative, m.p. 167°). J. L. D.

**Action of bromine on arylazobenzoylacetones.** F. R. CHATTAWAY and R. J. LYE (J.C.S., 1933, 480—482; cf. preceding abstract).—Benzeneazobenzoylacetone (I), m.p. 90—95° (lit., 99°) (1 mol.), and Br (2 mols.) in cold AcOH containing NaOAc afford  $\omega$ -bromophenylglyoxal-p-bromophenylhydrazone, m.p. 197° (converted by  $\text{NH}_2\text{Ph}$  in boiling EtOH into the  $\omega$ -anilino-compound, m.p. 165°), further brominated in hot AcOH to  $\omega$ -bromophenylglyoxal-2:4-dibromophenylhydrazone (II), m.p. 122° ( $\omega$ -anilino-compound, m.p. 137°). The following analogues of (I) are described: 2:4-dibromobenzene- (III), m.p. 160° (*Ac* derivative, m.p. 171°), which with 1 equiv. Br affords (II); 2:4:6-tribromobenzene-azobenzoylacetone, m.p. 112° (*Ac* derivative, m.p. 159°), which with Br (1 mol.) in cold AcOH-NaOAc affords  $\omega$ -bromo-, m.p. 132°, and with  $\text{Cl}_2$  in AcOH affords  $\omega$ -chloro-phenylglyoxal-2:4:6-tribromophenylhydrazone, m.p. 142° ( $\omega$ -anilino-derivative, m.p. 118°). (I) (1 mol.) with Br (3 mols.) in AcOH at about 40° affords  $\delta\delta$ -dibromo- $\alpha\beta\gamma$ -triketo- $\alpha$ -phenylbutane- $\beta$ -p-bromophenylhydrazone, m.p. 177° (decomp.) (the intermediate stages being difficult to realise). (III) (1 mol.) with Br (1 mol.) in boiling AcOH affords  $\delta$ -bromo- $\alpha\beta\gamma$ -triketo- $\alpha$ -phenylbutane- $\beta$ -2:4-dibromophenylhydrazone (IV), m.p. 170° (decomp.), whereas more extensive bromination gives the  $\delta\delta$ -dibromo-compound (V), m.p. 187° (decomp.).  $\delta$ -Bromo- (VI), m.p. 158° (decomp.), and  $\delta\delta$ -dibromo- $\alpha\beta\gamma$ -triketo- $\alpha$ -phenylbutane- $\beta$ -2:4:6-tribromophenylhydrazone (VII), m.p. 156° (decomp.), are similarly prepared. (IV) when boiled with EtOH containing excess of KOAc affords 4-hydroxy-3-benzoyl-1-(2':4'-dibromophenyl)pyrazole, m.p. 171°, brominated to a 5-*Br*-derivative, m.p. 127°, also obtained by the cyclisation of (V). (VI) is similarly cyclised to 4-hydroxy-3-benzoyl-1-(2':4':6'-tribromophenyl)pyrazole, m.p. 206° (*Ac* derivative, m.p. 140°), brominated to a 5-*Br*-derivative, m.p. 178° [*Ac* derivative, m.p. 117° (decomp.)], also obtained from (VII). J. L. D.

**Demethylating phenol ethers.** E. A. TZOFIN and K. A. TSOCHKIVADZE (Khim. Farm. Prom., 1932, 10, 376).—By a modification of Klemens' method, in which salts of aromatic amines are used together with dry HCl at 160—170°, 94% yields are obtained.

CH. ABS.

**Iodination of phenol under anhydrous conditions.** W. H. HUNTER and T. T. BUDROW (J. Amer. Chem. Soc., 1933, 55, 2122—2125).—Iodination of PhONa (from PhOH and Na) in dry xylene proceeds almost as rapidly as in presence of  $\text{H}_2\text{O}$ ; approx. 1 mol. of I is consumed and the products formed are (mainly)  $\text{o-C}_6\text{H}_4\text{I}\cdot\text{OH}$ , small amounts of  $\text{C}_6\text{H}_5\text{I}_2\cdot\text{OH}$  and  $\text{C}_6\text{H}_5\text{I}_3\cdot\text{OH}$ , and a trace of a halogen-free non-phenolic substance, m.p. 116—118°. Coffman's postulation (J.C.S., 1919, 115, 1040) of HOI as the active iodinating agent cannot apply in this case.

H. B.



Behaviour of mixed halogenated phenols in the Zincke method of nitration. L. C. RAIFORD and G. R. MILLER (J. Amer. Chem. Soc., 1933, 55, 2125—2131).—4-Chloro-2-bromophenol, b.p. 121—123°/10 mm., m.p. 33—34° (from  $p$ - $C_6H_4Cl \cdot OH$  and Br in  $CS_2$ ) (benzoate, m.p. 99—100°), is nitrated by  $NaNO_2$  and AcOH (the Zincke method) to its 6- $NO_2$ -derivative (I), whilst 2-chloro-4-bromophenol, b.p. 233—234°, m.p. 48—49° (lit. 50—51°) (from  $o$ - $C_6H_4Cl \cdot OH$ ), similarly gives its 6- $NO_2$ -derivative (II) and 2-chloro-4-nitrophenol. 2:4-Dichloro-6-bromo- and 2:6-dichloro-4-bromo-phenols similarly afford 2:4-dichloro-6-nitro- and 2:6-dichloro-4-nitro-phenols, respectively; 4-chloro-2:6-dibromophenol yields (I), whilst 2-chloro-4:6-dibromophenol furnishes (II) and 2-chloro-6-bromo-4-nitrophenol. 5-Chloro-3:4:6-tribromo-*o*-cresol (from 5-chloro-*o*-cresol and an excess of Br containing about 1% Al) is oxidised (fuming  $HNO_3$  at 0°) to 3:4:6-tribromotoluquinone, m.p. 238—240° (lit. 232°), and nitrated to 5-chloro-4:6-dibromo-3-nitro-*o*-cresol, m.p. 149—150° (benzoate, m.p. 131—132°), whilst 3-chloro-4:5:6-tribromo-*o*-cresol, m.p. 214—216° (lit. 209—211°), is nitrated to 3-chloro-4:6-dibromo-5-nitro-*o*-cresol, m.p. 182—183°. When both *o*- and *p*-positions are substituted by Cl and the other positions by Br, no replacement of halogen occurs (even with 2 mols. of  $NaNO_2$ ).

3-Chloro-5-bromo-*p*-cresol (III), b.p. 127—128°/5 mm., m.p. 30° (by chlorination of the bromocresol), is nitrated to 3-chloro-5-nitro-*p*-cresol, whilst 3-chloro-5:6-dibromo-*p*-cresol, m.p. 80—81° [from (III) and Br in  $CHCl_3$  containing a little I and Fe powder], gives 3-chloro-6-bromo-5-nitro-*p*-cresol, m.p. 109—110°, and 3-chloro-2:5:6-tribromo-*p*-cresol, m.p. 197—198° [from (III) and excess of Br containing Al], affords 3-chloro-2:6-dibromo-5-nitro-*p*-cresol, m.p. 157—158° (*Na* salt). 6-Chloro-4-bromo-*m*-cresol is nitrated to its 2- $NO_2$ -derivative, m.p. 103—104°, and 6-chloro-4-nitro-*m*-cresol (IV), m.p. 133—134°, whilst 6-chloro-2:4-dibromo-*m*-cresol gives 6-chloro-2-bromo-4-nitro-*m*-cresol, m.p. 87°, also prepared by bromination of (IV). Cl is not replaced by  $NO_2$  under the conditions now used.

5-Chloro-3-amino-*o*-cresol, m.p. 107° (ON- $Ac_2$ , m.p. 195—196°, N- $Ac$ , m.p. 110°, O- $Ac$ -N-Bz, m.p. 159°, and N-Bz, m.p. 203°, derivatives), 6-chloro-4-bromo-2-amino-*m*-cresol, m.p. 131—132° (ON- $Ac_2$ , m.p. 215°, N- $Ac$ , m.p. 184—185°, O- $Ac$ -N-Bz, m.p. 166—167°, and N-Bz, m.p. 247°, derivatives), 6-chloro-2-bromo-4-amino-*m*-cresol, m.p. 111—112° [ON- $Ac_2$ , m.p. 220°, N- $Ac$ , m.p. 180° (decomp.), O- $Ac$ -N-Bz, m.p. 189°, N-Bz, m.p. 192—193°, and ON-Bz<sub>2</sub>, m.p. 191°, derivatives], and 3-chloro-6-bromo-5-amino-*p*-cresol, m.p. 146—147° (ON- $Ac_2$ , m.p. 194—195°, N- $Ac$ , m.p. 149—149.5°, O- $Ac$ -N-Bz, m.p. 220—221°, and N-Bz, m.p. 178°, derivatives), are prepared by reduction of the corresponding  $NO_2$ -derivatives by the method previously described (A., 1911, i, 993). Only one (O-) $Ac$ -(N)-Bz derivative can be prepared from a substituted *o*-aminophenol regardless of the order of introduction of the groups. H. B.

Synthesis of chloromethyl derivatives of *p*-bromoanisole and the nitroanisoles. R. QUELET

(Compt. rend., 1933, 196, 1411—1413; cf. A., 1932, 943).— $p$ - $C_6H_4Br \cdot OMe$ ,  $(CH_2Cl)_2O$  [or, more conveniently,  $OMe \cdot CH_2Cl$  (I)], and  $ZnCl_2$  at room temp. give about 45% of 5-bromo-2-methoxybenzyl chloride; a larger proportion of 5:5'-dibromo-2:2'-dimethoxydiphenylmethane is formed with (I). With  $o$ - $NO_2 \cdot C_6H_4 \cdot OMe$  (II), reaction begins at about 40°, is rapid at 70°, and gives a good yield of 3-nitro-4-methoxybenzyl chloride (III);  $p$ - $NO_2 \cdot C_6H_4 \cdot OMe$  (IV) reacts more slowly, whilst  $m$ - $NO_2 \cdot C_6H_4 \cdot OMe$  (V) affords a trace only of condensation product. With  $SnCl_4$  for  $ZnCl_2$ , (II) gives a quant. yield of 3:3'-dinitro-4:4'-dimethoxydiphenylmethane (VI), m.p. 168°, which is oxidised ( $CrO_3$ ) to 3:3'-dinitro-4:4'-dimethoxybenzophenone, m.p. 190°; (IV) similarly affords the  $CH_2Cl$  derivative. Saturation of suspension of  $(CH_2O)_3$  and  $ZnCl_2$  in (II) with dry HCl gives 80% of (III) and a little (VI); (IV) similarly gives 70% of 5-nitro-2-methoxybenzyl chloride, whilst (V) affords a trace of 4-nitro-2-methoxybenzyl chloride, m.p. 90°. H. B.

Physico-chemical properties of *p*-aminophenol methosulphate. V. LUCAS (Bol. assoc. brasil. pharm., 1932, 12, 214).—The substance gives with  $FeCl_3$  a wine-red colour on boiling, reduces hot Fehling's solution and Nessler reagent, and gives ppts. with basic Pb acetate,  $BaCl_2$ , and  $Br \cdot H_2O$ .

CH. ABS.

Antiseptic activity and chemical constitution of the xylenols and their monohalogen derivatives. G. LOCKEMANN and T. KUNZMANN (Angew. Chem., 1933, 46, 296—301).—The following monohalogeno-xylenols are prepared by the action of  $SO_2Cl_2$  and Br on the corresponding xylenols and from the corresponding nitro-xylenols by reduction and diazotisation in presence of I, KI, and Cu powder, respectively: 6-chloro-, m.p. 98°, 6-bromo-, m.p. 92°, 6-iodo-, m.p. 84°, -*o*-3-; 5-chloro-, m.p. 87°, 5-bromo-, m.p. 84°, 5-iodo-, m.p. 71°, -*o*-4-; 5-chloro- (I), m.p. 72°, 5-iodo- (II), m.p. 68°, -*m*-2-; 5-iodo-*m*-4- (III), b.p. 108°; 2-bromo-, m.p. 82°; 2-iodo-, m.p. 74°, -*m*-5-; 5-chloro- (IV), and 5-iodo-*p*-2-xylenol. Action of the xylenols on *B. coli* (V), *Staphylococcus pyogenes aureus* (VI), and *B. typhosus* (VII) was not appreciably affected by the position of the Me and OH groups, but the effect of the position of halogen substitution was very marked. Whereas of the Cl-derivatives (I) and (IV) were most active against (V), the activity of the corresponding Br- and I-derivatives was much less, although still > that of the xylenols. (II) and (III) and the corresponding Br-derivatives were the most active of these two series, their activity being > that of the corresponding Cl-derivatives. Whilst the halogen derivatives of *m*-2- and *p*-2-xylenol were similar in activity towards (V), towards (VI) and (VII) the latter was much more active. A. L.

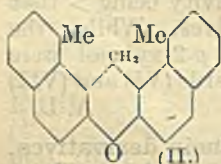
Nitrocyclohexylphenols and their derivatives. J. F. BARTLETT and C. E. GARLAND (J. Amer. Chem. Soc., 1933, 55, 2064—2068).—*o*-cyclohexylphenol (I) and  $HNO_3$  ( $d$  1.5) in EtOAc containing  $P_2O_5$  at <−15° and then at 0°, give a  $NO_2$ -derivative, b.p. 144—146°/3—4 mm.; at 0—5° and then at room temp., a  $(NO_2)_2$ -derivative, m.p. 106.5—107.5° [reduced ( $H_2$ ,  $PtO_2$ ,  $Ac_2O$ ) to the  $Ac_3$  derivative, m.p. 200—202°,



of the  $(\text{NH}_2)_2$ -compound], results. *p*-cyclohexylphenol (II) similarly affords a  $\text{NO}_2$ -derivative, b.p.  $140\text{--}142^\circ/2$  mm. (*Me ether*, b.p.  $148\text{--}152^\circ/4$  mm.; *Et ether*, b.p.  $146\text{--}150^\circ/4$  mm.), which is reduced (as above) to the  $\text{Ac}_2$  derivative, m.p.  $173\text{--}174^\circ$ , of the  $\text{NH}_2$ -compound, and a  $(\text{NO}_2)_2$ -derivative (III), m.p.  $84\text{--}85^\circ$  (*Me ether*, b.p.  $204\text{--}208^\circ/7$  mm.; *Et ether*, m.p.  $83\text{--}84^\circ$ ), which is reduced (as above) to the  $\text{Ac}_3$  derivative, m.p.  $212\text{--}213^\circ$ , of the  $(\text{NH}_2)_2$ -compound. It is probable that in the prep. of the ethers of (III) by Drew's method (J.C.S., 1920, 117, 1618), *aci*-ethers are first formed; these subsequently rearrange. (I) and (II) are prepared from cyclohexanol and PhOH in presence of  $\text{P}_2\text{O}_5$ ,  $\text{ZnCl}_2$ , or conc.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  (bath) for 2–3 days. H. B.

Butyl and amyl ethers of naphthols and some of their derivatives. S. D. WILSON, C. M. MA, and Y. L. T'YEN (J. Chinese Chem. Soc., 1933, 1, 11–16).—*n*-Bu and *n*-amyl bromides with K naphthoxides by an improved process give (50–65% yield) the following: 1-chloro-, m.p.  $28^\circ$ , 1-bromo-, m.p.  $29\cdot5^\circ$ , and 1-nitro- $\beta$ -naphthyl Bu<sup>a</sup> ether, m.p.  $55^\circ$ , and  $\alpha$ -naphthyl, m.p.  $29\cdot5\text{--}30\cdot0^\circ$ ,  $\beta$ -naphthyl, m.p.  $24\cdot0\text{--}24\cdot5^\circ$ , and 1-chloro-, m.p.  $31\cdot0\text{--}31\cdot5^\circ$ , 1-bromo-, m.p.  $25\cdot5^\circ$ , and 1-nitro- $\beta$ -naphthyl *n*-amyl ether.  $\alpha$ - and  $\beta$ -Naphthyl Bu<sup>a</sup> ethers have m.p.  $24^\circ$  and  $34\cdot5\text{--}35\cdot0^\circ$ , respectively. A. A. L.

7-Hydroxy-1-methylnaphthalene. V. VESELY and F. ŠTURSA (Coll. Czech. Chem. Comm., 1933, 5, 170–178).—Reduction of the 7- $\text{NO}_2$ -derivative (Schroeter and Laves, A., 1930, 1039) of 1-keto-1:2:3:4-tetrahydronaphthalene (prepared by a modification of Hock and Susemihl's method, this vol., 153) affords the 7- $\text{NH}_2$ -derivative, from which by diazotisation is obtained the 7-OH-compound, m.p.  $166^\circ$ , b.p.  $213\text{--}215^\circ/12$  mm., the *Me ether*, m.p.  $67\text{--}68^\circ$ , of which with  $\text{MeMgI}$  affords the *tert*-alcohol, which loses  $\text{H}_2\text{O}$  at  $100\text{--}110^\circ$  giving 7-methoxy-1-methyl-3:4-dihydronaphthalene, b.p.  $154\text{--}156^\circ/12$  mm. This is dehydrogenated by S at  $220^\circ$  to the *Me ether*, m.p.  $47\text{--}48^\circ$ , b.p.  $152\text{--}153^\circ/10$  mm., of 7-hydroxy-1-methylnaphthalene (I), m.p.  $69\text{--}70^\circ$ , b.p.  $176^\circ/10$  mm. (*Bz* derivative, m.p.  $88\text{--}90^\circ$ ), which is obtained by demethylation with  $\text{HBr}$  (*d* 1.49). (I) is converted by conc. aq.  $\text{NH}_3 + (\text{NH}_4)_2\text{SO}_3$  at  $170^\circ$  into 7-amino-1-methylnaphthalene, m.p.  $85\text{--}86^\circ$  (*Ac* derivative, m.p.  $157\text{--}158^\circ$ , identical with a specimen prepared from 7-nitro-1-methylnaphthalene), and couples with diazotised *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  to give 8-*p*-nitrobenzeneazo-1-methyl-7-naphthol, m.p.  $262\text{--}263^\circ$ . With 40%  $\text{CH}_2\text{O}$  in 50%  $\text{AcOH}$  (I) gives



the dimethyldinaphthopyran (II), m.p.  $216\text{--}217^\circ$ , and with  $\text{FeCl}_3$  it affords 7:7-dihydroxy-1:1-dimethyl-8:8'-dinaphthyl, m.p.  $238\text{--}239^\circ$ . The m.p. of (I) and its related compounds differ from those obtained by Dziewoński and

Waszkowski (A., 1930, 336).

J. W. B.

Bromo-derivatives of benzylphenols. I. Mono-, di-, and tri-bromo-derivatives of *o*- and *p*-benzylphenols. R. C. HUSTON, A. NEELEY, B. L. FAYERWEATHER, H. M. D'ARCY, F. H. MAXFIELD, M. M. BALLARD, and W. C. LEWIS (J. Amer. Chem.

Soc., 1933, 55, 2146–2149).—Br-derivatives of 2- and 4-hydroxydiphenylmethanes are prepared from benzyl (and the bromobenzyl) chloride and PhOH (and its Br-derivatives) by the Claisen method (A., 1925, i, 656) or by condensation with  $\text{AlCl}_3$ . The presence of Br in the ring of  $\text{CH}_2\text{PhCl}$  favours ether formation with  $\text{AlCl}_3$ , and affects the yield in the Claisen reaction (the retarding influence increases in the order: *p*-, *o*-, *m*-Br). Ethers are not produced from the bromophenols,  $\text{CH}_2\text{PhCl}$ , and  $\text{AlCl}_3$ . The  $\text{Br}_3$ -derivatives described are also prepared by bromination of the corresponding Br-compounds in the cold. The following derivatives are described: (a) of 2-hydroxydiphenylmethane: 3-, b.p.  $150\text{--}153^\circ/2$  mm. (*benzoate*, m.p.  $89\cdot5\text{--}90^\circ$ ; *p*-toluenesulphonate, m.p.  $85\text{--}85\cdot5^\circ$ ), 5-, m.p.  $55\text{--}56^\circ$ , 2'-, m.p.  $47\text{--}48^\circ$  (*benzoate*, m.p.  $39\text{--}40^\circ$ ), 3'-, b.p.  $167\text{--}169^\circ/3$  mm. (*benzoate*, m.p.  $69\text{--}70^\circ$ ), and 4'-, m.p.  $72\text{--}73^\circ$  (*benzoate*, m.p.  $50\text{--}51^\circ$ ), -Br-derivatives; 3:5- $\text{Br}_2$ -derivative, m.p.  $90\text{--}91^\circ$ ; 3:5:2'-, m.p.  $41\cdot5\text{--}42\cdot5^\circ$ , 3:5:3'-, m.p.  $76\text{--}77^\circ$  (*benzoate*, m.p.  $90\text{--}91^\circ$ ), and 3:5:4'-, m.p.  $80\text{--}81^\circ$  (*benzoate*, m.p.  $115\text{--}116^\circ$ ), - $\text{Br}_3$ -derivatives; (b) of 4-hydroxydiphenylmethane: 3-, b.p.  $148\text{--}150^\circ/2$  mm. (*benzoate*, m.p.  $63\text{--}64^\circ$ ; *benzenesulphonate*, m.p.  $56\text{--}57^\circ$ ), 2'-, m.p.  $71\text{--}73^\circ$  (*benzoate*, m.p.  $64\text{--}65^\circ$ ), 3'-, b.p.  $169\text{--}171^\circ/3$  mm. (*benzoate*, m.p.  $97\text{--}98^\circ$ ), and 4'-, m.p.  $82\text{--}83^\circ$  (*benzoate*, m.p.  $118\text{--}120^\circ$ ), -Br-derivatives; 3:5- $\text{Br}_2$ -derivative, m.p.  $56\text{--}57^\circ$ ; 3:5:2'-, m.p.  $78\text{--}80^\circ$ , 3:5:3'-, m.p.  $106\text{--}107^\circ$  (*benzoate*, m.p.  $131\cdot5\text{--}132\cdot5^\circ$ ), and 3:5:4'-, m.p.  $81\text{--}82^\circ$  (*benzoate*, m.p.  $144\text{--}145^\circ$ ), - $\text{Br}_3$  derivatives. The following ethers are prepared: 2:4-dibromophenyl benzyl, m.p.  $67\text{--}68^\circ$ ; *o*-, b.p.  $142\text{--}144^\circ/2$  mm., and *p*-, m.p.  $60\text{--}61^\circ$ , -bromophenyl benzyl; *Ph o*-, m.p.  $34\text{--}36^\circ$ , *m*-, m.p.  $36\text{--}37^\circ$ , and *p*-, m.p.  $92\cdot5\text{--}93\cdot5^\circ$ , -bromobenzyl; 2:4-dibromophenyl *o*-, m.p.  $62\text{--}64^\circ$ , *m*-, m.p.  $49\text{--}50^\circ$ , and *p*-, m.p.  $86\text{--}87^\circ$ , -bromobenzyl. In some cases the yield of hydroxydiphenylmethane in the Claisen reaction is much increased by addition of the corresponding Ph benzyl ether. H. B.

Derivatives of dihydroeugenol and pharmacological properties of some of the compounds.

D. E. LEVIN [with A. Lowy] (J. Amer. Chem. Soc., 1933, 55, 1995–2000).—Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOH}$ ) of eugenol [5- $\text{NO}_2$ -derivative (I), m.p.  $42\cdot8\text{--}43\cdot4^\circ$  (*K* salt)] gives dihydroeugenol (II), b.p.  $94\text{--}95^\circ/1$  mm.,  $126\text{--}127^\circ/15$  mm. (*acetate*, b.p.  $115^\circ/2$  mm.; *benzoate*, m.p.  $73^\circ$ ), which with  $\text{HNO}_3$  (*d* 1.5) in  $\text{Et}_2\text{O}$  at  $23\text{--}26^\circ$  affords 5-nitro-4-hydroxy-3-methoxypropylbenzene, m.p.  $33\cdot8\text{--}34\cdot2^\circ$  (*K* salt). This is reduced (as above) to 5-amino-4-hydroxy-3-methoxypropylbenzene (III), m.p.  $83\text{--}84^\circ$  (*hydrochloride*, decomp.  $191\text{--}192^\circ$ ; *ON-Ac*, m.p.  $155^\circ$ , *ON-Bz*, m.p.  $162^\circ$ , and *p*-nitrobenzylidene, m.p.  $133\text{--}134^\circ$ , derivatives), also prepared by similar reduction of (I). Dyes are prepared from diazotised (III) and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ , 1:8-aminonaphthol-3:6-disulphonic acid, 2-hydroxy-3-naphthanilide, and  $\alpha$ -naphthol-4-sulphonic acid. 2-Methoxy-4-propylphenoxyacetic acid, m.p.  $104^\circ$ , is obtained from (II),  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ , and aq.  $\text{KOH}$ . The effects of many of the above compounds on mucous membrane, cardiac muscle, turtle heart (*in situ*), blood pressure, and respiration are given. H. B.



Action of cyanogen on phenols and naphthols.

II. Trihydroxybenzenes. III. Naphthols. G. MACHEK (Monatsh., 1933, 62, 195—205; cf. A., 1932, 1245).—The following additive compounds are prepared by interaction of gaseous  $(\text{CN})_2$  with the appropriate OH-compound in  $\text{H}_2\text{O}$  or  $\text{EtOH}$  at  $0^\circ$ :  $2[1:2:3\text{-C}_6\text{H}_3(\text{OH})_3], (\text{CN})_2$ , decomp.  $125\text{--}135^\circ$ ;  $\beta\text{-C}_{10}\text{H}_7\text{-OH}, (\text{CN})_2$ , decomp.  $109\text{--}110^\circ$ ;  $3[2:3\text{-C}_{10}\text{H}_6(\text{OH})_2], (\text{CN})_2$ , m.p.  $150\text{--}180^\circ$  (decomp.);  $3[2:3\text{-C}_{10}\text{H}_6(\text{OH})_2], 2(\text{CN})_2$ , decomp.  $220\text{--}230^\circ$ ;  $2:7\text{-C}_{10}\text{H}_6(\text{OH})_2, (\text{CN})_2$ , decomp.  $135^\circ$ . PhOH reacts with  $(\text{CN})_2$  in  $\text{H}_2\text{O}$ , but not in  $\text{EtOH}$  or  $\text{CS}_2$ , to give a very unstable additive compound that could not be isolated pure on account of its ready loss of  $(\text{CN})_2$ . Negative results were also obtained with  $1:2:4\text{-}$  and  $1:3:5\text{-C}_6\text{H}_3(\text{OH})_3$ ,  $\alpha\text{-C}_{10}\text{H}_7\text{-OH}$ , and  $1:3\text{-}$  and  $1:4\text{-C}_{10}\text{H}_6(\text{OH})_2$ . H. A. P.

Podophyllin. III. W. BORSCHKE and J. NIEMANN (Annalen, 1933, 502, 264—272).—Veratraldehyde, Na methylsuccinate, and  $\text{Ac}_2\text{O}$  at  $115\text{--}125^\circ$  give  $\gamma\text{-}3:4\text{-dimethoxyphenyl-}\alpha\text{-methyl-}\Delta^8\text{-butenoic acid}$ , the Me ester of which when reduced catalytically and subsequently warmed with conc.  $\text{H}_2\text{SO}_4$  affords  $1\text{-keto-}6:7\text{-dimethoxy-}2\text{-methyl-}1:2:3:4\text{-tetrahydronaphthalene}$  (I), m.p.  $129\text{--}130^\circ$  [ $2:4\text{-dinitrophenylhydrazone}$ , m.p.  $259\text{--}260^\circ$  (decomp.)]. Clemmensen reduction of (I) and dehydrogenation (Se at  $250\text{--}280^\circ$ ) of the product gives  $6:7\text{-dimethoxy-}2\text{-methyl naphthalene}$  (II), m.p.  $98\text{--}99^\circ$  (picrate, m.p.  $118\text{--}120^\circ$ ), which is identical with phyllomerol  $\text{Me}_2$  ether (A., 1932, 1258). Veratrole, methylsuccinic anhydride, and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  give  $\beta\text{-}3:4\text{-dimethoxybenzoylbutyric acid}$  (III), m.p.  $107\text{--}108^\circ$  [Me ester, m.p.  $74\text{--}75^\circ$  ( $2:4\text{-dinitrophenylhydrazone}$ , m.p.  $155\text{--}156^\circ$ )], and non-cryst. material (A). Clemmensen reduction of (III) affords some  $\gamma\text{-}3:4\text{-dimethoxyphenyl-}\beta\text{-methylbutyric acid}$ , b.p.  $200\text{--}220^\circ/15\text{ mm.}$ , which with conc.  $\text{H}_2\text{SO}_4$  yields  $1\text{-keto-}6:7\text{-dimethoxy-}3\text{-methyl-}1:2:3:4\text{-tetrahydronaphthalene}$ , m.p.  $120\text{--}121^\circ$  [ $2:4\text{-dinitrophenylhydrazone}$ , m.p.  $200\text{--}201^\circ$  (decomp.)], convertible [as (I)] into (II). Esterification (MeOH) of (A) gives a Me ester,  $\text{C}_{14}\text{H}_{18}\text{O}_5$ , b.p.  $218\text{--}220^\circ/12\text{ mm.}$ , whilst reduction (Clemmensen) affords  $6:7\text{-dihydroxy-}2\text{-methyl-}1:2:3:4\text{-tetrahydronaphthalene}$  (?), m.p.  $76\text{--}80^\circ$ , and  $\text{tetrahydrophyllomerol Me}$ , m.p.  $98\text{--}101^\circ$ , and  $\text{Me}_2$  ethers. Phyllomeronic acid is converted partly into podophyllomeronic acid (*loc. cit.*) when heated with  $\text{CH}_2\text{I}_2$  and  $\text{MeOH-NaOMe}$  at  $100^\circ/20\text{ hr.}$  The optical activity of apocieropodophyllin is confirmed; vals. of  $[\alpha]_D^{25} +99.6^\circ$  and  $[\alpha]_D^{25} +107^\circ$  are found for preps. obtained using  $\text{Ac}_2\text{O-H}_2\text{SO}_4$  and  $\text{PCl}_5$ , respectively. H. B.

Reaction of halogen-substituted aryl alkyl and dialkyl sulphides with benzylamine. I. T. P. DAWSON (J. Amer. Chem. Soc., 1933, 55, 2070—2075).—The following are prepared [generally by methods already described (lit.)]: Et, b.p.  $63\text{--}65^\circ/47\text{ mm.}$ ,  $\text{Pr}^a$ , b.p.  $43\text{--}45^\circ/2\text{ mm.}$ ,  $\text{Bu}^a$ , b.p.  $58\text{--}59^\circ/1\text{ mm.}$ , isoamyl, b.p.  $68^\circ/1\text{ mm.}$ , Ph, b.p.  $88\text{--}89^\circ/0.637\text{ mm.}$ , and benzyl, b.p.  $113\text{--}115^\circ/1.01\text{ mm.}$ ,  $\beta\text{-chloroethyl sulphides}$ ;  $\text{CH}_2\text{Br-CH}_2\text{-SEt}$ , b.p.  $57\text{--}58^\circ/6\text{ mm.}$ ; di- $\beta$ , b.p.  $94\text{--}95^\circ/7\text{ mm.}$ , and di- $\gamma$ , b.p.  $111\text{--}112^\circ/7\text{ mm.}$ , -chloropropyl sulphides; Et  $\beta\text{-chloropropyl}$ , b.p.  $60^\circ/17\text{ mm.}$ , and Et  $\gamma\text{-chloro-}$

propyl, b.p.  $72^\circ/17\text{ mm.}$ , sulphides;  $\text{S}(\text{CH}_2\text{Cl})_2$ , b.p.  $51^\circ/11\text{ mm.}$ ; di- $\beta\text{-chloroethyl disulphide}$ , b.p.  $124\text{--}127^\circ/10\text{ mm.}$ ;  $\beta\text{-chloroethyl chlorovinyl sulphide}$  (mixture), b.p.  $83\text{--}84^\circ/4\text{ mm.}$ ;  $\beta\text{-chloroethyl } \alpha\beta\text{-dichlorovinyl sulphide}$ , b.p.  $79.5\text{--}80.5^\circ/4\text{ mm.}$ ; Et allyl sulphide, b.p.  $115\text{--}116^\circ$ . The following are prepared from  $\text{CH}_2\text{Ph-NH}_2$ , the appropriate alkyl (aryl) chloro- (or bromo-) alkyl sulphide, and  $\text{Na}_2\text{CO}_3$  in EtOH: Et, b.p.  $162\text{--}164^\circ/13\text{ mm.}$  (hydrochloride, m.p.  $214\text{--}215^\circ$ ),  $\text{Pr}^a$ , b.p.  $167\text{--}169^\circ/13\text{ mm.}$  (hydrochloride, m.p.  $175^\circ$ ),  $\text{Bu}^a$ , b.p.  $172\text{--}230^\circ/13\text{ mm.}$  (hydrochloride, m.p.  $152\text{--}153^\circ$ ), isoamyl, b.p.  $190\text{--}250^\circ/17\text{ mm.}$  (hydrochloride, m.p.  $161\text{--}162^\circ$ ), Ph, decomp. when heated (hydrochloride, m.p.  $152\text{--}153^\circ$ ), chlorovinyl (mixture), decomp. when heated (hydrochloride, m.p.  $211\text{--}212^\circ$ ), and  $\alpha\beta\text{-dichlorovinyl}$ , decomp. when heated (hydrochloride, m.p.  $174\text{--}176^\circ$ ),  $\beta\text{-benzylaminoethyl sulphides}$ ; Et  $\gamma\text{-benzylaminopropyl sulphide}$ , b.p.  $163\text{--}165^\circ/12\text{ mm.}$  (hydrochloride, m.p.  $172^\circ$ ); 3-benzyl-1:3-thiazetidine, b.p.  $175\text{--}185^\circ/16\text{ mm.}$  (hydrochloride, m.p.  $201\text{--}203^\circ$ ); di- $\beta\text{-benzylaminopropyl sulphide}$ , decomp. when heated (hydrochloride, m.p.  $239\text{--}240^\circ$ ); di- $\beta\text{-benzylaminoethyl disulphide}$ , decomp. when heated (hydrochloride, m.p.  $269^\circ$ ). Numerous other physical data are given.

H. B.

Preparation and properties of 2:4-dimethoxyphenyl alkyl sulphides. C. M. SUTER and H. L. HANSEN (J. Amer. Chem. Soc., 1933, 55, 2080—2082).— $m\text{-C}_6\text{H}_4(\text{OMe})_2$  and conc.  $\text{H}_2\text{SO}_4$  give 2:4-dimethoxybenzenesulphonic acid [*p-toluidine* salt, m.p.  $191\text{--}192^\circ$  (corr.)]; acid chloride (I), m.p.  $70.5^\circ$  (softens at  $69^\circ$ ); amide, m.p.  $166\text{--}167^\circ$ , the K salt of which with  $\text{Cl}_2$  in  $\text{H}_2\text{O}$  affords 4:6-dichlororesorcinol  $\text{Me}_2$  ether. Reduction (cf. Org. Synth., 1921, 1, 71) of (I) gives 2:4-dimethoxythiophenol (II), b.p.  $115\text{--}117^\circ/5\text{ mm.}$  (Pb salt). 2:4-Dimethoxyphenyl Me, b.p.  $115\text{--}118^\circ/4\text{ mm.}$ , m.p.  $38\text{--}39^\circ$ , Et, b.p.  $140\text{--}142^\circ/7\text{ mm.}$ ,  $\text{Pr}^a$ , b.p.  $157\text{--}160^\circ/8\text{ mm.}$ , and  $\text{Bu}^a$ , b.p.  $148\text{--}151^\circ/6\text{ mm.}$ , sulphides are prepared from (II) by the method previously described (A., 1932, 1244); the mol. refractions of these show considerable exaltation. Demethylation of these sulphides did not give the expected  $(\text{OH})_2$ -compounds. H. B.

Factors giving rise to the abnormal iodine value of cholesterol. J. O. RALLS (J. Amer. Chem. Soc., 1933, 55, 2083—2094).—When cholesterol (I) is treated with IBr or  $\text{C}_5\text{H}_5\text{N}$  sulphate dibromide (II) in AcOH the main reaction is the formation of the dihalide; this loses HHal at  $0^\circ$  and  $25^\circ$  (the elimination is facilitated by  $\text{C}_5\text{H}_5\text{N}$ ) to give dehydrocholestan-4-ol-7-one (III) (Windaus, A., 1904, i, 49) [ $2:4\text{-dinitrophenylhydrazone}$ , m.p.  $257^\circ$  (decomp.)]. (I) is also oxidised by IBr or (II) in AcOH at  $25^\circ$  to cholestenone (IV) ( $2:4\text{-dinitrophenylhydrazone}$ , m.p.  $231\text{--}232^\circ$ ). Elimination of HHal does not occur when IBr in  $\text{CCl}_4$  is used at  $25^\circ$ ; the amount of IBr consumed is more than is required for one double linking owing to concurrent substitution; at  $0^\circ$ , the theoretical val. is obtained. The reaction products from (I) and (II) or the Hanus reagent give the Lifschütz reaction (A., 1908, ii, 233) indicating that substances other than the dibromide of (I), (III), (IV) and its dibromide are formed. H. B.



**Dehydrogenation of cholesterol.** J. W. COOK and C. L. HEWETT (Chem. and Ind., 1933, 451—452).—The dehydrogenation product of cholesterol,  $C_{27}H_{44}$  (Diels *et al.*, A., 1927, 241), is probably impure 1:2-cyclopentenophenanthrene, m.p. 152—153° (picrate, m.p. 133—134.5°; *s*-trinitrobenzene derivative, m.p. 165.5—166.5°); the impurity may be the corresponding indene derivative. F. R. S.

**Constitution of cholesterol, and a new isomeride.** R. DE FAZI (Atti R. Accad. Lincei, 1933, [vi], 17, 166—172).—The literature on the constitution of cholesterol is discussed. The hydrochloride, m.p. 136—137° (A., 1932, 511), gives an *isomeride* of cholesterol, m.p. 141—143° (possibly a mixture of two *isocholesterols*, m.p. 138—139° and 142—144°). Another *hydrochloride*, m.p. 124—126°, is formed on treating cholesterol, in EtOH or Et<sub>2</sub>O, with gaseous HCl. The following conclusions are reached: the double linking of cholesterol is in the 6:7-position and that of *metacholesterol* at 5:6 or 7:8; for Diels' cholesterol, *allocholesterol*, and the new isomeride (or isomerides), m.p. 141—143°, the double linkings are in the 12:13-, 13:1-, 1:2-, and 2:3-positions, but it cannot be stated which is which. T. H. P.

**isoCholesterol.** I. Lanosterol and a new method for its preparation. C. DORÉE and D. C. GARRATT (J.S.C.I., 1933, 52, 141—143T).—Lanosterol (I) is obtained from a "neutral wool grease" extracted from sheep's wool with H<sub>2</sub>O. The grease is saponified in Et<sub>2</sub>O solution with NaOEt, the optically inactive alcohols are removed by treatment with COMe<sub>2</sub>, and (I) is separated from cholesterol by crystallisation from a 1:2-vol. mixture of MeOH and COMe<sub>2</sub> in which it is sparingly sol. Agnosterol (Windaus and Tschesche, A., 1930, 1179) was not present in the samples of wool grease employed, 1 kg. of which gave 40 g. of pure (I). Attempts to prepare "*isocholesterol*" from S. African rubber, the latex of *Euphorbia* species (Cohen, A., 1908, i, 884), gave negative results.

**Preparation of *allocholesterol* hydrochloride.** O. WAGNER (Biochem. Z., 1933, 261, 64—65).—The yield of this hydrochloride obtained by Mauthner's method (A., 1906, i, 579) is increased to 75% and the product is purer by working in CHCl<sub>3</sub>. W. McC.

**Coprosterol and lithobilianic acid.** R. LANGER (Z. physiol. Chem., 1933, 216, 189—192).—The dicarboxylic acid (I), m.p. 250°, obtained by oxidation of coprosterol (or cholesterol) gives on oxidation with CrO<sub>3</sub> lithobilianic acid (II). The observation by Windaus and Riemann that *isolithobilianic acid* (III) is produced was made with impure (I) containing isomerides which could give a mixture of (II) and (III). J. H. B.

**Action of  $\alpha\gamma$ -dichloropropylene on sodium derivatives of arylaliphatic alcohols.** P. C. DORIER (Compt. rend., 1933, 196, 1325—1327).— $\alpha\gamma$ -Dichloropropylene and the appropriate Na alkoxide at 130° in PhMe give *benzyl* (I), b.p. 123°/13 mm.,  $\beta$ -*phenylethyl*, b.p. 135°/13 mm., and  $\gamma$ -*phenylpropyl*  $\gamma$ -*chloroallyl ether* (II), b.p. 146°/13 mm. The Cl of these ethers is unreactive. (II) with Br liberates HBr which hydrolyses the ether to CH<sub>2</sub>PhBr.  $\gamma$ -Chloroallylbenzene does not react with Na phenoxides. R. S. C.

**Sterically hindered *tert.*-carbinols. 2:4:6-Tribromotriphenylcarbinol.** A. A. MORTON and L. V. PEAKES, jun. (J. Amer. Chem. Soc., 1933, 55, 2110—2112).—2:4:6-C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>·CO<sub>2</sub>Me and MgPhBr in Et<sub>2</sub>O-PhCl give 28% of 2:4:6-*tribromotriphenylcarbinol* (I), m.p. 116.5—117.5°; none is produced in Et<sub>2</sub>O alone and a trace only is obtained from 2:4:6-tribromobenzophenone and MgPhBr. No reaction occurs between *s*-C<sub>6</sub>H<sub>3</sub>Br<sub>3</sub>, CPh<sub>2</sub>Cl<sub>2</sub>, and AlCl<sub>3</sub> in CS<sub>2</sub>. (I) and PCl<sub>5</sub> in CCl<sub>4</sub> give a product, which with Ag in Et<sub>2</sub>O affords a yellowish-orange solution (becoming red when heated) which is decolorised by exposure to air. H. B.

**Heteropolarity. XXII. Constitution and colour.** W. DILTHEY (Ber., 1933, 66, [B], 825—826; cf. A., 1932, 1127).—A reply to Burawoy (this vol., 208). H. W.

**The two diastereoisomeric  $\alpha\beta\gamma$ -triphenyl-*n*-propyl alcohols. Exclusive preparation of each from stilbene and *isostilbene* oxides.** F. KAYSER (Compt. rend., 1933, 196, 1127—1129).—Stilbene oxide, obtained by oxidation of stilbene with BzO<sub>2</sub>H, reacts with CH<sub>2</sub>Ph·MgCl affording *r*-" $\beta$ "- $\alpha\beta\gamma$ -triphenyl-*n*-propyl alcohol (I), m.p. 87° (*phenylurethane*, m.p. 121.5°; *acetate*, m.p. 89°). *isoStilbene* oxide from *isostilbene*, obtained by catalytic hydrogenation of tolane, similarly yields *r*-" $\alpha$ "- $\alpha\beta\gamma$ -triphenyl-*n*-propyl alcohol (II), m.p. 92° (*phenylurethane*, m.p. 125°; *acetate*, m.p. 70°). Both (I) and (II) yield benzyldeoxybenzoin on oxidation with CrO<sub>3</sub>-AcOH. A. C.

**Dissymmetric influence exercised by an asymmetric carbon atom during the action of an organo-magnesium compound on an aldehyde group. Production of a single diastereoisomeride.** M. TIEFFENAU, (MLLE.) J. LÉVY, and F. KAYSER (Compt. rend., 1933, 196, 1407—1408).—*dl*- $\alpha\beta$ -Diphenylpropaldehyde and MgPhBr give  $\alpha$ -*dl*- $\alpha\beta\gamma$ -triphenylpropyl alcohol, m.p. 92° (cf. preceding abstract), whilst reduction (Na-Hg) of CH<sub>2</sub>Ph·CHPh·COPh affords  $\beta$ -*dl*- $\alpha\beta\gamma$ -triphenylpropyl alcohol, m.p. 87° (cf. *loc. cit.*). H. B.

**Derivatives of *p*-xylylene glycol.** R. QUELET (Bull. Soc. chim., 1933, [iv], 53, 222—234).— $\omega\omega'$ -Dichloro-*p*-xylene (I), m.p. 100°, b.p. 135°/16 mm., is obtained in 40% yield [calc. on (CH<sub>2</sub>O)<sub>2</sub>] by interaction of CH<sub>2</sub>PhCl, (CH<sub>2</sub>O)<sub>2</sub>, and gaseous HCl in presence of ZnCl<sub>2</sub>; a little  $\omega\omega'$ -dichloro-*o*-xylene, m.p. 55°, b.p. 130—135°/19 mm., is formed at the same time. With KOH in EtOH (I) gives, not (II) (below) alone (cf. Grimaux, Bull. Soc. chim., 1870, 14, 193), but mainly *p*-xylylene glycol Et<sub>2</sub> ether, b.p. 134°/15 mm., 252°/760 mm.; this and some Et ether (II), b.p. 154°/16 mm., are prepared in better yield by use of NaOEt in EtOH. The Me<sub>2</sub>, b.p. 124°/18 mm., 235°/1 atm.; Pr<sub>2</sub>, b.p. 148°/15 mm.; Pr<sub>3</sub>, b.p. 145°/15 mm.; Bu<sub>2</sub>, b.p. 180°/15 mm.; *di*-*isoamyl*, b.p. 185°/15 mm., and *dibenzyl ether*, m.p. 67°, are similarly prepared.

*p*-Xylylene glycol, m.p. 114°, is best prepared from (I) and aq. Na<sub>2</sub>CO<sub>3</sub> in an autoclave at 150°, allowing the CO<sub>2</sub> to escape from time to time, otherwise the white insol. polymeride is formed. Its monoalkyl ethers are obtainable from the Na deriv-



active and alkyl halides, but are better prepared by action of  $\text{AcCl}$  on an excess of the dialkyl ether in presence of  $\text{ZnCl}_2$  and hydrolysing the resulting half-chloride:  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{OR})_2 + \text{AcCl} \longrightarrow \text{AcOR} + \text{C}_6\text{H}_4(\text{CH}_2\cdot\text{OR})\cdot\text{CH}_2\text{Cl}$ . The *Me* ether, b.p.  $152^\circ/16$  mm. [*phenylurethane*, m.p.  $62^\circ$ ; *acetate*, b.p.  $150^\circ/16$  mm. (from chloride and  $\text{NaOAc}$ )], and (II) are thus prepared. The method does not work well with the higher ethers, but gives difficultly separable mixtures containing much (I). From the half-chloride and hexamethylenetetramine *p*-methoxymethylbenzaldehyde, b.p.  $125^\circ/16$  mm. [*semicarbazone*, m.p.  $186^\circ$  (block)], is prepared, and converted by the Cannizzaro reaction into *p*-methoxymethylbenzoic acid, m.p.  $123^\circ$ . H. A. P.

**Iodo-silver benzoate complex; its application to the oxidation of ethylenic compounds to  $\alpha$ -glycols.** C. PRÉVOST (Compt. rend., 1933, 196, 1129—1131).— $\text{AgOBz}$  and I combine to form the complex  $\text{AgI}(\text{OBz})_2$  (I), which liberates I from KI, oxidises  $\text{EtOH}$  to a mixture of aldehydes,  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$ ,  $\text{S}_2\text{O}_3^{--}$  to  $\text{SO}_4^{--}$ , and is decomposed by  $\text{H}_2\text{O}$  into  $\text{BzOH}$ ,  $\text{AgI}$ , and  $\text{O}_2$ . Unsaturated compounds,  $\text{R}\cdot\text{CH}:\text{CH}_2$ , are converted by (I) *in situ* into  $\alpha$ -glycol dibenzoates in accordance with the equation  $(\text{I}) + \text{R}\cdot\text{CH}:\text{CH}_2 \longrightarrow \text{AgI} + \text{R}\cdot\text{CH}(\text{OBz})\cdot\text{CH}_2\cdot\text{OBz}$ . The mechanism of the reaction is not regarded as addition of 2I to the double linking followed by reaction of the iodide with  $\text{AgOBz}$ . The reaction is applicable to the synthesis of erythritols and substituted glycerols. Stycerol,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , is obtained cryst., m.p.  $99.5^\circ$ . A. C.

**$\alpha$ -cyclopentylpropionic acid.** A. E. TSCHITSCHIBABIN and S. I. KORJAGIN (Bull. Acad. Sci. U.S.S.R., 1933, 273—276).—Et sodiomethylmalonate and cyclopentyl bromide in EtOH afford Et cyclopentylmethylmalonate, b.p.  $138\text{--}145^\circ/12$  mm., hydrolysed to the acid, m.p.  $150\text{--}151^\circ$  (decomp.), which when heated gives  $\alpha$ -cyclopentylpropionic acid, b.p.  $238.5\text{--}240^\circ$  (chloride, b.p.  $107^\circ/49$  mm.; *Me* ester, b.p.  $189.5\text{--}191^\circ$ ; *amide*, m.p.  $136.5\text{--}137^\circ$ ; *anilide*, m.p.  $115\text{--}116^\circ$ ; *p*-nitroanilide, m.p.  $167\text{--}168^\circ$ ). G. A. R. K.

**Effect of the medium "metallic nitrate-acetic anhydride" on the orientation of the nitro-group [introduced into] aromatic compounds.** G. BACHARACH, A. H. HAUT, and (MISS) L. CAROLINE (Rec. trav. chim., 1933, 52, 413—419).—Quinoline and  $\text{LiNO}_3$  with a trace of  $\text{Cu}(\text{NO}_3)_2$  in  $\text{Ac}_2\text{O}$  give 7-nitroquinoline.  $\text{Al}(\text{NO}_3)_3$  is less effective, and heavy metal nitrates are ineffective.  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  with  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Ac}_2\text{O}$  gives *m*- (50%) and *o*- (10%)  $\text{NO}_2$ -derivatives. The former result is explained on electronic grounds by co-ordination of the  $\text{Ac}_2\text{O}$  with the N atom. The latter confirms the views of Porter *et al.* (A., 1932, 511). R. S. C.

**Degradation of optically active carboxylic acids by azoimide and sulphuric acid.** J. VON BRAUN and E. FRIEHMELT (Ber., 1933, 66, [B], 684—685).—Addition of 10%  $\text{HN}_3$  in  $\text{CHCl}_3$  to optically active  $\alpha$ -benzylpropionic acid in conc.  $\text{H}_2\text{SO}_4$  at  $40\text{--}42^\circ$  affords  $\alpha$ -benzylethylamine hydrochloride, m.p.  $146^\circ$ ,  $[\alpha]_D^{25} +16.1^\circ$  (cf. Jones and Wallis, A., 1926, 279). The fenchylethylamine hydrochloride obtained

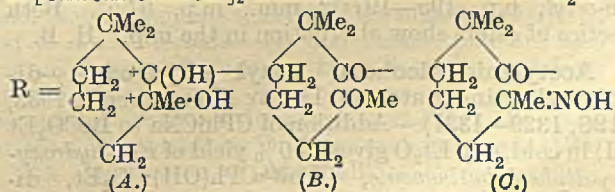
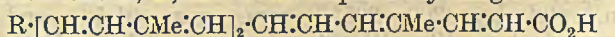
similarly from fencholic acid is identical with that derived from *d*-fenchone through fencholamide. With optically active acids this method of degradation can replace the Br-alkali or azide method.

H. W.

**Alkamine esters of cinnamic acid and derivatives. Novocaine analogues.** V. H. C. BRILL and C. F. COOK (J. Amer. Chem. Soc., 1933, 55, 2062—2064).—The hydrochlorides of  $\beta$ -diethylaminoethyl cinnamate,  $\beta$ -phenylpropionate, and phenylpropionate, and of  $\gamma$ -diethylaminopropyl  $\alpha$ - $\beta$ -dibromo- $\beta$ -phenylpropionate have m.p.  $135^\circ$ ,  $111^\circ$ ,  $163^\circ$ , and  $148^\circ$ , respectively. The narcotic effects (on goldfish) of these are compared with that of  $\gamma$ -diethylaminopropyl cinnamate (apothosin). H. B.

**Condensation of aromatic aldehydes and cyanoacetic acid.** V. M. RODIONOV and A. M. FEDOROVA (Arch. Pharm., 1933, 271, 292—296).—Benzhydramide and  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (I) in EtOH give  $\alpha$ -cyanocinnamic acid in 96% yield. (I) and the appropriate aldehyde in EtOH- $\text{NH}_3$  give the following substituted  $\alpha$ -cyanoacrylic acids in the yield stated:  $\beta$ -piperonyl-, 80.3;  $\beta$ -*p*-hydroxy-*m*-methoxyphenyl-, 78;  $\beta$ -*p*-anisyl-, 57; and  $\beta$ -furyl-, 58%. R. S. C.

**Constitution of azafrin.** R. KUHN and A. DEUTSCH (Ber., 1933, 66, [B], 883—892).—Further analyses of azafrin (I) and its *Me* ester (II) after purification by crystallisation and chromatographically coupled with determinations of the equiv. of tetradecahydroazafrin (III) lead to alteration of the formula of (I) from  $\text{C}_{28}\text{H}_{40}\text{O}_4$  to  $\text{C}_{27}\text{H}_{38}\text{O}_4$ . Cautious oxidation of (I) with  $\text{CrO}_3$  ( $\text{O}=1$ ) leads to azafrinone (IV),  $\text{C}_{27}\text{H}_{36}\text{O}_4$ , m.p.  $191^\circ$  (corr., Berl.). (IV) catalytically absorbs  $7\text{H}_2$  readily and a further  $2\text{H}_2$  with greater difficulty. It is optically inactive. The absorption spectrum of (IV) lies more toward the region of longer wave-length than that of (I); hence one OH of (I) is in immediate proximity to the system of conjugated double linkings and the CO formed by its oxidation is optically involved in the polyene system. Hence (I) is a glycol in which both OH groups are attached to a C ring. They are immediately proximate to the polyene chain, and the optical activity of (I) depends on the C atoms to which the OH groups are attached. (I) is a di-*tert*-glycol, since tetradecahydroazafrin reacts quantitatively with 1 mol. of  $\text{Pb}(\text{OAc})_4$  and the tetradecahydroazafrinone has no aldehydic properties. Oxidation of (I) with  $\text{KMnO}_4$  affords geronic [ $\delta$ -acetyl- $\alpha\alpha'$ -dimethyl-*n*-valeric] acid [semicarbazone, m.p.  $163^\circ$  (corr.) after softening] and considerable amounts of  $\alpha\alpha'$ -dimethylglutaric acid. The saturated ring system is therefore closely related to that of  $\beta$ -carotene. Drastic oxidation of (I) with  $\text{CrO}_3$  affords 3.5 mols. of  $\text{AcOH}$ . To (I), (IV), and azafrinonemonoxime, m.p.  $194^\circ$  (corr., Berl.), the constitutions A, B, and C are respectively assigned.





*Azafrinone Me ester*, m.p. 110° (corr., Berl), is reduced by Zn and AcOH in  $C_5H_5N$  to a dihydro-compound, this behaviour being characteristic of carotenoids containing CO at each end of the chain. (I) has  $[\alpha]_D^{20} -75.0^\circ$  in EtOH,  $-72.5^\circ$  in EtOH with 1% of  $B(OH)_3$ , whereas (II) has  $[\alpha]_D^{20} -32^\circ$ ,  $-73^\circ$ ,  $-158^\circ$ , and  $-210^\circ$  to  $-193^\circ$  ( $c=0.56$  to  $0.07$ ) in  $CHCl_3$ , EtOH,  $PhNO_2$ , and  $C_5H_5N$ , respectively.

H. W.

The monoamide of salicylacetic acid. E. A. TZOFIN and K. A. TSCHCHIKVADZE (J. Gen. Chem. Russ., 1933, 3, 17—20).—Salicylamide (I) and  $CH_2Cl \cdot CO_2Et$  condense in presence of NaOEt to *Et salicylamidoacetate* (II), m.p. 130—131°, hydrolysed with cold alkali to the acid, m.p. 213—215°, also obtained from (I) and  $CH_2Cl \cdot CO_2H$ . (II) is therefore isomeric with Merriman's compound, m.p. 164—165° (J.C.S., 1911, 99, 911; 1913, 103, 1838), which is shown to be *o*-carbethoxyphenylglycollamide by synthesis from Et salicylate and  $CH_2Cl \cdot CO \cdot NH_2$ . Unlike this compound, (II) can be allylated to an ester hydrolysable in the cold to *salicyl-N-allylamidoacetic acid*, m.p. 120—121°, also obtained from salicyl-*N*-allylamide,  $CH_2Cl \cdot CO_2Et$ , and NaOEt.

G. A. R. K.

Hydrate of *m*-5-xylenoxyacetic acid. A. R. ALBRIGHT (J. Amer. Chem. Soc., 1933, 55, 1736—1737).—*m*-5-Xylenoxyacetic acid has m.p. 111.2°, whilst the monohydrate has m.p. 81° (corr.); discrepancies in the m.p. (lit.) are thus explained. The acid is volatile in steam.

H. B.

Configuration of natural (—)-tyrosine. S. GOLDSCHMIDT and G. FREYSS (Ber., 1933, 66, [B], 784—785).—The laevo-configuration of (—)-tyrosine is established by the observation that (+)-benzoyl-tyrosine is oxidised by  $KMnO_4$  to the Bz derivative of *l*(+)-aspartic acid, m.p. 181°,  $[\alpha]_D +38.5^\circ$  in  $KOH-H_2O$ .

H. W.

Condensation of oxalic esters with benzyl cyanide. G. S. SKINNER (J. Amer. Chem. Soc., 1933, 55, 2036—2039).—The following data are reported: Et, m.p.  $-40.2^\circ$ ,  $Pr^a$ , b.p. 78—80°/3 mm., m.p.  $-46.3^\circ$ ,  $Bu^a$ , b.p. 95—97°/2 mm., m.p.  $-30^\circ$ , *n*-amyl, b.p. 131—132°/5 mm., m.p.  $-12.8^\circ$ , *n*-hexyl, b.p. 135—136°/2.5 mm., m.p.  $-9^\circ$ , *n*-heptyl, b.p. 142—144°/2 mm., m.p.  $12.5^\circ$ , and *n*-octyl, b.p. 167—169°/3 mm., m.p.  $11.2^\circ$ , oxalates; the higher esters ( $C_5-C_8$ ) are prepared by heating  $H_2C_2O_4 \cdot 2H_2O$  and the alcohol in vac.  $Alk_2C_2O_4$ ,  $CH_2Ph \cdot CN$ , and Na in  $Et_2O$  give the alkyl  $\beta$ -cyano- $\beta$ -phenylpyruvates; the following are prepared: *Me*, b.p. 152—154°/3 mm., m.p.  $115^\circ$ ; Et, b.p. 158—160°/4 mm., m.p.  $130^\circ$ ;  $Pr^a$ , b.p. 161—163°/3 mm., m.p.  $93^\circ$ ;  $Bu^a$ , b.p. 167—169°/3 mm., m.p.  $95^\circ$ ; *n*-amyl, b.p. 173—175°/3 mm., m.p.  $88^\circ$ ; *n*-hexyl, b.p. 181—183°/4 mm., m.p.  $94^\circ$ ; *n*-heptyl, b.p. 200—205°/8 mm., m.p.  $91.5^\circ$ ; and *n*-octyl, b.p. 195—197°/2 mm., m.p.  $97.5^\circ$ . Both series of esters show alternation in the m.p. H. B.

Acetylenic alcohols. Ethyl  $\alpha$ -hydroxy- $\alpha$ -*di*-phenylbutinenoate. M. LOURY (Compt. rend., 1933, 196, 1329—1331).—Addition of  $CPh:CHNa$  to  $BzCO_2Et$  (I) in cold, dry  $Et_2O$  gives a 50% yield of *Et*  $\alpha$ -hydroxy- $\alpha$ -*diphenylbutinenoate*,  $CPh:C(Ph)(OH) \cdot CO_2Et$ , di-

morphous, m.p. 55—56° and 80—81°, sol. in conc. alkalis and giving with hot 5%  $KOH$   $CPh:CH$ ,  $BzOH$ , and  $HCO_2H$ .  $COBz:C(Ph)$  is not formed.

R. S. C.

3 : 5-Dihydroxy-*p*-toluic acid. Y. ASAHINA and J. ASANO (Ber., 1933, 66, [B], 687—688).—*p*-Toluic acid is transformed by fuming  $H_2SO_4$  (50%  $SO_3$ ) at 170—180° into the 3 : 5-disulphonic acid [Ba salt,  $C_6H_4O_2(SO_3)_2Ba \cdot H_2O$ ], the K salt of which is converted by molten  $KOH$  at 250—270° into 3 : 5-dihydroxy-*p*-toluic acid (I), m.p. 262° after darkening (lit., m.p. 175—176°). (I) with  $KOH-Me_2SO_4$  and subsequently with  $Ag_2O-MeI$  affords *Me* 3 : 5-dimethoxy-*p*-toluate, m.p. 105°.

H. W.

Dehydrogenation of cholatrienic acid. II. H. RAUDNITZ, F. PETRÜ, and A. STADLER (Ber., 1933, 66, [B], 879—882; cf. A., 1932, 944).—Cholic acid is converted at about 300° into cholatrienic acid, which is mixed with Zn dust and distilled over Zn-pumice at a low red heat under slight vac. The presence of chrysene (I) in the distillate is placed beyond doubt; very probably picene is present also in the solid portion. The liquid distillate gives the reactions of indene. The formation of (I) is attributed to the enlargement of the 5-membered fourth ring of cholesterol and the bile acids.

H. W.

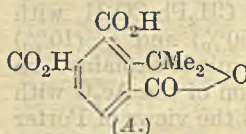
Bile acids. III. Enolisation of dehydrocholic acid and experiments on the structure of the acid. S. MINOVICI and M. VANGHELOVICI (Bul. Soc. Chim. România, 1933, 14, 171—178).—Dehydrocholic acid does not condense with  $CH_2(CO_2Et)_2$ , showing the absence of the CHO group, but gives  $Ac_2$ , m.p. 201°, and  $Bz_2$  derivatives, m.p. 115°, of the di-enol form of the acid.

F. R. S.

Bitter substances. V. Constitution of picrotoxin. K. F. W. HANSEN (Ber., 1933, 66, [B], 849—854).—Oxidation of picrotoxin, picrotin, or picrotoxinin with  $MnO_2$  and boiling 57%  $H_2SO_4$  yields an acid,  $C_{12}H_{10}O_6 \cdot H_2O$  (I), m.p. 286° after anhydride formation, and 1 : 2 : 3 : 4- $C_6H_2(CO_2H)_4$ , m.p. 240—241° ( $Me_4$  ester, m.p. 131—132°). (I) is converted by  $CH_2N_2$  into the  $Me_2$  ester, m.p. 103° (also obtained from  $MeI$  and the  $Ag$  salt); the  $Et_2$  ester has m.p. 93°. It is not affected by  $PhNCO$ , acetylation, or benzylation. When heated at 250° or boiled with  $AcCl$  (I) yields the anhydride  $C_{12}H_8O_5$ , m.p. 286°, transformed by  $CO(NH_2)_2$  into the imide  $C_{12}H_8O_4N$  (II), m.p. 325—327°. The Hofmann degradation of (II) affords the  $NH_2$ -acid  $C_{11}H_{11}O_4N$ , m.p. 219—220°, transformed by diazotisation and treatment with boiling EtOH into the monocarboxylic acid,  $C_{11}H_{10}O_4$ , m.p. 202—203°. Decarboxylation of (I) by Cu powder in boiling quinoline yields dimethylphthalide. (I) has probably the constitution A.

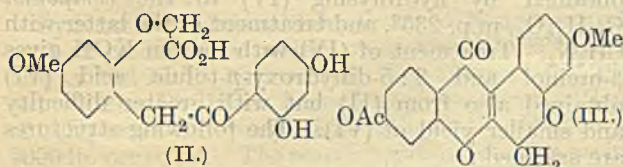
H. W.

Synthesis of rotenone and its derivatives. III. The dehydrorotenone nucleus. A. ROBERTSON (J.C.S., 1933, 489—493; cf. A., 1932, 751).—4-*O*-Methylresorcyraldehyde,  $CH_2Br \cdot CO_2Et$ , and  $K_2CO_3$  in  $COMe_2$  during 2 hr. afford *Et* 2-aldehydo-5-methoxyphenoxyacetate, m.p. 64° (semicarbazone, m.p. 222°),





which condenses with hippuric acid to give the *azlactone*, m.p. 128—129°, hydrolysed by boiling NaOH for 6 hr. and then heated with excess of dil. HCl for 3 hr. to give 5-methoxyphenoxycetic-2-pyruvic acid, m.p. 250—251° (decomp.) [oxime (I), anhydro-form, m.p. 128—130° and at 152—153° after solidifying at 140—145°]. Interaction of (I) with Ac<sub>2</sub>O affords 5-methoxy-2-cyanomethylphenoxycetic acid, m.p. 156°, the *Me* ester, m.p. 88°, of which with resorcinol in Et<sub>2</sub>O containing ZnCl<sub>2</sub> and HCl, followed by hydrolysis with H<sub>2</sub>O, affords 5-methoxy-2-2':4'-dihydroxybenzoylmethylphenoxycetic acid (II) (+H<sub>2</sub>O, m.p. 193°; *Me* ester, m.p. 89—90°). Cyclisation of (II) by boiling Ac<sub>2</sub>O containing NaOAc during 10 min. affords 7-hydroxy-7'-methoxychromeno-(3':4':2:3)-chromone acetate (III), m.p. 195°, hydrolysed by EtOH-HCl to the hydroxychromone, m.p. 258—260° (decomp.). With boiling NaOH (III) reverts to (II).



This reaction is identical with the formation of derrisic acid and deguelic acid from dehydrorotenone and dehydrodeguelin, respectively. Salicylaldehyde, CH<sub>2</sub>Br-CO<sub>2</sub>Et, and K<sub>2</sub>CO<sub>3</sub> in COMe<sub>2</sub> during 2 hr. afford *Et* 2-aldehydophenoxyacetate, m.p. 34—35° (semicarbazone, m.p. 178°), which affords with hippuric acid an *azlactone*, m.p. 131°, converted into 2-cyanomethylphenoxycetic acid, m.p. 136° [*Me* ester (IV), m.p. 68°], by hydrolysis of the *azlactone* to a pyruvic acid, followed by the action of Ac<sub>2</sub>O on its oxime. (IV) and resorcinol after the procedure of Hoesch afford 2-2':4'-dihydroxybenzoylmethylphenoxycetic acid (V), m.p. 206°, cyclised by Ac<sub>2</sub>O and NaOAc to 7-acetoxychromeno-(3':4':2:3)-chromone, m.p. 178°, hydrolysed to (V) by NaOH. 3-Hydroxycoumarin when boiled with NaOH affords with NH<sub>2</sub>OH.HCl the *oxime*, m.p. 126° (decomp.), of 2-hydroxyphenylpyruvic acid, which with Ac<sub>2</sub>O affords 2-hydroxyphenylacetonitrile, m.p. 122° (lit., 117—119°). Diacetylresorcyraldehyde and 2-acetyl-4-*O*-methylresorcyraldehyde condense with hippuric acid to give *azlactones*, m.p. 130° and 150°, respectively.

J. L. D.

**Bile acids. XXXIX.** M. SCHENCK (Z. physiol. Chem., 1933, 217, 68—74; cf. this vol., 609).—Catalytic hydrogenation of the NO-compound C<sub>24</sub>H<sub>34</sub>O<sub>8</sub>N<sub>2</sub> (I) (A., 1928, 764) gives bilianic acid oxime lactam (II), indicating the probability of a double linking between C<sub>7</sub> and C<sub>8</sub> in (I). With HNO<sub>3</sub> the oximinoamino-acid C<sub>24</sub>H<sub>38</sub>O<sub>9</sub>N<sub>2</sub> does not form the aminonitrile C<sub>24</sub>H<sub>36</sub>O<sub>10</sub>N<sub>2</sub> (III) and the aminoamide C<sub>24</sub>H<sub>38</sub>O<sub>11</sub>N<sub>2</sub> given by (I) and (II), but gives first a NO-compound (green coloration) and then as gel a tribasic acid, C<sub>24</sub>H<sub>36</sub>O<sub>9</sub>N<sub>2</sub>, decomp. 195°, which evolves a gas (? N<sub>2</sub>) on treatment with aq. NaOH in excess. Probably in the production of (III) from (I) or (II) the reaction at the NO- or N-OH group is first completed before the lactam ring is opened (if this occurs).

J. H. B.

**Lichen acids. V. Synthesis of methyl O-tetramethylgyrophorate.** F. W. CANTER, A. ROBERTSON, and R. B. WATERS (J.C.S., 1933, 493—495; cf. A., 1932, 1258).—Carbomethoxyisoevernic acid (prepared by methylation of *p*-monocarbo-methoxyorsellinic acid) and PCl<sub>5</sub> in CHCl<sub>3</sub> afford a chloride (*anilide*, m.p. 149—150°), which with *Me* isoevernic in C<sub>5</sub>H<sub>5</sub>N at room temp. during several days affords *Me* O-dimethyl-lecanorate (I), m.p. 142°. Interaction of orcyraldehyde Me<sub>2</sub> ether and KMnO<sub>4</sub> in warm COMe<sub>2</sub> affords orsellinic acid Me<sub>2</sub> ether, m.p. 145—146° (decomp.) (lit. 64—65°), converted by PCl<sub>5</sub> into a gummy chloride (II) (*anilide*, m.p. 131°). Interaction of (I) and (II) in dry C<sub>5</sub>H<sub>5</sub>N during 3 days affords *Me* gyrophorate Me<sub>4</sub> ether, m.p. 195° (cf. A., 1932, 851). *iso*Evernaldehyde (prep. described) with Ac<sub>2</sub>O and NaOAc during 3 hr. affords 2:4-diacetoxy-6-methylbenzylidene diacetate, m.p. 95—96°, which with KMnO<sub>4</sub> did not yield *O*-diacetylorsellinic acid.

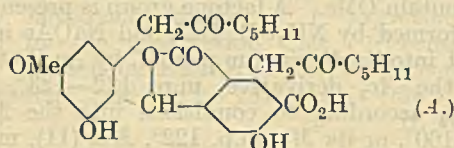
J. L. D.

**Lichen substances. XIX. Alecronic acid**, a new component of pale-coloured *Alectoria* species. Y. ASAHINA and A. HASHIMOTO. **XX. Collatolic acid**, an alecronic acid methyl ether. Y. ASAHINA, Y. KANAOKA, and F. FUJIKAWA. **XXI. Salazic acid.** I. Y. ASAHINA and J. ASANO [with M. FUSE and K. OKAMI]. **XXII. Cetraric acid.** Y. ASAHINA and Y. TANASE (Ber., 1933, 66, [B], 641—649, 649—655, 689—699, 700—703).—XIX. Extraction of *A. japonica*, Tuck., with Et<sub>2</sub>O and concn. of the extract leads to *l*-usnic acid, m.p. 203°, [α]<sub>D</sub><sup>20</sup> —482.1° in CHCl<sub>3</sub>, and alecronic acid (I), C<sub>23</sub>H<sub>34</sub>O<sub>8</sub>, m.p. 193° (monohydrate, m.p. 120—121°), which is optically inactive and does not contain OMe. A lactone group is present. (I) is transformed by NH<sub>2</sub>OH, HCl, and NaOAc in anhyd. EtOH into its *dioxime*, m.p. 194°, by Ac<sub>2</sub>O at 80—90° into the Ac<sub>3</sub> derivative, m.p. 122—123°, and by CH<sub>2</sub>N<sub>2</sub> according to conditions into the *Me* ester, m.p. 160°, or its *Me*, m.p. 122°, *Me*<sub>2</sub> (II), m.p. 136°, or *Me*<sub>3</sub> (III), m.p. 114°, *ether*. Conditions are given for the formation of (II) or (III) from (I), Ag<sub>2</sub>O, and MeI. Treatment of (I) with boiling HCO<sub>2</sub>H affords alecronic [alecronicolactone] (IV), C<sub>23</sub>H<sub>32</sub>O<sub>8</sub>, m.p. 198°. The Ac<sub>3</sub> derivative, m.p. 157—158°, from (I) or (IV), NaOAc, and boiling Ac<sub>2</sub>O, the *oxime*, m.p. 226°, and the *Me*<sub>3</sub> *ether* (V), m.p. 185°, from (IV) and an excess of CH<sub>2</sub>N<sub>2</sub>, or Ag<sub>2</sub>O and MeI, or from (III) and boiling HCO<sub>2</sub>H, are described. The *oxime* of (V) had m.p. 180°. Treatment of (V) or (III) with KOH or of (I) with Me<sub>2</sub>SO<sub>4</sub> and KOH leads to the dicarboxylic acid, C<sub>22</sub>H<sub>42</sub>O<sub>10</sub>, m.p. 119—120° (*Me*<sub>2</sub> ester, m.p. 68—70°). Treatment of (I) with molten KOH affords *n*-hexoic acid (*anilide*, m.p. 98°), orcinol, 5-hydroxy-*m*-xylene, and 3-hydroxy-5-methylbenzoic acid. The presence of 3 OH, 2 CO, CO<sub>2</sub>H, one lactone group, an orcinol and a *m*-cresol nucleus, and probably 2 CO-C<sub>5</sub>H<sub>11</sub> groups is established. The ready formation of an enol-lactone suggests that CO<sub>2</sub>H is vicinal to CO-C<sub>5</sub>H<sub>11</sub>. (I) is not a depside. (I) and *l*-usnic acid are also obtained from *A. japonica* from Sakhalin and from *A. sarmentosa*, Ach., from Europe. *A. ochroleuca* contains *d*-usnic and diffractaic acid (VI); the barbatinic acid reported by Zopf was probably crude (VI).

**XX. Maceration of the thalli of *Cetraria collata*,**

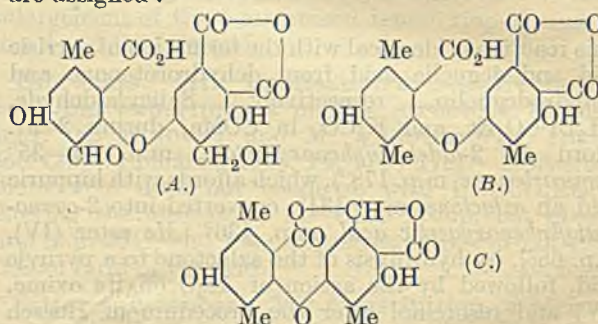


Nyl., with cold  $\text{Et}_2\text{O}$  leads to the isolation of atranorin, m.p.  $196^\circ$ ,  $\alpha$ -collatolic acid,  $\text{C}_{30}\text{H}_{36}\text{O}_9$  (I), m.p.  $124$ – $125^\circ$ , or +aq. m.p.  $90$ – $95^\circ$ , and traces of  $\beta$ -collatolic acid (II), m.p.  $162^\circ$  (see below). (I) is optically inactive, contains 1OMe and a lactone ring, and yields a *disemicarbazone*, m.p.  $212^\circ$  (decomp.). Regulated treatment with  $\text{CH}_2\text{N}_2$  transforms (I) into the Me ester (III), m.p.  $122^\circ$ , identical with Me alectoronate Me ether (see above), and thence into Me alectoronate  $\text{Me}_2$  (IV), m.p.  $136^\circ$ , and  $\text{Me}_3$ , m.p.  $114^\circ$ , ether. (I) and 95%  $\text{HCO}_2\text{H}$  at  $130^\circ$  afford collatolone [collatololactone],  $\text{C}_{30}\text{H}_{34}\text{O}_8$  (V), m.p.  $142^\circ$ , also obtained from (III). From (V) are derived a *monoxime*, m.p.  $175^\circ$ , and  $\text{Ac}_2$  derivative (VI), m.p.  $105^\circ$ , prepared from (V) and cold  $\text{Ac}_2\text{O}$  containing  $\text{H}_2\text{SO}_4$ , and an  $\text{Ac}$  compound, m.p.  $151^\circ$ , prepared similarly from (I) and transformed into (VI) by  $\text{NaOAc}$  and boiling  $\text{Ac}_2\text{O}$ . Treatment of (IV) with boiling  $\text{HCO}_2\text{H}$  affords collatololactone Me ether (VII), m.p.  $185^\circ$ . Collatololactone  $\text{Me}_2$  ether (VIII), m.p.  $185^\circ$ , identical with alectorolactone  $\text{Me}_3$  ether (see above), is obtained from (V) or (VII) with excess of  $\text{CH}_2\text{N}_2$  or from (V),  $\text{Ag}_2\text{O}$ , and  $\text{MeI}$  in  $\text{Et}_2\text{O}$ . (VIII) is hydrolysed by  $\text{KOH}$ – $\text{EtOH}$  to the dicarboxylic acid  $\text{C}_{32}\text{H}_{42}\text{O}_{10}$ ,  $0.5\text{H}_2\text{O}$ , m.p.  $125^\circ$  ( $\text{Me}_2$  ester, m.p.  $72^\circ$ ), identical with that derived from alectorolactone  $\text{Me}_3$  ether (see above). Hydrolysis of (III) with dil.  $\text{KOH}$ – $\text{EtOH}$  leads to  $\beta$ -collatolic acid, m.p.  $162^\circ$  (see above), readily transformed into (V) by  $\text{HCO}_2\text{H}$ . Preservation of (I) in cold  $\text{C}_5\text{H}_5\text{N}$  causes formation of  $\gamma$ -collatolic acid (IX),  $\text{C}_{30}\text{H}_{36}\text{O}_9$ , m.p.  $140$ – $141^\circ$ , converted by  $\text{HCO}_2\text{H}$  into (V). Oxidation of (IX) by  $\text{KMnO}_4$  in  $\text{COMe}_2$  affords olivetonide Me ether, m.p.  $57^\circ$ , and (?) a little hexoic acid. The constitution A is advanced provisionally for (I).

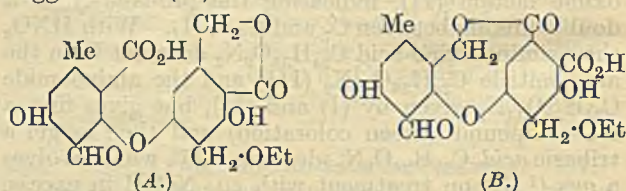


XXI. Extraction of *Parmelia conspersa* (Ehrh.), Ach., var. *hypoclysta*, Nyl., with  $\text{Et}_2\text{O}$  gives about 1% of *d*-usnic acid and traces of a colourless acid, m.p.  $205^\circ$  (decomp.), and subsequent treatment with  $\text{COMe}_2$  affords about 3% of salazic acid (I, A): Similar treatment of *P. cetrata*, Arch., var. *sorediifera*, Wain, gives atranorin, m.p.  $195^\circ$ , (?) cetratic acid, m.p.  $178$ – $180^\circ$ , and (I). (I),  $\text{C}_{18}\text{H}_{12}\text{O}_{10}$  (also + $\text{H}_2\text{O}$  and + $\text{MeOH}$ ), decomposes at about  $260^\circ$  after becoming discoloured at  $240^\circ$ . (I) is converted by boiling  $\text{Ac}_2\text{O}$  into the  $\text{Ac}_3$  derivative, m.p.  $206$ – $207^\circ$ , and by cold  $\text{Ac}_2\text{O}$  containing  $\text{H}_2\text{SO}_4$  into the  $\text{Ac}_6$  compound, m.p.  $178^\circ$ , which does not give a colour with  $\text{FeCl}_3$  and contains 2Ac as an aldehydiacetate. With  $\text{NH}_2\text{Ph}$  and  $\text{NHPh}\cdot\text{NH}_2$  in  $\text{COMe}_2$  it affords the *dianil*  $\text{C}_{30}\text{H}_{22}\text{O}_8\text{N}_2$ , decomp.  $280^\circ$  after darkening at  $240^\circ$ , and *diphenylhydrazone*,  $\text{C}_{30}\text{H}_{24}\text{O}_8\text{N}_4$ , decomp.  $295^\circ$  after blackening at  $270^\circ$ , respectively, indicating  $2\text{CO}$ . Dry distillation or distillation with Zn dust affords atranol. Molten  $\text{KOH}$  converts (I) into orcinol and  $\alpha$ -resorcylic acid. Catalytic hydrogenation of (I) (Pd–C) gives the product  $\text{C}_{18}\text{H}_{14}\text{O}_8$  (II, B), decomp. about  $280^\circ$  after becoming discoloured at  $240^\circ$ , which yields an  $\text{NH}_2\text{Ph}$  salt and gives  $\beta$ -orcinol

when dry distilled. It is transformed by  $\text{CH}_2\text{N}_2$  into the compound  $\text{C}_{18}\text{H}_{11}\text{O}_5(\text{OMe})_3$  (III), m.p.  $165^\circ$ , which does not contain an active H. Acidification of (III) after short treatment with  $\text{KOH}$ – $\text{MeOH}$  yields the substance  $\text{C}_{18}\text{H}_{12}\text{O}_5(\text{OMe})_4$ , converted by  $\text{CH}_2\text{N}_2$  into the compound  $\text{C}_{18}\text{H}_{11}\text{O}_4(\text{OMe})_5$ , m.p.  $146^\circ$ , obtainable in poor yield directly from (II). Reduction therefore causes the transformation of  $\text{CHO}$  into  $\text{Me}$  in the atranol nucleus and of  $\text{C}\cdot\text{OH}$  into  $\text{Me}$  in the second nucleus. Prolonged hydrogenation of (I) in warm solution or, preferably, short treatment of (II) with hot  $\text{AcOH}$  and Zn dust yields the substance  $\text{C}_{18}\text{H}_{14}\text{O}_7$  (IV, C), m.p. about  $300^\circ$  (also + $\text{COMe}_2$ ), converted by  $\text{CH}_2\text{N}_2$  into the  $\text{Me}_2$  ether  $\text{C}_{18}\text{H}_{12}\text{O}_5(\text{OMe})_2$  (V), m.p.  $283^\circ$ , which does not contain an active H. When warmed with  $\text{KOH}$ – $\text{MeOH}$  (V) gives an acid,  $\text{C}_{18}\text{H}_{13}\text{O}_5(\text{OMe})_3$ , m.p.  $178^\circ$ , transformed by  $\text{CH}_2\text{N}_2$  into the compound  $\text{C}_{18}\text{H}_{12}\text{O}_4(\text{OMe})_4$ , m.p.  $111^\circ$ , also obtained by hydrolysing (IV) to the compound  $\text{C}_{18}\text{H}_{16}\text{O}_8$ , m.p.  $235^\circ$ , and treatment of the latter with  $\text{CH}_2\text{N}_2$ . Treatment of (IV) with molten  $\text{KOH}$  gives  $\beta$ -orcinol and 3:5-dihydroxy-*p*-toluic acid (VI) obtained also from (II) but with greater difficulty and smaller yield of (VI). The following structures are assigned:



XXII. Thermal decomp. of fumarprotocetraric acid (I) yields atranol. (I), obtained by extraction of *Cetraria islandica*, Ach., with  $\text{COMe}_2$ , is converted into cetraric acid (II), decomp.  $255^\circ$  after darkening at  $220^\circ$ , by Simon's method (*anil*, decomp. about  $250^\circ$ ). Treatment of (II) with  $\text{KOH}$  at  $250$ – $310^\circ$  yields orcinol and  $\alpha$ -resorcylic acid. Catalytic hydrogenation (Pd–C) of (II) is accompanied by loss of  $\text{OEt}$  (therefore acetal form) and production of the compound  $\text{C}_{18}\text{H}_{16}\text{O}_7$ , m.p.  $242^\circ$  (decomp.) after becoming discoloured at  $215^\circ$ , which yields a  $\text{Me}_3$  derivative (III), m.p.  $170^\circ$ , in which active H is not present. (III) and molten  $\text{KOH}$  afford  $\beta$ -orcinol, 3:5-dihydroxy-*p*-toluic acid, and small amounts of a phenol,  $\text{C}_{16}\text{H}_{18}\text{O}_4$ , m.p.  $218$ – $219^\circ$ . The structure A or B is suggested for (II):

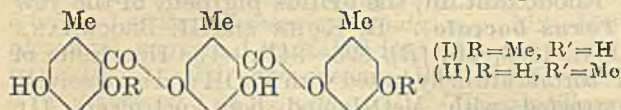


H. W.

Umbilicaric and ramalic acids. G. KOLLER and G. PFEIFFER (*Monatsh.*, 1933, 62, 241–251).—Umbilicaric acid, m.p.  $203^\circ$  (decomp.) [ $\text{Ac}_3$  derivative,



decomp. 197° (in vac.) (*Me* ester, decomp. 206—207°)], is converted by  $\text{CH}_2\text{N}_2$  into a  $\text{Me}_3$  ether *Me* ester, m.p. 196°, identical with *Me* tetramethylgyrophorate; it is therefore a *Me* ether of gyrophoric acid. Fission with 30%  $\text{NaOH}$  in  $\text{H}_2$  gives lecanoric, orsellinic, and isovernic acids; the last-named is identified by mixed m.p. of its *Me* ester and decarboxylation to orcinol. It is therefore represented by formula (I) or (II), (I) being preferred on account of the absence of a red coloration with  $\text{Ca}(\text{OCl})_2$ .



Fission of ramalic acid with  $\text{MeOH}$  at its b.p. gives *Me* rhizonate, m.p. 103°, therefore it is identical with obtusatic acid (cf. A., 1932, 613). H. A. P.

**Synthesis of benzaldehyde from benzene and carbon monoxide under pressure.** J. H. HOLWAY and N. W. KRASE (Ind. Eng. Chem., 1933, 25, 497—502).— $\text{PhCHO}$  is formed by direct combination of  $\text{C}_6\text{H}_6$  and  $\text{CO}$  in presence of  $\text{AlCl}_3$  at 25—50°/500—2000 lb. per sq. in. The reaction is dependent on rapid and thorough stirring to bring about intimate admixture of the gaseous and liquid phases and is accelerated by added  $\text{PhCHO}$  and by small amounts of  $\text{H}_2\text{O}$  or  $\text{HCl}$ . Above 25° the conversion decreases with rising temp., and at > 50° oils of high b.p. form in increasing amounts; the conversion increases rapidly with pressure up to 700—1000 lb. per sq. in. and then more slowly. With 1 mol.  $\text{AlCl}_3$ :1 mol.  $\text{C}_6\text{H}_6$ :0.12 mol.  $\text{H}_2\text{O}$  at 25°/1000 lb. per sq. in. a yield of 65.4% of theory is realised in 2 hr. H. A. P.

**Reimer-Tiemann reaction.** D. E. ARMSTRONG and D. H. RICHARDSON (J.C.S., 1933, 496—500).—The Reimer-Tiemann reaction carried out with many phenols, substituting  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  for  $\text{CHCl}_3$ , resulted in no improvement in the yields of aldehyde. Evidence is adduced of the formation of an acetal in the above reaction. Interaction of *p*-chlorophenol and  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  in  $\text{KOH}$  solution affords tri-*p*-chlorophenyl orthoformate and di(chlorosalicylaldehyde) and an acetal indicated by (a) the formation of a *p*-nitrophenylhydrazone after removal of aldehydes and subsequent hydrolysis with  $\text{NaHCO}_3$ , (b) reaction with  $\text{MeMgI}$ , and (c) methylation with  $\text{Me}_2\text{SO}_4$ . Analyses of the resinous products obtained indicate the existence of  $\text{CHPh}_3$  derivatives. J. L. D.

**Action of phenylcarbimide on aromatic amino-oximes.** C. V. GHEORGHIU (Ann. Sci. Univ. Jassy, 1933, 17, 188—194).—Two mols. of aryl-carbimide react with 1 mol. of amino-oximes, whereas only 1 mol. of -thiocarbimide reacts. This difference may be due to the difference in electronic structure, viz.,  $\text{R}\cdot\text{N}:\text{C}:\text{O}$  and  $\text{R}\cdot\text{N}:\text{C}:\text{S}$ , disclosed by Raman spectra.

*ON-Dicarbanilido*-derivatives are prepared from the following substances and have the m.p. quoted: *p*- [176—177° (decomp.)] and *m*-aminobenzaldoxime, 171° (decomp.); 3-amino-*p*-anisaldoxime ( $\text{CH}_3\cdot\text{N}:\text{OH}=\text{I}$ ), 170—171° (decomp.); *p*- [178—179° (decomp.)] and *m*- (I) -aminoacetophenoneoxime [175—176° (decomp.)]. (I), m.p. 129—130°, is prepared by

reduction of *m*-nitroacetophenoneoxime with  $(\text{NH}_4)_2\text{S}$ . *o*-Aminobenzaldoxime and  $\text{PhNCO}$  in  $\text{Et}_2\text{O}$  give 4-carbanilidohydroxylamino-2-keto-3-phenyl-1:2:3:4-tetrahydroquinazoline (II) (or *ON-dicarbanilido-o*-aminobenzaldoxime), m.p. (anhyd.) 195—196° (decomp.), (? +  $\text{Et}_2\text{O}$ ) 148° (decomp.); the cyclic structure  $\text{NH}\langle\text{C}_6\text{H}_4(\text{o})\rangle\text{CH}\cdot\text{NH}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$  for (II) is probable, since the substance has pale green fluorescence in  $\text{H}_2\text{SO}_4$ . R. S. C.

**Action of chlorides of the type  $\text{XCl}_3$  on vanillin and methyl anthranilate.** G. SOLLAZZO (Officina, 1932, 5, 270—273).—Condensation in presence of  $\text{XCl}_3\text{--Et}_2\text{O}$  affords compounds probably having the constitution  $(\text{R}\cdot\text{NH}_2\cdot\text{R}'\cdot\text{CHO})\text{XCl}_2$ .  $\text{AsCl}_3$  gives a reddish-yellow substance, m.p. 143° (decomp.);  $\text{AlCl}_3$  gives a citron-yellow substance, m.p. 178°.

Ch. Abs.

**Lignin content of cellulose products.** A. G. NORMAN and S. H. JENKINS (Nature, 1933, 131, 729).—A pentose on treatment with cold 72%  $\text{H}_2\text{SO}_4$  and then boiling with dil.  $\text{H}_2\text{SO}_4$  gave a quantity of material as resistant as lignin and determined as such by accepted methods. About 25% of the apparent lignin content of celluloses from cereal straws is secondarily produced from the cellulosan fraction, but there is some true lignin or other equally acid-resistant material present. The determination of lignin by the 72%  $\text{H}_2\text{SO}_4$  method should be critically examined. L. S. T.

**Lignin reactions.** P. KLASON (Arkiv Kemi, Min., Geol., 1932, 11 A, No. 1, 12 pp.; No. 3, 4 pp.).—A discussion of the composition and reactions of lignin and ligninsulphonic acid. Freudenberg's view that the aliphatic part of lignin contains a no. of linked alcohol groups is refuted, as 50% of his material certainly contained a free  $\text{CHO}$  group. H. F. H.

**Carbon rings. XXIII. Parachor and compressibility of multi-membered ring compounds.** L. RUZICKA, H. A. BOEKENOOGEN, and H. J. EDELMAN (Helv. Chim. Acta, 1933, 16, 487—492; cf. this vol., 230).—Vals. for the parachor of cyclooctane, cyclooctanone, methylcyclopentadecane, 1-methylcyclopentadecan-3-one, and  $\Delta^9$ -cycloheptadecen-1-one, and for the compressibility coeff. of cyclohexane, cyclohexanone, methylcyclopentadecane, and 1-methylcyclopentadecan-1-one, are given. Rings with more than about 8 members behave like aliphatic compounds with respect to both properties.

F. L. U.

**Selective catalytic reduction of ketones.** N. D. ZELINSKI, K. PACKENDORFF, and L. LEDER-PACKENDORFF (Ber., 1933, 66, [B], 872—874).—Hydrogenation of  $\text{COPhMe}$  in  $\text{EtOH}$  in presence of 10%  $\text{Pt-C}$  activated with  $\text{Pd}$  at room temp. and pressure affords  $\text{PhEt}$ . Homologues of  $\text{COPhMe}$  behave similarly, whereas the  $\text{CO}$  of cyclopentanone, cyclohexanone, hexahydroacetophenone and its homologues, and of ketones in which  $\text{CO}$  is separated from the  $\text{C}_6\text{H}_5$  ring by at least one  $\text{CH}_2$  remains unaffected. It is thus possible to separate aromatic ketones from cyclic ketones or those which do not contain  $\text{CO}$  in the  $\alpha$ -position to the  $\text{C}_6\text{H}_5$  ring. Accumulation of negative groups in the neighbourhood of  $\text{CO}$  does not



with  $\text{AcO}_2\text{H}$ ); by  $\text{H}_2$  and Cu chromite to a  $\beta$ - $\alpha$ -difacilitate its reduction, since  $\text{COPh}_2$  is not reduced. Change proceeds  $>\text{CO} \longrightarrow >\text{CH}\cdot\text{OH} \longrightarrow >\text{CH}_2$ , since  $\text{OH}\cdot\text{CHPhBz}$  affords successively  $\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{OH}$  and  $(\text{CH}_2\text{Ph})_2$  (also obtained from  $\text{COPhBz}$ ).  $\text{CH}_2\text{Bz}\cdot\text{OMe}$  affords  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COMe}$  exclusively. H. W.

Chlorination product obtained by condensation of methyl ethyl ketone with benzaldehyde [in presence of hydrogen chloride]. G. MASSARA (Gazzetta, 1933, 63, 199–206).—The interaction of  $\text{COMeEt}$ ,  $\text{PhCHO}$ , and  $\text{HCl}$  (cf. A., 1902, i, 295) yields the hydrochloride of dibenzylidenebutanone (A., 1916, i, 372), which is reduced ( $\text{Zn}\cdot\text{AcOH}$ ) to  $\beta$ -phenylethyl  $\alpha$ -benzylethyl ketone, m.p. 47–48° (oxime, m.p. 129–130°; semicarbazone, m.p. 215–216°).

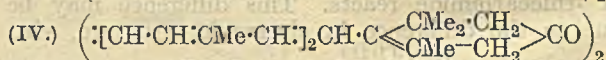
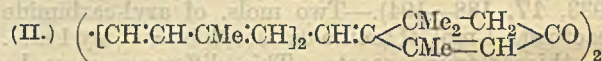
E. W. W.

Synthesis of  $\alpha\beta$ -aminoketones. A. SKITA, F. KEIL, and E. BAESLER (Ber., 1933, 66, [B], 858–866; cf. A., 1928, 1120; 1929, 808).—The catalytic action of Pd in the hydrogenation of  $\alpha\beta$ -diketones in the presence of bases is more selective than that of Pt and by suitable adjustment of the amount of metal the  $\text{NH}_2$ -ketone (I) can be readily prepared, whereas with larger amounts the  $\text{NH}_2$ -alcohol is obtained. By use of very small amounts of Pt, (I) can be prepared. *sec*-Amines can be used in place of primary amines in the synthesis of (I) if base and ketone have low mol. wt.  $\text{NH}_2$ -ketones, if liquid, are usually unstable and readily give viscous, red substances. Details are given for the reduction of  $\text{AcBz}$  in presence of  $\text{NH}_2\text{Me}$  and Pd or Pt to ephedrine (*loc. cit.*) or  $\beta$ -methylamino- $\alpha$ -phenylpropan- $\alpha$ -one, b.p. 120–121°/11 mm. (hydrochloride, m.p. 180°; picrate, m.p. 138°; chloroplatinate, m.p. 191–192°). The following are described:  $\beta$ -cyclohexylamino-, b.p. 185–195°/15 mm., m.p. 178° (picrate, m.p. 154°);  $\beta$ - $\beta'$ -hydroxyethylamino-, m.p. 78° (hydrochloride, m.p. 159–160°), and  $\beta$ -anilino- $\alpha$ -phenylpropan- $\alpha$ -one, m.p. 100–101° (hydrochloride, m.p. 191°);  $\beta$ -anilino- $\alpha$ -phenylpropan- $\alpha$ -ol, m.p. 122° (hydrochloride, m.p. 184°);  $\beta$ -methylamino-, b.p. 160°/11 mm. (picrate, m.p. 179–180°),  $\beta$ -cyclohexylamino-, m.p. 110° (hydrochloride, m.p. 193–194°), and  $\beta$ -p-toluidino- $\alpha$ -p-anisylpropan- $\alpha$ -one, m.p. 83° (hydrochloride, m.p. 182–183°);  $\beta$ -cyclohexylamino-, m.p. 107–108° [hydrochloride, m.p. 235–237° (decomp.)], and  $\beta$ - $\alpha'$ -ethylpropylamino- $\alpha\beta$ -diphenylethan- $\alpha$ -one, b.p. 200–201°/11 mm. (picrate, m.p. 148°);  $\beta$ -cyclohexyl-, b.p. 128–130°/13 mm. (hydrochloride, m.p. 176°),  $\beta$ -methyl-, b.p. 70–71°/18 mm. (picrolonate, m.p. 183–184°),  $\beta$ - $\beta'$ -hydroxyethyl-, b.p. 142–144°/14 mm., m.p. 68° (picrolonate, m.p. 217–218°), and  $\beta$ -p-ethoxyphenyl-aminohexan- $\gamma$ -one, b.p. 189–190°/15 mm. (hydrochloride, m.p. 148–149°);  $\beta$ -cyclohexylamino-, b.p. 118°/12 mm. (hydrochloride, m.p. 157–158°), and  $\beta$ -methylanilino-pentan- $\gamma$ -one, b.p. 148–150°/14 mm. (picrolonate, m.p. 182–183°);  $\beta$ -dimethylaminohexan- $\gamma$ -one, b.p. 89–90°/25 mm. (picrolonate, m.p. 163–164°). H. W.

Bromination of enols and enol ethers. T. FJÄDER (Suomen Kem., 1933, 6, 60–61).—Bromination of the appropriate  $\beta$ -diketone by Toivonen's

method (in suspension in cold  $\text{AcOH}$  in presence of  $\text{KOAc}$ ) affords the *Br*-derivatives of 4-methyl-, m.p. 103–104°, 4-ethyl-, m.p. 40–41°, and 4-isopropyl-, m.p. 80–81°, -menthone, 4-phenyl-1-methylcyclohexane-2:6-dione, m.p. 55–56°, and  $\text{CHAc}_2\text{Me}$ , b.p. 63°/11 mm., the appropriate enol ethers similarly giving 2-bromo-3-methoxy-, m.p. 103–104°, -3-ethoxy-, m.p. 112–113°, and -3-isopropoxy-, m.p. 89–90°, -5:5-dimethyl- $\Delta^2$ -cyclohexenone. J. W. B.

Rhodoxanthin, the arillus pigment of the yew (*Taxus baccata*). R. KUHN and H. BROCKMANN (Ber., 1933, 66, [B], 828–841).—The ripe fruits of *T. baccata* are dehydrated with  $\text{MeOH}$  and successively extracted with  $\text{MeOH}$  and light petroleum (I). Isolation by repeated distribution between 90%  $\text{MeOH}$  and (I) leads to rhodoxanthin (II),  $\text{C}_{40}\text{H}_{50}\text{O}_2$ , m.p. 219° (corr., vac., Berl), bluish-black in colour, unusually stable to air. It is not acidic and does not give the supposed alkali salts. It is unchanged by  $\text{CH}_2\text{N}_2$ . With  $\text{MgMeI}$  it evolves rather more than 1 mol. of  $\text{CH}_4$ , but the presence of the indicated OH is not confirmed by the action of  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$ . It is indifferent towards  $\text{KOH}\cdot\text{EtOH}$ . With  $\text{NH}_2\text{OH}$  in presence of a little  $\text{NaOH}$  it affords the dioxime (III),  $\text{C}_{30}\text{H}_{52}\text{O}_2\text{N}_2$ , m.p. 227–228° (corr., vac., Berl). The absorption spectra of (II) and (III) show the CO groups to be in conjugation with a system of conjugated double linkings. The difficulty of reaction with  $\text{NH}_2\text{OH}$  proves the presence of CO not CHO in (II). Catalytic hydrogenation of (II) [Pt-kieselguhr] causes rapid absorption of  $12\text{H}_2$  and ultimate absorption of  $14\text{H}_2$  showing the presence of 12 double linkings and reduction of CO to  $\text{CH}\cdot\text{OH}$ . The parent hydrocarbon and its perhydro-compound have therefore the formulae  $\text{C}_{40}\text{H}_{54}$  and  $\text{C}_{40}\text{H}_{78}$ , requiring the presence of two C rings. Reduction of (II) with Zn dust and  $\text{AcOH}$  yields dihydrorhodoxanthin (IV),  $\text{C}_{40}\text{H}_{52}\text{O}_2$ , m.p. 219° (corr., vac., Berl), which absorbs catalytically  $13\text{H}_2$  and differs from (II) mainly in colour and absorption spectrum. With  $\text{NH}_2\text{OH}$  it yields a dioxime (V),  $\text{C}_{40}\text{H}_{54}\text{O}_2\text{N}_2$ , m.p. 226–227° (corr., vac., Berl). The optical identity of (IV) and (V) shows that the conjugation of the CO groups is broken by the absorption of the two H atoms. Addition of  $\text{NaOH}\cdot\text{EtOH}$  to (IV) in  $\text{C}_5\text{H}_5\text{N}$  in high vac. gives a dark violet solution immediately, yielding (II) on exposure to air; reduction is therefore reversible. Oxidation of (II) with  $\text{CrO}_3$  affords 5.5 mols. of  $\text{AcOH}$ , whilst treatment with I yields about 0.2 mol. of  $\text{COMe}_2$ . To (II) and (IV) the following constitutions are assigned.



Rhodoxanthin is the first representative of a new type of polyene colouring matter, the polyene-ketone type.

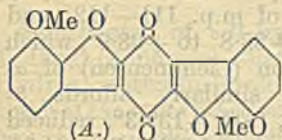
H. W.

Aromatic cyanohydrins and their transformation into quinomethide derivatives. I. GORSKI and S. MAKAROV (Ber., 1933, 66, [B], 674–680).—Treatment of *o*-methoxybenzaldehyde cyanohydrin in abs.  $\text{Et}_2\text{O}$  with  $\text{SOCl}_2$  affords chloro-*o*-methoxy-



phenylacetonitrile, b.p. 132—133°/9 mm., m.p. 43—44°. Vanillin (I) is transformed by anhyd. HCN in presence of a little KOH or KCN into the corresponding cyanohydrin (II), m.p. 80°, converted into its components by boiling KOH-EtOH and into homoprotocatechuic acid (III), m.p. 127°, by boiling HI (*d* 1.7). (II) in Et<sub>2</sub>O is transformed by PCl<sub>3</sub>, PCl<sub>5</sub>, or PBr<sub>5</sub> into *m*-methoxycyanoquinomethide (IV), 1 : 2 : 4-O:C<sub>6</sub>H<sub>3</sub>(OMe):CHCN, decomp. after incipient melting at 138°, transformed by 10% NaOH or dil. H<sub>2</sub>SO<sub>3</sub> into (I) and HCN. Br in CHCl<sub>3</sub> transforms (IV) into 5-bromo-3-methoxycyanoquinomethide, m.p. 172—174° (decomp.), converted by NaOH into 5-bromovanillin, m.p. 163.5°. (IV) and boiling HI (*d* 1.7) yield 4 : 4'-dihydroxy-3 : 3'-dimethoxy- $\omega\omega'$ -dicyanostilbene, m.p. 231—232°, whence, by protracted action of HI, 3 : 3' : 4 : 4'-tetrahydroxystilbene- $\omega\omega'$ -dicarboxylic acid, m.p. 204—212° (decomp.). The production of homovanillic acid and (III) from (IV) is described. H. W.

Condensation of *p*-benzoquinone with cresols and veratrole. R. PUMMERER, M. DALLY, and S. REISSINGER [with, in part, G. HUPPMANN] (Ber., 1933, 66, [B], 792—798).—Addition of a suspension of *p*-benzoquinone (I) in CS<sub>2</sub> to a solution of AlCl<sub>3</sub> in CS<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>Me·OH at 0° yields a quinol derivative, oxidised by FeCl<sub>3</sub> in AcOH to 2 : 5-di-6'-hydroxy-m-tolyl-*p*-benzoquinone [diacetate, m.p. 238—239°; Et<sub>2</sub> ether, m.p. 200° (from *o*-C<sub>6</sub>H<sub>4</sub>Me·OEt)]. (I), AlCl<sub>3</sub>, *m*-C<sub>6</sub>H<sub>4</sub>Me·OH, and CS<sub>2</sub> afford 2 : 5-di-5'-hydroxy-p-tolylquinol, m.p. 310—313° (under CO<sub>2</sub>) [Ac<sub>4</sub> derivative, m.p. 186—187°], oxidised with unusual difficulty by FeCl<sub>3</sub> in boiling AcOH to the corresponding quinone, incipient decomp. 260—270° (? + PhOMe). *p*-C<sub>6</sub>H<sub>4</sub>Me·OH does not afford a homogeneous condensation product, whereas its Me ether yields (?) 2 : 5-di-2'-methoxy-5'-methyl-phenylquinol, m.p. 138°. (I) and veratrole appear to yield the substance A, darkening about 245° and yielding a vat dye with NH<sub>2</sub>Ph in AcOH.



Synthesis of helminthosporin. H. RAISTRICK, R. ROBINSON, and A. R. TODD (J.C.S., 1933, 488—489).—In accord with Shah and Alimchandani (A., 1931, 1053),  $\gamma$ -coccinic acid Me ether is inaccessible by the method of Schleussner and Voswinkel (A., 1921, i, 111). 3-Methoxy-5-methylphthalic anhydride (modified prep. of acid; cf. Meldrum, J.C.S., 1911, 99, 1712), *p*-C<sub>6</sub>H<sub>4</sub>(OMe)<sub>2</sub>, and AlCl<sub>3</sub> in boiling CS<sub>2</sub> during 24 hr. affords a compound, m.p. 222—223° (suggested constitution), which with conc. H<sub>2</sub>SO<sub>4</sub> at 150° during 0.5 hr. affords 4 : 5 : 8-trihydroxy-2-methylanthraquinone, m.p. 226—227°, identical with helminthosporin, m.p. 225—226°. J. L. D.

Sugar-beet sapogenin. II. Oleanolic acid. V. PRELOG (Coll. Czech. Chem. Comm., 1933, 5, 165—169; cf. A., 1932, 46).—The substance C<sub>31</sub>H<sub>46</sub>O<sub>4</sub> obtained by CrO<sub>3</sub> oxidation of the sapogenin C<sub>30</sub>H<sub>48</sub>O<sub>2</sub> (A., 1930, 1044; all formulæ there given now having CH<sub>2</sub> less) is actually a diketolactone C<sub>30</sub>H<sub>44</sub>O<sub>4</sub> (identical with that obtained by Kitasato and Sone, A., 1932, 1035), since it affords a dioxime, m.p. 222—223°

(decomp.), and a monosemicarbazone, decomp. 292—294°. Me oleanolate (oxime, m.p. 239°) also gives 1 mol. of CH<sub>4</sub> by Zerevitinov's method, due to enolisation of the CO group. Partial formulæ for these derivatives are given. J. W. B.

Menthones and menthadienes. R. GACHARD (Bull. Inst. Pin, 1933, 42—48, 67—72, 79—87, 97—102).—The products described below are identified mainly by their Raman spectra. Menthol, dehydrated by the xanthate method, gives a mixture of  $\Delta^2$ - and  $\Delta^3$ -menthones, also obtained similarly, with carvomenthene, from carvomenthol, and, possibly with  $\Delta^{4(8)}$ -menthene, from menthyl chloride by EtOH-KOH or NH<sub>2</sub>Ph. This chloride, prepared by PCl<sub>5</sub>, is entirely the 4-Cl-compound, formed by rearrangement. Ozonisation and determination of the CH<sub>2</sub>O formed is not an accurate method of determining the CH<sub>2</sub> group. Turpentine and 50% H<sub>2</sub>SO<sub>4</sub> below 50° give cymene, limonene, camphene, dipentene,  $\alpha$ - and  $\gamma$ -terpinene, terpinolene, 1 : 4-cineole, and 3 unidentified substances. R. S. C.

"Terpinolene." Attempts to obtain pure terpinolene. (MLLE.) R. MAROT (Bull. Inst. Pin, 1933, 38—41, 61—66).—Commercial terpinolene (I) contains 80% of cineole. Dipentene (II),  $\alpha$ - (III) and  $\gamma$ - (IV) -terpinene, and terpinolene (V) are readily identified by their Raman spectra, the principal frequencies being : (II), 765, 1647, and 1676; (III), 876 and 1615; (IV), 1640; (V), 1672 and 1681. Pure terpinene dihydrochloride (from cineole) and NH<sub>2</sub>Ph give much (III) and traces of (V). The crude hydrochloride from (I) gives similarly much (II), some (III), and probably a little (V). Commercial terpineol and Al<sub>2</sub>O<sub>3</sub> give (II), (III), and much (V). Distillation at 12 mm. of the crude acetate from pinene gives limonene, (III), and (V). *iso*Cineole (VI) [H<sub>4</sub>Fe(CN)<sub>6</sub> compound, regenerates (VI) with cold KOH, but, when heated, gives also some hydrocarbon] is stable to cold 40% H<sub>2</sub>SO<sub>4</sub> and hot CrO<sub>3</sub>-dil. H<sub>2</sub>SO<sub>4</sub>, fairly stable to cold, conc. HNO<sub>3</sub>, polymerised by conc. H<sub>2</sub>SO<sub>4</sub>, oxidised by KMnO<sub>4</sub> to cineolic acid, m.p. 203—204° (lit. 156°), and dehydrated by H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to (III) and (IV). R. S. C.

Isomerisation of  $\alpha$ -pinene to an aliphatic terpene. I, II. Examination of the aliphatic terpene. B. A. ARBUSOV (J. Gen. Chem. Russ., 1933, 3, 21—27, 28—34).—I. When  $\alpha$ -pinene (I) is passed over Cu chromite (A., 1931, 598) at 300°, some 80% of (I) is recovered and 20% of an aliphatic terpene (II). At 375°, 23% of (I), 42% of dipentene, and 31% of (II) are produced, and at 400—410°, 20% of (I), 23% of dipentene, 20% of (II), and 36% of an unidentified monocyclic terpene C<sub>10</sub>H<sub>16</sub>. Dipentene is not isomerised under these conditions. (II) may be identical with the product obtained from (I) with an Al catalyst (B., 1932, 376). A Co-Th catalyst at 380° gives similar products in comparable yield.

II. (II), b.p. 87—87.5°/16 mm.,  $d_4^{25}$  0.8162,  $n_D^{25}$  1.5448,  $[\alpha]_D^{25}$  0, closely resembles alloocimene; it is readily oxidised in the air to a viscous product with the properties of a peroxide. (II) is reduced by Na and EtOH to a dihydro-compound, b.p. 168.5—170°/760 mm., containing two double linkings (titration



methyloctene, b.p. 165—166°/760 mm., and with  $H_2$  and Ni to *dl*- $\beta$ -dimethyloctane, b.p. 159.5°. (II) combines with maleic anhydride to an *anhydride*,  $C_{14}H_{18}O_3$  (III), m.p. 81—82°, hydrated to an *acid*,  $C_{14}H_{20}O_4$ , m.p. 154.5—155.5°, which is isomerised by HBr to an *acid*, m.p. 189—190°, dehydrated by Se to a compound, m.p. 77.5—80° (?=III). (II) and citraconic anhydride give an *anhydride*,  $C_{15}H_{20}O_3$ , m.p. 82°. G. A. R. K.

**Homologues in the camphor group. VIII. *tert*-Propylborneol and its reactions.** S. S. NAMETKIN and A. I. SCHAVRYGIN (J. Gen. Chem. Russ., 1933, 3, 35—42).— $MgPr^+Br$  does not yield the expected *tert*-alcohol with camphor, but reduction ( $H_2$ -Pt) of *tert*-allylborneol gives a good yield of *tert*-propylborneol (I), m.p. 34—36°. Dehydration of (I) with  $NaHSO_4$  gives a *hydrocarbon*, b.p. 100—101°/22 mm., oxidised by  $KMnO_4$  to camphoric acid. The hydrocarbon is only partly hydrated by  $AcOH-H_2SO_4$ , the greater part remaining unchanged and probably consisting of *propylidenecamphane*. The hydration product on hydrolysis gives 4-propylisoborneol, m.p. 57—58°, oxidised by  $HNO_3$  to 4-propylcamphor, m.p. 61—62° (*semicarbazone*, m.p. 203—204°); this in turn is oxidised by  $KMnO_4$  to *propylcamphoric acid*, m.p. 177—178° (with elimination of  $H_2O$ ). The dehydration of (I) therefore proceeds for the most part without isomerisation, although a part undergoes the "Nametkin" change.

G. A. R. K.

**Hydrocarbons corresponding with particular camphor-like substances. III. Hydrocarbons from dichlorides of the camphor series.** G. KOMPPA and T. HASSELSTRÖM (Annalen, 1933, 502, 272—281).—Reduction (Na, EtOH) of camphor dichloride (I), m.p. 155—156°, or chlorocamphene [from (I) and  $NH_2Ph$ ] gives a mixture of camphene, bornylene, and a little tricyclene. *dl*-Fenchone and  $PCl_5$  at 105—110° afford *fenchone dichloride* (II), b.p. 105—107°/11 mm., and a little *chlorofenchene*, m.p. 45—46° (cf. Gardner and Cockburn, J.C.S., 1896, 73, 704). (II) is reduced (Na, EtOH) to a mixture of  $\beta$ -,  $\gamma$ -, and  $\delta$ -fenchenes and *cyclofenchene*. The *chlorofenchene*, b.p. 84—87°/6.5 mm., from *dl*-isofenchone and  $PCl_5$  in the cold, is similarly reduced to  $\beta$ - and  $\delta$ -fenchenes. *dl*- $\alpha$ -Fenchocamphorone dichloride, b.p. 71—74°/22 mm., is reduced (Na, EtOH) to *apobornylene* and (probably) a little *apocyclene* (III), whilst  $\beta$ -fenchocamphorone dichloride, b.p. 87—92°/15 mm., similarly gives *apoisofenchene* and a little (III). The constitutions of the hydrocarbons are determined by oxidation ( $KMnO_4$ ).

H. B.

**New diterpene,  $\gamma$ -camphorene.** K. KAFUKU, T. OYAMADA, and M. NISHI (Bull. Chem. Soc. Japan, 1933, 8, 144—148).—Myrcene at 240—260° is partly converted into a monocyclic terpene (not isolated pure) and a mixture of  $\alpha$ - (I), b.p. 178°/4.5 mm.,  $d_4^{25}$  0.8864,  $n_D^{25}$  1.4998, and  $\gamma$ -camphorene (II), b.p. 176—178°/4.5 mm.,  $d_4^{25}$  0.8875,  $n_D^{25}$  1.5030, separated by the solubility in ligroin of the *tetrahydrochloride*, m.p. 96—98° (decomposed by hot EtOH), of (II), whence (II) is obtained by 10% KOH-EtOH (cf. A., 1913, i, 377). (I) and (II) give *tetrahydrobromides*, m.p. 133—134° and 111—114°, respectively; the

latter is unstable in hot EtOH. Both hydrocarbons form an *octabromide*, m.p. indefinite, 70—80°.

R. S. C.

**Ionic theory of organic reactions. III. Ring-chain tautomerism and conception of "synionie."** A. KIRRMANN and C. PRÉVOST (Bull. Soc. chim., 1933, [iv], 53, 253—260; cf. A., 1931, 670; 1932, 11).—The ionic theory is applied to ring-chain tautomerism and a no. of reversible and irreversible changes of similar type in the terpene series.

H. A. P.

**Essential oil from the wood of *Eremophila Mitchellii* (Bentham).** A. E. BRADFELD, A. R. PENFOLD, and J. L. SIMONSEN. Essential oils of three species of *Geijera* and the occurrence of a new hydrocarbon. II. A. R. PENFOLD and J. L. SIMONSEN.—See B., 1933, 445.

**Saponin series. XII. Parent hydrocarbons of the triterpene group.** A. WINTERSTEIN and G. STEIN (Annalen, 1933, 502, 223—236).— $\alpha$ -Amyrin and  $PCl_5$  in light petroleum give  $\alpha$ -amyrene I, m.p. 133—135° (all m.p. are corr.), reduced ( $H_2$ ,  $PtO_2$ ,  $AcOH$ -methylcyclohexane) to  $\alpha$ -amyrene I, m.p. 96—97.5°,  $[\alpha]_D^{25} +72.2^\circ$  (all rotations are in  $CHCl_3$ ), which is probably identical with the dihydro- $\alpha$ -amyrene of Ruzicka *et al.* (A., 1932, 517, 1254).  $\beta$ -Amyrin similarly gives  $\beta$ -amyrene I, m.p. 170—175°, reduced (as above) to a mixture of  $\beta$ -amyrene I, m.p. 89—91.5°,  $[\alpha]_D^{25} +77.6^\circ$  [probably identical with the dihydro- $\beta$ -amyrene of Ruzicka *et al.* (*loc. cit.*)], and  $\beta$ -amyrene Ia, m.p. 209—210°,  $[\alpha]_D^{25} +115^\circ$ . Decomp. of benzoyl- $\alpha$ -amyrin at 270—300° gives  $\alpha$ -amyrene II, m.p. 119—120°,  $[\alpha]_D^{25} +136.6^\circ$ , reduced (as above) to a non-homogeneous  $\alpha$ -amyrene II (fractions of m.p. 111—112° and 120—122° are isolated),  $[\alpha]_D^{25} +88.8^\circ$  to  $+98.9^\circ$ , which is also produced by reduction (Clemmensen) of  $\alpha$ -amyrene. Benzoyl- $\beta$ -amyrin similarly affords  $\beta$ -amyrene II, m.p. 148—150°,  $[\alpha]_D^{25} +139.3^\circ$ , reduced (as above) to  $\beta$ -amyrene II (A), m.p. 162°,  $[\alpha]_D^{25} +94.6^\circ$ . Reduction (Clemmensen) of  $\beta$ -amyrene gives  $\beta$ -amyrene III (B), m.p. 187—189.5°,  $[\alpha]_D^{25} -22^\circ$ , whilst the use of Zn and  $AcOH$ -conc. HCl affords  $\beta$ -amyrene IV (C), m.p. 159—161°,  $[\alpha]_D^{25} +57.3^\circ$ . (A) and (C) are converted into (B) by Zn-Hg and  $AcOH$ -conc. HCl, whilst (C) is produced from (A) by the action of HCl or  $Zn+HCl$ .

Oleanol and  $PCl_5$  give *oleanylene* I, m.p. 145—149°,  $[\alpha]_D^{25} +78.9^\circ$ , reduced catalytically to *oleanene* I, m.p. 113—116°, whilst Clemmensen reduction of oleanone, m.p. 168—172°,  $[\alpha]_D^{25} +95.8^\circ$ , affords *oleanone* III (D), m.p. 225—226°,  $[\alpha]_D^{25} +30.1^\circ$ . *Oleanylene* II (A., 1932, 61), Zn-Hg, and  $AcOH$ -conc. HCl give *oleanylene* III, m.p. 178—182°, which is reduced catalytically to (D). *Oleanene* II (*loc. cit.*) rearranges to (D) when treated with the Clemmensen reagents. Decomp. of dibenzoylhederagenol, m.p. 179—182°, gives resinous material and the *benzoate* of *anhydrohederagenol*,  $C_{29}H_{46}O$ , m.p. 193—195° (after sintering).

Reduction (Zn,  $AcOH$ -conc. HCl) of ergosterol gives a product,  $[\alpha]_D^{25} +48.5^\circ$ , whilst Clemmensen reduction affords a product,  $[\alpha]_D^{25} +56.2^\circ$ ; neither of these is pptd. by digitonin. Similar reductions of cholesterol



give products,  $[\alpha]_D^{25} +5.2^\circ$  and  $+23.2^\circ$ , respectively; the amounts pptd. by digitonin are 12 and 0.2%, respectively. H. B.

**Friedel-Crafts reaction with phenols and furoyl chloride.** H. GILMAN and J. B. DICKEY (Rec. trav. chim., 1933, 52, 389—394).—PhOH, furoyl chloride (I), and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  or  $\text{CS}_2$ - $\text{PhNO}_2$ , first at room temp. and then at  $60$ – $65^\circ$ , give *p*-furoylphenol [*p*-hydroxyphenyl 2-furyl ketone] (II), m.p.  $163$ – $164^\circ$  (Me ether, m.p.  $60^\circ$ , giving *p*-anisic acid when oxidised) ( $24$ – $32\%$  yield), and Ph furoate. In  $\text{CS}_2$  alone much *p*-furoylphenyl furoate, m.p.  $84^\circ$  [also obtained from (I) and (II)], is also formed. PhOBz gives a poor yield of (II). Resorcinol similarly gives 2-furoylresorcinol, m.p.  $123$ – $124^\circ$ , in  $80\%$  yield. Quinol gives *p*-hydroxyphenyl furoate, m.p.  $193$ – $195^\circ$ . R. S. C.

**Furanpolycarboxylic acids. II. Furan-2:3:5-tricarboxylic acid.** T. REICHSTEIN and A. GRÜSSNER (Helv. Chim. Acta, 1933, 16, 555—557).—7-Hydroxycoumarone-2-carboxylic acid (synthesis later) is oxidised ( $\text{H}_2\text{O}_2$ ,  $10\%$  KOH) to furan-2:3:5-tricarboxylic acid [Me ester, b.p.  $130$ – $131^\circ/0.3$  mm., m.p.  $76^\circ$  (corr.)], which when heated to  $250^\circ$  gives furan-2:4-dicarboxylic acid. H. B.

**2:2'-Di(furylmethyl) ether.** T. ISEKI (Z. physiol. Chem., 1933, 216, 130—132).—5-Hydroxymethylfurfuraldehyde yields 2:2'-di(furylmethyl) ether 5:5'-dialdehyde (I) more readily in presence of  $\text{AcCO}_2\text{H}$ . When heated with  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$ , (I) gives 2:2'-di(furylmethyl) ether 5:5'-diacrylic acid, m.p.  $190^\circ$ . (I) is oxidised in the animal organism to 2:2'-di(furylmethyl) ether 5:5'-dicarboxylic acid, m.p.  $206^\circ$ . J. H. B.

**Synthesis of *dl*-hydroxymethylfurylalanine.** T. ISEKI (Z. physiol. Chem., 1933, 216, 127—129).—5-Hydroxymethylfurfuraldehyde heated with hydantoin and  $\text{NaOAc}$  gives 5-hydroxymethylfurfuraldehydhydantoin (I), m.p.  $247^\circ$ , which on reduction with  $\text{Na-Hg}$  in aq.  $\text{NaOH}$  affords 5-hydroxymethylfurfurylhydantoin (II), m.p.  $167^\circ$ . Hydrolysis of (II) with aq.  $\text{Ba(OH)}_2$  yields *dl*-5-hydroxymethylfurylalanine, m.p.  $295^\circ$ . J. H. B.

**$\alpha$ - and  $\beta$ -Cinenic acids.** H. RUPE and H. HIRSCHMANN (Helv. Chim. Acta, 1933, 16, 505—514).—An improved method of separation (cf. A., 1909, i, 7) of  $\alpha$ -cinenic acid (I) (A., 1905, i, 409) (*p*-bromophenacyl ester, m.p.  $98$ – $99^\circ$ ) and  $\beta$ -cinenic acid (II) (A., 1901, i, 578) (*p*-bromophenacyl ester, m.p.  $66^\circ$ ) is given. The Me esters of (I) and (II) form compounds with  $\text{H}_3\text{Fe(CN)}_6$  and  $\text{H}_4\text{Fe(CN)}_6$  (in  $50$ – $64\%$  yield) indicating that they are oxido-compounds. (II) is converted [as is (I)] by cold conc.  $\text{H}_2\text{SO}_4$  into (mainly)  $\delta$ -acetyl- $\alpha\alpha$ -dimethylvaleric acid and the lactone, m.p.  $51^\circ$ , previously described (A., 1908, i, 390). (I) and (II) give the same Br-derivative (A., 1909, i, 7) when treated with aq.  $\text{HBr}$  (saturated at  $0^\circ$ ); this with  $\text{MgCO}_3$  and  $\text{H}_2\text{O}$  affords cinogenic ( $\alpha\alpha$ -dihydroxy- $\alpha\alpha$ -dimethylheptic) acid, which when distilled gives (I). H. B.

**isoBenzpyrylium ferrichloride.** B. K. BLOUNT and R. ROBINSON (J.C.S., 1933, 555—556).—Homophthalaldehyde, obtained by oxidation of *trans*-

1:2-hydrindenediol, gives with  $\text{HCl}$  and  $\text{FeCl}_3$  isobenzpyrylium ferrichloride, decomp.  $205$ – $208^\circ$ , which forms isoquinoline with  $\text{NH}_3$ . F. R. S.

**Dye of acacia wood.** K. C. GULATI and K. VENKATARAMAN (J. pr. Chem., 1933, [ii], 137, 53—56).—Treatment of synthetic 3:7:3':4':5'-penta-hydroxyflavone (Badhwar *et al.*, A., 1932, 621) with  $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  and crystallisation of the product from  $\text{MeOH}$  gives an  $\text{Ac}_5$  derivative (I), m.p.  $225^\circ$ , identical with that obtained by Brass *et al.* (this vol., 103) from natural source. Crystallisation from  $\text{MeOH-H}_2\text{O}$  and finally from  $\text{C}_6\text{H}_6$  yields the  $\text{Ac}_5$  compound, m.p.  $177$ – $178^\circ$ , described previously (*loc. cit.*). Dimorphism is assumed. Hydrolysis of (I) leads to a product, m.p.  $310$ – $312^\circ$  (decomp.) which could not be raised to  $325$ – $330^\circ$ . H. W.

**Comparison of the directive powers of elements having consecutive atomic numbers. V. Nitration of 9-phenylxanthylum perchlorate.** R. J. W. LE FÈVRE and J. PEARSON (J.C.S., 1933, 482—484).—Xanthylum ferrichloride is unaffected by  $\text{HNO}_3$  of a concn. which dinitrates xanthone. 9-Phenylxanthylum perchlorate, m.p.  $274$ – $275^\circ$ , is nitrated to the 9-*p*- $\text{NO}_2$ -derivative, m.p.  $257$ – $258^\circ$ , which gives the corresponding 9-*p*-nitrophenylxanthanol, m.p.  $116$ – $118^\circ$ . The Grignard reaction on *p*- $\text{C}_6\text{H}_4\text{ClBr}$  and xanthone affords 9-*p*-chlorophenylxanthanol, m.p.  $164^\circ$  (perchlorate, m.p.  $280$ – $281^\circ$ ), and on *p*- $\text{C}_6\text{H}_4\text{Br}_2$  forms the 9-*Br*-compound, m.p.  $132$ – $133^\circ$  (perchlorate, m.p.  $> 300^\circ$ ). 9-Phenyl-10-methylacridinium perchlorate (?), m.p.  $244$ – $245^\circ$  (hydrochloride, m.p.  $161$ – $162^\circ$ ; picrate, m.p.  $169$ – $170^\circ$ ), is nitrated to the  $\text{NO}_2$ -derivative, m.p.  $257$ – $262^\circ$  (decomp.). F. R. S.

**Synthesis of diflavones.** J. ALGAR, (MISS) I. B. MCCARTHY, and (MISS) E. M. DICK (Proc. Roy. Irish Acad., 1933, 41 B, 155—160; cf. A., 1915, i, 707).—Diacetoresorcinol (I),  $\text{Bz}_2\text{O}$ , and  $\text{NaOBz}$  at  $190$ – $200^\circ$  afford 3:3'-dibenzoyldiflavone, m.p.  $292^\circ$ , hydrolysed by  $\text{EtOH-KOH}$  to 4:6-dibenzoylacetoresorcinol (II), m.p.  $203$ – $204^\circ$ , converted by boiling  $\text{EtOH-HCl}$  into diflavone. (II) is cyclised by boiling  $\text{Ac}_2\text{O-NaOAc}$  to 2:2'-dimethyl-3:3'-dibenzoyldichromone, m.p.  $263$ – $264^\circ$ . Interaction of (I) with anisic anhydride and  $\text{Na}_2\text{CO}_3$  at  $190$ – $200^\circ$  affords the anisate, m.p.  $233$ – $235^\circ$ , of 7-hydroxy-4'-methoxy-6-anisoyl-aceto-3-anisoylflavone, hydrolysed ( $\text{EtOH-KOH}$ ) to 4:6-dianisoylacetoresorcinol, m.p.  $203$ – $204^\circ$ , converted by boiling  $\text{EtOH-HCl}$  into 4':4''-dimethoxy-diflavone, m.p.  $321$ – $322^\circ$ , different from the substance obtained by Gulati and Venkataraman (A., 1931, 1305). J. L. D.

**Preparation of *dl*-proline.** A. HEYMONS (Ber., 1933, 66, [B], 846—848).—Treatment of piperidone (I) with  $\text{PCl}_5$  in  $\text{C}_6\text{H}_5\text{Me}_2$  at  $100^\circ$  and subsequently at  $120^\circ$  affords the imido-chloride, hydrolysed by conc.  $\text{HCl}$  to  $\alpha\alpha$ -dichloro- $\delta$ -amino-*n*-valeric acid hydrochloride (II), whence the free acid (III) is isolated in  $60\%$  yield by cold  $2N\text{-Na}_2\text{CO}_3$ . Treatment of (I) with 1 mol. of  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  and subsequently with 2 mols. of  $\text{Br}$  followed by hydrolysis affords dibromopiperidone, m.p.  $172$ – $173^\circ$ , whence  $\alpha\alpha$ -dibromo- $\delta$ -amino-*n*-valeric acid, m.p.  $191^\circ$  (decomp.).



Treatment of (II) with EtOH affords (III), which when heated alone or with *tert.* bases causes lactamisation with ultimate production of 2-pyridone. In acid medium (III) is reduced to  $\delta$ -amino-*n*-valeric acid under very mild conditions, whereas with Na-Hg it affords pyrrolidine-2-carboxylic acid in 47% yield.

H. W.

**Amino-acids and related compounds. II. Electrolytic oxidation of pyrrolidonecarboxylic acids.** Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1933, 8, 137—143; cf. this vol., 681).—By determining changes in  $\text{NH}_2\text{-N}$  it is shown that equilibrium exists between glutamic (I) and pyrrolidone-2-carboxylic acid (II) in  $\text{N-H}_2\text{SO}_4$  at 35°. Electrolytic oxidation of (II) affords much succinimide and a little succinic acid, whilst (I) gives a little succinamic acid. R. S. C.

**Action of alkali hypiodites on pyrrolealdehydes.** P. PRATESI (Atti R. Accad. Lincei, 1933, [vi], 17, 173—177).—Towards KOI, pyrrole-2- and -3-aldehydes behave like phenol-*o*- and -*p*-aldehydes and naphtholaldehydes. Thus, Et 3-formyl-2:4-dimethylpyrrole-5-carboxylate gives Et 3-iodo-2:4-dimethylpyrrole-5-carboxylate; Et 3-formyl-2-methylpyrrole-5-carboxylate gives Et 3:4-di-iodo-2-methylpyrrole-5-carboxylate, m.p. 185°; pyrrole-2-aldehyde gives heptaiododipyrrol (A., 1922, i, 763); Et 3-iodo-2:4-dimethylpyrrole-5-carboxylate gives Et 3-iodo-2-formyl-4-methylpyrrole-5-carboxylate, m.p. 172.5 (aldazine, m.p. 232°), and Et 3-iodo-2-formyl-4-methylpyrrole-5-carboxylate a compound, m.p. 189°.

T. H. P.

**Hypnotic action of mixed ketones containing different types of aromatic nuclei.** H. GILMAN, L. W. ROWE, and J. B. DICKEY (Rec. trav. chim., 1933, 52, 395—398).—Mg pyrrol bromide and Et furoate give furoylpyrrole [furyl pyrrol ketone] (I), m.p. 69—70°, b.p. 141—144°/1.5 mm. (18% yield), also obtained (in 42% yield) from Mg pyrrol iodide and furoyl chloride (II). Thiophen, (II), and  $\text{SnCl}_4$  in  $\text{C}_6\text{H}_6$  give furoylthiophen [thienyl pyrrol ketone] (III), b.p. 134—136°/3 mm., in 66% yield. The following are hypnotic in large doses: CPhMe, acetyl- (slightly) and benzoyl-pyrrole, and (I). The following are not hypnotic: acetyl-thiophen and -furan, furoylthiophen, and benzoylfuran. The inhibition of hypnotic properties by the furan and thiophen nuclei may be due to the super-aromatic nature of these nuclei.

R. S. C.

**N-3-Nitropyridylpyridinium chloride.** E. KOENIGS and G. JUNG (J. pr. Chem., 1933, [ii], 137, 157—160).—4-Chloro-3-nitropyridine hydrochloride and  $\text{C}_5\text{H}_5\text{N}$  (with or without 4-aminopyridine) at 40—50° give N-3-nitropyridylpyridinium chloride, m.p. 175° (corresponding chloroaurate, m.p. 171—172°). In contrast to N-pyridylpyridinium chloride this is monobasic and more readily disrupted. With hot, dil. HCl, or better hot  $\text{H}_2\text{O}$ , it gives  $\text{C}_5\text{H}_5\text{N}$  and 3-nitro-4-hydroxypyridine, and with  $\text{NH}_2\text{Ph}$  at 100° glutacondianil. With cold aq.  $\text{NH}_3$  it affords the substance  $\text{C}_{10}\text{H}_9\text{O}_3\text{N}_3$ , m.p. 161° (A., 1904, i, 448), probably  $\delta$ -3-nitro-4-pyridylpentadienaldehyde (hydrochloride, m.p. 171°; phenylhydrazone, m.p. 147°). R. S. C.

**4:4'-Dipyridylamine and its derivatives.** E. KOENIGS and G. JUNG (J. pr. Chem., 1933, [ii],

137, 141—156).—4-Aminopyridine (I) and  $\text{PCl}_3$  in  $\text{C}_5\text{H}_5\text{N}$  give 4:4'-dipyridylamine (II) (72% yield) [hydrochloride, m.p. > 300°; picrate, m.p. 235° (decomp.)] and a little tri-N-4-aminopyridylphosphine,  $\text{P}(\text{NH}\cdot\text{C}_5\text{H}_4\text{N})_3$ , m.p. 305—308°. In quinoline or  $\alpha$ -picoline a poorer yield of (II) is obtained. The substances, m.p. about 130°, previously (A., 1926, 178) believed to be (II), contained much (I). 4:4'-Dipyridylamine-2:6-dicarboxylic acid, when prepared as described (*loc. cit.*), contains much of its (I) salt; when freed therefrom by crystallisation from HCl, it has m.p. 305° (decomp.); when distilled, it is partly decomposed into (I). (I) does not react with  $\text{PCl}_3$  alone,  $\text{POCl}_3$ , or  $\text{POCl}_3\text{-C}_5\text{H}_5\text{N}$ . (II) does not react with  $\text{HNO}_2$ ,  $\text{BzCl}$ -aq. NaOH, or EtI-EtOH. Addition of the nitrate, m.p. 226° (decomp.), of (II) to  $\text{H}_2\text{SO}_4$  at 110—120° gives 3-nitro-4:4'-dipyridylamine,  $+\text{H}_2\text{O}$ , m.p. 96° and (anhyd.) 122—123° [nitrate, m.p. 210° (decomp.)], which with Br and NaOAc in AcOH at 80—100° gives 5:3':5'-tribromo-3-nitro-4:4'-dipyridylamine, m.p. 181° (neutral), and is reduced by  $\text{Na}_2\text{S}$  at 70° to 3-amino-4:4'-dipyridylamine, m.p. 239° [nitrate, m.p. 195° (decomp.)]; picrate, m.p. 224°; reduces  $\text{HAuCl}_4$ , the constitution of which is proved by formation of 4'-pyridyl-3:4-pyridotriazole, m.p. 183° (chloroaurate, m.p. 249°; picrate, m.p. 197—198°), by  $\text{HNO}_2$ . With  $\text{HNO}_3$  (d 1.52) and oleum (60%  $\text{SO}_3$ ) at 100° (II) gives 3:3'-dinitro-4:4'-dipyridylamine, m.p. 195—196° [nitrate, m.p. 187—188° (decomp.)]; picrate, m.p. 202°; Na salt, red], which with Br and NaOAc in hot AcOH gives 5:5'-dibromo-3:3'-diamino-4:4'-dipyridylamine, m.p. 222—223° (neutral), and with  $\text{Na}_2\text{S}$  at 70° affords 3:3'-diamino-4:4'-dipyridylamine, m.p. 244—245° (decomp.) [dinitrate, m.p. about 300° (decomp.)]; dipicrate, m.p. 238° (decomp.), the constitution of which is proved by (i) formation of 3'-amino-4'-pyridyl-3:4-pyridotriazole, m.p. 244° (picrate, m.p. 192°; can be diazotised), by  $\text{HNO}_2$  and (ii) transformation of the dihydrochloride at 215° into di-3:4-pyridodihydrophenazine, m.p. 310° (dioxalate, dihydrochloride, and dinitrate, m.p. 310°; picrate, decomp. 300—301°), oxidised by  $\text{H}_2\text{O}_2$  to di-3:4-pyridopyrazine, m.p. about 290—300°, a feeble base. Bromination of (II), best with Br and NaOAc in hot AcOH, affords only 3:5:3':5'-tetra-bromo-4:4'-dipyridylamine, m.p. 222° (neutral).

R. S. C.

**N-Hydroxyethyl-2-pyridone and some of its derivatives.** J. A. GAUTIER (Compt. rend., 1933, 196, 1124—1127).—1-Hydroxyethylpyridinium chloride, m.p. 128—129° (lit. 125—126°), is converted by Decker's reaction into 1-hydroxyethyl-2-pyridone, m.p. 92°. The following derivatives are described: hydrochloride; chloroaurate ( $+2\text{EtOH}$ ), m.p. 92°; chloroplatinate, m.p. 205° (decomp.); picrate, m.p. 103°; phenylurethane, m.p. 132° [hydrochloride; chloroplatinate ( $+2\text{EtOH}$ ), m.p. 150° (decomp.)]; benzoate, m.p. 118° [chloroplatinate ( $+2\text{EtOH}$ ), m.p. 225° (decomp.)]. A. C.

**Mechanism of C. Mayer's triphenylpiperidone synthesis.** E. MACOVSKI and A. SILBERG (J. pr. Chem., 1933, [ii], 137, 131—140).—Benzylidene-aniline (I) and  $\text{H}_2\text{O}_2$  in boiling  $\text{COMe}_2$  give  $\beta$ -anilino- $\beta$ -



*phenylethyl Me ketone* (II), m.p. 91°, also obtained from  $\text{NH}_2\text{Ph}$ ,  $\text{PhCHO}$ , and  $\text{H}_2\text{O}_2$  in boiling  $\text{COMe}_2$ . The constitution of (II) is proved by (i) hydrolysis by hot  $\text{HCl}$  or cold, conc.  $\text{H}_2\text{SO}_4$  to  $\text{NH}_2\text{Ph}$  and benzylideneacetone (III), (ii) formation of 1:5-dimethylpyrazoline by  $\text{NH}_2\text{NPh}$  in hot  $\text{AcOH}$  [by preliminary hydrolysis to (III)], (iii) formation of tribromoaniline and a substance, m.p. 115°, by  $\text{Br}$  in  $\text{CHCl}_3$ , and (iv) synthesis from (III) and  $\text{NH}_2\text{Ph}$  in  $\text{EtOH}$ , best with addition of a little  $\text{NaOH}$ . (II) is presumed to be formed by hydrolysis of (I) to  $\text{NH}_2\text{Ph}$  and  $\text{PhCHO}$ , synthesis of (II), and subsequent addition of  $\text{NH}_2\text{Ph}$ . Similarly, formation of triphenylpiperidone from (I) and  $\text{COMe}_2$  is assumed to occur by hydrolysis of (I), formation of (II), and direct two-fold addition of unchanged (I) to (II); this view is supported by formation of styryl  $\beta$ -anilino- $\beta$ -phenylethyl ketone [obtained by single addition of (I) to (II)] as a by-product. Objections are raised to previously suggested mechanisms. R. S. C.

**Oxidation of magnesylindoles by hydrogen peroxide.** G. INGRAFFIA (Gazzetta, 1933, 63, 175—182).—The reaction of Oddo and Binaghi (A., 1922, i, 314) is extended. With 100-vol.  $\text{H}_2\text{O}_2$  in theoretical proportion,  $\text{Mg}$  indole gives 1-hydroxyindole, m.p. 160°,  $\text{Mg}$  2- and 3-methylindole give 3-hydroxy-2-, m.p. 40° (*picrate*, m.p. 128°; 2-methylindole *picrate* has m.p. 139°), and 1-hydroxy-3-methylindole, m.p. 120° (no *picrate* obtained), respectively. Colour reactions of the products are described. E. W. W.

**Indole series. I. Synthesis of 2-benzylindoles.** P. L. JULIAN and J. PIKL (J. Amer. Chem. Soc., 1933, 55, 2105—2110).— $\text{Et N-methylanilinoacetate}$ ,  $\text{CH}_2\text{Ph}\cdot\text{CN}$ , and  $\text{EtOH}\cdot\text{NaOEt}$  give  $\gamma\text{-N-methylanilino-}\alpha\text{-phenylacetoacetonitrile}$  (I),  $\text{CN}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NPhMe}$ , m.p. 121°, hydrolysed (90%  $\text{H}_2\text{SO}_4$  at 125°) to  $\gamma\text{-N-methylanilino-}\alpha\text{-phenylacetoacetamide}$ , m.p. 141°, which is hydrolysed (5%  $\text{HCl}$ ) to benzyl  $\text{N-methylanilinoethyl ketone}$  (II), m.p. 37° (*oxime*, m.p. 119°), and a little of a compound (III), m.p. 245°; (III) is the main product from (I) and conc.  $\text{HCl}$ . (I) and  $\text{MeOH}\cdot\text{HCl}$  afford *Me*  $\gamma\text{-N-methylanilino-}\alpha\text{-phenylacetoacetate}$ , m.p. 73° (*hydrochloride*, m.p. 158°), also hydrolysed (5%  $\text{HCl}$ ) to (II) and (III). (II) heated with  $\text{NH}_2\text{Ph}$  and  $\text{NH}_2\text{Ph}\cdot\text{HCl}$  gives 2-benzylindole, m.p. 86° (*picrate*, m.p. 115°), and a little 3-benzyl-1-methylindole, m.p. 61° (*picrate*, m.p. 120—121°) (also prepared from  $\beta$ -phenylpropaldehydephenylmethylhydrazone and  $\text{ZnCl}_2$  at 170—180°). Similarly, (II),  $\text{NHPhMe}$ , and  $\text{NHPhMe}\cdot\text{HCl}$  afford 2-benzyl-1-methylindole, m.p. 65° (*picrate*, m.p. 97°). The following are prepared by reactions similar to the above:  $\gamma\text{-N-methylanilino-}\alpha\text{:3:4-dimethoxyphenyl-acetoacetonitrile}$ , m.p. 110° (this and following m.p. are corr.), and *acetoacetamide*, m.p. 156° (accompanied by a substance, m.p. 214°); 3:4-dimethoxybenzyl  $\text{N-methylanilinoethyl ketone}$ , m.p. 79.5° (*oxime*, m.p. 120°); 2:3:4-dimethoxybenzylindole, m.p. 146° (*picrate*, m.p. 101°), and its 1-*Me* derivative, m.p. 96° (*picrate*, m.p. 97°). H. B.

**Spectroscopic study and assay of histamine.** B. LEWIS, E. VON GEBAUER-FUELNEGG, and C. J. FARMER (J. Amer. Chem. Soc., 1933, 55, 2025—

2027).—Histamine can be determined spectroscopically in concns. of 0.00367—1.82 g./100 c.c. H. B.

**Complex salts of 8-hydroxyquinoline.** A. ABLOV (Bull. Soc. chim., 1933, [iv], 53, 234—240).—The complex salt  $\text{Co}(\text{C}_9\text{H}_6\text{ON})_3$  is prepared by addition of  $\text{H}_2\text{O}_2$  to a solution of a  $\text{Co}^{\text{II}}$  salt and 8-hydroxyquinoline (I), or by direct combination of (I) with hydrated  $\text{Co}_2\text{O}_3$ . It is also formed from cobaltamines, e.g.,  $[\text{Co}(\text{NH}_2)_5]\text{Cl}_2$ , *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ , or  $[\text{Co}(\text{NH}_2)_6]\text{Cl}_3$  and (I), there being no evidence of the formation of a cobaltamine containing (I). *Co* salts are also prepared from 5-chloro- and 5:7-dibromo-8-hydroxyquinoline, and the salt  $\text{Cr}(\text{C}_9\text{H}_6\text{ON})_3$  from (I) and  $[\text{Cr}\{\text{CO}(\text{NH}_2)_2\}_6]\text{Cl}_3$ . H. A. P.

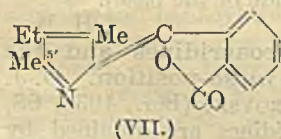
**Quinoline derivatives. IX. Photochemical oxidation of methylated 2-phenylquinolines.** H. JOHN and G. BEHMEL (Ber., 1933, 66, [B], 844—845; cf. A., 1926, 622).—Irradiation of 2-phenyl-3-methylquinoline (I) leads to dark resins, about 3% of 2-phenylquinoline-3-carboxylic acid, and 47% of unchanged (I). 2-Phenyl-6-methylquinoline yields amorphous products, and about 8% of 2-phenylquinoline-6-carboxylic acid, whereas 2-*p*-tolylquinoline gives no acid, resin, and 37.5% of unchanged base. H. W.

**Ring-chain conjugation in the quinoline series.** A. HOFFMAN, M. W. FARLOW, and R. C. FUSON (J. Amer. Chem. Soc., 1933, 55, 2000—2004).—2-Styrylquinoline (I) and  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  give 70% of 2- $\beta\beta$ -diphenylethylquinoline (II), m.p. 121—121.5° (*Br*-derivative, m.p. 131.5—132.5°; *picrate*, decomp. >200°), also obtained from (I),  $\text{C}_6\text{H}_6$ , and  $\text{AlCl}_3$ . 2-*p*-Chlorostyrylquinoline (III), m.p. 139.5° (*dibromide*, m.p. 175°), from 2-methylquinoline, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ , and  $\text{ZnCl}_2$  at 140—160°, and  $\text{MgPhBr}$  afford 64% of 2- $\beta$ -phenyl- $\beta$ -*p*-chlorophenylethylquinoline, m.p. 91.5—92.5°. (III),  $\text{C}_6\text{H}_6$ , and  $\text{AlCl}_3$  give (II); reaction does not occur when the reagents are kept free from moisture, but does take place when dry  $\text{HCl}$  is passed into the reaction mixture (indicating that condensation involves the hydrochloride of the base). H. B.

**Formation of mesochloroacridines and the mobility of chlorine in the meso-position.** O. J. MAGIDSON and A. M. GRIGOROVSKI (Ber., 1933, 66, [B], 866—872).—9-Chloroacridines are obtained by heating the requisite diphenylaminocarboxylic acid with  $\text{POCl}_3$ , removal of excess of the latter under diminished pressure, suspending the residue in  $\text{PhMe}$  or  $\text{C}_6\text{H}_4\text{Me}_2$ , and decomposing with  $\text{H}_2\text{O}$  at 0°. Thus are prepared: 9-chloroacridine, m.p. 119—120°, 2-ethoxy-, m.p. 142—144°, 6-nitro-2-ethoxy- (I), m.p. 187—188°, and 7-nitro-2-ethoxy- (II), m.p. 365—370°, -9-chloroacridine. The rates of hydrolysis of the acetates in  $\text{AcOH}$  have been measured. (I) is transformed by  $\text{PhOH}$  at 80° into 6-nitro-9-phenoxy-2-ethoxyacridine, m.p. 173—174°, and by  $\text{NH}_3\cdot\text{EtOH}$  at 130—135° into 6-nitro-9-amino-2-ethoxyacridine, m.p. 310°. Similar treatment of (II) yields 7-nitro-2-ethoxyacridone, but a modified procedure leads to 7-nitro-9-phenoxy-2-ethoxyacridine, m.p. 152—153°, and 7-nitro-9-amino-2-ethoxyacridine, m.p. >300°. H. W.



**Dipyrrolyl ketones.** II. H. FISCHER and H. ORTH (Annalen, 1933, 502, 237—264).— $\text{COCl}_2$  in PhMe converts the product from  $\text{Et}_2\text{O}$ - $\text{MgEtBr}$  and 2-methyl-, 2-ethyl-, 2:4-diethyl-, 2-methyl-4-ethyl-, 5-methyl-3:4-diethyl-, 4-methyl-2:3-diethyl-, 2:3-dimethyl-4-propyl-, 2:4-dimethyl-3-propyl-, 2:3-dimethyl-, and 2:3:4-trimethyl-pyrroles into *di*-(5-methyl-2-pyrrolyl), m.p. 250°, *di*-(5-ethyl-2-pyrrolyl), m.p. 175°, *di*-(3:5-diethyl-2-pyrrolyl) (I), m.p. 140°, *di*-(5-methyl-3-ethyl-2-pyrrolyl) (II), m.p. 186°, *di*-(5-methyl-3:4-diethyl-2-pyrrolyl) (III), m.p. 156°, *di*-(3-methyl-4:5-diethyl-2-pyrrolyl), m.p. 182°, *di*-(4:5-dimethyl-3-propyl-2-pyrrolyl) (IV), m.p. 160°, *di*-(3:5-dimethyl-4-propyl-2-pyrrolyl) (V), m.p. 177° (azine, m.p. 229°), *di*-(4:5-dimethyl-2-pyrrolyl), m.p. 275° [hydrazone, m.p. 173° (not sharp)], and *di*-(3:4:5-trimethyl-2-pyrrolyl) (VI), m.p. 252° (hydrazone, m.p. 174°; azine, m.p. 267°), ketones, respectively. (I),  $\text{AcCl}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$  give *di*-(4-acetyl-3:5-diethyl-2-pyrrolyl) ketone, m.p. 180—181°, whilst (II) similarly gives *di*-(4-acetyl-5-methyl-3-ethyl-2-pyrrolyl) ketone, m.p. 250°, which with Br in AcOH affords the *di*-(5-bromomethyl) derivative, m.p. 205° (decomp.) (darkens at 195°). (III) and 20%  $\text{COCl}_2$  in PhMe give 5:5'-*dimethyl-3:4:3':4'-tetraethyl-ms-chloropyrromethene hydrochloride*, m.p. 152° (Zn salt, sinters at 180°); 4:5:4':5'-*tetramethyl-3:3'-dipropyl-*, m.p. 245° [hydrochloride, m.p. 155—156° (Zn salt, m.p. 165°)]; 3:5:3':5'-*tetramethyl-4:4'-dipropyl-*, m.p. 105° [hydrochloride, m.p. 90—93° (Zn salt, darkens at 125°)], and 3:4:5:3':4':5'-*hexamethyl-*, unstable (hydrochloride, m.p. 148°), -*ms-chloropyrromethenes* are similarly prepared from (IV), (V), and (VI), respectively. The Zn salt, darkens and sinters at 171°, of 3:5:3':5'-*tetramethyl-4:4'-diethyl-ms-chloropyrromethene hydrochloride* (A., 1931, 1168) is also described. *Di*-(3:5-dimethyl-4-ethyl-2-pyrrolyl) ketone (*loc. cit.*) undergoes fission when treated with  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  and AcOH at 180—190° to give cryptopyrrolephthalide (VII) (cf. A., 1913, i, 93), which is also similarly prepared from Et 2:4-dimethyl-3-ethylpyrrole-5-carboxylate. (VII) and Br in AcOH afford the



5'-bromomethyl derivative, m.p. 192°, converted by boiling MeOH into a *OMe*-derivative, m.p. 157°, and by  $\text{NH}_2\text{Ph}$  into an *anilino*-derivative, m.p. 170°. Et 2:4-diethylpyrrole-5-carboxylate,  $\text{AcCl}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$  give the *Et* ester, m.p. 106° (*oxime*, m.p. 164°), of 3-acetyl-2:4-diethylpyrrole-5-carboxylic acid, m.p. 205°; the ester is reduced (Wolff-Kishner) to 2:3:4-triethylpyrrole, b.p. 103—104°/12 mm., which is converted (as above) into *di*-(3:4:5-triethyl-2-pyrrolyl) ketone, m.p. 134° (hydrazone, m.p. 130°), and with  $\text{HCO}_2\text{H}$  and  $\text{HBr}$  affords 3:4:5:3':4':5'-*hexaethylpyrromethene hydrobromide*, m.p. 155° (free base, m.p. 123°). *Di*-(4-carbethoxy-5-methyl-2-pyrrolyl) ketone, m.p. 216° (decomp.), and *Me xanthopyrrolecarboxylate picrate*, m.p. 102°, are described. *Di*-(3-methyl-5-ethyl-2-pyrrolyl) ketone (VIII), m.p. 150° (azine, m.p. 171°; *Ac* derivative, m.p. 136°, of hydrazone), prepared (as above) from xanthopyrrole, is brominated to the 4:4'-*Br*<sub>2</sub>-derivative, sinters at 163°, converted by  $\text{COCl}_2$  into 4:4'-dibromo-3:3'-dimethyl-

5:5'-diethyl-*ms-chloropyrromethene hydrochloride*, m.p. about 150°. (VIII),  $\text{AcCl}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$  give the 4:4'-*Ac*<sub>2</sub> derivative, m.p. 237°, which with Br (2 mols.) in AcOH affords *di*-(4-acetyl-3-methyl-5-β-bromoethyl-2-pyrrolyl) ketone, darkens at 182° and sinters at 196°, converted by boiling EtOH into the *di*-5-β-ethoxyethyl derivative, m.p. 216—217° (decomp.). *Di*-(4-acetyl-3:5-dimethyl-2-pyrrolyl) ketone (IX), m.p. 271° (*dioxime*, m.p. 269°), is brominated to the *di*-5-bromomethyl derivative, darkens at 180°, converted into the *di*-5-methoxy-, m.p. 218—219°, *di*-5-ethoxy-, m.p. 222° (sinters at 209°), and *di*-5-acetoxy-, m.p. 260° (darkens at 206°), -methyl derivatives by the action of  $\text{MeOH-KOH}$ ,  $\text{EtOH-KOH}$ , and  $\text{AcOH-AgOAc}$ , respectively. (IX) and  $\text{SO}_2\text{Cl}_2$  in  $\text{Et}_2\text{O}$  give a compound,  $\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_2\text{Cl}_8$ , m.p. 224—227°.

*Me opsopyrrolecarboxylate* and  $\text{COCl}_2$  in  $\text{Et}_2\text{O}$  afford 3-methyl-4-β-carbomethoxyethylpyrrole-2-carboxylic chloride (corresponding *anilide*, m.p. 141°), which with 3-acetyl-2:4-dimethylpyrrole (X) and  $\text{AlCl}_3$  in  $\text{CS}_2$  gives 4'-acetyl-3:3':5'-trimethyl-4-β-carbomethoxyethyl-*di*-2-pyrrolyl ketone, m.p. 156°. The acid chloride (XI) from  $\text{COCl}_2$  and  $\text{Me } \beta$ -2:4-dimethyl-3-pyrrolylpropionate with Et 2:4-dimethylpyrrole-3-carboxylate and  $\text{AlCl}_3$  in  $\text{CS}_2$  affords 4-carbethoxy-3:5:3':5'-tetramethyl-4'-β-carbomethoxyethyl-*di*-2-pyrrolyl ketone, m.p. 173—174°. Et 2-methylpyrrole-3-carboxylate (XII) and (XI) similarly give 4-carbethoxy-5:3':5'-trimethyl-4'-β-carbomethoxyethyl-*di*-2-pyrrolyl ketone, m.p. 188°, whilst 4-acetyl-3:5:3':5'-tetramethyl-4'-β-carbomethoxyethyl-*di*-2-pyrrolyl ketone, m.p. 186°, is prepared from (XI) and (X). The chloride from *Me* hampopyrrolecarboxylate and  $\text{COCl}_2$  with (X) and (XII) gives 4-acetyl-3:5:4':5'-tetramethyl-, m.p. 153°, and 4-carbethoxy-5:4':5'-trimethyl-, m.p. 170°, -3'-β-carbomethoxyethyl-*di*-2-pyrrolyl ketone, respectively. An improved method of prep. (cf. Hess and Anselm, A., 1921, i, 881) of *di*-2-pyrrolyl ketone (XIII) (*Br*<sub>4</sub>-derivative, darkens at 255°) is given. (XIII) and  $\text{SO}_2\text{Cl}_2$  in  $\text{Et}_2\text{O}$  afford (probably) *di*-(3:5-dichloro-2-pyrrolyl) ketone, m.p. 296—297° (sinters at 275°). Pyrrole-2-aldoxime,  $\text{Ac}_2\text{O}$ , and  $\text{NaOAc}$  give 2-cyano-5-acetylpyrrole, m.p. 74—75°.

H. B.

**New metallic complexes of cyanogen compounds.** J. FOUCHY (J. Pharm. Chim., 1933, [viii], 17, 432—433).—Unstable coloured complex salts are pptd. when a solution of Fe-antipyrine [antipyrine +  $\text{Fe}_2(\text{SO}_4)_3$ ] is added to  $\text{NaSCN}$  or  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ . The reaction is sp. for antipyrine, but similar ppts. are obtained with  $\text{UO}_2$ , Zn, Mn, or  $\text{Cu}^{\text{II}}$  in place of Fe.

J. W. B.

**Glyoxaline derivatives.** III. Occurrence of 4-hydroxymethylglyoxaline. T. YABUTA and K. KAMBE (J. Agric. Chem. Soc. Japan, 1932, 8, 815—820).—In presence of  $\text{O}_2$ , a solution of fructose and  $\text{NH}_3$  in presence of  $\text{Cu}(\text{OH})_2$  afford 4-hydroxymethylglyoxaline (I), which is also obtained from fructose,  $\text{CH}_2\text{O}$ ,  $\text{NH}_3$  phosphate, and aq.  $\text{NH}_3$ , or fructose,  $\text{CH}_2\text{O}$ , aq.  $\text{NH}_3$ , and methylene-blue, in presence of  $\text{O}_2$ . Hydroxygluconic acid,  $\text{Cu}(\text{OH})_2$ , and aq.  $\text{NH}_3$  afford (I) and glyoxaline-4-carboxylic acid.

CH. ABS.

**Hydro-orotic acid.** M. BACHSTETZ (Gazzetta, 1933, 63, 206—210).—Maleic acid heated with



$\text{CO}(\text{NH}_2)_2$  at  $132^\circ$  gives a small yield of *hydro-oroctic acid* (*hydrouracil-4-carboxylic acid*), m.p.  $247^\circ$  (corr.),  $K\ 6.19 \times 10^{-3}$ . E. W. W.

**Action of triphenylmethyl perchlorate on substituted barbituric acids.** H. ASPELUND (J. pr. Chem., 1933, [ii], 137, 1—8).—The action of  $\text{CPh}_3\text{ClO}_4$  on Na 5-ethyl- (I) or 5-benzyl- (II) -barbiturate in  $\text{CHCl}_3$  or  $\text{Et}_2\text{O}$  does not lead to the expected derivatives.  $\text{CPh}_3$  is recovered as  $\text{CHPh}_3$  or  $\text{CPh}_3\text{OH}$ , whilst (I) and (II) are recovered with a small amount of the corresponding dialuric acid. (II) is partly transformed into a *substance*, m.p. (indef.)  $183$ — $184^\circ$ .  $\text{CPh}_3\text{ClO}_4$  and Na 5:5-diethyl- (III) and 5-ethyl-5-allyl- (IV) -barbiturate afford 1:3-ditriphenylmethyl-5:5-diethyl-, m.p.  $220^\circ$ , according to rate of heating, and 1:3-ditriphenylmethyl-5-ethyl-5-allyl-, m.p.  $192$ — $196^\circ$ , *barbituric acid*, respectively, insol. in  $\text{H}_2\text{O}$  and alkali and very readily hydrolysed with much unchanged (III) and (IV) and  $\text{CPh}_3\text{OH}$ . (III) in  $\text{CHCl}_3$  at  $40^\circ$  gives the compound  $\text{C}_{16}\text{H}_{24}\text{O}_6\text{N}_4\text{NaClO}_4$ , m.p.  $229^\circ$ . (IV) is obtained in 85% yield from (I) suspended in  $\text{H}_2\text{O}$  and allyl chloride (V) (20% excess) at  $40^\circ$ . 5:5-Diallyl-barbituric acid results in 65% yield from Na barbiturate and (V) at  $70$ — $80^\circ$ . H. W.

**Interaction of cyclohexene oxide with piperazine and piperidine.** T. S. KUSNER (Ukrain. Chem. J., 1932, 7, [Sci.], 179—183).—On warming an aq. suspension of piperazine and cyclohexene oxide (I), *NN'*-bis-(2-hydroxycyclohexyl)piperazine, m.p.  $208$ — $208.5^\circ$ , is produced (picrate, m.p.  $232^\circ$ ; *dihydrochloride*, darkens about  $270^\circ$ , carbonises at  $276$ — $280^\circ$ ; *dihydrochloride of dibenzoate*, darkens at  $250$ — $260^\circ$ ) (cf. A., 1932, 404).  $\text{C}_5\text{H}_{11}\text{N}$  and (I) yield *N*-(2-hydroxycyclohexyl)piperidine, b.p.  $142$ — $143^\circ/21\text{ mm.}$ , m.p.  $34^\circ$  [*hydrochloride*, m.p.  $268^\circ$  (decomp.)]; *hydrochloride of benzoate*, m.p.  $265$ — $266^\circ$  (decomp.)]. Both the benzoates possess local anaesthetic properties.

G. A. R. K.

**Constitution of polypeptides and [action of] proteolytic enzymes.** I, II. J. MATSUI (J. Biochem. Japan, 1933, 17, 163—169, 253—258).—I. Treatment of glycylytyrosine Et ester with fumaryl chloride in  $\text{CHCl}_3$  yields *fumaryldi(glycylytyrosine) Et ester*, hydrolysed to *fumaryldi(glycylytyrosine)*, m.p.  $159$ — $160^\circ$ , which with aq.  $\text{NH}_3$  at  $100^\circ$  under pressure affords *asparagyldi(glycylytyrosine)*, m.p.  $183^\circ$ , hydrolysed by trypsin-enterokinase (I), but not by pepsin (II), erepsin, (III), or non-activated trypsin (IV). Thus glycylytyrosine is no longer a substrate for (III) when the  $\text{NH}_2$  group is linked with aspartic acid, but becomes a substrate for proteases such as (I).

II. Et aminomalonate in  $\text{Et}_2\text{O}$  solution shaken with  $\text{CH}_2\text{Cl}\cdot\text{COCl}$  and aq.  $\text{Na}_2\text{CO}_3$  yields *Et chloroacetamidomalonate*, m.p.  $98^\circ$ . The corresponding *acid*, m.p.  $113^\circ$ , on treatment with  $\text{NH}_3$  etc. affords *glycylaminomalononic anhydride*, m.p.  $193^\circ$ , which has a diketopiperazine structure, is hydrolysed by (IV) and, to a greater extent, by (I) but not by (II) or (III).

F. O. H.

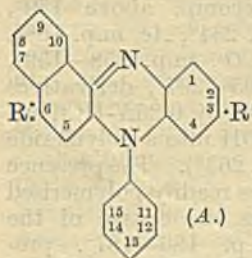
**Enzymic degradation of diketopiperazine rings.** T. ISHIYAMA (J. Biochem. Japan, 1933, 17, 285—297).—The anhydride of Et glycylaspartate (A., 1904, i, 31) is hydrolysed with  $\text{Ba}(\text{OH})_2$  to yield

*diketopiperazinediacetic acid*, m.p.  $270^\circ$ . Et glutamate hydrochloride is converted into the free base and treated with  $\text{CH}_2\text{Cl}\cdot\text{COCl}$  to give Et chloroacetylglutamate, which with  $\text{NH}_3$ -saturated EtOH yields *diketopiperazinepropionamide*, m.p.  $248$ — $250^\circ$  (decomp.), and with 0.93*N*- $\text{NH}_3$  in EtOH yields *Et glycylglutamate anhydride*, m.p.  $140^\circ$ . The latter with  $\text{Ba}(\text{OH})_2$  affords *diketopiperazinepropionic acid*, m.p.  $225^\circ$ . The action of trypsin and of trypsin-kinase on these and other diketopiperazine derivatives indicates that glycylglutamic acid on anhydride (diketopiperazine) formation is no longer hydrolysable by trypsin, but becomes a sp. substrate for trypsin. Diketopiperazine and pyrrolidone-2-carboxylic acid and its amide are not hydrolysed by trypsin.

F. O. H.

**Quinazolines. VI. Alkylation of benzoylene-carbamide [2:4-diketotetrahydroquinazoline].** N. A. LANGE and F. E. SHEIBLEY (J. Amer. Chem. Soc., 1933, 55, 2113—2116).—*o*- $\text{NHET}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (I) and  $\text{KNCO}$  in AcOH give 2:4-diketo-1-ethyltetrahydroquinazoline, m.p.  $215$ — $217^\circ$ , also obtained from (I) and  $\text{CO}(\text{NH}_2)_2$  at  $150^\circ$ , which is ethylated (EtI and EtOH-KOH;  $\text{Et}_2\text{SO}_4$  and *N*-NaOH) to the 1:3-Et<sub>2</sub> derivative, m.p.  $110$ — $111^\circ$  [this could not be prepared by Bogert and May's method (A., 1909, i, 329)], and methylated (MeI, MeOH-KOH) to 2:4-diketo-3-methyl-1-ethyltetrahydroquinazoline, m.p.  $138$ — $139^\circ$ . Ethylation (EtI; cf. Bogert and Scatchard, A., 1920, i, 184) of 2:4-diketotetrahydroquinazoline gives the 3-Et derivative, m.p.  $197.5$ — $198.5^\circ$ , which is methylated ( $\text{Me}_2\text{SO}_4$ , *N*-NaOH) to 2:4-diketo-1-methyl-3-ethyltetrahydroquinazoline, m.p.  $133$ — $134^\circ$  (softens at about  $110^\circ$ ). All m.p. are corr. H. B.

**Analysis of azine dyes.** R. BASS (Helv. Chim. Acta, 1933, 16, 403—418).—Naphthophenosafranines (A, where R and R' are basic groups) are hydrolysed by heating with AcOH-conc. HCl under pressure (cf. Fischer and Arntz, A., 1907, i, 94) to well-defined OH-derivatives. Thus, Wool Fast Blue BL (By) (I) and Novazol Acid Blue G. L. (Gy) (II) give compounds resembling (appearance; position of main absorption band) naphthosafranin (A, R=O, R'=OH); that from (II) has the composition  $\text{C}_{22}\text{H}_{14}\text{O}_3\text{N}_2$ , and contains 2 OH groups (Zerevitinov in PhOMe). Neutral Blue (C) (III) similarly gives a violet compound (the main absorption band of which differs from that of isorosindone), whilst Basle Blue R (DH) (IV) and dimethylisorosindulines containing a substituent in position 13 afford non-homogeneous products. Prolonged heating with 60—70%  $\text{H}_2\text{SO}_4$  causes the elimination of the 6-substituent; thus, (I) gives the compound (A with R=O, R'=NHPH, and  $\text{SO}_3\text{Na}$  at position 4 or 7), (II) affords the compound (A with R=O, R'=NEt<sub>2</sub>, Me at 11, and an undetermined  $\text{SO}_3\text{Na}$  group), whilst Indocyanine BF (A) yields a substance, the spectrum of which resembles that of dimethylnaphthosafraninone (A, R=O, R'=NMe<sub>2</sub>). (III) is unaffected by 60—70%  $\text{H}_2\text{SO}_4$

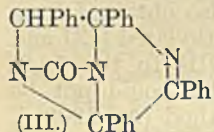




at 140–160°, whilst (IV) gives a non-homogeneous product. No useful information is obtained by reduction (Sn, HCl) of the dyes. The above methods of degradation give some idea of the constitutions, but do not establish the structures of the dyes.

H. B.

**Heterocyclic compounds obtained by the interaction of benzoin and hydrazine hydrochloride.** II. J. VAN ALPHEN (Rec. trav. chim., 1933, 52, 478–486; cf. this vol., 286).—The following derivatives of  $\Delta^2$ -1:3:4:6-tetraphenyl[dehydro]trimidine (I) are prepared: 5:7-*Me*<sub>2</sub>-, m.p. 189°, and -*Et*<sub>2</sub>-, m.p. 135°; 5- or 7- $\beta$ -bromoethyl-, m.p. 158° [reduced to (I) by Zn dust in hot AcOH], a complex (II) of the 5:7-oxalylo-derivative with 0.5(COCl)<sub>2</sub>, m.p. about 240°; 5:7-carbonylo- (III), m.p. about 335° [complex with 0.5COCl<sub>2</sub>, m.p. 158°, gives (I) at 250°]; 5:7-sulphono-, decomp. > 280° (by conc. H<sub>2</sub>SO<sub>4</sub> at 160°), gives (III) when boiled with 50% H<sub>2</sub>SO<sub>4</sub>. PhI, KOH, and Cu-bronze in boiling PhNO<sub>2</sub> give  $\Delta^2$ -1:3:4:5:6:7-hexaphenyl[dehydro]trimidine, m.p. 283°. Addition of ligroin to a C<sub>6</sub>H<sub>6</sub> solution of (II) or boiling (II) with NaOAc-EtOH gives the 5:7-oxalylo-derivative (IV), m.p. 268–269° (decomp.), which rapidly affords (I) when boiled with KOH-EtOH. Fusion of (II) or (IV) gives (III).



R. S. C.

**Polymerisation of alkylated indoles.** O. SCHMITZ-DUMONT and K. H. GELLER (Ber., 1933, 66, [B], 766–774; cf. A., 1931, 1165, 1429).—*Di*-7-methylindole hydrochloride (I) is obtained by passing HCl into 7-methylindole (II) in C<sub>6</sub>H<sub>6</sub> or by rapid addition of fuming HCl to (II) in EtOH at –10°. (I) and KOH yield *di*-7-methylindole, m.p. 88°, which contains 2 active H but affords only monoacyl derivatives. It is smoothly depolymerised at 225–240° vac. to (II). The *picrate*, decomp. above 130°, *phenylcarbamide* derivative, m.p. 234°, *Ac*, m.p. 186°, *CO<sub>2</sub>Et*, m.p. 195–196°, *CCl<sub>3</sub>CO*-, m.p. 158–159°, decomp. 160°, and *Bz*, m.p. 265–267°, derivatives are described. (II) is not affected by 0.25N-HCl, but is converted by HCl in H<sub>2</sub>O-EtOH into a polymeride (*Ac* derivative, C<sub>33</sub>H<sub>33</sub>O<sub>3</sub>N<sub>3</sub>, m.p. 263°). The presence of the 7-Me in (II) renders (II) less readily polymerised than indole and also influences the course of the change. *Tri*-7-methylindole, m.p. 186–187°, prepared by the prolonged action of SnBr<sub>4</sub> on (II) in C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>, contains 3 active H, is depolymerised to (II) at 240°/vac., and gives an *Ac* derivative, m.p. 250–251°. 1-Methylindole (III) in C<sub>6</sub>H<sub>6</sub> is converted by HCl into *tri*-1-methylindole (IV), m.p. 178–179° (*hydrochloride*), in very poor yield, the main reaction following a different course. (III) in EtOH is transformed by fuming HCl at –10° into *di*-1-methylindole, m.p. 133–135° (*hydrochloride*), a little (IV), and much other material. Increase in size of the alkyl groups diminishes the tendency towards polymerisation; 3-ethyl-, unlike 3-methylindole, is not polymerised.

H. W.

**Chlorophyll. XXXII. Neophæoporphyrin a<sub>6</sub>, hydroxymethylphæophorbide and its dihydro-derivative, and allophæoporphyrin a<sub>7</sub>.** H.

FISCHER and W. HAGERT (Annalen, 1933, 502, 41–74).—Allomerisation of phæophorbide *a* (I) with O<sub>2</sub> in AcOH and subsequent esterification (CH<sub>2</sub>N<sub>2</sub>) give *Me* esters, C<sub>36</sub>H<sub>38</sub>O<sub>6</sub>N<sub>4</sub>, m.p. 253° (previous sintering), and C<sub>36</sub>H<sub>38</sub>O<sub>5</sub>N<sub>4</sub>, m.p. 228° (previous sintering). Similar allomerisation of phæophytin and subsequent reduction (HI-AcOH at 60°) affords chloroporphyrin *e*<sub>6</sub> (II), phæoporphyrin *a*<sub>7</sub> (III), phæoporphyrin *a*<sub>5</sub> (IV) (*Me*<sub>2</sub> ester, m.p. 279°), phylloerythrin (V), and porphyrins of the *b*-series. Reduction (HI-AcOH) of chlorophyllide *a* and *b* gives only (V); when a solution in AcOH is kept under O<sub>2</sub> for 35 days and then reduced, 75% of (III) is produced (similar results are obtained using benzoquinone in N<sub>2</sub> for O<sub>2</sub>). Hydrolysis (MeOH-KOH-C<sub>5</sub>H<sub>5</sub>N) of the more sol. fraction from allomerised (I) gives a chlorin (*Me* ester, C<sub>37</sub>H<sub>42</sub>O<sub>6</sub>N<sub>4</sub>, m.p. 212°). (II) is converted by O<sub>2</sub> in 3% HCl into some (III) and by O<sub>2</sub> in conc. H<sub>2</sub>SO<sub>4</sub> into (IV), whilst (IV) and O<sub>2</sub> in AcOH give (V). Esterification (MeOH-HCl; CH<sub>2</sub>N<sub>2</sub>; Me<sub>2</sub>SO<sub>4</sub>) of (III) affords the *Me*<sub>2</sub> ester, m.p. 250–258° (according to method of prep.), of allophæoporphyrin *a*<sub>7</sub> (VI), C<sub>35</sub>H<sub>36</sub>O<sub>7</sub>N<sub>4</sub>, also formed when (III) is kept for 1 year or treated with EtOH-C<sub>5</sub>H<sub>5</sub>N or EtOH-NH<sub>3</sub>. (VI) is unaffected by benzoquinone in 4% HCl and N<sub>2</sub> and is converted by conc. H<sub>2</sub>SO<sub>4</sub> into (III). Short reduction (HI-AcOH) of allomerised (O<sub>2</sub>-AcOH) (I) and subsequent hydrolysis (HCl) give (IV) and (after esterification with CH<sub>2</sub>N<sub>2</sub>) dihydrohydroxymethylphæophorbide (VII), C<sub>36</sub>H<sub>40</sub>O<sub>6</sub>N<sub>4</sub>, m.p. 272° (sinters at 263°), and phæoporphyrin 658 (VIII), C<sub>36</sub>H<sub>40</sub>O<sub>6</sub>N<sub>4</sub>, m.p. 221–228° (blackens at 190°) (characterised by an absorption max. at 658 mμ); (VIII) is obtained also by further reduction (HI) of (VII) and is converted by 12–14% HCl or 10% aq. NH<sub>3</sub> into (III). Reduction of the allomerised (I) under slightly differing conditions gives (IV), (VII), (VIII), and neophæoporphyrin *a*<sub>6</sub> (*Me* ester, C<sub>36</sub>H<sub>36</sub>O<sub>6</sub>N<sub>4</sub>, m.p. 270–272°; *oxime*), which is hydrolysed (7% HCl) to (III). Phæoporphyrin *a*<sub>6</sub> ester is hydrolysed (MeOH-KOH in EtOH-C<sub>5</sub>H<sub>5</sub>N and N<sub>2</sub>) to (VI). Hydrolysis of allomerised (I) to chlorins and esterification of the fraction sol. in 10% HCl gives a compound (IX), C<sub>37</sub>H<sub>42</sub>O<sub>7</sub>N<sub>4</sub>, m.p. 300°. (I) heated with AcOH affords (V) and a more basic porphyrin [the *Me* ester of which is identical with (IX)]. Details of the prep. of phæophorbides *a* and *b* from methylchlorophyllide by extraction with HCl in N<sub>2</sub> are given. Structures are suggested for most of the above new compounds.

H. B.

**Ultra-violet absorption of porphyrins.** A. TREIBS (Z. physiol. Chem., 1933, 217, 38; cf. this vol., 76).—The work of Bois (A., 1928, 345) and van der Bom is acknowledged.

J. H. B.

**Relations between constitution and spectra of porphyrins. Fluorescence of ætioporphyrin.** H. HELLSTRÖM (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 11, 5 pp.).—Irradiation of ætioporphyrin (I) in C<sub>5</sub>H<sub>5</sub>N with light of the same wave-lengths as the absorption bands causes variations in the intensities of the non-equiv. fluorescence bands; this does not occur in Et<sub>2</sub>O. The former results are due to the production of photoporphyrin [obtained when a conc.



solution of (I) in  $C_5H_5N$  is exposed to sunlight], which is altered by 25% HCl and 14% HCl- $Et_2O$ , and is probably formed by dehydrogenation of (I). H. B.

**Production of urobilin by the action of ultra-violet rays on chlorophyll and porphyrins.** B. GOUZON (Compt. rend., 1933, 196, 1542—1544).—Urobilin is formed when solutions of chlorophyll and hæmato-, oo-, and proto-porphyrins in  $CHCl_3$  or  $CHCl_3-C_5H_5N$  are exposed to ultra-violet rays at  $< 40^\circ$ . H. B.

**Bile pigments. XII. Dihydromesobilirubin.** H. FISCHER and H. BAUMGARTNER (Z. physiol. Chem., 1933, 216, 260—263; cf. A., 1932, 627).—An intermediate product in the reduction of mesobilirubin to mesobilirubinogen is *dihydromesobilirubin*, blackens at  $250^\circ$ , m.p.  $278-284^\circ$  (decomp.). J. H. B.

**Formation of hydrindones from unsaturated ketones.** K. VON AUWERS and E. RISSE (Annalen, 1933, 502, 282—299).—*p*-Xylene, cinnamoyl chloride (I), and  $AlCl_3$  in  $CS_2$  give 3-phenyl-4:7-dimethyl- $\alpha$ -hydrindone, b.p.  $198-202^\circ/11$  mm., m.p.  $94-95^\circ$  [oxime, m.p.  $218-219^\circ$  (Ac derivative, m.p.  $127-127.5^\circ$ ); phenylhydrazone, m.p.  $193-194^\circ$ ; semicarbazone, m.p.  $232^\circ$ ], also obtained when *p*-xylyl styryl ketone, m.p.  $41-42^\circ$  (from aceto-*p*-xylene, PhCHO, and MeOH-KOH), is treated with  $AlCl_3$  in  $CS_2$ . *p*-Xylene and crotonyl chloride (II) similarly give a mixture (A) of *p*-xylyl propenyl ketone (III) (not obtained pure) and 3:4:7-trimethyl- $\alpha$ -hydrindone (IV), b.p.  $142^\circ/12$  mm., m.p.  $32-33^\circ$  [oxime, m.p.  $144.5^\circ$  (Ac derivative, m.p.  $74-75^\circ$ ); *p*-nitrophenylhydrazone, m.p.  $195^\circ$ ; benzylidene derivative, m.p.  $90.5-91.5^\circ$ ]; (IV) is isolated from the product from (A) and  $AlCl_3$  in  $CS_2$ . Aceto-*p*-xylene,  $CH_2BrCO_2Et$ , and Zn in  $C_6H_6$  give Et  $\beta$ -hydroxy- $\beta$ -*p*-xylylbutyrate, b.p.  $140-155^\circ/12$  mm., dehydrated by 90%  $HCO_2H$  to the Et ester, b.p.  $150-154^\circ/20$  mm., of  $\beta$ :2:5-trimethylcinnamic acid, m.p.  $68^\circ$  (which is probably the *trans*-form); the acid is reduced (Na-Hg, aq.  $Na_2CO_3$ ) to  $\beta$ -*p*-xylylbutyric acid, m.p.  $111-112^\circ$ , the chloride of which with  $AlCl_3$  in  $CS_2$  gives (IV).  $\alpha\beta$ -Dibromobutyryl-*p*-xylene, m.p.  $62-63^\circ$  (from *p*-xylene,  $CHMeBrCHBrCOCl$ , and  $AlCl_3$  in  $CS_2$ ), and EtOH-KI also afford impure (III). (IV) is also produced during the condensation of  $\beta$ -chlorobutyryl chloride and *p*-xylene.

*m*-Xylene and (I) give *m*-4-xylyl styryl ketone, b.p.  $218-219^\circ/11$  mm., m.p.  $71-72^\circ$ , which does not yield an oxime, semicarbazone, or phenylhydrazone, and is unaffected by  $AlCl_3$ ; in one condensation, a little 3-phenyl-5:7-dimethyl- $\alpha$ -hydrindone, m.p.  $101^\circ$  (semicarbazone, m.p.  $195-197^\circ$ ), was produced. *m*-4-Xylyl propenyl ketone, b.p.  $144-146^\circ/15$  mm., formed using (II), is polymerised by  $AlCl_3$ . *o*-Xylene and (I) afford *o*-4-xylyl styryl ketone, m.p.  $72-73^\circ$  (dibromide, m.p.  $87-88^\circ$ ), which with  $NH_2OH.HCl$  in EtOH gives 5-phenyl-3:3':4'-dimethylphenylisooxazoline, m.p.  $179.5-180.5^\circ$ ; and with  $p-NO_2.C_6H_4.NH.NH_2$  yields 5-phenyl-1-*p*-nitrophenyl-3:3':4'-dimethylphenylpyrazoline, m.p.  $172-173^\circ$ . *o*-4-Xylyl propenyl ketone, b.p.  $138-140^\circ/12$  mm., polymerises readily. PhMe and (I) give *p*-tolyl styryl ketone and a saturated additive compound (not isolated); with (II), *p*-tolyl propenyl ketone, b.p.

$132-134^\circ/11$  mm., results. *m*-Tolyl styryl ketone, b.p.  $214-216^\circ/11$  mm. (from *m*- $C_6H_4Me.COMe$  and PhCHO), is converted by  $AlCl_3$  at  $100^\circ$  into 3-phenyl-6-methyl- $\alpha$ -hydrindone, b.p.  $210-220^\circ/11$  mm. (*p*-nitrophenylhydrazone, m.p.  $236-238^\circ$ ). The production of Ph  $\beta\beta$ -diphenylethyl ketone and 3-phenyl- $\alpha$ -hydrindone from  $C_6H_6$  and (I) is confirmed.  $C_6H_6$  and (II) give Ph propenyl ketone, b.p.  $124-128^\circ/14$  mm. (cf. A., 1921, i, 466). 3-Methyl- $\alpha$ -hydrindoneoxime has m.p.  $99-100^\circ$  (lit.  $141.5^\circ$ ). The ring closures show that the *o*-H in PhMe is more reactive than the *p*-H atom, which is more reactive than a H in  $C_6H_6$ , which is more reactive than the *m*-H in PhMe (cf. von Braun *et al.*, A., 1929, 562). H. B.

[Hydroxylamine derivatives of ketones.] II. Derivatives of benzylideneacetone, ethylideneacetophenone, and benzoylacetone. III. *iso*-Oxazolines and *isooxazoles*. K. VON AUWERS and H. MÜLLER (J. pr. Chem., 1933, [ii], 137, 81—101, 102—130; cf. this vol., 611).—Styryl Me ketone does not form an oximino-oxime; the normal oxime, m.p.  $116^\circ$ , with HCl gives an isomeride, which usually has m.p.  $105-106^\circ$ , but often lower. The second oxime, when pure, gives by the Beckmann change acetylstyrylamine, but, when impure, methylcinnamamide. Ethylideneacetophenone does not form a simple oxime; with  $NH_2OH$  and a drop of HCl in hot abs. EtOH it gives  $\beta$ -hydroxylaminobutyrophenone-oxime (I), m.p.  $151-152^\circ$  ( $Bz_2$  derivative, m.p.  $124-125^\circ$ ), and a little "*B*-isooxazole," 3-phenyl-5-methylisooxazole (II), m.p.  $43^\circ$ . (I) is stable to hot, dil., or conc. HCl, and cold  $NH_3-MeOH$ ; when boiled for a day with  $2N-H_2SO_4$ , it gives  $NH_2OH$  and the "*A*-isooxazole," 5-phenyl-3-methylisooxazole (III), m.p.  $68^\circ$ ; when heated above the m.p., or boiled for 15 min. with AcOH, it gives (II); when kept in cold NaOH or oxidised by  $K_3Fe(CN)_6$ , it gives benzoylacetone-oxime (IV); when boiled for a few min. with  $HCO_2H$ , it forms  $NH_3$  and  $\beta$ -N-formylhydroxylaminobutyrophenone (*propio*phenone- $\beta$ -formylhydroxamic acid) (V), m.p.  $95-96^\circ$  ( $Cu$  salt; Ac derivative, m.p.  $96^\circ$ ), and some (III); when boiled for 15 min. with  $HCO_2H$ , (V) yields (III), also formed almost exclusively by similar treatment of (II). With hot NaOH (V) gives  $COPhMe$  and (?)  $CH_2O$ .  $CH_2BzAc$  (VI) and cold  $NH_2OH$  (2 mols.) in aq. EtOH give benzoylacetone-oxime (VII), an oil ( $Bz_2$  derivative, m.p.  $68-70^\circ$ ); when heated, however, (III) is formed (cf. A., 1926, 406); (III) is also obtained if  $NH_2OH.HCl$  (3 mols.) and KOH (1.5 mols.) in cold aq. MeOH are used. (VI),  $NH_2OH$  (2 mols.), and NaOH (2 mols.) in cold aq. EtOH give (II) and (VII); when this solution is boiled, (II), (IV), and  $COPhMe$  are obtained. Hot or cold  $K_3Fe(CN)_6$  oxidises (VII) to  $BzOH$ . (VI),  $NH_2OH$  (3 mols.), and NaOH (3 mols.) in cold aq. EtOH give (IV), m.p.  $86-87^\circ$  or  $95^\circ$  ( $Bz$  derivative, m.p.  $148-149^\circ$ , unchanged by  $PCl_5$ ), oxidised by  $K_3Fe(CN)_6$  to (II). *O*-Benzoylacetophenoneoxime, m.p.  $98-100^\circ$ , is also stable to  $PCl_5$ . With boiling  $HCO_2H$  or cold, dil. HCl (IV) gives (III), but with aq. NaOH more slowly (II). The constitutions of (IV) and (VII) are supported by refractometric data.

III. Ph styryl ketone (VIII) (1 mol.),  $NH_2OH.HCl$  (1 mol.), and NaOEt (1.5 mol.) in cold EtOH give



3:5-diphenylisooxazoline (IX); the oxime of (VIII), however, is unchanged by excess NaOH, with or without  $\text{NH}_2\text{OH}$ , in hot or cold solvents.  $\text{NN}'$ -Di-( $\alpha$ -phenyl- $\beta$ -benzoyl-ethyl)hydroxylamine is entirely or mostly unchanged by  $\text{NH}_2\text{OH}$  in cold EtOH, cold EtOH-NaOH, or hot, conc. HCl, but in hot EtOH-NaOH gives (II) and a little CPhMe. Styryl Me ketoxime (either isomeride) is stable to alkali, but with cold, conc.  $\text{H}_2\text{SO}_4$  gives 5-phenyl-3-methylisooxazoline, b.p. 151—152°/13 mm. This method gives a good yield of pure (IX) from (VIII), but fails with *Bz*- or  $\alpha$ -substituted derivatives. Crotonylbenzene in cold EtOH-NaOH yields 3-phenyl-5-methylisooxazoline (X), m.p. 49—50° (completely degraded by  $\text{CrO}_3$ -AcOH), but in hot solution a trace of oxaminoxime is also formed.  $\beta$ -Chloropropionic acid (XI) and NaOAc or KOAc in hot AcOH afford a little Ph vinyl ketone (XII) and much  $\beta$ -acetoxypropionic acid, m.p. 53—54° [hydrolysed by KOH to (XII)], which with  $\text{NH}_2\text{OH}$  and excess of hot KOH-EtOH gives 3-phenylisooxazoline, m.p. 66—67° (degraded by  $\text{CrO}_3$ ), also obtained similarly from (XI) together with  $\text{NN}'$ -di-( $\beta$ -benzoyl-ethyl)hydroxylaminedioxime, m.p. 154—155°. The dioxime reduces warm Fehling's solution, is sol. in acids and alkalis, and is also formed with the isooxazoline in the cold; with hot HCl (1:1) it gives  $\text{NN}'$ -di-( $\beta$ -benzoyl-ethyl)hydroxylamine, m.p. 140°, which with  $\text{NH}_2\text{OH}$  in cold EtOH-NaOH gives a mixture of isooxazolines, containing a substance, m.p. 58—59°, probably 5-phenylisooxazoline.  $\beta$ -Chlorobutyryl chloride, b.p. 51—53°/21 mm. (from the acid, b.p. 108—110°/11 mm.),  $\text{AlCl}_3$ , and  $\text{C}_6\text{H}_6$  in  $\text{CS}_2$  give a mixture of Ph propenyl ketone and  $\beta$ -phenylbutyrophenone. The former ketone and HCl in AcOH give  $\beta$ -chlorobutyrophenone, m.p. 24—25°. This, when kept with  $\text{NH}_2\text{OH}$ , HCl (3 mols.) and KOH (1.5 mols.) in cold EtOH for a day, gives (I), but after 2 days some (III) is also formed; with excess of NaOH in the cold (I) and (X) are obtained. Acetylacetonedioxime is unchanged by  $\text{PCl}_5$  in  $\text{Et}_2\text{O}$ ; with  $\text{K}_3\text{Fe}(\text{CN})_6$  it gives 3:5-dimethylisooxazole. The configurations of the isooxazolines are supported by refractometric data, only those substances having a N:CPh grouping giving a large exaltation. From the above and previously recorded data it is concluded that isooxazolines are not formed by direct ring-closure of *syn*-oximes, but by way of either oxaminoximes or disubstituted hydroxylamines, which, however, must be more reactive in the "nascent" state than after isolation. The mechanism of the formation of isooxazoles is discussed. R. S. C.

**Dioximes. XCIX.** G. PONZIO and F. BIGLIETTI (Gazzetta, 1933, 63, 159—171).—Dioximes of the type  $\text{CAr}(\text{NOH})\cdot\text{C}\begin{smallmatrix} \nearrow \text{CAr}(\text{NOH})\cdot\text{N} \\ \searrow \text{O} \end{smallmatrix}$  when heated with dil. NaOH, or even alone, isomerise to those of the type  $\text{CAr}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{C}\begin{smallmatrix} \nearrow \text{CAr}\cdot\text{N} \\ \searrow \text{O} \end{smallmatrix}$ . Thus, when  $\text{Ar}=\text{Ph}$ , 3:4-dibenzoyl-1:2:5-oxadiazoledioxime ( $\text{Ac}_2$ , m.p. 95°, and  $\text{Bz}_2$ , m.p. 148—149°, derivatives), of which the peroxide (A., 1927, 1207) is reduced by  $\text{SnCl}_2$ , gives rise to the  $\alpha$ -dioxime (I) of 3-benzoyl-formyl-4-phenyl-1:2:5-oxadiazole, m.p. 203—204° (decomp.) ( $\text{Ac}_2$ , m.p. 102—103°, and  $\text{Bz}_2$ , m.p. 119—

120°, derivatives), and to the  $\beta$ -dioxime (II), m.p. 189—190° ( $\text{Ac}_2$ , m.p. 113—114°, and  $\text{Bz}_2$ , m.p. 118—119°, derivatives), isolated through its *Ni* salt, m.p. 262—263° (decomp.). (I) is partly converted into (II) when heated; with  $\text{N}_2\text{O}_4$  or  $\text{HNO}_3$  both give peroxides, m.p. 135—136° and 131—132°, respectively. With  $\text{POCl}_3$  (II) yields 3:4'-diphenyl-5:3'-(1:2:4-oxadiazolyl)-1':2':5'-oxadiazole, m.p. 100—101°. Another product of heating (I) or of reducing the peroxides of (I) or (II) is 4:4'-diphenyl-3:3'-di-1:2:5-oxadiazolyl, m.p. 136—137°. When  $\text{Ar}=\text{p-C}_6\text{H}_4\text{Me}$ , the  $\alpha$ -dioxime, m.p. 218—219° (decomp.), of 3-*p*-toluoylformyl-4-*p*-tolyl-1:2:5-oxadiazole is separated from the  $\beta$ -dioxime, m.p. 199—200°, through the *Ni* salt of the latter. 4:4'-Di-*p*-tolyl-3:3'-di-1:2:5-oxadiazolyl has m.p. 147—148°. E. W. W.

**Naphthathiazole series. I. Constitution of the bromo-additive compounds of bromo-substituted alkylamino- $\beta$ -naphthathiazoles obtained in the bromination of *s*- $\alpha$ -naphthylalkylthiocarbamides.** C. HASAN and R. F. HUNTER (J. Indian Chem. Soc., 1933, 10, 81—89).—Extensive bromination of *s*- $\alpha$ -naphthylmethylthiocarbamide (I) in boiling  $\text{CHCl}_3$  affords 8-bromo-2-methylamino- $\beta$ -naphthathiazole hydropentabromide (II), m.p. 135° (decomp.), which easily loses Br to give the hydrotribromide (III), m.p. 163° (decomp.) (cf. A., 1927, 263), and is further reduced by  $\text{SO}_2$  to 8-bromo-2-methylamino- $\beta$ -naphthathiazole, m.p. 194—195° (*Ac* derivative, m.p. 208°). 4-Bromo- $\alpha$ -naphthylamine in  $\text{CHCl}_3$  and  $\text{CSCl}_2$  in  $\text{H}_2\text{O}$  afford 4-bromo- $\alpha$ -naphthylthiocarbimide, m.p. 90°, which with  $\text{NH}_2\text{Me}$  in aq. EtOH affords *s*-4-bromo- $\alpha$ -naphthylmethylthiocarbamide, m.p. 179°, converted into (II) when boiled with Br in  $\text{CHCl}_3$  during 5 min., and by less vigorous bromination into (III) [also obtained from (I)], which is further brominated to (II). Less exhaustive bromination of (I) affords 8-bromo-2-methylamino- $\beta$ -naphthathiazole hydrotetrabromide, m.p. 195° (decomp.) (cf. A., 1930, 483), also obtained by keeping (III) over KOH. *s*- $\alpha$ -Naphthylethylthiocarbamide similarly gives rise to 8-bromo-2-ethylamino- $\beta$ -naphthathiazole hydropentabromide (IV), m.p. 93° [also obtained from *s*-4-bromo- $\alpha$ -naphthylethylthiocarbamide (V), m.p. 82° (prep. as above)], and a hydrotribromide, m.p. 204° [also obtained from (IV) and (V)], both reduced by  $\text{SO}_2$  to 8-bromo-2-ethylamino- $\beta$ -naphthathiazole, m.p. 147° (*Ac* derivative, m.p. 172—173°). Similarly, *s*- $\alpha$ -naphthylisoamylthiocarbamide gives rise to 8-bromo-2-isoamylamino- $\beta$ -naphthathiazole hydropentabromide (VI), m.p. 79—80° [also obtained from *s*-4-bromo- $\alpha$ -naphthylisoamylthiocarbamide (VII), m.p. 128°], and a hydrotribromide, m.p. 121° [also obtained from (VI)], reduced by  $\text{SO}_2$  to 8-bromo-2-isoamylamino- $\beta$ -naphthathiazole, m.p. 126°.

J. L. D.

**Constitution of the so-called dithiourazole of Martin Freund. V. Isomerism of hydrazodithiodicarbonyl amides, iminothiolthiodiazoles, and di-*R*-iminothiodiazoles. VI. Isomerism of hydrazomonothiodicarbonyl amides, iminothiodiazolones, and monothiourazoles.** S. L. JANNIAH and P. C. GUHA (J. Indian Inst. Sci., 1933, 16 A, 11—18, 19—27).—V. Hydrazodithiodicarbonyl-



methyl-, -mono- and -di-phenyl- (I), and -o-tolyl- (II)-amide when boiled with 2*N*-HCl afford *isomerides*, m.p. 198°, 162° (III), 173°, and 178°, respectively (cf. A., 1931, 369). (III) is converted by HCl into iminothiolthiodiazole or *endoiminothiolthiodiazole* according to the concn. of the acid. (I) with boiling HCl (*d* 1.16) affords the alkali-sol. 5-*anilo*-4:5-*dihydro*-2-*thiol*-1:3:4-*thiodiazole*, m.p. 219° (cf. A., 1895, i, 400), and some PhNCS, whereas with HCl (*d* 1.19) alkali-insol. 2:5-*dianilo*-2:3:4:5-*tetrahydro*-1:3:4-*thiodiazole* (IV), m.p. 249° (decomp.) [Ac<sub>2</sub> derivative (V), m.p. 224°], identical with that of Guha (A., 1923, i, 607), is obtained. Hydrolysis of (V) with dil. HCl affords (IV), whereas HCl (*d* 1.19) affords PhNCS and 2-*anilino*-2:5-*endoanilo*-2:3-*dihydro*-1:3:4-*thiodiazole*, m.p. 208°. (II) and boiling HCl (*d* 1.16) afford some thiocarbimide and 5-*o*-tolylimino-4:5-*dihydro*-2-*thiol*-1:3:4-*thiodiazole*, m.p. 195° (oxidised by I to a disulphide), whereas with boiling HCl (*d* 1.19) it affords 2:5-*di*-*o*-tolylimino-2:3:4:5-*tetrahydro*-1:3:4-*thiodiazole* (VI), m.p. 217° (decomp.) (not oxidised by I). The Ac<sub>2</sub> derivative of (VI), m.p. 262°, with boiling dil. HCl affords (VI), whereas with HCl (*d* 1.19) it affords 2-*o*-tolylimino-2:5-*endo*-*o*-tolylimino-2:3-*dihydro*-1:3:4-*thiodiazole*, m.p. 133°.

VI. Hydrazomonothiodicarbonamide (I) with boiling 2*N*-HCl affords only NH<sub>2</sub>·NH·CS·NH<sub>2</sub>·HCl (see above), but with boiling 5*N*-HCl cyclises to 2:5-*endoxy*-1:3:4-*triazole* (II) (A., 1927, 784). Boiling HCl (*d* 1.19) with (I) affords both (II) and 2-*imino*-5-*keto*-1:3:4-*thiodiazole* (III), m.p. 177° [Ac derivative (IV), m.p. 295°]. (IV) is hydrolysed by boiling conc. HCl to 2-*amino*-2:5-*endoxy*-2:3-*dihydro*-1:3:4-*thiodiazole*, an isomeride of (III), previously obtained by Guha (A., 1923, i, 607). Hydrazomonothiodicarbon-phenyl- (V), -methyl- (VI), and -allyl- (VII) are isomerised (see above) by boiling dil. HCl to *substances*, m.p. 175°, 168°, and 192°, respectively. (V) with boiling HCl (*d* 1.19) affords 2-*thiol*-2:5-*endoxy*-1-*phenyl*-2:3-*dihydro*-1:3:4-*triazole* (VIII), m.p. 184° [disulphide, m.p. 196°; S-Me ether, m.p. 90—91°; Ac<sub>2</sub> derivative, hydrolysed (conc. HCl) to a product, m.p. 206°, identical with that obtained by Guha and Chakravarti (A., 1929, 582) and now assigned the structure 2-*anilino*-2:5-*endoxy*-2:3-*dihydro*-1:3:4-*thiodiazole*]. Similarly, (VI) and (VII) with boiling HCl (*d* 1.19) afford 2-*thiol*-2:5-*endoxy*-1-*methyl*-, m.p. 182° (disulphide, m.p. 265°; Ac derivative, m.p. 196—197°, hydrolysed by conc. HCl to 2-*methylamino*-2:5-*endoxy*-2:3-*dihydro*-1:3:4-*thiodiazole*, m.p. 232°), and 2-*thiol*-2:5-*endoxy*-1-*allyl*-2:3-*dihydro*-1:3:4-*triazole* (disulphide, m.p. 174°; Ac derivative, m.p. 171°, hydrolysed by boiling conc. HCl to 2-*allylamino*-2:5-*endoxy*-2:3-*dihydro*-1:3:4-*thiodiazole*, m.p. 210—211°), respectively.

J. L. D.

**Alkaloids of *Heliotropium lasiocarpum*. II. Degradation of heliotridine to heliotridane.** G. MENSCHIKOV (Ber., 1933, 66, [B], 875—878; cf. A., 1932, 865).—The presence of 2OH in heliotridine (I) is established by the isolation of the Bz<sub>2</sub> derivative as *hydrochloride*, m.p. 180°; NMe is not present. (I) is mainly resinified by red P and HI at 200—210°.

Cautious treatment of (I) with SOCl<sub>2</sub> causes replacement of 2OH by 2Cl and the unstable product is catalytically reduced (PtO<sub>2</sub>) to *chloroheliotridane* (II), C<sub>8</sub>H<sub>14</sub>NCl, b.p. 84—85°/10 mm., [α]<sub>D</sub> -133.5° [*picrate*, m.p. 242° (decomp.)], which, rapidly when heated, slowly when preserved, becomes cryst. and then contains ionisable Cl. (II) is stable to Zn and HI and to H<sub>2</sub> (Pd-CaCO<sub>3</sub>) but is transformed by NaOEt in boiling EtOH into *heliotridine* C<sub>8</sub>H<sub>13</sub>N, b.p. 54—55°/12 mm., [α]<sub>D</sub> -10.5°, reduced by Na and EtOH followed by H<sub>2</sub> (PtO<sub>2</sub>) to *heliotridane* C<sub>8</sub>H<sub>15</sub>N, b.p. 169—170°, [α]<sub>D</sub> -68° [*methiodide*, decomp. 240—250°; *picrate*, m.p. 236° (decomp.)].

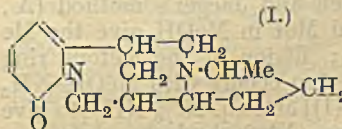
H. W.

**Alkaloids of *Salsola Richteri*.** A. OREKHOV and N. PROSKURNINA (Ber., 1933, 66, [B], 841—843).—Percolation of the foliage of *S. Richteri* with EtOH containing 2% of AcOH, evaporation of the solution to dryness, and treatment of the residue with 2% HCl in C<sub>6</sub>H<sub>6</sub> followed by K<sub>2</sub>CO<sub>3</sub> and CHCl<sub>3</sub> leads to *salsoline* (I), C<sub>11</sub>H<sub>15</sub>O<sub>2</sub>N, m.p. 218—211°, optically inactive (*hydrochloride* (+1.5H<sub>2</sub>O), m.p. indef. 141—152°; Bz<sub>2</sub>, m.p. 166—168°, and N-Bz, m.p. 172—174° derivatives). (I) and MeI in MeOH yield *methylsalsoline methiodide*, m.p. 232—235° (Bz derivative, m.p. 249—253°). (I) is therefore OH·C<sub>10</sub>H<sub>10</sub>(NH)·OMe.

H. W.

**Alkaloids of *Anagyris foetida* and their relation to the lupin alkaloids.** H. R. ING (J.C.S., 1933, 504—510).—Improved separation from the mixed alkaloids is described; anagyrine is more readily extracted by C<sub>6</sub>H<sub>6</sub> from aq. solution than is cytisine, and *anagyrine perchlorate*, decomp. 270°, is less sol. in H<sub>2</sub>O than *cytisine perchlorate*. Anagyrine, C<sub>15</sub>H<sub>20</sub>ON<sub>2</sub> (I), has not been obtained cryst., has [α]<sub>D</sub><sup>20</sup> -165.3°, and forms a Br<sub>2</sub>-derivative, m.p. 202—203°, which does not lose HBr with KOH. (I) is oxidised with Ba(MnO<sub>4</sub>)<sub>2</sub> to *anagryamide*, m.p. 201—202° (cf. Litterscheid, A., 1900, i, 514, "anagryne oxide"), which with HI and P gives *anagryamine*, m.p. 98—99° (Ac derivative, m.p. 134—135°; NO-derivative, m.p. 127—128°), and is ozonised to a *lactam*, m.p. 258° (*benzenesulphonyl* derivative, m.p. 141°). Anagyrine methiodide, m.p. 264° (decomp.), affords the methoxyhydroxide, which is reduced (Pd-H<sub>2</sub>) to *dihydromethyl-anagyrine*, b.p. 180—190°/1 mm.; two further degradations give *hexahydroanagryline*, C<sub>15</sub>H<sub>23</sub>ON, b.p. 155—160°/4 mm., ozonised to a *lactam*, C<sub>11</sub>H<sub>21</sub>ON, b.p. 140—150°/4 mm., which is hydrolysed and subsequently oxidised by KMnO<sub>4</sub> to an *acid*, C<sub>11</sub>H<sub>20</sub>O<sub>4</sub>, b.p. 180—200°/4 mm. This acid is converted through the anhydride into *α-methyl-α'-n-amyglutarimide*, m.p. 53—54°, identical with the synthetic specimen obtained from the corresponding -*glutaric acid*, b.p. 180—200°/4 mm.

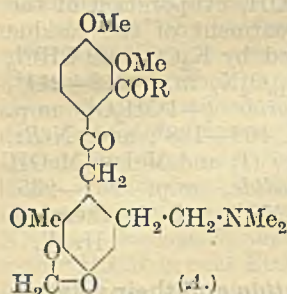
(I) is derived from cytisine with the addition of a new methylpyrrolidine ring. Anagyrine hydrochloride is reduced (Pd-H<sub>2</sub>) to *tetrahydroanagryline*, b.p. 186—190°/1 mm., [α]<sub>D</sub><sup>20</sup> -61.45°, identical with *L*-lupinane (*perchlorate*, m.p. 210°). Electrolysis of (I) in 50% aq. H<sub>2</sub>SO<sub>4</sub> gives *hexahydrodeoxyanagryline*, b.p. 130—135°/1 mm.,





$[\alpha]_D^{19} + 10.9^\circ$  (monoperchlorate, m.p. 169—170°), which appears to be identical with *d*-sparteine (*l*-sparteine monoperchlorate, m.p. 171—172°). Lupinane must be (I) with the N ring fully hydrogenated and sparteine is derived from it by replacing CO by CH<sub>2</sub>. F. R. S.

**Narcotine and hydrastine. Mechanism of their conversion into narceine, methylhydrastine, and their derivatives.** C. R. ADDINALL and R. T. MAJOR (J. Amer. Chem. Soc., 1933, 55, 2153—2163).—The *Me* ester *hydriodide*, m.p. 181—182°, hydrochloride, m.p. 150—151°, and *Me H sulphate*, m.p. 213—214°, of narceine (I) (*A*, R=OH) are obtained when narcotine methiodide (II), methochloride (III), and methosulphate (IV), respectively, are boiled with MeOH in dry NH<sub>3</sub>; the *Et* ester *hydriodide*, m.p. 212—213°, and *hydrochloride*, m.p.



208—210°, the *Pr*<sup>B</sup> ester *hydriodide*, m.p. 224—225°, and the *Bu* ester *hydriodide*, m.p. 185—186°, of (I) are similarly prepared from the requisite quaternary salt. (II) boiled with H<sub>2</sub>O containing a little C<sub>5</sub>H<sub>5</sub>N gives (I), also formed by hydrolysis of (III) and (IV) with boiling H<sub>2</sub>O. (II) and liquid NH<sub>3</sub> give the *hydriodide* (V), softens at 182° with evolution of gas and melts at 216—218° to a red gum, of *narceinamide* (VI) (*A*, R=NH<sub>2</sub>); the hydrochloride of (VI) is similarly prepared from (III). Repeated crystallisation of (V) from H<sub>2</sub>O gives *narceinimide hydriodide*, m.p. 228°, whilst boiling MeOH converts it into an *imide hydriodide* (+MeOH), m.p. 216° (decomp.). (II) heated with 28% aq. NH<sub>3</sub> affords (I) and (VI) (m.p. 178°); (VI) is also produced from (IV) and cold 28% aq. NH<sub>3</sub> and from (II) or (IV) and aq. EtOH-NH<sub>3</sub>. The diethylaminoethyl ester (+MeOH), m.p. 203°, of (I) is obtained by heating (II) with an excess of NEt<sub>2</sub>·C<sub>2</sub>H<sub>4</sub>·OH and dilution with H<sub>2</sub>O. Hydrastine methiodide (VII) boiled with H<sub>2</sub>O gives *methylhydrastine hydriodide*, m.p. 216—217°; with liquid NH<sub>3</sub>, *methylhydrastamide hydriodide*, m.p. 233—235° (converted by dil. aq. NH<sub>3</sub> into methylhydrastimide), results. (VII) and 28% aq. NH<sub>3</sub> afford methylhydrastamide, which is also obtained from methylhydrastine and 28% aq. NH<sub>3</sub> in presence or absence of dioxan. (VII) boiled with EtOH in NH<sub>3</sub> gives the *Et* ester *hydriodide* (VIII), m.p. 235—236°, of methylhydrastine. Mechanisms are advanced which explain the above changes.

Methylnarcotine (IX) is obtained by Rabe and McMillan's procedure (A., 1911, i, 77), but could not be prepared by Tambach and Jaeger's method (A., 1906, i, 879). (IX) and MeI in MeOH give the *Me* ester methiodide of (I); fission of the lactone ring first occurs. Similar fission occurs with MeOH-NH<sub>3</sub> [to give the *Me* ester of (I)] and aq. 28% NH<sub>3</sub> [to give (VI)]. Methylhydrastine (X) is hydrolysed by aq. NaOH (not by H<sub>2</sub>O) to methylhydrastine (XI); with MeOH-NH<sub>3</sub>, the *Me* ester, m.p. 175°, of (XI) results. Contrary to Schmidt (A., 1890, 1167), (X) and aq. EtOH do not give the *Et* ester, m.p. 194—

195° [*chloroplatinate*, m.p. 210° (decomp.)], of (XI), which is obtained from (X) and EtOH-NH<sub>3</sub>. The *hydriodide*, m.p. 257—258°, of (X) is unaffected by liquid NH<sub>3</sub> or boiling with H<sub>2</sub>O or EtOH; EtOH-NH<sub>3</sub> converts it into (VIII). Narcotine heated with BzCl gives *benzoylnarceine* (+MeOH), m.p. 174—175° (*A*, R=OH, and NMe<sub>2</sub>=NMeBz). H. B.

**Amine oxides of alkaloids. IX. Action of hydrogen peroxide on narcotimethine and hydrastimethine. Stereochemistry of hydrastine and narcotine.** MAX POLONOVSKI and MICHEL POLONOVSKI (Bull. Soc. chim., 1933, [iv], 53, 268—276).—Action of H<sub>2</sub>O<sub>2</sub> in COMe<sub>2</sub> on *hydrastimethine* (I) (the base from hydrastine methiodide), m.p. 157° (*hydrochloride*, m.p. 249°), gives *hydrasteimethine N-oxide* (II), m.p. 213° [*hydrochloride*, m.p. 230°], and a small amount of its *anhydro-base* (III), m.p. 186° (*hydrochloride*, m.p. 230°; *nitrate*, m.p. 235°). (III) is also formed by repeated evaporation of (II) with dil. HCl and treatment of the yellow insol. salt thus formed with dil. NaOH; on warming with NaOH it is reconverted into (II). SO<sub>2</sub> in COMe<sub>2</sub> or H<sub>2</sub>O converts (II) into *hydrasteimethine O-sulphate*, m.p. 249°, but is without action on (III); similarly, (II) gives with Ac<sub>2</sub>O at 100° *acetylnorhydrastimethine*, m.p. 200°, and an amorphous *Ac<sub>n</sub>* derivative: (II) and (III) are therefore considered to be OH-acid and lactone, respectively.

Reduction of (I) with Na-Hg in dil. NaOH gives *dihydrohydrasteimethine* (IV), m.p. 174°, readily converted by acids, even by SO<sub>2</sub>, into *dihydrohydrastimethine*, which is delactonised to (IV) by NaOH or H<sub>2</sub>O<sub>2</sub> without formation of an *N*-oxide in the latter case. The difference in behaviour between (I) and narcotimethine (cf. A., 1931, 969) is attributed to geometrical isomerism about the meconic acid-isoquinoline double linking. H. A. P.

**Alkaloids of fumaraceous plants. IV. *Adlumia fungosa*, Greene.** R. H. F. MANSKE (Canad. J. Res., 1933, 8, 210—216).—A general method for the separation of the alkaloids of fumaraceous plants is described. From *A. fungosa* are isolated fumaric acid, protopine, bicuculline, *adlumidine*, C<sub>19</sub>H<sub>15-17</sub>O<sub>6</sub>N, m.p. 235° (OMe-free), and *adlumine*, C<sub>21</sub>H<sub>21</sub>O<sub>6</sub>N, m.p. 180° [a (OMe)<sub>2</sub>-compound]. The last-named is probably not identical with the alkaloid previously described under the same name, m.p. 188° (cf. A., 1900, ii, 746; 1903, i, 512), which may be the impure isomeride of bicuculline, m.p. 198°.

H. A. P.

**Kurchi alkaloids. I. Bases from *Holarrhena anti-dysenterica*.** A. BERTHO, G. VON SCHUCKMANN, and W. SCHÖNBERGER (Ber., 1933, 66, [B], 786—790).—The following bases are obtained from the crude alkaloids sol. in light petroleum after removal of conessine (I) as the oxalate. (A) *Conessidine*, C<sub>21</sub>H<sub>32</sub>N<sub>2</sub>, m.p. 123°,  $[\alpha]_D^{25} -52.2^\circ$  in CHCl<sub>3</sub>, a di-acid base containing 1NMe, which very closely resembles (I) and probably imparts the feeble pharmacological activity to conessine preps.; *hydriodide*, m.p. 259° (decomp.) after becoming discoloured at 200°; *perchlorate*, C<sub>21</sub>H<sub>32</sub>N<sub>2</sub>·2HClO<sub>4</sub>·H<sub>2</sub>O, m.p. 243° (decomp.). (B) *Conkurchine*, C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>,



m.p. 153°,  $[\alpha]_D^{25}$  -67.4° in 96% EtOH, a very sensitive base which does not contain NMe, gives an amorphous *methiodide*, m.p. 274° after becoming discoloured at 220°, *sulphate*, m.p. 342°, *oxalate*, decomp. 325°, and *Ac* derivative, m.p. 233°. (C) *Kurchenine*,  $C_{21}H_{32}O_2N_2$ ,  $[\alpha]_D^{25}$  -92.0° in 2*N*-HCl, a di-acid base which does not contain NMe or OMe, is insol. in Et<sub>2</sub>O, sparingly sol. in MeOH or EtOH (*sulphate*,  $C_{21}H_{32}O_2N_2 \cdot H_2SO_4 \cdot EtOH$ ,  $[\alpha]_D^{25}$  -78.3° in H<sub>2</sub>O). Reasons are advanced for considering many of the *Kurchi* alkaloids to be non-homogeneous. H. W.

**Preparation and optical rotation of pure quinidine.** C. L. BUTLER and L. H. CRETCHER (J. Amer. Pharm. Assoc., 1933, 22, 414—415).—Pure quinidine, prepared from quinine ( $C_5H_{11} \cdot OH \cdot KOH$ ), had m.p. 170—171°,  $[\alpha]_D^{25}$  +262.0° in abs. EtOH, +323.8° in HCl. E. H. S.

**Strychnine and brucine. XXIV. Synthesis of dinitrostrycholamide.** P. HILL and R. ROBINSON (J.C.S., 1933, 486—488).—3:5-Dinitro-2-hydroxybenzaldehyde, m.p. 62—63° (lit., 58—60°) [*phenylhydrazone*, m.p. 228° (decomp.); *semicarbazone*, prisms, decomp. 231°, needles, decomp. 239°], condenses with hippuric acid to give 2-*phenyl*-4-(3':5'-dinitro-2'-hydroxybenzylidene)oxazolone, m.p. 302—303° (decomp.); 3:5-dinitro-2-methoxybenzaldehyde, m.p. 86—87° [methylation by CH<sub>2</sub>N<sub>2</sub>; *phenylhydrazone*, m.p. 214° (decomp.); *semicarbazone*, m.p. 205° (decomp.)], similarly forms the 2'-*methoxy*-oxazolone (I), m.p. 185.5°, and in one experiment, a substance, m.p. about 215° (decomp.), has been obtained. (I) is hydrolysed by aq. NaOH to 3:5-dinitro-2-hydroxy- $\alpha$ -benzamidocinnamic acid, m.p. 218° (decomp.), and affords with MeOH-NH<sub>3</sub>, 5:7-dinitroindole-2-carboxylamide, m.p. 263° (decomp.), identical with a specimen obtained from dinitrostrychol through the acid chloride. F. R. S.

**Solanidine.** A. SOLTYS (Ber., 1933, 66, [B], 762—765).—Solanine is heated with 10% HCl at 100° under conditions such that most of the solanidine hydrochloride (I), m.p. 345° (decomp.), separates on cooling, whereas *solanthrene hydrochloride* remains dissolved. Purification of (I) from 80% EtOH and subsequent decomp. with NaOH and crystallisation of the base from Et<sub>2</sub>O yields solanidine (II),  $C_{27}H_{43}ON$ , m.p. 170°,  $[\alpha]_D^{25}$  -27.3° in CHCl<sub>3</sub>, which does not contain NMe. The *Ac* derivative, m.p. 204°, and the *methiodide* (III), m.p. 280° (decomp.), of (II) are described. Treatment of (III) with Ag<sub>2</sub>O and decomp. of the base at 130° gives MeOH and (II), whereas rapid heating to 280° affords *isosolanidine*  $C_{27}H_{43}ON$ , m.p. 169°. Although indifferent toward KMnO<sub>4</sub>, (II) is converted by energetic hydrogenation (PtO<sub>2</sub>-AcOH) into *tetrahydrosolanidine*,  $C_{27}H_{47}ON_2$ , m.p. 222°,  $[\alpha]_D^{25}$  +28.8° in CHCl<sub>3</sub> [*hydrochloride*; *methiodide*, m.p. 280° (decomp.)]. (II) is therefore a doubly unsaturated, *tert.*-base with a *sec.*-OH. Solanthrene (IV),  $C_{25}H_{39}N$ , m.p. 170°,  $[\alpha]_D^{25}$  -92.3° in CHCl<sub>3</sub>, gives a *methiodide*, m.p. 260° (decomp.). Hydrogenation (PtO<sub>2</sub>) of (IV) leads to *tetrahydrosolanthrene*, m.p. 165°,  $[\alpha]_D^{25}$  +30.4° in CHCl<sub>3</sub> [*methiodide*, m.p. 285° (decomp.)]. (IV) is present as a glucoside in the initial material. H. W.

**Alkaloid from *Ceanothus americanus*.** A. BERTHO and W. S. LIANG (Arch. Pharm., 1933, 271, 273—276).—The bark of this plant contains *ceanothine*,  $C_{29}H_{36}O_4N_4$ , dimorphic, m.p. 227—228° and 234° (contains 1NMe, but no OMe, group; *hydriodide*, m.p. 189—190°, decomp. 250°; *methiodide*, cryst.; *perchlorate* and *chloraurate*, amorphous), and another alkaloid, m.p. 240°. R. S. C.

**Aromatic tropene derivatives. I. Derivatives of 8:9-benz- $\Delta^{8:9}$ -homogranatene.** B. K. BLOUNT (J.C.S., 1933, 553—555).—Tetrahydronaphthalene-1:2-diol (improved prep.) is oxidised by Pb(OAc)<sub>4</sub> to  $\beta$ -(*o*-formylphenyl)propaldehyde (*dioxime*, m.p. 116°), which condenses with Ca acetonedicarboxylate and NH<sub>2</sub>Me to give, after acidification and heating, 8:9-benz- $\Delta^{8:9}$ -homogranaten-3-one, m.p. 125° [*picrate*, m.p. 204° (decomp.); *hydrobromide*, m.p. 235° (decomp.)], reduced to the  $\psi$ -alcohol (+H<sub>2</sub>O), m.p. 105—110° [*Bz* derivative, m.p. 98°, and its *hydrobromide*, m.p. 257°, and *hydrochloride*, m.p. 258° (decomp.)]. Similar condensation of homophthalaldehyde gives 2-methylisoquinolinium hydroxide, identified as the *picrate*. F. R. S.

**Colorimetric determination of alkaloids.** R. SEIFFERT (Diss., Halle, 1930; Bied. Zentr., 1933, A, 3, 282).—Methods are based on the pptn. of alkaloids by appropriate reagents and the colorimetric determination of a suitable element or radical in the washed ppt. Suggested reagents include picric, silico- and phospho-tungstic acid for strychnine, quinine, emetine, and cinchonine; Mayer's reagent for strychnine and emetine; H<sub>4</sub>Fe(CN)<sub>6</sub> for strychnine. A. G. P.

**Arsenical azo-derivatives. VI.** S. BERLINOZZI (Annali Chim. Appl., 1933, 23, 168—173; cf. A., 1931, 105).—With 6 compounds obtained by coupling diazotised *p*-aminophenylarsinic acid with various derivatives of C<sub>6</sub>H<sub>5</sub>, C<sub>9</sub>H<sub>7</sub>N, etc., the toxicity towards rats, when injected intraperitoneally, depends mainly on the nature of the coupled grouping and not on the As content (cf. Arch. Sci. Biol., 1931, 16, 4). The 2-phenylquinoline grouping is most interesting in this connexion. 3-Amino-4-(4'-carboxy-2'-phenylquinoline-3'-azo)phenol-2-azophenylarsinic acid, prepared from *m*-aminophenol-6-azo-*p*-phenylarsinic acid and 3-diazo-2-phenylquinoline-4-carboxylic acid, and the analogous 2'-*p*-anisyl compound similarly prepared from 3-diazo-2-*p*-anisylquinoline-4-carboxylic acid, do not melt at 250°. T. H. P.

**3:4-Dimethoxy-2-anhydrohydroxymercurobenzoic acid.** New synthesis of veratric acid. V. M. RODIONOV and A. M. FEDOROVA (Arch. Pharm., 1933, 271, 287—292).—Hemipinic acid and Hg(OAc)<sub>2</sub> give 3:4-dimethoxy-2-anhydrohydroxymercurobenzoic acid, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>2</sub> $\begin{matrix} \text{CO} \\ \diagup \\ \text{Hg} \end{matrix}$ O (*Na* salt), in 90% yield and a substance, m.p. 118—120°. The former with hot, conc. HCl gives a 92% yield of veratric acid [sublimes in rhombic crystals (cf. lit.)]. R. S. C.

**Organomagnesium compounds containing solubilising amino-groups.** H. GILMAN, S. A. HARRIS, and C. LIU (Proc. Iowa Acad. Sci., 1931, 38, 167—168).—Compounds containing the  $\cdot\text{MgX}$  group attached to C in a mol. containing a basic group



( $\cdot\text{NR}_2$  or substituted  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{C}_7\text{N}_7\text{N}$ ) are formed from corresponding  $\text{RX}$  compounds less readily than when no basic group is present, but the presence of the basic group does not affect the general properties.

CH. ABS.

**Rearrangement reactions of organo-sodium and -lithium compounds.** H. GILMAN and F. W. BREUER (Proc. Iowa Acad. Sci., 1931, 38, 167).

**Catalytic decomposition of organo-metallic compounds.** G. A. RAZUVAIEV and M. M. KOTON (Ber., 1933, 66, [B], 854–858; cf. A., 1932, 409).—The catalytic effect of metals on the decomp. of organo-mercury compounds is most strongly marked with  $\text{HgPh}_2$  which undergoes slight decomp. at  $200^\circ$ , whereas  $\text{Hg}(\text{CH}_2\text{Ph})_2$  is unstable at its m.p. With the most active catalysts, decomp. is observed at room temp. For  $\text{HgPh}_2$  between  $200^\circ$  and  $25^\circ$  the activity sequence is  $\text{Pd} > \text{Pt} > \text{Ag} > \text{Au} > \text{Co} > \text{Cu} > \text{Fe} > \text{Ni}$ , whereas for  $\text{Hg}(\text{CH}_2\text{Ph})_2$  between  $75^\circ$  and  $25^\circ$  it is  $\text{Pd} > \text{Pt} > \text{Ag} > \text{Au} > \text{Cu} > \text{Ni} > \text{Fe} > \text{Co}$ . The change is  $\text{HgR}_2 \rightarrow \text{RR} + \text{Hg}$  (I). In presence of compressed  $\text{H}_2$  the reaction  $\text{HgR}_2 + \text{H}_2 = 2\text{RH} + \text{Hg}$  (II) also occurs, the ratio of (I) and (II) depending on the catalyst. For  $\text{HgPh}_2$  and  $\text{Hg}(\text{CH}_2\text{Ph})_2$  the sequences of decreasing activity calc. on decomposed material are respectively:  $\text{Pd} > \text{Pt} > \text{Ni} > \text{Ag} > \text{Au} > \text{Co} > \text{Cu} > \text{Fe}$  and  $\text{Pd} > \text{Pt} > \text{Ni} > \text{Au} > \text{Ag} > \text{Fe} > \text{Co} > \text{Cu}$ .  $\text{PbPh}_4$  and  $\text{SnPh}_4$  behave analogously to  $\text{HgPh}_2$ . In presence of a large amount of Ni,  $\text{PbPh}_4$  smoothly affords Ni and  $\text{C}_6\text{H}_6$  (cf. Zartman *et al.*, A., 1932, 1050).

H. W.

**Racemic and active cyclotetramethylenediselenidedicarboxylic acid.** A. FREDGA (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 15, 6 pp.).— $\text{dl-}\alpha\alpha'$ -Di(selenocyno)adipic acid (from the  $\text{dl-Br}_2$ -acid and  $\text{KSeCN}$ ) is converted by aq.  $\text{H}_2\text{SO}_4$  into  $\text{dl-cyclo-tetramethylene-1:2-diselenide-3:6-dicarboxylic acid}$ , decomp. about  $200^\circ$  [strychnine salt (+5 $\text{H}_2\text{O}$ )], which is resolved by quinine into the (–)-form, decomp. about  $200^\circ$ ,  $[\alpha]_D^{25} -351^\circ$  in dil.  $\text{Na}_2\text{CO}_3$  [quinine salt (+2 $\text{H}_2\text{O}$ )], and then by strychnine into the (+)-form,  $[\alpha]_D^{25} +351^\circ$  in dil.  $\text{Na}_2\text{CO}_3$ , +178.5° in  $\text{EtOH}$ , –244° in 0.2N-HCl [strychnine H salt (+2.5 $\text{H}_2\text{O}$ )]. H. B.

**Dilatometric investigation of the hydrolysis of proteins and their degradation products. I. Hydrolysis of dipeptides.** P. RONA and H. FISCHGOLD (Biochem. Z., 1933, 261, 66–75).—The change (I) in vol. which occurs during the hydrolysis of dil. (0.75%) solutions of dipeptides [glycylglycine (II), glycylalanine (III), alanylglycine (IV)], with dil. alkali (1.5N-NaOH) at  $37^\circ$  is about +9 c.c. per 0.001 mol., the reaction being unimol. When conc. HCl is used at  $50^\circ$  (I) is about –2.5 c.c. for (II) but cannot be determined for (III) and (IV) because the process is too slow. The difference in the type of ionisation in alkaline and acid solution is responsible for the different (I). The dilatometric method, which can also be used for kinetic determinations, gives here 10 times the accuracy of that obtained from determining N by Van Slyke's method.

W. McC.

**Relation between the chemical and colloidal structure of proteins.** A. FODOR (Kolloid-Z., 1933, 63, 203–214; cf. A., 1932, 529).—A general discussion of the structure of gelatin and casein, based

on results obtained by the author's method of non-hydrolytic degradation by heating with anhyd. glycerol or  $m\text{-C}_6\text{H}_4(\text{OH})_2$ , which are considered to cause the tautomeric change  $\cdot\dot{\text{C}}(\text{OH})\cdot\dot{\text{N}}\cdot \rightarrow \cdot\text{CO}\cdot\text{NH}\cdot$ , thus breaking down the lateral linking between adjacent polypeptide mols.

F. L. U.

**Physico-chemical properties of proteins separated from serum by the acetone method.** A. BOUTARIC (Protoplasma, 1933, 18, 286–298).—The viscosity and optical properties of proteins and their influence on the flocculation of  $\text{Fe}(\text{OH})_3$  are discussed. Separation of proteins at low temp. by the  $\text{COME}_2$  method does not involve the disturbance of mol. structure.

A. G. P.

**Action of ultra-violet rays on aqueous solutions of gelatin. Modification of physico-chemical properties. Probable photolysis.** P. PONTIUS (Compt. rend., 1933, 196, 1248–1250).—On irradiation (total ultra-violet) of 0.25–0.75% aq. solutions of gelatin (> 2 hr.) coagulation does not occur,  $n$  does not vary, electrical conductivity increases, and optical density ( $\delta$ ) and relative viscosity ( $\eta/\eta_0$ ) decrease, whilst the ratio  $\omega(=\eta/\eta_0-1)/\delta$  does not vary significantly. The results are explained by dehydration of gelatin particles, and the possibility of its photolysis is also suggested.

A. C.

**Adenylic acid and adenine nucleotide.** J. K. PARNAS and R. KLIMEK (Z. physiol. Chem., 1933, 217, 75–78).—The dissolution of  $\text{Cu}(\text{OH})_2$  by feebly alkaline solutions of adenylic and inosic acids and adenosine and its non-dissolution by adenine nucleotide and the guanylic acids is confirmed. Steudel's differing results (cf. this vol., 612) may be due to his having used too much NaOH.

J. H. B.

**Action of resorcinol on silk fibroin.** I. R. O. HERZOG and J. WEINDLING. II. A. DOBRY-KURBATOV (Z. physiol. Chem., 1933, 216, 248–250; 251–254).—I. Treatment of silk fibroin with resorcinol (I) at  $120^\circ$  for periods up to 6 hr. does not appreciably affect the N distribution on hydrolysis. The action of HCl at  $0^\circ$  slowly liberates more  $\text{NH}_2\text{-N}$  from the (I)-treated than from the untreated material.

II. Longer treatment with (I) at a higher temp. induces chemical combination, a greater proportion of the fibroin becoming sol. in  $m$ -cresol. The viscosity of the product decreases as the fusion time increases.

J. H. B.

**Physico-chemical studies on proteins. VII. Peptisation of gliadin by solutions of inorganic salts.** W. SINCLAIR and R. A. GORTNER (Cereal Chem., 1933, 10, 171–188).—Pure gliadin (I) prepared by Osborne's "70% EtOH method" and by Blish and Sandstedt's  $\text{AcOH}$  method (B., 1933, 894) was peptised with equi-ionic solutions of KI, KBr, and KCl. A lyotropic series was observed ( $\text{Cl} < \text{Br} < \text{I}$ ). The non-peptisable residue from repeated extractions with  $M\text{-KI}$ , when purified by repeated pptn. from EtOH, could then be further peptised by KI solution. Similarly the "KI-sol." fraction, when re-worked, furnished a "KI-insol." residue. The  $p_H$  of the fractions was practically unchanged. The treatment of (I) with these neutral salt solutions does not produce any "true hydrolysis," for no significant



change occurred in free  $\text{NH}_2\text{-N}$ , and in free  $\text{CO}_2\text{H}$ . The Hausmann N distribution vals. ( $\text{NH}_2\text{-N}$ , humin-N, basic N, and non-basic N) were practically the same as for untreated gliadin. The amount of (I) peptised by a particular salt solution depends both on the concn. of the solution and the amount of (I) present. (I) cannot be separated into chemically dissimilar fractions by differential dissolution in salt solutions and, therefore, from the viewpoint of org. chemistry, is probably a homogeneous protein, but the granules of the dry protein or the larger aggregates of the hydrated protein are not physically homogeneous.

E. A. F.

#### Use of the orcinol reaction for determination of the kind and amount of carbohydrate in proteins.

M. SØRENSEN and G. HAUGAARD (Biochem. Z., 1933, 260, 247—277).—In the usual determination the step photometer replaces the colorimeter, and the effects on the course of the reaction of variation of temp., orcinol and  $\text{H}_2\text{SO}_4$  concns., and time of warming with  $\text{H}_2\text{SO}_4$  are determined. The form and position of the extinction-time curves enable glucose, mannose, galactose, fructose, sorbose, arabinose, xylose, and rhamnose to be differentiated. The reactions of raffinose, lactose, glycogen, and inulin with orcinol- $\text{H}_2\text{SO}_4$  are shown to be additive processes and the glucose contents of amygdalin and salicin are determined. Finally the kind and amount of carbohydrate in various proteins are determined. Ovalbumin before crystallisation often contains 1.7% of mannose, serum albumin after several crystallisations and horse-serum globulin after several pptns. contain 0.47 and 1.82%, respectively, of a carbohydrate containing mannose and galactose, purified caseinogen and lactalbumin contain 0.31 and 0.44%, respectively, of galactose but no lactose, and wheat gliadin 0.20% of mannose.

P. W. C.

**Union of biocolloids. XVII. Combination of proteins, polysaccharides, and nucleic acids.** S. J. PRYZLECKI and M. D. GRYNBERG (Biochem. Z., 1933, 260, 395—402).—In systems nucleic acid (I) + polysaccharide (II) no affinity exists at higher  $p_{\text{H}}$  and it seems improbable that union between glycogen and (I) occurs in the animal body. When a multi-valent cation, protein, is present in addition to the negatively charged biocolloid (I+II) as anion, combination occurs, but only with small concns. of (I) and at a definite  $p_{\text{H}}$ . The existence of a four-component system at  $p_{\text{H}}$  7.3 is also detected using the system (I) + basic protein + neutral protein + (II).

P. W. C.

#### Röntgenographic investigation of proteins.

**I. Behaviour of silk against acids and bases.** C. TROGUS and K. HESS (Biochem. Z., 1933, 260, 376—394).—A no. of X-ray fibre diagrams of various kinds of silk are given and show that the different types of silk are composed of at least two crystal forms. Silk fibres show considerable resemblance to cellulose fibres in their behaviour with reagents.

P. W. C.

**Semi-micro-determination of carbon and hydrogen according to the method of Orthner and Reichel.** G. KOMPPA and W. ROHRMANN (Chem. Fabr., 1933, 6, 201—202).—A form of apparatus is described.

H. F. G.

**Loading combustion tube in carbon and hydrogen determination on liquids.** J. R. BAILEY (Ind. Eng. Chem. [Anal.], 1933, 5, 171).—The apparatus allows the drops of liquid to fall on to the layer of CuO without impinging on the sides of the combustion tube, thus ensuring complete combustion.

E. S. H.

**Nickel tubes in organic combustions.** F. E. RAY (Ind. Eng. Chem. [Anal.], 1933, 5, 220).—Tubes of Ni are recommended.

E. S. H.

**Micro-analytical methods.** E. P. CLARK (J. Assoc. Off. Agric. Chem., 1933, 16, 255—260).—The advantages of micro-analytical methods are discussed and semi-micro-methods are described for the determination of C, H, N, halogens, and OMe. T. McL.

**Determination of nuclear halogens in organic compounds. Critical study and standardisation of the Stepanov method.** W. A. COOK and K. H. COOK (Ind. Eng. Chem. [Anal.], 1933, 5, 186—188).—Certain details of procedure are standardised. The method is not suitable for volatile substances. With cryst. substances, sparingly sol. in EtOH, the state of subdivision affects the result.

E. S. H.

**Detection of mercury in organic compounds.** I. STONE (Ind. Eng. Chem. [Anal.], 1933, 5, 220).—A glass rod, coated with CuI, is introduced into a test-tube containing a heated mixture of the org. compound and  $\text{Na}_2\text{CO}_3$ . In presence of Hg the CuI turns pink. 0.02 mg. of Hg can be detected. As and Sb do not interfere. The interference due to N can be overcome by placing a layer of  $\text{K}_2\text{S}_2\text{O}_7$  over the alkaline mixture to absorb the  $\text{NH}_3$  produced. Similarly, a layer of PbO obviates the interference due to S.

E. S. H.

**Identification and determination of methyl alcohol in the presence of ethyl alcohol.** A. IONESCU-MATIU and C. POPESCU (Ann. Sci. Univ. Jassy, 1933, 17, 205—215).—MeOH in alcoholic liquors can be identified by distillation with acid and alkali, and application of known tests to the distillate. Determination of small amounts can be effected only approx., best by colorimetric examination of the oxidation products.

R. S. C.

**Formation of thiocyanates from cyanides [and analytical applications].** A. CASTIGLIONI (Gazzetta, 1933, 63, 171—175).—KCN reacts at once with S in  $\text{COMe}_2$ , MeOH, EtOH, or amyl alcohol to form KSCN. This may be used to detect and determine free S, and to detect  $\text{CN}'$ , e.g., that formed in a test for org. N.

E. W. W.

**Carbon tetrachloride: pyrolysis and analytical procedure.** KOHN-ABREST (Ann. Chim. Analyt., 1933, [ii], 15, 199—207).— $\text{CCl}_4$  passed with air through a quartz tube at  $1000^\circ$  decomposes (a)  $\text{CCl}_4 + 0.5\text{O}_2 = \text{CO} + 2\text{Cl}_2$ ; (b)  $\text{CCl}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{HCl}$ . Absorption of the HCl in  $\text{H}_2\text{O}$ ,  $\text{Cl}_2$  in KI permits of the determination of the  $\text{CCl}_4$ . For toxicological investigation, air is aspirated over the organs under examination and the HCl produced by pyrolysis absorbed in  $\text{AgNO}_3$ .

J. S. A.

**Micro-determination of citric acid by Thunberg's methylene-blue method.** A. C. KUYPER (Proc. Iowa Acad. Sci., 1931, 38, 172).—Use of the



sp. property of citric acid to accelerate the decolorisation of methylene-blue (I) by an enzyme present in cucumber seed is trustworthy only when the enzyme extracts are prepared in the same way and used at the same age. Na, Ca, and hexose diphosphate do not interfere unless present in concns.  $>$  those in blood.  $\text{H}_2\text{C}_2\text{O}_4$  interferes. The sensitivity is proportional to the amount of (I) present. CH. ABS.

**Kogan's method for determining citric acid.** E. EMILIANI (Annali Chim. Appl., 1933, 23, 188—192).—With slight modification, Kogan's method (A., 1930, 743) gives satisfactory results (cf. Romani, A., 1932, 144). T. H. P.

**Micro-determination of lactose by method of Hagedorn and Jensen.** C. FROMAGEOT and M. MOULIN (Bull. Soc. chim., 1933, [iv], 53, 266—267).—Vals. are given for the vol. of  $0.005N\text{-K}_3\text{Fe}(\text{CN})_6$  reduced per mg. lactose from 0 to 0.509 mg. The vol. is proportional to the lactose present up to 0.4 mg. H. A. P.

**Microanalytical detection and determination of fructose in presence of aldoses and sucrose.** F. FISCHL (Chem.-Ztg., 1933, 57, 393—394).—A solution of  $\text{CuSO}_4$ , Na K tartrate,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{HPO}_4$  is reduced by fructose but not by aldoses or sucrose; the resulting solution may be titrated iodometrically. F. R. S.

**Colour reaction and micro-determination of d-fructose.** K. YAMADA.—See this vol., 737.

**Night-blue as an indicator for use in volumetric titrations with silicotungstic acid.** H. L. FEINSTEIN and E. O. NORTH (J. Amer. Pharm. Assoc., 1933, 22, 415—419).—1.5 mg. of dye per c.c. of 7—8  $N\text{-H}_2\text{SO}_4$  is used as external indicator. The method described is applicable to the analysis of other amines which form insol. ppts. with silicotungstic acid. E. H. S.

**Colour tests for salicylic acid and its derivatives.** A. ZAGORSKIKH (Khim. Farm. Prom., 1932, 10, 377).— $(\text{NH}_4)_2\text{MoO}_4$  (1 g.) in  $\text{H}_2\text{SO}_4$  (100 c.c.) gives with acetylsalicylic acid a blue colour changing to violet, and with salol and salicylic acid a violet colour changing to olive-green. CH. ABS.

**Detection of saccharin and the composition of complexes with copper and pyridine.** J. J. L. ZWIKKER (Pharm. Weekblad., 1933, 70, 551—559).—Pptn. of saccharin (I) with  $\text{CuSO}_4\text{-C}_5\text{H}_5\text{N}$  gives three characteristic types of crystal depending on the concn. of (I). In dil. solution needles are formed of the compound,  $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2]_2(\text{C}_7\text{H}_5\text{O}_3\text{NS})$ , converted into the compound,  $[\text{Cu}2(\text{C}_7\text{H}_5\text{O}_3\text{NS}),\text{C}_5\text{H}_5\text{N},\text{H}_2\text{O}]$ , at  $150^\circ$ . More conc. solutions afford quadratic crystals and hexagonal prisms of compound (II),  $(\text{C}_7\text{H}_5\text{O}_3\text{NS})_6[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3\text{NS}),(\text{C}_5\text{H}_5\text{N})_2]_6, 11\text{H}_2\text{O}$ , converted into the compound  $(\text{C}_7\text{H}_5\text{O}_3\text{NS})_6[\text{Cu}(\text{C}_7\text{H}_5\text{O}_3\text{NS}),\text{C}_5\text{H}_5\text{N}]_6, 4\text{H}_2\text{O}$ , at  $150^\circ$ . The lattice structure of (II) is discussed. S. C.

**Determination of small quantities of benzyl alcohol.** J. CALLAWAY and S. REZNEK (J. Assoc. Off. Agric. Chem., 1933, 16, 285—289).—Tables are given showing the sp. gr. and  $\eta$  of aq. solutions containing up to 3% of  $\text{CH}_2\text{Ph-OH}$  (I). The (I) is

distilled with  $\text{H}_2\text{O}$  so that the distillate contains  $> 1.5\%$  of alcohol and its sp. gr. and  $\eta$  are determined. If necessary, owing to the presence of other volatile substances, the (I) may be oxidised to  $\text{BzOH}$  by  $\text{KMnO}_4$ , extracted, and titrated. T. McL.

**Micro-test for triarylcarbinols.** A. A. MORTON and L. V. PEAKES, jun. (Ind. Eng. Chem. [Anal.], 1933, 5, 185).—The carbinol is converted into the chloride and then into the free radical by treating with  $\text{AcCl}$  and dry, powdered Ag in a capillary. After centrifuging the Ag a coloured liquid layer is observed, due to the free radical. As  $\text{O}_2$  diffuses slowly into the open capillary the liquid becomes decolorised. E. S. H.

**Indirect enol titration.** T. FJÄDER (Suomen Kem., 1933, 6, 61—62).—The different behaviour of various bromoketones titrated by the Kurt Meyer method in presence of (a)  $\text{HBr} + \beta\text{-C}_{10}\text{H}_7\text{-OH}$  (I), (b)  $\text{HBr}$ , (c) (I), and (d)  $\text{H}_2\text{O}$ ,  $\text{HBr}$ , + (I), indicates that the reaction is complex. Thus with bromomethylmenthone the  $\text{Na}_2\text{S}_2\text{O}_3$  titre falls rapidly in (a) and much more slowly in (c), (b), and (d) (in this order). J. W. B.

**Azo-derivatives of hydroxyquinoline in inorganic analysis.** II, III. G. GUTZEIT and R. MONNIER (Helv. Chim. Acta, 1933, 16, 478—485, 485—486; cf. this vol., 479).—II. 4'-Sulpho-*o*-tolyl-, *o*-carboxyphenyl-, and *p*-tolyl-azo-5:8-hydroxyquinoline give characteristic ppts. or colorations with  $\text{Hg}^{++}$ ,  $\text{Pd}^{++}$ , and  $\text{Mo}$  (as  $\text{MoOCl}_5^{--}$ ), respectively. The reactions are sp. under conditions which are described. The corresponding Ph derivative is a sp. reagent for  $\text{Hg}^{++}$ ,  $\text{Cu}^{++}$ , and  $\text{Pd}^{++}$ . Limits of sensitivity are given.

III. A table showing the reactions of sixteen azo-derivatives of 8-hydroxyquinoline is given. Substitution of different radicals in the quinoline nucleus weakens or enhances the reactions with certain ions, but does not lead to new reactions. F. L. U.

**Quinoline and lignin.** A. CASTIGLIONI (Atti R. Accad. Lincei, 1933, [vi], 17, 469—473).—Lignin gives no coloration with isoquinoline, carbostyryl, or acridine in acid solution, but, contrary to Grandmougin's statement (Z. Farbenind., 1906, 5, 321), gives an intense wine-red colour with either 1% solution of quinoline in EtOH followed by conc.  $\text{HCl}$  or 10% aq. quinoline hydrochloride or sulphate solution. 4-Methylquinoline gives a faint colour and the reagent used by Ihl (B., 1891, 165) probably contained quinoline. T. H. P.

**Analytical notes.** II. L. ROSENTHALER (Pharm. Zentr., 1933, 74, 288—290; cf. this vol., 41).—(1) A 10% "Pantosept" solution dissolves As stains immediately but Sb stains only after several hr. Differences between the dissolution velocities, when using  $\text{NH}_2\text{Cl}$ , are small. (2) Ac can be detected as amyl acetate instead of  $\text{EtOAc}$  by esterification with amyl alcohol and *p*-toluenesulphonic acid. Sensitivity of the test is reduced by the characteristic odour of amyl alcohol. (3) Use of  $\text{CaCO}_3$  in place of alkali hydroxides and aq.  $\text{NH}_3$  for neutralisation of acids is recommended. (4) The transient green colour given by 8-hydroxyquinoline,  $\text{CHCl}_3$ , and  $\text{NaOH}$  can be used to detect  $\text{CHCl}_3$  and hydroxyquinolines, but is not given by chloriodohydroxyquinoline ("Vio-



form"). (5) Piperazine gives with aq. benzoquinone (I) a brownish-violet colour, and with alcoholic (I) a wine-red colour. Both solutions later become turbid. (6)  $\text{CCl}_3\text{-CO}_2\text{H}$  solution, neutralised with  $\text{CaCO}_3$ , gives characteristic crystals with (a) solid  $\text{Ti acetate}$ , (b)  $\text{HgNO}_3$ , (c) solid  $\text{AgNO}_3$ , (d)  $\text{UO}_2(\text{OAc})_2$ . (7) Cyanides heated with  $\text{NaOH}$  and colloidal  $\text{S}$  are converted into thiocyanates. (8) Descriptions with photographs are given of crystals deposited on treating (i)  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$  with (a)  $\text{KOH}$ , (b)  $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , (c) conc.  $\text{HNO}_3$ ; (ii) caffeine, theobromine, and theophylline with (a) Zwicker's reagent (4 c.c. of 10%  $\text{CuSO}_4$  solution, 1 c.c. of

$\text{C}_5\text{H}_5\text{N}$ , 5 c.c. of  $\text{H}_2\text{O}$ ), (b)  $\text{CdSO}_4\text{-C}_5\text{H}_5\text{N}$  solution; (iii) saccharin with  $\text{Ti acetate}$ . (9) Colour reactions given by apiol are: (a) violet, with  $\text{NH}_2\text{Cl}$  in glacial  $\text{AcOH}$ , (b) dirty red on heating with conc.  $\text{HBr}$ , (c) from yellow to reddish-brown to dark brown with  $\text{BzCl}$  and  $\text{ZnCl}_2$ . (10) Aldehydes accelerate the reaction between  $\text{CS}_2$  and alkali plumbites.

V. P. P.

**Determination of labile sulphur in gelatin.** N. V. KIRILENKO (J. Appl. Chem., Russia, 1932, 5, 1119—1126).—Sheppard and Hudson's method is subject to an error of 14%; the colorimetric standard should be replaced by methylene-blue. CH. ABS.

## Biochemistry.

**Mechanism of the action of pyocyanine on respiration.** K. G. STERN (Naturwiss., 1933, 21, 350—351).—Addition of neutral 0.0005*M*-pyocyanine (I) to dil. aq. oxyhaemoglobin gives rise to absorption bands characteristic of methaemoglobin (II) which are shifted 20  $\text{m}\mu$  towards the blue by addition of  $\text{NaF}$  or of  $\text{H}_2\text{PO}_4'$  at  $p_{\text{H}}$  6. With intact erythrocytes, formation of (II) occurs very slowly; haemolysis with piperazine accelerates the reaction, the fall in  $\text{O}_2$  consumption indicating a 50% conversion in 45 min. at 39°.

F. O. H.

**Specificity of haemoglobins, including embryonic haemoglobin.** H. TROUGHT (Arch. Dis. Childhood, 1932, 7, 259—262).—The rate of decomp. of haemoglobin by 0.25*N*- $\text{NaOH}$  depends on the source.

CH. ABS.

**Analysis. III. Detection of blood with 2:7-diaminofluorene hydrochloride.** L. ROSENTHALER (Pharm. Zentr., 1933, 74, 333—334).—Other oxidising agents and oxidases react with the reagent (cf. A., 1932, 242) to produce a blue colour (or other colour or ppt. in higher concns.). The presence of blood is confirmed if the blue colour is present in a  $\text{CHCl}_3$  extract after acidification with  $\text{AcOH}$ .

E. H. S.

**Conductivity method for the determination of the cell-volume of blood.** A. SLAWINSKI (Biochem. J., 1933, 27, 356—360).—Formulae are given whereby the cell-vol. of blood may be calc. from the ratio of the conductivities of blood after complete settling in two tubes, one horizontal and the other (I) vertical, together with a reading of the height of the settled cells in (I). The method is accurate to 0.1%.

W. O. K.

**Effect of ingestion of pure water and mineral diuretic water on blood-serum-protein.** C. AUGUSTE (Ann. Méd., 1933, 33, 25—60).—Ingestion of  $\text{H}_2\text{O}$  or of a mineral diuretic causes a marked oscillation in the "coeff. of hydræmia" (ratio of increase in plasma vol. to the initial vol.).

NUTR. ABS.

**Determination of blood-urea-nitrogen by direct nesslerisation.** W. F. TAYLOR and W. M. BLAIR (J. Lab. Clin. Med., 1932, 17, 1256—1263).—The blood is allowed to react with a very conc. urease

prep. which is pptd. with the proteins by  $\text{Na}_2\text{WO}_4$  and  $\text{H}_2\text{SO}_4$ . The filtrate may be nesslerised directly.

CH. ABS.

**Cystine content of human serum-proteins.** L. R. TRICHMAN and M. REINER (J. Biol. Chem., 1933, 100, 775—778).—The total cystine content of human sera averaged 4.82%, 3.64% being in globulin and 6.07% in albumin. Variations such as have been observed by other workers in the cystine content of oedematous sera were not apparent.

A. L.

**Tyrosine and cystine content of serum-proteins.** M. REINER and H. SOBOTKA (J. Biol. Chem., 1933, 100, 779—781).—Results of determinations of the tyrosine (I) and cystine (II) factors for the serum-albumin and -globulin of various animals are in agreement with those made by Wu and Ling (A., 1929, 88) except in the case of the pig. The (I) and (II) contents of several fractions of typhoid-immunised horse serum are also determined, the immuno-active factor being richer than the others in (I). The (I) content of horse serum-proteins rises on acid hydrolysis.

A. L.

**Micro-photometric method for determination of free cholesterol and cholesterol esters in blood-plasma.** E. OBERMER and R. MILTON (Biochem. J., 1933, 27, 345—350).—Cholesterol digitonide derived from the  $\text{EtOH-Et}_2\text{O}$  extract of 1 c.c. of plasma (or its hydrolysate) is treated with  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$  and  $\text{ZnCl}_2$  in  $\text{AcOH}$  at 100° and the colour is measured. The accuracy is comparable with that of a macro-gravimetric method.

R. K. C.

**Effect of diet on the plasma-phosphatase of sheep.** D. W. AUCHINACHIE and A. R. G. EMSLIE (Biochem. J., 1933, 27, 351—355).—The plasma-phosphatase (I) of sheep, on a diet poor in  $\text{Ca}$  but rich in  $\text{P}$ , rose before any detectable fall in serum- $\text{Ca}$  or deterioration of clinical condition. With a more adequate diet the rise in serum- $\text{Ca}$  precedes the return to normal of (I). Cod-liver oil is more effective than  $\text{Ca}$  salts in preventing the rise in (I).

W. O. K.

**Phosphatases and glycolysis in blood.** A. ROCHE and J. ROCHE (Bull. Soc. Chim. biol., 1933, 15, 520—530).—In haemolysates of red blood-corpuscles to which glucose monophosphate (I) and fructose mono- (II) and di-phosphate (III) have been



added, hydrolysis and glycolysis go on simultaneously. The liberated sugar in the case of (I) has the same reducing power as glucose, but with (II) and (III) a mixture of aldose and ketose is obtained. A. L.

**Sugar content of the blood of ruminants.** F. W. KRZYWANIEK and H. BRÜGGEMANN (Biochem. Z., 1933, 261, 170—175; cf. Pflüger's Archiv, 1929, 222, 89).—In sheep, administration (oral or direct into stomach) of glucose has little effect on the sugar content of the blood. Probably most of the sugar is not resorbed as such, but fermented. W. McC.

**Influence of proteins, amino-acids and their derivatives on the regulation of blood-sugar.** II. E. G. SCHENCK (Arch. exp. Path. Pharm., 1933, 170, 546—550).—Pure glycine administered orally to rabbits or to healthy and diabetic man has a hypoglycæmic action (cf. A., 1932, 1054; Paasch, A., 1928, 1151). W. O. K.

**Blood-sugar regulation by reflexes from the sinus caroticus.** P. THELEN (Z. ges. exp. Med., 1933, 86, 231—243). NUTR. ABS.

**Hormonal regulation of blood-sugar.** F. HÖGLER and F. ZELL (Z. ges. exp. Med., 1933, 86, 144—157).—Parathormone by itself or with ergotamine (sympathetic paralysis) or atropine (vagus paralysis) had no effect on blood-sugar (I) in rabbits. In some instances it weakened, in others it strengthened, insulin action. It increased the hyperglycæmic action of adrenaline and decreased or prevented that of  $MgSO_4$ . It had no effect on the rise of (I) following pyramidone or the ingestion of glucose or fructose. NUTR. ABS.

**Lactic acid, sugar, and inorganic phosphorus of the blood of ruminants.** W. M. ALLCROFT and R. STRAND (Biochem. J., 1933, 27, 512—522).—Fasting for 7 days did not change the lactic acid (I) or the sugar content (II) of the blood of sheep; the initial increase of blood-P (inorg.) (III) was followed by a fall. Ingestion of a carbohydrate-rich meal did not change (I) and (II) appreciably; (III) after rising slightly tended to decrease slowly. Vigorous exercise produced corresponding increases in (I) and (II) proportional to length of period; (III) rose quickly, fell, and then rose again sharply to normal. Moderate exercise left (I) unchanged, (II) and (III) rising slightly. Nervous excitement caused a significant increase in (I) and (II) depending on the degree of excitation, that of (I) being greater and the increase in (III) being similar to that of (I). A. L.

**Determination of calcium in blood-serum and cerebrospinal fluid.** A. H. TINGEY (Biochem. J., 1933, 27, 332—337).—Adsorbed org. matter and incomplete pptn. vitiate Ca determinations by  $KMnO_4$  or acidimetric methods in non-deproteinised serum or cerebrospinal fluid. The method of Halverson and Bergeim (A., 1918, i, 50) as modified by Peters and Van Slyke ("Quantitative Clinical Chemistry," 1932, 1, 767) including the Halverson and Bergeim washing with removal of the mother-liquors by suction, as modified by Van Slyke and Sendroy (A., 1929, 1476), is recommended and is successful with fatty and opaque sera. R. K. C.

**Chemical action of sodium citrate as a cause of certain transfusion reactions.** A. S. MINOT, K. DODD, and R. BRYAN (Amer. J. Dis. Children, 1933, 45, 32—40).—Transfusions of blood containing 0.5% Na citrate into dogs following reduction of blood-Ca are followed by indications of acute lack of Ca; the symptoms are relieved by injection of Ca salts. CH. ABS.

**Determination of chloride in blood.** J. H. NORRIS and G. AMPT (Biochem. J., 1933, 27, 321—325).—Fusion with NaOH is recommended for decomp. of org. matter in determination of Cl. The regular loss of Cl reported by others with  $HNO_3$  decomp. was not found, but the Van Slyke method sometimes gives low vals. R. K. C.

**Chlorine, total and residual nitrogen of the blood of the chick embryo.** K. YAMADA (Japan. J. Med. Sci., Biochem., 1933, 2, 81—83).—The Cl content of the blood rises during incubation; the reducing substances (as glucose) also increase. The total and residual N are less affected during the latter part of incubation, but a slight rise (7 mg. per 100 c.c.) occurs. P. G. M.

**Alkaline reserve of the blood of fishes.** FONTAINE and BOUCHER-FIRLY (Compt. rend., 1933, 196, 1439—1441).—For sea fish, the alkaline reserve (I) (expressed by the no. of c.c. of  $CO_2$  at 0° and 750 mm. liberated from 100 c.c. of plasma) of the blood of Teleosteans is always higher than for Selachians. Fresh-water Teleosteans have a much higher (I), whilst potamic fishes possess intermediate vals. H. B.

**Mineral composition of circulating fluids in marine animals.** K. BIALASZEWICZ (Arch. int. Physiol., 1933, 36, 41—53).—The mineral elements in the circulating fluids of marine invertebrates (I) and fish differ considerably from one another and from sea- $H_2O$  (II). The differences from (II) for (I) are most marked in the case of Mg and S. The greatest deficiency in Mg is shown in certain annelids and Crustacea, although Mg is always less conc. in (I) than in (II). The Mg : S ratio is const., showing that it is the  $MgSO_4$  which varies in the body-fluids. The Ca : Cl ratio is also fairly const. and the actual vals. are close to those in (II). K was only a little more conc. in most of the (I) than in (II). In the serum of selachian and teleostean fish the K : Cl ratio is considerably > in sea- $H_2O$  and the Mg very much lower. NUTR. ABS.

**Comparative value of chlorobenzene and thymol when used with fluoride as preservatives of blood for chemical analysis.** R. C. LEWIS and G. E. MILLS (Amer. J. Clin. Path., 1928, 3, 17—28).—PhCl and KF are more efficacious than thymol and KF. CH. ABS.

**Effect of tannin on hæmolysis, agglutination, and the action of toxins.** A. KLOPSTOCK and E. NETER (Biochem. Z., 1933, 261, 207—225).—Tannin (I), *in vitro* [(I) mixed with virus before adding to blood or added after mixing blood and virus] or injected with or before (even in another part of the body) cobra virus, rapidly and reversibly (reversal by dilution) inhibits the hæmolysis even when activation



by lecithin has preceded and hence acts as a certain prophylactic (for mice, at least). (I) also inhibits the action of ricin as well as those of saponin, Na oleate and Na glycocholate, and cobra virus-lecithin compound and prevents the agglutination of blood-corpuscles by anti-sera. The results support the view that the action of (I), although non-sp., resembles the second phase of action of anti-bodies and confirm the views of Sachs and Behrens (A., 1932, 1054).

W. McC.

**Purification of antitoxic sera in order to avoid serum shock.** E. SAVINO (Rev. soc. argentina biol., 1932, 7, 108).—Separation of the globulins with  $\text{Na}_2\text{SO}_4$  is followed by dialysis and pptn. at the isoelectric point. The prep. then contains only pseudo- and eu-globulins.

CH. ABS.

**Serological studies on iodinated sera. I. Precipitins and precipitinogens. II. Anaphylaxis.** J. JACOBS (J. Immunol., 1932, 23, 361—374, 375—384).—I. When I is added to animal sera in the absence of acid or alkali, substances are formed which give ppts. with antisera prepared from iodinated sera. Di-iodotyrosine (I), but not KI, inhibits pptn. specifically in systems of iodinated sera (II).

II. (I), but not I', inhibited anaphylaxis in animals sensitised to (II).

CH. ABS.

**Quantitative study of the precipitin reaction with special reference to crystalline ovalbumin and its anti-body.** J. T. CULBERTSON (J. Immunol., 1932, 23, 439—453).—Cryst. ovalbumin affords a single type of anti-body. The amount of precipitable antibody in unit vol. of rabbit anti-cryst.-ovalbumin serum can be determined by finding the amount of antigen necessary to neutralise the precipitin of a small vol. of the antiserum. At the neutralisation point antigen and antibody combine in const. ratio with max. pptn. Corresponding quant. relations are not found in the titration of anti-sera to horse serum.

CH. ABS.

**Antigenic property of gelatin-diazoarsanilic acid.** S. B. HOOKER, W. C. BOYD, O. E. ALLEY, and M. A. DEROW (J. Immunol., 1933, 24, 141—147).—Antigenicity may be conferred on gelatin (I) by coupling it with an unsaturated cyclic compound. Non-antigenicity of (I) is not necessarily due to its deficiency in aromatic  $\text{NH}_2$ -acids.

CH. ABS.

**Hypothetical mechanism of anti-body production.** S. MÜDD (J. Immunol., 1932, 23, 423—427).—Anti-bodies (I) are probably synthesised from less complex units, e.g., peptides and  $\text{NH}_2$ -acids. Synthesis of (I) probably occurs at the antigen (II) surface. Specificity of (I) is attributed to sp. stereochemical correspondence with the (II). Dissociation of (I) and (II) is then governed by equilibrium conditions, the (II) being left free to incite further production of (I).

CH. ABS.

**Quantitative aspect of the hypothetical incorporation of injected antigen in resulting anti-body.** S. B. HOOKER and W. C. BOYD (J. Immunol., 1932, 23, 465—479).—Buchner's hypothesis requires the presence of 2.5—2500 times as much As in immune serum, prepared by injection of an arsenical diazo-protein, as is found chemically.

CH. ABS.

**Union of serum-colloids. II. Binding of bile pigment, lipochrome, cholesterol, lecithin, and the anti-bodies of syphilis.** W. M. BENDIEN and I. SNAPPER (Biochem. Z., 1933, 261, 1—14; cf. this vol., 623).—Experiments with the membranes previously described show that bilirubin is not ultra-filterable. In sera from jaundiced patients it is very probably quantitatively combined with the albumin (I). The lipochrome of serum is neither combined with (I) nor distributed in combination over the whole globulin fraction (II), and the same holds for the cholesterol and lecithin, which are possibly partly combined with the euglobulin (III). In sera from syphilitics the anti-bodies are not united to (I) or (II), but may be to part of (III).

W. McC.

**Distribution of chlorine in the developing hen's egg.** K. YAMADA (Japan. J. Med. Sci., Biochem., 1933, 2, 71—79).—The Cl content of the fresh egg (White Leghorn) is approx. 170 mg. per 100 g.;  $\frac{3}{5}$  of the total is in the white. During the first half of incubation Cl migrates into the yolk from the white, a process which runs parallel to the  $k$  of the white and regulates the osmotic pressure for the developing embryo.

P. G. M.

**Inorganic constituents of nerve tissue.** K. HAYASI (Japan. J. Med. Sci., Biochem., 1933, 2, 1—5).—The spinal cord of the whale is richer in inorg. P than any other nerve tissue examined and has a higher ash content, but only traces of S are present. The lingual nerve is the richest in Na and Cl, and the brain in K. All nerve tissue in the whale is richer in Na and Cl than that of land mammals.

P. G. M.

**Cation and chlorine content of rabbit's brain.** M. MATSUMOTO (Japan. J. Med. Sci., Biochem., 1933, 2, 11—20).—Grey matter contains Ca 7.7, Mg 14.6, K 351.7, Na 131.9, and Cl 181.9 mg. per 100 g.; the vals. for white are Ca 6.6, Mg 16.1, K 340.1, Na 121.7, and Cl 165.4. The osmotic pressure in nerve tissues is regulated in a different manner from that in other tissues.

P. G. M.

**Inorganic and phosphagen-phosphorus content of the brain.** M. MATSUMOTO (Japan. J. Med. Sci., Biochem., 1933, 2, 85—91).—Grey matter of the rabbit's brain contains 42—45 mg. of inorg. P and 3—5 mg. of phosphagen-P, white matter 25—30 mg. and 8—11 mg. per 100 g., respectively. Some hydrolysis of org. P compounds occurs in 4%  $\text{CCl}_3\text{CO}_2\text{H}$  solution at room temp., but they are less labile than in muscle. Rat's brain contains 2—3 mg. of pyrophosphate per 100 g.

P. G. M.

**Muscle extractives. XXXIII. Extractives of crab's muscle (*Astacus fluviatilis*, L.). L. BROUDE. XXXIV. Oxalylmethylguanidine (creatone) as a constituent of muscle tissue.** V. GULEVITSCH (Z. physiol. Chem., 1933, 217, 56—62, 63—67).—XXXIII. The total N of crab-muscle extract was much >, and the N of the Ag-Ba(OH)<sub>2</sub> ppt. of the Hg fraction much <, in pig's muscle. Carnosine, creatinine, oxalylmethylguanidine, and xanthine could not be detected, but *dl*-arginine and *dl*-lactic acid were isolated.

XXXIV.  $\alpha$ -Oxalylmethylguanidine (+H<sub>2</sub>O), m.p. 182.5°, was isolated from the filtrate after carnosine



pptn. with basic Hg sulphate. It is probably not an artefact, but may be the precursor of the  $\text{H}_2\text{C}_2\text{O}_4$  found by Steudel (A., 1932, 1273) in ox-muscle.

J. H. B.

**Muscle extractives.** T. YAZAWA (Japan. J. Med. Sci., Biochem., 1933, 2, 37—41).—The following were obtained from a  $\text{H}_2\text{O}$  extract of finback-whale muscle: lactic acid, xanthine (or adenine), hypoxanthine, histidine, creatine, and a substance (m.p.  $259-261^\circ$ ; N 20.05%) similar to lysine.

P. G. M.

**Chemistry of muscle-adenosinetriphosphoric acid. Determination of muscle-adenosinetriphosphoric acid.** D. FERDMANN (Z. physiol. Chem., 1933, 216, 205—216).—Of the three P atoms of adenosinetriphosphoric acid, two are eliminated by hydrolysis for 7 min. with  $\text{N-HCl}$  at  $100^\circ$  and the third, remaining as adenylic acid, by ashing with conc.  $\text{H}_2\text{SO}_4$ . The pentose is estimated by Bial's method, hydrolysing with 4.5N-HCl for 5 min., which yields furfuraldehyde (I) giving the reaction with orcinol and  $\text{FeCl}_3$ , or accurately determined by the method of Simonokura (J. Biochem., Japan, 1931, 14, 343), hydrolysing in this case with 6N- $\text{H}_2\text{SO}_4$ . Longer hydrolysis with 20% HCl gives no (I); the pentose therefore differs from arabinose and xylose, which yield only (I) under these conditions.

J. H. B.

**Nitrogenous substances of the liver.** T. YAZAWA (Japan. J. Med. Sci., Biochem., 1933, 2, 43—46).—Tyrosine, guanine, and xanthine, but not hypoxanthine, were isolated. Autolysis increased the (arginine+histidine)-N and the N not pptd. by phosphotungstic acid. Free sugar increased.

P. G. M.

**Nitrogenous extractives of ox testes.** D. TRUBIZIN (Z. physiol. Chem., 1933, 217, 33—37).—Guanine, xanthine, adenine, hypoxanthine, but no carnosine were isolated from ox testes. The N distribution in the various ppts. was determined.

J. H. B.

**Composition of the lipins of normal and diseased organs. IV. Composition of the lipins of the corpus luteum, ovary, testis, and epididymis of cattle.** B. LUSTIG and E. MANDLER (Biochem. Z., 1933, 261, 132—155; cf. A., 1932, 959).—The corpus luteum (I) is richer in combined lipins (II) than are the other sex organs (III), but in all the amount of (II) is very small. In both (I) and (III) the fatty acids which are free, combined in phosphatides, and combined in neutral fats are, in each case, different. The organs also differ greatly as regards the quant. composition (IV) of the lipins which they contain. In the epididymis (IV) depends on the content of semen. Details of the composition and physical and chemical consts. of the fatty acids, neutral fats, phosphatides, and phosphatides pptd. by  $\text{COMe}_2$  are given.

W. McC.

**Composition of unsaturated fatty acids of animal tissues.** H. G. SMITH (Proc. Iowa Acad. Sci., 1931, 38, 171—172).—The fatty acids of ox heart-muscle and liver contain  $\Delta^4$ .

CH. ABS.

**Cytological fixation with the lower fatty acids, their compounds and derivatives.** C. ZIRKLE (Protoplasma, 1933, 18, 90—111).—Use of a no. of

fatty acids and their Cu and Ni salts in conjunction with  $\text{CH}_2\text{O}$  in the fixation of cellular structures is examined.

A. G. P.

**Cytolysis by fat solvents and the importance of calcium and lecithin in the physico-chemical behaviour of protoplasm.** B. HLUCHOVSKY and B. SEKLA (Protoplasma, 1933, 18, 130—140).—The antagonism of fat solvents with respect to their cytolytic action is discussed. In the structure of the protoplasm there is a Ca-lecithin equilibrium which is disturbed by the differential action on the components of the various solvents examined.

A. G. P.

**Insect wax. V. *Psylla* and *Schizoneura* wax.** F. N. SCHULZ and M. BECKER (Biochem. Z., 1933, 261, 165—169).—*Psylla* wax,  $\text{C}_{32}\text{H}_{64}\text{O}$ , has m.p.  $95-96^\circ$ . *Schizoneura* wax, m.p.  $47-49^\circ$ , is probably a triglyceride containing 2 mols. of myristic and 1 mol. of palmitic acid or a mixture of triglycerides in which these acids, or other saturated fatty acids of mol. wt. of this order, are present in that ratio. The  $n_D$  of the wax is 1.4351, that of a 2:1 mixture of the acids named 1.4350.

W. McC.

**Intestinal worms. I. Chemical composition of *Taenia saginata*.** I. A. SMORODINCEV, K. V. BEBESCHIN, and P. I. PAVLOVA (Biochem. Z., 1933, 261, 176—178).—The average composition of the worms is:  $\text{H}_2\text{O}$  87.8, org. matter 11.6, total N 0.64 (equiv. to 4% of protein), fat 1.36, ash 0.65%. Compared with that of earthworms the  $\text{H}_2\text{O}$  content is the same, the ash content much lower. The fat content exhibits very great variations, depending on the condition of the host. About 6.2% of the org. matter is probably glycogen, but chitin may also be present.

W. McC.

**Pigment of *Proctolepsis tessellata*.** G. GHEORGHIU (Bull. Soc. Chim. biol., 1933, 15, 552—554).—The colouring matter is of the bile-pigment type.

A. L.

**Enzymes of *Hydrochelidon nigra*.** L. A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1933, 260, 369—375).—The glycerol extracts of the blood, leg, breast, mucous membrane, and keratinoid layer of the gizzard of *H. nigra*, L., all contain amylase (cf. A., 1932, 1274) and an invertase which attains its max. action when the concns. of enzyme and sugar are approaching the equilibrium concns. The glycerol extracts of the keratinoid layer contain no protease, of the breast and gizzard musculature traces, and of the blood, leg, and mucous membrane of the gizzard considerable amounts.

P. W. C.

**Apatite structure of inorganic bone- and tooth-substance.** M. A. BREDIG (Z. physiol. Chem., 1933, 216, 239—243).—Comparison of X-ray diagrams of synthetic preps., especially of carbonate-apatite with bone- and tooth-substance, indicates that the latter consists of hydroxyapatite.

J. H. B.

**Phosphorescence in human tissues. II. Phosphorescence of human concretions and pathological calcific tissues, and effect of calcination temperature on phosphorescence.** S. HOSHJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 21, 15—21; cf. this vol., 411).—The phosphorescence



spectra (I) of the tissues of various animals calcined at different temp. are examined. The ashes of calcified bronchial glands and muscular tissues give intense (I). The (I) of ashed human bones is identical with that of a mixture of calcite and hepatite.

H. D.

**Chinese silks. I. Glycine, alanine, and tyrosine contents of Chekiang silk.** P. P. T. SAH, T. S. MA, and S. Y. MA (J. Chinese Chem. Soc., 1933, 1, 17—22).—The amounts are glycine 18.8, alanine 16.5, and tyrosine 10.5%.

A. A. L.

**Sugar of amniotic fluid. Observations in chick embryos.** K. YAMADA (Japan. J. Med. Sci., Biochem., 1933, 2, 47—69).—Fructose was identified. Creatine and creatinine are not present after 12 days' incubation, but lactic acid can be detected. A summary of the general physical and chemical properties is given.

P. G. M.

**Fructose in the amniotic fluid of chick embryos.** K. YAMADA (Japan. J. Med. Sci., Biochem., 1933, 2, 107—113).—Using the cryogenin colour reaction (cf. following abstract) fructose was detected.

P. G. M.

**Colour reaction and micro-determination of *d*-fructose.** K. YAMADA (Japan. J. Med. Sci., Biochem., 1933, 2, 93—105).—Cryogenin (I) (*m*-benzamidosemicarbazide) when heated at 100° for 3 min. with HCl and glucose (II) (>0.5%) gives a reddish-violet colour, whilst with fructose (III) a bluish-violet colour is produced (concn. >0.005%). For the determination of (III) 2 c.c. of solution are heated with 2 c.c. of 24% HCl [containing 2% of (I)] for 20 min. at 100°; the mixture is cooled rapidly, diluted to 25 c.c., and compared colorimetrically with a standard. A partial separation of (II) and (III) can be effected by treatment with an EtOH-Et<sub>2</sub>O (2:1) mixture; the solubility of (II) is 46.6 and of (III) 286.0 mg. per 100 c.c. For detection of (III) in blood the proteins are first removed with CCl<sub>3</sub>-CO<sub>2</sub>H. The method is more sensitive and sp. than the NHPH<sub>2</sub> test (0.002 mg. gives a positive reaction). Many other carbohydrates give different colours in 1% solution.

P. G. M.

**Lipase content of thoracic duct lymph.** A. KALLÓ (Z. ges. exp. Med., 1933, 86, 848—853).—The lymph usually contained much more lipase than the blood. Lymph-lipase, which contributes to the serum-lipase, is derived from pancreatic or hepatic lipase directly through the lymph vessels or by way of the bowel.

NUTR. ABS.

**Function of chloride secretion in the stomach.** S. KIN (Keijo J. Med., 1933, 4, 41—52).—Total chlorides, free HCl, and total acid have been determined in human gastric juice, fasting and after test meals.

W. O. K.

**Substances which stimulate secretion from the gastric juice of the dog.** S. A. KOMAROW (Biochem. Z., 1933, 261, 92—105).—From the gastric juice (I) of the dog, after removal of protein and inorg. matter, phosphotungstic acid ppts. nitrogenous bases (II) sol. as carbonates in EtOH, which stimulate secretion by the gastric glands. Some of (II) pass

into the histidine-arginine fraction when AgNO<sub>3</sub> and Ba(OH)<sub>2</sub> are used for pptn. The extent of the stimulation is proportional to the amount of (I) from which the active material injected is obtained.

W. McC.

**Changes in alkali reserve and sugar content of bile as affected by different physiological agents.**

**III. Effect of histamine, adrenaline, and insulin.** W. M. KARATYGIN and A. I. HEFTER (Z. ges. exp. Med., 1933, 86, 697—708).—Histamine and insulin, both of which lead to an increase in the alkali reserve (I) of the blood, caused a rise in the (I) and a fall in the sugar content (II) of the bile: the vol. of bile secreted was increased. Adrenaline, which tends to cause a fall in blood-(I), caused a fall in (I) and a rise in (II) of the bile: the vol. was decreased.

NUTR. ABS.

**Excretion of nitrogen by the bile.** H. LUCKE and J. FREY (Z. ges. exp. Med., 1933, 86, 1—11).—On ordinary diet only 0.1 g. N in 24 hr. (0.5—1% of total output) was excreted in the bile of dogs with bile fistulae. When urea (50 g.) was given very little extra appeared in the bile. After the production of a nephritis (HgCl<sub>2</sub>) the bile-N increased (usually 1—7% of total output). U nitrate nephritis often led to a greater % output of N in the bile because of the small amounts of urine excreted. Although the bile responds to excessive N retention, its output cannot significantly affect the amount retained.

NUTR. ABS.

**Proteins of the whey fraction in milk from normal and abnormal udders.** F. S. JONES and R. B. LITTLE (J. Dairy Sci., 1933, 16, 101—109).—After removal of caseinogen the whey-proteins are pptd. by means of CCl<sub>3</sub>-CO<sub>2</sub>H and determined by the vol. of the ppt. after centrifuging. This vol. is correlated with the proportion of protein present as determined colorimetrically. Vals. for normal milk are fairly uniform, but increase considerably under abnormal conditions. The proteins found in milk during mastitis probably originate in the blood. Differences are established between the albumin: globulin ratios of normal and abnormal milks.

A. G. P.

**Acid milk in bovine mastitis.** F. S. JONES and R. B. LITTLE (J. Dairy Sci., 1933, 16, 111—119).—Acidity in milk during mastitis is associated with high nos. of carbohydrate-decomposing streptococci and a poorly buffered condition in the altered milk. Lactic acid is always present under these conditions.

A. G. P.

**Acid changes in milk produced by certain bacteria.** L. H. LAMPITT and M. BOGOD (Biochem. J., 1933, 27, 361—369).—Milk was inoculated with various bacteria (100,000 per c.c.), including *E. coli* (I), *B. subtilis* (II), *A. aerogenes* (III), *B. alcaligenes faecalis*, *S. lactis*, and a lipase-producing micrococcus (IV) of unknown species, and incubated at 30°. (I) and (III) show a general resemblance in the formation of total acidity, but (III) produces more lactic acid, whilst (I) destroys citric acid more completely. The citric acid loss with (II) is very small. The free fatty acid formation (chiefly higher fatty acids) is greatest in the case of (IV). (I) produces the largest amount of volatile acids. The destruction of



citric acid appears to be correlated with formation of volatile acids. W. O. K.

**Source of volatile acidity produced in milk by citric acid-fermenting streptococci.** M. B. MICHAELIAN and B. W. HAMMER (J. Dairy Sci., 1933, 16, 157—164).—Volatile acids are produced from citric and not from lactic acid. Increased production of volatile acids following additions of lactic acid to milk cultures is due to the establishment of a more favourable  $p_{\text{H}}$ , and is also induced by appropriate additions of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , or tartaric acid. The amount of volatile acid thus produced is greatest in cultures yielding least titratable acidity and *vice versa*. A. G. P.

**Excretion of fat through the skin.** A. PERUTZ and B. LUSTIG (Biochem. Z., 1933, 261, 128—131; cf. A., 1932, 958).—The increase (I) in the excretion of fat through the skin in rabbits receiving repeated subcutaneous injections of olive oil reaches 40%, the I val. (II) of the fat being doubled. When the injections cease (I) decreases, but (II) remains unchanged. If the mid-brain is destroyed similar changes occur, but (I) reaches 200% and the cholesterol content of the fat is greatly diminished. W. McC.

**Identification of lactose in urine.** R. GOOTZ and H. TUNGER (Z. physiol. Chem., 1933, 217, 28—32).—Lactose identification in presence of monoses is based on the determination of reducing power before and after enzymic hydrolysis. The urine must previously be boiled for 15 min. J. H. B.

**Simultaneous determination of lactose and glucose in urine.** I. S. KLEINER and H. TAUBER (J. Biol. Chem., 1933, 100, 749—754; cf. Tauber and Kleiner, this vol., 295).—The method consists in determining the total reducing power (I) and the monose content (II) of the filtrate obtained by treating the urine with  $\text{CuSO}_4$  and  $\text{Ba(OH)}_2$ . For total reduction, Benedict's Cu reagent (A., 1931, 973) is used, and the  $\text{Cu}_2\text{O}$  formed is determined colorimetrically after addition of acid molybdate. The lactose val. is obtained by subtracting (II) + 0.02% from (I), and multiplying by 2.2. A. L.

**Colloid chemistry of Trommer's sugar test.** F. GEBHARDT, R. KÖHLER, and E. KÖRNER (Kolloid-Z., 1933, 63, 257—263).—Sedimentation and X-ray analysis of the reduction products of alkaline  $\text{Cu(OH)}_2$  preps. show that a red product of relatively low dispersity is obtained with glucose solution, whilst reduction with glucose in presence of gelatin gives a yellow product of high dispersity. Both ppts. consist of  $\text{Cu}_2\text{O}$ . The product obtained with glucose-containing urine is generally yellow and contains a mixture of Cu and  $\text{Cu}_2\text{O}$ . E. S. H.

**Is blood-protein amide-nitrogen a source of urinary ammonia? IV. Aëration set for use in the transfer and measurement of small quantities of ammonia.** E. F. WILLIAMS, jun., and T. P. NASH, jun. (J. Biol. Chem., 1933, 100, 737—741). A. L.

**Form in which uric acid is excreted.** M. RANGIER (Compt. rend., 1933, 196, 1441—1442).—The ureide previously described (A., 1925, i, 186) and

almost the whole of the urochrome are adsorbed from urine by C. Subsequent elution with dil. aq.  $\text{NH}_3$ , evaporation to dryness, and extraction of the residue with  $\text{H}_2\text{O}$  ( $\text{NH}_4\text{H}$  urate remains undissolved) gives glycine (I). Uric acid is thus excreted in the form of a complex with (I). H. B.

**Hæmoglobin content of the blood of healthy and anæmic "salt-sick" cattle.** W. M. NEAL and R. B. BECKER (J. Agric. Res., 1933, 46, 557—563).—The following vals. are recorded: normal  $10.94 \pm 1.54$  to  $11.06 \pm 1.40$ , anæmic cattle which subsequently recovered after administration of Fe and Cu, min. 3.02; anæmic calf shortly before death, 1.37 g. per 100 c.c. of blood. A. G. P.

**Action of insulin on experimental beriberi and experimental avitaminosis-B.** O. KAUFFMANN-COSLA and S. OERIU (Arch. exp. Path. Pharm., 1933, 170, 458—464).—The blood-sugar of pigeons on a diet deficient in vitamin- $\text{B}_1$  rises above normal, but falls when polyneuritic symptoms appear, and ultimately reaches 25—40% below normal. Administration of insulin (I) prevents the hyperglycæmia. The progressive rise of urea and other N compounds in the blood is not reduced by administration of (I). W. O. K.

**Aluminium as a cause of cancer.** O. BAUMANN (Chem.-Ztg., 1933, 57, 424—425).—No ill-effects were observed on rats and mice fed with so-called harmless Al salts or with Al powder. The strong reducing powers of Al may produce changes in food-stuffs which account for the taste produced but are not necessarily harmful. Cut nasturtiums flourished in enamel, but died in Al, containers. J. G.

**Aluminium as a cause of cancer.** H. ZELLNER (Chem.-Ztg., 1933, 57, 425).—A reply to Baumann (cf. preceding abstract). J. G.

**Lipin content of malignant tumours. II.** R. BIERICH and A. LANG (Z. physiol. Chem., 1933, 216, 217—223; cf. A., 1931, 1445).—Slow-growing Jensen sarcoma shows a large increase in cholesteryl ester (I) (up to 10 times the normal) and 100% increase in uncombined fatty acids (II). Flexner-Jobling carcinoma shows no increase in (I). The necrotic tissue of Jensen sarcoma of normal growth shows an increase in (I) and a decrease in (II). J. H. B.

**Heavy metals in the cell. Copper and vitamin-B; copper and iron in tumours.** S. G. ZONDEK and M. BANDMANN (Deut. med. Woch., 1933, 59, 91—94).—Cu had a similar distribution to that of vitamin-B. No Cu was found in Jansen's cryst. vitamin- $\text{B}_1$ . The liver-Cu is at its max. in the human foetus, and the blood-Cu rises considerably during pregnancy. The liver-Fe of the rat increased markedly to the end of the period of growth, when it became const. In the nervous system the grey matter contained most Fe, the white matter less, and the peripheral nerves practically none. Very little Cu or Fe was found in rat carcinoma or sarcoma. Similar findings were obtained with cellular human tumours. NUTR. ABS.

**Immune reactions in diabetes.** J. K. MOEN and H. A. REIMANN (Arch. Int. Med., 1933, 51, 789—



795).—Severity of diabetes decreases the development of agglutinins for *B. typhosus*. H. G. R.

**Reactions of respiratory exchanges of diabetics to ingestion of glucose and to insulin.** F. RATHERY, A. PLANTEFOL, and L. PLANTEFOL (Compt. rend., 1933, 196, 1250—1252).—The effect of the ingestion of glucose (50 g.) on the R.Q. and metabolism of diabetics who (a) have had no insulin (I), (b) received (I) at least 12 hr. previously, and (c) received (I) with the glucose, varies markedly among individuals. An increase of R.Q. from 0.75 to 0.85—1.0 is, however, generally observed in group (c).

A. C.

**Consumption of blood-sugar by muscle in the non-diabetic and in the diabetic state.** W. M. YATER, J. MARKOWITZ, and R. F. CAHOON (Arch. Int. Med., 1933, 51, 800—813).—Heart-muscle in a normal heart-lung perfusion consumes 4 mg. of glucose (I) per g. per hr. In the diabetic condition the val. is < 1 mg. The decline in blood-sugar following removal of the liver is the same in both the non-diabetic (II) and diabetic (III) state. It is suggested that in (III) the requirement of (I) of resting skeletal muscle is the same as in (II), but, in (III), contracting muscle is unable to utilise (I) for the purpose of obtaining extra energy.

H. G. R.

**Transient hyperglycæmia and glycosuria following discontinuation of insulin given non-diabetic patients.** W. D. PAUL, B. B. CLARK, and R. B. GIBSON (Proc. Soc. Exp. Biol. Med., 1932, 30, 353—354).—Insulin (I) given in increasing doses up to 25 units thrice daily before meals to five non-diabetic subjects gave rise to no hypoglycæmic symptoms. On discontinuing (I) all patients showed hyperglycæmia, in one case up to 0.253% after sugar ingestion, four had temporary glycosuria, and three showed reduced sugar tolerance in response to a test dose.

NUTR. ABS.

**Mottled enamel and brown stain.** G. MONTELIUS, J. F. McINTOSH, and Y. C. MA (J. Dent. Res., 1933, 13, 73—79).—Org. matter, Ca, P, and Fe in stained and mottled enamels gave vals. within the limits for normal unstained teeth. NUTR. ABS.

**Late lactose-fermenting coliform bacilli in dysentery.** F. F. TANG (Chinese Med. J., 1933, 97, 161—167).—From eight cases of dysentery late lactose-fermenting bacilli classified under the genus *Escherichia* and one non-lactose-fermenting bacillus (*Aerobacter*) were isolated.

H. D.

**Behaviour of the adrenal lipins in anæmia caused by hæmorrhage and by hæmolytic poisons.** S. MARINO (Arch. Farm. sperim., 1933, 55, 183—206).—During the early stages of anæmia caused by hæmorrhage, the free and combined cholesterol (I) of the adrenals (II) diminishes whilst the phosphatides (III), fatty acids (IV), and, sometimes, the lipin-P increase. Later, when the corpuscular blood-mass increases, all the lipin contents increase. With anæmia caused by hæmolytic poisons, during the period when small Heinz bodies or granules appear (12—18 hr. after the injection), the (I) and (IV) of the (II) increase, whilst (III) and (V) may rise or fall. During the period of hæmolysis (3—5 days

after injection), (I) decreases, the (III) and (IV) increase, and (V) varies little. T. H. P.

**Urea clearance in normal and in dehydrated infants. Renal function and intestinal intoxication.** L. SCHOENTHAL, D. LURIE, and M. KELLY (Amer. J. Dis. Children, 1933, 45, 41—53).—The reduction in urea clearance in intestinal intoxication in infants is attributed to dehydration. CH. ABS.

**Cholesterol content of blood in Indians and its significance in jaundice.** A. C. GHOSE (Indian J. Med. Res., 1933, 20, 883—888).—The average normal blood-cholesterol of healthy Indians is 146 mg. per 100 c.c. of whole blood and 140 mg. per 100 c.c. of blood-plasma, or 40 mg. per 100 c.c. < European and American standards. The vals. are the same on a vegetarian and on a mixed diet and show a temporary increase on feeding a rich fatty diet to a starving subject. Seasonal variations are small.

NUTR. ABS.

**Content of cholesterol, unsaponifiable fraction, and lipins in brain of lunatics.** M. POLONOVSKI and P. LAWRIE (Compt. rend. Soc. Biol., 1933, 112, 381—383).—Vals. for brains of psychotics were not appreciably different from the normal except perhaps for a small lowering in the H<sub>2</sub>O content and an increase in the unsaponifiable substances of the white matter.

NUTR. ABS.

**Bromine in blood in manic depressive psychoses.** C. L. URECHIA and RETEZEANU (Compt. rend. Soc. Biol., 1933, 112, 411—412).—Blood-Br is diminished in melancholia or manic depressive psychoses.

NUTR. ABS.

**Bromine in blood in psychoses.** H. ZONDEK and A. BIER (Klin. Woch., 1933, 12, 55—56).—Although a fall in blood-Br is characteristic of 85—90% of cases of manic depressive insanity, a fall also occurs in cases of org. disease involving the brain. In cases of manic depressive psychosis, but not in org. brain diseases, the Br of the cerebrospinal fluid also falls.

NUTR. ABS.

**Mineral metabolism in renal disease. II. Excretion of minerals in the urine on K- and Na-rich diet.** H. GLATZEL (Z. ges. exp. Med., 1933, 86, 103—129).—A normal subject showed on a Na-rich diet (I) an increase in Ca and Mg output due to the greater potential acidity of the diet, and a decrease in the urinary output of P, S, and org. acids attributed to the increase in Cl. On (I) the vol. of urine was greater and the molar concn. less. On both Na- and K-rich (II) diets the amount of anions excreted was < that of the cations, in contrast with the excess of anions found on ordinary diet. In nephritis the concn. of all the elements except Mg was decreased on (I) and (II). In health and in nephritis the state of the acid-base balance regulates the output of minerals.

NUTR. ABS.

**Effects of agave concentrate in the treatment of experimental nephritis induced in animals. I. Nephritis induced in rabbits by the use of tartrates.** H. D. JONES, K. D. CRANE, G. B. JOHNSTON, and C. R. HENRY. II. Nephritis induced in dogs by the use of uranium nitrate. H. D. JONES,



R. C. HUGHES, and G. B. JOHNSTON (J. Pharm. Exp. Ther., 1933, 48, 1—24, 25—50).—I. Agave concentrate (fresh unfermented juice from *A. atrovirens*, Karw., conc. in vac. at 35—38°), administered orally to rabbits in which a kidney lesion is produced by an injection of tartrate, has a therapeutic effect on the nephritis shown by decreased mortality, improvement in the blood composition, and by the histological findings.

II. Similar favourable results were obtained in the case of dogs in which an acute nephritis was produced as the result of administration of  $\text{UO}_2(\text{NO}_3)_2$ .

W. O. K.

**Experimental cedema in nephrectomised dogs.** C. J. FARMER, F. S. BARRY, A. REED, and A. C. IVY (Arch. Int. Med., 1933, 51, 704—713).—In the nephrectomised dog there is a marked decrease in total serum-protein and in the albumin fraction (I) with an increase in the globulin, on the day following the onset of cedema (II). The amount of (I) and the reversal of the serum-protein ratio have no direct relation to the development of (II). The effusion fluids of dogs treated with Ringer's solution have a protein content of 1.3—4.0%.

H. G. R.

**Relationship between plasma-protein content, plasma-specific gravity, and cedema in dogs maintained on a protein-inadequate diet and in dogs rendered cedematous by plasmapheresis.** A. A. WEECH, C. E. SNELLING, and E. GOETTSCH (J. Clin. Invest., 1933, 12, 193—216).—In dogs subjected to plasmapheresis each bleeding resulted in an immediate fall in plasma-protein concn. followed by a period of increase most marked in the first 24 hr., but continuing until the next bleeding. A diet producing a negative N balance led to gradual decrease of plasma-albumin which was not paralleled by decrease of total protein because the globulin tended to rise. Gradual retention of NaCl and  $\text{H}_2\text{O}$  is also indicated. With plasmapheresis cedema was present at plasma-albumin concns. < 1.0—1.5 g. per 100 c.c. and nutritional cedema at concns. < 1.5—2.0 g. per 100 c.c. The subcutaneous cedema fluid contained 0.10—0.35 g. of protein per 100 c.c. with a slightly higher average than the fluid in plasmapheresis cases.

NUTR. ABS.

**Effect of serum transfusion on the plasma-protein depletion associated with nutritional cedema in dogs.** A. A. WEECH, E. GOETTSCH, and E. B. REEVES (J. Clin. Invest., 1933, 12, 217—228).—The transfusion of normal dog serum to a dog with low plasma-albumin (I), due to low-protein diet, leads to an immediate rise in the concn. of (I) and a fall in globulin (II). When calc. as total circulating protein both (I) and (II) were increased. After the preliminary rise the concn. of (I) fell, whilst that of (II), after its initial fall, gradually increased; total protein and blood vol. gradually returned to the pre-transfusion vals.

NUTR. ABS.

**Hyperfunction of the thyroid in pregnancy. Effect of adrenaline on blood-iodine in pregnancy.** W. SCHERINGER (Klin. Woch., 1933, 12, 107—108).—During the second half of pregnancy intravenous injection of 0.005 mg. of adrenaline resulted in a marked fall in blood-I within 30 sec.

After 30 min. the vals. reached, or even exceeded, the original level.

NUTR. ABS.

**Mechanism of the formation of phyto bezoars (persimmon ball).** S. IZUMI, K. ISIDA, and M. IWAMOTO (Japan. J. Med. Sci., Biochem., 1933, 2, 21—35).—These may be composed either of fibrous matter (inio-bezoar) or of fruits (opo-bezoar), the latter being the commonest. The persimmon ball is formed from unripe fruit, the skins being cemented together by the sol. tannin, shibuol (I), which is coagulated by gastric acidity. On ripening, (I) becomes insol. and loses its astringent properties; (I)-protein complexes cannot be digested either by pepsin or trypsin. Bile salts are pptd. by sol. (I) in presence of NaCl.

P. G. M.

**Pathological excretion of oxyproteic acid.** H. TSUTSUI (Japan. J. Med. Sci., Biochem., 1933, 2, 185—187).—Oxyproteic acid constitutes normally about 3.4% of the total N of urine. The proportion is increased in kala-azar, diabetes, and carcinoma of the stomach, but lowered in acute yellow atrophy of the liver; it is not correlated with the neutral S content of the urine.

P. G. M.

**Urinary protein.** S. KOZAWA, R. IWATSURU, and T. ADACHI (Biochem. Z., 1933, 260, 313—325).—The isoelectric point of urinary protein is at  $p_H$  4.4 and the protein on hydrolysis gives 80—82% of  $\alpha\text{-NH}_2$ -acids, 1.04—1.29% of histidine, 0.86—1.12% of tryptophan, and 4.56—4.98% of tyrosine. These figures, together with the albumin:globulin ratio, are all closely related to the corresponding figures for serum-protein.

P. W. C.

**Relation between calcium-potassium equilibrium and antirheumatics. III. Influence of antirheumatics in rabbits with mustard-oil inflammation or experimental toothache.** K. IN (Keijo J. Med., 1933, 4, 56—72).—In rabbits blistering of the skin with mustard oil does not alter the K/Ca ratio (I) in the serum, but in animals so treated, administration of erycon (II), antipyrine (III), and Na salicylate (IV) but not cinnamon (V) decreases (I). In rabbits with experimental toothache (I) exceeds the normal val., and is reduced by (II)—(IV), but not by (V). The animals are soothed by injection of  $\text{CaCl}_2$ , but KCl has the opposite effect.

W. O. K.

**Treatment of endemic scurvy by the intravenous injection of citrus.** T. J. DRY (Arch. Int. Med., 1933, 51, 679—691).—Intravenous use of citrus juices is an efficient method of controlling scurvy.

H. G. R.

**Glycosuria in spirochaetosis icterohæmorrhagica.** M. KITAOKA (Japan. J. Med. Sci., viii, Int. Med. Ped. Psych., 1932, 2, 239—266).—Glycosuria appears frequently after ingestion of food.

CH. ABS.

**Chemical composition of heart muscle.** Water content, total nitrogen, total phosphorus, sterols, glycogen, and lipins (I) in normal and thyroidec-tomised animals; (II) in thyrotoxicosis; (III) after stimulation with adrenaline; (IV) in animals thyroidless or suffering from thyro-toxicosis. A. FIESCHI (Z. ges. exp. Med., 1933, 86, 387—397, 398—407, 408—412, 413—419).—I.



Heart muscle of rabbits thyroidectomised 2–4 months previously showed a slight increase in  $H_2O$  content, a slight reduction of glycogen, a definite decrease in EtOH-sol. P, but a normal or slight increase in  $COMe_2$ -sol. P.

II. Intravenous injections of thyroxine or feeding with dried thyroid greatly reduced the heart-muscle-glycogen; total N and total P increased with slight increase in phosphatide, chiefly the  $COMe_2$  fraction. Dried thyroid (thyroidin) caused an increase in sterol content of heart muscle which was not found after thyroxine.

III. Intravenous injection of adrenaline (1 : 10,000) led to a marked increase in the  $H_2O$  content of heart muscle, but little change in the other constituents.

IV. Intravenous adrenaline produced in thyroidectomised rabbits a considerable increase in  $H_2O$  content and a reduction of EtOH-sol. P; in thyrotoxicosis (thyroid feeding or thyroxine injections) little change in  $H_2O$  content, increase in total P and phosphatide, and great diminution of glycogen.

NUTR. ABS.

Excretion of iodine in experimental hyperthyroidism. B. O. BARNES (Amer. J. Physiol., 1933, 103, 699–703).—When desiccated thyroid or thyroglobulin was fed to dogs, 50% of the I was eliminated through the urine and very little in the bile, but after thyroxine (I) intravenously, most of the injected I was excreted in the bile. It is concluded that free (I) is not liberated during the course of thyroid feeding.

NUTR. ABS.

Growth, reproduction, and lactation in the absence of the parathyroid glands. F. L. KOZELKA, E. B. HART, and G. BOHSTEDT (J. Biol. Chem., 1933, 100, 715–729).—In parathyroidectomised puppies fed on a complete diet including thyroxine and just sufficient vitamin-D to maintain the normal serum-Ca and inorg. P, Ca and P deposition in the soft tissues did not occur and calcification of the bones was normal. Mature dogs in similar circumstances were able to survive a complete reproductive cycle. It is believed that vitamin-D toxicity is due to increased blood-Ca, since the lactating animals were able to withstand up to 66,000 rat units per day (the amount necessary to maintain normal serum-Ca) without ill effect.

A. L.

Effect of acids and other substances on the production of acute gastric ulcers. J. FRIEDENWALD, M. FELDMAN, and S. MORRISON (J. Exp. Med., 1933, 57, 203–213).

CH. ABS.

Tissue respiration and its relation to morphological changes, oxidase reaction, and hydrogen-ion concentration in tissues. H. NAKAMURA (Trans. Japan. Path. Soc., 1931, 21, 282–295).—Respiration and oxidase reaction decreased in dying or starved liver and kidney tissue of rats, in tissues treated with HCl or  $NaHCO_3$ , or poisoned with U,  $HgCl_2$ ,  $K_2Cr_2O_7$ , As, P, or cantharidin.

CH. ABS.

Relation between degenerative changes and tissue respiration. Various toxins. M. NAKAMURA and K. SUZUKI. Inorganic poisons and ligation of the excretory duct. K. SUZUKI and M. NAKAMURA (Trans. Japan. Path. Soc., 1931, 21,

298–302, 302–305).—Degenerative changes caused by bacterial toxins were accompanied by decreased tissue respiration (I) and oxidising granules. Those caused by inorg. poisons are generally so accompanied; in many cases the decrease in (I) is parallel with the decrease in oxidase content. The change in (I) is related to the appearance of fat.

CH. ABS.

Iron as a cation in relation to reducing power of tissues. A. CANONICO and J. A. TAIANA (Compt. rend. Soc. Biol., 1933, 112, 493–494).—The power of rat-liver tissue to reduce  $m-C_6H_4(NO_2)_2$  was decreased by  $Fe^{II}$ .

NUTR. ABS.

Carbohydrate metabolism and the function of the grey matter of the central nervous system. E. G. HOLMES (Biochem. J., 1933, 27, 523–536).—The central nervous system of frogs functions, as shown by the convulsive response of the animals to strychnine injections, after 20 min. perfusion with 0.04%  $CH_2I \cdot CO_2H$  (I), the min. level of lactic acid having almost been reached by this time. Perfusion with 0.1% (I) for 1½ hr. is necessary for complete destruction of the function. 0.5% Na lactate and 0.05% AcCHO partly prevent the effect of (I). The labile P of the central nervous system is likewise reduced by (I) more rapidly than the tissue function is affected. The activity of the grey matter is therefore not immediately dependent on phosphocreatine breakdown or lactic acid formation or oxidation.

A. L.

Oxalic acid metabolism. R. JÜRGENS and G. SPEHR (Deut. Arch. klin. Med., 1933, 174, 456–467).—The blood-serum- $H_2C_2O_4$  of the fasting dog was 5.4–19.3 mg. per 100 c.c., and in man, 5.2–9.7 mg.; in disease these vals. may be increased by 68%. Perorally,  $H_2C_2O_4$  (I) and its salts produced in dogs a sharp rise of blood-(I), with a return to normal in the 5th hr. after administration. Jaundice and blood-(I) ran parallel courses, suggesting a connexion between the liver and (I) metabolism. A daily intake of 2.74 g. of (I), derived from food, did not raise the normal fasting val. in the blood during 5 days. The blood-(I) increased in some cases of renal calculus, in diabetes (in which it varied with the blood-sugar), in uræmia, and in leucæmia. Glucose rapidly produced a considerable rise of blood-(I) which persisted after the fall of blood-sugar. There appeared to be some connexion between sugar tolerance and degree of oxalæmia. The results suggest a relationship between sugar and (I) metabolism.

NUTR. ABS.

Metabolism of tissues. Rôle of glycolysis in the metabolism of embryonic cells. F. LIPMANN (Biochem. Z., 1933, 261, 157–164).—Quant. measurements of the respiration (I) and glycolysis (II), under aerobic and anaerobic (III) conditions and at low  $O_2$  pressures (IV), of growing embryonic (osteoblast, fibroblast) cells (V) *in vitro* have been made. The metabolism of (V) varies considerably with their origin. Under (III), development of too great acidity being prevented, very slight growth is possible. At (IV) reduction of (I) by one third is accompanied by reduction of growth by one half with corresponding increase in (II) which provides the min. amount of



energy required for growth (VI), but is apparently not the sp. reaction of (VI). W. McC.

**Anaërobic formation and disappearance of pyruvic acid in muscle.** O. MEYERHOF and D. McEACHERN (*Biochem. Z.*, 1933, **260**, 417—445).—In minced muscle in  $\text{PO}_4'''$  solution with max. lactic acid (I) formation,  $\text{AcCO}_2\text{H}$  (II) amounting to 2—4% of (I) is formed. This amount is increased at the expense of (I) in finely minced muscle and still further by addition of sulphite, when it amounts to 35% of (I). Formation of (II) is only transiently increased by addition of (I), but is strongly increased by addition of glycogen or hexose diphosphate. (II) added to muscle disappears to a slight extent, especially just after addition. In carbohydrate-free enzyme extracts, added (II) does not disappear, but the yield of (II) in presence of sulphite is increased several times. (II) arises therefore during the conversion of carbohydrate into (I) and not from (I). It is formed by the mutation of hexose diphosphate, the oxidised product being (II) and the reduced,  $\alpha$ -glycero-phosphoric acid. P. W. C.

**Mechanism of deamination in heart and skeletal muscle.** P. OSTERN and T. MANN (*Biochem. Z.*, 1933, **260**, 326—353).—With heart-muscle pulp (I) of man, dog, hare, rabbit, pigeon, etc., deamination of adenosine (II) is considerably more rapid than of adenylic acid (III), the reverse being true only of frog's (I). Adenine nucleotide is deaminated by (I), but not by skeletal muscle pulp (IV). The reaction is slower than with (III) and is decreased or completely inhibited by  $\text{PO}_4'''$ . Presence of salts ( $\text{Cl}'$ ,  $\text{PO}_4'''$ ,  $\text{SO}_4''$ ) accelerates deamination of (III) by (I). With (IV) formation of  $\text{NH}_3$  from (II) is much < from (III) and from (III) is much greater with (IV) than with (I) of the same animal. The dependence of  $\text{NH}_3$  formation on  $p_{\text{H}}$  is investigated. Adenosinetriphosphoric acid (V) is more slowly deaminised by (IV) than (III), the reaction being accelerated by alkali,  $\text{Cl}'$ ,  $\text{PO}_4'''$ ,  $\text{SO}_4''$ , and inhibited by  $\text{F}'$ . Mg salts inhibit deamination by (IV) both in the tissue pulp and of added (V) and (III). P. W. C.

**Variation of volume of muscle in relation to the chemistry of contraction. I. Methods. II. Change of volume with various forms of contraction.** O. MEYERHOF and W. MÖHLE (*Biochem. Z.*, 1933, **260**, 454—468; 469—489).—I. Apparatus for determination and photographic registration of the change in vol. of muscle on stimulation is described.

II. Of many such photographic registrations, a few characteristic curves and tables are given showing the change of vol. with the single muscle twitch, tetanus, isometric, isotonic, and auxotonic contraction, etc. P. W. C.

**Theory of muscular contraction.** P. FABRE (*Compt. rend. Soc. Biol.*, 1931, **106**, 951—953; *Chem. Zentr.*, 1933, i, 632).— $\text{H}'$  and lactate ions diffuse with different velocities into the contractile element, forming an electric double layer and producing a change in surface tension. Relaxation takes place when the more slowly diffusing ion has neutralised the other. A. A. E.

**Fat metabolism. II.** P. E. VERKADE and J. VAN DER LEE (*Proc. K. Akad. Wetensch. Amsterdam*, 1933, **36**, 314—323; cf. this vol., 417).—When glyceryl triononoate (A., 1932, 1018) is fed to man on a diet poor in carbohydrate, azelaic acid is excreted in the urine. Similarly, tridecain, triundecain (I), and trilaurin yield respectively sebacic, nonane- $\alpha$ - and decane- $\alpha\alpha$ -dicarboxylic acids. With tristridecain the corresponding diacid was not detectable. The conversion is most marked with (I). The significance of this  $\omega$ -oxidation in fat metabolism and the therapeutic importance of (I) are discussed. F. O. H.

**Combustion of fat in the lungs.** L. BINET, E. AUBEL, and M. MARQUIS (*Compt. rend. Soc. Biol.*, 1933, **112**, 540—542).—In lung perfusion experiments using citrated blood, the R.Q. after 1, 2, and 3 hr. was 0.95, 0.95, 1.00, whilst on perfusing with blood containing 0.5%  $\text{PrCO}_2\text{Na}$  (I), it was 0.90, 0.73, and 0.64, respectively. In the first series, therefore, carbohydrate (II) only was burned, whilst in the second, (II) was burned in the first hr., both (II) and (I) in the second, and almost exclusively (I) in the third hr. NUTR. ABS.

**Functions of the pancreas in fat resorption.** M. NOTHMANN and H. WENDT (*Klin. Woch.*, 1932, **11**, 2137—2139; *Chem. Zentr.*, 1933, i, 627).—A discussion. The pancreas plays an important part in removal of fat from the stomach, but not in its resorption in the intestine after cleavage. A. A. E.

**Effect of ultra-violet light on cholesterol metabolism. III. Methods.** R. HUBERT (*Arch. Gynäkol.*, 1932, **151**, 681—685).—The colorimetric method for determination of cholesterol (I) (Autenrieth and Funk, modified by Pincussen) gives results averaging 11.9% > those by the gravimetric (Windaus) method. The same changes of (I) metabolism are, however, detected by both methods. NUTR. ABS.

**Purine metabolism in man.** F. CHROMETZKA (*Z. ges. exp. Med.*, 1933, **86**, 483—528).—Feeding with uric acid (I) or its precursors led to an increase in the output of total creatinine. Even on meat-free diet small amounts of allantoin (II) were present in the urine (10—20 mg. in 24 hr.). In patients with disturbances of nucleoprotein metabolism (pituitary obesity) there was an increase in urinary (II). Feeding with (II) led to an increase in urinary urea; some of the urea must have been derived from the (II) by way of substances of the type of oxaluric acid. Evidence is given of an unknown nitrogenous end-product (III) (pptd. by  $\text{CuSO}_4$ ) and of purine metabolism, probably an intermediate stage between (I) and (II). Feeding with nucleic acid, purine bases, or (I) leads to appearance in the urine of a labile form of (I) which readily undergoes hydrolysis, and it is suggested that this is the parent substance of (III). NUTR. ABS.

**Production of kynurenic acid from tryptophan derivatives.** C. P. BERG (*Proc. Iowa Acad. Sci.*, 1931, **38**, 169).—Tryptophan Et ester hydrochloride, when administered orally or subcutaneously, gave rise to an output of kynurenic acid comparable with that afforded by an equiv. amount of free tryptophan;



the Ac derivative afforded a small, and the methylene and Bz derivatives an inappreciable, quantity.

CH. ABS.

**Labile rôle of sulphur in metabolism.** H. E. C. WILSON (J. Physiol., 1933, 77, 240—246).—Experimental evidence does not support the view that the labile nature of S in protein metabolism is due to preferential excretion of the S by the kidney, or that cystine is more easily attacked than other  $\text{NH}_2$ -acids. The hypothesis that a S compound, such as cystine, occupies a key position in the protein mol. and is the first to be eliminated in catabolism, or to be retained in anabolism, seems best to explain the peculiar metabolic behaviour of S.

NUTR. ABS.

**Digestibility of cheese.** A. MOEN (Tidsskr. norske Landbruk, 1933, 40, 3—5).—A fresh half-fat Gauda cheese contained 14.8% water-sol. and 92.0% digestible (HCl and pepsin) N; the ripe (6 months) cheese contained 52.0 and 99.3%, respectively.

NUTR. ABS.

**Relative digestibility by rats of the milk of five breeds of dairy cattle.** W. B. NEVENS and D. D. SHAW (J. Agric. Res., 1933, 46, 463—472).—With rats receiving milk only, no significant differences were observed in the digestibility of milks from different breeds of cattle. The % digestibilities of milk constituents were: fat 99, protein 91, total solids 92—93, sugars 100.

A. G. P.

**Nutritive value of the proteins of leguminous seeds.** V. ZAGAMI and V. FAMIANI (Atti R. Accad. Lincei, 1933, [vi], 17, 485—490; cf. this vol., 89).—Rat experiments show that the protein deficiency of grain may be supplied as well by the proteins of peas, beans, lentils, and the like as by caseinogen.

T. H. P.

**Digestive power of, and nitrogen retention by, four types of pigs.** J. SCHMIDT, M. F. VON LAGNEAU, and C. ZIMMERMANN (Arch. Tierernähr. Tierzucht, 1933, 8, 453—496).—The digestive power of pigs was not affected by age or type. N retention varied considerably among individual animals, but average vals. for 6—8 individuals of each of four types showed significant type differences.

A. G. P.

**Edible bird's-nests.** A. HEIDUSCHKA and L. GRAEFE (Biochem. Z., 1933, 260, 406—413).—The nest substance is a member of the group of salivary mucins of composition, C 49, H 6.9, N 9.8, S 0.9%, and is present chiefly as the sparingly sol. Ca and to a small extent as the Na salt. Traces of salivary enzymes are also present. On hydrolysis the substance yields 18% of carbohydrate (probably chitosamine) and the hydrolysate contains tyrosine 5.6, tryptophan 1.4, cystine 2.4, histidine 2.7, and arginine 2.7%. The heat of combustion of the swallow's nest is 4400 g.-cal. The nest substance is almost completely unattacked by pepsin and trypsin *in vitro*, and although intestinal bacteria attack it to a somewhat greater extent, the amount digested in the animal is very small.

P. W. C.

**Digestibility, metabolism, and energy exchange in hens as a basis for rational feeding.** M. J. DIAKOW (Arch. Tierernähr. Tierzucht, 1932, 7, 571—637).—Data are given showing respiratory and heat

exchanges in hens receiving varied diets. Unbroken grain is most advantageous when used in such quantities that it is wholly utilised for heat maintenance.

A. G. P.

**Mineral metabolism in rabbits fed on a cabbage diet.** S. RANGANATHAN (Indian J. Med. Res., 1932, 20, 651—662).—The finding of Baumann *et al.*, that the hyperplastic goitres produced in rabbits on an exclusive cabbage diet are associated with Ca, Mg, and P retention, has not been confirmed in cases where the goitres so produced range between 150 and 170 mg. per kg. body.-wt.

NUTR. ABS.

**Mineral metabolism of farm animals.** K. C. SEN (J. Indian Chem. Soc., 1933, Ray No., 143—159).—A summary.

H. J. E.

**Influence of the chief mineral nutrients on the structure and hygiene of the animal.** U. DUERST (Ernähr. Pflanze, 1933, 29, 141—145).—Effects of mineral salts on the digestive, metabolic, and reproductive changes in animals are discussed. Antagonism between  $\text{Ca}^{++}$  and  $\text{K}^+$  is considered.

A. G. P.

**Significance of calcium and phosphorus in the development and growth of pigs.** J. H. W. T. REIMERS and D. B. SMUTS (Arch. Tierernähr. Tierzucht, 1932, 7, 471—531).—Pigs developed rickets with a ration low in Ca and optimum in P (Ca : P = 1 : 4). The corrective action of cod-liver oil resulted from increased Ca and decreased P retention. Rations having excessive Ca and optimum P (Ca : P = 3.5 : 1) induced fits and blindness, high Ca and very low P contents in blood-serum, and decreased Ca and P retention. The Ca and P of the bones were unaltered. A ration having Ca : P = 1.8 : 1 produced no abnormal effects. The effects of excess-Ca rations were corrected by administration of  $\text{Na}_2\text{HPO}_4$ . Addition of CaO to a rachitic diet to produce Ca : P = 1.2 : 1 gave excellent results, which were not further improved by supplying cod-liver oil. Addition of Ca and P above certain limits to a ration having a normal Ca : P ratio increased the total ash content of bones without alteration of the % Ca and P.

A. G. P.

**Magnesium deficiency in animals. III. Chemical changes in the blood following magnesium deprivation.** D. H. KRUSE, E. R. ORENT, and E. V. MCCOLLUM (J. Biol. Chem., 1933, 100, 603—643; cf. A., 1932, 773).—In the blood of dogs fed on a diet containing 1.8 p.p.m. of Mg but adequate amounts of other constituents, serum-Mg decreases, this being followed by an increase in total cholesterol, particularly in the cholesteryl ester fraction, with a corresponding decrease in fatty acids, so that the total fat remains the same. Finally, before death, the non-protein-N rises. No change is observed in Na, K, Ca, inorg. P, lipin-P, bilirubin,  $\text{CO}_2$  capacity,  $\text{Cl}^-$ , fibrinogen, albumin, globulin, glucose, creatine, or creatinine.

A. L.

**Salt economy in extreme dry heat.** D. B. DILL, B. F. JONES, H. T. EDWARDS, and S. A. OBERG (J. Biol. Chem., 1933, 100, 755—767).—The changes in urinary output of  $\text{H}_2\text{O}$ , Cl, Na, K, N, and inorg. P of individuals under conditions of extreme dry heat indicate that high concn. similar to that of serum is not maintained in profuse and continued perspir-



ation (I). The organism adapts itself, and the salt content of (I) decreases after the first few days, so that 10 litres of (I) may be excreted per day without the necessity of having a greater salt intake than 15 g. per day, except before acclimatisation. The (I) for the entire period of dry heat had the average composition Cl 14, Na 14, K 2 milli-equiv. per litre.

A. L.

**Resorption of water and of water from salt solutions in the intestine.** W. STRAUB and E. LEO (Arch. exp. Path. Pharm., 1933, 170, 534—545).—In the intestine of a guinea-pig the rate of resorption of  $H_2O$  (I) is decreased by the presence in it of salts, the effect being dependent on the osmotic pressure and not on the nature of the salt. When the concn. is isotonic with the tissue fluids (I) does not occur, whilst with hypertonic solutions secretion takes place into the intestine. (I) is more rapid from the large than from the small intestine and is increased by free  $CO_2$ .

W. O. K.

**Metabolism of alcohol.** H. E. HIMWICH, L. H. NAHUM, N. RAKIETEN, J. F. FAZIKAS, D. DU BOIS, and E. F. GILDEA (J. Amer. Med. Assoc., 1933, 100, 651—654).—Ingestion of 10 c.c. of 19% EtOH (I) per kg. body-wt. by man and 50 c.c. by dogs was followed by a slight rise in blood-sugar, a marked rise in blood-lactic acid, and a decrease in blood- $CO_2$  and  $p_H$ . (I) acts as a glycogenolytic agent on liver- and muscle-glycogen. The fall in  $p_H$  due to accumulation of lactic acid and lag in  $CO_2$  excretion varied with the concn. of (I) in the blood. In patients suffering from the effects of excessive ingestion of alcohol the lactic acid of the arterial blood was increased. Intraperitoneal injection of 50 c.c. of 19% (I) per kg. of rat lowered the R.Q. of the cerebral cortex from 0.98 to < 0.9, indicating an oxidation of (I) and lactic acid.

NUTR. ABS.

**Determination of alcohol in blood.** A. HEIDUSCHKA and E. FLOTOW (Pharm. Zentr., 1933, 74, 329—333).—A modified Widmark method is recommended for forensic purposes. The blood-EtOH content is a more accurate measure of the EtOH consumed than is that of the urine. If the body-wt. and the time of consumption are known then the quantity of EtOH taken can be accurately calc. from the blood-EtOH.

E. H. S.

**Physiology of pyrimidines. VII. Metabolism of isobarbituric acid in man.** J. S. STEKOL and L. R. CERECEDO (J. Biol. Chem., 1933, 100, 653—656).—*iso*Barbituric acid fed to man is partly broken down to urea and partly excreted as an ethereal sulphate at the expense of the inorg.  $SO_4$  normally excreted. Neutral S remains unaffected.

A. L.

**Effect of soporifics on blood-sugar.** J. LERMAN (Z. ges. exp. Med., 1932, 85, 536—546; Chem. Zentr., 1933, i, 255).—In dogs the barbituric acid group tends to lower the blood-sugar. Chloretone causes a rise followed by a fall; chloralformamide and dionine have no effect.

A. A. E.

**Hypnotic action of mixed ketones containing different types of aromatic nuclei.** H. GILMAN, L. W. ROWE, and J. B. DICKEY.—See this vol., 720.

**Alteration of the blood-[H<sup>+</sup>] and mineral metabolism during narcosis. I. Calcium and phosphorus in blood during narcosis.** J. BEČKA (Arch. exp. Path. Pharm., 1933, 170, 377—383).—Of many hypnotics administered to rabbits, the greatest fall in the serum-Ca was effected by Mg salts, avertin (—4 mg. per 100 c.c.) whilst  $CHCl_3$  caused the greatest increase (+3 mg.). Post-narcotic effects were < those during narcosis. The serum-inorg. P exhibited only slight changes except with  $Mg_3(PO_4)_2$  (+5 mg.). The total P was increased by  $Mg_3(PO_4)_2$  (+14 mg.), avertin (+12 mg.), chloralformamide (+10 mg.), and urethane (+7 mg.). The post-narcotic effects on total P were somewhat irregular and sometimes reversed.

W. O. K.

**Action of veratrine and urethane on tissue oxidations.** F. BERNHEIM and M. L. C. BERNHEIM (J. Pharm. Exp. Ther., 1933, 48, 73—78).—Veratrine (a mixture of cevadine and veratridine) (I) inhibits the  $O_2$  uptake of mammalian muscle, kidney, and liver (ground or sliced tissue), being about 100—150 times as toxic as urethane (II), but has no effect on the R.Q. Its action is greater on broken than on intact cells. It has no effect on the oxidation of lactic and succinic acids by liver tissue, completely inhibits that of proline and xanthine, and accelerates that of tyramine. The  $O_2$  uptake of yeast is accelerated by small and inhibited by large concns. of (I) or (II).

W. O. K.

**Test for the presence of novocaine in nervous tissue.** M. GRODINSKY, M. BEBER, and C. P. BAKER (Science, 1933, 77, 450).—Novocaine in nervous tissue can be detected by diazotisation and the formation of an orange-red colour when  $\beta\text{-C}_{10}\text{H}_7\text{OH}$  is added.

L. S. T.

**Antagonism of paraldehyde to strychnine.** I. SIMON (Arch. Farm. speriment., 1933, 55, 214—218).—The antagonism of paraldehyde to strychnine (cf. Cervello, Arch. Sci. Med., 1883, 7, 1) is confirmed.

T. H. P.

**Combination experiments on magnesium and calcium with morphine with regard to the influence on blood-sugar.** K. AKIMOTO (Folia Pharmacol. Japon., 1933, 15, No. 3, 185—192).—Rabbit's blood-sugar is increased by subcutaneous injection of  $MgSO_4$  (0.2 g. per kg.) or  $CaCl_2$  (0.01 g. per kg.); much smaller doses have no effect, but the hyperglycaemic action of morphine is greatly increased, whilst larger doses have no such action.

CH. ABS.

**Pharmacological action of narcotine and its derivatives.** M. HAYASHI (Japan. J. Med. Sci., [iv], Pharmacol., 1932, 6, 203—257).

CH. ABS.

**Physiological action of norconessine.** A. C. WHITE (J. Pharm. Exp. Ther., 1933, 48, 79—87).—The pharmacological action of norconessine (cf. Haworth, A., 1932, 406) is very similar to that of conessine.

W. O. K.

**Pharmacology of anabesine.** H. B. HAAG (J. Pharm. Exp. Ther., 1933, 48, 95—104).—Anabesine (2-3'-pyridylpiperidine) resembles nicotine generally in its pharmacological actions, but it is somewhat less exciting and more depressing.

W. O. K.



Effects of some quaternary ammonium and analogous compounds on the autonomic nervous system. R. HUNT and R. R. RENSCHAW (J. Pharm. Exp. Ther., 1933, 48, 51—66).—The following compounds are approx. in order of decreasing muscarine-like action:  $[\text{NMe}_3\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2]\text{I}$  (I),  $[\text{NMe}_3\cdot(\text{CH}_2)_2\text{Ph}]\text{Br}$  (II),  $[\text{NMe}_3\cdot\text{CHPhMe}]\text{Br}$  (III),  $[\text{NMe}_3\cdot\text{CH}_2\cdot\text{NO}_2]\text{Br}$ ,  $[\text{NMeEt}_2\cdot\text{CHPh}\cdot\text{CN}]\text{I}$ ,  $[\text{NEt}_3\cdot(\text{CH}_2)_2\text{Ph}]\text{I}$  (IV),  $[\text{NEt}_3\cdot\text{CHPh}\cdot\text{CN}]\text{Br}$  (V), the last two compounds being inactive. (I), (II), and (III) have a nicotine stimulating action whilst (IV) and (V) have a paralysing nicotine action.

W. O. K.

[Pharmacology of] ethers and thio-ethers of triethylammonium compounds. R. HUNT and R. R. RENSCHAW (J. Pharm. Exp. Ther., 1933, 48, 105—125).—The compounds  $[\text{R}\cdot\text{CH}_2\cdot\text{NEt}_3]\text{X}$  ( $\text{R}=\text{OMe}$ ,  $\text{OEt}$ ,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{O}$ ,  $\text{OMe}\cdot\text{CH}_2$ ,  $\text{OEt}\cdot\text{CH}_2$ ,  $\text{OBu}\cdot\text{CH}_2$ ,  $\text{OPh}\cdot\text{CH}_2$ ,  $\text{SMe}$ ,  $\text{SEt}$ ,  $\text{SPi}^\beta$ ,  $\text{SBu}^\beta$ ;  $\text{X}=\text{Br}$  or  $\text{I}$ ) are all devoid of muscarine-like action or stimulating nicotine action, but exert a paralysing nicotine action.  $\text{R}=\text{OPh}$  was more active than the aliphatic ethers, of which  $\text{R}=\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{O}$  and  $\text{R}=\text{OBu}\cdot\text{CH}_2$  were the most active. Of the thiols the most active was  $\text{R}=\text{SBu}^\beta$ , which had a powerful and brief curare-like action.

W. O. K.

Depressor substance in extract of mistletoe. E. DRESSLER, H. KWIATKOWSKI, and E. SCHILF (Arch. exp. Path. Pharm., 170, 428—431).—The depressor action of an acid  $\text{EtOH}$  mistletoe extract on cats is inhibited by atropine. Acetylation of the crude extract increases its activity. A leech prep. treated with eserine reacts only to the acetylated extract (cf. A., 1932, 966). The depressor principle in the crude extract is therefore probably choline.

W. O. K.

Depressor action of stimulation of the chorda lingualis and influence of atropine. W. FELDBERG (Arch. exp. Path. Pharm., 1933, 170, 560—570).—The lowering of blood-pressure which occurs on stimulation of the chorda fibres to the salivary gland or of the chorda lingualis fibres to the tongue in a cat injected with eserine takes place in 10—15 sec. after the beginning of stimulation and is inhibited by atropine. Acetylcholine, probably, is produced locally, enters the blood-stream, and thus produces the depressor action.

W. O. K.

Substances regulating circulation and their significance in hypertonus. F. LANGE (Klin. Woch., 1933, 12, 173—176).—A hypotensive substance (I) can be isolated from blood, urine, and all tissues, of which  $5\text{--}7\times 10^{-6}$  g. has a marked effect on the blood-pressure of the cat. In essential hypertension the blood contains less, the urine considerably more, of (I) than that of healthy subjects. When hypertension is due to chronic nephritis the blood contains more and the urine less (I) than that of normals.

NUTR. ABS.

Substances regulating circulation. K. FELIX (Klin. Woch., 1933, 12, 176—179).—The hypotensive substance (preceding abstract) is a (mono)Me methylenediguandine compound.  $5\text{--}7\times 10^{-6}$  g. of the cryst. flavianate lowers the blood-pressure of a cat by 20—30 mm.

NUTR. ABS.

Physiological action of cystinyl peptides and guanidine derivatives. H. J. HARWOOD (Iowa State Coll. J. Sci., 1932, 6, 431—433).—Guanidine derivatives are classified as hyperglycæmic, hypoglycæmic, and inactive; in no case did the hypoglycæmic action approach that of insulin or synthalin, and it was usually accompanied by toxic effects. The prep. of dicarboxytyrosylcystine  $\text{Et}_2$  ester, dicarboethoxy-cystinyltyrosine  $\text{Et}$  ester, -cystinyl chloride, -cystinyltyrosine, -cystinylhistidine  $\text{Me}$  ester, and -cystinylarginine is described.

CH. ABS.

Influence of "anticoman" on carbohydrate metabolism. K. FRÖHLICH (Arch. Verdauungskrankh., 1932, 52, 434—440; Chem. Zentr., 1933, i, 629).—In non-toxic doses "anticoman" has no effect on the blood-sugar of fasting dogs and rabbits, but the glucose tolerance of normal animals is increased during several hr. For diabetic dogs insulin can be partly substituted by "anticoman."

A. A. E.

Interaction of histamine and nicotine on the intestine. F. BERNHEIM (J. Pharm. Exp. Ther., 1933, 48, 67—72).—The action of histamine on the isolated guinea-pig intestine is quantitatively antagonised by nicotine.

W. O. K.

Carbon dioxide changes in alveolar air and blood-plasma or -serum after subcutaneous histamine injection in man. L. MARTIN and M. MORGENSTERN (J. Lab. Clin. Med., 1932, 17, 1228—1236).—The  $\text{CO}_2$  contents of alveolar air and blood-plasma of individuals with normal gastric secretion are usually increased following injection of histamine, whilst those of individuals whose gastric juice contains no  $\text{HCl}$  may be increased or decreased.

CH. ABS.

Perfusion of the stomach. M. TSUDJI. I. Perfusion with histamine. Y. YOSHIDA. II. Perfusion with *dl*- and *d*-alanine. Y. MATSUOKA. III. Ketonic substances in gastric juice and the fate of *l*-leucine in the stomach wall. K. IKEBE (J. Biochem. Japan, 1933, 17, 259—260, 261—266, 267—274, 275—283).—The significance of the constituents of gastric juice is discussed.

I. Perfusion of the isolated dog's stomach (I) with defibrinated blood containing histamine (II) leads to the appearance of (II) in the mucous membrane.

II. Lactic acid is formed in the stomach wall by oxidative deamination of *dl*- or *d*-alanine.

III. Intravenous injection of *l*-leucine (III) produces a higher content of ketonic substances in the gastric juice than does subcutaneous injection of (II). Perfusion of (I) with defibrinated blood containing (III) increases the levels in the blood of  $\text{COMe}_2$ ,  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ , and  $\beta$ -hydroxybutyric acid, whilst the  $\text{NH}_2\text{-N}$  level falls to approx. half of the initial val. (III) appears to be catabolised in the stomach wall.

F. O. H.

Anaphylaxis in the rabbit. I. Factors concerned in the establishment of maximal hypersensitiveness in rabbits to egg-white and horse-serum. II. Effect of histamine, barium chloride, and adrenaline on unstriated muscle of the guinea-pig and rabbit. III. Sensitisation of rabbits with fowl corpuscles. IV. Simonds' explanation of the different pathologies of acute



anaphylactic shock in different animal species. V. Rôle of unstriped muscle in acute anaphylaxis in the rabbit. E. F. GROVE (J. Immunol., 1932, 23, 101—123, 125—138, 139—145, 147—152).—II. Histamine, adrenaline, and  $\text{BaCl}_2$  may produce a characteristically different effect on the same unstriated muscular tissue in the same animal.

CH. ABS.

Action of hashish. H. MARZ and G. ECKHARDT (Arch. exp. Path. Pharm., 1933, 170, 395—406).—The doses of crude cannabinal and of certain fractions and derivatives required to anaesthetise the rabbit's cornea have been determined. Hashish does not raise the body-temp. in dogs as in the case of men nor does it cause diuresis, whilst the pulse rate is lowered. The hæmoglobin content of the blood falls and other blood-constituents are also affected.

W. O. K.

[Toxicity of] *Senecio riddelli*. F. S. BUKEY and R. W. CUNNINGHAM (J. Amer. Pharm. Assoc., 1933, 22, 399—404).—Observations on horses are recorded.

E. H. S.

Cattle poisoning by the feeding of rape cake. C. KUČERA (Int. landw. Rundsch., 1931, 37, 915; Bied. Zentr., 1933, A, 3, 261—262).—In samples of rape cake having a toxic action on cattle the mustard-oil content was low, but probably there was a deficiency of myrosin. Data are given showing the amounts of mustard oil developed by rations containing rape cake and various myrosin-containing feeding-stuffs.

A. G. P.

Character of the dermatitis-producing factor in dietary egg-white as shown by certain chemical treatments. H. T. PARSONS and E. KELLY (J. Biol. Chem., 1933, 100, 645—652).—The capacity of egg-white (I) to produce a pellagra-like condition in the rat is destroyed by peptic digestion or by mild treatment with aq. HCl. The toxicity persists after denaturation with conc. aq. EtOH. On saturation of the (I) with  $(\text{NH}_4)_2\text{SO}_4$ , the toxicity remains in the protein, but is absent from purified ovalbumin. (I) denatured by EtOH and dialysed is as active as before.

A. L.

Toxic substances of *Amanita* species. H. A. RAAB and J. RENZ (Z. physiol. Chem., 1933, 216, 224—228).—Several species of *Amanita*, including *phalloides*, contained no hæmolysin acting on ox-blood. The apparent destruction of the lysin of *A. excelsis* by heating is due to its adsorption on the pptd. protein. The sensitivity to HCl was confirmed. Only *A. phalloides* and *verna* contain the toxin.

J. H. B.

Influence of theocin on the action of ephedrine and hypophysin. R. KOHN (Arch. exp. Path. Pharm., 1933, 170, 432—442).—Theocin (I) does not inhibit the pressor action of ephedrine (II) or of hypophysin (III) to the same extent as that of adrenaline or sympatol. (I) has a paralysing effect on the intestine and uterus. The stimulating action of (III) and (II) on the intestine and uterus is decreased by (I), whilst the inhibiting action of (II) is reinforced by that of (I).

W. O. K.

Amino-alcohols. IX. Biological assay of propadrin and ephedrine. T. S. GITHENS (J. Amer.

Pharm. Assoc., 1933, 22, 391—399).—Propadrin is of approx. the same activity as ephedrine and is equally stable in solution.

E. H. S.

Comparison of two xanthine diuretics. Theophylline sodium acetate and theobromine sodium salicylate. A. R. BLISS, jun., and R. W. MORRISON (J. Amer. Pharm. Assoc., 1933, 22, 404—410).—The two drugs are about equal in promptness of action (in rabbits) and both increase the vol. of urine. Uric acid and total solids are also increased. The theobromine compound is the safer of the two and produces no irritation.

E. H. S.

Nature of phloridzin diabetes. I. Metabolism of individual organs after administration of phloridzin. E. S. LONDON and N. P. KOTSCHNEFF (Arch. exp. Path. Pharm., 1933, 170, 384—394).—Phloridzin administered to dogs influences the metabolism of many organs, and the metabolism of fat, protein, and carbohydrate is disturbed. The  $\text{NH}_2$ - and polypeptide-N of the arterial blood is raised, the  $\text{NH}_2$ -N being given up by the muscle and retained by kidneys and liver. The fatty acid content of the arterial blood is also raised. Fatty acid is given up by the subcutaneous tissue, intestine, and kidney and is retained by the liver and lungs. Sugar is produced by the liver and taken up by the intestine, muscles, and kidneys.

W. O. K.

Effect of intravenous injection of hypertonic glucose. E. VON GYÖRGY and L. VESZELSZKY (Arch. Kinderheilk., 1932, 98, 70—74).—Intravenous injection of 4% glucose in amounts equiv. to 0.3—0.4 g. per kg. body-wt. produced in children no glycosuria (I). When 0.5—2.0 g. per kg. was given, (I) was present. In infants (I) was present when the dose exceeded 0.5 g. per kg.

NUTR. ABS.

Calcium : magnesium ratio of blood-serum in oxalic acid poisoning. M. JACOBY and H. FRIEDEL (Biochem. Z., 1933, 260, 451—453).—The serum-Mg content of dogs poisoned with  $\text{H}_2\text{C}_2\text{O}_4$  increases, whilst the Ca content and the Ca : Mg ratio decrease.

P. W. C.

Pharmacology of acetylsalicylic acid. I. SIMON (Arch. Farm. sperim., 1933, 55, 151—182).—The min. lethal dose (intravenous) is for rabbits 0.7 g. per kg. of body-wt. The toxicity is greatly diminished by contact of the acid with NaCl in  $\text{H}_2\text{O}$  for a few hr. The acid has an intense hæmolytic action on human or rabbit blood both *in vivo* and *in vitro*. It has a toxic effect on the isolated heart of the frog, but only very large doses produce vaso-constriction. When 1 g. is ingested by a healthy man, 90% passes out in the urine, about one half of this being unchanged. It increases the elimination of uric acid with healthy individuals in purine equilibrium.

T. H. P.

Microchemical colour reaction of *m*-dinitrobenzene for the forensic detection of benzene. F. KIRCHHOF (Chem.-Ztg., 1933, 57, 425—426).—If Peltzer's reaction (B., 1931, 433; this vol., 532) is carried out by adding to a mixture of equal vols. of a solution of the  $\text{NO}_2$ -compound and 96% EtOH (instead of  $\text{COMe}_2$ ) 1 drop of KOH in EtOH, a colour stable for 3—4 hr. is obtained. The reaction is also obtained with technical  $\text{PhNO}_2$ , presumably owing



to the presence of  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ . The chemistry of the reaction is discussed. J. G.

**Microchemical reaction of *m*-dinitrobenzene for the forensic detection of benzene.** I. PELTZER (Chem.-Ztg., 1933, 57, 426).—The modified reaction described by Kirchhof (preceding abstract) is not confirmed. A violet colour changing to carmine was obtained by the original method from  $\text{PhNO}_2$ , although it was weaker than that from  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ . J. G.

**Toxic action of cations on fibroblasts cultivated *in vitro*.** J. VERNE and C. SANNIÉ (Compt. rend., 1933, 196, 1246—1247).—Alkali, Ca, and Mg chlorides are not toxic to fibroblasts in Ringer solution containing plasma.  $\text{NH}_4$ , Sr, Ba, and Mn inhibit growth at concns. between  $N/120$  and  $N/150$ . Fe, Pb, Al, U, Be, Y, Pr, La, Dy, and Th are toxic at  $N/200$ —1000; Ce, Tl, Ni, Co, Au, Pt, Cu, and Zn at  $N/1000$ —5000; Cd and Hg at  $N/10,000$ . Plasma-protein protects the fibroblasts from the toxic action of Cu, Pb, and Pt, and, to a smaller degree, from that of U, Cr, Fe, and Au, which are more toxic in the absence of plasma. There is no protective action with Tl, Cd, and Hg; Zn, Ni, and Co are more toxic in the presence than in the absence of plasma. A. C.

**Iodine storage in [animal] organs.** W. WEBER (Diss., Basle, 1930; Bied. Zentr., 1933, A, 3, 258).—Administration of I, even in considerable quantities, does not increase the I content of the internal organs by > a few mg. per 100 g. Elimination of I is rapid and in some cases amounts in 1 day to 75% of the quantity ingested. A. G. P.

**Metabolism of tissues growing in culture. V. Effect of radium on the metabolism of cultures of embryonic kidney tissue.** B. E. HOLMES (Biochem. J., 1933, 27, 391—396).—When kidney tissue in artificial culture is subjected to suitable degrees of irradiation by  $\gamma$ -rays from Ra, the oxidation of carbohydrate (glucose and galactose) is inhibited, although very small doses of radiation may produce a small acceleration. The utilisation of protein with the formation of  $\text{NH}_3$  and urea does not appear to be affected by  $\gamma$ -rays. W. O. K.

**Mercury poisoning. I. Influence of water and Ringer solution.** M. KUSE (Folia Pharmacol. Japon., 1933, 15, No. 3, 244—258).—Rabbits fed on oats are more resistant to Hg poisoning than those fed on bean jelly. Injection of Ringer solution soon after that of novasurol had a good effect. CH. ABS.

**[Arsenical poisoning from] dangerous wall coverings.** A. W. VERVLOET (Pharm. Weekblad, 1933, 70, 578—584).—A case of As poisoning from wall panelling made from sugar-cane fibre is recorded. S. C.

**Toxicity of osmium tetroxide.** F. R. BRUNOT (J. Ind. Hyg., 1933, 15, 136—143).—Rabbits exposed to an atm. containing  $\text{OsO}_4$  vapour (0.25—1.0 g. in 190 litres) suffer bronchopneumonia, inflammation of the cornea, and ultimately death. Industrial protective measures are indicated. F. O. H.

**Chemotherapy of organo-metalloid compounds.** S. C. NIXOGY (J. Indian Chem. Soc., 1933,

Rây No., 135—140).—Trypanocidal action is discussed. H. B.

**Chemotherapy of paludism. Tests on the Java sparrow.** E. FOURNEAU, J. TRÉFOUEL, D. BOVET, and G. BENOIT (Ann. Inst. Pasteur, 1933, 50, 731—744).—A no. of derivatives of 8-aminoquinoline were tested for parasitocidal activity; the most effective were of the type 8-R-amino-6-methoxyquinoline ( $\text{R}=\text{NEt}_2\text{[CH}_2\text{]}_x$ ;  $x=4, 5$ , or 6). These compounds, in which the alkyl group is a straight chain, have a chemotherapeutic index of  $\frac{1}{100}$  to  $\frac{1}{150}$ . Substitution of Me for OMe in the 6-position destroys the activity, whilst OEt is also much less effective. Activity is also reduced when the 8- $\text{NH}_2$  group of quinoline is substituted with a branched-chain alkyl group. All the products tested were much less toxic in the rabbit. P. G. M.

**Determination of diffusion coefficients of substances of high mol. wt. Diffusion of catalase.** K. ZEILE (Biochem. Z., 1933, 261, 156; cf. this vol., 425).—Stern claims to have determined the mol. wt. of catalase by the diffusion method. W. McC.

**Presence in cells of adipose tissues of a dehydrogenase acting on higher fatty acids.** G. QUAGLIARIELLO (Atti R. Accad. Lincei, 1932, [vi], 16, 552—554).—The adipose tissue of the dog contains a dehydrogenase which acts on higher fatty acids, causing either oxidation of existing double linkings or formation of new double linkings (cf. this vol., 413). T. H. P.

**Dehydrogenase of the higher aliphatic acids in the liver.** F. P. MAZZA and G. STOLFI (Atti R. Accad. Lincei, 1933, [vi], 17, 476—480).—Confirmation is obtained of the presence in liver extracts of an enzyme capable of mobilising the H of higher fatty acids (cf. Quagliariello, this vol., 413), the point of attack being the ionised  $\text{CO}_2\text{H}$  of the acid. The enzyme is not found in muscle, kidneys, or pancreas, and differs from succino-dehydrogenase. A mechanism of its action is suggested. T. H. P.

**Enzymic dehydrogenation of fat.** N. BEREND (Biochem. Z., 1933, 260, 490—498).—The detection, prep., determination, and properties of an enzyme from ox pancreas which on activation with bile is able to dehydrogenate tristearin, are described. P. W. C.

**Glucose-dehydrogenase. Preparation and properties of the enzyme and its co-enzyme.** D. C. HARRISON (Biochem. J., 1933, 27, 382—386).—Dialysed aq. extracts of  $\text{COMe}_2$ -treated liver are mixed with an equal vol. of saturated  $(\text{NH}_4)_2\text{SO}_4$  and the pptd. protein, which contains the enzyme (I), is separated from the mother-liquor in which the co-enzyme (II) remains. (II) is pptd. with protein on complete saturation with  $(\text{NH}_4)_2\text{SO}_4$ , the product taken up in  $\text{H}_2\text{O}$ , and the protein removed by heat-coagulation, a solution of (II) being obtained. (II) is not adenyl pyrophosphate. W. O. K.

**Chemical nature of the active group in glucose-dehydrogenase.** D. C. HARRISON (Proc. Roy. Soc., 1933, B, 113, 150—160).—Xanthine-oxidase (Schar-dinger) (I) completely inhibits the oxidation of glucose by glucose-dehydrogenase (II). This is shown to be



due to oxidative destruction of (II). Since (I) acts on aldehyde and purine substrates, and the activity of (II) is reversibly inhibited by low concns. of  $\text{NaHSO}_3$ , the activity of (II) may be associated with an aldehyde group. A. C.

**Effect of adenosinephosphoric acids on dehydrogenation processes by vegetable and animal enzymes.** II. H. J. DEUTICKE (Pflüger's Archiv, 1932, 230, 556—562; Chem. Zentr., 1933, i, 622).—Embsden's heart nucleotide behaves like adenosine-triphosphoric acid towards methylene-blue in presence of dehydrogenases. A. A. E.

**Co-enzyme of lactic acid oxidation.** I. BANGA and A. SZENT-GYÖRGYI (Z. physiol. Chem., 1933, 217, 39—43).—The co-enzyme of lactic acid oxidation was further purified (cf. A., 1932, 1165) by pptn. with phosphotungstic acid followed by prep. of the picrate. It is a  $\alpha'$  monoadenyl nucleotide monophosphate, not identical with muscle-adenylic acid or adenyl pyrophosphate, but possibly with Euler's co-enzyme. J. H. B.

**Oxidation of lactic and  $\beta$ -hydroxybutyric acids by heart-muscle.** I. BANGA, K. LAKI, and A. SZENT-GYÖRGYI (Z. physiol. Chem., 1933, 217, 43—51).—In presence of the dehydrogenase (I) of heart-muscle activated by co-enzyme (II), lactic acid (III) is reversibly oxidised to  $\text{AcCO}_2\text{H}$  (IV). (I), (II), (III), and (IV) form a thermodynamically reversible oxidation system with  $E_0$  —181 mv.  $\beta$ -Hydroxybutyric acid (V) is dehydrogenated to the  $\beta$ -keto acid (VI). The dehydrogenation of (III) and (V) is activated by the same (II). Oxidation of (V) also forms a reversible system. Except (III), (V), and fructose diphosphate, no acid examined is oxidised by the enzyme. In each case of oxidation the enzyme requires its co-enzyme, but the hydrogenation of (IV) is unaffected by the co-enzyme. J. H. B.

**Free energy of lactic acid oxidation. Scale for biological oxidation-reduction potentials.** A. SZENT-GYÖRGYI (Z. physiol. Chem., 1933, 217, 51—53).—The  $\text{O}_2$  electrode is proposed as reference electrode for biological oxidation-reduction potentials. All biological potentials ( $EO_2$ ) become negative and the sign may be neglected. In the system lactic acid- $\text{AcCO}_2\text{H}$ -activated dehydrogenase  $EO_2$  = 991 mv. and the change of free energy in the oxidation is 45.7 g.-cal. J. H. B.

**Properties of glyoxalase and mechanism of antiglyoxalase action.** J. O. GIRŠAVIČIUS (Biochem. Z., 1933, 260, 278—312).—Complete inhibition of glyoxalase (I) occurs with such very small amounts of pancreatin that the direct action of the latter on  $\text{BzCHO}$  (II) can be neglected, and the non-enzymic conversion of (II) can thus be determined. A portion of (II) added to liver extract cannot be recovered, the amount being const. for one set of conditions. This loss decreases with increasing dilution of liver extract, but is independent of the concn. of (II). The loss is caused by substances present in both the  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  ppt. and filtrate, and is partly or wholly due to glutathione (III).  $\text{Na H}$  malcate buffer inhibits (I) more strongly than does  $\text{PO}_4'''$ , whilst  $\text{PrOH}$  (optimum concn. 1.8%) activates. A concn.

of (II) of 0.2% is optimal for (I) activity. The inhibition of (I) by pancreatin shows an induction period and is antagonised by addition of (III). (III) on incubating with pancreatin and liver extract loses its power to activate (I). P. W. C.

**Glyoxalase activity of the red blood-cell. Function of glutathione.** M. JOWETT and J. H. QUASTEL (Biochem. J., 1933, 27, 486—498).—Whilst the high glyoxalase (I) activity of human red blood-corpuscles disappears on lysis of the cells with  $\text{H}_2\text{O}$ , it is completely restored by the addition of glutathione (II) at a similar concn. to that present in the intact cell. The liberation of  $\text{CO}_2$ , and the change of the I titre of (II) when (II) is mixed with  $\text{AcCHO}$  (III), and a study of the reaction velocity of (I) in presence of (II), indicate that (II) and (III) combine reversibly. The (I) activity of red blood-cells lysed and intact under anaërobic is  $>$  that under aërobic conditions, the effect of  $\text{O}_2$  being reversible. Glucose decreases the inhibition by  $\text{O}_2$  only on the intact cell. These effects are believed to be due to interference with the equilibrium between oxidised and reduced (II). The (I) activity of red blood-cells is compared with the glycolytic activity of tissues under similar conditions. A. L.

**Muscle-glyoxalase.** J. WATANABE (J. Biochem. Japan, 1933, 17, 307—313).—The incomplete transformation of  $\text{AcCHO}$  (I) into lactic acid (II) by muscle-glyoxalase preps. (A., 1928, 796) is due to creatine in the enzyme solution reacting with a part of (I) and inhibiting its conversion into (II). F. O. H.

**Enzymic fission of polysaccharides. I. Specificity of cellulose- and hemicellulose-splitting enzymes.** W. GRASSMANN, R. STADLER, and R. BENDER (Annalen, 1933, 502, 20—40).—The enzyme prep. (I) used (cf. A., 1932, 1062) is obtained from fungi and is purified by dialysis (cf. Karrer *et al.*, A., 1924, i, 471). (I) effects hydrolysis (max. at  $p_{\text{H}}$  4.5) of cellulose, lichenin, and xylan; the crude (I) also hydrolyses hydropectin, mannan, inulin, and chitin. Max. hydrolysis of cellobiose occurs at  $p_{\text{H}}$  4.5—5. The relationships between the amounts of (I) used and the substrate hydrolysed are investigated. Varying amounts of lichenase and xylanase are adsorbed from (I) by  $\text{Al}_2\text{O}_3$ , C, and kaolin. H. B.

**Saccharification of starch.** A. TYCHOWSKI (Przemysł Chem., 1933, 17, 65—74).—The saccharification of dextrins by malt or barley diastase is due chiefly to  $\alpha$ -diastase; the action of a mixture of purified  $\alpha$ - and  $\beta$ -diastase is considerably  $<$  that of the unpurified malt extract, pointing to the presence of activators in the latter; such activators are also present in aq. extracts of yeast. The concn. of maltose in the reaction mixture does not affect the equilibrium point, the attainment of which depends solely on exhaustion of hydrolysable dextrins. R. T.

**Takadiastase. II. Inactivation by heat and reactivation.** E. OHLSSON and O. EDFELDT (Bull. Soc. Chim. biol., 1933, 15, 470—481).—The enzyme is inactivated by heating in various buffer solutions. For max. reactivation, the inactivation must be



carried out rapidly. For a temp. of 90°, a  $p_H$  of 5.63—6.03 during deactivation gives max. reactivation at a fixed  $p_H$ , whilst for a fixed  $p_H$  during inactivation the optimum  $p_H$  for reactivation is 7.0. Reactivation occurs only between  $p_H$  5.5 and 8.7.

A. L.

**Specificity of  $\alpha$ -glucosidase.** R. WEIDENHAGEN (Z. physiol. Chem., 1933, 216, 255—259).— $\alpha$ -Glucosidase from takadiastase or from barley malt hydrolyses  $\alpha$ -methylglucoside,  $\alpha$ -phenylglucoside, and maltose, again indicating its identity with maltase.

J. H. B.

**Action of amylase.** E. M. MYSTKOWSKI and M. LANDAU (Biochem. Z., 1933, 261, 116—127).—At  $p_H$  other than the optimum (I) glycine (II) accelerates the action of amylase (III) on starch (IV), the effect being the greater the further the  $p_H$  is from (I). (II) does not increase the reaction velocity beyond that observed at (I), nor does it affect the degree of dispersion of (III).  $\text{CaCl}_2$  counteracts the effect of (II) and also inhibits the degradation of (IV), colloidal factors being probably involved. The action of (II) is probably chemical.

W. McC.

**Separation of the two malt-amylases by adsorption.** O. HOLMBERG (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 4, 6 pp.).—Max. adsorption of a dialysed amylase prep. (from kiln-malt) on starch occurs in 50% EtOH,  $\alpha$ -amylase (I) being adsorbed in preference to  $\beta$ -amylase (II) (A., 1930, 955). Adsorption in 30% EtOH followed by washing of the complex with 50% EtOH yields a solution rich in (I), whilst the residual solution is rich in (II). Prolonged adsorption is attended by destruction of the enzymes. Pptn. of malt extract by 30—45% EtOH gives a ppt. rich in (I). Increase of acidity increases the adsorption of amylase, but destruction of the enzyme is accelerated.

F. O. H.

**"Sisto-amylase," a natural inhibitor of amylase.** T. CHRZASZCZ and J. JANICKI (Biochem. Z., 1933, 260, 354—368).—During germination of buckwheat a substance ("sisto-amylase") (I) is formed in the roots and leaves which paralyses the liquefying, dextrinifying, and saccharifying power of amylase. (I) is insol. in  $\text{H}_2\text{O}$  and EtOH, is fairly sensitive to rise in temp., and is protein-like in character, its action being rapid and due either to adsorption of, or formation of a complex compound with, amylase. (I) is not present in the seeds before germination.

P. W. C.

**Reaction velocity-temperature constant of yeast-invertase in supercooled solutions.** Z. I. KERTESZ.—See this vol., 679.

**Maltase. I. Blood-maltase. II. Origin of blood- and urine-maltase. III. Conditions for blood-maltase activity. IV. Maltase of human urine.** T. KOKURYO (Japan. J. Med. Sci., Biochem., 1933, 2, 115—130, 131—159, 161—174, 175—184).—I. Maltose is absent from the blood of the cat, guinea-pig, rabbit, and man; in the horse, sheep, and dog it is almost exclusively associated with the pseudoglobulin fraction, whilst in the pig it is conc. in the albumin and euglobulin fractions.

II. Maltase in the blood and urine has its origin in the pancreas and intestine. The diastase content

is unaffected by starvation, but the maltase content is variable.

III. Substitution of 0.5% of NaF for PhMe as preservative increases the hydrolysis of a 2.5% solution of maltose by blood-maltase from 78.6 to 92.9% in 24 hr. A combination of 0.5% NaF and 0.9% NaCl is even more effective. The optimum  $p_H$  is 6.6.

IV. The urine-maltase in man has been investigated in health and disease. The occurrence is most frequent in an acid urine ( $p_H$  4.0—4.9) and in cases of tuberculosis.

P. G. M.

**Digestion and inactivation of maltase by trypsin and the specificity of maltase.** H. TAUBER and I. S. KLEINER (J. Gen. Physiol., 1933, 16, 767—771).—Maltase (I) of saliva and of *B. coli* hydrolyses maltose but not  $\alpha$ -methylglucoside or sucrose. (I) is rapidly inactivated by trypsin.

H. G. R.

**Glucosulphatase.** V. T. SODA and F. EGAMI (Bull. Chem. Soc. Japan, 1933, 8, 148—160; cf. this vol., 534).—A modified prep. of a very active, solid glucosulphatase is described. The enzyme acts purely hydrolytically on glucose sulphate, is completely adsorbed by kaolin, but not by  $\text{BaSO}_4$ ,  $\text{Al}(\text{OH})_3$  gel, or C. Its action is inhibited by glucose, galactose,  $\text{MgCO}_3$ ,  $\text{SO}_4^{--}$ , or  $\text{PO}_4^{---}$  (very greatly). It is not identical with pheno-sulphatase, which, however, is always present as an impurity.

R. S. C.

**Proteolytic enzymes and the coagulation of caseinogen.** S. NISHIMURA (J. Agric. Chem. Soc. Japan, 1932, 8, 1323—1334).—Caseinogen (I) or milk is coagulated by takadiastase, papain, and pancreatin. When (I) is partly hydrolysed by protease of the tryptase type in presence of Ca, coagulation may occur. With pepsin, coagulation is accompanied by slight hydrolysis.

CH. ABS.

**Fractional enzymic degradation of ovalbumin.** H. O. CALVERY, E. WALDSCHMIDT-LEITZ, and A. SCHÄFFNER (Naturwiss., 1933, 21, 316).—The successive action of pepsin, carboxy- (or amino-)poly- and di-peptidase on ovalbumin liberates 24% of the original total N as  $\text{NH}_2$ -groups at each stage. Pancreatic proteinase (I), carboxy- (or amino-)poly- and di-peptidase liberate 24, 36, and 12% in successive stages. Pepsin or (I) followed by protaminase (II) liberate 24 and 6%, respectively. Pepsin has no action after (I) and *vice versa*. It is concluded that peptic hydrolysis yields chiefly tripeptides, (I) yields also higher peptides, whilst (II) hydrolysis yields  $\text{NH}_2$ -groups corresponding with the  $\alpha$ - $\text{NH}_2$ -groups of arginine, histidine, and lysine.

R. K. C.

**Effect of halogen salts on tryptic digestion.** W. M. CLIFFORD (Biochem. J., 1933, 27, 326—331).—The digestion of fish protein by trypsin is depressed by addition of halides of Li, Na, K, and  $\text{NH}_4$  in the order  $\text{F}^-$  and  $\text{Cl}^- > \text{I}^- > \text{Br}^-$ . The depressing action decreases as the concn. falls from 0.5M to 0.008M, but no accelerating action is observed. In conc. solutions  $\text{NH}_4$  salts are the most depressant. NaF is less depressant than KF or  $\text{NH}_4\text{F}$ .

R. K. C.

**Action of high pressures on pancreatic juice.** J. BASSET, M. LISBONNE, and M. A. MACHEBEUF (Compt. rend., 1933, 196, 1540—1542).—After sub-



jection to pressures of 11,000—13,500 atm. for 30—40 min., pancreatic juice (I) is activated by kinase and Ca but not by acid; trypsinogen (II) and amylase (III) remain normal, whilst lipase is destroyed. (II) and (III) are partly destroyed at 15,500 atm./45 min. The trypsin content of activated (I) is reduced by 50% after 45 min. at 13,500 atm.; (III) is destroyed.

H. B.

**Enzymic degradation of diketopiperazine rings.** T. ISHIYAMA.—See this vol., 723.

**Tyrosinase from the skin of certain black rabbits.** C. E. M. PUGH (Biochem. J., 1933, 27, 476—479).—Mammalian tyrosinase (I) is shown to exist by the fact that tyrosinase extracts can be made from the skins of certain recessive black rabbits. Black Rex rabbits and black rabbits of unknown pedigree failed, however, to yield (I), although pyrocatechol-oxidase was present in all the skins examined.

A. L.

**Supposed oxidase activity of cobaltammines with particular reference to tyrosinase.** C. E. M. PUGH (Biochem. J., 1933, 27, 480—485).—Examination of a no. of cobaltammines has shown that they cannot imitate the action of tyrosinase. The colour change produced on tyrosine and *p*-cresol by  $[3\text{NH}_3, \text{CoCl}_2, \text{H}_2\text{O}]\text{Cl}$  (I) does not require  $\text{O}_2$ ; that, however, on pyrocatechol by (I),  $[4\text{NH}_3, \text{CoCl}_2]\text{Cl}$ , and  $[3\text{NH}_3, \text{Co}(\text{NO}_3)_3]$  does.

A. L.

**Concentration of soya-bean urease. New method for the purification of enzymes.** J. S. KIRK (J. Biol. Chem., 1933, 100, 667—670).—Soya-bean urease (I) is completely pptd. from soya-bean extracts by adding excess of antiurease. By making such a pptn. fractionally, (I) has been purified 850 times.

A. L.

**Urea-splitting enzyme found in gastric juice.** L. MARTIN (Bull. Johns Hopkins Hosp., 1933, 52, 166—172).—Normal gastric juice contains a urease which is active between  $p_{\text{H}}$  1.4 and 8.3 (optimum  $p_{\text{H}}$  8.0).

NUTR. ABS.

**Thrombase. Preparation and properties.** J. MELLANBY (Proc. Roy. Soc., 1933, B, 113, 93—106).—Prothrombase (A., 1931, 111) undergoes spontaneous transformation into thrombase (I), the prep. and purification of which are described. (I) is a  $\text{H}_2\text{O}$ -sol., slowly dialysable (collodion) protein, destroyed by 0.01N-NaOH and 0.01N-HCl; 1 mg. coagulates 100 c.c. of oxalated plasma in 30 sec., and intravenous injection of 2 mg. into a 2-kg. rabbit rapidly causes intravascular coagulation and death. The time of coagulation of plasma varies inversely as the amount of (I), and directly as its dilution. When (I) converts fibrinogen into fibrin, the latter adsorbs (I) in proportion to its original concn. It is suggested that (I) is an essential factor in blood coagulation *in vivo*, and that it causes fission of fibrinogen into fibrin and serum-globulin.

A. C.

**Digestion in Selachians.** H. BEAUVALET (Compt. rend., 1933, 196, 1437—1439).—An extract of the anterior portion of the stomach of *Scyllium canicula* hydrolyses fibrin (I) in acid medium to albumoses and peptones, whilst the extract of the posterior portion hydrolyses (I), starch (II), and olive oil (III)

in alkaline media. The pancreatic extract hydrolyses (II) and (III), whilst the liver extract and bile hydrolyse (I) (to peptones), (II), and (III).

H. B.

**Rate of oxygen utilisation by yeast as related to temperature.** T. J. B. STIER (J. Gen. Physiol., 1933, 16, 815—840).—The ratio of consumption of  $\text{O}_2$  to temp. for *S. cerevisiae* gave a reproducible "temp. characteristic" over a wide range. Plotted according to the Arrhenius equation, the const.  $\mu$  has the following vals.:  $35\text{--}30^\circ$   $8290$ ,  $30\text{--}15^\circ$   $12,440 \pm 290$ ,  $15\text{--}3^\circ$   $19,530 \pm 154$ . The crit. temp. are at  $29.0^\circ$  and  $15.7^\circ$ . A close similarity exists between these vals. for  $\mu$  and those usually obtained for respiratory activities in other organisms.

H. G. R.

**Yeast growth in absence of oxygen.** R. KOCH (Woch. Brau., 1933, 50, 169—172).—Yeast grown under completely anaërobic conditions in a sealed drop culture containing also a culture of *B. putrificus* to remove  $\text{O}_2$  develops initially at a rate slightly less than the aërobic control. After 1—3 days, however, the yeast decays and loses its power of propagation. Vigorous aëration of a fermenting wort produces a yeast of low fermentative power, and thus excessive aëration is as unsuitable as complete lack of  $\text{O}_2$ .

R. H. H.

**Fermentation of hexose monophosphate and glyceraldehyde- $\gamma$ -phosphoric acid.** C. V. SMYTHE and W. GERISCHER (Biochem. Z., 1933, 260, 414—416).—For the same mol. concn. the initial velocity of hexose monophosphate fermentation using Lebedev's extract is at least as great as for glucose. At the corresponding concn. (same C content) the velocity of elimination of  $\text{CO}_2$  from glyceraldehyde- $\gamma$ -phosphoric acid is half that of glucose or hexose phosphate. When the concn. of triose ester is doubled, the total  $\text{CO}_2$  formation is the same as for glucose or hexose phosphate, and the velocity of formation is the same. Glyceraldehyde itself is only very slowly fermented by the juice.

P. W. C.

**Zymophosphate and alcoholic fermentation.** B. HVIETENDAHN (Angew. Chem., 1933, 46, 335—337).—A discussion. The Harden-Young hexose diphosphate is probably a maltose tetraphosphate.

W. O. K.

**Decomposition of amino-acids by yeast.** I—III. M. YAMADA (J. Agric. Chem. Soc. Japan, 1932, 8, 428—432, 498—505, 506—508).—I. Leucine, glycine, alanine, and  $\alpha$ -aminobutyric acid substituted for asparagine in Hayduck solution affect the production of fusel oil (I) by saké yeast (II). Valine and norvaline, but not asparagine, glutamic acid, and  $(\text{NH}_4)_2\text{SO}_4$ , produce traces of (I).

II. (I) from a solution containing glucose, *d*-alanine (0.4%), and Hayduck mineral solution fermented by (II) contained *isobutyl* and a little amyl alcohol. When *dl*-alanine was added the same result was obtained and *l*-alanine was recovered. Brewer's yeast afforded only amyl alcohol.

III. Replacement of the asparagine by *dl*- $\alpha$ -aminobutyric acid led with (II) to the formation principally of active amyl alcohol. The recovered  $\text{NH}_2$ -acid had  $[\alpha]_{\text{D}}^{20} -1.14^\circ$  (in 20% HCl solution).

CH. ABS.



**Rôle of iron in alcoholic fermentation.** F. ZUCKERKANDL and L. MESSNER-KLEBERMASS (Biochem. Z., 1933, 261, 55—63).— $\alpha\alpha'$ -Phenanthroline (I), which forms very stable complex  $\text{Fe}^{\text{II}}$  compounds, reversibly inhibits fermentation by yeast, but does not combine with Fe which is already bound in a complex such as hæmin.  $\alpha\beta$ -Phenanthroline neither forms such complexes nor inhibits the fermentation. It follows that Fe is necessarily a constituent of holozymase and that it is probably  $\text{Fe}^{\text{II}}$  which is active, whilst Fe in hæmin complexes does not partake in the fermentation.  $\text{Fe}'$  inhibits the fermentation probably by preventing the conversion of  $\text{Fe}^{\text{III}}$  into  $\text{Fe}^{\text{II}}$ . (I) resembles  $\text{CH}_3\text{I}-\text{CO}_2\text{H}$  (II) in the concn. at which it acts, but its activity increases with increasing  $p_{\text{H}}$ , whereas the activities of (II) and of  $\text{Fe}'$  then decrease. Two complementary systems of fermentation involving Fe probably exist. One, which catalyses respiration, is sensitive to  $\text{CN}'$ ; the other, which activates fermentation, is relatively insensitive to  $\text{CN}'$ .

W. McC.

**Action of organic compounds on alcoholic fermentation.** III. Compounds with condensed nuclei and their reduction products. E. MAMELI and A. MOSSINI (Giorn. Chim. Ind. Appl., 1933, 15, 161—167; cf. A., 1932, 1288).—Compounds containing condensed nuclei with olefinic linkings in nuclei ( $\text{C}_{10}\text{H}_8$ , indene, acenaphthene, phenanthrene, cholesterol) determine or accelerate alcoholic fermentation, whereas the corresponding saturated compounds have little or no effect in this direction. An olefinic linking in such compounds appears to exert less influence on the fermentation when in the nucleus than when in a side-chain, and when the latter has this linking at its extremity the effect increases with the length of the side-chain.

T. H. P.

**Influence of organic dyes on cell and organ function.** III. Fermentation by yeast cells and press juices in presence of organic dyes. F. AXMACHER (Arch. exp. Path. Pharm., 1933, 170, 476—491).—Certain basic dyes inhibit the fermentation (I) of glucose and fructose by beer- and top yeasts, and have practically no effect on fermentation by cell-free zymase filtrate (II). Certain acid disazo-dyes are without action on (I) by yeast cells but inhibit that by (II).

W. O. K.

**Action of different kinds of light on glycolysis.** E. KEESER (Arch. exp. Path. Pharm., 1933, 170, 500—509).—Irradiation (red light) for 30 min. of 0.1% glucose solution (buffered with  $\text{PO}_4'''$ ) in presence of yeast cells accelerated the decrease in reducing power (I); white, green, or blue light had little effect. Similar results were obtained with fructose as well as in the glycolysis of glucose or fructose by guinea-pig serum. Irradiation (5 hr.) of ox-serum with visible light did not alter its (I) or its content in inorg. P (II), but ultra-violet irradiation increased (I) but did not change (II). Rabbits irradiated with visible light exhibited a reduction in the no. of white blood-corpuscles, but apart from a temporary eosinophilia no change in the differential count occurred.

W. O. K.

**Effect of monochromatic light on yeast fermentation.** R. MURAKAMI (J. Agric. Chem. Soc.

Japan, 1932, 8, 1237—1247).—In the fermentation of koji extract at 25—28°, EtOH production was max. in red light ( $> 6200 \text{ Å.}$ ); that of aldehydes was max. at 3960—5400 Å. Acetal was produced abundantly in white light. The production of volatile acids was max. in the dark, whilst that of non-volatile acids was max. at 3900—5800 Å.

CH. ABS.

**Relation of inorganic salts to growth and reproduction in *Amœba proteus*.** D. M. PACE (Arch. Protistenk., 1933, 79, 133—145).—A stimulatory effect on reproduction is shown by  $\text{FeCl}_2$  in concns.  $< 0.0001N$  and by  $\text{SO}_4''$ ,  $< 0.00007N$ . Above these limits inhibition occurs. The stimulatory action of  $\text{SiO}_3''$  was very marked. Increasing concns. of chlorides of Na, K, Ca, and Mg, or of  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SiO}_3$  have at first a stimulatory and at higher concns. an inhibitory effect. In still greater concns. a second optimum is reached. Similar effects are produced by solutions of mixed salts. The action of salts is ascribed to electrolytic effects rather than to sp. ionic properties.

A. G. P.

**Aspergillin, the spore pigment of *Aspergillus niger*.** II. A. QUILICO and A. DI CAPUA (Atti R. Accad. Lincei, 1933, [vi], 17, 177—182; cf. this vol., 536).—When extracted with 1—2% aq.  $\text{NH}_3$  and pptd. with HCl, aspergillin forms shining black lumps with brown reflexion. EtOH or MeOH dissolves 12—14%, and the residue, containing 0.23—0.26% Fe, has C:H:O=5:4:2 and behaves like certain oxypyrrrole-blacks when heated (A., 1932, 1266). It contains an OH and forms *Me*, *Et*, and *Bz* derivatives.

T. H. P.

**Occurrence of the growth-promotor *B* in urine.** V. HARTELIUS (Biochem. Z., 1933, 261, 76—88; cf. this vol., 189).—The substance *B* which promotes the growth of *A. niger* occurs in human urine (I) in amounts (II) proportional to the solid content. Age, sex, and pregnancy have no effect on (II). *B* is probably derived from food, since (II) increase after meals. (I) also contains a complementary substance (*co-B*), possibly a Zn compound, but in amount insufficient to enable *B* to produce its max. effect (III). (III) is produced by addition of filter-paper ash. *B*, which is insol. in  $\text{Et}_2\text{O}$  and resists destruction by heat or  $\text{H}_2\text{O}_2$ , is probably identical with similar substances previously described.

W. McC.

**Occurrence of the growth-promotor *B*.** V. HARTELIUS (Biochem. Z., 1933, 261, 89—91).—Foods (*e.g.*, cabbage, potatoes, apples, barley, milk) and also blood contain abundant quantities of *B*, but only small amounts of *co-B*. At least part of the *B* content of urine may therefore come from the food consumed.

W. McC.

**Biochemistry of filamentous fungi. I. Colouring matters of *Monascus purpureus*, Went.** H. NISHIKAWA (J. Agric. Chem. Soc. Japan, 1932, 8, 1007—1015).—The  $\text{Et}_2\text{O}$  extract afforded *monascorubin* (I),  $\text{C}_{22}\text{H}_{24}\text{O}_5$ , m.p. 136°, reduced (Pd-BaSO<sub>4</sub>) to  $\text{C}_{22}\text{H}_{26}\text{O}_5$ , m.p. 95—96°. (I) with Br gave  $\text{C}_{21}\text{H}_{23}\text{O}_3\text{Br}_3$ , and with  $\text{H}_2\text{O}_2$  or  $\text{KMnO}_4$  gave *monascoflavin* (II),  $\text{C}_{17}\text{H}_{22}\text{O}_4$ , m.p. 145°. Reduction of (II) (Pd-BaSO<sub>4</sub>) gives *dihydromonascoflavin*, m.p.



120°, phenolic. (II) affords  $C_{17}H_{22}O_4Br_2$ , m.p. 175—183°, and  $C_{17}H_{21}O_4Ac$ , amorphous. CH. ABS.

**Biochemistry of micro-organisms. XXVII.** Production of luteic acid from various sources of carbon by *Penicillium luteum*, Zukal. J. H. BIRKINSHAW and H. RAISTRICK (Biochem. J., 1933, 27, 370—375).—Luteic acid which is produced by *P. luteum* when grown on glucose (A., 1931, 1092) is also produced by this organism when grown on fructose, galactose, mannose, xylose, arabinose, and glycerol as the sole source of C. A similar product is also formed from succinic and from citric acids.

W. O. K.

**Biochemistry of micro-organisms. XXVIII.** Helminthosporin and hydroxyisohelminthosporin, metabolic products of the plant pathogen *Helminthosporium gramineum*, Rabenhorst. J. H. V. CHARLES, H. RAISTRICK, R. ROBINSON, and A. R. TODD (Biochem. J., 1933, 27, 499—511).—The dried mycelium of *H. gramineum* responsible for the leaf-stripe disease of barley, when extracted with  $CHCl_3$  gives 30% of a mixture of helminthosporin,  $C_{15}H_{10}O_5$  (I), m.p. 225—226° [ $Ac_3$  derivative (II), m.p. 223—224°], and hydroxyisohelminthosporin,  $C_{15}H_{10}O_6$  (III), m.p. 238° ( $Ac_4$  derivative, m.p. 234—235°), (I) being 2—3 times in excess of (III). (I) gives on distillation with Zn dust 2-methylantracene. (II) with  $CrO_3$  in AcOH yields triacetylhelminthosporic acid,  $C_{21}H_{14}O_{10}$ , m.p. 235—236° (Et ester, m.p. 205—206°), hydrolysed to helminthosporic acid (IV),  $C_{15}H_8O_7$ , m.p. 359—360° (Et ester, m.p. 194—195°). (IV) when heated with quinoline and  $CuCr_2O_4$  gives 1:4:5-trihydroxyanthraquinone, m.p. 268—269° (triacetate, m.p. 224—225°), also prepared synthetically from 1:4:5-trichloroanthraquinone with  $Ca(OH)_2$  and Cu-bronze. (I) with aq.  $HNO_3$ ,  $d$  1.42, gives a substance, m.p. 225—227° (decomp.), probably trinitrohelminthosporin, and also 2:4:6-trinitro-5-hydroxy-3-methylbenzoic acid. (I) is therefore 2-methyl-4:5:8-trihydroxyanthraquinone. (III) may be 1:8-dihydroxy-2-hydroxymethylantracene. Colour reactions of (I) and (III) are described, and the optimum cultural conditions for the production of the pigments by the fungus are determined.

A. L.

**Carbon metabolism of *Fusarium oxysporum* on glucose.** A. K. ANDERSON, E. L. EVERITT, and P. D. ADAMS (J. Agric. Res., 1933, 46, 473—482).—The principal products of the metabolism of glucose by *F. oxysporum* are  $CO_2$  and EtOH, but this organism, unlike *F. lini*, utilises EtOH as a food source only to a very slight extent.

A. G. P.

**Comparative growth rates of different strains of *Rhizobium meliloti*.** R. H. WALKER and D. A. ANDERSON (Proc. Iowa Acad. Sci., 1931, 38, 333—334).—Organisms which are less efficient in fixing N grow faster in presence of combined N or require it for growth; more efficient organisms grow faster in its absence, or may be inhibited by it. CH. ABS.

**Production of gum by certain species of *Rhizobium*.** D. A. ANDERSON (Iowa Agric. Exp. Sta. Res. Bull., 1933, No. 158, 27—56).—The amount of gum produced in *Rhizobium* cultures may be calc. from the alteration in viscosity of the medium. An

equilibrium is indicated between the amount of gum formed and the quantity of sugar destroyed, irrespective of the size of the inoculum. Gum formation is a normal process in the metabolism of the organism, and increases with the exposed surface area of the cultures. Differences in the viscosity changes in cultures of different species of *Rhizobium* may be due in part to chemical differences in the gums produced.

A. G. P.

**Conditions governing the production of the plant-growth hormone by *Rhizopus* cultures.** K. V. THIMANN and H. E. DOLK (Biol. Zentr., 1933, 53, 149—166).—Aeration of cultures increases the production of the hormone (I). Formation of (I) is either dependent on sp. peptones or is greatly inhibited by impurities in crude peptone. The production of coloured carotenoid substances proceeds approx. parallel with that of (I). Formation of (I) is associated with the formation of sporangia and (I) may be utilised, wholly or in part, by the germinating spores.

A. G. P.

**Conditions of culture and synthetic power of *Saprolegnia* sp.** Carbon, nitrogen, and sulphur nutrition. M. VOLKONSKY (Ann. Inst. Pasteur, 1933, 50, 703—730).—A typical basic culture medium contains NaOAc 0.1,  $K_2HPO_4$  0.1,  $MgCl_2$  0.01%, a trace of  $FeCl_3$ , and NaOH to  $p_H$  7.0. Muscle peptone supplies complete org. nutriment. AcOH,  $OH \cdot CHMe \cdot CO_2H$ , and  $AcCO_2H$  are poor sources of C; alanine, cysteine, and histidine are good sources. Glycine, sarcosine, and valine will not support development. In the presence of an unfavourable  $NH_2$ -acid a fermentable sugar is essential. Most of the  $NH_2$ -acids which are poor sources of C are good sources of N in the presence of glucose. Cysteine is the only source of S which is effective alone;  $H_2S$  and  $AcSH$  require the presence of glucose in addition. The synthetic power is greatly modified by the composition of the nutrient medium.

P. G. M.

**Fermentation of glucose by legume bacteria.** A. I. VIRTANEN, M. NORDLUND, and E. HOLLO (Suomen Kem., 1933, B, 6, 62).—Fermentation is of the  $PrCO_2H$  type.

A. G. P.

**Methane fermentation of carbohydrates.** G. E. SYMONS [with A. M. BUSWELL] (J. Amer. Chem. Soc., 1933, 55, 2028—2036).—The  $CH_4$  fermentation of 45 substances (carbohydrates, alcohols, aldehydes, ketones, acids) is studied. Fermentation is an anaerobic oxidation-reduction reaction involving  $H_2O$  and is catalysed by bacteria.  $CO_2$  and  $H_2$  appear to be the primary products and the reaction  $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$  occurs to some extent; org. acids are probable intermediates. For compounds containing C, H, and O, the general reaction is  $C_nH_aO_b + (n - a/4 - b/2)H_2O \rightarrow (n/2 - a/8 + b/4)CO_2 + (n/2 + a/8 - b/4)CH_4$ ; an equation is formulated also for compounds containing C, H, O, N, S, and metal. Thermodynamic considerations indicate that if  $H_2O$  is the only source of O (other than that in the compound undergoing fermentation), then  $CH_4$  and  $CO_2$  are the expected end-products, since the greatest decrease in free energy occurs with their formation. Reaction



proceeds in the same manner at both 33–35° and 58–60°.  
H. B.

**Hydrogen-producing organism from spoiled cream style maize.** J. J. HARRIS (Zentr. Bakt. Par., 1933, 88, II, 54–57).—Swelled tins of maize contained CO<sub>2</sub> 31.5, O<sub>2</sub> 0.5, H<sub>2</sub> 54.0%. A H<sub>2</sub>-producing organism (probably *Es. pseudocoscrobali*) was isolated and examined.  
A. G. P.

**Cellulose-decomposing bacteria requiring iron.** R. BOJANOVSKY (Zentr. Bakt. Par., 1933, 88, II, 1–16).—Optimum growth of certain aerobic cellulose-decomposing bacteria isolated from soils occurred in media containing 0.0012–0.0026% Fe, supplied as Mohr's salt. On either side of this range development was retarded.  
A. G. P.

**Activity of non-pathogenic bacteria utilising mineral matter in the thermal water of Aix-les-Bains and Aix-Burtscheid.** I. A. SCHLOEMER.—See this vol., 691.

**Kinetics of intracellular carbohydrate oxidation of *Sarcina lutea*.** B. B. RUBENSTEIN (J. Cell. Comp. Physiol., 1932, 2, 27–40).—The O<sub>2</sub> consumption (I) of *S. lutea* in darkness is expressed by the equation for a unimol. reaction. The rate of (I) increases during irradiation at < 30° and decreases at 35° with substrates of low concn.  
A. G. P.

**Fermentative properties of the *Zymosarcina* group.** J. SMIT (Ann. Inst. Pasteur, 1933, 50, 675–694).—This group can be regarded as allied to the bacilli of lactic fermentation and is frequently found in the stomach in cases of pyloric ulcer. In the presence of HCl the optimum *p*<sub>H</sub> for growth is 0.9. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> will not allow growth below *p*<sub>H</sub> 3.4, nor will AcOH below *p*<sub>H</sub> 4.1. *Z. ventriculi* (I) is the only member of the group which contains catalase; none contains tyrosinase or will liquefy gelatin. From a glucose medium (I) produces CO<sub>2</sub> and EtOH, and *Z. maxima* yields CO<sub>2</sub> and BuOH with a trace of EtOH. All of the group are sensitive to antiseptics and to heating at 55°; they remain viable for long periods in the ground in some unknown form.  
P. G. M.

**Oxygen-transporting enzyme of lactic acid bacilli.** O. WARBURG and W. CHRISTIAN (Biochem. Z., 1933, 260, 499–501).—The respiration of *B. Delbrücki* behaves both qualitatively (non-inhibition by HCN and CO, formation of H<sub>2</sub>O<sub>2</sub>, replaceability of O<sub>2</sub> by methylene-blue) and quantitatively in the same way as the oxidation *in vitro* of hexose monophosphate by the yellow oxidation enzyme. Irradiation of aerobic and anaerobic bacterial suspensions gives yellow and colourless solutions, respectively. The respiration of the bacillus is due to O<sub>2</sub> transference by the yellow oxidation enzyme.  
P. W. C.

**Degradation of arginine to citrulline by *Bacillus pyocyaneus*.** F. HORN (Z. physiol. Chem., 1933, 216, 244–247).—*B. pyocyaneus*, but not *B. coli*, converts arginine into citrulline.  
J. H. B.

**Bacterial degradation of choline.** K. POLLER (Z. physiol. Chem., 1933, 217, 79–82).—By the action of putrefactive organisms on choline NMe<sub>3</sub>, EtOH, and

probably neurine are formed. Neurine is not attacked.  
J. H. B.

**Cultures and broth filtrates of *Staphylococci*.** E. L. BURKY (J. Immunol., 1933, 24, 93–133).—Certain strains of *Staphylococcus* produce independently of haemolysins in non-protein media, and not as the result of bacterial autolysis or the decomp. of protein constituents of the culture medium, a filterable substance lethal for rabbits > 4 months old. Production of the lethal factor is associated with high initial acidity and high end alkalinity. Immunity in rabbits can be induced by intradermal injection of the toxic filtrates.  
CH. ABS.

**Substance causing *Staphylococcus* food poisoning.** E. O. JORDAN and W. BURROWS (Proc. Soc. Exp. Biol. Med., 1933, 30, 448–449).—The active principle is not volatile nor readily dialysable, and is best extracted by Et<sub>2</sub>O or CHCl<sub>3</sub> from an acid aq. solution. It is not identical with the haemolytic substance present in many *Staphylococcus* filtrates, and does not produce a skin reaction.  
NUTR. ABS.

**Detection of *B. coli* in water.** T. WATABIKI and S. HIMENO (Keijo J. Med., 1933, 4, 73–75).—The H<sub>2</sub>O is incubated in a modified U-tube (with the longer limb closed) with neutral-red-lactose bouillon and *B. coli* are recognised by the production of acid, gas, and fluorescence.  
W. O. K.

**Active immunisation of white mice by a non-polysaccharide and probably non-protein derivative of the pneumococcus.** L. D. FELTON (J. Immunol., 1932, 23, 405–421).—White mice can be immunised with a fraction sol. in Cu(OAc)<sub>2</sub> in presence of saturated aq. NaCl and extractable from the dried Cu-free filtrate with EtOH. The antigen gives a negative Molisch reaction and is free from protein. No pptn. occurs with antipneumococcus horse serum.  
CH. ABS.

**Relationship of the tuberculin proteins of different acid-fast bacilli to sensitisation as indicated by their reactivity in sensitised animals.** F. B. SEIBERT and N. MORLEY (J. Immunol., 1933, 24, 149–156).—Tuberculin proteins from 3 different strains of human type tubercle bacilli induced skin-sensitivity approx. parallel to the virulence of the bacilli. On the basis of N content the 3 proteins possessed the same potency for tuberculous guinea-pigs. Proteins made by the same method from cultures of bovine, avian, and timothy bacilli produced skin reactions of decreasing severity in that order in guinea-pigs infected with the human strain.  
CH. ABS.

**Are antiviruses specific?** A. BESREDKA (J. Immunol., 1932, 23, 349–360).—Antiviruses are as strictly sp. as the bacteria from which they originate.  
CH. ABS.

**Effect of meat-curing solutions on anaerobic bacteria.** I. Sodium chloride. F. W. TANNER and F. L. EVANS (Zentr. Bakt. Par., 1933, 88, II, 44–54).—The tolerance towards NaCl of various strains of *Cl. botulinum* (I), *Cl. putrificum*, and *Cl. sporogenes* are recorded. Toxin production by (I) may occur in salt concns. much > those permitting growth.  
A. G. P.



**Antiseptic activity and chemical constitution of the xlenols and their monohalogen derivatives.** G. LOCKEMANN and T. KUNZMANN.—See this vol., 707.

**Grinder [for bacteria].** A. HOW (Ind. Eng. Chem. [Anal.], 1933, 5, 219).—The apparatus is designed to break up bacteria without causing degenerative protoplasmic changes. E. S. H.

**Effect of liver extract on bile-pigment formation.** M. S. KIM (J. Lab. Clin. Med., 1932, 17, 1223—1227).—Oral administration of therapeutically active liver extracts does not affect the nutritional condition of, or output of bile-pigment from, dogs with biliary fistulas. CH. ABS.

**Action of liver extracts on carbohydrate metabolism.** K. ZIFF and H. DRINGENBERG (Arch. exp. Path. Pharm., 1933, 170, 465—475).—Commercial anti-anæmic preps. exert no const. action on the fasting blood-sugar (rabbit), do not affect or only slightly diminish the hyperglycaemia following administration of glucose or fructose, do not alter the blood-sugar level of rabbits during insulin hypoglycaemia, and do not change the body-temp. W. O. K.

**Effect of spleen extract on blood-sugar in man.** N. FRESSINGER and S. GOTHIE (Compt. rend. Soc. Biol., 1933, 112, 171—172).—Intravenous injection of a deproteinised, fat-free extract caused a 6—26% fall of blood-sugar in normal and diseased persons. Some cases, notably two splenomegalics, showed a small rise. NUTR. ABS.

**Attempted peptic synthesis of insulin.** A. M. FISHER and D. A. SCOTT (J. Gen. Physiol., 1933, 16, 741—755).—A physiologically inactive plastein is obtained by the action of pepsin on the products of peptic hydrolysis of insulin (I). The physiological activity of (I) is not destroyed by repeated freezing and melting of aq. or EtOH solution, nor by incubation with pepsin at 37° and  $p_H$  4. H. G. R.

**Extraction of adrenal cortical hormone-like substance from urine.** D. PERLA and J. MAR-MORSTON (Science, 1933, 77, 432—433).—The substance obtained from urine by the method detailed increases the resistance of adrenalectomised rats to histamine poisoning, but proof that it is identical with the life-prolonging hormone is lacking. L. S. T.

**Variations in blood-cholesterol on injection of adrenaline.** E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1933, 107, 1546—1547; Chem. Zentr., 1933, i, 626).—Injection of adrenaline increases the blood-cholesterol in normal, but not in splenectomised, persons. Blood-fat is unaltered. A. A. E.

**Effect of the separated fractions of the posterior lobe of the pituitary on the fat content of the liver.** A. C. WHITE (J. Pharm. Exp. Ther., 1933, 48, 89—94).—Administration to rabbits of the oxytocic fraction of posterior pituitary lobe extract produced no apparent change in the liver, whereas a fraction containing predominantly pressor and some melanophore-active substance produced fatty infiltration accompanied by an increase in the Et<sub>2</sub>O-extractable material. W. O. K.

**Point of attack of pituitrin on antidiuresis and on sodium chloride excretion.** Y. FUJIMOTO (Folia Pharmacol. Japon., 1933, 15, No. 3, 19—26).—The point of attack is the kidney. CH. ABS.

**Effect of anterior pituitary extract on blood-lipins.** J. M. MUNOZ (Compt. rend. Soc. Biol., 1933, 112, 502—504).—Repeated injection of anterior pituitary extract produced a marked increase of blood-fatty acid, -cholesterol, and -phospholipin in normal and thyroidectomised dogs. Removal of the pituitary caused a small decrease of these substances in the blood. NUTR. ABS.

**Secretion of the thyreotropic hormone of the pituitary.** G. KUSCHINSKY (Arch. exp. Path. Pharm., 1933, 170, 510—533).—The secretion of thyreotropin (the hormone which stimulates secretion of the thyroid) by the anterior lobe of the pituitary is itself inhibited by the presence in the blood stream of high concns. of thyroxine. W. O. K.

**Effect of thyroxine on tissue oxidation.** G. MYHRMAN (Klin. Woch., 1932, 11, 2139—2140; Chem. Zentr., 1933, i, 627).—The oxidation process in isolated tissue is not increased by thyroxine (I) in concns. of 10<sup>-4</sup> to 10<sup>-14</sup>, neither does injection of (I) into guinea-pigs affect tissue oxidation as determined by the methylene-blue method. A. A. E.

**Oxygen consumption of animal tissues following administration of thyroxine.** H. VON EULER and R. ENDERLEIN (Biochem. Z., 1933, 261, 226—234; cf. this vol., 195).—In rats, repeated injection of thyroxine (I) results in a 25% increase in the O<sub>2</sub> consumption (II) of the liver, but the (II) of kidney and muscle seems to be scarcely, if at all, affected. The effect of (I) may also depend, to some extent, on concurrent action of vitamin-A or carotene. W. McC.

**Preparation, properties, and occurrence of an antithyroid protective substance from blood and tissues.** K. J. ANSELMINO and F. HOFFMANN (Klin. Woch., 1933, 12, 99—103).—The protective substance (I) is found in the saponifiable fraction of the Et<sub>2</sub>O extract of blood and tissues. Foetal blood contains > adult, human > that of animals. Extracts prepared were 1000 times as active as serum. Ingestion of (I) prevented the rise of basal metabolism and of ketones and loss of liver-glycogen following injection of thyroxine or the thyreotropic hormone of the pituitary, but has no effect on the diminution of liver-glycogen due to hunger. The potency of the serum of patients suffering from Graves' disease is diminished. NUTR. ABS.

**Method of estimating the functional activity of the thyroid by means of urine or serum. I. Relations between the thyroid and the other endocrine organs.** M. KOH (Keijo J. Med., 1933, 4, 1—24).—The mydriatic action of atropine sulphate (I) on the cat's eye is neutralised by previous incubation at 37° for 2 hr. with the serum or urine of normal rabbits. Thyroidectomy of the rabbit results in a decrease in the (I)-inactivating substance which is partly compensated for in about 2 weeks, whilst administration of thyroxine or implantation of thyroid tissue restores the (I)-inactivating power.



The (I)-inactivating substance exists in human serum and urine, and is increased in Basedow's disease and in pregnancy. Thymectomy, splenectomy, parathyroidectomy, or administration of adrenaline increases the (I)-inactivating substance in rabbit's serum and urine, whilst administration of suprarenal cortex, insulin, folliculin, prolant, or Indian ink, as well as starvation, has the opposite effect. The substance is stable at 80°, but destroyed at 100° and is associated with the serum-albumin. It is considered that the quantity of (I)-inhibiting substance in the serum and urine is a measure of thyroid activity.

W. O. K.

**Hormones and growth-promoting substances.** H. VON EULER, H. HELLSTRÖM, L. PULKKI, and D. BURSTRÖM (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 5, 5 pp.).—Apples were extracted with 95% EtOH, the extract was conc. and extracted with Et<sub>2</sub>O, and the extract (absorption max. at 284–285 mμ) was washed with dil. alkali, acid, and H<sub>2</sub>O and finally dried when it had max. at 265, 274, and 282 mμ. Parallel experiments were made with the leaves and floral parts of begonia (I), alder, hawthorn, and elder. Application of the purification method of Butenandt for oestrin (II) to the extracts of stamens or pistils of (I) gave solutions showing absorption spectra not characterised by any max. and also sensitive to acid or alkali. Comparison of the absorption data with those for (II) (max. at 278 and 289 mμ for EtOH solutions and at 280 mμ for aq. solutions) indicates that some of these plant products resemble (II) in structure and act as precursors for the hormone in the animal body.

F. O. H.

**Oestrogenic substance from plant material.** B. SKARZYŃSKI (Nature, 1933, 131, 766).—The female flowers of the willow yield a semi-cryst. substance (I) having a strength of 35,000 mouse units of the follicular hormone. Extraction of (I) with 60% EtOH gave crystals identical with trihydroxy-oestrin (from female urine) in respect of mixed m.p., absorption spectra, m.p. of Ac derivatives, but not of biological activity, which was 1000 mouse units per mg. of plant material and 4000 units per mg. of (I).

L. S. T.

**Sensitivity to light of sexual hormone and chlorophyll.** G. KÖGEL (Strahlenther., 1932, 45, 587–589; Chem. Zentr., 1933, i, 625).—Both sexual hormones are sensitive to light; the effect is attributed to reversible reduction of the keto-group by activated H. The photo-sensitivity of chlorophyll *a* and *b* is also attributed to the keto-group.

A. A. E.

**Effect of sex hormones on creatine metabolism.** F. BÜHLER (Z. ges. exp. Med., 1933, 86, 638–649).—About 70% of intravenously injected creatine (I) was excreted unchanged. When testicular (proviron) or ovarian (progynon) hormone was injected on the same day as (I), practically none of the injected (I) appeared in the urine; in children the hormones had no effect on creatinuria, indicating that they act through the corresponding sexual glands, proviron only on testes, since it had no action on the creatinuria of females, and similarly progynon only on the ovaries.

A method of determining (I) and creatinine by the step photometer is described.

NUTR. ABS.

**Effect of prolant on the magnesium balance and on the magnesium content of organs.** L. CANNAVO and R. INDOVINA (Biochem. Z., 1933, 261, 45–46; cf. A., 1932, 1068).—Previous findings are confirmed. In rabbits administration of prolant (I) has very little effect on the excretion of Mg, which seems rather to be retained in the blood-plasma. The Mg content of the organs of rabbits receiving (I) and of controls has been determined.

W. McC.

**Effects observed in mice under continued treatment with oestrin.** H. BURROWS, E. C. DODDS, and N. M. KENNAWAY (Nature, 1933, 131, 801–802).—Male mice treated with superficial applications or subcutaneous injections of oestrin develop hernia. Female mice are kept in oestrus by superficial applications.

L. S. T.

**New hydrogenation products of the follicular hormone.** W. SCHOELLER, E. SCHWENK, and F. HILDEBRANDT (Naturwiss., 1933, 21, 286).—A vitreous mixture of octahydro-derivatives, C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>, has been obtained which yields cryst. fractions on distillation. The mixture and part of the fractions promote comb-growth (1 capon unit=8–10 mg.). This supports Butenandt's hypothesis that the male hormone is derived from the female hormone by hydrogenation of the aromatic ring.

R. K. C.

**Vitamin-A, thyroxine, and oestrin.** H. VON EULER and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 1, 6 pp.).—The corpus luteum (I) of cows contains only traces of xanthophyll (II), whilst β-carotene (III) but not vitamin-A (IV) is detectable. A growth of 6.5 g. per week is induced in rats by feeding with 0.17 g. of (I) per day. Cow's placenta appears to contain (III), whereas human placenta contains (II). The nerve tissue of rabbits fed with large doses of carotene is free from carotenoids (V). The follicle probably plays some part in the conversion of (V) into (IV) during maturation of the ovum. The antagonism of carotene and (IV) towards thyroxine (A., 1932, 782) is confirmed. Vitamin-E concentrates do not promote growth in young rats.

F. O. H.

**Substances interfering with the antimony trichloride test for vitamin-A.** R. E. CORBET, H. H. GEISINGER, and H. N. HOLMES (J. Biol. Chem., 1933, 100, 657–666).—The effect on the SbCl<sub>3</sub> colour test (I) for vitamin-A (II) of boiling cod-liver oil in CHCl<sub>3</sub> solution with certain org. compounds, and the interference produced on (I) by mixing various substances with (II) concentrate, are studied, the max. amounts of the substances investigated which cause no interference being given. Among the most active substances are PhCHO, CH<sub>3</sub>Ph·OH, cyclohexene, benzoquinone, oleic acid, lecithin, C<sub>5</sub>H<sub>5</sub>N, indole, and terpenes. The extent of the interference depends on the configuration of the mol. and increases with the degree of unsaturation.

A. L.

**Chinese citrus fruits. I. Vitamin-A and -B in the peel of Fu Chü (Chinese tangerine).** P. P. T. SAH (J. Chinese Chem. Soc., 1933, 1, 23–28).—Tangerine oil is rich in vitamin-A, and the peel also



contains vitamin-B. Analyses for moisture, ash, essential oil, and non-volatile oil are recorded.

A. A. L.

**Vitamins-B<sub>1</sub> and -B<sub>2</sub>.** B. C. GUHA (J. Indian Chem. Soc., 1933, Rây No., 185—188).—A survey.

H. B.

**Adsorption of vitamin-B<sub>1</sub> by plant tissue.** I. C. D. MILLER and M. G. ABEL (J. Biol. Chem., 1933, 100, 731—735).—*Brassica chinensis* lost approx. 50% of its original vitamin-B<sub>1</sub> content (I) and the  $p_H$  of the leaf extract changed from 6.3 to 4.91 after 3 days' pickling in aq. NaCl. After pickling for the same time, however, in a paste of salt and rice bran, the (I) increased to 4 times the original val., and the  $p_H$  became 4.74.

A. L.

**Glycolytic enzyme in liver of animals with vitamin-B deficiency. Effect of iodine in avitaminosis-B.** T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1932, 8, 756—764).—The livers of white rats fed on synthetic diets without vitamin-B (I) contained 10% less glyoxalase than those of normal rats, but the same quantity as those of starved rats. Liver-glycolase is also low in avitaminosis-B and starvation. NaI (hypodermic) or thyroxine (oral) checks the antineuritic symptoms produced by a diet free from (I).

CH. ABS.

**Influence of diet and vitamins on blood-glycolysis. II. Glycolysis and the distribution of free and combined cholesterol. III. Glycolysis in rabbits fed on polished rice.** J. CHIWAKI (J. Biochem. Japan, 1933, 17, 171—213, 215—251).—II. The feeding of cholesterol to rabbits produces a decrease in blood-glycolysis (I) together with increases in the free (II) and combined cholesterol (III), that of (II) being most marked in the plasma and that of (III) in the corpuscles. The amount of vitamin-B in the diet does not influence the effect. The decrease in (I) appears to be related to the amount of (III) in the corpuscles. When normal erythrocytes are suspended in serum from cholesterol-fed rabbits, (I) decreases and the corpuscular content of (III) simultaneously increases.

III. Neither (I) nor the blood-sugar level (IV) is appreciably changed by extreme starvation of rabbits. The survival period of starvation averages 18 days, during which period the body-wt. decreases by approx. 37%. Feeding with polished rice produces a marked decrease in (I) of both serum and corpuscles and in (IV). The low (I) is increased by administration of vitamin-B concentrate, but not by that of insulin, lecithin, or  $PO_4'''$  buffer.

F. O. H.

**Vitamin-C.** P. KARRER, H. VON EULER, and H. HELLSTRÖM (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 6, 6 pp.).—Aq. 1.00, 1.62, 2.00, and 4.00% vitamin-C (I) have  $[\alpha]_{578}^{25} +32.8^\circ$ ,  $+27.2^\circ$ ,  $+23.7^\circ$ , and  $+18.5^\circ$ , respectively (cf. A., 1932, 548). Heating at 60—80° has no effect on  $[\alpha]$ . The Na salt of (I) has  $[\alpha] +102.2^\circ$ . Strongly acidic or alkaline solutions of (I) show decreases in  $[\alpha]$ . The absorption max. for solutions in EtOH is at 245  $m\mu$ , in dil. HCl at 245  $m\mu$ , and in 0.0002—0.01N-NaOH at 263—301  $m\mu$ . Vals. for galactose and fructose are 264—275 and 265—295  $m\mu$ , respectively. On oxidation of (I) the loss in reducing power is not proportional to the diminution

in absorption coeff. Parallel data for methylnornarcotine (A., 1932, 310) are given. Addition of (I), its Na salt, or the  $COMe_2$  derivative to hæmin in  $C_5H_5N$  and in presence of  $O_2$  produces absorption spectra characteristic of hæmochromogen and finally of green hæmin (A., 1930, 1199).

F. O. H.

**Vitamin-C and sugar derivatives.** H. VON EULER and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 7, 6 pp.).—Relatively to the adrenal gland (I), the liver is poor in vitamin-C (II), whilst the thymus has a comparatively high content. Intraperitoneal injection of (II) into guinea-pigs increases the content of (II) in (I) by approx. 30%, whilst administration of adrenaline considerably lowers it. When tested by the 2:6-dichlorophenol-indophenol reagent, normal human urine has an appreciable reduction val. (III) which is not increased by fever. Suspensions of dried or living yeast have a high (III) due to cell constituents. Glucose, on fermentation with yeast, produces derivatives with high (III).

F. O. H.

**Vitamin-C and related substances.** H. VON EULER and M. MALM (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 9, 5 pp.).—Heating simple sugars with 0.2N-alkali produces a substance (I) which in reducing properties and absorption spectrum resembles vitamin-C (II). (I) in  $PO_4'''$  buffer decolorises methylene-blue (III), a min. velocity occurring at  $p_H$  7, whilst addition of KCN inhibits the reaction. The decolorisation of (III) by (II) is accelerated by presence of Cu. Suspensions of adrenal gland and of liver also decolorise (III). The mechanism of the reduction and the probable constitution of (I) and (II) are discussed.

F. O. H.

**Vitamin-C and ascorbic acid.** V. DEMOLE (Z. physiol. Chem., 1933, 217, 83—88).—Various preps. of ascorbic acid (I) cured scurvy in guinea-pigs in daily doses of 1 mg. The activity of dehydroascorbic acid was slightly less, but the regenerated (I) was fully active. Methylnornarcotine, dihydroxyphenylalanine, dihydroresorcinol, and alloxantin were inactive.

J. H. B.

**Oxygen uptake by organs containing vitamin-C and by gluco-reductone.** H. VON EULER, K. MYRBÄCK, and H. LARSSON (Z. physiol. Chem., 1933, 217, 1—22).—The velocity of  $O_2$  uptake by ascorbic acid (I) increases rapidly above  $p_H$  9. Cu, Ni, and Mn catalyse the oxidation. The  $O_2$  uptake is activated by constituents of Ringer's solution ( $NaCl$ ,  $CaCl_2$ ), also slightly by KCN. The velocity of methylene-blue reduction by (I) shows a min. at 5—6 which is a combined function of the  $p_H$  effects of (I) and methylene-blue. The  $O_2$  uptake of gluco-reductone (enol tartronaldehyde) formed by the action of alkali on sugars is of the same order as that of (I). The  $O_2$  uptake of the medulla of the adrenals far exceeds that of the cortex.

J. H. B.

**Oxidation-reduction potential of ascorbic acid.** K. LAKI (Z. physiol. Chem., 1933, 217, 54—55).—Ascorbic acid (I) does not form a thermodynamically reversible system, i.e., the oxidised form does not show a definite oxidation potential. The potential of 0.2% solution of (I) falls 53 mv. per  $p_H$  unit increase.

J. H. B.



**Vitamin formation in plants.** S. VON HAUSEN (Suomen Kem., 1933, B, 6, 62).—The carotene (I) and vitamin-C (II) contents of plants are largely dependent on the nature of the N source, high vals. for both in sand-cultured peas being associated with N supplied as  $\text{KNO}_3$ , glutamic or aspartic acid. The proportions of N, P, and K in the nutrient which produce max. plant growth are also optimal for the formation of (I) and (II). With increasing divergence of N, P, and K concns. from the optimum, there was a corresponding decline in (I) and (II) in the plants. Changes in the latter were observed where differences in nutrient ratios were too small to produce differences in plant yields. Excessive N supplies did not affect the formation of (I) and (II), but concns. of P and K above the optimum led to reduced production of these. A. G. P.

**Determination of vitamin-D by the preventive method. The preventive dose established as curative.** P. SCHULTZER (Biochem. J., 1933, 27, 376—381).—The development of rickets in rats on a rachitic diet, examined radiographically, is inhibited by the addition of sufficient quantities of irradiated ergosterol or of cod-liver oil. The dose of the latter required to prevent completely any signs of rickets is practically the same as the curative dose. W. O. K.

**Toxicity of preparations of irradiated ergosterol.** M. SCHIEBLICH (Deut. tierärztl. Woch., 1931, 39, 750; Bied. Zentr., 1933, A, 3, 254—255).—Administration of excessive amounts of irradiated ergosterol causes hypercalcaemia in dogs and hyperphosphataemia in Herbivora. Heating to  $200^\circ$  destroys the antirachitic properties of the prep. without affecting its toxicity. The toxic action is ascribed directly to vitamin-D rather than to secondary substances present. A. G. P.

**Photo-electric measurement of the penetration of light of various wave-lengths into the sea and the physiological bearing of the results.** W. R. G. ATKINS and H. H. POOLE (Phil. Trans., 1933, B, 222, 129—164).—The antirachitic portion of the spectrum is reduced to 0.001% of the sub-surface val. at 2.9—5.5 m., and appears inadequate to account for the vitamin-D content of zooplankton. J. S. A.

**Diet and reproduction. IV. Bipartite nature of vitamin-E.** G. GRIJNS and E. DINGEMANSE (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 242—248; cf. A., 1929, 359).—Wheat germ is extracted with 40% EtOH in presence of  $\text{Ca}(\text{OH})_2$  and kieselguhr. The extract contains an  $\text{Et}_2\text{O}$ -sol. fraction which is dissolved in petrol and extracted with 90% EtOH. On evaporating the petrol an oil is obtained which cures sterility in male (but not female) rats on a diet free from vitamin-E (I). With (I) concentrates from wheat germ, fractionation with org. solvents yields two fractions, one extractable with 90% EtOH and responsible for fertility in female rats, and the other non-extractable with 90% EtOH and responsible for fertility in male rats. F. O. H.

**Carotenoids, vitamin-E, and sex hormones.** H. VON EULER, B. ZONDEK, and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1933, 11 B, No. 2, 5 pp.).—

The livers of human foetuses of 2—7 months contain no carotene (I), but are rich in vitamin-A (II). The placenta probably converts (I) into (II). (I) is also found in ox pituitary gland, the anterior lobe containing  $2.2 \times 10^{-6}$  g. per 278 g. and the posterior lobe  $0.3 \times 10^{-6}$  g. per 52 g. Wheat oil, xanthophyll, and (I) neither influence the dioestrous condition of spayed rats nor modify the action of oestrin in such animals. F. O. H.

**Root respiration of young coffee plants.** E. HERNDLHOFFER (Z. Pflanz. Düng., 1933, 29 A, 290—298).—Respiration increases with light intensity. In darkness respiration is small and tends to maintain a const. rate throughout the day. A. G. P.

**Photosynthesis in maize.** W. E. LOOMIS and K. H. BURNETT (Proc. Iowa Acad. Sci., 1931, 38, 150).—The upper leaves of maize are more efficient than the lower; removal of leaves tends to reduce the yield of grain and total dry matter. Removal of the ear produces a stiff stalk and much anthocyanin. The rate of photosynthesis in maize is affected by grain production and therefore depends on soil fertility and genetic factors. CH. ABS.

**Carbon dioxide assimilation of leaves of *Oryza sativa*, L.** R. H. DASTUR and J. J. CHINYOY (Indian J. Agric. Sci., 1932, 2, 431—454).—Photosynthetic activity rises rapidly soon after transplantation, remains fairly const. in August, is depressed in September, rises again in October, and thereafter falls rapidly. CH. ABS.

**Relations between various physiological phenomena in plants and the occurrence of colouring matter in different vegetative organs. IV. Presence of anthocyanin and assimilation in cultivated plants.** H. KOSAKA (J. Dept. Agric. Kyushu, 1933, 3, 251—267).—In plants in which anthocyanins occur in leaves or skins assimilation is stimulated by the presence of the pigment or chromogen. A. G. P.

**Organic matter and the life of the green plant.** N. A. CLARK (Proc. Iowa Acad. Sci., 1931, 38, 168—169).—*Lemna major* grows and reproduces in absence of org. matter. Stimulation of reproduction by org. matter does not occur in absence of micro-organisms. CH. ABS.

**Mechanism of the action of growth substance of plants.** K. V. THIMANN and J. BONNER (Proc. Roy. Soc., 1933, B, 113, 126—149).—The growth produced in decapitated *Avena* coleoptiles is linearly related to the added growth promoter (I). The calc. relation between the amount of (I) entering the cells and the cell-wall material produced shows that (I) is not stoichiometrically concerned in the formation of cellulose or cell wall, and that (I) does not influence growth by effecting permeability changes in the cell wall. The growth-promoting effect is indirect and one in which the mol. of (I) reproduces its action several times. A. C.

**Ash constituents of the apple during the growing season.** E. F. HOPKINS and J. H. GOURLEY (Ohio Agric. Exp. Sta. Bull., 1933, No. 519, 30 pp.).—Physiological breakdown of apples is not closely related to either the N or ash content of the fruit.



Deficiency of mineral nutrient in soil is likely to show itself in foliage, top, and root growth and in the character of the fruit. Breakdown is largely affected by seasonal conditions. A. G. P.

**Progressive changes in the cuticle of apples during growth and storage.** K. S. MARKLEY and C. E. SANDO (J. Agric. Res., 1933, 46, 403—412; cf. B., 1931, 775).—A new method for determining cutin is described. The % of cutin in the cuticle at maturity and at the end of storage was > in the earlier stages of growth. Variations in the ratio cutin: total  $\text{Et}_2\text{O}$  extract are considerable, but the average val. for a no. of samples was approx. 56:44. The proportions of ursolic acid, oily fraction, and total  $\text{Et}_2\text{O}$  extract in the cuticle are to some extent characteristic of the locality in which the fruit is grown. A. G. P.

**Electrical resistance of pear tissue as an index of maturity.** J. C. MOORE (Oregon Agric. Exp. Sta. Bull., 1932, No. 300, 18 pp.).—Changes in resistance of pear tissue with advancing maturity are generally similar to those of the customary pressure test and may be utilised in assessing the state of maturity. A. G. P.

**Formation of betaine and alkaloids in plants. II. Stachydrine and trigonelline.** G. KLEIN and H. LINSE (Planta [Z. wiss. Biol.], 1933, 19, 366—388; cf. A., 1932, 975).—Variations in the trigonelline (I) content throughout the growth of several plants are recorded. Formation of (I) was not increased by injection of tyrosine, arginine, asparagine, aspartic acid,  $\text{NH}_4\text{NO}_3$ , alanine, leucine, or citrulline. Increases produced by ornithine and proline were confirmed. The action of proline was markedly accentuated by the simultaneous injection of  $(\text{CH}_2)_6\text{N}_4$  as a source of  $\text{CH}_2\text{O}$ . Formation of (I) was also increased by injection of substances intermediate in its formation from  $\text{NH}_2$ -acids. A. G. P.

**Variations in nitrogen content of lilac during forcing.** R. QUETEL (Compt. rend., 1933, 196, 1243—1245).—Exposure of lilac plants to an atm. containing  $\text{Et}_2\text{O}$  during a forcing process lowers the protein-N content ( $P$ ) of the branches from about 0.95 to 0.75%. The content of sol. N ( $S$ ) shows no marked variation from about 0.13%. In the buds  $P$  remains approx. const., whilst  $S$  increases from 0.28 to 1.66%, the ratio  $P/S$  at the commencement of flowering being much < in normal plants. A. C.

**Assimilation of atmospheric nitrogen by the root fungus of *Coralliorrhiza innata*, R. Br., and of the epiphytes *Cattleya Bowringiana*, Veit, and *Laelia anceps*, Ldl.** H. WOLFE (Jahrb. wiss. Bot., 1933, 77, 657—684).—The organisms from *Coralliorrhiza* utilise tannin and glucose and those from *Cattleya* and *Laelia*, tannin, glucose, mannose, and arabinose. The presence of N compounds did not influence the fixation of free N. A. G. P.

**Relationship between nitrogen assimilation and hydrogen-ion concentration of some fungi.** K. RIPPPEL (Diss., München, 1930; Bied. Zentr., 1933, A, 3, 223—224).—Interrelationships between  $[\text{H}^+]$ , isoelectric point, and N assimilation are estab-

lished. The organism plays a passive rôle and possesses no "selective" power in assimilation.  $\text{NH}_2$ -acids are not preferentially assimilated. A. G. P.

**Changes in fibre in a peat bog.** E. V. RAKOVSKI and V. A. VUISOTSKAYA (Khim. Tverd. Topl., 1931, 2, No. 11—12, 80—92).—Vals. for a freshly-cut pine tree (air-dry) and a tree submerged in a peat bog for 1500—2000 years were: ash 0.65—0.68, 0.26—0.77;  $\text{Et}_2\text{O}$  extract 4.57—6.08, 10.19—12.57;  $\text{EtOH}$ - $\text{C}_6\text{H}_6$  extract 0.16—0.05, 0.1; pentosans 6.82—9.78, 5.79—8.45; hemicellulose 15.69—18.41, 11.08—16.31; cellulose 28.25—32.08, 27.73—34.93; lignin 29.05—29.84, 29.12—32.33; OMe (Willstätter) 11.29—13.77, 11.98—12.37; humic substances 0, 19.5%. The solubilities of the fibre and the properties of the resins, composition of extracts, etc. are recorded. CH. ABS.

**Rôle of organic acids in plant metabolism. I.** T. A. BENNET-CLARK (New Phytologist, 1933, 32, 37—71).—Common org. acids present in various species of plants are discussed and methods of analysis noted. Three groups of plants are distinguished, (a) plants containing malic acid (I) and having the crassulacean type of acid metabolism [(I) formed from carbohydrate in darkness and reconverted into it in light], (b) (I) plants in which  $\text{H}_2\text{C}_2\text{O}_4$  gradually replaces (I) with increasing age, (c)  $\text{H}_2\text{C}_2\text{O}_4$  plants which may be represented as special cases of (b) in which the change  $(\text{I}) \rightarrow \text{H}_2\text{C}_2\text{O}_4$  is accelerated. Acid production by moulds is not strictly comparable with that by higher plants. A. G. P.

**Micro-gas analysis and its application particularly for biological purposes.** H. SCHWARZ and F. RAPPAPORT (Mikrochem., 1933, 13, 235—273).—A summary.

**Electrical resistance thermometers as applied to human calorimetry.** G. F. SODERSTROM.—See this vol., 689.

**Biochemical gravimetric methods. III. Weighing of heat-dried filters and precipitates on the torsion balance.** L. JENDRASSIK and A. BOKRÉTÁS (Biochem. Z., 1933, 261, 106—109).—To prevent absorption of  $\text{H}_2\text{O}$  when using the torsion balance, the material is weighed in the oven or a drying agent ( $\text{CaCl}_2$ ) is introduced into the weighing chamber on the balance. W. MCC.

**Nephelometric determination of cholesterol.** W. KRÖNER (Biochem. Z., 1933, 260, 403—405).—Details concerning the prep. of MeOH for successfully carrying out the nephelometric determination of cholesterol by the method of Mühlbock, Kaufmann, and Wolff (A., 1932, 666) are given. P. W. C.

**Determination of cystine in biological material.** F. T. G. PRUNTY (Biochem. J., 1933, 27, 387—390).—The cystine is reduced with Zn dust in acid solution to cysteine, which is then determined colorimetrically by means of Sullivan's Na  $\beta$ -naphthoquinonesulphonate reagent. The results agree well with those obtained by the method of Folin and Marenzi (A., 1929, 1093). W. O. K.