

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

APRIL, 1933.



### General, Physical, and Inorganic Chemistry.

**Continuous spectra of the hydrogen molecule.** L. GOLDSTEIN (J. Phys. Radium, 1933, [vii], 4, 44—53).—Mathematical. The intensity distribution of the continuous  $H_2$  bands is calc. N. M. B.

**Excitation functions of atomic hydrogen.** L. S. ORNSTEIN and H. LINDEMAN (Z. Physik, 1933, 80, 525—533).—Excitation functions are given for the Balmer lines of H. A. B. D. C.

**Dispersion and absorption of helium.** J. A. WHEELER (Physical Rev., 1933, [ii], 43, 258—263).—Mathematical. The strength of the absorption continuum below the 507 Å. series limit and of the resonance line at 584 Å., and the at. absorption coeff. for X-rays, are calc. and discussed. N. M. B.

**Dependence of the excitation of the spectral lines of helium and mercury on pressure under a high-frequency discharge.** E. MATUYAMA (Sci. Rep. Tōhoku, 1932, 21, 928—935).—The intensities of spectral lines of Hg and He under high-frequency oscillatory discharge have been measured under various pressures. The results are discussed in relation to the excitation probabilities of these lines, the velocity of electrons, and other conditions of excitation. J. W. S.

**Effect of gradient of potential of alternating current on the glowing potential of inert gases and air in discharge tubes.** W. SPIELHAGEN (Physikal. Z., 1933, 34, 164—168).—For both inert gases and air the glowing potential decreases with increasing potential gradient, and reaches a const. val. A. J. M.

**Glowing potential of discharge tubes (nitrogen) with varying electrode separation. I. Straight tubes.** H. FRICKE (Physikal. Z., 1933, 34, 168—172). A. J. M.

**Characteristics of metallic spectra excited by active nitrogen.** H. HAMADA (Sci. Rep. Tōhoku, 1932, 21, 554—563).—In the metallic spectra excited by active N (cf. A., 1929, 615) no evidence is found of the resonance enhancement of the lines due to collisions between the metallic atoms and either the metastable atoms (2.37 and 3.56 volts) or the metastable mols. (8.2 volts) in the active N. The concns. of such metastable species must therefore be small. The half-val. width of the D line excited by active N was found to be 0.07 Å., and hence the mean translational energy which the Na atom and the  $N_2$  mol. receive during the triple collisions is  $\approx$  0.35 volt. O. J. W.

**Spectrum of the corona discharge in air, oxygen, and nitrogen.** A. C. YOUNG and A. G. CREELMAN (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 39—42).—The spectra of corona discharges in air,  $O_2$ , and  $N_2$  are of mol. origin, no at. spectra being observed (cf. A., 1930, 5; 1931, 1103). The results indicate that this discharge gives a low degree of excitation. J. W. S.

**Spectrum of the discharge through oxygen and hydrogen mixtures.** A. S. ROY (Phil. Mag., 1933, [vii], 15, 421—426).—The Balmer lines  $H_\beta$  and  $H_\gamma$  are enhanced in Geissler discharges through  $O_2$  containing  $H_2$ ; this is attributed to excitation and ionisation of H atoms by  $O^+$  or  $O_2^+$ . H. J. E.

**Continuous spectrum of sodium.** H. HAMADA (Phil. Mag., 1933, [vii], 15, 574—592; cf. A., 1932, 1193).—The intensity distribution in the continuous spectrum of a discharge in Na vapour has been measured. The origin of the continuum is discussed. H. J. E.

**Interaction of configurations:  $sd-p^2$ .** R. F. BACHER (Physical Rev., 1933, [ii] 43, 264—269).—Mathematical. The possibility of the presence of singlets below their triplets as observed in the two-electron spectrum of Mg I is demonstrated. N. M. B.

**Arc spectrum of sulphur.** R. FRERICHS (Z. Physik, 1933, 80, 150—160).—The arc spectrum of S was measured between 4000 and 11,000 Å. A. B. D. C.

**Quantitative intensity determinations in the spectra of normal and of singly-ionised vanadium V I and V II.** G. R. HARRISON (Physical Rev., 1931, [ii], 38, 1921).—The relative intensities of lines of V I and V II between 5200 and 2500 Å. have been determined under different conditions of excitation in the vac. arc. L. S. T.

**Interferometer measurements in the extreme ultra-violet region of copper.** J. C. McLENNAN and (Miss) F. M. QUINLAN (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 19—24; cf. this vol., 2).—The wave-lengths of the lines in the ultra-violet spectrum of Cu are suggested as standards for the region 2300—2000 Å. J. W. S.

**Spectra of bromine: Br V, VII, and IV.** A. S. RAO and K. R. RAO (Nature, 1933, 131, 170).—The chief multiplets belonging to the higher spark spectra of Br have been identified. L. S. T.

Deviations from the sum rule in the spectrum of strontium. W. KAST (Z. Physik, 1933, 80, 414).—Correction of an earlier paper (this vol., 200).

A. B. D. C.

Optical constants of transparent silver. H. MURMANN (Z. Physik, 1933, 80, 161—177).—The optical consts. of Ag were determined from reflexion and transmission measurements on layers deposited by sublimation on transparent substances. Anomalies appear similar to those known for cathodic and chemical layers. Variation of the consts. with thickness shows that beyond 15  $m\mu$  the layer is identical with massive Ag.

A. B. D. C.

Relative intensity of spectral lines in indium and gallium. R. PAYNE-SCOTT (Nature, 1933, 131, 365—366).—Results for the doublet  $2p_{3/2}-2s_{1/2}$  and  $2p_{1/2}-2s_{1/2}$  are given for each element.

L. S. T.

Absorption bands of iodine vapour at high temperatures. E. SKORKO (Nature, 1933, 131, 366).—Details of the absorption bands of I vapour in the region 2900—5000 Å. at 800—1050° are recorded.

L. S. T.

Effect of foreign gases on the relative intensities of the mercury triplet  $2^3P_{0,1,2}-2^3S_1$  under conditions of optical excitation. R. T. MACDONALD and G. K. ROLLEFSON (Physical Rev., 1933, [ii], 43, 177—180).—Anomalous effects on the intensity ratio of 5461 to 4358 or 4046 Å. were found when  $N_2$  or  $N_2-CO_2$  mixture was introduced.

N. M. B.

Atomic energy levels and Zeeman effect. D. R. INGLIS and N. GINSBURG (Physical Rev., 1933, [ii], 43, 194—196).—Results of applying the theory of complex spectra are compared with experimental data.

N. M. B.

Line groups and fine structure. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss., 1932, 32, 502—513).—The configurations of line groups with narrow coarse structure and simultaneous fine structure are discussed.

A. J. M.

Broadening of spectral lines. W. LENZ (Z. Physik, 1933, 80, 423—447).—A crit. review is given of present theories of broadening, displacement, and asymmetry of spectral lines, and a general theory is developed by statistical mechanics. It is applied to the particular cases of disturbance due to foreign gases, the gas itself, and to the presence of ions; comparison with experiment is made for A,  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CO_2$ , and  $H_2O$ .

A. B. D. C.

Integrals required for the theory of pressure broadening of spectral lines. H. JENSEN (Z. Physik, 1933, 80, 448—450).

A. B. D. C.

Spectra emitted during the early stages of a condensed discharge through nitrogen at low pressure. H. HAMADA (Sci. Rep. Tôhoku, 1932, 21, 549—553).—The second positive and the negative bands begin to be emitted after  $0.4 \times 10^{-8}$  sec. from the beginning of the discharge, and the intensity is greatest during  $1.7 \times 10^{-8}$  sec. The first positive bands are emitted mainly  $>7 \times 10^{-7}$  sec. after beginning of the discharge.

O. J. W.

Electrical discharge in gases at normal pressures and temperatures. J. D. STEPHENSON (Phil.

Mag., 1933, [vii], 15, 241—262).—Theories of discharge are reviewed in the light of three fundamental experimental equations for the crit. conditions for discharge with the principal types of electrode shape and field distribution. A new theory is proposed showing the dependence of the breakdown strength on the electron mean free path.

N. M. B.

Variations in visible solar light during submarine measurements. C. L. UTTERBACK (Science, 1933, 77, 118—119).—Marked variations in the intensity of visible solar light measured beneath the surface of ocean waters are recorded.

L. S. T.

Long-wave part of the visible spectrum of the night sky. L. A. SOMMER (Z. Physik, 1933, 80, 273—276).—Long wave-length lines reported by Vegard (*ibid.*, 1932, 77, 574) in Northern lights have the same wave-lengths as lines in the spectrum of the night sky, but the relative intensities of the lines are different.

A. B. D. C.

Efficiency effect of X-ray K-fluorescence radiation for light elements. M. HAAS (Ann. Physik, 1933, [v], 16, 473—488).—The efficiency effect (ratio of no. of excited atoms to no. of emitted atoms) for the K-fluorescence radiation from Mg, Si, S, Cl, Ca, and Cr was measured.

A. J. M.

Weak lines in the K-spectra of 42 Mo and 47 Ag. E. CARLSSON (Z. Physik, 1933, 80, 604—609).

A. B. D. C.

X-Ray satellites. H. C. WOLFE (Physical Rev., 1933, [ii], 43, 221—223).—Calc. energies and frequencies for the 5  $K\alpha$  satellites of K based on Druyvestyn's theory are in agreement with observed vals.

N. M. B.

M series of tantalum obtained by means of an ionic tube. V. DOLEJSEK and (MLLE.) D. FILCAKOVA (Compt. rend., 1933, 196, 388—389).—Using an improved form of Dolejsek's ionic tube at 3400 volts, the Ta lines  $M_{I}N_{III}$  5385,  $M_{III}O_{I}$  5820, and  $M_{IV}N_{III}$  8875 X, corresponding with the W lines found by Lindberg (cf. A., 1928, 1078), and also the lines  $M_{V}O_{III}$  (7280 for Ta, and 6990 X for W) have been measured.

C. A. S.

Properties of X-radiation. C. G. BARKLA (Nature, 1933, 131, 166).—The present position with regard to the J-phenomenon is discussed.

L. S. T.

Theory of X-ray absorption by molecular gases. II. H. PETERSEN (Z. Physik, 1933, 80, 258—266; cf. A., 1932, 892).—Kronig's theory of fine structure of absorption edges due to mol. gases is more fully worked out.

A. B. D. C.

Spectral composition of an X-ray radiation determined from its filtration curve. L. SILBERSTEIN (Phil. Mag., 1933, [vii], 15, 375—394).—Theoretical.

H. J. E.

Ionisation of solid dielectrics on X-irradiation. M. BENDER (Z. tech. Physik, 1932, 13, 431—432; Chem. Zentr., 1932, ii, 3206).—Ionisation of S and paraffin on X-irradiation was observed. Ohm's law was obeyed.

A. A. E.

Higher ionisation potentials of atoms according to the Thomas-Fermi model. A. SOMMERFELD (Z. Physik, 1933, 80, 415—422).—An earlier

calculation (*ibid.*, 1932, 78, 283) is corrected, and calculations of the second and third ionisation potentials are given for atoms between Li and Cs.

A. B. D. C.

**Ionisation and scattering accompanying positive ion impact in gases.** C. A. FRISCHE (Physical Rev., 1933, [ii], 43, 160—168; cf. Mouzon, A., 1932, 1184).—Ionisation and scattering curves and data are given for the ionisation produced by  $K^+$  ion impact in A, Ne, He,  $N_2$ , CO,  $H_2$ , and Hg for the range 0—4000 volts.

N. M. B.

**Photo-electric and metastable atom emission of electrons from surfaces in the rare gases.** C. KENTY (Physical Rev., 1933, [ii], 43, 181—193).—The causes, and relative effects under various conditions, of conductivity at considerable distances beyond the end of a discharge in Ne, He, and A were investigated for the pressure range 0.5—2 mm.

N. M. B.

**Conservation of energy and the impulse in the photo-electric effect.** J. KUNZ (Physikal. Z., 1933, 34, 218).—Mathematical.

A. J. M.

**Classical distribution of electrons in the photo-electric effect with X-rays.** J. KUNZ (Physikal. Z., 1933, 34, 219—220).—Mathematical.

A. J. M.

**Adsorbed films of caesium on tungsten. I. Space charge sheath and the image force.** I. LANGMUIR (Physical Rev., 1933, [ii], 43, 224—251).—Mathematical. For a W-walled heated enclosure containing Cs vapour in thermal equilibrium the image force in the sheath close to the surface acting on an electron, and the image force on a given electron due to electrons near the surface which have a Fermi distribution, are calc. by a perturbation method.

N. M. B.

**"Electric diffusion" of ions in gases with unipolar charge.** N. VOLODKEVITSCH (Ann. Physik, 1933, [v], 16, 431—467).—The theory and method for the production of a unipolar charged air stream are given, and an instrument (the ionometer) for determining the charge density is described.

A. J. M.

**Electron diffraction by films of grease.** G. P. THOMSON and C. A. MURISON (Nature, 1933, 131, 237).—The patterns produced by films of grease and waxes when used to reflect electrons are discussed.

L. S. T.

**Electron emission by metals under the influence of monochromatic X-rays.** H. HASE (Z. Physik, 1933, 80, 670—689).—Electron emission from the incident side was determined for Fe, Cu, Mo, Ag, Sn, Ta, W, Au, Pb, and Bi, and from the exit side for Cu, Sn, and Au. Electrons emitted by the heavier metals are almost all of the third kind.

A. B. D. C.

**Positive ion emission from oxide catalysts.** C. F. POWELL and L. BRATA (Nature, 1933, 131, 168).—Positive ion sources of Tl and In have been produced by evaporation on to an Fe oxide base (cf. A., 1932, 670). For a given metal the emission characteristic of the saturated surface increases rapidly with a rise in temp. until the Fe oxide sinters, when emission becomes unstable. The bearing of the

results on the catalytic action of the Kunsman source in the production of  $NH_3$  is discussed. L. S. T.

**Energetics of the reciprocal effect in corpuscular impact.** R. DÖPEL (Ann. Physik, 1933, [v], 16, 1—38).—The excitation of He by H canal rays was investigated between 2 and 40 kv. Other experiments were carried out with H impact on Hg, Na, K, and He charged with  $H^+$ . A simple mechanical-elastic theory of the collision is discussed.

W. R. A.

**Investigation of negatively-charged hydrogen atoms by light emission in the photographic range.** R. DÖPEL (Physikal. Z., 1933, 34, 199—200).—An attempt was made to show the existence of H atoms by photographs of their light emission. No sign of light emission due to this cause was found, and it is concluded that if a negatively-charged H atom produces light, discrete or continuous, within the wave-length range 7111 Å. to the Lyman region, it is < 1% of that due to neutral H atoms in this range.

A. J. M.

**Ionisation by positive ions.** J. S. TOWNSEND and F. L. JONES (Phil. Mag., 1933, [vii], 15, 282—294).—Experiments are described to determine separately the effects of the ionisation of gas mols. or atoms by collisions of positive ions, and the setting free of electrons from the negative electrode by positive ions, in currents between parallel plates at a gas pressure corresponding with the min. sparking potential.

N. M. B.

**At. wt. of caesium.** G. P. BAXTER and J. S. THOMAS (J. Amer. Chem. Soc., 1933, 55, 858—859).—Determinations of the CsCl:Ag ratio using specially pure CsCl lead to the at. wt. 132.91, which is consistent with vals. from mass-spectrographic data.

J. G. A. G.

**Relative abundance of the carbon isotope,  $C^{13}$ .** F. A. JENKINS and L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 1212—1219).—The relative intensities of the 1,0 bands of  $C^{12}C^{13}$  and  $C^{12}C^{12}$  indicate an abundance ratio of 106:1 for  $C^{12}:C^{13}$ , corresponding with an at. wt. of 12.010. Lines due to  $C^{13}N$  in the CN band at 3883 Å. have been detected in the C arc in air.

D. R. D.

**Isotopes (oxygen, neon, and chlorine).** H. KALLMANN and W. LASAREV (Z. Physik, 1933, 80, 237—241).—Mass-spectrograph measurements on CO,  $H_2O$ , and  $O_2$  gave the intensity ratio  $O^{18}:O^{16}$  as 1:630; Ne gave  $Ne^{23}:Ne^{20}$  as 1:2000, and HCl gave  $Cl^{40}$  and  $Cl^{39}:Cl^{36}$  as 1:6000.

A. B. D. C.

**Masses of  $O^{17}$ .** W. D. HARKINS and D. M. GANS (Physical Rev., 1931, [ii], 37, 1671—1672).—New vals. are discussed (cf. A., 1931, 783).

L. S. T.

**Existence of barium isotopes 136 and 137.** R. C. GIBBS and P. G. KRUGER (Physical Rev., 1931, [ii], 38, 1921).—The satellites of the Ba II lines 4554 and 4934 Å. may be due to  $Ba^{137}$  and the parent line to  $Ba^{136}$  and  $Ba^{138}$  (cf. A., 1932, 979).

L. S. T.

**Zero-point energy and the separation of isotopes.** H. EYRING (Proc. Nat. Acad. Sci., 1933, 19, 78—81).—Theoretical. It is shown that the higher zero-point energy of the lighter isotope of H makes it the more reactive of the two in the special case of

processes involving adsorption and desorption at electrode surfaces. The bearing of this on isotope separation is discussed. M. S. B.

**Nuclear moments of the gallium isotopes 69 and 71.** J. S. CAMPBELL (*Nature*, 1933, **131**, 204).—An examination of the hyperfine structure in the visible lines of the Ga  $\pi$  spectrum has shown the patterns due to the individual isotopes to be separated by a difference in the magnetic moments of the nuclei. From this the mechanical moments have been separately determined as  $i=3/2$  for both isotopes. The ratio of the  $g(i)$  factors from the hyperfine separations is 1.27, isotope 71 having the greater magnetic moment. The abundance ratio  $c_{69}/c_{71}$  is 1.5/1. The only other example of isotopes with equal spins and unequal hyperfine separations is that of Tl. L. S. T.

**Mass defect of helium.** E. WIGNER (*Physical Rev.*, 1933, [ii], **43**, 252—257).—Mathematical. A connexion between the mass defect of  $H_2$ , the width and depth of a simple potential hole, and the mass defect of He and higher nuclei is obtained. N. M. B.

**Artificial disintegration.** D. VAN DER VEEN (*Chem. Weekblad*, 1933, **30**, 66—75, 146).—A review of recent work on at. disintegration by  $\alpha$ -particle bombardment and by means of H canal rays. H. F. B.

**Mobilities of molecular aggregates in gases containing radon.** E. L. HARRINGTON and E. O. BRAATEN (*Trans. Roy. Soc. Canada*, 1932, [iii], **26**, III, 177—186).—The mobilities of mol. aggregates in gases containing radon have been studied by two methods employing an ultramicroscope and also a modified Erikson apparatus. The results show a wide range of mobilities and suggest the importance of ionic winds and inconstancy of ionic charge in the study of mobilities. J. W. S.

**Influence of distillation on the grouping of radioactive atoms.** (MLLE.) M. I. ARCHINARD (*J. Chim. phys.*, 1933, **30**, 56—60).—The nature of the radioactive layers condensed on a cold surface from Po or active Th deposit volatilised under various conditions was investigated photographically. N. M. B.

**Amplification of the ionisation produced by radioactive sources.** J. A. C. TEEGAN (*Nature*, 1933, **131**, 277—278). L. S. T.

**Energy distribution of  $\beta$ -rays from atoms of known age.** B. W. SARGENT (*Trans. Roy. Soc. Canada*, 1932, [iii], **26**, III, 205—216).—By collecting Th- $C''$  atoms from a Th- $B+C$  prep. under the action of an electric field on a moving Cu strip, atoms of known age have been obtained and the absorption of the  $\beta$ -rays emitted by these atoms at ages of 21 sec. to 10.7 min. for papers of various thicknesses has been measured. No dependence of energy distribution on the age of the atoms could be detected. J. W. S.

**Scattering of  $\beta$ -rays.** I. B. W. SARGENT and A. J. O'LEARY (*Trans. Roy. Soc. Canada*, 1932, [iii], **26**, III, 217—232).—The average angles of scattering of  $\beta$ -rays from Ra- $E$  by gases and vapours are  $60^\circ$  and  $90^\circ$ . For gaseous compounds of H, C, N, and O the intensities of the scattered  $\beta$ -rays are proportional

to their mol. scattering nos., in accordance with theory. For gaseous compounds of S, Cl, Br, and I the intensities relative to  $CO_2$  are in some cases  $>$  theoretical, suggesting plural scattering. Scattered  $\beta$ -rays are the more penetrating the higher is the at. no. of the scattering atoms. J. W. S.

**Absorption of  $\beta$ -rays by, and molecular structure of, organic compounds.** G. FOURNIER and M. GUILLOT (*Compt. rend.*, 1933, **196**, 412—414).—The mass absorption coeffs. ( $\mu/\rho$ ) of 19 hydrocarbons calc. additively from those of C and H deduced from the authors' formula (cf. A., 1932, 210) compared with the coeff. determined experimentally show differences of 1.0—2.3 units. The difference increases with length of chain whether principal or lateral, is decreased by an ethylenic linking ( $C_6H_6$  behaves as if it contained three such linkings), and approx. double as much by an acetylenic linking. The differences in saturated hydrocarbons are similar to that for C in diamond, in unsaturated hydrocarbons to that for C in graphite (cf. A., 1917, ii, 437). C. A. S.

**Magnetic spectra of the  $\beta$ -rays emitted by thorium- $B+C+C'+C''$  and actinium- $B+C+C'+C''$ .** S. SHIH-YUAN (*Ann. Physique*, 1933, [x], **19**, 59—85; cf. A., 1932, 443).—Using the method described previously,  $H_p$  and intensity have been measured for the  $\beta$ -rays emitted by the active deposits of Th and Ac, and the corresponding energy levels deduced. The energies of the  $\gamma$ -rays emitted in the changes Th- $C \rightarrow$  Th- $C'$  and Ac- $C \rightarrow$  Ac- $C'$  are equal to the differences in energy between the groups of  $\alpha$ -rays from Th- $C$  and Ac- $C$ , respectively. J. W. S.

**$\gamma$ -Radiation from Th- $C$  and Th- $C'$  and fine structure of the  $\alpha$ -rays.** L. MEITNER and K. PHILIPP (*Z. Physik*, 1933, **80**, 277—284).— $\gamma$ -Lines belonging to the transitions Th- $C \rightarrow$  Th- $C''$  and Th- $C'' \rightarrow$  Th-Pb were distinguished; the results fit Gamow's relation of  $\alpha$ -ray fine structure to  $\gamma$ -ray emission. 21  $\beta$ -ray groups were measured for Th- $C''$ . A. B. D. C.

**$\gamma$ -Rays emitted on disintegration of lithium.** H. R. VON TRAUBENBERG, A. ECKARDT, and R. GEBAUER (*Z. Physik*, 1933, **80**, 557—558).—Li disintegrated with protons emits  $\gamma$ -rays. A. B. D. C.

**$\gamma$ -Radiation of radium.** E. STAHEL and W. JOHNER (*Helv. phys. Acta*, 1932, **5**, 310—311; *Chem. Zentr.*, 1932, ii, 3197).—Ionisation measurements show that the no. of  $\gamma$ -quanta emitted by Ra is 1.3%. The no. of secondary  $\beta$ -rays is 5%; hence 100 disintegrating Ra atoms emit 6.3  $\gamma$ -quanta. A. A. E.

**Neutron, atomic nucleus, and mass defect.** W. D. HARKINS (*J. Amer. Chem. Soc.*, 1933, **55**, 855—857).—Theoretical. The energies of union of 13 atoms with either a proton, neutron, or  $H^2$  nucleus are recorded. The mass defect per  $\alpha$ -particle increases rapidly with the no. of  $\alpha$ -particles up to mass 52 and then decreases slowly. J. G. A. G.

**Conditions of emission of neutrons by the action of  $\alpha$ -particles on light elements.** (MME.) I. CURIE and F. JOLIOT (*Compt. rend.*, 1933, **196**, 397—399).—The relation between the radiation

(neutrons) emitted by Be, B, and Li under the influence of  $\alpha$ -particles from Po and the energy,  $w\alpha$  (expressed in  $eV \times 10^6$ ), of the  $\alpha$ -particles, has been determined by means of the ionisation produced in  $CH_4$ . For Be excitation begins when  $w\alpha=1.3$ , is a max. for  $w\alpha=2.6$ , and a min. for  $w\alpha=3.2$ ; corresponding figures for B are 2.0, 2.2, and 2.85, figures near to those for excitation of  $\gamma$ -rays (cf. A., 1932, 895, 1073). The radiation from Li is much less, and extends from  $w\alpha=3$  to 5; emission of  $\gamma$ -rays before neutrons is explicable by transmutation without capture of an  $\alpha$ -particle. Under similar conditions Al emits feebly,  $CaF_2$  very, penetrating radiation, the latter due to F, and in both cases consisting mainly of neutrons, so that  $Al^{27}$  and  $F^{19}$  are able to emit both protons and neutrons (cf. A., 1931, 142). C. A. S.

**Possibility of spontaneous emission of neutrons from certain non-radioactive elements.** W. SWIENTOSEAWSKI and A. DORABIALSKA (Rocz. Chem., 1933, 13, 1—4).—The existence of certain isotopes cannot be explained solely on the basis of  $\alpha$ -,  $\beta$ -, and  $H$ -radiation from predecessors, but requires the postulation of neutron radiation, to which the thermal radiation found by Dorabialska (A., 1932, 927) for certain elements is tentatively ascribed. R. T.

**Emission of neutrons by aluminium under action of  $\alpha$ -particles.** P. AUGER and G. M. HERZEN (Compt. rend., 1933, 196, 543; cf. preceding abstracts).—500 photographs of the rays emitted by powdered Al, obtained by the Wilson method, showed two trajectories due to rapid and two to slow protons, indicating emission of neutrons by Al, although much more rarely than by Be under similar conditions. C. A. S.

**Experimental proofs of the existence of the neutron.** (MNE.) I. CURIE and F. JOLIOT (J. Phys. Radium, 1933, [vii], 4, 21—33).—Evidence of the existence and properties of radiations of particles of unit mass and zero charge in the transmutation of Be, B, and Li by  $\alpha$ -rays was obtained by the cloud-track method and by the ionisation of A-He and  $N_2$ -He mixtures and absorption in Pb. N. M. B.

**Diffusion of neutrons.** J. SOLOMON (Compt. rend., 1933, 196, 607—609).—The applicability of Born's first approximation (cf. A., 1926, 1078) to the equation  $V(r)=Ze^2e^{-r/a}/r$  (cf. A., 1932, 443, 672) for the interaction energy of an electron and a neutron is shown to be limited to the case of H. C. A. S.

**Chemical nature of the neutron.** P. ACHALME (Compt. rend., 1933, 196, 614—616).—Assuming that the negative charge of the electron is double the positive charge of the proton (cf. A., 1912, ii, 322) it is suggested that the neutron is identical with para-H, and consists of two protons and one electron; and further that  $X_3$  (cf. A., 1913, ii, 820) and  $\alpha$ -particles consist of one electron and three and four protons, respectively. C. A. S.

**Neutrons.** D. MEKSYN (Nature, 1933, 131, 366).—Theoretical. An electron and a proton are held together in a neutron by combined forces of attraction and repulsion which are in statical equilibrium. The size of the neutron is  $r=1.4 \times 10^{-13}$

cm. and the binding energy is  $mc^2 \sim 5 \times 10^5$  electron-volts. L. S. T.

**Structure of atomic nuclei. III.** W. HEISENBERG (Z. Physik, 1933, 80, 587—596; cf. A., 1932, 1074).—The Thomas-Fermi method is applied to neutrons and protons constituting at. nuclei.  $\gamma$ -Ray scattering is treated on lines developed for Raman scattering, and finally the anomaly of  $\beta$ -ray emission without exchange energy of electrons within the nucleus is discussed. A. B. D. C.

**Models of atomic nuclei.** E. N. GAPON (J. Gen. Chem. Russ., 1932, 2, 862—863).—Models of the structure of nuclei are given, based on the assumption that  $\alpha$ -particles are composed of 2 neutrons and 2 protons. R. T.

**Theory of atomic nuclei. I—IV.** E. N. GAPON (J. Gen. Chem. Russ., 1932, 2, 837—842, 843—848, 849—850, 851—861).—I. See this vol., 111.

II. Variations in the velocity of  $\beta$ -particles are ascribed to the mass defect of intra-nuclear electrons. The law of conservation of energy applies to  $\beta$ -particles.

III. Mass defect is ascribed to entrance into protons of electrons of negative wt.

IV. Mass defect and mechanical moment of at. nuclei are discussed with reference to a theory of the structure of the at. nucleus, based on Rutherford's model. R. T.

**Theory of superconductivity. II.** R. DE L. KRONIG (Z. Physik, 1933, 80, 203—216; cf. this vol., 15).—A three-dimensional electron lattice must traverse very high potential barriers in passing through a crystal; this difficulty is obviated by assuming that the electrons form a one-dimensional lattice which melts at the superconductive temp. A. B. D. C.

**Electron spin.** S. SHIMASAKI (Sci. Rep. Tokyo Bunrika Daigaku, 1933, 1, 251—273).—Mathematical. Treating the impulse in a linear form and the spin angular momentum as a vector gives a result similar to that of the perturbation theory, and leads to the Dirac fine structure for the  $H_2$  spectrum. N. M. B.

**Most probable values of the atomic constants,  $e$  and  $h$ .** R. LADENBURG (Ann. Physik, 1933, [v], 16, 468—472).—The vals. regarded as most probable are  $e=4.770 \pm 0.004 \times 10^{-10}$  and  $h=6.547 \pm 0.009 \times 10^{-27}$ . A. J. M.

**Earth's magnetic effect and corpuscular nature of cosmic ultra-radiation. IV.** J. CLAY (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 1282—1290).—The variation of intensity with magnetic latitude suggests that cosmic rays consist primarily of a charged corpuscular radiation. D. R. D.

**Electronic theory of metals.** R. PEIERLS (Ergebn. exakt. Naturwiss., 1932, 11, 264—322; Chem. Zentr., 1932, ii, 2923).—A discussion. A. A. E.

**Uncertainty relations and volume of photons.** D. MEKSYN (Phil. Mag., 1933, [vii], 15, 592—601).—Theoretical. H. J. E.

**Physical proof of existence of Gurwitsch radiation by means of a differential arrangement.**

W. W. SIEBERT and H. SEFFERT (Naturwiss., 1933, 21, 193—194).—An experiment is described for this purpose. A. J. M.

**Band spectra and dissociation of molecules.** R. SAMUEL (Proc. Muslim Assoc. Adv. Sci., 1932, 2, 55—67).—An address.

**Spectro-photometry in the ultra-violet.** H. ARENS (Z. Physik, 1933, 80, 629—635).—Methods are given for sensitising plates for the extreme ultra-violet, and the sensitivity of AgI emulsions in relation to AgI absorption bands is discussed. A. B. D. C.

**Total radiation of oxides and mixtures of oxides.** K. HILD (Mitt. Kaiser-Wilh.-Inst. Eisenforsch., 1932, 14, 59—70; Chem. Zentr., 1932, ii, 3055).—The total radiation at 800—1400° of Al<sub>2</sub>O<sub>3</sub>, MgO, CaO, SiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and ZnO in relation to particle size, and of mixtures in relation to composition, was investigated. A. A. E.

**Continuous absorption spectrum of some polyatomic molecules.** I. Y. HUKUMOTO (Sci. Rep. Tôhoku, 1932, 21, 906—927).—A continuous absorption spectrum without a neighbouring band spectrum and convergence limit is accounted for by the excited electronic state of the mol. being unstable or much less stable than the normal state.

The continuous absorption spectra of this type of a no. of alkyl halides which have been investigated in the ultra-violet region are very similar, excepting that the absorption regions are displaced towards the long-wave side in the order RCl, RBr, RI. I-compounds show some selective absorption. J. W. S.

**Chappuis bands of ozone and the boric acid spectrum.** E. WALLIS (Z. Physik, 1933, 80, 267—272).—The H<sub>3</sub>BO<sub>3</sub> spectrum is identical with Chappuis' bands of O<sub>3</sub>. A new spectrum in the red was obtained from the C arc in O<sub>2</sub>. A. B. D. C.

**Absorption spectra of cobaltous chloride in alcoholic solutions.** O. SPECCHIA (Nuovo Cim., 1932, 9, 164—167; Chem. Zentr., 1932, ii, 3362—3363).—The fundamental frequencies of the vibration components of the COCl<sub>2</sub> band at 6950—6100 Å. and the multiplicities are, respectively; MeOH 416, 36—40; EtOH 417, 36—41; PrOH, 472, 32—36; BuOH 371 cm.<sup>-1</sup>, 39—44. A. A. E.

**Absorption spectra of complex salts of Cr, Mn, Ru, Rh, Pd, Re, Os, Ir, and Pt.** R. SAMUEL and A. R. R. DESPANDE (Z. Physik, 1933, 80, 395—401).—Absorption curves are given for 13 complex cyanides and chlorides of the above metals in the region 650—200 mμ. A. B. D. C.

**Line absorption spectra of chromium complex salts.** G. JOOS and K. SCHNETZLER (Z. physikal. Chem., 1933, B, 20, 1—10; cf. A., 1932, 983).—Most of the salts examined exhibit sharp absorption lines, showing that the differences in the Cr<sup>+++</sup> ion in the various salts are merely quant. In the hexacyano- and -thiocyano-complexes, however, there is a qual. change in the electron envelope of the central ion, for these salts give no lines. The introduction of a charged group into aquo-, ammino-, or en-complexes displaces the absorption by about 500 cm.<sup>-1</sup> towards the red. R. C.

**Effect of crystal symmetry and chemical composition on the energy levels of solids.** F. H. SPEDDING and G. C. NUTTING (J. Amer. Chem. Soc., 1933, 55, 496—504).—Absorption spectra of 6 Gd<sup>+++</sup> salts have been determined. The lines arise from electronic transitions from the <sup>8</sup>S<sub>7/2</sub> level to excited levels which are non-degenerate through the influence of the fields of neighbouring ions. The degree of splitting depends on the symmetry and separation of the ions in the lattice. J. G. A. G.

**Ultra-violet absorption spectra of simple benzene derivatives. II.** F. W. KLINGSTEDT (Z. physikal. Chem., 1933, B, 20, 125—141; cf. A., 1928, 1304).—Absorption measurements down to 2000 Å. have been made in hexane solution. With PhBr there are regions of selective absorption at 2800—2420 and 2240—2100, and a third commences at about 2075 Å., resembling those of PhCl displaced about 50 reciprocal Å. towards longer wave-lengths. PhI has a structureless flat band at about 2680—2460 Å., and a region of strong absorption at 2420—2170 Å., the former being ascribed to the nucleus. *p*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> has a region of selective absorption at 2900—2560 Å. and a superimposed region extending to 2170 Å.; the vibration frequency of the nucleus averages 1035 cm.<sup>-1</sup> The excitation energy of mono-substituted C<sub>6</sub>H<sub>6</sub> and PhMe derivatives increases fairly regularly with the nuclear charge of the element directly attached to the nucleus. R. C.

**Ultra-violet absorption of hydroxyazo-compounds in aqueous solution and its relation to  $p_H$ .** I. T. UYEMURA (Bull. Tokyo Univ. Eng., 1932, 1, 327—347).—The effect of various groups was examined. Me has little effect. NO<sub>2</sub> *para* to the azo-group is bathochromic; when *o*- or *m*- it shows similar absorption spectra. The position of OH relative to the azo-group is important. The band due to Ph is absent in *p*-cresol, possibly owing to the effect of the position of OH. In general, absorption bands are shifted towards longer wave-lengths with increase in  $p_H$ . CH. ABS.

**Spectrographic study of phloridzin and its derivatives. Ultra-violet absorption.** A. LAMBRECHTS (Compt. rend., 1933, 196, 295—297).—In H<sub>2</sub>O phloridzin has a band max. at 2852 Å. ( $\epsilon$ , 16,250) at  $p_H$  1.7, and bands with max. at 3225 ( $\epsilon$ , 27,000) and 2300 Å. at  $p_H$  10.04, whilst at  $p_H$  7.5 both bands appear as small max. in a more general absorption. In EtOH only the band at 2852 Å. is seen. These effects are due to keto-enol tautomerism. R. S. C.

**Pleochroism of calcite in the infra-red.** P. LE ROUX (Compt. rend., 1933, 196, 394—396; cf. A., 1928, 934).— $K_0$ ,  $K_0'$ , the coeffs. of absorption of calcite for propagation parallel and perpendicular to the axis for  $\lambda$  2.2—4.4  $\mu$ , are respectively 0.6—30.7 and 0.7—34.8,  $K_0$  being always slightly  $< K_0'$ . C. A. S.

**Infra-red absorption spectrum of nitrogen dioxide.** C. R. BAILEY and A. B. D. CASSIE (Nature, 1933, 131, 239).—At room temp. the absorption spectrum of N<sub>2</sub>O<sub>4</sub>  $\rightleftharpoons$  2NO<sub>2</sub> shows bands at 15.6, 13.4, 7.92, 6.17, 5.75, 3.22, and 2.91  $\mu$ . At 100°, the max. of radiation emission characteristic of this temp. is

beyond  $20 \mu$ ; all bands except those at  $15.6$  and  $6.17 \mu$  disappeared. These two bands are ascribed to  $\text{NO}_2$ , the mol. of which is thus probably rectilinear and symmetrical. The N-O force const. is approx.  $7 \times 10^5$  dynes per cm., the deformation force const. is approx.  $6 \times 10^{-12}$  dyne per cm., and the moment of inertia is  $60 \times 10^{-40}$  g.-cm.<sup>2</sup> with an interat. separation of  $1.1 \text{ \AA}$ . This structure is confirmed by the Raman spectrum of inorg. nitrites in aq. solution which show an intense line at  $1303 \text{ cm.}^{-1}$ , a val. of the same order as that calc. from the above. L. S. T.

**Envelopes of infra-red absorption bands.** S. L. GERHARD and D. M. DENNISON (Physical Rev., 1933, [ii], 43, 197—204).—The intensity formulæ for the fine-structure absorption lines of mols. of the symmetrical rotator type are approximated to determine line intensities or envelopes. Application of results gives for the moment of inertia perpendicular to the symmetry axis for MeF, MeCl, MeBr, and MeI, vals.  $\times 10^{40}$ , 32, 61, 89, and 99, respectively. N. M. B.

**Vibration spectra and molecular structure of methyl and ethyl alcohols.** R. TITÉICA (Compt. rend., 1933, 196, 391—394).—The infra-red spectra of MeOH and EtOH in the low-pressure gaseous condition have been measured for  $\lambda = 2.10$ — $14.70 \mu$ , and compared with previous results (cf. A., 1925, ii, 351; 1929, 236) and the Raman spectra. For MeOH eight fundamental frequencies (four single, four double) are inferred, leading to a structure in which C-H=1.08, C-O=1.46, O-H=0.96 Å, and the angle of H-C-H=106° (cf. A., 1932, 670); in EtOH C-O=C=1.53 Å, and the angle of C-C-O=108° 16'. C. A. S.

**Raman effect of the ions  $\text{SO}_4''$  and  $\text{SO}_3''$  and the electrolytic dissociation of sulphuric and sulphurous acids.** P. FADDA (Nuovo Cim., 1932, 9, 168—179; Chem. Zentr., 1932, ii, 3363).—Saturated aq.  $\text{Na}_2\text{SO}_4$ , irradiated with  $\lambda$  4358 Å, gave Raman frequencies: 460, 617, 984, 1104  $\text{cm.}^{-1}$ . 25%  $\text{H}_2\text{SO}_4$  gives 984; more conc.  $\text{H}_2\text{SO}_4$  gives frequencies of  $\text{HSO}_4'$  (421, 574, 1047),  $\text{H}_2\text{SO}_4$  (912, 1522), and  $\text{SO}_2$  (1166). The  $\text{H}_2\text{SO}_4$  frequencies diminish rapidly in intensity on dilution. The  $\text{SO}_3''$  frequencies in saturated aq.  $\text{Na}_2\text{SO}_3$  (471, 602, 984  $\text{cm.}^{-1}$ ) do not appear in the Raman spectrum of  $\text{H}_2\text{SO}_3$ , which indicates that  $\text{H}_2\text{SO}_3$  contains chiefly free  $\text{SO}_2$  (1142), together with some  $\text{HSO}_4'$  (569, 1047) formed by atm. oxidation. The line 1199 may be due to  $\text{HSO}_3'$ . A. A. E.

**Polarisation of light-scattering. II.** S. VENKATESWARAN (Phil. Mag., 1933, [vii], 15, 263—282; cf. A., 1932, 898).—Polarisation measurements of vibrational Raman lines are reported, and results are discussed in relation to mol. structure for the following 27 liquids:  $\text{H}_2\text{S}$ , HCN,  $\text{H}_2\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{PCl}_3$ ,  $\text{CS}_2$ , MeOH,  $\text{HCO}_2\text{H}$ , MeCl, MeBr, MeI, MeSH,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_5\text{H}_{12}$ ,  $(\text{C}_3\text{H}_5)_2\text{S}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{PhNO}_2$ , PhCl, PhBr, mesitylene, salol,  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{C}_4\text{H}_4\text{S}$ , and  $\text{C}_4\text{H}_4\text{NH}$ . Raman lines from transverse oscillations are highly depolarised, all showing the limiting depolarisation val. 6/7. N. M. B.

**Raman effect in liquids.** A. CARRELLI and J. J. WENT (Z. Physik, 1933, 80, 232—236).—Investigation of the Rayleigh continuum shows that there is no

relation between depolarisation and optical anisotropy of mols. Broadening of Raman lines was studied for  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{H}_2\text{O}$ , and glycerol. A. B. D. C.

**Raman effect.** T. CUMJUMZELIS (Praktika, 1932, 7, 242—247; Chem. Zentr., 1932, ii, 3202).—The following frequencies were detected:  $\text{C}_6\text{H}_6$ ,  $\Delta\nu$  1038; PhCHO 2971, PhMe 1237, and two anti-Stokes lines. Three PhMe lines reported by Pringsheim and Rosen as excited by 5461 Å. were not confirmed. A. A. E.

**Raman effect of methyl esters of silicic acid.** R. SIGNER and J. WEILER (Helv. Chim. Acta, 1933, 16, 115—121; cf. this vol., 23).—Raman frequencies of  $\text{Si}(\text{OMe})_4$ , and of the di-, tri-, and deca-polymerides, are given and compared with those of quartz and of crown glass. The results are discussed. F. L. U.

**Normal vibrations of the  $\text{SiO}_4$  group.** J. WEILER (Z. Physik, 1933, 80, 617—628).—Raman spectra of the polymerides of  $\text{Si}(\text{OMe})_4$  gave four fundamental frequencies near 1200, 1070, 800, and 500  $\text{cm.}^{-1}$  for the  $\text{SiO}_4$  group, and combinations of these frequencies give the bands of cryst. quartz. A. B. D. C.

**[Raman spectra of]  $\alpha$ -ethylene oxides.** R. LESPIEAU and (MLLE.) B. GREDY (Compt. rend., 1933, 196, 399—401).—The Raman spectra of  $\alpha$ -mono- and -di-substituted ethylene oxides have been determined. The  $\alpha$ -ethylene oxide group is characterised by a line near 1250  $\text{cm.}^{-1}$ ; the spectra of most of the derivatives are similar, but the presence of  $\text{Pr}^{\beta}$  or of a halogen introduces a difference. C. A. S.

**Raman effect in the terpene series. III. Products of sulphuric acid isomerism of pinene.** G. DUPONT and R. GACHARD (Bull. Soc. chim., 1932, [iv], 51, 1579—1594; cf. A., 1932, 1076).—The following constituents of terebene have been recognised: cymene, camphene, limonene,  $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene, 1:4-cineole, and four unidentified substances for which Raman data are given. E. S. H.

**Raman spectra and chemistry.** ANON. (Nature, 1933, 131, 263—265).—A summary. L. S. T.

**Temperature effect of the molecular polarisation of gases and vapours.** R. SANGER, O. STEIGER, and K. GACHTER (Helv. phys. Acta, 1932, 5, 200—210; Chem. Zentr., 1932, ii, 2949—2950).

**Negative polarisation in fluorescence.** K. S. KRISHNAN and S. M. MITRA (Nature, 1933, 131, 204—205).—Vavilov's experiments (Z. Physik, 1929, 55, 690) on the polarisation of fluorescence of dyes in glycerol when excited by radiations of different wave-lengths have been repeated and the general conclusions confirmed. L. S. T.

**Inhibitory action of certain ions on fluorescence of uranine.** J. ROUCHARD (Compt. rend., 1933, 196, 485—487; cf. A., 1927, 609).—The intensity of fluorescence in NaOH solution is inhibited by ions in the order  $\text{S}'' > \text{CNS}'' > \text{I}'' > \text{S}_2\text{O}_4'' > \text{S}_2\text{O}_3'' > \text{NO}_2'' > \text{HAAsO}_3''$ ;  $\text{NO}_3'$ ,  $\text{Cl}'$ ,  $\text{Br}'$ ,  $\text{F}'$ ,  $\text{CN}'$ ,  $\text{CO}_3''$ ,  $\text{SO}_3''$ ,  $\text{SO}_4''$ ,  $\text{AsO}_4'''$ ,  $\text{PO}_4'''$ , and  $\text{AcO}'$  are inactive. The active salts are all antioxygenic. C. A. S.

**Triboluminescence in mercury vapour.** S. DE WALDEN (Acta phys. Polonica, 1932, 1, 223—236;

Chem. Zentr., 1932, ii, 3203).—The spectrum of the triboluminescence of Hg in a SiO<sub>2</sub> vessel with carefully cleaned walls was studied at 90–400°. Arc lines first appeared, followed at >115° by the band spectrum. At 200–300° spark lines appeared. At >200° the Steubing band at 2345 Å. was observed. The spectrum of the electrodeless discharge in Hg at 100° resembles the triboluminescence spectrum, without spark lines. A. A. E.

Investigations of the ultra-violet rays. L. ZEHNDER (Z. Physik, 1933, 80, 699–700).—A weak radiation observed by the author (1899) is now confirmed in the mitogenetic rays, and methods of spectral analysis are suggested. A. B. D. C.

Potential curves for mercury hydride. R. RYDBERG (Z. Physik, 1933, 80, 514–524; cf. A., 1932, 104).—This method is applied to HgH, which is shown to dissociate by rotation. A. B. D. C.

Existence of a barrier layer photo-effect for lead sulphide? E. TIEDE and G. BRÜCKMANN (Z. Physik, 1933, 80, 302–304).—Only thermo-electric e.m.f. could be obtained from thin PbS layers. A. B. D. C.

Spectral sensitivity of caesium oxide photo-electric cathodes. G. DÉJARDIN and R. LATARJET (Compt. rend., 1933, 196, 470–473).—The Cs<sub>2</sub>O–Ag cell is prepared by treating a Ag plate oxidised superficially with Cs vapour at >200° in a closed vessel, which may or may not contain A, excess Cs being absorbed by Pb glass at the base of the vessel at 350°. It is stable, the sensitivity being a min. at 5000 Å., a max. at 8000, and then decreasing to 12,000 Å. (the threshold). If insufficiently heated the sensitivity varies with time, becoming const. after about 7 weeks; excessive heating decreases sensitiveness uniformly (cf. B., 1933, 26). C. A. S.

Reversal of current in rectifier photo-cells. J. GUILD (Nature, 1933, 131, 327–328; cf. this vol., 209).—The Cu<sub>2</sub>O–Cu junction is the essential factor in producing reversal in Au–Cu<sub>2</sub>O–Cu cells of the Auger type. Cells with no Cu backing to the Au–Cu<sub>2</sub>O layer show reversal in ultra-violet light, but not near 0.6 μ. A silvered Cu<sub>2</sub>O cell without Cu backing shows reversal at the blue end of the visible spectrum. L. S. T.

Distinction between electronic and photo-chemical effects in photo-voltaic elements. R. AUDUBERT (Compt. rend., 1933, 196, 475–477).—An oxidised Cu plate heated at 1000° in N<sub>2</sub> becomes coated uniformly with Cu<sub>2</sub>O. In an oxidising electrolyte, e.g. aq. Na<sub>2</sub>BO<sub>3</sub>, this gives a negative photo-potential, indicating absence or at least insignificance of the photolytic effect (cf. A., 1930, 173) in comparison with the intense photo-electronic process whereby the electrons under the action of light pass from the semi-conducting Cu<sub>2</sub>O into the metal. The essential difference between the two processes is supported by the fact that the photo-voltaic characteristics of such a plate for light of different wavelengths are or are not concurrent according as X=KI or Na<sub>2</sub>BO<sub>3</sub> in the cell Cu|Cu<sub>2</sub>O|X.m/100|KCl sat. Hg<sub>2</sub>Cl<sub>2</sub>|Hg in which it has been polarised. C. A. S.

Thermodynamic analysis of electromotive forces. J. VILLEY (J. Phys. Radium, 1933, [vii], 4, 10–20).—Theoretical. N. M. B.

Theory of conductivity of polarisable media. G. JAFFÉ (Ann. Physik, 1933, [v], 16, 217–248, 249–284).

Conductivity of highly insulating oxides and nitrides at very high temperatures. E. PODSZUS (Z. Elektrochem., 1933, 39, 75–81).—Data are given for Al<sub>2</sub>O<sub>3</sub>, MgO, CaO, ZrO<sub>2</sub>, ThO<sub>2</sub>, and BN from 1700° to 2400° abs., in vac. and in N<sub>2</sub> and H<sub>2</sub>. The conductivity, *k*, varies with the pressure and nature of the gas and the time of heating, and falls with increasing energy of formation of the compound. Normally, gases cause rise in *k*, but the val. for BN is depressed by N<sub>2</sub>, probably owing to its chemical identity with the anion. When the materials are pure, the variation with temp. is given by  $k=Ae^{-B/T}$ . D. R. D.

Electrical conductivity of tridymite and cristobalite at their transformation temperatures. S. SHIMIZU (Sci. Rep. Tôhoku, 1932, 21, 882–905).—The conductivity of SiO<sub>2</sub> plates changes abruptly in a direction parallel to the optical axis during the change β-quartz → tridymite, but in a direction at right angles it shows only continuous change. The conductivity of cristobalite is discontinuous at 225–245° in heating, but not in cooling, whilst that of tridymite changes abruptly in the range 175–202°. J. W. S.

Liquid crystal character of dipole liquids at the m.p. L. S. ORNSTEIN, W. KAST, and P. J. BOUMA (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 1209–1212).—The electrical conductivity of *p*-azoxyanisole is abnormally high throughout the temp. range within which it is in the liquid crystal state, passing through a max. in this region. A similar phenomenon occurs with CPh<sub>2</sub>, but extends over a range of only 2°. D. R. D.

Existence of limiting resistance in mixed crystals having a disordered atom arrangement. U. DEHLINGER and R. GLOCKER (Ann. Physik, 1933, [v], 16, 100–110). W. R. A.

Recovery of electrical resistance and the hardness of copper, silver, gold, platinum, and palladium after cold working. G. TAMMANN and K. L. DREYER (Ann. Physik, 1933, [v], 16, 111–119). W. R. A.

Method of determining dielectric constants of powders. K. HØJENDAHL (Z. physikal. Chem., 1933, B, 20, 54–64).—At the temp. at which a condenser filled with the powder with the air between the grains displaced by a pure liquid has the same capacity as when filled with the liquid, the dielectric consts. of the liquid and powder are equal. C<sub>6</sub>H<sub>6</sub> is recommended as the liquid. The dielectric consts. of solid alkali halides, Cu<sub>2</sub>O, and Ag<sub>2</sub>O have been measured. R. C.

Dipole moment of hydrogen peroxide. W. THEILACKER (Z. physikal. Chem., 1933, B, 20, 142–144; cf. this vol., 8).—The observed dipole moment agrees with that deduced from the formula HOOH if the angle between the O–O–H valencies is 110° and there is free rotation of the OH groups about the O–O axis. R. C.



**Electric moments of hydrazine and its derivatives.** L. F. AUDRIETH, W. NESPITAL, and H. ULICH (J. Amer. Chem. Soc., 1933, 55, 673—678).—Dielectric consts. of dil. solutions in  $C_6H_6$  were determined in the range  $17.5-20^\circ$ . The following dipole moments ( $\times 10^{-18}$  e.s.u.) were evaluated:  $N_2H_4$  1.83—1.85,  $NHPh \cdot NH$ , 1.65—1.79,  $NPhMe \cdot NH_2$  1.79,  $NPh_2 \cdot NH_2$  1.87,  $NHPh \cdot NHPh$  1.53 (cf. Bergmann *et al.*, A., 1931, 82),  $CHPh \cdot N \cdot NHPh$  1.97,  $CHPh \cdot N \cdot N \cdot CHPh$  1.0. J. G. A. G.

**Possibility of dipole rotation in crystalline solids.** S. E. KAMERLING and C. P. SMYTH (J. Amer. Chem. Soc., 1933, 55, 462—465; cf. this vol., 209).—Dielectric consts. at 0.2—50 kilocycles were determined in the range  $-91^\circ$  to  $36^\circ$ . Neither *n*-heptyl bromide, *p*- $C_6H_4(OMe)_2$ , or anisole mols., nor their polar groups turn in the applied field. Traces of impurities may account for effects attributable to such turning in  $PhOH$  and  $BzCl$ . J. G. A. G.

**Dipole moment and structure of organic compounds. XII.** A. WEISSBERGER and R. SANGEWALD (Z. physikal. Chem., 1933, B, 20, 145—157; cf. A., 1932, 718).— $CPh:CPh$  has zero dipole moment. In *p*-xylylene dichloride the  $CH_2Cl$  groups are apparently freely rotatable. The dipole moments of the meso- and *dl*-forms of *p*-di-( $\alpha$ -chlorobenzyl)benzene differ only slightly, showing that the interposition of the  $C_6H_6$  ring between the  $CHPhCl$  groups has decoupled them, permitting practically free rotation. In the monochlorodiphenyls the polarisation of the  $C_6H_4Ph$  residue varies with the position of the substituent relative to the diphenyl linking, as is shown by the differences in the dipole moments. A similar effect probably operates in the dichlorodiphenyls. R. C.

**Dipole moments of stannic chloride and some derivatives.** M. E. SPAGHT, F. HEIN, and H. PAULING (Physikal. Z., 1933, 34, 212—214).— $SnCl_4$  in  $CCl_4$  and in  $C_6H_{14}$  has zero dipole moment (cf. A., 1932, 793), showing the tetrahedral structure of this mol.  $SnEt_4$  gives the same result. For the ratio of dipole moments of singly- and doubly-substituted compounds the val. 1:1.12 was found (theoretical, 1:1.15). In contrast to C compounds, there is no marked deformation of the tetrahedral angle. A. J. M.

**Dependence of dipole moment of  $\alpha\beta$ -dichloroethane on the temperature and solvent.** S. MIZUSHIMA and K. HIGASI (Proc. Imp. Acad. Tokyo, 1932, 8, 482—485).—The dielectric const. of  $Et_2O$  solutions of  $CH_2Cl-CH_2Cl$  was measured between  $20^\circ$  and  $-60^\circ$ . The dipole moment increases with rise of temp. The rotation of the  $CH_2Cl$  groups in the mol. about the axis joining them is considered, and it is shown that the only case corresponding with the observed temp. effect is when interaction between the groups is not weak, but not strong enough completely to stop rotation. An expression is derived connecting the dipole moment with temp. on this assumption, giving satisfactory vals. A. J. M.

**Polarity in hydrocarbon vapours.** K. B. McALPINE and C. P. SMYTH (J. Amer. Chem. Soc., 1933, 55, 453—462).—Dielectric consts. have been deter-

mined at pressures between 10 and 1100 mm. in the temp. range  $226-486^\circ$  abs. The electric moments are  $C_6H_6$  0,  $PhMe$  0.37,  $C_3H_8$  0, propylene  $0.35 \times 10^{-18}$  e.s.u. The absence of temp. coeffs. of the polarisation of  $C_6H_6$  and  $C_3H_8$  indicates that those observed in liquid paraffins are due to decrease in intermol. action. The moments found for  $PhMe$  and propylene are attributed to inductive effects in the mols. J. G. A. G.

**Dispersion experiments with undamped ultrashort waves.** M. SEEBERGER (Ann. Physik, 1933, [v], 16, 77—99).—Three methods for the direct determination of the refractive index of liquids were investigated. Measurements were carried out with undamped waves of 12.6, 13.6, 14, 19, and 24 cm. The refractive and absorption indices, and the dielectric consts. of  $H_2O$  and aq.  $NaCl$ ,  $CuSO_4$ ,  $ZnSO_4$ ,  $Pb(OAc)_2$ , and glucose were determined at room temp. and 14 cm. Several alcohols were also measured. W. R. A.

**Molecular theory of the simultaneous optical effects of rotatory magnetic polarisation and of magnetic birefringence.** G. DUPOUY and M. SCHÉRER (Ann. Physique, 1933, [x], 19, 5—46; cf. A., 1931, 787).—The mathematical theory is developed for the optical effects when a beam of polarised light is passed through a liquid in a magnetic field. J. W. S.

**Compact molecules.** J. J. VAN LAAR (Chem. Weekblad, 1932, 29, 763—764).—A criticism of Backer's views (this vol., 211). H. F. G.

**New theory of chemical compounds.** M. REBEK (Coll. Czech. Chem. Comm., 1933, 5, 36—48).—The theory is based on the electronic conception of the atom. The system distinguishes between polar and non-polar combination, but avoids the use of those secondary valencies the nature and application of which are not clear. M. S. B.

**Electronic structures of polyatomic molecules and valency. IV. Electronic states, quantum theory of the double linking.** R. S. MULLIKEN (Physical Rev., 1933, [ii], 43, 279—302; cf. A., 1932, 1190).—Types of electronic states of polyat. mols. are tabulated. The determination of possible electronic states corresponding with any given electron configuration for any type of symmetry, and the selection rules for transitions between electronic states of mols. is shown. Mols. having all their electrons in closed shells or electron-pair linkings, and the approx. construction of mol. orbitals as linear combinations of at. orbitals are discussed. The quantum theory of the double linkings is illustrated and extended. N. M. B.

**New photo-magnetic effect.** D. M. BOSE and P. K. RAHA (Z. Physik, 1933, 80, 361—375).—Light absorption by solutions increases the paramagnetic susceptibility of the ions  $Cr^{+++}$ ,  $Fe^{++}$ ,  $Co^{++}$ ,  $Ni^{++}$ , and  $Cu^{++}$ , but leaves unchanged  $Ti^{+++}$  and  $Ce^{+++}$ . The increase is attributed to the absorbed light destroying the *l*-coupling of the ion to its associated  $H_2O$  mols. A. B. D. C.

**Absorption centres in crystals containing paramagnetic ions, and the mechanism of their**

**light absorption.** D. M. BOSE and S. DATTA (*Z. Physik*, 1933, 80, 376—394).—It is shown that in aq. solutions and in crystals containing  $H_2O$ , the absorption centre is the complex  $[M_nH_2O]^{m+}$ , and that this also causes the paramagnetic effects. The effect of *l*-coupling within the complex (cf. preceding abstract) is discussed, and it is shown that the energy required to destroy the *l*-couplings displaces the absorption frequency to higher wave nos.  $NH_3$ ,  $N_2H_4$ ,  $CN$ , etc. may replace  $H_2O$  in the complex, and if the coupling energy be increased, the magnetic moment is decreased and the absorption displaced to the violet. Rise of temp. increases the energy of the complex, tending to destroy the *l*-couplings and so affect the phenomena. A. B. D. C.

**Diamagnetic susceptibility of inorganic compounds. III. Oxyacidic salts and chlorides.** K. KUDO (*Sci. Rep. Tôhoku*, 1932, 21, 869—881; cf. A., 1932, 1077).—Measurements have been made of the magnetic susceptibility of salts of the oxyacids and of the chlorides and oxychlorides of the elements of groups IV, V, VI, and VII, and the susceptibilities of the oxyacidic ions calc. The susceptibility of an ion with a similar co-mol. structure decreases with increase of the nuclear charge on the central atom in the same group and increases with increase of the nuclear charge on the central atom in the same series. J. W. S.

**Diamagnetic susceptibility and refractivities according to wave mechanics.** B. MROWKA (*Z. Physik*, 1933, 80, 495—505).—The susceptibility of  $H_2$  is given in terms of universal constns. Ionic susceptibilities are deduced from ionic refractivities for  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Mg^{++}$ ,  $Sr^{++}$ , and  $Ba^{++}$ . A. B. D. C.

**Magne-crystallic action. I. Diamagnetics.** K. S. KRISHNAN, B. C. GUHA, and S. BANERJEE (*Phil. Trans.*, 1933, A, 231, 235—262).—The magnetic anisotropy of 13 inorg. and 12 org. crystals was determined by oscillating them about different axes in a uniform magnetic field. Results are tabulated for quartz, calcite, aragonite, strontianite, witherite,  $NaNO_3$ ,  $KNO_3$ ,  $KClO_3$ ,  $S$ , barite, celestite, anhydrite, and gypsum (the nitrates and carbonates showed large anisotropy, the sulphates were almost completely isotropic);  $C_{10}H_8$ , anthracene,  $\beta$ -naphthol, acenaphthene,  $Ph_2$ ,  $(CH_2Ph)_2$ ,  $COPh$ , benzil, salol, azo- and hydrazo-benzene. Except for the two last-named, for which the mean val. is lower, these follow the Pascal additive relations. The susceptibility of  $COPh_2$  decreases  $2\frac{1}{2}\%$  in the fused state. A correlation of the magnetic constns. of a crystal with those of its individual mols. by means of magnetic birefringence and light-scattering data, leading to a determination of the orientations of the mols. in the crystal lattice, is examined. N. M. B.

**Paramagnetic properties of rare-earth crystals. I.** H. A. KRAMERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1932, 35, 1272—1281).—The author's theoretical views (A., 1930, 401; 1931, 287) have been modified and extended. D. R. D.

**Paramagnetism of rhenium.** N. PERAKIS and L. CAPATOS (*Compt. rend.*, 1933, 196, 611—612).—The coeff. of magnetisation of Re at  $20^\circ$ ,  $-23^\circ$ , and

$-79^\circ$  is alike  $0.369 \pm 0.006 \times 10^{-6}$ , giving an at. coeff. of  $68.7 \times 10^{-6}$  (cf. A., 1931, 153). C. A. S.

**Ferromagnetism of trigonal ferric oxide.** V. DANILOV, G. KURDJUMOV, E. PLUSCHNIK, and T. STELLEZKY (*Naturwiss.*, 1933, 21, 177).—By heat treatment of some alloys containing  $Fe_2O_3$ , the latter may be converted from the para- into the ferromagnetic state. The lattice of the  $Fe_2O_3$  is unaltered by this change in magnetic properties, remaining trigonal. The change takes place only when the  $Fe_2O_3$  is present in an alloy. A. J. M.

**Interpretation of Weiss' law.** H. FAHLENBRACH (*Physikal. Z.*, 1933, 34, 204—207).—Explanations alternative to those of Gorter (A., 1932, 900) are given. A. J. M.

**Interpretation of Weiss' law.** E. VOGT (*Physikal. Z.*, 1933, 34, 207).—An addition to the paper of Fahlenbrach (cf. preceding abstract). A. J. M.

**Preliminary photographs of emission and absorption spectra with bent crystals as transmission gratings.** A. SANDSTRÖM and E. CARLSSON (*Z. Physik*, 1933, 80, 597—603).—Emission spectra Mo-*K* and Ag-*K* were obtained in four orders, and absorption spectra of *K*-edges of Br and Mo were obtained with bent gypsum crystals. A. B. D. C.

**Correction calculations for X-ray spectrometers.** M. SIEGBAHN (*Z. Physik*, 1933, 80, 413—414).—Polemical against Seemann (this vol., 108). A. B. D. C.

**Calculation of X-ray spectrographs. I.** D. BORISOV (*Ukrain. Chem. J.*, 1932, 7, [Sci.], 84—93).—Mathematical. R. T.

**Direct determination of the indices and locations of the spots in a Laue pattern of calcite.** G. F. H. HARKER (*Phil. Mag.*, 1933, [vii], 15, 512—527).—A calculation from first principles, assuming the lattice type and the lattice constns. H. J. E.

**Errors due to photographic development in spectrograms, particularly in measurement of band edges.** H. SEEMANN (*Z. Physik*, 1933, 80, 506—513).—Errors introduced by photographic development have been reinvestigated using a microphotometer. A. B. D. C.

**Improvement of X-ray quantitative chemical analysis.** F. VOGES (*Z. Physik*, 1933, 80, 542—556).—Measurement of intensity by ionisation combined with the Küstner monochromator (A., 1931, 993) gives quant. chemical analysis accurate to within a few parts per thousand, the time required for one measurement being 2—3 hr. A. B. D. C.

**Bitter's striations with an iron-silicon plate.** R. BECKER and H. W. F. FREUNDLICH (*Z. Physik*, 1933, 80, 292—298).—A study of the deposition of a colloidal suspension of  $Fe_2O_3$  particles on to the surface of magnetised Si-Fe. The particles are deposited in regular patterns in the form of striations. A. B. D. C.

**Co-operative phenomena.** F. ZWICKY (*Physical Rev.*, 1933, [ii], 43, 270—278).—Phenomena due to the interaction over large distances of elementary particles, a generalisation of thermodynamics from

static to stationary systems, the existence of crystals and their secondary structure, and ferromagnetic substances are discussed. N. M. B.

**Deposits of metallic mercury by high-frequency discharge.** D. BANERJI and R. GANGULI (Phil. Mag., 1933, [vii], 15, 676—681).—The deposits are explained in terms of the space potential distribution. H. J. E.

**Fusion of carbon.** A. EGERTON and M. MILFORD (Nature, 1933, 131, 169).—Under certain conditions in the C arc C is deposited as small spherules of graphite,  $d$  2.25, indicating that the C has existed for a finite time in the molten state. L. S. T.

**Electron diffraction photographs of microcrystalline carbon.** R. FRISCH (Naturwiss., 1933, 21, 173—177).—The method previously described (A., 1932, 980) was used, employing spider's web as basal substance instead of Au foil. Investigation of the photographs obtained with various preps. of "amorphous" C shows these to be microcryst. A. J. M.

**Change of lattice constant and conductivity of palladium by electrolytic charging with hydrogen.** F. KRÜGER and G. GEHM (Ann. Physik, 1933, [v], 16, 174—189).—The lattice const. and resistance of Pd charged with  $H_2$  by an electrolytic method were simultaneously determined as a function of the  $H_2$  concn. In the concn. range 0.03—0.77H/Pd, two phases exist, both showing an extended Pd lattice. The conclusion was confirmed by resistance measurements. The two phases are two solid solutions of  $H_2$  in Pd. A. J. M.

**Dependence of lattice constants and electrical conductivity of electrolytically charged palladium-silver alloys on the hydrogen concentration.** F. KRÜGER and G. GEHM (Ann. Physik, 1933, [v], 16, 190—202).—As concn. of  $H_2$  increases there is an extension of the Pd lattice up to 0.1H/Pd. For greater concns. two lattices are present, one weak, the other strong, in  $H_2$ . In this range there are two phases, which may be regarded as solid solutions of  $H_2$  in the alloy. Resistance measurements confirm this conclusion. With increase of Ag concn., the lattice consts. approach each other, and ultimately coexist; limiting concn. for this is 45% Ag. Discrepancies in the previous work on the solubility curve of  $H_2$  in Pd-Ag alloys are explained. A. J. M.

**Precision measurements of crystal parameters.** E. A. OWEN and E. L. YATES (Phil. Mag., 1933, [vii], 15, 472—488; cf. A., 1932, 557, 990).—Parameters of the following elements, showing cubic symmetry, were measured: Au 4.0699, Pt 3.9158; Pd 3.8824; Rh 3.7957; Pb 4.9396 Å. (all  $\pm 0.0003$ ); Ir 3.8312  $\pm 0.0005$  Å.; Fe 2.8607<sub>5</sub>; Al 4.0406<sub>5</sub>; Cu 3.6077<sub>5</sub>; Ag 4.0772<sub>4</sub> Å. (all  $\pm 0.0002$ ). Crystal densities at 0° and 20° were calc. H. J. E.

**X-Ray investigation of molten metals and alloys.** I. F. SAUERWALD and W. TESKE (Z. anorg. Chem., 1933, 210, 247—256).—X-Ray data are given for molten Hg in  $H_2$  and in vac., Tl in vac., Sn in vac., Pb in  $H_2$ ,  $Hg_5Tl_2$  in  $N_2$ , and  $KHg_2$  in A. Observations with the pure metals support the view that within a small region above the m.p. the melts contain struc-

tures similar to those observed in the solid state. The existence of intermetallic compounds is recognised in the longer periods of the alloys. E. S. H.

**Metals and alloys.** VII. Crystal structure of indium. VIII. Crystal structure of  $\beta$ -lanthanum. IX. Alloy phases of the type  $NaPb_3$ . E. ZINTL and S. NEUMAYR (Z. Elektrochem., 1933, 39, 81—84, 84—86, 86—97).—VII. In has a face-centred tetragonal structure with  $a$  4.583,  $c$  4.936 Å.,  $d_{calc}$  7.308.

VIII. Mixtures of rare-earth metals with NaCl or KCl, suitable for X-ray investigation, may be prepared by action of Na or K vapour on their anhyd. chlorides. In some cases formation of mixed crystals (e.g., Ce-K) causes error. Hence, La was first prepared electrolytically, converted into the  $\beta$ -form by heating for some days at 350°, and then mixed mechanically with KCl.  $\beta$ -La forms face-centred cubes with  $a$  5.296,  $r$  1.872 Å.

IX. The following are cubic:  $CaPb_3$  ( $a$  4.891 Å.),  $CePb_3$  (4.864),  $CaTl_3$  (4.794),  $CaSn_3$  (4.732),  $CeSn_3$  (4.711).  $SrPb_3$  is tetragonal with  $a$  4.955,  $c$  5.025 Å.

D. R. D.

**Effect of lattice distortion and fine grain on the X-ray spectra of metals.** W. A. WOOD (Phil. Mag., 1933, [vii], 15, 553—562; cf. A., 1932, 1193).—A method is given for differentiating between the broadening of X-ray diffraction lines due to fine grain and to lattice distortion, and is applied for electrodeposited Ni, for which both factors must be considered. H. J. E.

**Recrystallisation power and shear hardening in aluminium single crystals.** W. G. BURGERS (Nature, 1933, 131, 326—327).—Recrystallisation of stretched Al single crystals indicates that for the same amount of shear the no. of crystallites formed under identical conditions of heat treatment is the smaller the greater is the no. of slip-planes involved in the distortion. L. S. T.

**Preparation and crystal structure of lithium hydroxide.** T. ERNST (Z. physikal. Chem., 1933, B, 20, 65—88).—LiOH has a layer lattice with the space-group  $D_{2h}^2$  and  $d$  1.462,  $Z$  2,  $a$  3.549  $\pm 0.004$ , and  $c$  4.334  $\pm 0.008$  Å.  $n$  has been measured for various wave-lengths. R. C.

**Crystal structure of manganous sulphides and their mixed crystals with zinc sulphide and cadmium sulphide.** H. SCHNAASE (Z. physikal. Chem., 1933, B, 20, 89—117; cf. A., 1932, 986).—The Mn sulphides pptd. from aq. solution are all forms of  $MnS$ . The green sulphide has NaCl structure, and  $a$  5.212  $\pm 0.002$  Å. The rate of transformation of the red forms into the stable green form is appreciable at about 200°. Whilst the red forms are completely miscible in the solid state with CdS, there is apparently a gap with ZnS. R. C.

**Determination of the structure of the hexafluorides of sulphur, selenium, and tellurium by the electron diffraction method.** L. O. BROCKWAY and L. PAULING (Proc. Nat. Acad. Sci., 1933, 19, 68—73).—The diffraction patterns obtained when a beam of electrons intersects a jet of gas (cf. Mark and Wierl, A., 1930, 1336; 1931, 13, 665) give the

following separations for the elements in  $SF_6$ ,  $SeF_6$ , and  $TeF_6$ : S-F  $1.58 \pm 0.03$  Å.; Se-F  $1.70 \pm 0.03$  Å.; Te-F  $1.84 \pm 0.03$  Å. These agree very well with the vals. expected for an ionic structure. M. S. B.

**Crystal structures of fluorides. II.  $HgF$ ,  $HgF_2$ ,  $CuF$ , and  $CuF_2$ .** F. EBERT and H. WOITNEK (Z. anorg. Chem., 1933, 210, 269—272).—Lattice constns. have been determined:  $HgF$ ,  $a$  3.66,  $c$  10.9;  $HgF_2$ ,  $a$  5.54;  $CuF$ ,  $a$  4.26;  $CuF_2$ ,  $a$  5.40.

E. S. H.

**Planar structure of platinous complexes.** F. ROSENBLATT and A. SCHLEED (Naturwiss., 1933, 21, 178).—After repeated recrystallisation, the third isomeride of  $Pt(NH_3)_2Cl_2$  (Drew *et al.*, A., 1932, 562) gave the Debye diagram of the *trans*-compound. It can be obtained by crystallising together the *cis*- and *trans*-compounds. The more easily sol. *cis*-compound is found in greater amount in the mother-liquor; since the crystals give the Debye diagram of the new isomeride, it is concluded that this is a new cryst. form of *trans*- with some *cis*-compound.

A. J. M.

**Linear thermal expansion of a single crystal of sodium nitrate.** J. B. AUSTIN and R. H. H. PIERCE, jun. (J. Amer. Chem. Soc., 1933, 55, 661—668; cf. A., 1931, 1359).—The linear expansion accompanying the gradual transition between  $150^\circ$  and  $278^\circ$  was most marked in the direction of the  $c$  axis and was not detected along the  $a$  axis. This indicates a separation of the layers of  $NO_3$  ions resulting from the increasing amplitude of the oscillations and transition to rotation of these ions. The phenomena are reversible except along the  $a$  axis when the crit. point has been passed. At  $280^\circ$ ,  $\alpha = 45^\circ 34'$ .

J. G. A. G.

**Vacant positions in the iron lattice of pyrrhotite.** G. HÄGG (Nature, 1933, 131, 167—168).—X-Ray measurements support the assumption that the excess of S is due to vacant positions in the Fe lattice.

L. S. T.

**X-Ray studies of fatty acids and of mixtures of fatty acids.** E. OTT and F. B. SLAGLE (J. Physical Chem., 1933, 37, 257—258).—The spacings observed with mixtures show a linear relation with composition, in accordance with the usual behaviour of mixed crystals. Only one definite combination spacing may be observed in an equimol. mixture of nine fatty acids. The spacings recognised in highly polymerised substances may indicate an average chain-length.

E. S. H.

**Magnetostriction of ferromagnetic crystals.** R. GANS and J. VON HARLEM (Ann. Physik, 1933, [v], 16, 162—173).—Mathematical. The Heisenberg principle can be applied to magnetostriction.

A. J. M.

**Cross-sectional magnetostriction.** W. FRICKE (Z. Physik, 1933, 80, 324—341).—Magnetostriction hysteresis and remanence were established using the cross-section of cylindrical rods of Fe, Co, and Ni. The saturation magnetostriction for Ni agreed with Becker's theoretical val.

A. B. D. C.

**Kerr effect in Rochelle salt.** H. MÜLLER (Physikal. Rev., 1931, [ii], 38, 1922).

L. S. T.

**Change in the thermal power during the recovery of metals from cold work.** G. TAMMANN and G. BANDEL (Ann. Physik, 1933, [v], 16, 120—128).—Changes for Ag, Cu, Au, Mg, Fe, Ni, Pt, and Pd and the influence of the amount of cold work are discussed.

W. R. A.

**Change in resistance of bismuth crystals in magnetic fields.** O. STIERSTADT (Z. Physik, 1933, 80, 636—665).—A method was used which gave change in resistance with any orientation of the crystal; change in resistance was found, in directions normal to the principal axis of the crystal, which was very sensitive to structural changes in the crystal. This might be applied to determination of crystal form.

A. B. D. C.

**Electrical Barkhausen effect with crystals of sodium potassium tartrate.** M. KLUGE and H. SCHÖNFELD (Naturwiss., 1933, 21, 194).—The analogy between the dielectric properties of the salt and the magnetic properties of Fe is shown. De-electrification of the crystal shows an effect similar to the Barkhausen effect for Fe.

A. J. M.

**Magnetism of the metals.** E. VOGT (Ergebn. exakt. Naturwiss., 1932, 11, 323—351; Chem. Zentr., 1932, ii, 2935).—A discussion of the magnetic properties of metals in relation to the quantum states of the atoms in the crystal lattice.

A. A. E.

**Strength properties of moistened salt crystals. IV. Commencement of plasticity in rock-salt rods wholly subjected to water.** K. H. DOMMERICH (Z. Physik, 1933, 80, 242—251).

A. B. D. C.

**Tensile strength of synthetic rock-salt crystals at low temperatures.** W. BURGSMÜLLER (Z. Physik, 1933, 80, 299—301).—An investigation of the tensile strength and plasticity of synthetic rock-salt between  $-190^\circ$  and  $90^\circ$ .

A. B. D. C.

**Effect of water on the plasticity of rock-salt.** R. B. BARNES (Naturwiss., 1933, 21, 193).—By investigating the absorption bands in the ultra-violet of a rock-salt crystal made plastic by  $H_2O$  it is possible to show that the plasticity is due to entrance of  $H_2O$  into the crystal, as stated by Polanyi and Ewald, and not to a surface phenomenon (Joffé *et al.*).

A. J. M.

**Plasticity and tensile strength of rock-salt crystals stretched under water.** L. PIATTI (Nuovo Cim., 1932, 9, 102—124; Chem. Zentr., 1932, ii, 2786).—Plastic deformability differs not only in different crystals, but also in the parts of the same specimen. There is no clear relation between elastic limit, plastic extension, and tensile strength.

A. A. E.

**Isomeric compounds and their mixtures as solvents for micro-mol. wt. determination by the method of molar depression of f.p.** J. PIRSCH (Ber., 1933, 66, [B], 349—355; cf. this vol., 172).—The val.,  $E = 58.7$ , for isobornyl bromide (I) falls into line with those determined previously. In the neighbourhood of its m.p., (I) is isomerised to a slight extent to camphene hydrobromide. With mixtures of (I) and bornyl bromide (II) the val of  $E$

increases as a nearly linear function of the percentage of (II). H. W.

Electrical conductivity of mercury at high temperatures. W. BRAUNBEK (Z. Physik, 1933, 80, 137—149).—The electrical conductivity of Hg was determined up to 900° and 300 atm.; the pressure coeff. of conductivity was determined between 300 and 600 atm. up to 600°. A. B. D. C.

Absorption of sound in polyatomic gases. H. O. KNESER (Ann. Physik, 1933, [v], 16, 337—349). W. R. A.

Dispersion theory of sound. A. J. RUTGERS (Ann. Physik, 1933, [v], 16, 350—359).—Mathematical. W. R. A.

[Dispersion theory of sound.] H. O. KNESER (Ann. Physik, 1933, [v], 16, 360—361).—Polemical against Rutgers (cf. preceding abstract). W. R. A.

Physical properties of high-melting compounds. K. BECKER (Physikal. Z., 1933, 34, 185—198).—A summary of the physical properties of high-melting compounds, especially carbides, nitrides, and borides, either singly, or in alloys. The physical properties of alloys of WC and Co, and TaC and metals of the Fe group are specially considered. A. J. M.

Thermal conductivity of air. H. S. GREGORY and C. T. ARCHER (Phil. Mag., 1933, [vii], 15, 301—309).—Previous work (cf. A., 1926, 231) is amplified and discussed in relation to the investigations of Curie and Lepape on the rare gases (cf. A., 1932, 13). N. M. B.

Surface energy of molecules, and their physico-chemical properties. II. Surface energy and b.p. of members of homologous series. S. G. MOKRUSCHIN. III. Surface energy and b.p. of homologues of acyclic series. S. G. MOKRUSCHIN and E. I. KRILOV (J. Gen. Chem. Russ., 1932, 2, 911—915, 916—920).—II. The b.p.  $T$  of liquids belonging to a homologous series are given by  $T = \omega n + \phi n^2 + \pi$ , where  $n$  is the no. of atoms in the mol. of liquid, and  $\omega$ ,  $\phi$ , and  $\pi$  are consts.

III. The formula derived theoretically  $T = \alpha(M/d)^{2/3} + b$ , where  $\alpha$  and  $b$  are consts.,  $M$  is the mol. wt., and  $d$  the density of a member of a homologous series, gives results in good agreement with experiment. R. T.

Physical constants of 20 organic compounds. J. TIMMERMANS and (MME.) HENNAUT-ROLAND (J. Chim. phys., 1932, 29, 529—568).—Collection of physical consts., including b.p., f.p., density, refractive indices, viscosity, and surface tension, for the following substances: diisobutyl,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{I}_2$ , allyl chloride and alcohol, PhI,  $n$ -amyl alcohol,  $\text{CH}_2\text{Et}_2\text{OH}$ ,  $\text{CHMePrOH}$ ,  $\text{CMe}_2\text{EtOH}$ ,  $\text{COEt}_2$ ,  $\text{PrCO}_2\text{H}$ ,  $n$ - and *iso*-valeric acids,  $\text{HCO}_2\text{Et}$ ,  $\text{PrCO}_2\text{Et}$ ,  $\text{NEt}_3$ ,  $\text{MeNO}_2$ , and allylthiocarbimide. A. S. C. L.

Specific heat of oxygen at high temperatures from ozone explosions and the energy of the  $^1\Delta$  level of the neutral oxygen molecule. B. LEWIS and G. VON ELBE (J. Amer. Chem. Soc., 1933, 55, 511—519; cf. this vol., 16).—The sp. heat of  $\text{O}_2$  in the range 1400—2500° abs. has been determined by exploding  $\text{O}_3$ - $\text{O}_2$  mixtures in a const.-vol. bomb.

The discrepancy between the theoretical vals. calc. from the known vibration-rotation levels of  $\text{O}_2$  and the experimental vals., corr. for dissociation, is explained by the existence of the hitherto unknown  $^1\Delta$  state of the neutral  $\text{O}_2$  mol. at a level  $0.75 \pm 0.05$  volt, or  $17,200 \pm 1000$  g.-cal., above the ground state. Sp. heats,  $C_p$ , in the range 200—3000° abs. are recorded. J. G. A. G.

Temperature variation of the specific heat ( $C_p$ ) of carbon dioxide at 65.3 kg./cm.<sup>2</sup> pressure; specific heat of helium as a function of pressure. E. J. WORKMAN (Physical Rev., 1931, [ii], 38, 587).—The ratio  $C_p$  at 65.3 kg. per sq. cm. to  $C_p$  at 1 atm. is 1.87, 1.58, 1.38, and 1.27 at 45°, 50°, 80°, and 100°, respectively. At 180 kg. per sq. cm. the ratio may increase to 10 or 12 between 40° and 50°.  $C_p$  for He at 50° does not vary with pressure over the range 10—120 kg. per sq. cm. L. S. T.

Temperatures of sublimation of twelve amino-acids. (Miss) J. W. BROWN (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 173—175).—When heated in vac.  $\text{NH}_2$ -acids begin to sublime at temp. (which are tabulated) about 50—165° below the m.p. The sublimate collected on microscope slides 4 mm. above the surface of the substance form characteristic crystals, photographs of which are given. J. W. S.

Electrical differential method for measuring  $C_p$  in gases. V.  $C_p$  for carbon dioxide. M. TRAUTZ and H. BLUM (Ann. Physik, 1933, [v], 16, 362—375).—Modifications in the technique of measurement are described and the dependence of the measured  $C_p$  vals. on temp. and the initial heating current intensity were investigated. For  $\text{CO}_2$  the vals. of  $C_p$  are 6.77, 6.79, and  $6.80 \pm 0.02$  g.-cal. per mol. at 15.3, 18.0, and 19.0°, respectively. W. R. A.

Accurate determination of specific heats at high temperatures: the Neumann-Joule-Kopp-Regnault law concerning the additivity of the atomic heats of elements in chemical compounds. IV. F. M. JAEGER and J. A. BOTTEMA (Rec. trav. chim., 1933, 52, 89—111).—The sp. heat of mixed crystals of Au and Ag is almost exactly equal to the sum of the at. heats of the elements, but this is not true for the compounds PtSn, AuSn, and AuSb<sub>2</sub>, except in the case of  $\gamma$ -AuSb<sub>2</sub>. The deviations, which usually increase with rise of temp. and sometimes exceed 60%, may be positive or negative and show no correlation with the vol. changes on compound formation. Determinations of the crystal structure of AuSn, PtSn, and  $\gamma$ -AuSb<sub>2</sub> (A., 1927, 815; 1928, 574, 1079) have been confirmed. AuSb<sub>2</sub> is trimorphous, transition temp.  $\gamma$ - $\beta$  355.2°,  $\beta$ - $\alpha$  405°. Sb is dimorphous, transition temp.  $\beta$ - $\alpha$  413°. The sp. heats of  $\alpha$ - and  $\beta$ -AuSb<sub>2</sub> and  $\alpha$ -Sb change rapidly with temp. D. R. D.

Heat capacity data for durene, pentamethylbenzene, stilbene, and dibenzyl. J. D. FERRY and S. B. THOMAS (J. Physical Chem., 1933, 37, 253—255).—The sp. heats (in the solid and liquid states) and heats of fusion have been determined. E. S. H.

Calorimetric evidence for a term separation in gadolinium sulphate. N. KÜRTI and F. SIMON

See Paris  $T_B = K \log P + \lambda$

(Naturwiss., 1933, 21, 178—179).—Using the method of Simon *et al.* (A., 1930, 282), the determination of sp. heat at low temp. has been used as an indication of small term separations in  $Gd_2(SO_4)_3$ . The sp. heat decreases between  $10^\circ$  and  $6^\circ$  abs. as  $T^3$ , followed by a rapid rise, so that at  $1.6^\circ$  abs. the val. is 500 times normal. This gives  $0.2^\circ$  abs. as the characteristic temp. There is thus fairly complete equilibrium between all states at  $1.3^\circ$ . Neither susceptibility nor magneto-caloric effect shows any deviation from the Curie-Langevin law. Different results are, however, obtained if adiabatic demagnetisation of  $Gd_2(SO_4)_3$  is used for the attainment of very low temp. By using strong fields it is possible to reach temp. below those obtainable with liquid He. A. J. M.

**Physico-chemical measurements on hydrogen fluoride.** K. FREDENHAGEN (Z. anorg. Chem., 1933, 210, 210—224).—Densities of the saturated vapour have been determined between  $-78^\circ$  and  $19.5^\circ$ , and of the unsaturated vapour at atm. pressure between  $20^\circ$  and  $80^\circ$ . Heat of vaporisation of 20 g. of liquid to saturated vapour is 1704.6 g.-cal. at  $4.40^\circ$  and 1751 at  $15.76^\circ$ . V.p. between  $15^\circ$  and  $25^\circ$  are given by  $\log p = -1345.3/T$  (abs.) + 7.48. The association factor at the b.p. is 3.5, and has a max. 4.27 at  $-34^\circ$ . The same degree of association obtains in the liquid phase. F. L. U.

**Vapour pressures of BaO, SrO, CaO, and their mixtures from measurements of velocity of evaporation.** A. CLAASSEN and C. F. VEENEMANS (Z. Physik, 1933, 80, 342—351).—Formulae are given relating the v.p. of the three oxides with temp., and observations for mixtures suggest that the three are completely miscible. A. B. D. C.

**Vapour pressures of  $CF_4$  and  $NF_3$  and the triple point of  $CF_4$ .** W. MENZEL and F. MOHR (Z. anorg. Chem., 1933, 210, 257—263).— $CF_4$  has b.p.  $-128.0 \pm 0.1^\circ$ ;  $NF_3$  has b.p.  $-129.0 \pm 0.3^\circ$ . The heats of vaporisation have been calc. Trouton's consts. are, respectively, 20.3 and 19.9. The triple point of  $CF_4$  is  $-183.6 \pm 0.2^\circ$ . E. S. H.

**Vapour pressure of crystalline benzene and cyclohexene.** V. R. DEITZ (J. Amer. Chem. Soc., 1933, 55, 472—475).—Data obtained by means of a modified Knudsen procedure for the range  $165$ — $200^\circ$  abs. are recorded. J. G. A. G.

**Value of  $\sqrt{a}$  for elements, in correlation with the periodic system.** J. A. M. VAN LIEMPT (Rec. trav. chim., 1933, 52, 123—128).—The following relationships hold approx. for homopolar compounds:  $\alpha = 3.6r^5 \times 10^{-24}$ ,  $R = 9.3r^5$ ,  $\sqrt{a/b}$  lies between 30 and 50 (mean 38.5),  $p_c$  between 33 and 93 atm. (mean 55), and  $T_c$  between  $0.7$  and  $2.0 \times b_c \times 10^5$ , where  $\alpha$  = polarisability,  $r$  = at. or ionic radius in Å.,  $R$  = mol. refractivity, and  $a$  and  $b$  are van der Waals consts. D. R. D.

**Kinetic theory of liquids.** R. O. HERZOG and H. C. KUDAR (Z. Physik, 1933, 80, 217—231).—A kinetic hydrodynamic method is used to deduce the mean free path, the diffusion coeff., and the empirical viscosity formula of Batschinski. The results are applied to dipole-free liquids, to metals and salts. A heat of fluidity is introduced. A. B. D. C.

**Viscosity of nitrobenzene.** W. M. COX and J. H. WOLFENDEN (J.C.S., 1933, 118—119; cf. A., 1932, 329).—The previously recorded decrease in viscosity of  $PhNO_2$  with time is shown to depend on the absorption of  $H_2O$  vapour, in the absence of which no change is observed. The viscosity is unaffected by thermal pretreatment, thus rendering improbable the existence of internal equilibria (cf. A., 1931, 148, 899). F. L. U.

**Single crystals of the intermediate compound antimony-tin.** H. S. VAN KLOOSTER and M. O. DEBACHER (Met. and Alloys, 1933, 4, 23—24).—A single crystal of  $SbSn$  5 cm. long was obtained by cooling the molten alloy from  $480^\circ$  to  $300^\circ$  in 15 hr. The compound has a simple cubic structure, 4 mols. in unit cell,  $a$  3.061 Å.;  $d_{calc}$  6.918;  $d_{obs}^{20}$  6.9104 ± 0.005. C. A. K.

**Thermal and electrical conductivity of some magnesium alloys and their behaviour towards the Wiedemann-Franz law.** R. KIKUCHI (Sci. Rep. Tohoku, 1932, 21, 585—593).—The thermal ( $\lambda$ ) and electrical ( $\chi$ ) conductivities of Mg and Fe are: Mg,  $2.31 \times 10^5$ , 0.382 at  $18.1^\circ$ ; Fe,  $0.96 \times 10^5$ , 0.158 at  $16.4^\circ$ . The corresponding vals. for binary alloys of Mg with Ag, Al, Cu, Ni, Sn, and Zn, and for electron metal, Dow metal, and nichrome are also recorded. The addition of the second metal lowers both  $\lambda$  and  $\chi$  in the case of Mg; the effect decreases in the order Al, Sn, Zn, Ag, Ni, Cu. The alloys show considerable deviations from the Wiedemann-Franz law. O. J. W.

**Atomic arrangement and magnetic behaviour in the copper-gold, copper-palladium, and copper-platinum systems.** H. J. SEEMANN (Z. Metallk., 1932, 24, 299—301).—The diamagnetic susceptibility of the analogous phases  $Cu_3Au$ ,  $Cu_3Pd$ , and  $Cu_3Pt$  increases when the at. arrangement becomes regular on annealing, whereas that of  $CuAu$  decreases. Compared with the susceptibilities of the alloys with random orientation of the atoms the changes are +20, +50, +25, and  $-20\%$ , respectively. A. R. P.

**Binary systems cobalt-tungsten and cobalt-molybdenum.** W. KÖSTER and W. TONN (Z. Metallk., 1932, 24, 296—299).—The reactions have been investigated by dilatometric, magnetometric, and micrographic methods. The solubility of CoW in Co ( $a$ ) falls from 39% at the eutectic temp. ( $1480^\circ$ ) to 14% at room temp., the transformation temp. of  $\epsilon$ -Co into  $\gamma$ -Co is raised by addition of W to  $1040^\circ$  at 28.5% W ( $b$ ), where it ends in the 3-phase reaction:  $\gamma + CoW \rightleftharpoons \epsilon$  solid solution, and the magnetic transformation of Co at  $1140^\circ$  takes place at progressively lower temp. with addition of W until at 16% W ( $c$ ) it merges into the  $\gamma$  change. Alloys in the miscibility gap between  $\epsilon$  and CoW undergo a magnetic transformation at  $825^\circ$  ( $d$ ). The Co-Mo system is similar, but the corresponding temp. and compositions are as follows: ( $a$ ) 25% ( $1320^\circ$ )—8% Mo ( $20^\circ$ ); ( $b$ ) 20% Mo,  $920^\circ$ ; ( $c$ ) 10% Mo; ( $d$ )  $750^\circ$ . Quenching of Co alloys with > 14% W or > 8% Mo from the homogeneous  $\gamma$ -range followed by ageing at 800— $900^\circ$  results in an increase in hardness which exceeds 600 Brinell units with 28% Mo or 40% W. A. R. P.

**X-Ray investigations of BaO-SrO mixtures when heated to redness.** W. G. BURGERS (Z. Physik, 1933, 80, 352—360).—Mixtures of BaCO<sub>3</sub> and SrCO<sub>3</sub> when heated to redness yield completely mixed BaO and SrO with a lattice const. which is a function of the mixture. Anomalies in the velocity of evaporation are due to the fact that the velocity of diffusion of the oxides into one another is < the velocity of evaporation of BaO. A. B. D. C.

**Binary liquid systems and the mixture rule.** W. MACFARLANE and R. WRIGHT (J.C.S., 1933, 114—118).—Various physical properties of mixtures of chemically similar liquids have been determined and plotted against the composition expressed as (a) wt., (b) vol., and (c) mol.-%. The results indicate that (b) should be used for density or refractive index, and (c) for surface tension. None of the three is satisfactory in the case of viscosity. F. L. U.

**[Magnetic] susceptibility of mixtures of substances of high electric moment.** J. E. GARSSEN (Compt. rend., 1933, 196, 541—543).—The diamagnetic susceptibility of mixtures of COMe<sub>2</sub> with PhNO<sub>2</sub> and with *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub> (I) is not a linear function of the concn., the deviation being approx. 12% for a 50:50 (mol.) mixture of COMe<sub>2</sub> and PhNO<sub>2</sub>, and 11% for a 15:85 mixture of COMe<sub>2</sub> and (I), due possibly to changes in the degrees of association. C. A. S.

**M.p. of mixtures of ethyl alcohol and ether.** A. LALANDE (Compt. rend., 1933, 196, 402—404; cf. this vol., 247).—M.p. of 21 mixtures of EtOH and Et<sub>2</sub>O are given; the m.p. of EtOH, Et<sub>2</sub>O, and of the eutectic (57·85 wt.-%) are respectively -116·3°, -114·5°, and -125·0°. C. A. S.

**Examination of binary liquid mixtures.** W. A. WRIGHT (J. Physical Chem., 1933, 37, 233—243).—Apparatus designed to give more complete data for the pressure-temp.-composition relations of binary liquid mixtures is described. Results are given for the system PhMe-EtOH over a wide range of pressure and temp. The data obtained permit the prediction of equilibrium conditions and the calculation of heats of vaporisation. E. S. H.

**Binary systems of *m*-nitrotoluene and *p*-nitrotoluene with naphthalene, *p*-toluidine, and *o*-toluidine.** H. D. CROCKFORD and N. L. SIMMONS, jun. (J. Physical Chem., 1933, 37, 259).—The temp.-composition diagrams do not reveal the existence of compounds or solid solutions. The logarithm of the mol. fraction of solvent varies linearly with the reciprocal of abs. temp., showing that the systems are ideal. The calc. heats of fusion, eutectic temp., and eutectic compositions are given. E. S. H.

**F.p.-solubility relations of geometrical isomerides. II. Dynamic isomerism of the anisaldoximes.** E. L. SKAU and B. SAXTON (J. Physical Chem., 1933, 37, 197—207; cf. A., 1928, 1328).—The f.p.-composition diagram for *cis*- and *trans*-anisaldoxime is described, and has been adapted to the analysis of unknown mixtures. Either form, when heated at or above 100°, undergoes a reaction involving the formation of a compound, which has been isolated, but not identified. The "natural f.p." of

the simple binary system is 58·4±0·2°, corresponding with 12·3% of the *cis*-form. The equilibrium composition does not vary perceptibly with temp. up to 90°. E. S. H.

**Errors inherent in the usual determination of the binary f.-p. diagram.** E. L. SKAU and B. SAXTON (J. Physical Chem., 1933, 37, 183—196).—When the f.p.-composition diagram for the system β-chlorocrotonic acid-β-chloroisocrotonic acid (constructed without correcting for the amount of solid crystallising) is compared with accurate data, it is shown that the errors involved cause a shift of the observed eutectic along the temp. and composition axes. In some cases false indications of compound formation may be given. Cooling curves have shown that it is possible to follow a branch of the temp.-composition diagram to temp. below the eutectic. The causes of increased errors near the eutectic point are discussed. E. S. H.

**Binary azeotropic mixtures.** I. RABECWICZ-ZUBKOWSKI (Rocz. Chem., 1933, 13, 16—19).—A classification of azeotropic mixtures is given. R. T.

**Systems of four immiscible liquid layers.** E. L. SMITH (Nature, 1933, 131, 167).—Mainly a reply to criticism (cf. this vol., 120). The system previously described (A., 1931, 159) plus Hg still separates into five layers even after repeated shaking during a period of 2 years. L. S. T.

**Solubility of potassium ferrocyanide.** E. FABRIS (Gazzetta, 1932, 62, 909—912).—Data are given for temp. between 70° and 87·3° (the transition temp.) and for the stable and metastable forms at temp. up to 104° and 95·5°, respectively. H. F. G.

**Solubility. IV. Solubilities of slightly soluble organic compounds in water.** P. M. GROSS, J. H. SAYLOR, and M. A. GORMAN (J. Amer. Chem. Soc., 1933, 55, 650—652).—Data for 16 compounds at 30° are recorded. J. G. A. G.

**Solubility of nitrates in anhydrous acetic acid.** A. W. DAVIDSON and H. A. GEER (J. Amer. Chem. Soc., 1933, 55, 642—649).—The data refer to the nitrates of Ag, Na, NH<sub>4</sub>, and Ba in the range 16·45—167·5°. The NH<sub>4</sub>NO<sub>3</sub> solutions deviate widely from Raoult's law. J. G. A. G.

**Effect of lecithin and sodium chloride on the solubility of fatty acids in salts of bile acids.** O. FÜRTH and R. SCHOLL (Biochem. Z., 1933, 257, 151—159; cf. A., 1930, 1212; 1931, 1084; 1932, 871).—The solubility of oleic or linoleic acid in solutions of bile acids is increased by lecithin (from eggs, brain, or liver) and by small amounts of NaCl, KCl, or Na<sub>2</sub>SO<sub>4</sub>. Much NaCl causes pptn. 100 c.c. of a 5% Na taurocholate solution dissolve 4·5 g. of oleic acid if 0·8% of lecithin and 0·9% of NaCl are present. W. McC.

**Optical antipodes and velocity of crystallisation: non-existence of racemic form in liquid state.** G. RUMEAU (Compt. rend., 1933, 196, 410—412; cf. A., 1932, 22).—The velocity of crystallisation (*v*) at 28° of the α<sub>1</sub>-form [apparently α<sub>2</sub> of the previous paper] of *d*-Me<sub>2</sub> tartrate has been raised by purification from 3·20 to 3·95 (1·05 at 33°), that of the

$\beta$ -form [apparently  $\alpha_1$  of previous paper] at 33° to 0.35 mm. per min. The effects on  $v$  of additions of various substances have been examined, those for H<sub>2</sub>O and *l*-Me<sub>2</sub> tartrate explaining the difficulty of obtaining concordant results, since heat causes partial racemisation and the esters are very hygroscopic. *d*-, *l*-, and *r*-Me<sub>2</sub> tartrates and *l*- and *r*-malic acids have respectively identical effects on  $v$  of Me<sub>3</sub> citrate, indicating that racemates do not exist in the liquid state. Variation of  $v$  with time after addition of a foreign substance is a delicate method of detecting chemical action. C. A. S.

**Influence of X-rays on formation of crystal nuclei.** D. SAMUICAS (Compt. rend., 1933, 196, 418—420).—Supersaturated solutions of S and P in CS<sub>2</sub> and fused betol and santonin, when rapidly cooled, produce crystal nuclei in much greater no. (3—7 times), and much more rapidly (about 1/15th the time), when irradiated with X-rays (*K $\alpha$*  and *K $\beta$*  of Fe) than when not so irradiated. C. A. S.

**Rhythmic precipitates.** T. ISEMURA (Bull. Chem. Soc. Japan, 1933, 8, 11—14).—Optimum conditions are described for the formation of rhythmic ppts. of CaC<sub>2</sub>O<sub>4</sub>, SrC<sub>2</sub>O<sub>4</sub>, Cu(OH)<sub>2</sub>, and PbCrO<sub>4</sub> in SiO<sub>2</sub> gel, and of Ag<sub>2</sub>CrO<sub>4</sub> in gelatin. J. W. S.

**Periodic precipitation of ferrous carbonate.** R. J. HARTMAN, E. W. CANNING, and F. J. GALLION (J. Physical Chem., 1933, 37, 229—232).—Conditions favouring the formation of periodic structures of FeCO<sub>3</sub> have been elucidated. The bands are formed readily in SiO<sub>2</sub> gels prepared by bubbling CO<sub>2</sub> through aq. Na<sub>2</sub>SiO<sub>3</sub>, but only with difficulty in gelatin gels, using a salt of Fe<sup>++</sup> as diffusing agent. The results support the theory advanced to explain the formation of geological deposits (cf. A., 1932, 596). E. S. H.

**Action of radiations on Liesegang rings.** T. KOFMAN (J. Chim. phys., 1932, 29, 586—598).—Neither radiations from Ra nor X-rays affect the formation of Liesegang rings. The influence of ultraviolet light and mitogenetic rays (from onion) is described and discussed. A. S. C. L.

**Liesegang rings.** E. S. HEDGES (Nature, 1933, 131, 169).—A reply to criticism (this vol., 122). L. S. T.

**Adsorption from the gas phase by solid adsorbents.** F. KLEIN (Metallbörse, 1932, 22, 1021—1022, 1085—1086, 1118—1119, 1182—1183, 1277—1278; Chem. Zentr., 1932, ii, 3374).—A review. A. A. E.

**Influence of temperature and pressure on the adsorption of hydrogen by nickel.** I. J. SMITENBERG (Rec. trav. chim., 1933, 52, 112—122).—Isotherms, isobars, and velocity curves are given for 15—300° and 10—760 mm. D. R. D.

**Adsorption and amount of adsorbent.** I. A. RABINERSON (Kolloid-Z., 1933, 62, 157—162).—The amount of adsorbed Ba<sup>++</sup> or Ca<sup>++</sup>,  $x$ , varies with the amount of adsorbent (Na- or H-kaolin, Napermutite),  $m$ , in accordance with  $x = Km^{1/n}$ , where  $K$  and  $n$  are consts. The dependence of sp. adsorption,  $X$ , on  $m$  is given by  $X/m = Km^{1/p}$ , where  $p = -n$ . Kroecker's equation is applicable as a first approximation to exchange adsorption. An anomalous rise in

the curve connecting  $X/m$  with  $m$  occurs in the system Na-kaolin + BaCl<sub>2</sub>, but not in H-kaolin + BaCl<sub>2</sub>. The anomaly is attributed to a diminution of H<sub>2</sub>O adsorption by Ba<sup>++</sup> exchange and to coagulation of small amounts of kaolin by excess of Ba<sup>++</sup>. E. S. H.

**Adsorption measurements with streaming gases.** H. REMY [with W. HENE] (Kolloid-Z., 1933, 62, 154—157).—The results differ from those reported for the same adsorbent C, using a static method of measurement (cf. this vol., 120). The ratio of the adsorbabilities of SO<sub>2</sub> and CO<sub>2</sub> is also different. The discordance may be due to different H<sub>2</sub>O contents of the C. E. S. H.

**Specific surface and adsorbent properties of lead sulphate.** I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1933, 55, 851; cf. A., 1922, ii, 618, 619).—The constancy of the sp. surface shows that PbSO<sub>4</sub> adsorbs neither Pb<sup>++</sup> from dil. Pb(NO<sub>3</sub>)<sub>2</sub> solution nor SO<sub>4</sub><sup>'</sup> from dil. Na<sub>2</sub>SO<sub>4</sub> solutions. Since PbSO<sub>4</sub> adsorbs only dye ions from solutions of the Na salt of ponceau-4R, it would seem that SO<sub>4</sub><sup>'</sup> ions on the surface are replaced by ponceau ions. J. G. A. G.

**Sorption of gases, vapours, and mists.** H. REMY (Angew. Chem. 1933, 46, 101—104).—The amount of the solid phase removed from a NH<sub>4</sub>Cl mist by CaCl<sub>2</sub> and cotton-wool may be calc. additively from the results obtained with the two adsorbents separately. The relation between the vols.  $V_1$  and  $V_2$  of two gases adsorbed by a given material at temp.  $T_1$  and  $T_2$  such that in the liquid state the two substances have the same v.p., is given by  $V_1 = V_2 + 10^{(\tau_1 - \tau_2)/\alpha} - 1$ , where  $\alpha$  is a const.; if  $T_1$  and  $T_2$  do not differ greatly,  $V_1 = V_2$ . Adsorption from a stream of gas is considerably less than from stationary gas. The total quantity of gas adsorbed from a binary mixture is approx. equal to the mean of the quantities of each adsorbed at the pressure of the mixture, especially if the adsorbent possesses approx. the same power of adsorption for the two gases; it is not directly related to the partial pressures of the components. H. F. G.

**Adsorption of nitrophenol and iodine on calcium fluoride films.** J. H. DE BOER (Z. physikal. Chem., 1933, B, 20, 11—16; cf. A., 1932, 689).—A CaF<sub>2</sub> film can take up as many *p*-nitrophenol mols. as I atoms. It seems certain that I cannot form a multimol. adsorbed layer, but such a layer may perhaps be formed with nitrophenol. R. C.

**Inner adsorption in crystal salts.** V. D. BALAREV (Kolloid-Beih., 1933, 37, 180—214; cf. A., 1932, 332).—A review of published work on numerous aspects of crystal growth supports the author's theory. E. S. H.

**Extension of phase rule for adsorption under equilibrium and non-equilibrium conditions.** I. LANGMUIR (J. Chem. Physics, 1933, 1, 3—12).—A surface phase rule is based on the postulate that all the intrinsic properties of a surface phase possess  $C + E + 1$  degrees of freedom, even under non-equilibrium conditions ( $C$  = no. of components in surface phase,  $E$  = degree of freedom corresponding with an inde-



pendently variable external electric force). When the val. of these variables is chosen, all other properties such as contact potential, rates of evaporation, surface spreading force, etc. are fixed. A condition of validity is mobility of the atoms in a surface phase. The rule holds for transient states only when their duration is large compared with the time of relaxation of surface mobility. A no. of cases are discussed and illustrated by experiments with Cs on W filaments.

F. L. U.

**Application of the Gibbs adsorption theorem to solid-liquid interfaces.** F. E. BARTELL, F. L. MILLER, and E. G. ALMY (J. Amer. Chem. Soc., 1933, 55, 466—471; cf. A., 1929, 999).—Adhesion tensions against  $\text{SiO}_2$  and interfacial tensions against  $\text{H}_2\text{O}$  have been determined for binary mixtures of  $\text{Et}_2\text{CO}_3$  (I) with  $\text{C}_6\text{H}_6$  (II),  $1\text{-C}_{10}\text{H}_7\text{Br}$  (III), and  $\text{NPhMe}_2$  (IV). The adsorption of (I) from the solute decreases in the order (II), (III), and (IV), both for  $\text{H}_2\text{O}$  and  $\text{SiO}_2$  interfaces, and the calc. areas of the adsorbed mols. of (I) for the six cases are concordant. J. G. A. G.

**Chemical action of electrolytes in changing surface energy at the boundaries: metal-mineral oil-aqueous salt solution.** I. M. S. GOLOMBIK, D. S. LEV, and N. N. PETIN (J. Gen. Chem. Russ., 1932, 2, 880—888).—Mineral oil is best removed from metal surfaces by immersion in solutions of phosphates, with the addition of alkali or of Na silicates; the process is accelerated by agitation, increase in concn. of salts, and higher temp. No close parallelism is observed between depression of surface tension at the boundary oil-water, and degreasing action. The facility of removal of oil diminishes with its duration of contact with the metal surface.

R. T.

**Adhesion forces brought into play in freezing.** A. SELLERIO (Physikal. Z., 1933, 34, 180—181).—Three methods for measuring the adhesive force between a metal surface and ice are described. The variation of the adhesive force with temp. has been measured for S on Al.

A. J. M.

**Permeability of quartz and Pyrex and other glass to helium.** J. C. MCLENNAN and J. O. WILHELM (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 119—122).—Comparative experiments with a series of discharge tubes show that the permeability is in the order quartz > Pyrex glass > soft glass. The rate of transmission is not increased at low temp.

J. W. S.

**Kinetics of penetration. V. Kinetics of a model as related to the steady state.** W. J. V. OSTERHOUT (J. Gen. Physiol., 1933, 16, 529—557).—In a system consisting of (A), aq. solution of K guaiacoxide, (B), a non-aq. layer containing 70% guaiacol and 30% *p*-cresol, and (C), an aq. layer through which  $\text{CO}_2$  is bubbled (A., 1932, 1180) K moves from (A) through (B) to (C), and this is followed by migration of  $\text{H}_2\text{O}$  in the same direction. Quant. observations with regard to (C) and its K content made while all three layers were effectively stirred fit a formula obtained on the assumption that two distinct processes are proceeding. The first is the entry of K into (C), the vol. remaining unchanged, the second is the entry of  $\text{H}_2\text{O}$  into (C) in consequence of the high

osmotic pressure resulting from the increased concn. of K, and both processes are assumed to follow exponential laws.

W. O. K.

**Electro-osmosis and electrophoresis. II.** N. SCHÖNFELDT (Z. Elektrochem., 1933, 39, 103—116).—A review and bibliography.

D. R. D.

**History of modern solution theories and the theory of adhesion pressure.** J. TRAUBE (Kolloid-Beih., 1933, 37, 119—153).—Theories of solution are criticised. The adhesion pressure theory attributes osmotic pressure to the different adhesion intensities of the solute mols. from those of the solvent. This view is discussed in relation to interfacial tension, solubility, colloidal behaviour, adsorption and distribution, electro-potential, and mol. vol. The conclusions reached are applied to biological problems, especially permeability, narcosis, and the sp. effects of ions.

E. S. H.

**Cryoscopy of paraldehyde, acetone, and ether in solutions of ammonium and magnesium sulphates.** F. BOURION and (Mlle.) O. HUN (Compt. rend., 1933, 196, 480—482; cf. this vol., 223).—Further f.-p. data are recorded; paraldehyde depolymerises with increased dilution.

C. A. S.

**Cryoscopic studies on the transition points of the compounds of organic solvents with salts. II.** H. ŌOSAKA (Sci. Rep. Tokyo Bunrika Daigaku, 1933, A, 1, 241—249).—The lowering of the transition point of  $\text{NaI}\cdot 3\text{MeOH}$  (I) by addition of  $\text{NHPhAc}$ ,  $\text{BzOH}$ ,  $\text{COMe}_2$ , camphor,  $\text{PhNO}_2$ , and  $\text{H}_2\text{O}$  has been investigated, the mean val. for the mol. depression being 20.0 for polar and 18.3 for non-polar compounds. This is attributed to the difference in the influence of polarity of the solute on the activity of the alcohol. The heat of fusion of (I) calc. from the cryoscopic const. is 7276 g.-cal. per mol. or 29.6 g.-cal. per g.

J. W. S.

**Diffusion of electrolytes.** R. J. DAVIES (Phil. Mag., 1933, [vii], 15, 489—511).—Diffusion coeffs. of  $\text{MgSO}_4$  and  $\text{CdSO}_4$ , determined by measuring  $n$  (cf. A., 1924, ii, 523), show min. vals. at 1.4*N* and 1.8*N*, respectively, attributed to complex ion formation. The results indicate ionic solvation.

H. J. E.

**Equation relating density and concentration.** W. C. ROOT (J. Amer. Chem. Soc., 1933, 55, 850—851).—The equation  $D = D_0 + c_1N + c_2N^{3/2}$ , where  $c_1$  and  $c_2$  are additive consts.,  $D_0$  is the density of  $\text{H}_2\text{O}$ , and  $N$  the normality of the solution, holds for solutions of alkali and alkaline-earth halides up to 10*N*, and for  $\text{H}_2\text{SO}_4$  up to 25*N*.

J. G. A. G.

**Viscosity of aqueous solutions as a function of concentration.** G. JONES and S. K. TALLEY (J. Amer. Chem. Soc., 1933, 55, 624—642).—Full details are given for determining to within 0.01 sec. the time of flow of the liquid in a viscosimeter of the Ostwald type by means of a photo-electric cell. Viscosities of 0.002—0.2*M* aq. solutions of  $\text{KClO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{KBrO}_3$ ,  $\text{CsNO}_3$ ,  $\text{NH}_4\text{Cl}$ , sucrose, and  $\text{CO}(\text{NH}_2)_2$  have been determined at 25°. The results are in agreement with the Jones and Dole equation (A., 1929, 1385) for the viscosity of solutions of electrolytes, and confirm the prediction that all salts increase the viscosity of

H<sub>2</sub>O if measured at sufficiently low concn., including those salts which give a diminishing viscosity at moderate concn. The theoretically predicted absence of the square-root term in the equation for non-electrolytes is confirmed for sucrose and CO(NH<sub>2</sub>)<sub>2</sub>.

J. G. A. G.

**Determination of mass of electrolytic ions.** P. DEBYE (J. Chem. Physics, 1933, 1, 13—16).—The dynamical reactions due to the masses of electrolytic ions when subjected to periodic acceleration are calc. They may be expected to give rise to electric oscillations of the order 10<sup>-6</sup> volt under suitable experimental conditions.

F. L. U.

**Solvation. Determination of radii of ions in solution.** R. FLATT and A. JORDAN (Helv. Chim. Acta, 1933, 16, 37—53).—An expression which takes account of the charge and size of the ions, and of the dielectric const. of the solvent, has been deduced for the relative solubilities of a completely ionised binary electrolyte in different solvents. Measurement of the solubilities of CsClO<sub>4</sub>, RbClO<sub>4</sub>, KClO<sub>4</sub>, KCl, NaCl, and NaBr.2H<sub>2</sub>O in H<sub>2</sub>O and aq. EtOH, in conjunction with this expression, indicate that all the ions in question, excepting Na<sup>+</sup>, have the same radius in solution as in the cryst. salts. It is therefore concluded that they are not hydrated.

F. L. U.

**Exceptional tendency of the sodium ion to form hydrates, and its significance in the theory of combination of water of crystallisation.** M. A. RAKUSIN (Ukrain. Chem. J., 1932, 7, [Sci.], 65—74).—A discussion.

R. T.

**Investigation of influence of solute on solvent by means of infra-red absorption spectrum. I. Effect of dissolved salts on state of association of solvent water.** R. SUHRMANN and F. BREYER (Z. physikal. Chem., 1933, B, 20, 17—53; cf. A., 1931, 1211).—In presence of alkali halides and various other salts which do not absorb in the short infra-red the absorption bands of H<sub>2</sub>O in this region become steeper and are displaced towards shorter waves. Both cations and anions contribute to this effect, which in general increases with the ionic radius, and is to be ascribed to depolymerisation of the H<sub>2</sub>O mols. Ionic hydration, however, superimposes on the displacement of the bands towards shorter waves a displacement in the opposite direction, the influence of the cation in this connexion usually preponderating over that of the anion. MgCl<sub>2</sub> and some other salts cause a flattening of the H<sub>2</sub>O bands, which is attributed to chemical effects. The relations between depolymerisation effects, as revealed by spectroscopy, hydration pressure, contraction of the H<sub>2</sub>O in the solution, and chemical influences of solute on solvent, are surveyed.

R. C.

**Absorption of light by aliphatic carboxylic and amino-acids in presence of neutral salts.** F. LEUTHARDT [with M. PFISTER] (Helv. Chim. Acta, 1933, 16, 228—232; cf. A., 1932, 573).—The absorption curve of AcOH is unaffected by the addition of neutral salts, but that of the Na or K salts of AcOH, CH<sub>2</sub>Cl·CO<sub>2</sub>H, CCl<sub>3</sub>·CO<sub>2</sub>H, and PrCO<sub>2</sub>H is displaced towards shorter wave-lengths by addition of MgCl<sub>2</sub>. The effect is considered to be due to attachment of Mg<sup>++</sup> to the ·CO<sub>2</sub>' group.

F. L. U.

**Is hydrotropy a special property of organic salts?** F. V. VON HAHN (Kolloid-Z., 1933, 62, 202—207).—The so-called hydrotropic salts show no essential difference from alcohols, aldehydes, acids, etc. in their influence on the solubility of sparingly sol. substances.

E. S. H.

**Colloidal sulphur.** O. VON DEINES (Kolloid-Z., 1933, 62, 145—151).—The systems obtained by acidifying solutions of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> etc. or by interaction of H<sub>2</sub>S and H<sub>2</sub>SO<sub>4</sub> consist of solutions of S in highly dispersed persulphides of H. True sols of S are obtained by dispersion methods or by pouring an EtOH solution of S into H<sub>2</sub>O.

E. S. H.

**Highly concentrated fluoride sols.** W. BACHMANN and P. PINNOW (Kolloid-Z., 1933, 62, 131—145).—The prep. of conc. sols of CaF<sub>2</sub>, with or without the presence of MgF<sub>2</sub>, is described. The viscosity of these sols decreases slightly at first during dialysis, but at a later stage increases strongly; addition of HCl produces a rapid fall in viscosity. Thixotropy is highly developed. The particles are positively charged, and their mobility and size have been determined by several methods. The coagulating influence of univalent anions is small; that of bivalent anions is greater, but the Schulze-Hardy rule is not followed strictly.

E. S. H.

**Active oxides. LX. Dispersoid analysis of precipitates of zinc oxalate dihydrate prepared in different ways.** G. F. HÜTTIG and E. HERMANN (Kolloid-Z., 1933, 62, 151—153; A., 1932, 1211).—Sedimentation analysis of ppts. of ZnC<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O prepared under different conditions shows that small particles are favoured by low pptn. temp. and rapid mixing. With slow pptn. at high temp. or rapid pptn. at low temp. the particles of ppt. produced from Zn(NO<sub>3</sub>)<sub>2</sub> are smaller than those from ZnCl<sub>2</sub>.

E. S. H.

**Mol. wt., viscosity, and conductivity of hydrous silicic acid.** W. D. TREADWELL and W. KÖNIG (Helv. Chim. Acta, 1933, 16, 54—69; cf. A., 1930, 1537).—The f.-p. depression, viscosity, and electrical conductivity of purified sols of SiO<sub>2</sub> have been measured at various ages of the sol. From the results it is inferred that gelatinisation begins with polymerisation of simple mols. accompanied by a decrease in the no. of free H ions, the polymerised mols. afterwards coagulating to form a network which immobilises the whole of the liquid.

F. L. U.

**Emulsion systems containing phenols, water, and gelatin.** R. M. WOODMAN (J.S.C.I., 1933, 52, 44—46T).—Aq. solutions of gelatin yield dual emulsions with phenols and hydrogenated phenols. The mechanics of dual emulsion formation are discussed.

**Dispersion of Hertz waves in solvated colloids.** J. ERRERA (J. Chim. phys., 1932, 29, 577—585).—The time of relaxation is discussed in relation to the orientation of dipoles. Dielectric consts. have been measured with wave-lengths from 2 to 30,000 m. Results are given for several colloids with λ 2—30 m.

A. S. C. L.

**Optical anomalies and fine structure. Double refraction of paracrystalline (especially organic), colloidal materials. Shrinkage effects in albu-**

min. F. RINNE (Kolloid-Z., 1933, 62, 216—226).—A review of published work. E. S. H.

**Diffusion of colloidal electrolytes; sodium oleate.** M. E. L. MCBAIN (J. Amer. Chem. Soc., 1933, 55, 545—551; cf. A., 1931, 301).—The diffusion coeffs. of Na oleate (0.025—0.5*N*) through a sintered glass membrane into 0.0015*N*-NaOH at 20° and 25° are < those of K laurate, although the primary particles of the latter are only slightly smaller. The viscosity and gelatinising power of Na oleate are due to loose linking of primary particles, and this does not appreciably affect the rate of diffusion.

J. G. A. G.

**Method of separating different disperse systems by cataphoresis.** H. BENNHOLD (Kolloid-Z., 1933, 62, 129—131).—Apparatus and technique are described, and examples of application to hydrophilic colloids are given. E. S. H.

**Cataphoresis. Improved cylindrical cell.** S. MATTSO (J. Physical Chem., 1933, 37, 223—227).—Modifications are described (cf. A., 1928, 1323).

E. S. H.

**Electrokinetic phenomena. X. Electric mobility and charge of proteins in alcohol-water mixtures.** J. DANIEL (J. Gen. Physiol., 1933, 16, 457—474).—The electrophoretic mobility of quartz particles covered with a film of gelatin, ovalbumin, or gliadin in EtOH-H<sub>2</sub>O mixtures (up to 60%) is independent of the field strength. The mobility of gelatin-covered quartz particles in EtOH-H<sub>2</sub>O mixtures is independent of size and shape, and is equal to the electro-osmotic mobility of the same EtOH-H<sub>2</sub>O mixture in contact with protein-covered quartz surfaces. The electrophoretic mobility corrected for viscosity, and hence the charge, of gelatin-covered quartz particles, in 35% and 60% EtOH is proportional to the combining power of the gelatin. In aq. EtOH (up to 35%), the charge calc. by means of the Debye-Henry approximation employing the dielectric const. and the viscosity of the medium in bulk is, in the neighbourhood of the isoelectric point, proportional to the combining power of the gelatin. Hence the bulk, dielectric const., and viscosity may be employed in the application of the Debye-Henry equation. In presence of aq. EtOH, the isoelectric point of gelatin is shifted to a higher *p<sub>H</sub>* val., the shift being approx. proportional to the change in the dielectric const. of the medium.

W. O. K.

**Electrochemical investigations on gum arabic sol.** W. PAULI and E. RIPPER (Kolloid-Z., 1933, 62, 162—175).—Potentiometric and conductometric measurements have been made on highly-purified sols of gum arabic and gum tragacanth, and the effect of adding electrolytes has been studied. In the pure acidoid sols the conductivity calc. from H<sup>+</sup> activity is much greater than the obs. conductivity. Activities of the compounds of the sols with Ag<sup>+</sup> have been determined. With rising temp. the conductivity of the acidoid sols passes through a max., whilst a linear relation is observed in neutral sols. E. S. H.

***p<sub>H</sub>* of gelatin solutions.** J. G. MALONE and M. G. MALONE (J. Physical Chem., 1933, 37, 219—221).—

The electrometric method is preferred to the colorimetric method (cf. A., 1932, 700). E. S. H.

**Absorption and scattering of light by gelatin.** J. H. F. CUSTER, J. H. DE BOER, and C. J. DIPPEL (Rec. trav. chim., 1933, 52, 195—213).—The true absorption coeff., *k*, of isoelectric gelatin sols at 40° is independent of the concn., but the scattering coeff.,  $\sigma$ , falls with increase in concn. For gels at room temp., *k* and  $\sigma$  both fall with increasing concn. The sols and gels have similar but not identical absorption spectra. Dil. sols when cooled to room temp. give spectra of the gel type and show increased scattering. These results support the view that gelatin exists in two forms, an *A*-form stable at high temp. and a *B*-form stable at low temp.; gelation occurs only with the latter (cf. A., 1919, i, 179; this vol., 125). At 40°, *k* is independent of *p<sub>H</sub>* between 2.5 and 8.6, whereas  $\sigma$  passes through a max. at the isoelectric point. When *p<sub>H</sub>* > 8.6, *k* varies with *p<sub>H</sub>*, but the change to the *B*-form still occurs on cooling. The isoelectric point, which is the same for both *A*- and *B*-forms, corresponds with min. optical rotation of the former and max. rotation of the latter. D. R. D.

**Structural viscosity in some lyophilic sols. I. Flocculation of gelatin and casein by agar. II. Rubber sols.** W. GALLAY (Canad. J. Res., 1932, 7, 662—670, 671—676).—I. Comparative measurements have been made of the viscosities of mixtures of 0.2% agar and 1% gelatin sols at varying pressures, using the overflow viscosimeter. Wide deviations from Poiseuille's law occur, structure effects and turbulence effects being in evidence at low and high rates of flow, respectively. A min. viscosity is observed for 20—40% agar sol, indicating a dehydrating effect of the agar on the gelatin. In a corresponding series with 0.25% agar and 2% basic casein sol this effect is masked by the greater difference in relative viscosity. Structural turbulence is observed in the structure region. The velocity of flow and pressure are related by a parabolic equation.

II. Relative viscosities of sols of natural and purified rubber of different concn. in C<sub>6</sub>H<sub>6</sub> have been measured at varying pressures. The limiting concns. above which structure is evident are in agreement with those calc. theoretically by Staudinger (A., 1932, 619). Regions of structure and turbulence are observed at all concns. Exposure to ultra-violet light lowers considerably the viscosity of a purified rubber sol.

J. W. S.

**Lyophilic colloids. XVII. Influence of neutral salts on gelatin sols.** H. R. KRUYT and H. P. GALEMA (Kolloid-Beih., 1933, 37, 154—179; cf. A., 1929, 1381).—The viscosity of gelatin sols is influenced by all the ions investigated, which differ in effect from H<sup>+</sup> and OH<sup>-</sup> only quantitatively. The usual influence of valency is observed, suggesting a capillary-electric process. Some peculiarities noted with starch sols (cf. A., 1932, 1087) are also observed. Differences in viscosity under isoelectric conditions are attributed to ion hydration of the bound electrolyte. This explanation is supported by EtOH-pptn. experiments. E. S. H.

**Intermicellar combination and hydration in gelatin gels.** J. H. DE BOER and C. J. DIPPEL (Rec.

trav. chim., 1933, 52, 214—224).—When a gelatin gel is kept for some time at 25° an elevation of the apparent m.p. is observed. This is related to changes in the viscosity of gelatin sols (A., 1903, ii, 721; 1915, ii, 752), but not to the transformation from *B*- to *A*-gelatin (see this vol., 349). An electrostatic explanation is offered of the swelling, gelatinisation, etc. of gelatin.

D. R. D.

**Change of solvation medium in gelatin sols.** A. SARLUY (Kolloid-Z., 1933, 62, 176—180).—The relative viscosities of gelatin sols in PhOH—H<sub>2</sub>O mixtures have been determined at 70°. As the amount of PhOH is increased the viscosity falls, remains steady up to about 25%, and then rises sharply; the viscosity in anhyd. PhOH is very high. The high viscosities at extreme compositions are attributed to solvation by PhOH or H<sub>2</sub>O, whilst coacervation occurs in the intermediate region.

E. S. H.

**Complex coacervation. XIV. Autocomplex flocculation of sodium nucleate (yeast) sols.** H. G. B. DE JONG and F. A. MENALDA (Biochem. Z., 1933, 257, 62—77).—A study of the flocculation produced by 6-, 3-, and 2-valent cations.

H. W. D.

**Complete growth functions, particularly photographic.** L. HAMBURGER (Chem. Weekblad, 1933, 30, 115—133).—A discussion of growth phenomena in colloidal systems, with special reference to the similarity between animate and inanimate systems. A general equation is developed for both individual and collective growth, in which various well-known laws are embodied as special cases. The case of the photographic plate is considered at length, as regards both the growth of the separate nuclei and the increase of the no. of nuclei.

H. F. G.

**Thixotropic viscosity of cellulose esters.** S. A. GLIKMAN (Plast. Massi, 1932, No. 2—4, 16—23).—The phenomenon is observed with sols approaching gelatinisation and is attributed to the disturbance, by mechanical action, of the orientation of the mols. of the solvent by the vectorial forces of the field produced by mols. of the disperse phase.

T. H. P.

**Structure of cellulose gel. IV. Mechanism of sorption of vapours by cellulose gels.** K. ATSUKI, H. SOBUE, and K. KITAJIMA (J. Soc. Chem. Ind. Japan, 1932, 35, 584—587B).—A study of the mechanism of the sorption by normal and hydrated celluloses of vapours of H<sub>2</sub>O, alcohols, ketones, esters, ethers, and acids. Sorption and saturated v.p. run parallel. The sorption of vapours by cellulose is due to sorption and swelling; the former is governed by v.p., surface tension, and density, the latter by the polarity of the OH groups and bridge O in the cellulose mol.

V. E. Y.

**Radiographical introduction to the cellulose symposium [Delft, May, 1932].** J. R. KATZ (Chem. Weekblad, 1933, 30, 26—44).—A review of the theory and practice of the X-ray method of investigating the structure of cellulose, and of the results obtained, with an extensive bibliography.

H. F. G.

**Cellulose from the viewpoint of colloid chemistry.** H. R. KRUYT (Chem. Weekblad, 1933, 30,

24—26).—A discussion of the nature of cellulose, particularly in the light of the behaviour of such materials as stannic acid.

H. F. G.

**Thermal equilibrium between oxygen molecules and atoms.** G. VON ELBE and B. LEWIS (J. Amer. Chem. Soc., 1933, 55, 507—511; cf. this vol., 229).—Vals. of the equilibrium const. of the reaction  $2O=O_2$  and the degree of dissociation at 1 atm. in the range 1400—5000° abs. have been evaluated from optical and sp. heat data. At the higher temp. the contribution to the sp. heat of mol. O<sub>2</sub> in the <sup>1</sup>Δ state becomes significant.

J. G. A. G.

**Deacon equilibrium and the entropy of chlorine.** A. R. GORDON and C. BARNES (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 171).—See A., 1932, 997.

J. W. S.

**Chemical equilibria of reactions between hydrocarbons. IV.** A. A. VEDENSKI (J. Gen. Chem. Russ., 1932, 2, 826—828).—The v.p. of methylcyclohexane is given by  $\log P = -1460/T + 1.75 \log T + 0.0011T + 1.7040$ , where *T* is the abs. temp. The vals. of *P* for PhEt found by Woringer (A., 1900, ii, 709) are confirmed.

R. T.

**Dissociation constant of acetic acid from 0° to 60°.** H. S. HARNED and R. W. EHLERS (J. Amer. Chem. Soc., 1933, 55, 652—656; cf. A., 1932, 695).—An extension of previous work. The dissociation const., *K*, is given by  $\log K = -1500.65/T - 6.50923 \log T - 0.0076792T^2 + 18.67257$  and the heat of dissociation, Δ*H*, by  $\Delta H = 6871.0 - 12.9436T - 0.035161T^2$ .

J. G. A. G.

**Equilibrium between lactic and pyruvic acids.** R. WURMSER and (MME.) N. MAYER-REICH (Compt. rend., 1933, 196, 612—614; cf. A., 1932, 809).—More detailed investigation shows that the normal potential of the system  $OH \cdot CHMe \cdot CO_2' \rightleftharpoons AcCO_2 + H_2$  at 37° is -0.196 volt at *p*<sub>H</sub> 7.3 and +0.252 volt at *p*<sub>H</sub> 0, whence  $\Delta F = +11,600 \pm 100$  g.-cal., or 58% of the heat of reaction at const. pressure (+20,000 g.-cal.).

C. A. S.

**Hydrolysis of acetonesemicarbazone.** J. E. W. RHODES (J.C.S., 1933, 204—208).—Partial pressures of COMe<sub>2</sub>—H<sub>2</sub>O mixtures have been measured by a transpiration method. Henry's law is not obeyed over the range 0.16—76.6 g. per litre at 30° and 50°. From the partial pressure of COMe<sub>2</sub> over aq. solutions of acetonesemicarbazone the degree of hydrolysis has been calc. The val. of the hydrolysis const. is 0.00398 at 30.8° and 0.00974 at 49.7°, whence the heat of reaction is calc. to be 9179 g.-cal.

F. L. U.

**Equilibrium constants in terms of activities derived from cryoscopic data: dissociation of pyridine *o*-chlorophenoxide in benzene.** H. M. GLASS and W. M. MADGIN (J.C.S., 1933, 193—198).—The equilibrium const. for this dissociation ( $AB \rightleftharpoons A+B$ ), when calc. with activities instead of concns., shows remarkable consistency, whereas vals. of  $[AB]/[A][B]$  are widely divergent. Determinations were made at different concns. The activities were derived from independent cryoscopic measurements.

F. L. U.

**Rapid derivation of thermodynamic relations.** A. N. SHAW (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 187—204).—Theoretical. J. W. S.

**Equations for the application of the law of homogeneous chemical equilibrium.** E. DENINA (J. Chim. phys., 1933, 30, 47—55).—Theoretical. N. M. B.

**Internal effect in thermodynamic transformations.** V. NJEGOVAN (Arh. Hemiju, 1933, 7, 23—29; cf. A., 1932, 1206).—Mathematical. A modification of the Clausius-Clapeyron and Helmholtz equations explains certain apparent anomalies in the Nernst theorem. N. M. B.

**Higher-valency ions and activity. II. Theoretical discussion on the basis of the Poisson-Boltzmann equation.** J. B. CHLOUPEK, V. Z. DANĚŠ, and B. A. DANĚŠOVA (Coll. Czech. Chem. Comm., 1933, 5, 21—35).—The solubility data (this vol., 26) for  $\text{Ce}(\text{IO}_3)_3$  in aq. solutions of various salts cannot be represented quantitatively by any of the existing theories. M. S. B.

**Debye-Hückel ion size parameter in terms of individual ionic radii. Activity coefficient of lead chloride in solutions of cadmium nitrate.** H. D. CROCKFORD and H. C. THOMAS (J. Amer. Chem. Soc., 1933, 55, 568—574).—The e.m.f. of the cell  $\text{Pb-Hg}|0.002-0.016M\text{-PbCl}_2, 0.002-0.017M\text{-Cd}(\text{NO}_3)_2|\text{AgCl-Ag}$ , with  $[\text{PbCl}_2]/[\text{Cd}(\text{NO}_3)_2]$  const., has been determined at 25°. The vals. of the activity coeff. of  $\text{PbCl}_2$  in  $\text{Cd}(\text{NO}_3)_2$  solutions are consistent with the mean distance of closest approach of ions in dilute solutions of strong electrolytes derived mathematically as a function of quantities which depend on the valency types of the dissolved compounds and the size of individual ions. J. G. A. G.

**Reaction between osmium tetroxide and hydrobromic acid. I. Equilibrium.** H. D. KIRSCHMAN and W. R. CROWELL (J. Amer. Chem. Soc., 1933, 55, 488—495).—When the concns. are expressed in mols. per 1000 g.  $\text{H}_2\text{O}$  the val. of  $[\text{Os}^{\text{VII}}][\text{Br}_3^-]^{1/2}/[\text{Os}^{\text{VIII}}][\text{H}^+][\text{Br}^-]^5\gamma^2$  at 100° is  $4.5 \times 10^{-6}$ ,  $\gamma$  being the activity coeff. of the HBr. At high  $[\text{HBr}]$ ,  $\text{Os}^{\text{IV}}$  is probably formed. The reaction mechanism is discussed. J. G. A. G.

**System manganese-nitrogen.** R. SCHENCK and A. KORTENGRÄBER (Z. anorg. Chem., 1933, 210, 273—285).—Equilibrium isotherms below 800° are characterised by two rising branches connected by a horizontal portion. The latter diminishes with rising temp. and disappears at about 800°. In the horizontal region two solid solutions co-exist in equilibrium with  $\text{N}_2$ ; these become completely miscible at the crit. temp. 800°. X-Ray analysis establishes a N-rich, hexagonal  $\zeta$ -phase and a face-centred cubic  $\epsilon$ -phase, containing less N. Only the  $\epsilon$ -phase is ferromagnetic. The dissociation pressures of Mn-Fe alloys (10% Fe) in equilibrium with  $\text{N}_2$  are higher than those observed under the same conditions in the Mn- $\text{N}_2$  system. Horizontal portions of the isotherms are not observed. E. S. H.

**Equilibrium diagram of the system chromium-carbon.** K. HATSUTA (Tech. Rep. Tôhoku,

1933, 10, 186—194).—Four carbide phases exist, viz.,  $\text{Cr}_4\text{C}$  (cubic),  $\text{Cr}_7\text{C}_3$  (trigonal),  $\text{Cr}_3\text{C}_2$  (orthorhombic), and, probably, CrC. The eutectic between the  $\alpha$ -phase (solid solution) and  $\text{Cr}_4\text{C}$  lies at 1485° and 3.7% C. The peritectic temp. of the change  $\text{Cr}_7\text{C}_3 + \text{melt} \rightarrow \text{Cr}_4\text{C}$  is 1530°, and that of the change  $\text{Cr}_3\text{C}_2 + \text{melt} \rightarrow \text{Cr}_7\text{C}_3$  is  $> 1600^\circ$ ;  $\text{Cr}_7\text{C}_3$  separates in the form of primary crystals in the range 4.5—8.5% C.  $\text{Cr}_3\text{C}_2$  probably has the max. m.p. (about 1800°) on the liquidus curve, and it forms a eutectic with CrC at about 17.5% C. A transition takes place in the  $\text{Cr}_3\text{C}_2$  phase at about 1505°. H. F. G.

**Thermal study of the systems KCl-BaCl<sub>2</sub> and KCl-LiCl.** E. ELCHARDUS and P. LAFFITTE (Bull. Soc. chim., 1932, [iv], 51, 1572—1579).—An automatic apparatus for registering the thermal behaviour of systems is described. The system KCl-BaCl<sub>2</sub> has a eutectic at 340° (42.75 mol.-% BaCl<sub>2</sub>) and a transition point at 347° corresponding with the compound  $\text{KCl}_3\text{BaCl}_2$ . No evidence for the compound  $\text{KCl}_2\text{BaCl}_2$  was obtained. The system KCl-LiCl has a eutectic at 180° (41.7 mol.-% KCl). E. S. H.

**Dissociation of cubic ferric oxide.** A. GIRARD and G. CHAUDRON (Compt. rend., 1933, 196, 406—408; cf. A., 1932, 133).—The amount of FeO formed when samples of cubic  $\text{Fe}_2\text{O}_3$  prepared in various ways are heated in vac. to 300—600°, and magnetisation-temp. curves have been determined. The irregular results are thought to point to formation of solid solutions of the various oxides. C. A. S.

**Thermal dissociation of certain oxides and peroxides. V. Magnesium, strontium, and barium peroxides.** M. BLUMENTHAL (Rocz. Chem., 1933, 13, 5—15).—The dissociation pressure of  $\text{MgO}_2$  is given by  $\log P = 12,000/4.57T + 1.75 \log T + 2.8$ . For anhyd.  $\text{MgO}_2$   $P = 760$  mm. at 160°; for  $\text{MgO}_2 \cdot 1.14\text{H}_2\text{O}$  the temp. is 46°. Decomp. of  $\text{MgO}_2$  yields successively  $2\text{MgO}_2, 3\text{MgO}, \text{MgO}_2, 2\text{MgO}, \text{MgO}_2, 4\text{MgO}$ , and finally MgO. The thermal dissociation of  $\text{MgO}_2$ , but not of  $\text{SrO}_2$ , is an irreversible reaction.  $\text{O}_3$  reacts with MgO to yield an ozonide, different from  $\text{MgO}_2$ , and with SrO to yield ordinary  $\text{SrO}_2$ . For  $\text{SrO}_2$   $\log P = 13,500/4.57T + 1.75 \log T + 2.8$ , and for anhyd.  $\text{BaO}_2$   $\log P = -16,960/4.57T + 1.75 \log T - 0.0053T/4.57 + 2.8$ ; for hydrated  $\text{BaO}_2$   $P$  is considerably higher. The heats of dissociation of  $\text{MgO}_2, \text{SrO}_2$ , and  $\text{BaO}_2$  are respectively +12, +13.5, and +16.96 kg.-cal. R. T.

**Free energy of formation of iodine monobromide in carbon tetrachloride solution.** D. M. YOST, T. F. ANDERSEN, and F. SKOOG (J. Amer. Chem. Soc., 1933, 55, 552—555).—The partial pressures of IBr above solutions in  $\text{CCl}_4$  at 25° are given by  $p_{\text{IBr}}(\text{mm.})/\text{mol. fraction}_{\text{IBr}} = 114$ . The free energy changes at 25° are  $\frac{1}{2}\text{I}_2(\text{in CCl}_4) + \frac{1}{2}\text{Br}_2(\text{in CCl}_4) = \text{IBr}(\text{in CCl}_4) - 1746$  (equilibrium const. 19.0) and  $\frac{1}{2}\text{I}_2(\text{s}) + \frac{1}{2}\text{Br}_2(\text{l}) = \text{IBr}(\text{in CCl}_4) - 221$  g.-cal. J. G. A. G.

**Beryllium. VI. Reactions of sulphur dioxide with organic beryllium compounds.** H. S. BOOTH and V. D. SMILEY (J. Physical Chem., 1933, 37, 171—181; cf. this vol., 267).—Examination of the pressure-concn. relations in the systems  $\text{SO}_2\text{-Be}$

acetylacetonate and  $\text{SO}_2$ -Be Et acetoacetate at  $25^\circ$  has shown that in each case 1:1 compounds are formed. The structure of these compounds is discussed. E. S. H.

**Equilibrium in the system calcium-sulphur-oxygen. II.** R. SCHENCK and F. HAMMERSCHMIDT (Z. anorg. Chem., 1933, 210, 305—312; cf. A., 1929, 399).—Equilibrium data are given for the reaction  $\text{CaS} + 2\text{SO}_2 \rightleftharpoons \text{CaSO}_4 + \text{S}_2$  at 1 atm. and  $851$ — $1075^\circ$ . E. S. H.

**Equilibrium in the systems strontium-sulphur-oxygen and barium-sulphur-oxygen.** R. SCHENCK and F. HAMMERSCHMIDT (Z. anorg. Chem., 1933, 210, 313—315; cf. preceding abstract).—In the general reaction  $\text{M}^{\text{II}}\text{S} + 2\text{SO}_2 \rightleftharpoons \text{M}^{\text{II}}\text{SO}_4 + \text{S}_2$  the equilibrium partial pressure of S increases in the order Ca, Sr, Ba. E. S. H.

**X-Ray studies of the system nickel-oxygen-water. I. Nickelous oxide and hydroxide. II. Compounds containing tervalent nickel.** R. W. CAIRNS and E. OTT (J. Amer. Chem. Soc., 1933, 55, 527—533, 534—544; cf. A., 1931, 549).—I. The existence of more than one form of NiO could not be confirmed. The lattice const. is  $a_0$   $4.1684 \pm 0.001$  Å. The lattice const. of hexagonal  $\text{Ni}(\text{OH})_2$  are  $a_0$   $3.114$ ,  $c_0$   $4.167 \pm 0.005$  Å. Hydrates of  $\text{Ni}(\text{OH})_2$  do not exist. The two cryst. forms of anhyd.  $\text{NiSO}_4$  differ only in habit.

II. X-Ray diffraction patterns of  $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  have been obtained. The modes of decomp. of these compounds show that they are not true hydrates, but contain the  $\text{H}_2\text{O}$  bound as OH groups. Analogous "hydrates" of the hypothetical oxides  $\text{Ni}_2\text{O}_4$  and  $\text{Ni}_6\text{O}_7$  have been isolated. The results of Hüttig and Peter (A., 1930, 700) are criticised. J. G. A. G.

**Ternary systems. XVII. Sodium iodide, potassium iodide, and water. XVIII. Sodium iodide, sodium iodate, and water.** A. E. HILL, H. S. WILLSON, and J. A. BISHOP (J. Amer. Chem. Soc., 1933, 55, 520—522, 522—526).—XVII. The data refer to  $8^\circ$ ,  $25^\circ$ , and  $40^\circ$ . The solid phases are KI and  $\text{NaI} \cdot 2\text{H}_2\text{O}$  only.

XVIII. The data refer to  $8^\circ$ ,  $25^\circ$ , and  $40^\circ$ . The solubility of  $\text{NaIO}_3$  is greatly decreased by NaI, and solid solutions of the type  $(\text{NaIO}_3 \cdot 5\text{H}_2\text{O})_n \cdot (\text{NaI} \cdot 2\text{H}_2\text{O})_m$ , where  $n:m$  varies from 1:1 to 1:2, are shown to exist over a wide range of concn. J. G. A. G.

**Ternary systems mercuric chloride-water-alkaline-earth chloride or cupric chloride.** H. BASSETT, G. W. BARTON, A. R. FOSTER, and C. R. J. PATEMAN (J.C.S., 1933, 151—164).—The systems have been studied at  $25^\circ$ , and that containing Cu also at  $35^\circ$ . Complex salts of the types  $\text{MCl}_2 \cdot \text{HgCl}_2 \cdot x\text{H}_2\text{O}$ ,  $\text{MCl}_2 \cdot 3\text{HgCl}_2 \cdot x\text{H}_2\text{O}$ , and  $\text{MCl}_2 \cdot 6\text{HgCl}_2 \cdot x\text{H}_2\text{O}$  have been found. The  $\text{SrCl}_2$  system shows a region of mixed crystals of  $\text{SrCl}_2 \cdot 3\text{HgCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ , whence it is inferred that the latter is  $(\text{SrCl}_2 \cdot 2\text{H}_2\text{O})_4$ . Probable structures of the various complex salts, and the solubility curves, some of which are of an unusual type, are discussed. A new form of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  has been obtained. F. L. U.

**Liquidus and solidus studies. II. Ternary system  $\text{KNO}_3$ - $\text{NH}_4\text{NO}_3$ - $\text{Pb}(\text{NO}_3)_2$ .** H. M. GLASS, K. LAYBOURN, and W. M. MADGIN (J.C.S., 1933, 199—202; cf. A., 1932, 468, 1205).—F.p. of ternary mixtures, and compositions of conjugate phases relating to the  $150^\circ$ ,  $160^\circ$ , and  $190^\circ$  isotherms have been determined. There is a ternary eutectic of f.p.  $127.5^\circ$ .  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  form a discontinuous series of mixed crystals with a break between 8 and 35%  $\text{KNO}_3$ . F. L. U.

**The equilibrium  $\text{FeO} + \text{Ni} \rightleftharpoons \text{NiO} + \text{Fe}$  in the melt.** W. JANDER and H. SENF (Z. anorg. Chem., 1933, 210, 316—324).—Analyses have been made at temp. between  $1560^\circ$  and  $1790^\circ$ . With rising temp. the equilibrium is displaced towards the left. The temp. variation of the equilibrium const. is logarithmic. E. S. H.

**Dissociation pressures of magnesium ammonium phosphate hexahydrate and related substances. VII.** S. J. KIEHL and H. B. HARDT (J. Amer. Chem. Soc., 1933, 55, 605—618).—A method for determining the partial pressures of two volatile dissociation products is described. Dissociation pressures for the systems: (1)  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  (below  $60^\circ$ ), (2)  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  (above  $60^\circ$ ), (3)  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MgNH}_4\text{PO}_4$ ,  $\text{Mg}_2\text{P}_2\text{O}_7$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , (4)  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{MgHPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ , and (5)  $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ , have been determined. In a vessel exposed to the atm., all volatile material is rapidly removed from these substances at  $250^\circ$ . J. G. A. G.

**Thermal dissociation of serpentine minerals.** (MILE.) S. CAILLÈRE (Compt. rend., 1933, 196, 628—630).—The cooling curves for various serpentine minerals show in all cases absorption of heat due to dehydration at about  $650^\circ$ . Some show no other irregularity, but others show also an evolution of heat at about  $750^\circ$ , whilst a chrysotile from Quebec shows absorption at  $650^\circ$  and at  $400^\circ$ , the latter being due to dehydration of contained brucite. The results afford a means of classifying these minerals, but their classification does not fall into line with that based on their optical properties. Seven complete analyses are given, all agreeing fairly well with the formula  $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ . C. A. S.

**Gradation of heat of dilution at great dilution.** E. LANGE and J. MONHEIM (Naturwiss., 1933, 21, 24).—The heat of dilution of  $\text{CdSO}_4$  is greater than that of  $\text{ZnSO}_4$  even at a dilution of  $0.001M$ . This is a reversal of the usual order. The heat of dilution in the series  $\text{ZnSO}_4$ ,  $\text{CdSO}_4$ ,  $\text{CuSO}_4$ , shows no uniform increase with increasing radius of the cation, as would be expected from the assumptions of Debye and Hückel. The anomalous behaviour is shown in other properties. A. J. M.

**Determination of integral heats of dissolution. XIII.** N. A. KOLOSOVSKI and E. V. GRISCHKUN (J. Gen. Chem. Russ., 1932, 2, 906—910).—Kolosovski and Meshinin's method (A., 1932, 115) for the determination of latent heat of vaporisation has been applied to saturated solutions; the integral heat of dissolution  $L$  is derived from Kirchhoff's formula:

$L = M(\lambda - \lambda_0)$ , where  $M$  is the mol. wt. of  $H_2O$ , and  $\lambda$  and  $\lambda_0$  are respectively the latent heats of vaporisation for saturated solution and for pure  $H_2O$ . The results obtained for  $NaCl$ ,  $NH_4Cl$ , and  $CO(NH_2)_2$  are in good agreement with those given by direct measurement. R. T.

**Diffusion in liquids.** J. ZIRKLER (Z. Physik, 1933, 80, 412).—The results of Sitte (this vol., 17) for the % association of  $LiCl$ ,  $NaCl$ , and  $KCl$  are discussed in relation to the heat of hydration of ions. A. B. D. C.

**Thermodynamic data on zinc chloride and cadmium chloride.** F. ISHIKAWA, G. KIMURA, and T. MUROOKA (Sci. Rep. Tôhoku, 1932, 21, 455—473).—The e.m.f. of the cell  $Zn(Hg, 10\%)|ZnCl_2$ , saturated solution,  $HgCl|Hg$  from  $25^\circ$  to  $42.5^\circ$  is given by  $E = 0.82378 + 0.0001409(t - 30) - 0.00000039(t - 30)^2$ . For  $ZnCl_2 + 400H_2O = ZnCl_2 \cdot 400H_2O$   $\Delta H_{298} = -16,706$  g.-cal., and for  $Zn + Cl_2 = ZnCl_2$ ,  $\Delta H_{298} = -98,415$  g.-cal. For  $Hg + 0.5Cl_2 = HgCl$ ,  $\Delta H_{298} = -31,300$  g.-cal. Recorded v.p. at  $25^\circ$  are:  $CdCl_2 \cdot 2.5H_2O$ -saturated solution 19.64 mm.,  $CdCl_2 \cdot 2.5H_2O - CdCl_2, H_2O$  16.94 mm.,  $CdCl_2, H_2O - CdCl_2$  1.7 mm. The composition of the saturated solution is  $CdCl_2 \cdot 9.203H_2O$ , and its heat of dilution to  $CdCl_2 \cdot 400H_2O$ ,  $\Delta H_{298} = 37$  g.-cal. For  $\alpha - Cd + Cl_2 = CdCl_2$ ,  $\Delta H_{298} = -92,149$  g.-cal. Other recorded data are:  $\Delta F_{298}$ ,  $ZnCl_2$ ,  $-88,256$ ,  $CdCl_2$ ,  $-81,857$  g.-cal.;  $S_{298}$ ,  $HgCl$  24.1,  $ZnCl_2$  29.6,  $CdCl_2$  31.2. O. J. W.

**Thermodynamic studies of zinc bromide.** F. ISHIKAWA and T. YOSHIDA (Sci. Rep. Tôhoku, 1932, 21, 474—483).—The e.m.f. of the cell  $Zn(10\% Hg)|ZnBr_2$ , saturated solution in  $EtOH$ ,  $HgBr|Hg$  is given by  $E = 0.68133 + 0.00013897(t - 25) - 0.000000334(t - 25)^2$  between  $20^\circ$  and  $45^\circ$ , and that of the cell  $Zn(10\% Hg)|ZnBr_2 \cdot 2H_2O$ , saturated solution in  $H_2O$ ,  $HgBr|Hg$  from  $20^\circ$  to  $35^\circ$  by  $E = 0.68741 - 0.0004584(t - 25) - 0.000001533(t - 25)^2$ , and by  $E = 0.68328 + 0.0001348 \times (t - 40) + 0.000001739(t - 40)^2$  above  $35^\circ$  (transition point  $ZnBr_2 \cdot 2H_2O \rightarrow ZnBr_2$ ). V.-p. data for the system  $ZnBr_2 - H_2O$  are also given. The following thermodynamic data have been calc.:  $Zn + Br_2(l) = ZnBr_2$ ,  $\Delta F_{298} - 74,142$  g.-cal.,  $\Delta H_{298} - 78,470$  g.-cal.;  $ZnBr_2 + 2H_2O(l) = ZnBr_2 \cdot 2H_2O$ ,  $\Delta F_{298} - 3093$  g.-cal.;  $Zn + 2HgBr = ZnBr_2 + 2Hg$ ,  $\Delta S_{298} 6.41$  g.-cal./per degree; entropy of  $ZnBr_2 = 35.04$ . O. J. W.

**Thermodynamic study of cadmium hydroxide.** F. ISHIKAWA and E. SHIBATA (Sci. Rep. Tôhoku, 1932, 21, 499—510).—The activity product  $[Cd^{++}][OH^-]^2$  has been derived from (a) e.m.f. measurements of the cell  $Cd(10\% Hg)|Cd(OH)_2, 1.0N-NaOH, HgO|Hg$ ,  $E_{298} = 0.8598$  volt, (b) electrometric titration of  $CdSO_4$  solutions with  $NaOH$ , and (c) conductivity measurements of  $Cd(OH)_2$  solutions. The results do not agree, but method (a), which is the most trustworthy, gives  $1.17 \times 10^{-14}$ , according to which the solubility of  $Cd(OH)_2$  is  $1.4 \times 10^{-5}M$  at  $25^\circ$ . The following thermodynamic data have been obtained:  $Cd(s) + H_2(1 \text{ atm.}) + O_2(1 \text{ atm.}) = Cd(OH)_2(s)$ ,  $\Delta F_{298} - 112,469$  g.-cal.;  $Cd(s) + HgO(s) + H_2O(l) = Cd(OH)_2(s) + Hg(l)$ ,  $\Delta F_{298} - 42,100$  g.-cal.;  $Cd(OH)_2(s) + H_2(1 \text{ atm.}) = Cd(s) + 2H_2O(l)$ ,  $\Delta F_{298} - 949$  g.-cal. O. J. W.

**Heats of combustion of salicylic acid and of naphthalene with a view to their possible use as a second calorimetric standard.** L. J. P. KEFFLER (Bull. Soc. chim. Belg., 1932, 41, 607—621).—Mainly polemical against Beckers (A., 1932, 125), and a discussion of methods used in the determination of heats of combustion. The val.  $5235 + 2$  g.-cal. at  $15^\circ$  is proposed as the standard val. for salicylic acid. O. J. W.

**Heats of combustion.** M. BECKERS (Bull. Soc. chim. Belg., 1932, 41, 621—629).—A reply to Keffler (cf. preceding abstract). The adoption of a mean val. for the heat of combustion of salicylic acid is considered to have no significance. O. J. W.

**Organic thermochemical measurements. Velocities and heats of saponification of amides.** E. CALVET (J. Chim. phys., 1933, 30, 1—26; cf. A., 1932, 344).—The theory of the Tian microcalorimeter is discussed. The solubilities of five aliphatic amides in  $NaCl$  and  $KNO_3$  are recorded. The concn. of amide and electrolyte for max. reaction velocity has been determined. N. M. B.

**Free energies of formation of aqueous *d*-alanine, *l*-aspartic acid, and *d*-glutamic acid.** H. BORSOOK and H. M. HUFFMAN (J. Biol. Chem., 1933, 99, 663—676).—Vals. are calc. for the entropy, heat, and free energy of formation of the  $NH_2$ -acids and their ions at  $25^\circ$ . The free energy change calc. for the reaction  $l\text{-aspartate}'' \rightleftharpoons \text{fumarate}'' + NH_4^+$  agrees with the equilibrium which is attained in presence of micro-organisms (A., 1929, 850); the data indicate that the enzyme acts as a perfect catalyst. F. O. H.

**Transport numbers of solid alkali halides.** W. JOST and H. SCHWETZER (Z. physikal. Chem., 1933, B, 20, 118—124).—Transport no. measurements with  $NaCl$  at  $550$ — $700^\circ$  have confirmed the theory that the share of the cation and anion in the conduction can be represented by the terms of a two-term conductivity formula (A., 1926, 231; Joffé, Z. Physik, 1930, 62, 730). Measurements have also been made with  $KI$  and  $KBr$ . R. C.

**Electrical conductivity of aqueous solutions of sodium and potassium hydroxides and the limiting mobility of the hydroxyl ion at  $25^\circ$ .** G. H. JEFFERY and A. I. VOGEL (Phil. Mag., 1933, [vii], 15, 395—408).—Conductivities at  $25^\circ$  below  $0.01N$  are recorded. The limiting mobility of  $OH^-$  at  $25^\circ$  is  $211.9 \pm 0.1\%$ . H. J. E.

**Electrolytic solutions. II. Evaluation of  $\Lambda_0$  and  $K$  for incompletely dissociated electrolytes.** R. M. FUOSS and C. A. KRAUS (J. Amer. Chem. Soc., 1933, 55, 476—486).—The equations connecting the conductance and concn. of solutions of incompletely dissociated binary electrolytes are solved on certain assumptions. The validity of the method is confirmed for ion concns. as large as  $0.002N$ . J. G. A. G.

**Properties of mixtures of electrolytes. II.** V. K. SEMENTSCHENKO, B. V. EROFEEV, and V. V. SERPENSKI (J. Gen. Chem. Russ., 1932, 2, 893—905).—A modification of Shedlovsky's method (A., 1930, 862) gives results for the conductivity of

0.00025—2*N*-KCl solutions accurate to within 0.02%, which agree with those of Shedlovsky, and with those calc. from Onsager's formula (A., 1927, 517). R. T.

Effect of small water additions on the conductivity of electrolytes in non-aqueous solvents. O. L. HUGHES and (Sir) H. HARTLEY (Phil. Mag., 1933, [viii], 15, 610—637).—Additions of H<sub>2</sub>O up to 1% decrease the conductivity of KCl, AgNO<sub>3</sub>, and NEt<sub>3</sub>ClO<sub>4</sub> (I) in MeOH, of (I) in EtOH, and of (I), HClO<sub>4</sub>, and KCNS in COMe<sub>2</sub>, but increase that of Ag picrate, NaCNS, AgNO<sub>3</sub>, NH<sub>4</sub>CNS, LiCNS, and of picric acid in COMe<sub>2</sub>. The effect in each case is proportional to the concn. of H<sub>2</sub>O. Its influence on the association and solvation of the ions is discussed. Viscosity measurements for the mixed solvents, and the densities of COMe<sub>2</sub>-H<sub>2</sub>O mixtures, are recorded. H. J. E.

Connexion between complex formation, solvation, and formation of electrically conducting systems. V. S. FINKELSTEIN and M. S. ASCHKINAZI (J. Gen. Chem. Russ., 1932, 2, 790—799).—Electrolysis in the system NH<sub>2</sub>Ac-PhNO<sub>2</sub>-Br<sub>2</sub> is due to complex formation and ionisation represented by NH<sub>2</sub>Ac+Br<sub>2</sub> → NH<sub>2</sub>AcBr<sub>2</sub> ⇌ (NH<sub>2</sub>AcBr)<sup>+</sup>+Br<sup>-</sup>. R. T.

Electrochemistry of ethereal solutions. VII. Arsenic tribromide-methyl ethyl ether. M. USANOVITSCH and P. ROZENTRETER. VIII. Arsenic trichloride-ethyl ether. F. I. TERPUGOV. IX. Acetic acid-ethyl ether. A. G. PISAREV. X. Phosphorus trichloride-ethyl ether. P. G. ROZENTRETER (J. Gen. Chem. Russ., 1932, 2, 864—867, 868—874, 875—877, 878—879).—VII. The sp. conductivity and its temp. coeff. are at a max. for solutions which contain about 50 mol.-% of AsBr<sub>3</sub>, indicating that the electrolyte is AsBr<sub>3</sub>MeOEt.

VIII. The viscosity ( $\eta$ )-composition and conductivity ( $C$ )-composition isotherms show that for a given concn.  $\eta = Ae^{B/T}$ , where  $T$  = abs. temp. and  $A$  and  $B$  are consts. Max. vals. for  $C$  are obtained for mixtures which contain 80 mol.-% AsCl<sub>3</sub>; in view of the negative temp. coeff. of  $C$  this result is ascribed to a compound, AsCl<sub>3</sub>Et<sub>2</sub>O, which readily decomposes on dilution and with rising temp.

IX. Conductivity and viscosity measurements indicate the absence of compound formation in the system AcOH-Et<sub>2</sub>O.

X. Viscosity measurements suggest the absence of compound formation in the system PCl<sub>3</sub>-Et<sub>2</sub>O. R. T.

Anomalous electrolytes. I. Electrical conductivity of solutions of iodine and cyanogen iodide in pyridine [at 25°]. L. F. AUDRIETH and E. J. BIRR (J. Amer. Chem. Soc., 1933, 55, 668—673).—The conductivity of the solutions increases to max. vals. on keeping. Solvent and solute first form a non-conducting additive compound which slowly changes to a true quaternary pyridonium salt. The mol. conductivity of the I<sub>2</sub> solution at infinite dilution is 130 and this high val. is attributed to ternary salt formation. J. G. A. G.

Calcium electrodes of the third order. J. VELÍŠEK and A. VAŠÍČEK (Coll. Czech. Chem. Comm., 1933, 5, 10—20).—Previous data for Ca electrodes of the third order are discussed and other electrodes

are investigated, but none is found to be entirely satisfactory. It is unlikely that a satisfactory method will be found for determining [Ca<sup>++</sup>] electrometrically. The electrode studied in most detail was Hg|Hg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>|Ca<sup>++</sup>. For [Ca<sup>++</sup>] between 0.2 and 0.01*N* the hypothetical normal potential of Ca against the normal H electrode is approx. const. = 0.6100, but increases below these concns. owing to the solubility of the depolariser Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. The solubility of the latter corresponds with 0.003*N*-Ca<sup>++</sup>. There is a slow increase of potential with time due to decomp. of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> by H<sub>2</sub>O to form Ca(OH)<sub>2</sub> and also to the reduction of the Hg<sup>++</sup> salt. It cannot be used in physiological solutions because of the presence of Cl<sup>-</sup> and PO<sub>4</sub><sup>'''</sup>. M. S. B.

Diffusion in standard cells. G. A. HULETT and R. B. ELLIOTT (J. Physical Chem., 1933, 37, 245—252).—The concn. of Hg<sub>2</sub><sup>++</sup> in standard cells may be explored at any point in the electrolyte or paste by means of an amalgamated Pt point electrode. The cathode systems of Cd cells are shown not to be equilibrium systems. The concn. gradient of Hg<sub>2</sub><sup>++</sup> varies with the age of the cell; 4—18 years are required to establish a steady state of diffusion. Diffusion is greater when the depolariser is cryst. Hg<sub>2</sub>SO<sub>4</sub> than when electrolytically pptd. Hg<sub>2</sub>SO<sub>4</sub> is used. Attention is directed to the importance of diffusion of Hg<sub>2</sub><sup>++</sup> in determining the e.m.f. E. S. H.

E.m.f. and temperature coefficient of cell Cu|CuSO<sub>4</sub>|Hg<sub>2</sub>SO<sub>4</sub>|Hg at 25°. (MLLE.) M. GUINTIN (Compt. rend., 1933, 196, 473—475, 538—540, 652).—The e.m.f. of the cell Cu amalgam (two phases)|CuSO<sub>4</sub>(c)|Hg<sub>2</sub>SO<sub>4</sub>(solid)|Hg, special care being taken to exclude O<sub>2</sub>, has been determined at 25° for  $c=1.1300-0.00113$ .

The temp. coeffs. ( $\Delta E/\Delta t \times 10^4$ ) for  $c=0.525$ , 0.105, 0.02625, 0.0105, 0.00525, and 0.00105 are respectively -4.0, -3.3, -2.1, -1.2, +0.3, and +0.5. C. A. S.

Lead-mercurous acetate voltaic cell with acetic acid as solvent. G. TARBUTTON and W. C. VOSBURGH (J. Amer. Chem. Soc., 1933, 55, 618—624; cf. this vol., 126).—The e.m.f. of cells with the solid phases Pb(OAc)<sub>2</sub>·3H<sub>2</sub>O, Pb(OAc)<sub>2</sub>·0.5H<sub>2</sub>O, and Pb(OAc)<sub>2</sub>·0.5AcOH, and with solvents for which the wt. ratio, AcOH/H<sub>2</sub>O, ranges from 0.1969 to 90 has been determined between 16° and 50°. For cells with almost pure AcOH the e.m.f. is const. and reproducible. The temp. coeff. changes from negative to positive as the AcOH/H<sub>2</sub>O ratio is increased. The heat of formation of Pb(OAc)<sub>2</sub>·0.5H<sub>2</sub>O is 271.35 kcal. J. G. A. G.

Potential [at metallic electrodes] in electrolytes with foreign ions. III, IV. A. SCHMID, W. WINKELMANN, and P. VÖGELE (Helv. Chim. Acta, 1933, 16, 20—22, 22—28; cf. A., 1930, 705; this vol., 28).—III. C.d.-potential curves for amalgamated Al in Na<sub>2</sub>SO<sub>4</sub> and for Cu in NaCl and NaBr show that polarisation occurs which is determined, not by the concn. of ions of the electrode material, but by the concn. and nature of the foreign ions present.

IV. Experiments on the evolution of H<sub>2</sub> by amalgamated Al in various foreign electrolyte solutions



indicate that the purely chemical reaction is essentially different from the corresponding electrochemical change, the electrolyte acting in opposite senses in the two cases.

F. L. U.

So-called heats of transfer ( $Q^*$  values) in Peltier heats. E. LANGE and T. HESSE (J. Amer. Chem. Soc., 1933, 55, 853—855; cf. A., 1932, 814).—Preliminary. The Peltier effects at 25° for the system  $\text{Ag}|\text{AgCl}|\text{Cl}'$  in presence of  $\text{K}'$ ,  $\text{H}'$ ,  $\text{Li}'$  vary with the cation, and thus the existence of heats of transfer is established. The conclusions of Bruzs (*ibid.*, 1000) are criticised.

J. G. A. G.

Electrolysis of glass at high temperatures. R. SCHWARZ and J. HALBERSTADT (Z. anorg. Chem., 1933, 210, 286—288; cf. A., 1932, 230).—Conduction of electricity in glass up to 1000° is purely electrolytic. A Cu anode dissolves as  $\text{Cu}'$  above 700° and as a mixture of  $\text{Cu}'$  and  $\text{Cu}''$  at lower temp. The Na liberated at the cathode forms a blue sol in the glass.

E. S. H.

Influence of organic substances on the deposition of metallic ions at the dropping mercury cathode. G. DEVOTO and A. RATTI (Gazzetta, 1932, 62, 887—893).—The deposition potentials of Ni and Co from 0.01—0.1M solutions of the sulphate or chloride are depressed by 0.1—0.2 volt if 0.3 g. per litre of  $\text{C}_5\text{H}_5\text{N}$  is added to the electrolyte, and the form of the c.d.—voltage curves is somewhat modified. With Zn the effect is observed only at relatively high c.d. Deposition of Cd from a  $\text{CdSO}_4$  solution is retarded if the electrolyte is saturated with  $\text{COPhMe}$ , probably because of adsorption of the ketone on the Hg surface.

H. F. G.

Electrochemistry of polonium. M. HAÏSSINSKY (J. Chim. phys., 1933, 30, 27—46; cf. this vol., 128).—The crit. anodic deposition potential in acid solution varies with the acidity and the nature of the electrode, but this is not the case for the crit. cathodic potential. Po shows a strong tendency to form complex ions with the anions. The crit. cathodic potential is due in non-reducing media to the discharge of  $\text{Po}^{\text{III}}$  ions, in reducing media to the discharge of  $\text{Po}^{\text{IV}}$  ions, and in alkaline media to the electrolytic reduction of  $\text{PoO}_3$  ions. Anodic deposition in alkaline solution is due to discharge of  $\text{PoO}_3$  ions with formation of a peroxide, whilst in acid solution this peroxide is formed by nascent O.

N. M. B.

Initial electrolytic over-voltage of evolution of hydrogen over mercury. R. DUFOUR (Compt. rend., 1933, 196, 483—485).—Observations on the cell  $\text{Hg}|\text{N-H}_2\text{SO}_4|\text{Pt}$  are recorded.

C. A. S.

Passivity phenomena during the dissolution of copper in a mixture of nitric and sulphuric acids. A. KUTZELNIGG (Z. Elektrochem., 1933, 39, 67—73).—Cu becomes passive on immersion in a mixture of conc.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , owing to deposition of a layer of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . When present in high concn. HCl inhibits passivation, especially in presence of soot.

D. R. D.

Reaction cells in chain reactions. A. R. UBBELOHDE (Nature, 1933, 131, 328).—Theoretical.

L. S. T.

Upper pressure limit in the explosive chain reaction between hydrogen and oxygen. C. N. HINSHELWOOD and G. H. GRANT (Nature, 1933, 131, 361—362).—The upper limit is governed by ternary collisions in the gas phase and the particles which recombine or are deactivated in this process must be much more massive than pairs of H atoms. A theory which accounts quantitatively for many known facts concerning the upper limit is developed.

L. S. T.

Combustion of an inflammable gas mixture by a hot wire. J. D. MORGAN (Phil. Mag., 1933, [vii], 15, 440—442).—Dil. coal-gas-air or  $\text{Et}_2\text{O}$ -air mixtures reacting on hot wires of Pt, Fe, or Cu will not discharge an electroscope until the mixture inflames. Ionisation is a consequence and not a cause of inflammation.

H. J. E.

Ignition of explosive gaseous mixtures by small flames. J. M. HOLM (Phil. Mag., 1933, [vii], 15, 329—359; cf. A., 1932, 915).—Measurements were made on the change of flame velocity with tube diam., the limiting diams. for  $\text{H}_2$ -air and  $\text{Et}_2\text{O}$ -air mixtures, the effect of inert diluents on the limiting diam., and the extinction of moving flames by partitions in tubes. The previous theory of the cause of extinction of flames has been developed.

H. J. E.

Oxidation of carbonyl sulphide. C. E. H. BAWN (J.C.S., 1933, 145—151).—The influence of pressure, surface of vessel, method of mixing, etc. on the ignition temp. of  $\text{COS-O}_2$  mixtures has been investigated. The explosion gives rise to  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ , S, and possibly CS. There is an induction period, decreased by drying, during which a surface reaction occurs. Branched reaction chains are initiated and destroyed at the walls of the vessel. It is suggested that they are initiated by the formation of  $\text{COS}_2\text{O}_2$  on the walls. Addition of  $\text{O}_2$  to a mixture  $\text{COS-2O}_2$  depresses the ignition temp., whereas  $\text{COS}$ ,  $\text{He}$ ,  $\text{N}_2$ , and A have the reverse effect, and  $\text{H}_2\text{O}$  is without influence. The action of the inert gases is attributed to their cooling effect on the walls. Irradiation with ultra-violet light does not facilitate reaction, possibly owing to the opacity of the S deposited on the walls.

D. R. D.

Oxidation of carbonyl sulphide. H. W. THOMPSON, F. L. HOVDE, and A. C. H. CAIRNS (J.C.S., 1933, 208—216).—This investigation covers the same field as that described in the preceding abstract. Data are also given for the upper limiting pressure. In general, the results agree, but  $\text{N}_2$  and A are found to produce a depression of the lower explosion limit.  $\text{SO}_2$  and  $\text{CO}_2$  act similarly in low concn., but at higher concn. they have the opposite effect. Similar results have been obtained with  $\text{CS}_2$ . No appreciable reaction occurs in the absence of an explosion.

D. R. D.

Explosion of mixtures of carbon disulphide and nitric oxide. I. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1933, 52, 160—168).—Explosion limits have been determined for total pressures up to 400 mm. No explosion occurs if  $p < 35$  mm. For a given mixture, the quantity of light emitted  $\propto p^2$  (approx.). For a given pressure,

the light intensity is greatest when  $\text{CS}_2:\text{NO}$  lies between 2.25 and 2.75. The ignition temp. is of the order of  $1900^\circ$ . D. R. D.

**Explosion limits and ensurement of safety in the propagation of gas explosions.** E. BERL and K. BARTH (Z. Elektrochem., 1933, 39, 73—75).—Explosion limits are given for mixtures of air with coal gas,  $\text{C}_2\text{N}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CS}_2$ ,  $\text{Et}_2\text{O}$ ,  $\text{EtOH}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{COMe}_2$  vapours. A glass filter diaphragm serves to prevent backward propagation of an explosion. D. R. D.

**Explosion pressure of air-benzene mixtures in a closed vessel.** Y. LAURE (Compt. rend., 1933, 196, 385—387).—Pressure-time curves have been determined for explosions of the same air- $\text{C}_6\text{H}_6$  mixture in a sphere and three cylinders of vols. 288, 432, 500, and  $729 \times \pi$  c.c., but all having the same ratio of surface to vol. ( $0.5 \text{ cm.}^{-1}$ ). Duration of reaction increased and max. pressure decreased in the above order, but delay in ignition was const. Curves relating max. pressure to richness of mixture were all superposable. The effect of introducing metal plates into the bombs depended on their position. C. A. S.

**Homogeneous unimolecular decomposition of mixtures of gaseous aliphatic ethers.** E. W. R. STEACIE (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 103—110).—In the homogeneous unimol. decomp. of mixtures of  $\text{Et}_2\text{O}$  and  $\text{Me}_2\text{O}$  on a Pt filament at  $478^\circ$ , the efficiency of energy transfer between mols. of the two substances is zero in so far as production of activated mols. is concerned. The rates of decomp. of the separate reactants are therefore additive. J. W. S.

**Energy transfer between complex gas molecules and solid surfaces.** E. W. R. STEACIE and H. A. REEVE (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 75—85).—The homogeneous unimol. decomp. of  $\text{EtOH}$ ,  $\text{COMe}_2$ ,  $\text{PrCHO}$ , and  $\text{MeOH}$  on a heated Pt filament has been investigated. The reactions occur in the gas layer surrounding the filament and are not catalysed. For  $\text{EtOH}$  and  $\text{COMe}_2$  the gas layer is in thermal equilibrium with the filament and the apparent heat of activation calc. from the temp. coeff. of the reaction agrees with that for a homogeneous reaction. The apparent heat of activation of  $\text{PrCHO}$  and  $\text{MeOH}$  is much  $>$  that of the homogeneous reaction. This is explained by assuming that the accommodation coeffs. for these gases are low and hence thermal equilibrium with the filament is not attained by colliding gas mols. J. W. S.

**Dithionates. I. Sodium dithionate. II. Velocity of decomposition of sodium dithionate and potassium dithionate.** F. ISHIKAWA and M. OKU (Sci. Rep. Tôhoku, 1932 21, 727—746, 747—771).—I. The solubility of  $\text{Na}_2\text{S}_2\text{O}_6$  has been measured at temp. between  $100^\circ$  and  $-1.14^\circ$  (the cryohydric point). The following hydrates exist:  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 8\text{H}_2\text{O}$ , the transition points being  $9.1$ — $9.2^\circ$  and  $0^\circ$ , respectively. The velocity of dehydration of  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  at  $50^\circ$  as measured by both dynamic and static methods suggests that both mols. of  $\text{H}_2\text{O}$  of crystallisation are equally bound to the  $\text{Na}_2\text{S}_2\text{O}_6$  mol. and that the dehydration is controlled by the diffusion velocity of the  $\text{H}_2\text{O}$

vapour. The v.p. of  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  has also been measured, the changes in heat content and free energy for the hydration process being calc.

II. The velocity of decomp. of these compounds has been measured by determining the vol. of  $\text{SO}_2$  evolved. Its course cannot be explained on Langmuir's interfacial theory alone, as the effect of the disintegration of the particles must be taken into account. J. W. S.

**Velocity of decomposition of dithionic acid and its volumetric determination.** F. ISHIKAWA and H. HAGISAWA (Sci. Rep. Tôhoku, 1932, 21, 484—498).—Velocity measurements in aq. solution at  $60$ — $100^\circ$  show that the reaction  $\text{H}_2\text{S}_2\text{O}_6 = \text{H}_2\text{SO}_4 + \text{SO}_2$  is unimol., the temp. coeff. varying between 3 and 4. The reaction is greatly accelerated by  $\text{HCl}$ .  $\text{H}_2\text{S}_2\text{O}_6$  can be determined by heating with conc.  $\text{HCl}$  in a sealed tube and titrating with I the  $\text{H}_2\text{SO}_3$  formed. O. J. W.

**Velocity of reaction of potassium cyanide with thiosulphate or tetrathionate.** F. ISHIKAWA, T. MUROOKA, and H. HAGISAWA (Sci. Rep. Tôhoku, 1932, 21, 511—526; cf. A., 1927, 1147).—The reaction  $\text{S}_2\text{O}_3'' + \text{CN}' = \text{SO}_3'' + \text{CNS}'$  is bimol. at  $25^\circ$  and  $70^\circ$ , and the velocity coeff.,  $k$ , varies linearly with initial total KCN concn. and with added  $\text{NaOH}$  concn., *i.e.*  $k = 0.0269 + 0.06[\text{KCN}]$  and  $k = 0.0461 + 0.033[\text{NaOH}]$ . The velocity of the reaction  $\text{S}_4\text{O}_6'' + \text{CN}' + 2\text{OH}' = \text{S}_2\text{O}_3'' + \text{CNS}' + \text{SO}_4'' + \text{H}_2\text{O}$  at  $70^\circ$  is controlled by the velocity of the secondary reaction  $\text{S}_2\text{O}_3'' + \text{CN}' = \text{SO}_3'' + \text{CNS}'$ , which is accelerated by the  $\text{KCNS}$  formed in the primary reaction. O. J. W.

**Regularities in acid and salt effects in alcoholic aqueous solutions. II. Oxidation of ethyl alcohol by chromic acid.** M. BOBTELSKI and R. COHN (Z. anorg. Chem., 1933, 210, 225—240; cf. A., 1931, 1245).—In absence of acids or in presence of weak acids, reaction between  $\text{EtOH}$  and  $\text{CrO}_3$  occurs at measurable speed only when the concn. of  $\text{EtOH}$  is  $> 60$  vol.-%. In general, the influence of acids or salts depends on the concn. of  $\text{EtOH}$  and three regions are recognised, according as the latter is  $< 30$ ,  $30$ — $60$ , or  $> 60$  vol.-%. In the upper region,  $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$ ,  $\text{CHCl}_2 \cdot \text{CO}_2\text{H}$ , and  $\text{CCl}_3 \cdot \text{CO}_2\text{H}$  accelerate the reaction in the ratio 1 : 2 : 6 for equiv. consns. The acceleration is also proportional to the concn. of acid. Sp. differences in the effect of the acids are shown particularly when the  $\text{EtOH}$  concn. is  $> 60\%$ .  $\text{Al}'''$  has a marked accelerating effect, especially in absence of strong acids; the velocity is proportional to the concn. of  $\text{Al}'''$  at high consns. of  $\text{EtOH}$ .  $\text{Mn}''$ ,  $\text{Cl}'$ , and  $\text{Br}'$  exert an exhibiting influence on the reaction. E. S. H.

**Velocity of liberation of hydrocarbons by the action of indene on aliphatic organo-magnesium compounds. Method of measuring the attraction between alkyl radicals and the magnesyl group.** D. IVANOV and I. ABDOULOV (Compt. rend., 1933, 196, 491—493).—The velocity of the reaction between indene and  $\text{RMgX}$  is determined by measuring the vol. of the hydrocarbon  $\text{RH}$  liberated. This is an inverse measure of the affinity between  $\text{R}$  and  $\text{MgX}$ . This affinity decreases in the order  $\text{Bu}^\beta$ ,  $\text{Me}$ ,

Buc, sec.-Bu, Pr<sup>a</sup>, Et, Pr<sup>β</sup>, which is similar to that deduced from the reaction between RMgX and CH<sub>2</sub>Ph·CO<sub>2</sub>MgCl (A., 1932, 816). A. C.

**Invertase action as a heterogeneous reaction.** T. A. WHITE (J. Amer. Chem. Soc., 1933, 55, 556—568).—Kinetic expressions are developed on the assumption that sucrose and H<sub>2</sub>O are adsorbed by invertase, the inversion occurs in the adsorbed layer, and adsorption of the products inhibits the reaction. Consistent with theory, it is found that the velocity is const. for the first 10% of hydrolysis and then decreases. The unimol. coeff. decreases with increase of  $p_H$  from 4.7 to 7.4, and passes through a max. at a definite % of hydrolysis which decreases with decrease of initial sucrose concn., increase of  $p_H$  and temp., and is independent of enzyme concn. The existence of a max. initial velocity with 6% sucrose is interpreted as corresponding with the optimum ratio of adsorbed sucrose to adsorbed H<sub>2</sub>O. J. G. A. G.

**Combustion of graphite in a current of gas.** V. SIHVONEN (Suomen Kem., 1932, 5, 51B).—The combustion of graphite in cold and preheated O<sub>2</sub>, CO<sub>2</sub>, and steam has been studied. In O<sub>2</sub> either of two first-order reactions may occur, according to the condition of the surface; the one occurs at 800—1400° at the normal porous surface, and results in the formation of CO<sub>2</sub>+2CO, and the other at 900° at the surface modified by the action of CO, the product being pure CO. With preheated steam the reaction is initiated by O resulting from dissociation. In cold steam vigorous combustion does not occur below 1500°, whilst at temp. > 1600° the rate of reaction diminishes owing to a change of the surface and decrease of adsorption of the steam. Cold (i.e., undissociated) CO<sub>2</sub> does not react with graphite below 1500°. H. F. G.

**Action of chlorine on metal oxides.** W. KANGRO and R. JAHN (Z. anorg. Chem., 1933, 210, 325—336).—The rate of reaction of Cl<sub>2</sub> with BeO, ZnO, CdO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, WO<sub>3</sub>, and U<sub>3</sub>O<sub>8</sub> has been determined at high temp. The oxides of Ta and B do not react with Cl<sub>2</sub>. Regularities in the temp. at which chlorination begins are observed only when the product is completely volatile at that temp. Under these conditions the chlorination temp. rises with increasing at. no. in each group of elements. E. S. H.

**Law of combustion of mixtures of powders.** H. MURAOUB and G. AUNIS (Compt. rend., 1933, 196, 478—480).—Substitution of part of the powder of a charge by another powder of different velocity of combustion had no effect on  $spdt$  for a density of loading of 0.2 owing to the small variation in  $t$  (cf. Appl. Chem. Rep., 1930, 15, 677), but for lower densities the expected increase in  $spdt$  has been experimentally demonstrated, the  $spdt-t$  curve being a straight line inclined to the axes. C. A. S.

**Rate of absorption of nitrous gases by sulphuric acid.** II. L. SZEGŐ and M. LOMBARDI.—See B., 1933, 188.

**Dynamics and catalysis of the thermal decomposition of hydrogen carbonates in aqueous**

**solution.** VIII. Decomposition of sodium hydrogen carbonate. R. STUMPER (Z. anorg. Chem., 1933, 210, 264—268; cf. A., 1932, 1095).—The decomp. in boiling aq. solutions (0.005—0.05*N*) is unimol., both with and without application of a CO<sub>2</sub>-free air stream. Fe, dextrin, starch, and agar accelerate the decomp. The thermal decomp. of Ca(HCO<sub>3</sub>)<sub>2</sub> is accelerated by many finely-divided solids, which act as nuclei, but inhibited by hydrophilic colloids. E. S. H.

**Chronic poisoning by oxalic acid. Volatilisation of oxalic acid from aqueous solution.** C. D. HOWARD (J. Ind. Hyg., 1932, 14, 283—290).—Volatilisation occurs at the b.p. at a rate dependent on the rate of boiling and concn. In a glass vessel, Cu and Al increase the rate, which is low if a Cu flask is used or when steam is passed through the solution. In presence of Al, HCO<sub>2</sub>H, H<sub>2</sub>, and CO<sub>2</sub>, and in presence of Cu only CO<sub>2</sub>, are formed.

CH. ABS.

**Heavy metal catalysts. II. Influence of cystine on artificial peroxidases.** T. OMORI (J. Biochem. Japan, 1932, 16, 483—497; cf. A., 1932, 346).—Addition of cystine (I) to systems containing H<sub>2</sub>O<sub>2</sub> and Fe or Cu (but not Mn, Ni, or Co) accelerates the oxidation of the substrate (starch). The acceleration is proportional to the concn. of (I) and is effective at concns. >  $M/19,200$ . The  $p_H$  optimum for the system (I)-H<sub>2</sub>O<sub>2</sub>-Fe-starch is 3.3; outside the range 1.0—5.6 there is no action. Citrates and narcotics inhibit the reaction. (I) can be replaced by tyrosine and, in the Fe-containing systems, by glutathione or thioglycolic acid, but not by caseinogen or ovalbumin. F. O. H.

**Comparison of organic inhibitors in chain reactions.** K. K. JEU and H. N. ALYEA (J. Amer. Chem. Soc., 1933, 55, 575—588).—The photopolymerisation of vinyl acetate, the thermal autoxidation of Na<sub>2</sub>SO<sub>3</sub>, and the photolysis of H<sub>2</sub>O<sub>2</sub> are first-order chain reactions. The results in the presence of inhibitors are represented by the general equation  $(1/t) \log_e 1/(1-x) = K/(k_2 + kC)$ , where  $x$  is the fraction reacting during time  $t$ ,  $K$  includes the number of chains initiated at  $t=0$  and the probability of continuing the chains, whilst  $k_2 + kC$  is the probability of breaking the chains by a const. factor,  $k_2$ , or by an inhibitor of concn.  $C$  and inhibiting power  $k$ . Relative vals. of  $k$  for 16 inhibitors are approx. identical for the first two reactions, but bear no relation to those obtained in the photolysis of H<sub>2</sub>O<sub>2</sub>. Chain lengths agreeing with experimental vals. were calc. from vals. of  $k_2$ . Many org. substances photosensitise the polymerisation of vinyl acetate to visible light. J. G. A. G.

**Theory of ammonia catalysis. II. Kinetics.** W. FRANKENBURGER (Z. Elektrochem., 1933, 39, 97—103).—A discussion. D. R. D.

**Influence of traces of a salt of tin in acid solution on the rate of corrosion of mild steel.** T. N. MORRIS and J. M. BRYAN.—See B., 1933, 231.

**Interface catalysis in the reduction of metallic oxides.** A. R. UBBELOHDE (Trans. Faraday Soc., 1933, 29, 532—534).—The possibility of interface

catalysis, or the catalysis of a reaction in the solid phase by the presence of one of the resultants, is discussed in connexion with the reduction of metallic oxides. Thermochemical data indicate that interfacial catalysis is to be expected in the reduction of oxides of Cu, Ni, Pt, Pd, and Pb. Experimental data confirm this for Cu, Ni, and Pt. M. S. B.

**Mechanism of chemical reactions. IV. Specific hydrogenation with combined hydrogen.** K. KINDLER and W. PESCHKE (Annalen, 1933, 501, 191—198; cf. A., 1932, 944).—4-Methyl- and 4-methoxy-cinnamic acids, Me 4-methoxy- (I), 3:4-methylenedioxy- (II), and 3:4-dimethoxy-cinnamates are reduced to the corresponding propionic acid derivatives (in almost quant. yield) by Pd-black and boiling dihydrophellandrene (III); in all these cases, the same amount of H<sub>2</sub> is evolved as with Pd-black and (III) alone. It is suggested that the affinity of the acceptor and catalyst is small; an adduct is produced which is able to add the donor [*i.e.*, (III)], thereby forming a system in which part of the H of (III) and the reducible portion of the acceptor are activated. Cinnamic acid (IV), Et *p*-nitrocinnamate, and Me, Et, and *iso*amyl cinnamates are not reduced by Pd-black and (III); little H<sub>2</sub> is evolved. In these cases, the affinity of the acceptor and catalyst is great; the adduct formed is unable to add the donor. No reduction of (I) and (II) occurs when they are admixed with an equimol. amount of (IV). 3:4-Dimethoxymandelonitrile benzoate is reduced by Pd-black and (III) to 3:4-dimethoxyphenylacetone; reduction of mandelonitrile benzoate is slower (less H<sub>2</sub> is evolved). H. B.

**Corrosion and local current.** F. TÖDT (Z. Elektrochem., 1933, 39, 146—147; cf. A., 1930, 1125).—A reply to criticisms by Eckell (A., 1932, 231). F. L. U.

**Electro-reduction of perrhenic acid.** W. F. JAKÓB and B. JEZOWSKA (Ber., 1933, 66, [B], 461—462).—Reduction of K perrhenate in 6*N*- or 8*N*-HCl takes place with poor current yield and marked cathodic polarisation. In these solutions or those containing KI a sudden fall in potential marks the completion of the change, Re<sup>VII</sup>+2e=Re<sup>V</sup>. The isolation of the salt K<sub>2</sub>[Re(OH)<sub>2</sub>Cl<sub>5</sub>] is described. With thiocyanates it yields an intensely green compound, sol. in Et<sub>2</sub>O. With alkalis, the black oxide ReO(OH)<sub>3</sub>·*x*H<sub>2</sub>O, rapidly oxidised by air, is pptd. H. W.

**Behaviour of mercuric halides during anodic oxidation.** G. ILLARI (Gazzetta, 1932, 62, 1166—1176).—HgI<sub>2</sub> is oxidised almost quantitatively to Hg(IO<sub>3</sub>)<sub>2</sub> at a Pt anode in HNO<sub>3</sub> solution, and this forms a convenient method of preparing the latter salt. HgBr<sub>2</sub> is oxidised to bromate, which undergoes decomp. by the HNO<sub>3</sub> with evolution of Br. HgCl<sub>2</sub> is not oxidised anodically. O. J. W.

**Electrodeposition of nickel with insoluble anodes.** V. I. LATNER and others.—See B., 1933, 194.

**Electrolytic separation of lead as peroxide in non-ferrous alloys. I. Determination of small amounts of lead in copper and copper-rich alloys.** B. JONES.—See B., 1933, 193.

**Electrodeposition of iron-cobalt alloys. II.** S. GLASSTONE and J. C. SPEAKMAN.—See B., 1933, 231.

**Electrochemical behaviour of palladium. I. Electrolytic deposition of palladium and palladium-silver alloys from solutions of complex salts.** G. GRUBE and D. BEISCHER (Z. Elektrochem., 1933, 39, 131—139).—Ag and Pd can be deposited simultaneously from a bath containing KAg(CN)<sub>2</sub>+K<sub>2</sub>Pd(CN)<sub>4</sub> with a current yield of 5—6%. The deposit is greyish-black and non-coherent. From a bath of the corresponding (CNS) compounds similar deposits are obtained, containing S in addition to org. substances. Satisfactory deposits of Ag could not be obtained from NH<sub>3</sub>-AgNO<sub>3</sub> baths. The process [Pd(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]+2NH<sub>3</sub>→[Pd(NH<sub>3</sub>)<sub>4</sub>](NO<sub>2</sub>)<sub>2</sub> has been followed by conductivity measurements. F. L. U.

**Anodic oxidation of benzene.** R. M. ARCHIBALD (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 69—73).—Electrolysis of a solution of C<sub>6</sub>H<sub>6</sub> in AcOH using an anode of Ni, Pt, Cu, or Fe yields an equilibrium mixture of PhOH and higher oxidation products. The PhOH concn. is highest when a relatively high voltage (>15 volts) is used, when a diaphragm is used between the electrodes, and in presence of traces of salts such as CuSO<sub>4</sub> and NH<sub>4</sub>VO<sub>3</sub>. The max. yield of PhOH (1.76%) was obtained in 5% solution. The use of a.c., alone or superimposed on the d.c., results in lower yields. Large concns. of salts also lower the yield. Rapid oxidation for a short period is preferable to slower oxidation over longer periods. The voltage-current curve with C<sub>6</sub>H<sub>6</sub>-AcOH solutions is smooth over the range 0—5 volts, indicating the absence of a definite decomp. potential. Electrolysis of suspensions of C<sub>6</sub>H<sub>6</sub> in aq. NaOH or EtOH-H<sub>2</sub>SO<sub>4</sub> yielded no PhOH. J. W. S.

**Dissociation of nitrous oxide in the glow discharge.** E. A. STEWARDSON (Nature, 1933, 131, 364—365).—With a high-frequency discharge and fields of average peak intensity of 100—400 volts/cm. and initial pressures of 0.1—3.0 mm. results in substantial agreement with those of Hinshelwood and Hutchison (A., 1928, 30) have been obtained. At the lowest discharge intensity the initial rate varies little with the initial pressure, but at the highest p.d. there is a small pressure range over which dissociation is unimol. Beyond this region the rate of dissociation increases for 3—4 sec. after initiation, rapidly attains a max., and then proceeds normally in a manner dependent on pressure. A similar effect has been observed with NO<sub>2</sub>. L. S. T.

**Effect of water on the photosynthesis of hydrogen chloride.** G. K. ROLLEFSON and J. C. POTTS (J. Amer. Chem. Soc., 1933, 55, 860—861; cf. this vol., 34).—Experiments at 145—200° abs. indicate no decrease in reaction velocity when the v.p. of H<sub>2</sub>O becomes <10<sup>-5</sup> mm. With fall of temp., the reaction velocity ∝ I<sub>abs.</sub> probably changes to velocity ∝ I<sub>abs.</sub><sup>1/2</sup>. Baker's experiments (*ibid.*, 132) are criticised. J. G. A. G.

**Reaction of hydrogen atoms with oxygen and the hydrogen-chlorine reaction.** J. R. BATES (Proc. Nat. Acad. Sci., 1933, 19, 81—85).—Theoretical. The part played by the reaction between H and O<sub>2</sub>

in the HCl reaction is discussed on the basis of results obtained from the photo-oxidation of HI (this vol., 237).

M. S. B.

**Primary photochemical processes. II. Absorption spectrum and photochemical decomposition of diazomethane.** F. W. KIRKBRIDE and R. G. W. NORRISH (J.C.S., 1933, 119—126).—The absorption spectrum of  $\text{CH}_2\text{N}_2$  is similar to that of

$\text{Me}\cdot\text{N}_2\cdot\text{Me}$  and supports the structure  $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{N} \end{array}$

The photochemical decomp. of  $\text{CH}_2\text{N}_2$  is a unimol. reaction of quantum efficiency approx. 4 at 365 and 436  $\text{m}\mu$ . The main products are  $\text{N}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , and a non-volatile liquid (possibly a pyrazoline derivative). In presence of  $\text{H}_2$ , much  $\text{CH}_4$  is formed and the liquid N compound is absent. In presence of  $\text{O}_2$ , liquid compounds, believed to be oxidation products of  $\text{CH}_2$ , are obtained, but no oxides of N. These observations support the view that the primary process is  $\text{CH}_2\text{N}_2 + h\nu = \text{CH}_2 + \text{N}_2$ .

D. R. D.

**Influence of X-rays on the oxidation of graphite by oxygen at very low pressures.** V. SIHVONEN (Suomen Kem., 1932, 5, 51B).—When graphite reacts with  $\text{O}_2$  (at  $3.6\text{--}15.7 \times 10^{-3}$  mm. pressure) which is subjected to X-ray irradiation, the product is  $\text{CO}_2 + 2\text{CO}$ . If, on the other hand, the X-rays fall directly on the graphite, a considerable excess of  $\text{CO}_2$  is formed; at low pressures ( $5\text{--}12 \times 10^{-3}$  mm.) this excess is not formed from  $\text{O}_2$  in the gas phase, but appears to be derived from the breakdown of adsorption complexes on the graphite surface, whereas at higher pressures ( $25\text{--}32 \times 10^{-3}$  mm.) part of the excess arises from reaction of the graphite with the gas phase.

H. F. G.

**Silver nucleus theory of the latent image. II. Size and nature of [latent image] nuclei and [primary silver] nuclei in silver bromide emulsions.** W. REINDERS and L. HAMBURGER (Z. wiss. Phot., 1933, 31, 265—284; cf. A., 1932, 821).—Theoretical. Primary Ag nuclei ["sensitivity specks" (Sheppard), "prokeime"] formed during ripening of AgBr emulsions become developable when aggregates of 3 or 4 atoms are produced. The Ag is replaceable by  $\text{Ag}_2\text{S}$  and other S-containing complexes. The proportion of such aggregates, among the primary Ag adsorbed on the surface of grains of a normal AgBr emulsion, is very small. Ag formed on exposure is preferentially deposited on these nuclei, which form weak spots in the crystal lattice. The desensitising action of methylene-blue is also discussed.

J. L.

**Photochemical studies. III.** C. WINTHER (Z. wiss. Phot., 1933, 31, 285—293).—Various types of sensitisation are discussed, and simple experiments illustrating their chief features are described.

J. L.

**Herschel effect as a result of simultaneous forward and reverse reactions.** K. M. JOEHNCK and J. M. BLAIR (J. Opt. Soc. Amer., 1933, 23, 67—69).—The Herschel effect is explained on the basis of Blair and Leighton's hypothesis (cf. A., 1932, 1006) that the formation of the latent image is the equilibrium of two opposed reactions. Then for light of given wave-length and intensity, the max. develop-

able Ag is const., and a higher latent density (obtained by previous exposure to a stronger light) is reducible to this const. by prolonged exposure. Experiments showing these effects are described.

J. L.

**Blue and green sensitivity of photographic emulsions in absolute measure.** M. BILTZ (Physikal. Z., 1933, 34, 200—204).—The determination of the blue and green sensitivity of a series of Agfa films gave for the blue sensitivity 77—4 sq. cm. per erg. The ratio of the green to blue sensitivity for unsensitised emulsions was 0.006, but for sensitised emulsions it could be increased to about 100 times this val.

A. J. M.

**Mechanism of hypersensitisation.** B. H. CARROLL and D. HUBBARD.—See B., 1933, 252.

**Photochemical reaction between quinine and dichromic acid. II. Kinetics of the reaction.** G. S. FORBES, L. J. HEIDT, and F. P. BRACKETT, jun. (J. Amer. Chem. Soc., 1933, 55, 588—596; cf. A., 1932, 480).—The reaction in the system  $0.00016\text{--}0.003M\text{-K}_2\text{Cr}_2\text{O}_7$ ,  $0.0\text{--}1.7M\text{-H}_2\text{SO}_4$ ,  $0.00001\text{--}0.02M$ -quinine has been investigated at temp. between  $5^\circ$  and  $29^\circ$  with monochromatic light of seven wavelengths between 405 and 208  $\text{m}\mu$ . The reaction proceeds by way of clusters and is of zero order with respect to quinine, approx. first order with respect to  $\text{H}_2\text{CrO}_4$  (or 0.5 for  $\text{H}_2\text{Cr}_2\text{O}_7$ ), and 0.07 with respect to  $\text{H}_2\text{SO}_4$ . At 208  $\text{m}\mu$ ,  $\text{H}_2\text{Cr}_2\text{O}_7$  may be photosensitive also. The absorption band of  $0.0001M$ -quinine is shifted  $200\text{ cm}^{-1}$  towards the red by increasing the concn. of  $\text{H}_2\text{SO}_4$  from 0.004 to  $4M$ . On one view, the temp. coeff. accords with a bimol. reaction between activated quinine and  $\text{H}_2\text{CrO}_4$  (or  $\text{H}_2\text{Cr}_2\text{O}_7$ ) without additional energy of activation.

J. G. A. G.

**Photo-active emanations from some irradiated organic substances.** C. SERONO and A. CRUTO (Gazzetta, 1932, 62, 1203—1209; cf. A., 1928, 1071).—Lecithin, which has been exposed for a few min. to ultra-violet radiation, affects a photographic plate. The emission of radiation is related to the absorption of O by the lecithin during the irradiation. Similar results are described for oleic acid.

O. J. W.

**Haber-Willstätter chain mechanism of organic and enzymic processes.** H. S. TAYLOR and A. J. GOULD (J. Amer. Chem. Soc., 1933, 55, 859).—Preliminary. In agreement with the theory (A., 1932, 352), OH produced by photo-decomp. of  $\text{H}_2\text{O}_2$  sensitises the interaction of  $\text{O}_2$  with EtOH and MeCHO. The oxidations are chain reactions sensitive to inhibitors.

J. G. A. G.

**Chemical and biological effects of ultra-sonic radiation.** A. SZENT-GYÖRGYI (Nature, 1933, 131, 278).—Ultra-sonic radiation decomposes sucrose into monosaccharides, but has no effect on  $\text{Ph}_2\text{O}$ , succinimide, etc. Judged by a fall in viscosity, starch, gum arabic, and gelatin are depolymerised.

L. S. T.

**Action of potassium nitroacetate on some metallic salts.** A. DANSI (Gazzetta, 1932, 62, 1177—1183).—The products obtained by the action of Hg and Cu salts on nitroacetic acid are very

unstable. With  $\text{HgCl}_2$  and  $\text{Hg}(\text{NO}_3)_2$  the final product contains Cl or  $\text{NO}_3$ , respectively, and either one or both Hg atoms are joined directly by a single linking to the C atom. With the corresponding Cu salts basic salts are obtained which contain no org. group. The pure neutral Ag nitroacetate could not be obtained (cf. A., 1924, i, 254). O. J. W.

**Coprecipitation. III. Water content of calcium oxalate monohydrate.** E. B. SANDELL and I. M. KOLTHOFF (J. Physical Chem., 1933, 37, 153—170; cf. A., 1932, 457).— $\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  is pptd. at room temp. from 0.1N- $\text{Ca}^{++}$  solutions, but is transformed completely into  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (I) when left in contact with the mother-liquor for 1—2 days. This transformation is accelerated by rise of temp. and by excess of  $\text{C}_2\text{O}_4^{--}$ . The higher hydrates are converted into (I) rapidly at  $100^\circ$  and more slowly at room temp.; the ppt. formed from boiling solutions consists of (I) alone. Ppts. formed under any conditions always contain adsorbed  $\text{H}_2\text{O}$ . This  $\text{H}_2\text{O}$  is contained in internal capillaries in the crystals, and adsorption and desorption are not quite reversible, as the  $\text{H}_2\text{O}$  tends to become trapped with the ageing of the crystals. (I) is not an ideal form in which to weigh Ca, even after drying at  $110^\circ$ . The least hygroscopic ppt. is formed from relatively conc. solutions, digesting the mixture for about 20 hr. at  $90^\circ$  before filtering. (I) sometimes loses  $\text{H}_2\text{O}$  of hydration on prolonged drying at  $115$ — $125^\circ$ , especially when the ppt. is formed in neutral or ammoniacal solutions, and at  $100^\circ$ . E. S. H.

**Dissolution of fluorite.** W. KLEBER (Neues Jahrb. Min., 1932, 65, A, 447—478; Chem. Zentr., 1932, ii, 2948).—The effect of concn. and temp. on dissolution by HCl was determined. A new end-form, probably due to the slight solubility of  $\text{CaSO}_4$ , was obtained with  $\text{H}_2\text{SO}_4$ . A. A. E.

**Basic salts. II. Simple basic chlorides of bivalent heavy metals.** E. HAYEK (Z. anorg. Chem., 1933, 210, 241—246; cf. A., 1932, 914).—In general, bivalent heavy metals can form compounds of the type  $\text{M}^{II}(\text{OH})_2 \cdot \text{M}^{II}\text{Cl}_2$ . The prep. of such compounds is described in the cases where  $\text{M}^{II} = \text{Mn}^{II}$ ,  $\text{Sn}^{II}$ , or  $\text{Fe}^{II}$ . The compounds  $3\text{CdCl}_2 \cdot \text{ZnCl}_2 \cdot 8\text{H}_2\text{O}$  and  $2\text{HgCl}_2 \cdot 5\text{ZnCl}_2 \cdot 12\text{H}_2\text{O}$  are described. E. S. H.

**Chloro-complex salts of bivalent copper.** H. REMY and G. LAVES (Ber., 1933, 66, [B], 401—407).—The following salts have been prepared by admixture of solutions of their components in hot  $\text{H}_2\text{O}$ :  $[\text{NH}_3\text{Me}]_2[\text{CuCl}_4]$ , m.p. (indef.)  $248^\circ$ ;  $[\text{NH}_3\text{Et}]_2[\text{CuCl}_4]$ , m.p.  $249^\circ$ ;  $[\text{NH}_3\text{Pr}^n]_2[\text{CuCl}_4]$ , m.p. (indef.)  $242^\circ$ ;  $[\text{NH}_3\text{Bu}]_2[\text{CuCl}_4]$ , m.p.  $250$ — $251^\circ$ ;  $[\text{NH}_2\text{Me}_2][\text{CuCl}_3]$ ,  $[\text{NH}_2\text{Me}_2]_2[\text{CuCl}_4]$ , and  $[\text{NH}_2\text{Me}_2]_3[\text{CuCl}_5]$ ;  $[\text{NHMe}_3][\text{CuCl}_3] \cdot 2\text{H}_2\text{O}$  and  $[\text{NHMe}_3][\text{CuCl}_3]$ , m.p. about  $158^\circ$ ;  $[\text{NHMe}_3]_2[\text{CuCl}_5]$ , m.p.  $201^\circ$ ;  $[\text{NHMe}_3][\text{CuCl}_4]$ ;  $[\text{NHMe}_3]_3[\text{Cu}_2\text{Cl}_7]$ ;  $[\text{NHMe}_4]_2[\text{CuCl}_4]$ ;  $[\text{NH}_3\text{Pr}^n][\text{CuCl}_3]$ , m.p. about  $190^\circ$  (decomp.);  $[\text{NH}_3\text{Pr}^n]_2[\text{CuCl}_4]$ , m.p. about  $154^\circ$  after darkening at  $55$ — $60^\circ$ . The region of existence is greatest for the salts with the complex for which the max. energy of formation is calc. H. W.

**Changes in properties of chemical compounds due to complex formation. VIII. Compounds of boron fluoride and the synthetic application of boron fluoride.** H. MEERWEIN (Ber., 1933, 66, [B], 411—414).— $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ , b.p.  $46^\circ/1$  mm., f.p.  $46$ — $5^\circ$ , is obtained by passing  $\text{BF}_3$  (1 mol.) into  $\text{H}_2\text{O}$  (2 mols.). It is strongly acidic, dissolves metals, their hydroxides and carbonates, and decomposes  $\text{CHN}_2 \cdot \text{CO}_2\text{Et}$  explosively. It adds olefines and is characterised by cryst. *dioxan*,  $\text{BF}_3 \cdot 2\text{H}_2\text{O} \cdot \text{C}_4\text{H}_8\text{O}_2$ , m.p.  $142^\circ$ , and *cineole*,  $\text{BF}_3 \cdot 2\text{H}_2\text{O} \cdot (\text{C}_{10}\text{H}_{18}\text{O})_2$ , m.p.  $59.5$ — $61^\circ$ , salts. It adds  $\text{BF}_3$  yielding  $\text{BF}_3 \cdot \text{H}_2\text{O}$ , f.p.  $5.4$ — $6^\circ$ , not volatile without decomp. The following compounds with aliphatic alcohols are described:  $\text{BF}_3 \cdot 2\text{MeOH}$ , b.p.  $58$ — $59^\circ/4$  mm.,  $\text{BF}_3 \cdot 2\text{EtOH}$ , b.p.  $51$ — $52^\circ/1.5$  mm.;  $\text{BF}_3 \cdot 2\text{Pr}^n\text{OH}$ , b.p.  $56^\circ/2$  mm.;  $\text{BF}_3 \cdot 2\text{BuOH}$ , b.p.  $64$ — $65^\circ/3$  mm.;  $\text{BF}_3 \cdot 2\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{OH}$ , b.p.  $59^\circ/2$  mm.;  $\text{BF}_3 \cdot \text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , m.p.  $40$ — $42^\circ$ . Compounds with primary alcohols are volatile in vac. without decomp.; those with sec. alcohols yield  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$  and partly polymerised olefine. The dialcoholates are strongly acidic and conduct electricity in  $\text{PhNO}_2$ . In the cold they absorb  $\text{BF}_3$ , giving compounds  $\text{BF}_3 \cdot \text{ROH}$ , not volatile without decomp. Salts  $\text{BF}_3 \cdot \text{ROX}$  are obtained by addition of  $\text{BF}_3$  to alkali alkoxides. With acids,  $\text{BF}_3$  yields the types  $\text{BF}_3 \cdot 2\text{RCO}_2\text{H}$  (those derived from the simple acids of the acetic series are liquid and distillable in vac.) and  $\text{BF}_3 \cdot \text{RCO}_2\text{H}$ , solid and losing half the combined  $\text{BF}_3$  when heated. Stability of the compounds decreases with increasing strength of the org. acid;  $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$  loses its combined  $\text{BF}_3$  completely at  $80^\circ/\text{vac.}$ , whilst  $\text{CHCl}_2 \cdot \text{CO}_2\text{H}$  absorbs  $\text{BF}_3$  only below  $-15^\circ$ , and loses it completely at room temp., and  $\text{CCl}_3 \cdot \text{CO}_2\text{H}$  does not unite with  $\text{BF}_3$ .  $\text{BF}_3$  and cold  $\text{Ac}_2\text{O}$  afford the compound  $(\text{CHAc}_2 \cdot \text{CO})_2\text{O} \cdot 3\text{BF}_3$ , m.p.  $192$ — $193^\circ$ , smoothly transformed by warm water into  $\text{CO}_2$  and  $\text{CH}_2\text{Ac}_2$ . With  $(\text{EtCO})_2\text{O}$ ,  $(\text{PrCO})_2\text{O}$ , and  $(\text{CHMe}_2 \cdot \text{CO})_2\text{O}$  production of diacyl derivatives recedes in favour of the monoacyl compounds,  $(\text{COR} \cdot \text{CHR} \cdot \text{CO})_2\text{O} \cdot 3\text{BF}_3$ , which yield mainly monoketones with relatively small amounts of  $\beta$ -diketones. In many respects the action of  $\text{BF}_3$  resembles that of  $\text{AlCl}_3$ . Thus  $\text{PhMe}$ ,  $\text{PhOMe}$ , and  $\text{PhOH}$  with  $\text{Ac}_2\text{O}$  and  $\text{BF}_3$  afford  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{Me}$  (*p*),  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , and  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , respectively.  $\text{CHMe}(\text{OAc})_2$  and  $\text{PhOMe}$  give  $\alpha\alpha$ -dianisylethane.  $\text{PhOH}$  and  $\text{AcOH}$  or  $\text{EtOAc}$  yield  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ .  $\text{COMePh}$  and  $\text{Ac}_2\text{O}$  afford  $\text{CH}_2\text{AcBz}$  in 85% yield. *cyclo*Hexanone and  $\text{Ac}_2\text{O}$  yield 2-acetyl*cyclo*hexanone. *Me styryl* ketone and  $\text{Ac}_2\text{O}$  give  $\alpha$ -phenyl- $\Delta^a$ -hexene- $\gamma\epsilon$ -dione.  $\text{BF}_3$  causes the benzidine transformation, conversion of diazoamino- into aminoazo-benzene, of  $\text{PhOAc}$  into  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , and the Beckmann change.

H. W.  
**Preparation of metallic praseodymium.** G. CANNERI and A. ROSSI (Gazzetta, 1932, 62, 1160—1163).—A max. yield of Pr was obtained by the electrolysis of a fused mixture (m.p.  $535^\circ$ ) of 55%  $\text{PrCl}_3$ , 27%  $\text{NaCl}$ , and 18%  $\text{KCl}$ , using a W cathode and Acheson graphite anode. The temp. must be kept  $< 600^\circ$  to avoid polarisation and formation of  $\text{PrO}_2$ . The Pr contains  $< 0.2\%$  of other rare-earth metals and only traces of Si and C;  $d$   $6.765 \pm 0.008$ , m.p.  $932 \pm 2^\circ$ . O. J. W.

**Thallium iodides.** R. LYDÉN (Finska Kem. Medd., 1932, 41, 34—53).—TII reacts with I in EtOH giving  $TlI_3$  (sol. in presence of excess of I) and ppts.  $Tl_3I_4$  ( $Tl_6I_8$ ?) alone or mixed with TII. In  $H_2O$   $Tl_3I_4$  is formed as black a ppt.  $TlCl$  (or  $K_3TlCl_6$ ) and aq. I ppts. higher Tl iodides of varying composition, and forms in solution I and  $K_3TlCl_6$ .  $K_3TlCl_6$  is decomposed partly by  $H_2O$  giving I and higher Tl iodides, but is stable in presence of excess of I. Higher Tl iodides and KI give I and  $K_3TlCl_6$ .

R. P. B.

**Ammines of lower chlorides of titanium.** W. C. SCHUMB and R. F. SUNDSTRÖM (J. Amer. Chem. Soc., 1933, 55, 596—604; cf. A., 1923, ii, 868).—Anhyd.  $TiCl_3$  is dimorphous. Anhyd.  $TiCl_2$  decomposes slowly in vac. at  $475^\circ$  forming  $TiCl_4$  and Ti. Contrary to Meyer and others (A., 1923, ii, 769),  $TiCl_2$  is non-volatile in the range  $300$ — $600^\circ$ .  $TiCl_3$  combines with  $NH_3$  at low temp. to form a white *hexammine* which loses  $4NH_3$  at  $300^\circ$ , giving a black residue, probably a *diammine*, which ignites on exposure to air. At low temp.,  $TiCl_2$  forms with  $NH_3$  a pearl-grey *tetrammine* which, at  $300^\circ$ , loses  $NH_4Cl$  leaving a black nitride (?).

J. G. A. G.

**Phosphorescence of zirconium oxide preparations.** K. HOLZINGER.—See B., 1933, 188.

**Preparation of  $HNO$  or  $[HNO]_n$ .** P. HARTECK (Ber., 1933, 66, [B], 423—426).— $NO$  is passed at the temp. of liquid air into a stream of  $H_2$  at 0.5 mm. split into atoms to the extent of 60%, whereby, when wide vessels are used to avoid explosions, the product ( $H:N:O=1:1\pm 10\%:1$ ) separates as a pale yellow, translucent deposit on the walls; it is precisely similar to that formed from  $NH_3$  and  $O$ , so that identity is assumed. When the temp. is very gradually raised, the deposit becomes white; decomp. commences at  $-95^\circ$ , and thence to room temp. is accompanied by evolution of  $N_2O$  with traces of  $H_2$  and  $NO$ . Small local explosions occasionally caused marked evolution of the latter gases. Analysis shows the product to be mainly hyponitrous acid, accompanied, however, by nitroamide.

H. W.

**Additive compound of vanadium tetrachloride and sulphur tetrachloride.** G. CANNARI and R. SALANI (Gazzetta, 1932, 62, 1164—1165).—By the action of dry  $Cl_2$  on  $V_2S_5$  or on a mixture of  $SCl_2$  and  $VCl_4$  black crystals of the compound  $VCl_4 \cdot SCl_4$ , m.p.  $32^\circ$  (approx.), are obtained.

O. J. W.

**Autoxidation. III. Initial act in autoxidation.** H. N. STEPHENS (J. Physical Chem., 1933, 37, 209—217).—Theoretical. A crit. discussion of published work indicates that the formation of the intermediate peroxide in autoxidation reactions does not consist of two stages, but is a single act.

E. S. H.

**Oxidation of sodium hyposulphite by free oxygen.** M. NICLOUX (Compt. rend., 1933, 196, 616—618).— $Na_2S_2O_4$  acts as a reducer in three ways: (a)  $2Na_2S_2O_4 + O_2 + 2H_2O = 4NaHSO_3$ ; (b)  $Na_2S_2O_4 + O_2 + H_2O = NaHSO_3 + NaHSO_4$ ; and (c)  $2Na_2S_2O_4 + 3O_2 + 2H_2O = 4NaHSO_4$ . (a) occurs when it removes O from a substance containing it, (b) when in contact with free  $O_2$ , and (c) when treated with an energetic

oxidiser. (b) applies also to the action of  $Na_2S_2O_4$  on oxyhæmoglobin, and enables its amount to be determined (cf. A., 1873, 936; 1903, ii, 225).

C. A. S.

**Aqueous solutions of thiocyanate- $SO_2$  complexes.** C. J. HANSEN (Ber., 1933, 66, [B], 447—450).—Thiocyanates, including HCNS, add  $SO_2$  in  $H_2O$ , the mol. proportion rising to about 1:2 near the f.p. of the solution. The compounds are very freely sol. in  $H_2O$ . The solutions have marked  $SO_2$  tension and, when evaporated, leave the homogeneous thiocyanate. Thiocyanate solutions are suitable for the absorption of  $SO_2$  from the gases obtained by roasting sulphides. The thiocyanate- $SO_2$  solutions very readily remove  $H_2S$  from its mixtures with pptn. of S. The behaviour of  $NH_4$ , K, Na, Ca, Ba, and H thiocyanates is described in detail.

H. W.

**Preparation of molybdenum oxide and some sulphides (molybdenum, tellurium, arsenic) in the crystalline state.** L. DEBUCQUET and L. VELLUZ (Bull. Soc. chim., 1932, [iv], 51, 1571—1572).—Cryst.  $MoO_3$  is obtained by igniting  $MoS_3 \cdot C_4H_{10}N_2 \cdot H_2S$  (cf. this vol., 401). Cryst.  $MoS_3$ ,  $TeS_2$ ,  $As_2S_3$ , or  $As_2S_5$  is obtained when the corresponding compound with piperazine is treated with cold, dil. HCl or AcOH.

E. S. H.

**Polyhalides. IV. Reactions in absence of a solvent.** H. W. CREMER and D. R. DUNCAN (J.C.S., 1933, 181—189).—The action of various gases and vapours on solid polyhalides has been investigated. In some cases the polyhalide reacts as such; in others, dissociation into monohalide and halogen or halogen halide occurs prior to reaction (cf. action of  $NH_3$ , A., 1931, 182). The reactions between polyhalides and halogens or halogen halides are explained on this basis.  $O_3$  acts on  $KIBr_2$  thus:  $KIBr_2 + O_3 = KIO_3 + Br_2$ . Amines form additive compounds with polyhalides. The action of a halogen or halogen halide on a monohalide may follow one of three courses: (1) reversible direct addition (e.g.,  $CsBr + IBr \rightleftharpoons CsIBr_2$ ); (2) irreversible direct addition (e.g.,  $CsI + Br_2 \rightarrow CsIBr_2$ ); (3) irreversible replacement, often followed by a reversible additive reaction (e.g.,  $2KI + Br_2 \rightarrow 2KBr + I_2$ ;  $I_2 + Br_2 \rightleftharpoons 2IBr$ ;  $KBr + IBr \rightleftharpoons KIBr_2$ ; all the iodides investigated, except  $CsI$ , reacted in this way). The formation of any polyhalide from its dissociation products follows course (1), the reaction  $CsBr + Cl_2 \rightarrow CsBrCl_2$  follows course (2), and  $KI + 2Cl_2 \rightarrow KICl_4$ ,  $KI + 2ICl \rightarrow KICl_2 + I_2$ , and  $RBr + 2ICl \rightarrow RICl_2 + IBr$  ( $R = Cs$  or  $K$ ) follow course (3). Velocity data are given and certain generalisations deduced. None of the reported cases of isomerism ( $CsICl_2$ ,  $CsIBr_2$ , and  $RbBrCl_2$ , cf. A., 1892, 773; 1917, ii, 531) can be confirmed.

D. R. D.

**Working up iodine residues.** G. A. STUTTERHEIM (Chem. Weekblad, 1933, 30, 166).—The  $Cu_2O$  recovered in van Voorst's method (A., 1931, 448, 1022) is preserved out of contact with air and re-used to work up fresh residues.

S. C.

**Reduction and oxidation of manganese silicates.** B. BOGITCH (Compt. rend., 1933, 196, 414—416; cf. A., 1929, 400, 1409).—Mn silicates at  $1300^\circ$  in presence of a reducing (e.g.,  $CO$ ,  $H_2$ ) or

neutral (e.g.,  $\text{CO}_2$ ,  $\text{N}_2$ ) gas are reduced to  $\text{Mn}^{\text{II}}$  silicates which are colourless with  $< 4\%$   $\text{MnO}$  and with more are green. In presence of  $\text{O}_2$  a violet  $\text{Mn}^{\text{III}}$  silicate is formed, the tint being the deeper the greater is the excess of  $\text{O}$ . Na silicates fused with  $\text{Mn}_2\text{O}_4$  evolve  $\text{O}_2$  at the moment of fusion, forming a frothy mass, but the  $\text{O}_2$  is reabsorbed on cooling, the amount of  $\text{O}_2$  retained being the smaller the higher is the temp. and the greater the duration of fusion. Na silicates rich in Mn when powdered absorb  $\text{O}_2$  rapidly above  $200^\circ$ ; on fusion these retain the less  $\text{O}_2$  the less Mn is present, the higher the temp. of fusion, and the less is the  $\text{O}_2$  in the atm. C. A. S.

Formation of alkali-soluble substances in the carbon monoxide reaction on iron. T. BAHR (Ges. Abhandl. Kenntn. Kohle, 1932, 10, 160—163; Chem. Zentr., 1932, ii, 2805—2806).—The C deposited at  $400$ — $600^\circ$  contains substances similar to humic acid. A. A. E.

Magnetic iron oxide and its hydrate. O. BAUDISCH (Biochem. Z., 1933, 258, 69—75; cf. A., 1932, 709).—Improved methods of preparing  $\gamma$ - $\text{Fe}_2\text{O}_3$  and its hydrate from purest Fe (from Fe carbonyl) and purest HCl ( $\text{FeCl}_2$  and  $\text{FeCl}_3$ ) by pptn. with  $\text{C}_5\text{H}_5\text{N}$  and the magnetic and other physical properties of these compounds are described. Dehydration of the hydrate at  $250$ — $270^\circ$  gives a strongly magnetic oxide, but if heating at this temp. is continued for 12—24 hr. the magnetic property disappears. W. McC.

Determination of hydrogen by combustion. A. J. ANTHONY (Z. Biol., 1933, 93, 405—406).—Combustion is effected in a 1-c.c. glass chamber containing a Pt spiral, 10—12 mm. long, of 0.2 mm. diam. wire. When a small current is passed through the wire the KOH level in the final absorption vessel, to which the combustion chamber is sealed by capillary tubing, falls owing to expansion of the gas, and then rises as combustion begins. The current is then increased until the spiral glows, and the gas is allowed to pass. By following in this manner the initiation of the combustion, the danger of explosion is greatly reduced. H. F. G.

Stick antimony electrode for the measurement of hydrogen-ion concentration. T. UEMURA and H. SUEDA (Bull. Chem. Soc. Japan, 1933, 8, 1—10).—The stick Sb electrode in an unstirred solution in contact with air gives trustworthy  $p_{\text{H}}$  vals. for  $p_{\text{H}}$  1—9 and approx. vals. for  $p_{\text{H}}$  9—12, the e.m.f. against a  $\text{Hg}_2\text{Cl}_2$  electrode being approx.  $(53.8p_{\text{H}} - 0.7) \times 10^{-3}$  volt. The e.m.f. increases with rise of temp. The surface of the electrode turns black in solutions of  $p_{\text{H}}$  1—8 and whitish in solutions of  $p_{\text{H}}$  9—12. Some time is required in order to establish equilibrium with the solution. The concn. of  $\text{Sb}_2\text{O}_3$  has only a slight effect on the e.m.f. J. W. S.

Potentiometric analysis. W. HILTNER (Chem. Fabr., 1933, 6, 111—113).—Details are given of a thermionic valve potentiometer in which a double grid valve is employed. The potential to be measured is applied across the two grids and the reading of a milliammeter connected across the two plates is observed, the reading when a Weston cell is connected

to the grids being taken as standard. Suitable electrodes are described. H. F. G.

Detection of hydrogen peroxide by means of spot reactions. F. FEIGL and E. FRAENKEL (Mikrochem., 1933, 12, 303—306).—Formation of Prussian-blue from  $\text{Fe}^{\text{III}}$  ferricyanide solution detects  $0.08 \times 10^{-6}$  g.  $\text{H}_2\text{O}_2$ . Bleaching of Ni oxides (used as paste of  $\text{Ni}_2\text{O}_3$  and  $\text{BaSO}_4$ ) detects  $0.01 \times 10^{-6}$  g. Yellow coloration with alkali vanadate paper detects  $3 \times 10^{-6}$  g. Warming with a drop of 0.01%  $\text{AuCl}_3$  gives red or blue colloidal Au, sensitive to  $0.07 \times 10^{-6}$  g. Warming with acidified 5%  $\text{NH}_4\text{SCN}$  gives an orange ppt. or coloration, sensitive to  $0.7 \times 10^{-6}$  g. J. S. A.

Gravimetric separation of chlorine, bromine, and iodine. G. BÜRGER (Z. anal. Chem., 1933, 92, 19—23).—The halogens in one portion of the sample are all pptd. and weighed as Ag salts. I<sup>-</sup> is removed from another portion by oxidation to I<sup>+</sup> with  $\text{KIO}_3$  in presence of  $\text{H}_2\text{SO}_4$  and Cl<sup>-</sup> and Br<sup>-</sup> are then pptd. as Ag salts and weighed. This mixture is next transformed into AgBr or AgI by calcining with the corresponding  $\text{NH}_4$  salt and again weighed. From these data the proportion of the different Ag salts in the mixture, and hence of halogens in the original product, may be determined indirectly. A "cella" filter is recommended. M. S. B.

Determination of periodic acid in presence of iodic acid. P. FLEURY and J. LANGE (J. Pharm. Chim., 1933, [viii], 17, 107—113).—(1) 5—25 c.c. aq.  $\text{IO}_4^-$  neutral to phenolphthalein, representing not more than 5—6 c.c. 0.1M- $\text{HIO}_4$ , is mixed with 5—10 c.c. of saturated aq.  $\text{NaHCO}_3$ , 15 c.c. of 0.1N- $\text{H}_3\text{AsO}_3$  containing  $\text{NaHCO}_3$ , and 1 c.c. of 20% aq. KI to act as catalyst. After 15 min. at room temp. the excess of  $\text{H}_3\text{AsO}_3$  is titrated with 0.1N-I.  $\text{HIO}_4$  only, and not  $\text{HIO}_3$ , is reduced. (2) 10 c.c. of the neutralised  $\text{HIO}_4$  and  $\text{HIO}_3$  solution, equiv. to  $\approx 3$  g. 0.1N- $\text{HIO}_4$ , is mixed with 3 c.c. of 14.3% aq.  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  and 10 c.c. of 1% aq.  $\text{MnSO}_4$ , the ppt. is centrifuged, the liquid decanted, and the oxidised Mn ppt. washed by centrifuging, using 5% aq.  $\text{Na}_2\text{SO}_4$  to prevent peptisation. 2 c.c. 20% aq. KI and 0.4—0.5 c.c. 20%  $\text{H}_2\text{SO}_4$  are added to the ppt., which dissolves, liberating I and  $\text{CO}_2$ . The former is titrated with 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$  without addition of starch. 3% should be subtracted from the result. M. S. B.

Reagent for determination of oxygen. V. I. PANASIUK (Ukrain. Chem. J., 1932, 7, [Sci.], 94—97).—Pyrogallol is replaced by a solution of 35.4 g. of  $\text{FeSO}_4$  in 120 c.c. of  $\text{H}_2\text{O}$ , to the filtrate from which 10 g. of tartaric acid and 45 c.c. of 25% aq.  $\text{NH}_3$  are added. R. T.

Determination of ozone by absorption measurements, using the photoelectric cell. R. RUYSSSEN (Natuurwetensch. Tijds., 1933, 15, 6—13, and Bull. Acad. roy. Belg., 1932, [v], 18, 1085—1094).—The max. in the visible absorption band of  $\text{O}_3$  coincides approx. with the D line. Apparatus for determining  $\text{O}_3$  at concns. of 2—5% by measuring the absorption of a 100 cm. layer by means of a Na lamp and a K photoelectric cell is described. The absorption coeff. for the D line is  $3.94 \times 10^{-4}$ , the max. deviation being about 2%. H. F. G.



**Potentiometric determination of sulphates by indirect titration with benzidine.** I. A. ATANASIU and A. J. VELCULESCU (Z. anal. Chem., 1932, 90, 337—340; cf. A., 1932, 955).—A standard solution of benzidine in dil. HCl is added in excess to a solution of the sulphate, and the excess of benzidine in the filtrate is determined potentiometrically by titration with  $\text{KNO}_3$ . The error is within 0.0006 g. in 0.01—0.12 g.  $\text{H}_2\text{SO}_4$ . F. L. U.

**Volumetric and potentiometric determination of tri- and tetra-thionate by means of silver nitrate.** F. ISHIKAWA and T. MUROOKA (Sci. Rep. Tôhoku, 1932, 21, 527—536).—Reaction between  $\text{AgNO}_3$  and a tri- or tetra-thionate takes place quantitatively: (1)  $\text{S}_x\text{O}_6^{2-} + 2\text{Ag}^+ = \text{Ag}_2\text{S}_x\text{O}_6$ , and (2)  $\text{Ag}_2\text{S}_x\text{O}_6 + 2\text{H}_2\text{O} = \text{Ag}_2\text{S} + 2\text{H}_2\text{SO}_4 + (x-3)\text{S}$ , where  $x=3$  or 4, respectively. These reactions can be used for the volumetric and potentiometric titration of the polythionates. O. J. W.

**Dumas technique for substances difficult to burn.** J. F. CROUCH (J. Amer. Chem. Soc., 1933, 55, 852—853).—The substance is mixed with a large excess of CuO and packed into a Cu tube 15 cm. long and 1 cm. in diameter, and the whole is placed in the position usually occupied by the combustion boat. J. G. A. G.

**Antimony electrode. V. Electrometric micro-determination of "formol"-titratable nitrogen with the antimony electrode.** A. ROCHE and J. ROCHE (Arch. Phys. biol. Chim.-Phys., 1932, 9, 273—276; Chem. Zentr., 1932, ii, 2489).—The neutral solution is brought to  $p_{\text{H}}$  8.3 with slightly alkaline  $\text{CH}_2\text{O}$ , when  $(\text{CH}_2)_6\text{N}_4$  and  $\text{NH}_2$ -acids are formed from the  $\text{NH}_3$ , but visual titration cannot be employed in presence of hydrolysed protein-N compounds or when only traces of N are present. By means of the Sb electrode  $\pm 0.05$  mg. N can be determined ( $\pm 1\%$  for  $> 1$  mg.,  $\pm 1$ — $2\%$  for 0.1—1 mg.,  $\pm 3$ — $4\%$  for 0.1—0.05 mg.). A. A. E.

**Acidimetric determination of alkali nitrites.** B. STEMPEL (Z. anal. Chem., 1933, 91, 413—415).—A measured excess of standard aq.  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  is heated with the neutral nitrite solution. The excess is then titrated with NaOH in presence of  $\text{CH}_2\text{O}$  (see below). F. L. U.

**Potentiometric investigation of the oxidimetric determination of hydrazine.** O. STELLING (Svensk Kem. Tidskr., 1933, 45, 4—9).— $\text{N}_2\text{H}_4$  and  $\text{KMnO}_4$  do not react quantitatively according to the equation  $\text{N}_2\text{H}_4 + \text{O}_2 = \text{N}_2 + 2\text{H}_2\text{O}$  (cf. Kolthoff, A., 1924, ii, 871). In dil. aq.  $\text{H}_2\text{SO}_4$  less, in HCl more,  $\text{KMnO}_4$  than the theoretical reacts. Side reactions are prevented by adding KI in acid solution before titrating, when three sudden potential changes are found, corresponding with  $\text{N}_2\text{H}_4 \rightarrow \text{N}_2$ ,  $\text{I}^- \rightarrow \text{I}$ , and  $\text{I} \rightarrow \text{ICl}$ . After correcting the  $\text{KMnO}_4$  titre for the amount used by the KI, quant. results are obtained. KBr has no effect, and titration in alkaline solution cannot be used.  $\text{N}_2\text{H}_4$  and I react quantitatively in  $\text{NaHCO}_3$  solution (cf. Gilbert, A., 1925, ii, 239) and the reaction can be followed potentiometrically.  $\text{KBrO}_3$  reacts quantitatively with  $\text{N}_2\text{H}_4$  in hot HCl solution and the reaction is specially suited to potentiometric titration.

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$\text{N}_2\text{H}_4$  and  $\text{KIO}_3$  give I in  $\text{H}_2\text{SO}_4$  solution and ICl in HCl solution. R. P. B.

**Formaldehyde titration of hydrazine sulphate.** B. STEMPEL (Z. anal. Chem., 1933, 91, 412).— $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ , when titrated with NaOH in presence of neutral  $\text{CH}_2\text{O}$ , behaves as a dibasic acid. Neutral EtOH produces the same effect. F. L. U.

**Determination of phosphorus in aluminium.** K. STEINHÄUSER and J. STADLER.—See B., 1933, 194.

**Rapid determination of boric acid in arsenic-free borosilicates.** W. MYLIUS (Chem.-Ztg., 1933, 57, 173—175, 194—195).—The powdered sample (0.5 g.) is heated with KOH+NaOH at about 500° for 6—7 min., and the melt is dissolved in 75 c.c. of  $\text{H}_2\text{O}$ . The solution is rendered slightly acid (Congored), and saturated aq.  $\text{Ba(OH)}_2$  is added to ppt.  $\text{CO}_3^{2-}$ ,  $\text{SiO}_2$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ , etc.; the ppt. is redissolved and repptd. twice, to free it from  $\text{B}_2\text{O}_3$ , and the combined filtrate is titrated with  $\text{Ba(OH)}_2$  after addition of fructose. If the sample is a Zn borosilicate,  $\text{K}_3\text{Fe(CN)}_6$  should be used to ensure removal of all the zinc. The error is  $\pm 0.05\%$  on the wt. of the sample. H. F. G.

**Determination of potassium by titration of the cobaltinitrite with potassium permanganate.** P. L. HIBBARD and P. R. STOUT (J. Assoc. Off. Agric. Chem., 1933, 16, 137—140).—The material (0.2—2.0 mg. K) is freed from org. matter and the K pptd. as  $\text{K}_3\text{Co(NO}_2)_6$  from AcOH solution. After 12—15 hr. the ppt. is collected on a talc-covered filter, washed, and added to excess of acidified  $\text{KMnO}_4$ , the excess of which is reduced with standard  $\text{Na}_2\text{C}_2\text{O}_4$  and titrated back with  $\text{KMnO}_4$ . J. W. S.

**Recovery of platinum in potash determinations.** L. D. HAIGH and A. R. HALL (J. Assoc. Off. Agric. Chem., 1933, 16, 147—148).—Residues are treated with conc.  $\text{NH}_4\text{Cl}$ ; the  $(\text{NH}_4)_2\text{PtCl}_6$  is collected and combined with  $\text{K}_2\text{PtCl}_6$  residues. These ppts. are dissolved in hot  $\text{H}_2\text{O}$ , 5 vol.-% of conc. HCl is added, and pieces of mossy or granular pure Zn are added until no more Pt is pptd. Base metals are removed with HCl and the Pt is dissolved in aqua regia and converted into  $\text{H}_2\text{PtCl}_6$  in the usual way. J. W. S.

**Conductometric and electrometric titration of mixtures of sodium hydroxide and carbonate.** M. AUMÉRAS and J. MARCON (Bull. Soc. chim., 1932, [iv], 51, 1594—1605).—Titration with HCl by the conductometric method indicates the neutralisation points of NaOH,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaHCO}_3$ , and gives satisfactory results in dil. solutions. The influence of dissolved  $\text{CO}_2$  has been examined and the observations provide a means of determining small amounts of free  $\text{CO}_2$ . The electrometric method, using the H electrode, is less accurate and is suitable only when the concn. of the solution is  $> 0.01N$ . E. S. H.

**Photographic sensitivity of lines of alkali metals in the oxy-acetylene flame.** R. BOSSUET (Compt. rend., 1933, 196, 469—470; cf. A., 1932, 825).—The method previously described is rendered more sensitive by using rapid panchromatic plates and a Bourguet spectrograph. The most sensitive line and min. amount of the chloride detectable are:

for Li 6708,  $3 \times 10^{-7}$  mg.; Na 5890 and 5896, traces; K 4044,  $1.3 \times 10^{-3}$  mg.; Rb 4216,  $10^{-3}$  mg.; Cs 4555,  $10^{-3}$  mg. C. A. S.

**Potentiometric determination of free alkali hydroxide in phenoxides.** V. A. KARGIN and M. I. USANOVICH.—See B., 1933, 215.

**Quantitative analysis of calcite-aragonite mixtures by X-rays.** E. G. COX and T. H. GOODWIN (Chem. and Ind., 1933, 172).—Relative intensities of calcite and aragonite lines in X-ray photographs of the mixture by the powder method give the proportions with an accuracy of  $\pm \frac{1}{2}\%$  to 2%, according to the composition. H. J. E.

**Volumetric determination of calcium oxide in lime.** I. TANANAEV.—See B., 1933, 226.

**Determination of calcium oxide in magnesium compounds.** P. ACKERMANN.—See B., 1933, 226.

**Rapid determination of calcium in phosphorite and limestone.** S. N. ROSANOV and A. G. FILIPPOVA (Z. anal. Chem., 1932, 90, 340—350).—For routine analysis the methods of Chapman (B., 1929, 142) and of Passon (A., 1898, ii, 642; 1899, ii, 246) are shown to be suitable and nearly as accurate as the standard methods. F. L. U.

**Separation of the cations of the alkali, alkaline-earth, and ammonium sulphide groups.** A. P. KRĚŠČKOV (Z. anal. Chem., 1933, 92, 92—95).—A strongly ammoniacal solution of the cations is treated with  $(\text{NH}_4)_3\text{PO}_4$ , when pptd. are obtained of  $\text{FePO}_4$ ,  $\text{AlPO}_4$ ,  $\text{CrPO}_4$ ,  $\text{Mn}(\text{NH}_4)\text{PO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Sr}_3(\text{PO}_4)_2$ ,  $\text{Ba}_3(\text{PO}_4)_2$ , and  $\text{Mg}(\text{NH}_4)\text{PO}_4$ , whilst  $[\text{Ni}^{II}(\text{NH}_3)_6]^{++}$ ,  $[\text{Co}^{II}(\text{NH}_3)_6]^{++}$ ,  $[\text{Zn}^{II}(\text{NH}_3)_6]^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$  remain in solution. The latter are separated in the usual way. A solution of the ppt. in a little dil. HCl is almost neutralised, NaOAc and  $\text{FeCl}_3$  are added until it is reddish-brown, and it is diluted, boiled, and filtered. This removes  $\text{PO}_4^{---}$ ,  $\text{Fe}^{+++}$ ,  $\text{Cr}^{+++}$ , and  $\text{Al}^{+++}$ , and these, and the cations in solution, can be separated by any method. J. W. S.

**Precipitation and determination of calcium in the presence of Ag, Hg, Pb, Cu, Bi, Cd, As, Sb, Sn, Co, Ni, Fe, Al, Mn, and Zn.** E. ERDHEIM (Rocz. Chem., 1933, 13, 64—69).—25 c.c. of a solution of 100 g. of citric acid and 350 c.c. of aq. 25%  $\text{NH}_3$  in 650 c.c. of  $\text{H}_2\text{O}$  are added to the acid solution under examination, followed by 10 drops of aq.  $\text{NH}_3$ . The vol. is made up to 250 c.c., and 1 g. of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  is added to the boiling solution, pptd.  $\text{CaC}_2\text{O}_4$  is dissolved in  $\text{H}_2\text{SO}_4$ , and the solution is titrated with  $\text{KMnO}_4$ . Under these conditions, salts of the above heavy metals do not interfere;  $\text{Cr}^{+++}$ , if present, should first be removed, and  $\text{Fe}^{++}$  should be oxidised to  $\text{Fe}^{+++}$ . The experimental error is  $> 1\%$ . R. T.

**Occlusion by precipitates.** B. TEŽAK (Bull. Soc. Chim. Yougoslav., 1932, 3, 147—156).—The  $\text{BaCl}_2$  content of  $\text{BaSO}_4$  pptd. from aq.  $\text{Na}_2\text{SO}_4$  by  $\text{BaCl}_2$  varies periodically with the concn. of  $\text{Na}_2\text{SO}_4$ ; this effect is ascribed to differences in adsorptive power for  $\text{BaCl}_2$  of particles of  $\text{BaSO}_4$  in different stages of aggregation. R. T.

**Semi-micro- and micro-determination of magnesium.** A. BLANCHETIÈRE and M. ARNOUX (J.

Pharm. Chim., 1933, [viii], 17, 97—107).—A white cryst. ppt. of  $\text{MgI}_2 \cdot 10\text{H}_2\text{O} \cdot 2(\text{CH}_2)_6\text{N}_4$  is obtained by the action of  $(\text{CH}_2)_6\text{N}_4$  on aq.  $\text{MgSO}_4$  in presence of excess of KI after all other cations except alkalis and alkaline earths have been removed. The solution must be neutral or slightly acid with AcOH, and  $\text{PO}_4^{---}$  must be absent. Pptn. must take place at a low temp., about  $8^\circ$ , as solubility increases fairly rapidly with rise of temp. After filtering on a micro-filter, washing with  $\text{COMe}_2$  saturated with the product, and then with  $\text{CHCl}_3$ , the compound is redissolved in  $\text{H}_2\text{O}$  and the amount determined either by (1) titrating I<sup>-</sup> with  $\text{AgNO}_3$  by adding excess and titrating the excess with  $\text{NH}_4\text{CNS}$ , or (2) boiling with an excess of  $\text{H}_2\text{SO}_4$  to decompose  $(\text{CH}_2)_6\text{N}_4$  and titrating the excess acid with NaOH using K alizarinsulphonate as indicator. The latter method gives more consistent results. The concn. of Ca must not exceed 0.2 mg. per c.c. of solution to be analysed. M. S. B.

**Volumetric determination of lead.** A. TRAVERS and LU (Compt. rend., 1933, 196, 548—549).—Determination of Pb as  $\text{PbSO}_4$  in presence of Bi or Ba is unsatisfactory; a satisfactory method is to bring the Pb into neutral solution and boil with aq. NaOCl, whereby the Pb is pptd. as  $\text{PbO}_2$ , which is determined iodometrically. To analyse a Pb-Bi or Pb-Bi-Cd alloy the Bi is separated as basic formate (cf. A., 1928, 388), and the Cd remaining with the Pb is converted into  $\text{Cd}(\text{OH})_2$  by the NaOCl, and then dissolved out by aq.  $\text{NH}_3$  free from  $\text{CO}_2$  (cf. A., 1931, 453). Pb is quantitatively separated from Ba as PbS by saturating the solution under pressure with  $\text{H}_2\text{S}$ , and then heating for 2 hr. at  $100^\circ$ . C. A. S.

**$\beta$ -Naphthol test for copper.** C. C. FULTON (Amer. J. Pharm., 1933, 105, 62—63).—The pink colour of a solution of  $\beta\text{-C}_{10}\text{H}_7\text{-OH}$  in ammoniacal aq. EtOH becomes cloudy yellowish-green in presence of Cu.  $3 \times 10^{-6}$  pt. of Cu can be detected. E. H. S.

**Precipitation of copper and tin groups using hydrogen sulphide.** I. Influence of increasing concentrations of ammonium chloride on the complete precipitation of lead and cadmium sulphides at 0.3N-HCl. II. Metals other than lead and cadmium. L. LEHRMAN. III. Effect of ammonium salts. L. LEHRMAN and H. WEISSBERG (J. Chem. Educ., 1933, 10, 50—53, 53—54, 54—55).— $\text{CaS}$  and  $\text{PbS}$  are incompletely pptd. when  $\text{H}_2\text{S}$  is passed into a strongly acid (HCl) solution afterwards diluted to 0.3N-HCl, the quantity unpptd. being greater if much  $\text{NH}_4\text{Cl}$  is present.  $\text{Sn}^{IV}$  when present alone in 0.3N-HCl is incompletely pptd. by  $\text{H}_2\text{S}$  to the extent of a few mg., but when all the elements of the group are present,  $< 1$  mg. escapes pptn.  $\text{NH}_4$  salts other than  $\text{NH}_4\text{Cl}$  do not prevent pptn. of Pb, Cd, and  $\text{Sn}^{IV}$ ; two methods for removing  $\text{Cl}^-$  are described. CH. ABS.

**Micro-volumetric analysis using diphenylcarbazide and diphenylcarbazone as indicators (mercurimetry).** J. V. DUBSKÝ and J. TRTÍLEK (Mikrochem., 1933, 12, 315—320).—Hg ions give an intense violet-blue coloration with diphenylcarbazide (I) and diphenylcarbazone (II). Chlorides may be titrated in dil. acid solution with 0.01N- $\text{Hg}(\text{NO}_3)_2$ ,

using (I), or better (II), as indicator, in consequence of formation of non-ionised  $\text{HgCl}_2$ . Heavy metals have little disturbing effect; in presence of Cu results were 0.5% low. J. S. A.

**Acetates as a means of separating the yttrium group rare-earth elements from each other.** J. A. HARRIS and A. H. CAMERON (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 61—62).—On fractional crystallisation of the acetates of the Y group, Er concentrates in the head fraction and Nd and Sm in the most sol. fraction. J. W. S.

**Comparison of the efficiencies of bromates and nitrates in the separation of the rare-earth elements from one another.** J. A. HARRIS and (Miss) D. E. WYLIE (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 63—68).—The order of the solubilities of the  $\text{BrO}_3'$  salts differs from that of the  $\text{NO}_3'$  salts. Bromates are recommended for the rapid separation of Er or of Nd and Sm from a mixture of the Y group. The nitrates afford a means for the rapid concn. of Eu, Tb, and Gd from a general mixture. J. W. S.

**Analytical behaviour of gallium.** E. S. VON BERGKAMPF (Z. anal. Chem., 1932, 90, 333—335).—Details with regard to separation of Ga from its alloys with Al, and to its pptn. by "cupferron," are given. The limits of  $p_{\text{H}}$  within which Ga can be pptd. as  $\text{Ga}(\text{OH})_3$  are 3.4 and 9.7. F. L. U.

**Test for aspirin, salicylic acid, and manganese.** C. C. FULTON (Amer. J. Pharm., 1933, 105, 59—61).—Aspirin or salicylic acid treated with  $\text{H}_2\text{O}_2$ ,  $\text{NH}_3$ , and a dil. solution of a  $\text{Mn}^{++}$  salt develops a pink or red colour changing to brown. By suitable modification Mn may be detected in concns. of from  $5 \times 10^{-6}$  to  $5 \times 10^{-4}$ . E. H. S.

**Determination of manganese, iron, and titanium by B. Lange's photo-electric colorimeter.** M. BENDIG and H. HIRSCHMÜLLER (Z. anal. Chem., 1933, 92, 1—7).—A colorimeter is described in which a Se half-conductor photo-cell, giving sufficient current to affect an ordinary pointer galvanometer, is used for detection. The sensitivity is increased by using colour filters of the same colour as the solution when this is strongly coloured and of the complementary colour for a weakly coloured solution. A special "substitution" method is employed for great precision. Mn is determined as  $\text{MnO}_4'$  obtained by oxidation with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in presence of  $\text{AgNO}_3$ . The concn. of  $\text{H}_2\text{SO}_4$  is kept const. at 10%.  $\text{KCN}^{\text{S}}$  is used for the determination of Fe. A green filter is used for concns. up to 1 mg.  $\text{Fe}_2\text{O}_3$ , and a red filter for higher concns. Ti is determined by oxidation to  $\text{TiO}_3$  by  $\text{H}_2\text{O}_2$ . If Fe is present it must be decolorised by addition of  $\text{H}_3\text{PO}_4$ . Since this also affects the colour due to Ti, a suitable standardisation curve must be prepared to allow for this. If monochromatic light is used, the relation between extinction and concn. is linear, and so facilitates the determination of the standardisation curve. M. S. B.

**Determination of metallic iron, ferrous oxide, and ferric oxide in mixtures.** F. KAUFMANN (Chem.-Ztg., 1933, 57, 122—123).—The finely powdered material (2.5 g.) is dissolved in freshly pre-

pared "bromoacetate" solution (60 c.c.) (cf. Mathesius, Stahl u. Eisen, 1914, 868) and after subsequent gentle boiling for 10—15 min., the cooled solution is filtered. After removing Br by boiling in  $\text{H}_2\text{O}$  under  $\text{CO}_2$  for 5 min., the insol. material is dissolved in conc.  $\text{HCl}$  (50 c.c.) and  $\text{HF}$  (1 c.c.), when the difference between its  $\text{Fe}^{\text{II}}$  and total Fe content gives the  $\text{Fe}^{\text{III}}$  content of the material. The total Fe content of the original material is determined in the usual way and the metallic Fe by the  $\text{HgCl}_2$  method.

D. F. T.

**Determination of cobalt in cobaltamines.** W. M. McNABB (Z. anal. Chem., 1933, 92, 7—11).—The  $\text{SO}_4''$  method for the determination of Co cannot be applied in the analysis of complex amines which are salts of a non-volatile acid. A modification of the method for the determination of Co in steel is therefore used.  $\text{Co}^{\text{II}}$  is oxidised to  $\text{Co}(\text{OH})_3$  by heating with  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$ . After filtering by suction and washing with hot  $\text{H}_2\text{O}$  the ppt. is dissolved in  $\text{H}_2\text{SO}_4$  in presence of  $\text{KI}$ .  $\text{Co}^{\text{III}}$  is thus reduced to  $\text{Co}^{\text{II}}$  again and the liberated I is titrated with  $\text{Na}_2\text{S}_2\text{O}_3$ . The method cannot be used for  $\text{C}_2\text{H}_4(\text{NH}_2)_2$  salts because they are not completely decomposed with  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$ . M. S. B.

**Microacidimetric determination of nickel.** J. V. DUBSKÝ and E. HAUER (Mikrochem., 1933, 12, 321—326).—Ni dicyanodiamidine (I) is readily sol. in dil. acid. For the determination of Ni, excess of dicyanodiamidine sulphate is added to the solution of Ni, and (I) pptd. by neutralisation with  $\text{KOH}$ . The washed ppt. is titrated with 0.1N-HCl, using Me-red as indicator. J. S. A.

**Qualitative analysis with small quantities. III. Analysis of the ammonium sulphide group in presence of phosphate.** A. SCHEINKMANN (Z. anal. Chem., 1933, 91, 415—418; cf. A., 1932, 1223).—A method of procedure based on addition to the filtrate from the  $\text{H}_2\text{S}$  ppt. of excess of  $(\text{NH}_4)_2\text{HPO}_4$ , aq.  $\text{NH}_3$ , and  $(\text{NH}_4)_2\text{S}$ , and subsequent digestion of the resulting ppt. with 2N-AcOH, whereby Mn, Mg, Ca, Sr, and Ba go into solution, is described.

F. L. U.

**Sodium sulphide in qualitative analysis; modified Fresenius-Vortmann method.** A. SOLDI (L'Ind. Chimica, 1933, 8, 159—162).—The difficulties encountered in the qual. analysis of mixtures containing Co and Ni, and  $\text{PO}_4''''$  etc. are discussed. In the scheme described, Pb, Ag, and Hg are pptd. as chlorides, org. matter is oxidised with  $\text{Br-H}_2\text{O}$ , and  $\text{NH}_3$  is removed from the filtrate by boiling with  $\text{NaOH}$ .  $\text{Na}_2\text{S}$  is added to the cooled mixture, and the resulting ppt. is extracted with  $\text{HCl}$  (1:1), leaving a residue of Pb, Bi, Cu, and Cd sulphides, which are separated by the usual procedure. The filtrate from the  $\text{Na}_2\text{S}$  ppt. is treated with  $\text{NH}_4\text{Cl}$  and the Al and Hg are removed, the As, Sb, and Sn remaining in solution. The  $\text{HCl}$  extract is diluted and treated with  $\text{Na}_2\text{S}$  to remove traces of Bi and Pb, concn., treated with solid  $\text{Na}_2\text{CO}_3$  in excess, and boiled;  $\text{PO}_4''''$ ,  $\text{BO}_3'$ , etc. remain in solution, and the ppt. is separated by the standard methods into groups containing Fe, Cr, and Mn, Zn, Co, and Ni, and Ca, Sr, and Ba, respectively. H. F. G.

**8-Hydroxyquinoline for the determination of tungsten.** S. HALBERSTADT (Z. anal. Chem., 1933, 92, 86—89).—A dil. alkaline or neutral solution containing the W as  $WO_4^{2-}$  is treated with excess of a 4% solution of 8-hydroxyquinoline in EtOH, heated nearly to boiling, and acidified with AcOH. The solution is then boiled and the yellowish ppt. of  $WO_2(C_9H_6ON)_2$  collected, washed until the washings are colourless, dried at 120°, and weighed (1 g. = 0.3650 g. W). J. W. S.

**Quantitative complete microanalysis of uraninites.** F. HECHT and W. REICH-ROHRWIG (Mikrochem., 1933, 12, 281—292).—A detailed account of procedure, using 25—40 mg. of material. J. S. A.

**Colorimetric determination of titanium.** R. SCHWARZ (Z. anorg. Chem., 1933, 210, 303).—The coloration produced when  $TiOSO_4$  and  $H_2O_2$  react in presence of  $H_2SO_4$  is probably due to  $[TiO_2(SO_4)_2]H_2$ . E. S. H.

**Simple and complex iodates of titanium. A correction.** P. R. RAY (Z. anorg. Chem., 1933, 210, 304).—Cf. A., 1932, 1099. E. S. H.

**Determination of zirconium in steel. Selenic acid method.** S. G. SIMPSON [with W. C. SCHUMB].—See B., 1933, 231.

**Sensitive test for gold with  $\alpha$ -naphthylamine hydrochloride.** H. HOLZER and W. REIF (Z. anal. Chem., 1933, 92, 12—15).—5 c.c. of filtered aq.  $\alpha$ - $C_{10}H_7\cdot NH_2\cdot HCl$  and 2—3 c.c. EtOAc are shaken with 5—10 c.c. of aq.  $AuCl_3$  which is either neutral or slightly acid with HCl. After a short time a violet-to rose-red additive product,  $AuCl_3\cdot C_{10}H_7\cdot NH_2\cdot HCl$ , is formed in the EtOAc layer. The reaction may be obtained with 0.008 mg. of Au diluted to 1 in  $10^6$ . A similar colour is formed with  $FeCl_3$ , but it is due to oxidation of the  $\alpha$ - $C_{10}H_7\cdot NH_2\cdot HCl$ , and the disturbing influence of Fe can be prevented by tartaric acid or Na K tartrate. The sensitivity of the test is reduced, but 1 part of Au in 700 parts of Fe can still be detected. The additive compound formed with  $PdCl_2$ ,  $Pd[C_{10}H_7\cdot NH_2]_2Cl_2$ , is orange-yellow. M. S. B.

**Analysis of platinum minerals. I—VIII.** INSTITUT DE PLATINE, B. G. KARPOV, and A. N. FEDEROVA.—See B., 1933, 232.

**Detection of free metal particles in dust etc.** T. J. WARD.—See B., 1933, 194.

**Use of potassium hydroxide as a fusion agent.** P. F. THOMPSON.—See B., 1933, 194.

**Coiled-filament resistance thermometers.** C. H. MEYERS (Bur. Stand. J. Res., 1932, 9, 807—813).—The strain-free coiled windings of a 25-ohm thermometer are wound in a space 5 mm. diam. and 2 cm. long, which is hermetically sealed, and filled with He to reduce lag. C. W. G.

**Accuracy of freezing-point determination by means of the Beckmann thermometer.** H. C. S. SNETHLAGE (Rec. trav. chim., 1933, 52, 139—150).—The sources of error are discussed and methods described for obtaining an accuracy of  $\pm 0.0005^\circ$ . D. R. D.

**Determination of specific heats of liquids. Specific heats of aniline and benzene over the approximate range 20—50°.** A. FERGUSON and J. T. MILLER (Proc. Physical Soc., 1933, 45, 194—207).—The electrical power necessary to maintain the calorimeter and its contents at various temp. is measured. The sp. heat of  $NH_2Ph$  is  $0.495_0 + 0.000275(T-20) + 0.0000035(T-20)^2$  and of  $C_6H_6$  is  $0.395_8 + 0.00125(T-20)$ . C. W. G.

**Glass autoclave to facilitate observation of reactions at high temperature and pressure.** O. GERNGROSS, K. M. HOFFMANN, and G. KLEIN (Chem. Fabr., 1933, 6, 93).—A vertical cylinder of special glass is closed above and below by end-plates, the joints being made with asbestos and tightened evenly by a screw working on 10 rods. An upper cover plate is separately held by a screw and bow with another asbestos joint, and only the latter need be removed to withdraw a sample of the contents of the autoclave. The capacity of this is 750 c.c. and it can be used up to 170° and 7 atm. An agitator can be fitted if required. C. I.

**Measurement of low-voltage X-ray intensities.** L. S. TAYLOR and C. F. STONEBURNER (Bur. Stand. J. Res., 1932, 9, 769—780).—The ionisation produced by 3—12 kv. rays is measured in a very small guarded field ionisation chamber. C. W. G.

**Colorimetry.** F. L. HAHN (Z. anal. Chem., 1932, 90, 330—332; cf. A., 1931, 54).—A criticism of a paper by Pestov (A., 1932, 920). F. L. U.

**Photo-electric absorption measurement of coloured and cloudy solutions.** R. SEIFERT (Pharm. Zentr., 1933, 74, 97—102).—The comparison and adjustment of the intensities of two colours or turbidities may be carried out photo-electrically. With the aid of the circuit and apparatus described the relationships between the current and the light absorption at varying concns. can be expressed graphically and an equation developed which enables accurate vals. for the concn. to be calc. from any galvanometer reading. E. H. S.

**Colour filters for altering colour temperature. Pyrometer absorption and daylight glasses.** H. P. GAGE (J. Opt. Soc. Amer., 1933, 23, 46—54).—Analysis of the Wien equation gives formulæ applicable to colour filters suitable for transforming light of one colour temp. to another. The formulæ for daylight glasses are also calc. J. L.

**Self-registering spectrometer.** C. LEISS (Physikal. Z., 1933, 34, 172—175).—The apparatus and its use are described. A. J. M.

**Innovations in photomicrography with ultra-violet light.** A. KÖHLER (Naturwiss., 1933, 21, 165—173).—A new monochromator for ultra-violet light is described. A. J. M.

**Multi-range potentiometer and its application to the measurement of small temperature differences.** H. B. BROOKS and A. W. SPINKS (Bur. Stand. J. Res., 1932, 9, 781—798).—The "second method" of Pogendorff is used. C. W. G.

**Universal direct-reading hydrogen-ion potentiometer.** C. MORTON (J.S.C.I., 1933, 52, 6—St).—

A universal  $H^+$  potentiometer, reading directly in  $p_H$  units, is described. The instrument is applicable to all reversible electrode systems (including glass electrode systems) at any temp. between  $10^\circ$  and  $30^\circ$ . Alternative ranges of 0—14  $p_H$  units and 0—1400 mv. are provided on the same scale, readings being obtained directly to 0.01  $p_H$  unit and 1 mv., respectively. Using the glass electrode, readings are obtained directly in  $p_H$  units with an accuracy of  $\pm 0.01 p_H$  over the range  $p_H$  2—10. Erroneous results are obtained with the Sb electrode, the e.m.f.— $p_H$  relationship of which is non-linear.

**Metal-connected glass electrode.** M. R. THOMPSON (Bur. Stand. J. Res., 1932, 9, 833—853).—Glass electrodes with direct metallic connexion can be constructed with substantial walls and have satisfactory accuracy and sensitivity. C. W. G.

**Temperature coefficient of the standard Weston cell.** P. VIGOUREUX and S. WATTS (Proc. Physical Soc., 1933, 45, 172—179).—The difference in microvolts from the e.m.f. at  $20^\circ$  can be represented by  $363 - 1.5(t-3)^2 + 1.68 \times 10^{-2}(t-3)^3 - 1.5 \times 10^{-4}(t-3)^4$ . C. W. G.

**Simple electrolytic generation of hydrogen and oxygen.** D. VON KLOBUSITZKY (Biochem. Z., 1933, 257, 478—479).—A simple cell using Ni and 20% NaOH is described. P. W. C.

**Apparatus for cathode sputtering.** J. A. DARBYSHIRE (J. Sci. Instr., 1933, 10, 83—85).—The danger of over-heating has been eliminated. C. W. G.

**Magnet for  $\alpha$ -ray spectroscopy.** J. D. COCKROFT (J. Sci. Instr., 1933, 10, 71—75).—Fields up to 18,000 gauss can be obtained, using 300 watts. Groups of  $\alpha$ -particles having an energy difference of 5000 electron volts can be separated and their relative energies measured by bending the tracks into semi-circles. C. W. G.

**Use of sintered Jena glass filters in gravimetric microanalysis.** Application to gravimetric determination of sulphur as benzidine sulphate and of carbamide as dixanthylcarbamide. R. GUILLEMET (Bull. Soc. chim., 1932, [iv], 51, 1611—1615).—Practical notes are given. E. S. H.

**Gas-volumetric method.** E. ELION (Z. anal. Chem., 1933, 92, 89—92).—The gas is drawn into an aspirator, the vol. of  $H_2O$  displaced from the aspirator being measured, whilst the pressure of the gas can be observed by means of a two-bottle regulator attached to a side tube. J. W. S.

**Wet-and-dry bulb hygrometry: relation to theory of the experimental researches of Awbery and Griffiths.** F. J. W. WHIPPLE (Proc. Physical Soc., 1933, 45, 307—309).—August's formula holds from  $30^\circ$  to  $100^\circ$ . C. W. G.

**Receiver for fractional distillation in vacuum.** A. HANAK (J. pr. Chem., 1933, [ii], 136, 202—204).—The receiver described has one tap with three independent borings. R. S. C.

**Distillation apparatus for water with feed-water regulator and preheater.** F. FRIEDRICH (Chem.-Ztg., 1933, 57, 123).—The apparatus includes

a special  $H_2O$ -jacket between the main condenser and the flask, which serves as the preheater, and an overflow regulator for supplying the heated  $H_2O$  to make good the evaporation losses. Steady continuous distillation is thereby ensured.

D. F. T.

**Apparatus for washing with boiling water.** H. REIDT (Woch. Brau., 1933, 50, 59).—The efflux tube of a wash-bottle is lengthened so as to act as a siphon, and is provided with a pinch-cock. E. S. H.

**Measurement of the viscosity of liquids; new universal viscosimeter.** F. HÖPPLER (Chem.-Ztg., 1933, 57, 62—63).—A general account is given of viscosity and its measurement. In a new falling-sphere type of instrument, the sphere is maintained in contact with the wall of the tube by inclining the latter at  $80^\circ$  to the vertical; as a result, errors due to variation of the distance between the sphere and wall are obviated. The tube is surrounded by a const.-temp.  $H_2O$ -jacket. Results are accurate to within 0.1%, and may readily be converted into abs. units. By using a sphere of diam. only slightly < that of the tube, the viscosity of gases also may be determined to within 0.1%. It is possible with the apparatus to demonstrate the difference between the viscosities of distilled and conductivity  $H_2O$ . H. F. G.

**Equilibrium forces acting on free drops in irregular capillaries.** H. MOUQUIN and S. NATELSON (Mikrochem., 1933, 12, 293—302).—A method for measuring surface tension by measurement of the length of drops in open, non-uniform capillary tubes is described. J. S. A.

**Capillary depressions of mercury in cylindrical tubes and some errors of glass manometers.** W. CAWOOD and H. S. PATTERSON (Trans. Faraday Soc., 1933, 29, 514—523).—Measurements have been made of the capillary depressions of Hg in cylindrical glass tubes of various sizes. These must be thin-walled to eliminate refraction errors. Measurements agreeing to within  $< 0.01$  mm. are thus obtained. A table shows the relationship between capillary depression and meniscus height for tubes varying in diam. from 10 to 19 mm. and for meniscus heights from 0 to 1.8 mm. The refraction errors in cylindrical glass tubes have been investigated and considered in relation to the design of glass manometers. M. S. B.

**Adjustable greaseless [gas] valve.** L. WOLF and S. VON REICHEL (Z. Elektrochem., 1933, 39, 143—145).—The action of the valve depends on the passage of gas through a porous porcelain cone, any desired fraction of which can be Hg-sealed by a simple mechanism. A full description and diagram are given. F. L. U.

**Extractor for large quantities of organic material.** J. J. T. GRAHAM (J. Assoc. Off. Agric. Chem., 1933, 16, 148—149).—An inverted bell-jar closed with a desiccator top is used. Solvent vapour from a flask enters by the side opening of the bell-jar, whilst a  $\cup$ -shaped tube furnishes a return tube from the bottom of the extractor to the flask. The charge to be extracted is supported by a layer of absorbent cotton on a porcelain desiccator plate. J. W. S.

**Recording pressure and time in gas explosions.** B. LEWIS and G. VON ELBE (J. Amer. Chem. Soc., 1933, 55, 504—507).—The construction of a hysteresis-free Ni steel diaphragm indicator of const. sensitivity for determining pressures developed in explosions is described. Calibration by a dynamic method *in situ* affords results in accord with vals. determined statically. J. G. A. G.

**Electrical heating equipment in Pregl's method of microanalysis:** (a) combustion furnace, (b) bomb for micro-Liebig [determination]. R. GUILLEMET (Bull. Soc. chim., 1932, [iv], 51, 1615—1619).—Apparatus and procedure are described. E. S. H.

**Flow of liquid suspensions.** E. G. RICHARDSON and E. TYLER (Proc. Physical Soc., 1933, 45, 142—151).—A hot-wire anemometer is used to measure the velocity of a liquid between a rotating cylinder and a concentric fixed cylinder. In a suspension the velocity gradients are abnormal and can be explained in terms of a viscosity which is a function of the velocity gradient. C. W. G.

**Vacuum work [in the laboratory].** P. HARTECK (Chem. Fabr., 1933, 6, 104—106).—Inflammable gases which are not readily liquefied can be burnt by admitting a regulated O<sub>2</sub> supply and passing over Pt foil in a sufficiently wide SiO<sub>2</sub> tube. The H<sub>2</sub>O and CO<sub>2</sub> are then condensed with liquid air. O<sub>2</sub> can be removed by the inverse process. A gas holder with floating gas bell and Hg seal for pure gases can be

fitted with a check valve which is Hg-tight but not gas-tight. The use of gas for washing out the last traces of air can then be avoided. Amongst other devices mentioned are flexible tubes to replace wide glass tubes, a Hg seal to reduce pressure when removing gases from a bomb to high vac., and a Hg-vapour trap for use with Hg jet pumps. C. I.

**Practical laboratory improvements.** G. GOLLNOW (Chem. Ztg., 1933, 57, 163—164).—Burettes, a micro-filter, a shaker, a rubber pipette-bulb, and a grease pencil are described and illustrated. P. G. M.

**Cause of fire in the laboratory.** H. FINCK (Woch. Brau., 1933, 50, 59).—A wash-bottle filled with H<sub>2</sub>O acts as a lens in strong sunlight, and may cause ignition of CS<sub>2</sub>, Et<sub>2</sub>O, etc. E. S. H.

**Neutralisation diagram.** M. SETA (L'Ind. Chimica, 1933, 8, 11—13).—The vol. of acid is plotted against the vol. of alkali of equiv. concn. Any point on a line at 45° to the axes and passing through the origin represents stoichiometric neutrality, whereas for an acid and a base of different strengths, points of ionic neutrality ( $p_H$  7) lie on a line inclined at an angle to the axes which may be calc. from the ionisation consts. concerned. Various typical cases are discussed in relation to the indicator which should be used in each case. H. F. G.

**Scientific work of Joseph Priestley.** J. R. PARTINGTON (Nature, 1933, 131, 348—350). L. S. T.

## Geochemistry.

**Fulminating matter: expansion on decomposition at atmospheric pressure and constant temperature.** E. MATHIAS (Compt. rend., 1933, 196, 455—458; cf. A., 1932, 358).—From an observation of globular lightning it is inferred that the fulminating matter which caused the manifestation expands to approx. eight times the initial vol. on destruction, temp. and pressure remaining unchanged. C. A. S.

**Carbon dioxide in the sea.** L. H. N. C. (Nature, 1933, 131, 282—283). L. S. T.

**Gold in sea-water.** A. GOURÉVITCH (Chim. et Ind., 1933, 29, 284).—Rags, after being mordanted with tannin, were steeped in a solution of SnCl<sub>2</sub>. 1 g. of such material is capable of fixing 0.0005 mg. Au per mg. in 1 ton of sea-water. Tests 0.5 km. from the coast of Brittany gave a negative result. W. J. W.

**Radium content of ocean-bottom sediments.** C. S. PIGGOT (Amer. J. Sci., 1933, [v], 25, 229—238).—Ra contents of ocean-bottom sediments, mainly from the Pacific, have been determined, and their origin is discussed. C. W. G.

**Origin of Chile saltpetre.** C. T. KAUTER (Chem.-Ztg., 1933, 57, 133—134).—A recapitulation of the evidence for Stoklasa's theory of the volcanic origin of the nitrate deposits. The presence of KIO<sub>3</sub> is explained by the "fog" theory of formation,

whereby the I is derived from the air in contact with the sea-surface. P. G. M.

**Julienite.** V. CUVELIER (Natuurwetensch. Tijds., 1933, 15, 17—20).—Julienite is free from Cu and Ni; it consists of almost pure Na<sub>2</sub>Co(CNS)<sub>4</sub>·8H<sub>2</sub>O. The Co(CNS)<sub>2</sub> ion forms a blue compound with NHPPh<sub>2</sub>. H. F. G.

**Metamorphism of the Deeside limestone, Aberdeenshire.** A. G. HUTCHISON (Trans. Roy. Soc. Edin., 1932, 57, 557—592).—From numerous observations on microscopic sections and a few chemical analyses of rocks, the mineral transformations occurring in a group of limestones have been traced and are described in detail. Interchange of mineral constituents has occurred between the pegmatite intrusions and the ground rock, resulting in extensive metamorphosis. Certain unstable associations are observed which probably result from the relief of static pressure during the growth of the lime-silicate minerals. W. O. K.

**Occurrence of rubidium, caesium, and thallium in some Western Australian micaceous minerals.** D. G. MURRAY and F. E. CHAPMAN (J. Roy. Soc. W. Australia, 1930—1931, 17, 151—155). CH. ABS.

**Vogtite, isomorphous with wollastonite.** N. L. BOWEN (J. Washington Acad. Sci., 1933, 23, 87—94).—Vogtite (Ca, Fe, Mn, Mg)SiO<sub>3</sub> is probably a wollastonite solid solution. C. W. G.

**Thermal dissociation of serpentine minerals.** S. CAILLÈRE.—See this vol., 352.

**Crystals of iron-rich pyroxene from a slag.** N. L. BOWEN (J. Washington Acad. Sci., 1933, 23, 83—87).—An analysis and optical and crystallographic details are given. C. W. G.

**Crystal structure of silicates.** E. SCHIEBOLD (Ergebn. exakt. Naturwiss., 1932, 11, 352—434; Chem. Zentr., 1932, ii, 2925).—Mineralogical relationships of structural types are considered. The structures and physical constants of the most important rock-forming silicates are tabulated. A. A. E.

**Study of contact metamorphism by means of the heavy minerals.** L. BERTHOIS (Compt. rend., 1933, 196, 493—495).—The investigation of the exo- and endo-morphic changes due to metamorphism caused by intrusion of granite etc. is greatly facilitated by examination of the heavy minerals separated from the powdered rock by, e.g.,  $\text{CHBr}_3$ , or from the sand formed therefrom. The method enables a much larger amount to be examined than that of thin sections. C. A. S.

**Fibrous sepiolite from Madagascar.** (MILLE.) CAILLÈRE (Compt. rend., 1933, 196, 416—418).—Cryst. sepiolite occurs, associated with gypsum and calcite, in a bed of mica at Ampandrandava, as flexible silky yellow fibres resembling chrysotile, and also as an asbestiform mass. Either form when heated evolves  $\text{H}_2\text{O}$ , mainly at  $150^\circ$ , but in smaller amounts at  $440^\circ$  and  $800^\circ$ . Analysis:  $\text{SiO}_2$  52.50,  $\text{Al}_2\text{O}_3$  0.60,  $\text{Fe}_2\text{O}_3$  2.99,  $\text{FeO}$  0.70,  $\text{CaO}$  0.47,  $\text{MgO}$  21.31,  $\text{H}_2\text{O} + 12.06$ , — 9.21%, corresponding with  $\text{H}_8\text{Mg}_2(\text{SiO}_4)_3$ ;  $n_r - n_a$  0.012,  $n$  (mean) 1.4997,  $d$  2.08; after heating at  $1100^\circ$   $n_r$  becomes 1.59 and  $d$  2.78. C. A. S.

**Difference between mica and clay as regards possible orientation of crystals growing thereon.** L. ROYER (Compt. rend., 1933, 196, 552—554; cf. this vol., 213).—The micas, clintonites, and chlorites (group *a*) and talc, kaolin, and pyrophyllite (group *b*) are all geometrically similarly constructed of thin parallel planes, but differ in that in (*a*) these planes are alternately electrically positive and negative, but in (*b*) uniformly neutral. Numerous substances when cryst. on a mineral of group (*a*) exhibit epitaxy, but in no case on one of group (*b*). This indicates that for epitaxy not merely must there be geometrical agreement, but also similarity of polarity of the particles that replace one another at the points of union. C. A. S.

**Formation of "anomalous mixed crystals" as the cause of geochemical "enclosure" and luminescence.** H. SEFFERT (Naturwiss., 1933, 21, 194).—The presence of foreign substances in the crystal lattice of a mineral may take the form of submicroscopic crystals oriented in certain planes, to which the name "anomalous mixed crystals" is applied. The application of this principle can explain the "enclosure" of certain substances in the crystal lattices of other minerals, e.g., the presence of  $\text{NaIO}_3$  in  $\text{NaNNO}_3$ , etc. Numerous artificial phosphors have their origin in the same cause. A. J. M.

**Chemical study of aluminosilicates.** W. VERNADSKY (Z. Krist., 1933, 84, 337—372; cf. A., 1901, ii, 249).—A ring structure,  $-\text{Al} \begin{matrix} \text{O} \cdot \text{SiO} \cdot \text{O} \\ \text{O} \cdot \text{SiO} \cdot \text{O} \end{matrix} \text{Al}-$ , in which Al has one supplementary valency, is suggested as the fundamental kaolin nucleus, the general formula of which is  $\text{Al}_2\text{Si}_{2+n}\text{O}_{7+2n}$ , with possible addition of  $\text{H}_2\text{O}$ ,  $\text{M}^{\text{I}}\text{O}$ , or  $\text{M}^{\text{II}}\text{O}$  to form kaolinic acid,  $\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8$ , and its derivatives. To this group are ascribed chromophoric properties to explain the colour of the "additive products," e.g., sodalite,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{Si}_2\text{O}_7 \cdot \text{NaCl}$ , in which neither "nucleus" nor "radical" ( $\text{NaCl}$ ) is coloured. The colour of ultramarine, hauyne, garnet, epidote, beryl, cordierite, etc. is thus explained. The application of these views to the micas is discussed, as also is the replacement of Si by Al and of Al by Mg, it being held that, e.g., sillimanite,  $\text{Al}_2\text{Si}_2\text{O}_5$ , is not a silicate of Al, but a complex acid anhydride, thus explaining the formation of an aluminosilicate by the action of  $\text{K}_2\text{CO}_3$  thereon, and the stereochemical identity of Al and Si; Mg can replace Al only in the "radical."

C. A. S.

**Measurement of reflecting powers of natural tellurides by the photo-electric method.** P. FASTRÉ (Compt. rend., 1933, 196, 630—632).—The reflecting powers for monochromatic light ( $\lambda$  5890, 5270, and 4659 Å.) of coloradoite, petzite, altaite, hessite, nagyagite, sylvanite, calaverite, and krennerite characterise the minerals (cf. B., 1927, 15).

C. A. S.

**Trends of differentiation in basaltic magmas.** W. Q. KENNEDY (Amer. J. Sci., 1933, [v], 25, 239—256).—The two primary basaltic magmas are olivine-basalt and tholeiitic-basalt, which give rise respectively to the alkaline rock suite and the calc-alkaline suite. No common source of the two primary magmas can be found, nor is there any evidence that one is derived from the other. C. W. G.

**Movement of gases through soil as a criterion of soil structure.** T. F. BUEHRER (Arizona Agric. Exp. Sta. Tech. Bull., 1932, No. 39, 57 pp.).—Apparatus is described for determining the rate of flow of air of controlled temp. and humidity through soils under standardised pressure conditions. From results obtained the "structural const." is calc. Its use as a single-val. const. is discussed. A. G. P.

**Descriptive soil map.** A. TILL (Z. Pflanz. Düng., 1933, 27 A, 402—407).—A system of notation representing the principal characteristics of soils and of parent rocks in soil maps is described.

A. G. P.

**Soil structure and pan formation with examples from soil maps of the Palatinate.** K. SCHLACHT (Z. Pflanz. Düng., 1933, 27 A, 303—385).—The nature and distribution of soil types of this area are recorded and formation of pans in each type is examined. Ground  $\text{H}_2\text{O}$  levels and the nature of the clay fraction are important factors. No apparent relationship exists between pan formation and the CaO or humus contents of the soils. Cropping, notably with lucerne and potatoes, tends to break up the pan, which may, however, re-form in some cases within 1—2 years. A. G. P.

**Formation and transformation of coal.** K. LEHMANN and E. HOFFMANN (Glückauf, 1932, 68, 793—800, 818—821; Chem. Zentr., 1932, ii, 3035).

**Origin of coal and mineral oil.** R. POTONIE and C. WICHER (Angew. Chem., 1932, 45, 802—803).—A

crit. discussion of the views of Stadnikov (Brennstoff Geol., 1930, No. 5/6). H. F. G.

**Origin and environment of petroleum source sediments.** M. E. KELLY (J. Inst. Petrol. Tech., 1933, 19, 117—141).—A review.

## Organic Chemistry.

**Reaction mechanism rule and its application to the action of fused alkali hydroxides on carbon compounds.** H. S. FRY and R. J. BUTZ (Rec. trav. chim., 1933, 52, 129—138).—The reactions of C compounds with fused NaOH—KOH which have been studied previously (A., 1924, i, 1277; 1926, 710; 1928, 615) are summarised and show (with certain exceptions) that with compounds containing H·C·O and Me·C·O, the H and Me are liberated as H<sub>2</sub> and CH<sub>4</sub>, respectively (by combination with H from the alkali hydroxide). The reactions also involve the formation of Na<sub>2</sub>(K<sub>2</sub>)CO<sub>3</sub>. The exceptions to this "rule" are (CH<sub>2</sub>·OH)<sub>2</sub>, which reacts as MeOH + CH<sub>2</sub>O, and glycerol, which reacts partly as MeOH + 2CH<sub>2</sub>O and partly (by an oxidation-reduction process) as EtOH + HCO<sub>2</sub>H. The amounts of H<sub>2</sub> and CH<sub>4</sub> formed from lactic and glycolic acids, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Me<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, HCO<sub>2</sub>Et, EtOAc, Et lactate, Et<sub>2</sub>CO<sub>3</sub>, and Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> agree with the predicted vals. H. B.

**Tautomerism in the light of recent investigations.** R. F. HUNTER (Proc. Muslim Assoc. Adv. Sci., 1932, 2, 1—41).—A review.

**Reactivity of aliphatic and alicyclic hydrocarbons.** A. SCHAARSCHMIDT and M. MARDER (Angew. Chem., 1933, 46, 151—154).—In homogeneous solution, SbCl<sub>5</sub> reacts with hydrocarbons (I) containing a *tert.*-H atom ( $\beta$ -methylpentane, methylcyclohexane) after a short period, whereas H in primary or *sec.* union in normal and quaternary hydrocarbons (II) (*n*-heptane,  $\beta\beta$ -dimethylbutane, cyclopentane or -hexane) is attacked only at a higher temp. The presence of 0.1% of (I) in (II) can thus be detected. The incidence of the reaction is frequently greatly delayed, but the difficulty is overcome by addition of a contact substance formed from SbCl<sub>5</sub> and the attackable hydrocarbon. Reaction with substances of group (II) is induced by the presence of those of group (I), and quant. separation of the members of the different groups cannot be effected simply by use of the theoretical amount of SbCl<sub>5</sub>; this is achieved by repeated application of the theoretical amount of SbCl<sub>5</sub> with intermediate purification of the unattacked hydrocarbon fractions. H. W.

**Photochemical chlorination of methane.** C. PADOVANI and F. MAGALDI (Giorn. Chim. Ind. Appl., 1933, 15, 1—7).—The influence of Hg arc radiation, particularly rich in the line at 2530 Å., on the reaction between CH<sub>4</sub> and Cl<sub>2</sub> has been studied. With a CH<sub>4</sub>:Cl ratio of 2:1 the Cl consumption increases with increase of the duration of irradiation to an approx. const. val. of 79% at 9 sec.; for a 7:1 mixture the const. val. is about 94%, whilst with a greater proportion of CH<sub>4</sub> the percentage increases steadily with time. The ratio of MeCl to other pro-

ducts is about 0.2 for the Cl-rich mixtures, but rises steadily to nearly 1.8 for 15:1 mixtures; if the reaction proceeds in a large vessel, this ratio is extremely small. H. F. G.

**Vapour-pressure measurements with isobutane.** W. HÜCKEL and W. RASSMANN (J. pr. Chem., 1933, [ii], 136, 30—40).—The isobutane prepared from Bu<sup>*β*</sup>I and Zn—Cu is shown by fractional distillation and v.-p. measurements to be impure, but concordant vals. of v.p. are obtained from two differently prepared fractions. These differ slightly from those for the gas from Bu<sup>*β*</sup>I and Al—Hg, and also from the vals. of Hückel and Ackermann (this vol., 372), but markedly from those of Burrell and Robertson (A., 1916, i, 6). It is concluded that their isobutane was contaminated with a more volatile substance, and it is suggested that Hückel and Ackermann's isobutane was slightly contaminated with *n*-butane on account of the mode of prep. H. A. P.

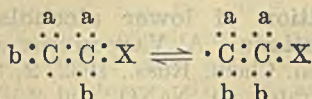
**Catalytic vapour-phase oxidation of tetraalkylmethanes.** W. L. FAITH, S. SWANN, jun., and D. B. KEYES (Ind. Eng. Chem., 1933, 25, 224).—Oxidation of  $\gamma\gamma$ -dimethyl- and  $\gamma\gamma$ -diethyl-*n*-pentanes with air and Cu, V<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub> (cf. A., 1932, 28) under a variety of conditions gave only CO<sub>2</sub>, CO, H<sub>2</sub>O, traces of aldehydes of low mol. wt., and unsaturated hydrocarbons, their behaviour in this respect resembling that of *n*-hydrocarbons. H. A. P.

**Highly-polymerised compounds. LXXVI. Viscosity of solutions of thread molecules with branched chains.** H. STAUDINGER and W. KERN (Ber., 1933, 66, [B], 373—378).—The sp. viscosity in CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, dioxan, or EtOAc of the following substances has been measured at 20°, 40°, and 60°: pentatriacontane,  $\sigma$ -ethylpentatriacontane (I), b.p. 260—265°/0.5 mm., m.p. 20—21° or m.p. 27—28° after long preservation;  $\sigma$ -ethylpentatriacontan- $\alpha$ -ol, m.p. 38—41°, obtained from stearone and a large excess of MgEtI and reduced by red P and HI to (I);  $\sigma$ -phenylpentatriacontane, m.p. 61—62°;  $\sigma$ -phenylpentatriacontan- $\sigma$ -ol, m.p. 50—51°; Me<sub>2</sub>, m.p. 30—34°, and Et<sub>2</sub>, m.p. 39—42°, dicetylmalonate; Me dicetylacetate, m.p. 47—49°. It is found that mols. with branched chain have the tendency when dissolved to assume the most extended form. The viscosity of dil. solution of compounds with the same length of chain is independent of the structure of the mol. H. W.

**Attempted explanation of unexpected reactions of geometrical isomerides of ethylenic compounds.** A. BERTHOUD (Bull. Soc. neuchâteloise Sci. nat., 1931, 56, 413—424).—The occurrence of *trans*-addition to ethylenic compounds is partly explained by the assumption that prior dissociation



of the mols. of the addendum occurs and that the subsequent stages of the reaction involve the intermediate formation of a free radical, e.g.,  $\text{CHPh}\cdot\text{CHPh} + \text{Br} \longrightarrow \cdots\text{CHPh}\cdot\text{CHBrPh}$  (I);  $(\text{I}) + \text{Br}_2 \longrightarrow \text{CHBrPh}\cdot\text{CHBrPh} + \text{Br}$  etc. The presence of an incomplete octet in the free radical allows the existence of two forms (independently of free rotation):



one of which gives rise to the *cis*- and the other to the *trans*-isomeride. This theory is equally applicable to acetylenic compounds and to the dehalogenation of halogenoethanes, and is extended to conjugated compounds; it does not, however, explain the difference in behaviour of some geometrical isomerides, e.g., maleic and fumaric acids, in additive reactions.

H. A. P.

**Number of structurally isomeric hydrocarbons of the ethylene series.** H. R. HENZE and C. M. BLAIR (J. Amer. Chem. Soc., 1933, 55, 680—686).—Theoretical. A relationship is established between the no. of structural isomerides and the alkyl groups attached to the C:C linking. Formulæ are advanced for calculating the no. of isomerides of each of the structural types from their C content, but their use involves the knowledge of the total no. of alkyl groups (i.e., structurally isomeric mono-substituted paraffins) of *N*—2 and all smaller C contents.

H. B.

**Pyrolysis of  $\alpha$ -unsaturated hydrocarbons.** C. D. HURD and H. T. BOLLMAN (J. Amer. Chem. Soc., 1933, 55, 699—702).—Pyrolysis of diallyl (425—650°),  $\delta$ -methyl- $\Delta^{\alpha}$ -pentene (600—675°), allyl-cyclohexane (500—650°) (dibromide, b.p. 129—131°/11 mm.), and  $\delta$ -phenyl- $\Delta^{\alpha}$ -butene (500—700°) at the temp. quoted gives  $\text{C}_3\text{H}_6$  as the predominating product; allene is not formed. Saturated gaseous hydrocarbons,  $\text{C}_2\text{H}_4$ ,  $\text{H}_2$ , and liquid products are also formed. The primary change in the pyrolysis of hydrocarbons is probably not a simple fission into two compounds (even though these may be isolated).

H. B.

**Preparation of  $\beta\delta$ -dimethyl- $\Delta^{\alpha\gamma}$ -pentadiene.** H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1933, 52, 234—238).—When the alcohol from mesityl oxide and  $\text{MgMeI}$  is heated, a mixture of  $\text{H}_2\text{O}$  and hydrocarbon distils at about 80°; the latter is finally dehydrated by repeated distillation from  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  and then from Na in  $\text{N}_2$ , thus giving  $\beta\delta$ -dimethyl- $\Delta^{\alpha\gamma}$ -pentadiene, b.p. 93.1—93.2  $\pm$  0.1°, i.p. —114°, which is readily oxidised in air and is reduced to  $\beta\delta$ -dimethylpentane, b.p. 78.9—80°. Other data (lit. and revised) are given.

H. B.

**$\alpha\zeta$ -Dimethyl- $\Delta^{\alpha\epsilon}$ -hexatriene.** URION (Compt. rend., 1933, 196, 353—354).— $\Delta^{\beta\epsilon}$ -Octadiene- $\delta\epsilon$ -diol by catalytic decomp. with reduced Cu gives  $\Delta^{\beta\epsilon}$ -octatriene, fractionated into two stereoisomeric forms, (I) (*trans-cis-trans*-), b.p. 137—143°/764 mm. [slightly contaminated with (II); liquid  $\text{Br}_2$ -compound], and (II), m.p. 52.5°, b.p. 147—148°/764 mm. ( $\text{Br}_2$ -derivative, m.p. 122°), which rapidly oxidises to an aldehydic resin in air.

J. W. B.

**Effect of high temperatures and pressures on unsaturated hydrocarbons. II. Hexadecene.** G. HUGEL and KOHN (Ann. Office Nat. Combust. liq., 1932, 7, 239—277; Chem. Zentr., 1932, ii, 3076).—At  $>400^\circ$  polymerisation and cracking, particularly of polymerides, occur. The decomp. takes place only in the vapour phase, and hence depends on the pressure below the crit. temp. (for  $\text{C}_{16}\text{H}_{32}$ , 458°).  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -Octene undergo polymerisation and fission with formation of hexadecane or octane and diolefines. At 500° and high pressures  $\text{C}_6\text{H}_{14}$  and  $\text{C}_7\text{H}_{16}$  are unaffected. Mineral oils are decomposed in the vapour phase at 400—450°, and also in the liquid phase above 450°.

A. A. E.

**Crystalline rubber hydrocarbon.** E. W. WASHBURN (Physical Rev., 1931, [ii], 38, 1790—1791).—Rubber crystals, m.p. —35° to 0°, have been obtained.

L. S. T.

**Number of stereoisomeric and non-stereoisomeric alkenes.** D. D. COFFMAN (J. Amer. Chem. Soc., 1933, 55, 695—698).—Theoretical. The no. of stereoisomeric and non-stereoisomeric acetylenes,  $\text{CH}\cdot\text{CR}$ , is deduced from the no. of stereoisomeric and non-stereoisomeric mono-substituted paraffins. Formulæ are advanced for calculating the no. of stereoisomeric and non-stereoisomeric acetylenes  $\text{CR}\cdot\text{CR}'$ , but their use involves a knowledge of the no. of stereoisomeric and non-stereoisomeric mono-substituted paraffins of *N*—3 and all smaller C contents.

H. B.

**Acetylene polymerides and derivatives. IV. Addition of hydrogen bromide to vinylacetylene: bromoprene [ $\beta$ -bromo- $\Delta^{\alpha\gamma}$ -butadiene] and  $\beta\delta$ -dibromo- $\Delta^{\beta}$ -butene. V. New synthetic rubbers. III. Polymerisation of bromoprene.** W. H. CAROTHERS, A. M. COLLINS, and J. E. KIRBY (J. Amer. Chem. Soc., 1933, 55, 786—788, 789—795).—IV. The primary product from vinylacetylene, conc. HBr, and CuBr is considered to be  $\delta$ -bromo- $\Delta^{\alpha\beta}$ -butadiene (not isolable), which then rearranges to  $\beta$ -bromo- $\Delta^{\alpha\gamma}$ -butadiene (bromoprene) (I), b.p. 42—43°/165 mm.; some  $\beta\delta$ -dibromo- $\Delta^{\beta}$ -butene, b.p. 168—169° (with loss of HBr)/760 mm., from (I) and HBr, is also formed. Maleic anhydride and (I) give 4-bromo- $\Delta^4$ -tetrahydrophthalic acid, m.p. 186.5—187°, whilst  $\alpha$ -naphthaquinone and (I) afford (probably) 2-bromo-1:4:11:12-tetrahydroanthraquinone, m.p. (block) 138° (turns blue at 115°) (cf. A., 1932, 1232), which is oxidised by air in dil. EtOH-NaOH to 2-bromoanthraquinone.

V. The polymerisation of (I) is closely analogous to, but occurs more rapidly than, that of chloroprene (B., 1932, 156). Spontaneous polymerisation in presence of a little air gives (after 8—10 days)  $\mu$ -polybromoprene (II), which is tough, resilient, and elastic, and when kept becomes harder and less resilient owing to atm. oxidation (preventible by application of anti-oxidants to the surface). Exposure of (I) to light from a Cooper-Hewitt lamp at 25° affords plastic  $\alpha$ -polybromoprene (pptd. from the mixture by EtOH), which when heated passes into (II). (I) heated at 80°/5 days in presence of a little thiodiphenylamine yields  $\beta$ -polybromoprene, b.p. 104—110°/11 mm., whilst slow polymerisation of (I)

in presence of *e.g.*  $\beta$ -C<sub>10</sub>H<sub>7</sub>-NHPh affords the granular  $\omega$ -polybromoprene. (I) is readily dispersed in H<sub>2</sub>O; the resulting emulsion polymerises rapidly to form a stable latex (*cf. loc. cit.*). H. B.

**Reaction of atomic hydrogen with chloroform.** H. FROMHERZ and H. SCHNELLER (*Z. physikal. Chem.*, 1933, **B**, 20, 158—160).—HCl, MeCl, and an apparently polymerised solid containing Cl are formed, with luminescence and considerable heat evolution. R. C.

**Formation of hexafluoroethane and tetrafluoroethylene from carbon tetrafluoride.** O. RUFF and O. BRETSCHNEIDER (*Z. anorg. Chem.*, 1933, **210**, 173—183).—The products formed by a C arc burning in CF<sub>4</sub> contain C<sub>2</sub>F<sub>6</sub> and C<sub>2</sub>F<sub>4</sub>, separated after converting the latter into *dibromotetrafluoroethane*, m.p. —111.5°, b.p. 47.4°, which, when treated with Zn and AcOH, yields C<sub>2</sub>F<sub>4</sub> m.p. —142.5°, b.p. —76.3°. Chemically, C<sub>2</sub>F<sub>6</sub> is inert, and C<sub>2</sub>F<sub>4</sub> resembles C<sub>2</sub>H<sub>4</sub>. V.p., *d*, and heats of vaporisation are recorded. F. L. U.

**Change of molecular structure during chemical reaction. II. Rearrangement of butyl bromides.** W. HÜCKEL and P. ACKERMANN (*J. pr. Chem.*, 1933, [ii], 136, 15—29).—The formation of *sec.*-BuBr (in addition to *tert.*-BuBr; *cf. A.*, 1911, i, 250) when Bu<sup>*β*</sup>Br is heated at 210—230° is proved by treatment of the product with AgOAc, which gives the corresponding acetates and butenes (the latter preponderating in glacial AcOH at the b.p.), hydrogenation of the latter to butanes, and determination of the v.p.-temp. curve, which is found to lie between those of *n.*- and *iso.*-butanes. *sec.*-BuBr is found to be unchanged under the same conditions. Redeterminations of the v.p.-temp. curves of *n.*- and *iso.*-butanes give results at variance with those of Burrell and Robertson (*A.*, 1916, i, 6) in the case of the latter. The degree of homogeneity of the butenes is determined by measuring the v.p. of the total hydrocarbon and of the residue after the bulk has been distilled. Catalytic dehydration of Bu<sup>*β*</sup>OH (*phenylurethane*, m.p. 86°) over graphite at 400° gives pure *isobutene* (*nitroschloride*, m.p. 98°; *nitrosopiperidide*, m.p. 137—138°); *sec.*-BuOH (*phenylurethane*, m.p. 64.5°) gives *trans.*- and a little *cis-n.*- $\Delta^{\beta}$ . containing approx. 10% of *n.*- $\Delta^{\alpha}$ -butene (composition from b.p./1 atm.), but free from *isobutene*, as pure *n.*-butane is formed on hydrogenation. *sec.*-BuBr gives with AgOAc in AcOH a mixture of *n.*- $\Delta^{\beta}$ - and - $\Delta^{\alpha}$ -butenes containing more  $\Delta^{\beta}$ -butene than the above; Bu<sup>*β*</sup>Br gives a mixture converted by H<sub>2</sub> into pure *isobutane*, whence the impurities are regarded as polymerides.

H. A. P.

**Rotatory powers of the chlorides produced by heating certain chloroformates in solvents.** (MISS) M. B. HARFORD, J. KENYON, and H. PHILLIPS (*J.C.S.*, 1933, 179—181).—Decomp. of *l.*- $\beta$ -octyl chloroformate (I) (*A.*, 1932, 611) and *l.*-Et phenylchloroformoxyacetate (II) (*A.*, 1931, 1291) when heated in various solvents affords *l.*-rotatory chlorides, CO<sub>2</sub>, and HCl [also octylene from (I)]. The chlorides from (I) have approx. the same rotation, but those from (II) vary, which supports the view that the cationic  $\beta$ -octyl radical affords an unsaturated

compound rather than inverts to a *d.*-chloride, whereas with (II) the opposite reaction is the more facile.

J. L. D.

**Identification of alcohols in dilute aqueous solution.** H. HENSTOCK (*J.C.S.*, 1933, 216).—A method of identifying alcohols in low concns. (> 1.5%) by their *p.*-nitrobenzoates is described. J. L. D.

**Determination of lower alcohols in dilute aqueous solutions.** A. VANSCHIEDT and O. EREMEEVA (*J. Gen. Chem. Russ.*, 1932, **2**, 800—805).—1 c.c. of saturated aq. NaNO<sub>2</sub> and 2 c.c. of H<sub>3</sub>PO<sub>4</sub> are added to 5—10 c.c. of solution, containing 10—60 mg. of EtOH or MeOH, and a stream of CO<sub>2</sub>-free air is passed through the solution at 35°. The mixture of air, alkyl nitrite, and oxides of N is passed through a heated Cu spiral, and successively through absorption tubes containing a solution of Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in conc. H<sub>2</sub>SO<sub>4</sub> at 135—140°, and 50% KOH. The gain in wt. of the KOH tube represents CO<sub>2</sub> originating from oxidation of alkyl nitrite, and the alcohol content is hence calc. The presence of small quantities of MeCHO does not interfere; Et<sub>2</sub>O, if present, should first be removed by aëration.

R. T.

**Action of calcium hypochlorite on alcohols aldehydes, and ketones.** I. F. SUKNEVITSCH and A. A. TSCHILINGARIAN (*J. Gen. Chem. Russ.*, 1932, **2**, 783—789).—EtOH and aq. Ca(OCl)<sub>2</sub> containing 10% of available Cl give on distillation CHCl<sub>3</sub> and EtOCl; the latter is transformed into CH<sub>2</sub>Cl·OEt by passing C<sub>2</sub>H<sub>4</sub> into the receiver, whilst if it is passed through the reaction mixture, practically no CHCl<sub>3</sub> is formed. HOCl and Et<sub>2</sub>O also give EtOCl, subsequently converted into MeCHO with evolution of heat and disappearance of the yellow colour. No CHCl<sub>3</sub> is formed from Ca(OCl)<sub>2</sub> and CMe<sub>3</sub>·OH, only the corresponding hypochlorite. Pr<sup>*β*</sup>CHO, Bu<sup>*β*</sup>CHO, and heptaldehyde do not give CHCl<sub>3</sub>, but are oxidised to the corresponding acids, and no yellow colour, due to the formation of a hypochlorite, is observed. Pr<sup>*α*</sup>OH, Bu<sup>*α*</sup>OH, and Bu<sup>*β*</sup>OH, which have no *tert.*-C next to OH, yield CHCl<sub>3</sub> and the corresponding hypochlorite, subsequently giving an aldehyde and the ester of the corresponding acid with the alcohol employed. The first step in the reaction between Ca(OCl)<sub>2</sub> and EtOH is the formation of EtOCl, which then gives MeCHO, and the enolic form of the latter is chlorinated to CCl<sub>3</sub>·CHO, which decomposes with alkali into CHCl<sub>3</sub> and a formate. A second reaction is the addition of EtOCl to the enol of MeCHO, giving CH<sub>2</sub>Cl·CH(OH)·OEt, which splits off EtOH with alkali and the enol formed reacts again in the same way, finally giving CCl<sub>3</sub>·CHO. The reaction with COMe<sub>2</sub> is explained similarly, as is also the inability of paracetaldehyde, MeOH, and CMe<sub>3</sub>·OH to yield CHCl<sub>3</sub>. G. A. R. K.

**Tertiary aliphatic carbinols containing an adjacent tertiary hydrogen, the related chlorides, and dehydration products.** F. C. WHITMORE and W. L. EYERS (*J. Amer. Chem. Soc.*, 1933, **55**, 812—816).—The following carbinols are prepared from COMePr<sup>*β*</sup> and the appropriate Mg alkyl bromide:  $\beta$ - $\gamma$ -dimethylpentan- $\gamma$ -ol, b.p. 38—39°/7 mm. (*chloride*, b.p. 133—138°), dehydrated by heating with a little

I to  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ - and - $\Delta^{\gamma}$ -pentenes;  $\beta\gamma$ -dimethylhexan- $\gamma$ -ol, b.p. 42—43°/6 mm. (chloride, b.p. 41—43°/12 mm.), dehydrated to  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ - and - $\Delta^{\gamma}$ -hexenes;  $\beta\gamma$ -dimethylheptan- $\gamma$ -ol, b.p. 56—57°/5 mm., 42°/2 mm. (chloride, b.p. 54°/8 mm.), dehydrated to  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ , b.p. 136.2—136.8°/743 mm., and - $\Delta^{\gamma}$ , b.p. 138.4—138.8°/740.5 mm., -heptenes;  $\beta\gamma$ -dimethyloctan- $\gamma$ -ol, b.p. 69—70°/5 mm. (chloride, b.p. 53—55°/3 mm.), dehydrated to  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ , b.p. 158.4—158.8°/733 mm., and - $\Delta^{\gamma}$ , b.p. 161.2—161.4°/739 mm., -octenes. The  $\Delta^{\beta}$ - and  $\Delta^{\gamma}$ -olefines (structures determined by ozonolysis) are formed in the ratio 2 : 1.

H. B.

#### Additive properties of secondary $\alpha\alpha'$ -diacetylenic alcohols and their alcoholic properties.

C. K. LIANG (Bull. Soc. chim., 1933, [ii], 53, 33—41, 41—47).—MgEtBr and excess of an acetylenic hydrocarbon give a Grignard reagent, which with  $\text{HCO}_2\text{Et}$  (0.5 mol.) yields compounds (A) of the type  $(\text{CR}:\text{C})_2\text{CH}\cdot\text{OH}$ . Thus are prepared:  $\Delta^{\beta\gamma}$ -undecadien- $\zeta$ -ol, b.p. 138—139°/19 mm.;  $\Delta^{\theta}$ -tridecadien- $\eta$ -ol, b.p. 155—156°/15 mm.;  $\Delta^{\delta}$ -pentadecadien-0-ol (I), b.p. 150—151°/5 mm.;  $\Delta^{\gamma\epsilon}$ -heptadecadien-1-ol, b.p. 192—193°/8 mm.;  $\Delta^{\alpha\omega}$ -tricosadien- $\nu$ -ol, m.p. 24°;  $\alpha\epsilon$ -diphenyl- (II), m.p. 69—70°, -di-*p*-tolyl- (III), m.p. 95—96°, and -di-2 : 4-dimethylphenyl- (IV) - $\Delta^{\delta\theta}$ -pentadien- $\gamma$ -ol, m.p. 93—94°. The aromatic, but not the aliphatic, compounds show a large exaltation of  $n$ . Unless an excess of acetylenic hydrocarbon is used in these preps., the resultant Grignard reagent contains MgEtBr, which with  $\text{HCO}_2\text{Et}$  leads to  $\text{CHEt}_2\cdot\text{OH}$  and mixed Et mono-acetylenic alcohols. In this way are obtained:  $\Delta^{\delta}$ -octinen- $\gamma$ -ol, b.p. 80—82°/25 mm.,  $\Delta^{\delta}$ -decinen- $\gamma$ -ol, b.p. 100—102°/15 mm., and  $\Delta^{\delta}$ -undecinen- $\gamma$ -ol, b.p. 96—97°/4 mm., also obtained from EtCHO and the Mg or Na derivatives of the acetylenic hydrocarbons. Compounds (A) are decomposed by  $\text{H}_2\text{SO}_4\text{-AcOH}$ . (II) is oxidised by 6%  $\text{KMnO}_4$  to BzOH only, but with  $\text{O}_3$  gives also tartaric acid. (I), (II), and (IV) with hot 20%  $\text{HgCl}_2\text{-EtOH}$  add only 1 mol. of  $\text{HgCl}_2$ ; the compounds from (I) and (IV) are destroyed by hydrolysis, but the compound from (II) with hot 15%  $\text{HCl}$  gives  $\alpha\epsilon$ -diphenyl- $\Delta^{\alpha}$ -pentinen- $\gamma$ -ol- $\epsilon$ -one, m.p. 96—97°, oxidised to BzOH by  $\text{KMnO}_4$ . With hot 12%  $\text{KOH-EtOH}$  (II) and (III) give much resin and  $\alpha\epsilon$ -diphenyl-, m.p. 131°, and  $\alpha\epsilon$ -di-2 : 4-dimethylphenyl-pentan- $\gamma$ -ol- $\beta\delta$ -dione, m.p. 180°, respectively, giving on oxidation the expected aromatic acid. (III) in EtOAc with aq. colloidal Pd and  $\text{H}_2$  is reduced at each acetylenic linking successively, affording  $\alpha\epsilon$ -di-*p*-tolylpentan- $\gamma$ -ol, m.p. 96°, -di-*p*-tolyl- $\Delta^{\alpha}$ -penten- $\Delta^{\delta}$ -inen- $\gamma$ -ol, m.p. 94° (probably the *trans* form, since it is unchanged by illumination), and (?) *cis*- $\alpha\epsilon$ -di-*p*-tolyl- $\Delta^{\alpha}$ -penten- $\gamma$ -ol, an oil, b.p. 180—182°/4 mm., changed by illumination into the (?) *trans* form, m.p. 93°.

Compounds,  $(\text{CR}:\text{C})_2\text{CH}\cdot\text{OH}$ , show one reactive OH group with  $\text{ZnEt}_2$ . The following derivatives were prepared by the usual methods:  $\zeta$ -bromo- $\Delta^{\beta\gamma}$ -undecadienene, b.p. 126—127°/21 mm.; 0-chloro- $\Delta^{\delta}$ -pentadecadienene (by  $\text{SOCl}_2$  in  $\text{C}_5\text{H}_5\text{N}$ ), b.p. 130—133°/5 mm.; *ν*-ethoxy-, b.p. 165—166°/6 mm., and *ν*-acetoxy- $\Delta^{\gamma\epsilon}$ -heptadecadienene, b.p. 188—189°/8 mm.; and  $\alpha\epsilon$ -di-*p*-tolyl- $\Delta^{\delta\theta}$ -pentadien- $\gamma$ -ol diphenylurethane,

m.p. 154°. The acetylenic linkings are oxidised by  $\text{KMnO}_4$ ,  $\text{HNO}_3$ , etc., but with cold  $\text{CrO}_3\text{-AcOH}$   $\Delta^{\gamma\epsilon}$ -heptadecadien- $\nu$ -one, b.p. 155—158°/5 mm. [semicarbazone, m.p. 305° (decomp.)], and  $\alpha\epsilon$ -diphenyl- $\Delta^{\delta\theta}$ -pentadien- $\gamma$ -one, m.p. 64—65°, are obtained in 75—90% yield. MgEtBr and  $\Delta^{\delta}$ -pentadecadien-0-ol in hot  $\text{Et}_2\text{O}$  give the Grignard reagent, which with PhCHO gives a little  $\text{CH}_2\text{Ph}\cdot\text{OH}$  and  $\Delta^{\delta}$ -pentadien-0-one [semicarbazone, m.p. 290° (decomp.)], but by further reaction only resins and more  $\text{CH}_2\text{Ph}\cdot\text{OH}$ .

R. S. C.

Identification and biochemical oxidation of  $\alpha$ -glucoheptulitol. (MME.) Y. KHOUVINE and G. NITZBERG (Compt. rend., 1933, 196, 218—220).—The individuality of  $\alpha$ -glucoheptulitol (I), obtained by reduction of  $\alpha$ -glucoheptulose (II) (Bertrand and Nitzberg, A., 1928, 620), is established by fractionation and X-ray analysis. Cultures of sorbose bacteria in yeast extract oxidise 80% of (I) in 1.5 months to (II), and not to  $\beta$ -glucoheptulose, anticipated if (I) were identical with  $\beta$ -glucoheptitol.

A. C.

Explosion of ethereal extracts. N. KRASOVSKI (Ukrain. Chem. J., 1932, 7, [Sci.], 98—104).—The causes of explosion of  $\text{Et}_2\text{O}$  extracts during their distillation are discussed.

R. T.

Apparatus for the micro-determination of ethoxyl and methoxyl groups, and of glycerol. R. GUILLEMET (Bull. Soc. chim., 1932, [iv], 51, 1547—1551).—Micro-determination of OEt groups by Pregl's technique gives low vals. owing to retention of EtI by moist P. Condensation of the liberated I in a dry U-tube or, better, absorption by moist KI crystals (in a special apparatus) allows accurate determination of OEt and OMe groups. Aq. glycerol can be evaporated and determined by the same technique within  $\pm 1\%$ .

R. S. C.

Mechanism of polymerisation. H. HIBBERT and S. Z. PERRY (Canad. J. Res., 1933, 8, 102).— $(\text{CH}_2)_2\text{O}$  polymerises in presence of aq. alkali to polyethylene glycol ethers,  $\text{H}\cdot[\text{O}\cdot\text{CH}_2\cdot\text{CH}_2]_n\cdot\text{OH}$ , the compounds where  $n=1-9$  having been isolated in addition to *cryst.* higher polyethylene glycols. With MeOH in place of  $\text{H}_2\text{O}$  the terminal groups are  $\cdot\text{OMe}$  and  $\cdot\text{OH}$ , and with amines ( $\text{NH}_2\text{R}$ ) they are probably  $\cdot\text{NHR}$  and  $\cdot\text{OH}$ . "Polymerisation" in this case therefore occurs by addition of the unstable ring to the OH group.

H. A. P.

Oxides of isoprene and butadiene. R. PUMMERER and W. REINDEL [with, in part, K. TRAUlsen] (Ber., 1933, 66, [B], 335—339).—Isoprene is converted by  $\text{BzO}_2\text{H}$  (prep. described) in EtCl into  $\beta$ -methylbutadiene  $\alpha\beta$ -oxide (I), b.p. 81°/735 mm., in which the presence of a double linking is established by reaction with ICl. (I) is violently isomerised by mineral acids, particularly  $\text{H}_2\text{SO}_4$ , to tiglaldehyde (II) (*p*-nitrophenylhydrazone, m.p. 181°; semicarbazone, m.p. 219°), accompanied by a non-distillable polymeride of (I) or (II). Hydrogenation of (I) (Pd-C) gives a non-homogeneous, saturated product with an intense odour of amyl alcohol. Under similar conditions, butadiene affords  $\Delta^{\gamma}$ -butene  $\alpha\beta$ -oxide, b.p. 66.5°/735 mm.

H. W.

Unsaponifiable matter from the oils of elasmobranch fish. IX. Structure of batyl and selachyl alcohols. W. H. DAVIES, I. M. HEILBRON, and W. E. JONES (J.C.S., 1933, 165—167; cf. following abstract).—Oxidation of batyl alcohol by Criegee's method (A., 1931, 461) affords  $\text{CH}_2\text{O}$  and *glycollaldehyde octadecyl ether*, m.p.  $51^\circ$  (2 : 4-dinitrophenylhydrazone, m.p.  $73^\circ$ ) [also formed by treating octadecyl allyl ether (A., 1931, 62) with  $\text{O}_3\text{-O}_6$  in AcOH during 3.5 hr.], which with  $\text{CrO}_3$  in hot AcOH during 0.5 hr. affords *glycollic acid octadecyl ether*, m.p.  $62\text{--}63^\circ$  (Et ester, m.p.  $41\text{--}42^\circ$ ; *methylamide*, m.p.  $83\text{--}84^\circ$ ). Contrary to Toyama (A., 1924, i, 604), batyl alcohol is optically active, having  $[\alpha]_{\text{D}}^{20} +2.6^\circ$  in  $\text{CHCl}_3$  (acetate,  $[\alpha]_{\text{D}}^{20} -8.5^\circ$  in  $\text{CHCl}_3$ ). As batyl alcohol is obtained by hydrogenation of selachyl alcohol, the latter is represented as  $\alpha$ -oleyl glyceryl ether. J. L. D.

Evidence from surface films on the constitution of batyl and chimyl alcohols. N. K. ADAM (J.C.S., 1933, 164—165).—Batyl alcohol and synthetic  $\alpha$ -octadecyl glyceryl ether form identical unimol. films, on  $\text{H}_2\text{O}$ , which supports the view (A., 1930, 852) that they are identical. Chimyl alcohol gives similar films, but the transition point between the condensed and expanded films is about  $15^\circ$  lower because the C chain is shorter by 2 C atoms. J. L. D.

Sulphonated oils. XIV. Sulphonated oil made from sperm oil. Preparation of salts of pure cetyl hydrogen sulphate and their properties. XV. Properties of aqueous solutions of pure salts of cetyl hydrogen sulphate. K. NISHIZAWA (J. Soc. Chem. Ind. Japan, 1931, 35, 548—550B, 550—551B).—XIV. [With T. TOMITSUKA.] Crystallographic data for the Na, K,  $\text{NH}_4$ , Mg, and Ca salts of cetyl H sulphate are detailed (with illustrations).

XV. The K, Mg, and Ca salts are very sparingly sol. in  $\text{H}_2\text{O}$ , but their solutions possess an appreciably lower surface tension to air or kerosene than  $\text{H}_2\text{O}$ . The lowering of the surface tension by the more sol. Na and  $\text{NH}_4$  salts is of the same order as that obtained by Na ricinoleate or Na sulphoricinoleate. Data for relative  $\eta$  of the solutions are also plotted. E. L.

Synthetic glycerides. IV. Esters of aromatic and aliphatic acids. D. T. JACKSON and C. G. KING (J. Amer. Chem. Soc., 1933, 55, 678—680).—The  $\beta$ -palmitate, m.p.  $71.5^\circ$ , -stearate, m.p.  $78.5\text{--}79.5^\circ$ , -laurate, m.p.  $47^\circ$ , and -*p*-nitrobenzoate (I), m.p.  $187.5^\circ$ , of glycerol  $\alpha\gamma$ -( $\text{CPh}_3$ )<sub>2</sub> ether (II) are prepared from (II) and the requisite acid chloride in  $\text{C}_6\text{H}_6$ -quinoline; removal of the  $\text{CPh}_3$  groups from (I) by  $\text{HBr-CHCl}_3$  gives glyceryl  $\beta$ -*p*-nitrobenzoate, but in the other cases the  $\alpha$ -monoglyceride results. The  $\beta\gamma$ -dipalmitate, m.p.  $40.5\text{--}41.5^\circ$ , -distearate, m.p.  $46\text{--}48^\circ$ , and -dibenzoate (III), m.p.  $92\text{--}94^\circ$ , of glycerol  $\alpha$ - $\text{CPh}_3$  ether are similarly prepared; removal of  $\text{CPh}_3$  from (III) affords glyceryl  $\alpha\beta$ -dibenzoate, whilst the others give the  $\alpha\gamma$ -diglycerides. H. B.

Lecithins. Y. YOKOYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, 8, 490—491).—Photomicrographs of three  $\alpha$ - and three  $\beta$ -lecithin derivatives (two from human brain and four from soya bean), *cryst.*, are reproduced. R. S. C.

Synthesis of lecithins and kephalins. I. Synthesis of dipalmityl- $\beta$ -kephalin and - $\beta$ -lecithin. I. KABASHIMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, 8, 492—495).—The double salt of Ba  $\beta$ -glycerophosphate and  $\text{Ba}(\text{NO}_3)_2$  with  $\text{K}_2\text{SO}_4$  gives  $\text{BaSO}_4$  and the  $\text{K}_2$  salt; the latter with palmityl chloride and KOH, or, better,  $\text{Ba}(\text{OH})_2$ , gives *dipalmityl- $\beta$ -glycerophosphoric acid*, isolated as Ag salt (I).  $\text{CH}_2\text{Br-CH}_2\text{Br}$  and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$  at  $150^\circ$  give *N- $\beta$ -bromoethylphthalimide*, m.p.  $82^\circ$ , whence  *$\beta$ -bromoethylamine picrate*, m.p. (anhyd.)  $130\text{--}131^\circ$ , ( $+0.5\text{H}_2\text{O}$ )  $99^\circ$ , is obtained. This with (I) in  $\text{COMe}_2\text{-C}_6\text{H}_6$  at  $85\text{--}90^\circ$  affords *dipalmityl- $\beta$ -kephalin*, *cryst.*, quantitatively hydrolysed to  *$\beta$ -glycerophosphoric acid* (II).  $\text{CH}_2\text{Br-CH}_2\text{Br}$  and  $\text{NMe}_3$  at  $125\text{--}130^\circ$  give " *$\beta$ -bromocholine bromide*" [*trimethyl- $\beta$ -bromoethylammonium bromide*], the *picrate*, m.p.  $158\text{--}159^\circ$ , of which with (I) affords *dipalmityl- $\beta$ -lecithin*, *sinters* at  $81^\circ$ , darkens at about  $170^\circ$ , and decomp. at about  $190^\circ$ , which is quantitatively hydrolysed to (II). The solubilities of the products and their complex salts are those of natural  $\beta$ -kephalins and -lecithins. R. S. C.

Enzymic scission of lysochitin and lecithin. Isomeric of the lecithins. A. CONTARDI and A. ERCOLI (Gazzetta, 1933, 63, 37—46).—When lecithinase-B free from -C (obtained from rice husks after long keeping) is added to aq. solutions of lysochitin a *substance*, m.p.  $183^\circ$  (decomp.), separates, which contains N and P in the proportions corresponding with a palmitostearolecithin. The synthesis of the *stearate* and *palmitate* of lysochitin is described. These substances have no haemolytic action. E. E. J. M.

Thermal decomposition of ethyl mercaptan and ethyl sulphide. N. R. TRENNER and H. A. TAYLOR (J. Chem. Physics, 1933, 1, 77—88; cf. A., 1931, 175).—Products of the thermal decomp. of  $\text{EtSH}$  and  $\text{Et}_2\text{S}$  at  $380\text{--}410^\circ$  are  $\text{H}_2\text{S}$ ,  $\text{C}_2\text{H}_4$ , and polysulphides. An intermediate product, b.p.  $48\text{--}49.5^\circ$ , with mercaptan properties, has been isolated in both cases. This product undergoes unimol. decomp. with energy of activation of about 40 kg.-cal. F. L. U.

Derivatives of selenium diethyl. T. SMEDSLUND (Finska Kem. Medd., 1932, 41, 13—26).—Se di- $\beta$ -chloroethyl dichloride (I) and  $\text{H}_2\text{O}$  (or dil. alkali) give *Se di- $\beta$ -chloroethyl oxide* (II), m.p.  $88^\circ$ , and then *Se di- $\beta$ -hydroxyethyl oxide* (III), m.p.  $121^\circ$  (decomp.). *Se di- $\beta$ -bromoethyl dibromide* (IV) similarly treated gives *Se di- $\beta$ -bromoethyl oxide* (V), m.p.  $61^\circ$ , and (III). (II) and (V) decompose on keeping. *Se di- $\beta$ -hydroxyethyl dichloride* (VI), m.p.  $85\text{--}86^\circ$ , is obtained by boiling an aq. solution of (I), and the *dibromide* (VII), m.p.  $94\text{--}95^\circ$  (decomp.), by boiling an aq. solution of (IV), or from (III) and conc. HBr. (I) and (IV) heated to  $130\text{--}160^\circ$  give Se and ethylene chloride or bromide. (VII) at  $170^\circ$  gives  $\text{CH}_2\text{Br-CH}_2\text{-OH}$ . Se di- $\beta$ -bromoethyl (VIII) and di- $\beta$ -chloroethyl with aq.  $\text{COMe}_2$  give *Se di- $\beta$ -hydroxyethyl*, b.p.  $143^\circ/2$  mm. (corresponding *phenylcarbimide*, m.p.  $130^\circ$ ), which adds Cl and Br in  $\text{CHCl}_3$  giving (VI) and (VII). *Se di- $\beta$ -methoxyethyl*, b.p.  $94^\circ/7$  mm. (*dichloride*, m.p.  $71\text{--}72^\circ$ ; *dibromide*, m.p.  $60\text{--}61^\circ$ ), is obtained from (VIII) and  $\text{NH}_3$  in EtOH. R. P. B.

**Constitution and structure of fatty acids.** E. L. LEDERER (Fettechem. Umschau, 1933, 40, 2—6).—A review. E. L.

**Preparation and decomposition of mixed acid anhydrides.** A. BARONI (Gazzetta, 1933, 63, 23—37).—Interaction in  $\text{Et}_2\text{O}$  of an acid chloride with the Na salt of a different acid gives acetomono- (I), -di-, and -tri-chloroacetic and mono- (II) and *s*-di-chloroacetic anhydrides, b.p. 80—83°/16 mm., 79—80°/16 mm., 88—89°/20 mm., 117°/16 mm., and 100—102°/15 mm., respectively. (I) and (II) are also obtained by heating  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  with  $\text{Ac}_2\text{O}$ . Butyric, trichlorobutyric, and benzoic acids when heated with  $\text{Ac}_2\text{O}$  give acetobutyric, b.p. 165°, *acetotrichlorobutyric*, b.p. 110—111°/20 mm., and acetobenzoic and *s*-butyric, b.p. 191°, *trichlorobutyric*, b.p. 138—140°, and benzoic anhydrides. Decomp. of a mixed anhydride with acid or with EtOH gives mainly the acyl derivative corresponding with the stronger acid. E. E. J. M.

**Preparation of pure formic acid.** A. A. PRILANISCHNIKOV and Z. F. SCHACHOVA (J. Gen. Chem. Russ., 1932, 2, 821—825).—The vals. given by the Internat. Bureau of Standards for the m.p., b.p., and *d* of pure  $\text{HCO}_2\text{H}$  are confirmed. R. T.

**Determination of acetic acid.** M. MUGDAN and J. WIMMER (Angew. Chem., 1933, 46, 117—118).—AcOH is determined by oxidation with KOH and CuO at 200—240° to  $\text{H}_2\text{C}_2\text{O}_4$ , which is then titrated with  $\text{KMnO}_4$ . Ca, if present, must be removed with  $\text{K}_2\text{CO}_3$  and  $\text{SO}_3$  must be oxidised with  $\text{H}_2\text{O}_2$ .  $\text{HCO}_2\text{H}$  and mineral acids do not interfere. A. G.

**Preparation of ethyl  $\beta$ -iodopropionate.** J. W. BAKER (J.C.S., 1933, 216).— $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  with NaI in boiling EtOH during 24 hr. affords  $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  in 81% yield. J. L. D.

**Dimorphism of aliphatic compounds. III. Ethyl margarate. IV. Ethyl esters [of fatty acids].** J. W. C. PHILLIPS and S. A. MUMFORD (Rec. trav. chim., 1933, 52, 175—180, 181—194).—III. The  $\alpha$ -form (I), f.p. 25·25°, of Et margarate forms unbroken series of solid solutions (showing neither max. nor min.) with  $\alpha$ -modifications of Et penta- and nona-decoates, palmitate, and stearate. The f.p. (17·2°) of the  $\beta$ -form (II), *i.e.*, the temp. at which the exothermic transition (I)→(II) occurs, and the m.p. (20·6°) of (II), *i.e.*, the temp. at which the transition (II)→(I) takes place, are both lowered by addition of higher or lower homologues, as is the rate of the transition (I)→(II). The f.p. curves of (I) with the above  $\alpha$ -homologues show two arrests; the data suggest that the transition (I)→(II) is complex. Et penta- and nona-decoates exhibit enantiotropic dimorphism similar to that of Et margarate, whilst tetra- and octa-decyl alcohols show the same dimorphism as does cetyl alcohol (A., 1931, 1003). Data are also given for tetradecyl, cetyl, and octadecyl acetates; each of these exists in two monotropic forms.

IV. The alternation of dimorphic type previously shown (A., 1932, 451) for the Et esters of high fatty acids occurs only above Et myristate. Both odd- and even-membered esters below this exist in monotropic modifications; the m.p. of the stable  $\beta$ -forms alternate,

whilst the f.p. of the metastable  $\alpha$ -forms lie on a smooth curve, the f.p. increasing with rise in C content. Examination of 10 binary systems of Et esters (decoate—nonadecoate) (including even—even, even—odd, and odd—odd) shows that in all the cases studied, the  $\alpha$ -forms give unbroken series of solid solutions showing neither max. nor min. An equation is derived connecting the f.p. of the binary mixture and its  $\alpha$ -components. Et undecoate, tridecoate, and nonoate probably exist in  $\gamma$ -modifications which resemble the third ( $\text{C}_1$ ) modification of the higher esters ( $\text{C}_{17}$ — $\text{C}_{21}$ ); the change  $\gamma$ → $\beta$  is effected by rubbing. H. B.

**Unsaturated acids and their derivatives. IX. Configuration of tetrabromostearic acid, m.p. 60°.** T. MARUYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, 8, 486—489; cf. A., 1932, 832).—The following prefixes (the historical order of discovery) are adopted for the tetrabromostearic acids:  $\alpha$ -, m.p. 114°;  $\beta$ -, liquid;  $\gamma$ -, m.p. 60° (I);  $\delta$ -, m.p. 58°. (I) (modified prep. from soya-bean oil) with Zn and  $\text{H}_2\text{SO}_4$  gives  $\Delta^{\alpha\lambda}$ -octadecadienoic acid [reconverted into (I) and other isomerides by Br], the constitution of which is proved by oxidation of the Me ester to azelaic (II), *n*-hexoic, and a little malonic acid (partly oxidised further to  $\text{H}_2\text{C}_2\text{O}_4$ ). (I) and KOH—EtOH at different temp. give: (a) at 28° a liquid acid,  $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Br}_2$ , either  $0\lambda$ - or  $\lambda\lambda$ -dibromo- $\Delta^{0\mu}$ -octadecadienoic acid, since it gives, when oxidised, (II) and valeric (III), but not oxalic acid; (b) at 80° an acid,  $\text{C}_{18}\text{H}_{29}\text{O}_2\text{Br}$ , either  $0$ - or  $\lambda$ -bromo- $\Delta^{0\mu}$ -octadecatrienoic acid, since oxidation affords (II), (III), and  $\text{H}_2\text{C}_2\text{O}_4$ ; (c) at 150°, the acid,  $\text{Me}[\text{CH}_2]_3[\text{CH}:\text{CH}]_2\text{C}:\text{C}[\text{CH}_2]_7\text{CO}_2\text{H}$ , oxidised to (II), (III), and  $\text{H}_2\text{C}_2\text{O}_4$ . On the principle that HBr is eliminated from *cis* positions it follows that (I) is  $0\lambda\mu$ -tetrabromostearic acid and that the  $0\lambda$ - and  $\lambda\mu$ -Br atoms are in the *trans* and *cis* positions, respectively; no choice can be made between the two steric formulæ thus possible for (I). In the parent  $\gamma$ -linoleic acid the configurations at the  $0$ - and  $\lambda$ -ethylenic linkings are probably *trans* and *cis*, respectively. R. S. C.

**Isomerism in the  $\beta$ -elæostearic acid series.** E. EIGENBERGER (J. pr. Chem., 1933, [ii], 136, 75—116).—Hydrolysis of freshly-prepared  $\beta$ -elæostearin (I) with EtOH—KOH (containing a little  $\text{H}_2\text{O}$  only) gives *K*  $\beta$ -elæostearate (II); the acid obtained (in solution) under carefully defined conditions can be reconverted into (II), but the free acid, m.p. 71—71·5°, isolated is a mixture. Crystallisation of (II) from 50% EtOH gives *K*  $\beta_1$ -elæostearate (III) [convertible into a *Ag* salt which with EtOH—KOH regenerates (III)], which when crystallised from EtOH rearranges into (II); a *K*  $\beta_1$ -acid salt,  $\text{C}_{18}\text{H}_{29}\text{O}_2\text{K}\cdot\text{C}_{18}\text{H}_{30}\text{O}_2$ , is described. Samples of (I) which have been allowed to autoxidise in the dark contain  $\text{COMe}_2$ -sol. and -insol. material; hydrolysis of the insol. part with EtOH—KOH causes evolution of  $\text{O}_2$  and gives *K*  $\beta_2$ -elæostearate (IV), also formed by autoxidation of (II) or (III); the  $\beta_2$ -acid is produced when the above acid mixture is heated above the m.p. When the acid from (III) is heated at 250° in  $\text{CO}_2$ , the resulting product sublimed, the sublimate extracted with

light petroleum, and the extract evaporated in  $\text{CO}_2$ , cryst. material is first obtained; the filtrate contains  $\beta_3$ -*elaeostearic acid*, an oil [amorphous K salt, also formed when (III) is heated to  $210^\circ/\text{vac.}$ ], which changes into the  $\beta_2$ -acid on keeping. Numerous other inter-conversions are studied. A corresponding series of Na salts is prepared. (IV) has the max. solubility and min. sp. conductivity in 94.6% (wt.) EtOH at  $20^\circ$  and  $25^\circ$ , respectively; (II) has the max. conductivity and (III) has min. solubility. H. B.

**Polymerisation of methyl esters of higher unsaturated fatty acids. XI. Structure of the dimerides of the methyl ester of linoleic acid.** K. KINO (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1933, 20, 103—108).—Ozonolysis of dimeric Me linoleate (I) (obtained by heating in  $\text{H}_2$  at  $290$ – $300^\circ$ ) affords Me H azelaate and an aldehyde oxidised to an acid  $(\text{Me}[\text{CH}_2]_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ . If hydrolysed prior to ozonolysis, subsequent esterification of the acid product gives Me<sub>2</sub> azelaate. Hence (I) has the structure  $(\text{Me}[\text{CH}_2]_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}[\text{CH}_2]_7\cdot\text{CO}_2\text{Me})_2$ . J. W. B.

**Oxidation of hydroxy-acids and sugars by periodic acid.** P. FLEURY and J. LANGE (Compt. rend., 1932, 195, 1395—1397).—MeOH, EtOH, pentaerythritol, glycollic, malic, and citric acids are not oxidised by cold  $\text{HIO}_4$ , but compounds containing  $\alpha$ -diol groupings are oxidised in 1—2 hr. (cf. Malaprade, A., 1928, 269),  $\text{CH}_2\cdot\text{OH}$  groups being converted into  $\text{CH}_2\text{O}$  (I),  $\text{CH}\cdot\text{OH}$  into  $\text{HCO}_2\text{H}$  (II) or into glyoxylic acid (III) when adjacent to  $\cdot\text{CO}_2\text{H}$  in the original mol. Tartaric acid (1 mol.) is oxidised to (III) (2 mols.); gluconic acid to (I) (1 mol.), (II) (3 mols.), and (III) (1 mol.); saccharic acid to (II) (2 mols.) and (III) (2 mols.), glucose to (I) (1 mol.) and (II) (5 mols.). Dihydroxyacetone is abnormal, affording (I) and glycollic acid. Similarly, fructose gives (I), (II) (3 mols.), and glycollic acid. A. C.

**Alkoxy-acids and their esters.** S. SABETAY (Bull. Soc. chim., 1932, [iv], 51, 1619—1620).—Concerning priority (cf. Rothstein, A., 1932, 832; Sabetay, A., 1928, 1130 *et seq.*). R. S. C.

**Emetics derived from lactic acid.** VOLMAR and BETZ (Compt. rend., 1933, 196, 355—357).—Max. fixation of  $\text{Sb}_2\text{O}_3$  by *N*-lactic acid at  $100^\circ$  in the presence of increasing concn. of *N*-NaOH under otherwise standard conditions occurs with equimol. concn. of lactic acid and its Na salt, and under such conditions the time curve for the fixation of Sb exactly resembles that of an ordinary esterification. Using these optimum conditions is obtained cryst. *Na antimonyl lactate*,  $\text{Sb}(\text{OH})(\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na})_2$ , m. p.  $230^\circ$  (decomp.), completely hydrolysed by  $\text{H}_2\text{O}$ . J. W. B.

**Hydroxy- and bromo-esters derived from the hydrogenation of  $\omega$ -acetyl esters.** E. J. LEASE and S. M. McELVAIN (J. Amer. Chem. Soc., 1933, 55, 806—808).—The rate of reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , EtOH) of  $\text{Ac}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{Et}$  ( $n = 1$ – $5$ ) to  $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{Et}$  (converted by  $\text{PBr}_3$  in  $\text{C}_6\text{H}_6$  into  $\text{CHBrMe}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{Et}$ ) generally decreases with rise in the val. of  $n$ . The following are new: *Et  $\delta$ -acetylvalerate*, b. p.  $107$ – $108^\circ/9$  mm.; *Et  $\epsilon$ -acetyl-*

*hexoate*, b. p.  $121$ – $122^\circ/9$  mm.; *Et  $\delta$ -hydroxy-*, b. p.  $94$ – $95^\circ/2$  mm., and  *$\delta$ -bromo-*, b. p.  $69$ – $71^\circ/2$  mm., *-hexoates*; *Et  $\epsilon$ -hydroxy-*, b. p.  $103$ – $104^\circ/2$  mm., and  *$\epsilon$ -bromo-*, b. p.  $85$ – $87^\circ/2$  mm., *-heptoates*; *Et  $\zeta$ -hydroxy-*, b. p.  $111$ – $113^\circ/2$  mm., and  *$\zeta$ -bromo-*, b. p.  $95$ – $96^\circ/2$  mm., *-octoates*; *Et  $\gamma$ -bromovalerate*, b. p.  $52$ – $54^\circ/2$  mm. Rapid distillation of *Et  $\gamma$ -hydroxyvalerate*, b. p.  $85$ – $86^\circ/2$  mm., does not give  $\gamma$ -valerolactone. H. B.

**Carbon suboxide.** C. D. HURD and F. D. PILGRIM (J. Amer. Chem. Soc., 1933, 55, 757—759).— $\text{C}_3\text{O}_2$ , conveniently prepared in 35—49% yield by passing diacetyltartaric anhydride through a Pyrex-glass tube at  $625$ – $650^\circ$ , reacts with 2 mols. of  $\text{NH}_2\cdot\text{OH}$  (at  $-15^\circ$ ) and  $\text{NPh}\cdot\text{OH}$  (in EtOAc at  $0^\circ$ ) to give malonhydroxamic acid and its  $\text{NN}'\text{-Ph}_2$  derivative, m. p.  $128^\circ$ , respectively. H. B.

**Properties of *d*-xylonolactone.** V. HASENFRATZ (Compt. rend., 1933, 196, 350—353).—The action of  $\text{H}_2\text{S}$  on *Pb d-xylonate* ( $+5\text{H}_2\text{O}$ ), m. p.  $59^\circ$ ,  $[\alpha]_D^{25} -5.9^\circ$  in  $\text{H}_2\text{O}$ , affords cryst. *d-xylono- $\gamma$ -lactone*, m. p.  $99$ – $103^\circ$ ,  $[\alpha]_D^{25} +85.5^\circ$  to  $+24.2^\circ$  (39 days), which, like *l-arabo-* and *l-ribo-*lactones (A., 1927, 229), affords a mixture of pyromucic and isopyromucic acids by thermal decomp., and with  $\text{Ac}_2\text{O}\text{-ZnCl}_2$  yields a  $\text{Ac}_3$  derivative, m. p.  $99^\circ$ ,  $[\alpha]_D^{25} +62.4^\circ$  in EtOH, but does not give cryst. Me and Et esters. J. W. B.

**Complexes of hydroferro- and hydroferri-cyanic acids with aldehydes and ketones.** P. DUPRAT (Bull. Inst. Pin, 1933, 37, 17—24, 36—37).—In extension of Baeyer and Villiger's work (A., 1902, i, 355) the formation of cryst. additive complexes between aldehydes and ketones (A) and  $\text{H}_4\text{Fe}(\text{CN})_6$  (B) (obtained pure and cryst. by decomp. of its  $\text{Et}_2\text{O}$  complex over  $\text{H}_2\text{SO}_4$  in a vac.), either in the pure liquid, in ligroin, or, sometimes, aq. solution, is investigated. Thus are obtained complexes with  $\text{MeCHO}$ ,  $\text{CCl}_3\cdot\text{CHO}$ , *n*-heptaldehyde,  $\text{PhCHO}$ , anisaldehyde,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ ,  $\text{CH}_2\text{Ph}\cdot\text{CHO}$ , citral, furfuraldehyde, all of type AB.  $\text{COEt}_2$  and menthone give complexes  $\text{A}_2\text{B}$ ; in O-free solvents camphor gives the complex  $\text{A}_2\text{B}$ , fenchone gives the complexes  $\text{A}_2\text{B} + 3\cdot4\text{H}_2\text{O}$  and anhyd., and  $\text{AB} + \text{EtOH}$  and solvent-free; camphenilone affords the complex  $\text{A}_2\text{B} + 2\text{H}_2\text{O}$  and  $+0\cdot5\text{H}_2\text{O}$ ; whereas no additive compound could be isolated with  $\text{CH}_2\text{O}$ ,  $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$ ,  $\text{CH}_2\text{PhAc}$ ,  $\text{CO}(\text{CH}_2\text{Ph})_2$ , benzylidene- and furfurylidene-camphor, products of indefinite composition being obtained with  $\text{COMe}_2$  and  $\text{COMeEt}$ . These complexes are only slowly hydrolysed by  $\text{H}_2\text{O}$ . The earlier results using  $\text{H}_3\text{Fe}(\text{CN})_6$  (*loc. cit.*) are confirmed, most of the above giving cryst. complexes; thus fenchone gives  $\text{A}_2\text{B} + 2\text{H}_2\text{O}$ ; camphor,  $\text{A}_2\text{B} + 0\cdot5\text{H}_2\text{O}$ ; menthone,  $\text{A}_2\text{B} + \text{H}_2\text{O}$ , and  $\text{PhCHO}$  affords  $\text{AB} + 4\cdot5\text{H}_2\text{O}$ . J. W. B.

**Action of phosphoryl chloride on aldehydes.** M. BACKÈS (Compt. rend., 1933, 196, 277—279).—Aldehydes, when treated with  $\text{POCl}_3$ , form aldols if the C atom adjacent to the CHO group carries a H atom. If the H atom is absent, chlorination occurs. Thus,  $\beta$ -hydroxy- $\alpha$ -methylvaleraldehyde (I) (semicarbazone, a gum; 2 : 4-dinitrophenylhydrazone, m. p.  $161^\circ$ ) and its dimeride (semicarbazone, a gum) are formed from EtCHO,  $\beta$ -hydroxy- $\alpha\alpha\gamma$ -trimethylvaler-

aldehyde (2:4-dinitrophenylhydrazone, m.p. 177°) and its dimeride, cryst., b.p. 160°/4 mm., from  $\text{CHMe}_2\text{CHO}$ ,  $\beta$ -hydroxy- $\alpha$ -n-amylnonaldehyde, b.p. 103—106°/0.5 mm. (2:4-dinitrophenylhydrazone, m.p. 124.5°), and its dimeride, b.p. 185°/0.5 mm., from *n*-heptaldehyde. (I) and  $\text{POCl}_3$  give  $\alpha$ -methyl- $\Delta^1$ -pentenaldehyde, also obtained from  $\text{Pr}^a\text{CHO}$ .

R. S. C.

General method for the preparation of aldehydes by degradation of acids. G. DARZENS and A. LÉVY (Compt. rend., 1933, 196, 348—350).— $\alpha$ -Alkoxy-acids are converted by distillation under atm. pressure in the presence of a little reduced Cu into aldehydes;  $\text{R}\cdot\text{CH}(\text{OR}')\cdot\text{CO}_2\text{H} \rightarrow \text{R}\cdot\text{CHO} + \text{R}'\cdot\text{OH} + \text{CO}$ . Thus  $\alpha$ -methoxy-*n*-heptoic, b.p. 122°/15 mm.,  $\alpha$ -methoxy-*n*-dodecoic, m.p. 52°, b.p. 145°/4 mm., and  $\alpha$ -methoxystearic acid, m.p. 62.5°, b.p. 190°/5 mm., afford respectively *n*-hex-, undec-, and *n*-heptadec-aldehyde in 70%, 75%, and 100% yield.

J. W. B.

Synthesis of  $\alpha\alpha$ -dimethylated aliphatic aldehydes of high mol. wt. G. DARZENS and A. LÉVY (Compt. rend., 1933, 196, 184—187).—If R of  $\alpha$ -glycol Me ethers is large, boiling in  $\text{HCO}_2\text{H}$  causes migration with formation of an aldehyde,  $\text{CMe}_2\text{R}\cdot\text{CHO}$ . If R is small, the ketone  $\text{CHMe}_2\cdot\text{COR}$ , or a mixture of it and the aldehyde, is obtained. The following examples of these reactions are given:  $\alpha$ -bromostearic acid  $\rightarrow$  Me  $\alpha$ -methoxystearate, b.p. 184—185°, m.p. 17.5° and 34°,  $\rightarrow$   $\gamma$ -methoxy- $\beta$ -methylnonadecan- $\beta$ -ol, m.p. 0° and 18°,  $\rightarrow$   $\alpha\alpha$ -dimethylstearaldehyde, b.p. 165—177°, m.p. 14.5°; Me  $\alpha$ -methoxylaurate, b.p. 124°/2 mm.,  $\rightarrow$   $\gamma$ -methoxy- $\beta$ -methyltridecan- $\beta$ -ol, b.p. 134°/3 mm.,  $\rightarrow$   $\alpha\alpha$ -dimethyldodecaldehyde; Me  $\alpha$ -bromo-, b.p. 116°/2 mm.,  $\rightarrow$  Me  $\alpha$ -methoxy-hexanoate, b.p. 126°/15 mm.,  $\rightarrow$   $\gamma$ -methoxy- $\beta$ -methylundecan- $\beta$ -ol, b.p. 112°/?,  $\rightarrow$  a mixture of 30% of  $\alpha\alpha$ -dimethyldec-aldehyde and 70% of  $\text{Pr}^b$  octyl ketone; Me  $\alpha$ -methoxyheptanoate, b.p. 90°/12 mm.,  $\rightarrow$   $\gamma$ -methoxy- $\beta$ -methyl-octan- $\beta$ -ol, b.p. 86°/11 mm.,  $\rightarrow$   $\text{Pr}^b$  amyl ketone.

A. C.

Action of hydrogen cyanide on methylglyoxal. C. V. SMYTHE (Biochem. Z., 1933, 257, 371—384).—When  $\text{CN}'$  is added to a solution of  $\text{AcCHO}$  a double compound is formed which is readily oxidised by  $\text{O}_2$  giving  $\text{AcOH}$ ,  $\text{CO}_2$ , and a small amount of  $\text{HCO}_2\text{H}$ . In the absence of  $\text{O}_2$  or other oxidising agents, a mol. of free  $\text{AcCHO}$  may be used as oxidising agent,  $\text{AcCO}_2\text{H}$  (0.5 mol. per mol.  $\text{AcCHO}$  disappearing) and a product containing at least 6 C atoms being formed. The velocities of the aerobic and anaerobic reactions are of the same order, and in presence of both  $\text{O}_2$  and free  $\text{AcCHO}$  both reactions proceed simultaneously. With excess of  $\text{CN}'$  the reaction with  $\text{O}_2$  proceeds almost quantitatively.

P. W. C.

Rapid pyrogenation of keten. J. A. MULLER and (Miss) E. PEYTRAL (Compt. rend., 1933, 196, 279—280).—Keten, when in contact with Pt at 1150° for 0.002—0.003 sec., decomposes to  $\text{C}_2\text{H}_4$  (19.6—22.8%),  $\text{C}_2\text{H}_2$  (1.9—4.3%),  $\text{CO}$  (60.9—66.1%),  $\text{CH}_4$  (8.0—10.6%),  $\text{H}_2$  (2.0—3.3%), and C. The amount of C formed increases with the time of contact. Primary decomp. into  $\text{CO}$  and  $\text{CH}_2$  is postulated.

R. S. C.

Metallic compounds of the enolic forms of monocarbonyl compounds. XV. Preparation of keten diethylacetal. H. SCHEIBLER (Ber., 1933, 66, [B], 428).—In reply to Snell and McElvain (this vol., 259), an improved prep. of the compound is described. Analysis is best effected by determination of  $\text{OEt}$  according to Vieböck and Schwappach.

H. W.

Alleged specific test for acetone. R. J. W. LE FÈVRE and J. PEARSON (J.S.C.I., 1932, 51, 433—434T).—The test of Raw (A., 1932, 1235) is not sp. for  $\text{COMe}_2$  but gives positive results (indigotin formation) with ketones  $\text{R}\cdot\text{COMe}$ , where the group R does not materially diminish the incipient polarisation of the CO group on which the reaction evidently depends.

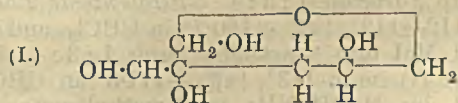
Preparation of the ketol  $\text{C}_6\text{H}_{10}\text{O}_3$  and of methylglyoxal. M. HENZE and R. MÜLLER (Z. physiol. Chem., 1933, 214, 281—284; cf. this vol., 88).—Details of the prep. of  $\text{AcCHO}$  (I) from  $\text{COMe}_2$  (cf. Riley *et al.*, A., 1932, 833) and of  $\gamma$ -hydroxyhexane- $\beta\epsilon$ -dione from (I) and  $\text{COMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  are given.

J. H. B.

Stereochemistry of aliphatic ketoximes. S. FURUKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 20, 71—86).—The oximes of Me palmityl, m.p. 73—74°, and Me lauryl, m.p. 56—57°, ketones could each be obtained in only one form and by the Beckmann change ( $\text{H}_2\text{SO}_4$  in  $\text{AcOH}$ ) and subsequent hydrolysis of the acid amide afford pentadecylamine and palmitic acid, and undecylamine and lauric acid, respectively. *Et palmityl ketoxime* is separated by fractional crystallisation into two stereoisomeric forms (I), m.p. 58—59° [converted into a mixture containing (II) by irradiation] and (II), m.p. 44—45°, from which similarly different proportions of pentadecylamine and palmitic acid are obtained. Similar differences in the proportion of the products were obtained in the case of the stereoisomeric forms, m.p. 52.5—53.5° (*Bz* derivative, m.p. 32.5—33°) (converted into the high-m.p. form by  $\text{HCl}$  in dry  $\text{Et}_2\text{O}$ ) and m.p. 64—65° (*Bz* derivative, m.p. 37.5°), of *Et stearyl*, and with the two forms, m.p. 43.5—44.5°, and m.p. 26.5—27.5°, of *Pr palmityl ketoxime*. In these cases both low- and high-m.p. forms are unchanged after fusion at 100°. In agreement with these results hydrolysis of the amide obtained by the Beckmann change from ginnoxime (A., 1932, 1138) gives *n*-decoic acid and *n*-nonadecylamine in addition to the products previously recorded. *Dipalmityl ketoxime*, m.p. 50—60°, similarly gives *palmitpentadecylamide*, m.p. 92—93°.

J. W. B.

isoSaccharinose. P. SCHORIGIN and N. N. MAKAROVA-SEMLIANSKAJA (Ber., 1933, 66, [B], 387—389).—Reduction of isosaccharine by  $\text{Na-Hg}$  in faintly



acid solution leads to non-cryst. isosaccharinose (I) (*p*-nitrophenylhydrazone, m.p. 168—169°;  $\text{Ac}_3$  derivatives, m.p. 98° and 85—86°, respectively).

H. W.

**3:5-Benzylidene- and 5:6-benzylidene-1:2-isopropylidene-glucose.** P. A. LEVENE and A. L. RAYMOND (Ber., 1933, 66, [B], 384—386).—Contrary to Brigl, 3:5-benzylidene-1:2-isopropylidene-glucose (I) (Brigl and Grüner, A., 1932, 1115) is not identical with the 5:6-benzylidene-1:2-isopropylidene-glucose (II) of Levene and Meyer (A., 1923, i, 92). The Bz derivatives of (I) and (II) have m.p. 124°,  $[\alpha]_D^{20} + 3.5^\circ$ , and m.p. 111.5—112°,  $[\alpha]_D^{20} - 43.6^\circ$  in  $\text{CHCl}_3$ , respectively, whilst the  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$  compounds have m.p. 121—121.5° and  $[\alpha]_D^{20} + 13.5^\circ$  in  $\text{CHCl}_3$  and (non-cryst.)  $[\alpha]_D^{20} - 16.5^\circ$  in  $\text{CHCl}_3$ , respectively. The supposition that (I) is unstable and passes into (II) under the influence of high temp. is supported by the observation that Brigl's compound is obtained in diminished yield when his directions are followed but a higher temp. is used, and that the process of Levene and Meyer, if continued for only a short time, leads to (I). H. W.

**Attempted preparation of esters of sugars and chloroacetic acid.** K. BRASS and E. KURZ (Ber., 1933, 66, [B], 442—446).—Attempts to prepare cellulose trimonochloroacetate leads to esters of the greatly degraded carbohydrate.  $\beta\text{-D}$ -Glucose is transformed by  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  and  $(\text{CH}_2\text{Cl}\cdot\text{CO})_2\text{O}$  in presence of  $\text{ZnCl}_2$  or conc.  $\text{H}_2\text{SO}_4$  into esterified and condensed products, whereby partial isomerisation occurs. Fructose appears to yield a  $(\text{CH}_2\text{Cl}\cdot\text{CO})_3$  derivative and to be anhydrided.  $\beta$ -Glucose penta-acetate (I) when heated for 20 min. at 130° with  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  and  $(\text{CH}_2\text{Cl}\cdot\text{CO})_2\text{O}$  affords  $\alpha$ -glucopyranose 2:3:4:6-tetra-acetate 1-chloroacetate, m.p. 129—130°,  $[\alpha]_D^{20} + 100.74^\circ$  in  $\text{C}_2\text{H}_2\text{Cl}_4$ , converted by  $\text{HBr}\cdot\text{AcOH}$  at 5—17° into acetobromoglucose (II), m.p. 87.2—88°,  $[\alpha]_D^{25} + 199.84^\circ$  in  $\text{CHCl}_3$ ; when the temp. is restricted to 120°, (I) gives  $\beta$ -glucopyranose 2:3:4:6-tetra-acetate 1-chloroacetate (II), m.p. 134—134.5°,  $[\alpha]_D^{25} - 1.39^\circ$  in  $\text{C}_2\text{H}_2\text{Cl}_4$ , also transformed into (II). (III) is partly converted into (I) by treatment with  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  and  $(\text{CH}_2\text{Cl}\cdot\text{CO})_2\text{O}$  at 120°. (I),  $(\text{CH}_2\text{Cl}\cdot\text{CO})_2\text{O}$ , and conc.  $\text{H}_2\text{SO}_4$  at 65° yield  $\alpha$ -glucopyranose 2:3:4-triacetate 1:6-dimono-chloroacetate, m.p. 93.5—94°,  $[\alpha]_D^{20} + 95.46^\circ$  in  $\text{C}_2\text{H}_2\text{Cl}_4$ . Cellobiose octa-acetate is transformed by  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  and  $(\text{CH}_2\text{Cl}\cdot\text{CO})_2\text{O}$  at 120° into cellobiose hepta-acetate 1-chloroacetate, m.p. 218—219°,  $[\alpha]_D^{17} + 46.55^\circ$  in  $\text{C}_2\text{H}_2\text{Cl}_4$ , whence acetobromocellobiose, m.p. 170—171.5°,  $[\alpha]_D^{25} + 94.70^\circ$  in  $\text{CHCl}_2$ . H. W.

**Carbohydrates. XV. Benzoyl and benzylidene derivatives of fructose.** P. BRIGL and R. SCHINLE (Ber., 1933, 66, [B], 325—330; cf. this vol., 148).—Fructose is converted by  $\text{BzCl}$  (4 mols.) and  $\text{C}_5\text{H}_5\text{N}$  in  $\text{CHCl}_3$  at  $-10^\circ$  and finally at room temp. into  $\beta$ -fructose 1:3:4:5-tetrabenzoate, m.p. 174—175°,  $[\alpha]_D^{20} - 164.9^\circ$  in  $\text{CHCl}_3$ , which rapidly reduces warm Fehling's solution, is transformed by  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$  into  $\beta$ -fructose 1:3:4:5-tetrabenzoate 2-acetate, m.p. 112—113°,  $[\alpha]_D^{20} - 160.7^\circ$  in  $\text{CHCl}_3$ , and by  $\text{Ag}_2\text{O}$  and  $\text{MeI}$  into  $\beta$ -methylfructoside 1:3:4:5-tetrabenzoate (I), m.p. 113°,  $[\alpha]_D^{20} - 171.3^\circ$  in  $\text{CHCl}_3$ , hydrolysed by  $\text{MeOH}\cdot\text{NH}_3$  to  $\beta$ -methylfructoside, m.p. 119°,  $[\alpha]_D^{20} - 171.8^\circ$ . An isomeric tetrabenzoate (II), m.p. 123—124°,  $[\alpha]_D^{20} - 6.10^\circ$  to  $-13.7^\circ$  in  $\text{CHCl}_3$ , is best obtained by complete benzoylation of fructose and subsequent treatment of the product with

$\text{HBr}\cdot\text{AcOH}$  followed by  $\text{Ag}_2\text{CO}_3$  in  $\text{MeOH}$ ; the yield is poor. Fructose and  $\text{BzCl}$  (5 mols.) in  $\text{CHCl}_3$  afford ketofructose 1:3:4:5:6-pentabenzoate, m.p. 124—125°,  $[\alpha]_D^{20} + 40.9^\circ$  in  $\text{CHCl}_3$ , which slowly reduces boiling Fehling's solution. The open structure is established by its transformation by  $\text{HCl}$  and  $\text{EtSH}$  into 2:3-diethylthiofructose 1:3:4:5:6-pentabenzoate, m.p. 128—129°,  $[\alpha]_D^{20} + 51.5^\circ$  in  $\text{CHCl}_3$ ; (I) and (II) do not react with  $\text{HCl}$  and  $\text{EtSH}$ .

Treatment of fructose with  $\text{PhCHO}$  and  $\text{ZnCl}_2$  at room temp. affords dibenzylidene-fructose, m.p. 160°,  $[\alpha]_D^{20} - 22.9^\circ$  in  $\text{CHCl}_3$  (*Ac*, m.p. 145—146°,  $[\alpha]_D^{20} - 37.5^\circ$  in  $\text{CHCl}_3$ , and *Bz*, m.p. 147°,  $[\alpha]_D^{20} - 18.05^\circ$  in  $\text{CHCl}_3$ , derivatives). H. W.

***am*-Hexose which occurs in the organism.** Y. KOTAKE and M. NISHAGAKI (Proc. Imp. Acad. Tokyo, 1932, 8, 507—510).—The liquid in the chamber of the eye, the cerebro-spinal fluid, and various other organs contain vitamose (I). The concn. of (I) in the extract from ox testicles (chiefly by pptn. by  $\text{CdSO}_4$ ) is described. Solutions of (I) yield a hexosazone, m.p. 205°, and di-2:4-dinitrophenylhydrazone, decomp. about 240° (rapid heating) (photomicrographs), give Trommer's reaction in the cold, Folin and Denis' reaction in very dil. solution, Selivanov's reaction rapidly when boiled, reduce  $\text{KMnO}_4$ ,  $\text{HIO}_3$ , and  $\text{HIO}$ , are decomposed by  $\text{O}_2$  (to give a little hexose), and are readily fermented by much yeast, but do not give pentose reactions. (I) is considered to be an *am*-hexose. R. S. C.

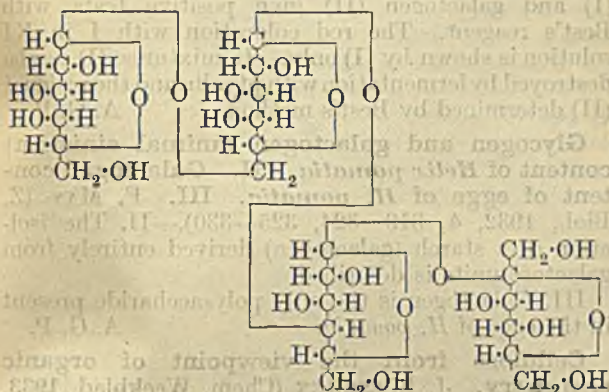
**Synthetic hexose phosphates. II.** K. JOSEPHSON and S. PROFFE.—See this vol., 428.

**New structural type of polysaccharides.** H. H. SCHLUBACH, H. KNOOP, and M. LIU (Naturwiss., 1933, 21, 62—63).—Methylirisin, containing 3 OMe groups to each hexose unit, yields on acid hydrolysis tetra- and di-methylfructose in about equal amount; irisin is, therefore, made up of two differently arranged fructose units. R. K. C.

**Constitution of stachyose.** M. ONUKI (Proc. Imp. Acad. Tokyo, 1932, 8, 496—499).—Stachyose (I),  $\text{C}_{24}\text{H}_{42}\text{O}_{21}$ ,  $+1.5\text{H}_2\text{O}$  (lost at 115° in vac.) (cf. lit.) [ $\text{Ac}_{14}$  ( $p\text{-NO}_2\text{C}_6\text{H}_4\cdot\text{CO}$ ) $_{14}$ , and  $(\text{CPh}_3)_4$  derivatives], has 14 free OH groups, of which 4 are primary. The  $\text{Me}_{14}$  ether with 0.5%  $\text{HCl}\cdot\text{MeOH}$  (1 mol.) gives 1:3:4:6-tetramethyl-*D*-fructose, 2:3:4:6-tetramethyl-*D*-galactose (II), and a fraction, b.p. 108—112°/0.02 mm., which, when methylated and hydrolysed with 7%  $\text{HCl}$ , affords 2:3:4:6-tetramethyl-*D*-glucose and (II). With 20%  $\text{AcOH}$  (I) yields fructose and mannitriose; the triose is oxidised by  $\text{Br}$  to mannitronic acid, affording the *Me* ester, b.p. 220°/0.02 mm., which with  $\text{HCl}$  (2 mols.) at 90° gives 2:3:5:6-tetramethyl-*D*-gluconic acid, (II), and 2:3:4-trimethyl-*D*-galactose (III), b.p. 132°/0.02 mm., m.p. 85°,  $[\alpha]_D^{20} + 154.07^\circ \rightarrow +122.02^\circ$  in 30 hr. in  $\text{H}_2\text{O}$ . The structure of (III) is proved by the following reactions: it reduces Fehling's solution, but does not give an osazone or anilide; when methylated, hydrolysed, and treated with  $\text{NH}_2\text{Ph}$ , it gives 2:3:4:6-tetramethylgalactopyranoseanilide; with  $\text{Br}$  it affords trimethylgalactonic acid (phenylhydrazide, m.p. 170—171°), the lactone



of which has the mutarotation curve of a  $\delta$ -lactone; with  $\text{CPh}_3\text{Cl}$  it gives 6-triphenylmethyl-2:3:4-trimethylgalactose. (I) is, therefore,



(III), obtained from uronic acid, has been crystallised (cf. A., 1931, 465). R. S. C.

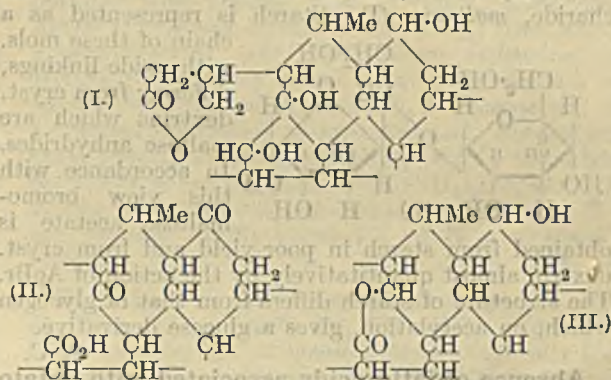
**Synthesis of phenolic glucosides.** B. HELFERICH and E. SCHMITZ-HILLEBRECHT [with E. GÜNTHER, F. STRAUSS, O. PETERS, and S. PETERSEN] (Ber., 1933, 66, [B], 378—383).—Acetates of reducing sugars are converted fairly rapidly and at a moderate temp. by phenols into phenolic glucosides and  $\text{AcOH}$  in the presence of acid catalysts.  $\alpha$ - and  $\beta$ -Forms are simultaneously produced, but their amounts are frequently so dissimilar that little difficulty is experienced in their separation. The steric direction is influenced by the nature of the sugar and phenol, but the selection of the  $\alpha$ - or  $\beta$ -acetate as initial material has little or no influence. The conditions of condensation, in particular the nature and amount of catalyst, control the direction. Active catalysts are acids, acid salts, or salts which tend to complex formation and give acidic complexes with  $\text{OH}$ -compounds. Anhyd.  $\text{ZnCl}_2$  and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  are particularly useful. The following examples are cited: phenol- $\alpha$ - $d$ -glucoside tetra-acetate, m.p. 114—115° (corr.),  $[\alpha]_D^{25} +168^\circ$  in  $\text{CHCl}_3$ , from  $\beta$ - $d$ -glucose-penta-acetate (I),  $\text{PhOH}$ , and  $\text{ZnCl}_2$ ; phenol- $\beta$ - $d$ -glucoside tetra-acetate, from (I),  $\text{PhOH}$ , and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  at 100°;  $\alpha$ -naphthol- $\beta$ - $d$ -glucoside tetra-acetate, m.p. 178—179° (corr.),  $[\alpha]_D^{25} -72^\circ$  in  $\text{CHCl}_3$ ; 2- $\beta$ -naphthol- $\beta$ - $d$ -glucoside tetra-acetate, m.p. 135—136° (corr.),  $[\alpha]_D^{25} -19^\circ$  in  $\text{CHCl}_3$ ; methyl-arbutin tetra-acetate, m.p. 103—104° (corr.),  $[\alpha]_D^{25} -16^\circ$  in  $\text{CHCl}_3$ ; guaiacol- $\beta$ - $d$ -glucoside tetra-acetate, m.p. 155—156°,  $[\alpha]_D^{25} -29^\circ$  in  $\text{CHCl}_3$ ; phenol- $\alpha$ - $d$ -galactoside tetra-acetate; phenol- $\beta$ - $d$ -galactoside tetra-acetate, m.p. 123—124° (corr.),  $[\alpha]_D^{25} -26.4^\circ$  in  $\text{CHCl}_3$ ;  $o$ -cresol- $\beta$ - $d$ -galactoside tetra-acetate, m.p. 113—114° (corr.),  $[\alpha]_D^{25} -4^\circ$  in  $\text{CHCl}_3$ ; phenol- $\beta$ - $d$ -xyloside triacetate, m.p. 147.5—148.5° (corr.),  $[\alpha]_D^{25} -50^\circ$  in  $\text{CHCl}_3$ ; phenol- $\beta$ - $d$ -fructoside tetra-acetate, m.p. 128—130.5°,  $[\alpha]_D^{25} -146^\circ$  in  $\text{CHCl}_3$ ; phenol- $\beta$ - $d$ -fructoside, m.p. 172.5—173.5° (corr.),  $[\alpha]_D^{25} -210^\circ$  in  $\text{H}_2\text{O}$ ; phenol- $\alpha$ -cellobioside hepta-acetate, m.p. 228° (corr.),  $[\alpha]_D^{25} +83^\circ$  in  $\text{CHCl}_3$ ; phenol- $\beta$ -gentiobioside hepta-acetate, m.p. 194—195° after softening at about 186°,  $[\alpha]_D^{25} -29^\circ$  in  $\text{CHCl}_3$ , whence phenol- $\beta$ -gentiobioside, m.p. 190—193° after softening at about 185°,  $[\alpha]_D^{25} -67^\circ$  in  $\text{H}_2\text{O}$ . H. W.

c c

**Emulsin.** X. B. HELFERICH, H. APPEL, and R. GOOTZ (Z. physiol. Chem., 1933, 215, 277—284).—The following glucosides were prepared: phenol- $\beta$ - $l$ -arabinoside, m.p. 176—179°,  $[\alpha]_D^{25} +243^\circ$  in  $\text{H}_2\text{O}$ ; - $\beta$ - $d$ -arabinoside, m.p. 177—179° (corr.),  $[\alpha]_D^{25} -244^\circ$  in  $\text{H}_2\text{O}$ ; - $\alpha$ - $d$ -arabinoside, m.p. 152.5—154.5° (corr.),  $[\alpha]_D^{25} -5.5^\circ$  in  $\text{H}_2\text{O}$ ; - $\alpha$ - $l$ -rhamnoside (I), m.p. 75—77° (corr.),  $[\alpha]_D^{25} -106^\circ$  in  $\text{H}_2\text{O}$  [triacetate, m.p. 130—131° (corr.),  $[\alpha]_D^{25} -80^\circ$  in  $\text{CHCl}_3$ ]; - $\beta$ - $l$ -rhamnoside, m.p. 159—161° (corr.),  $[\alpha]_D^{25} +87.5^\circ$  in  $\text{H}_2\text{O}$  [triacetate, m.p. 147—148° (corr.),  $[\alpha]_D^{25} +52.5^\circ$  in  $\text{CHCl}_3$ ]. Only (I) is hydrolysed appreciably by emulsin.

F. O. H.

**Digitalis glucosides. VI. Oxidation of anhydrodihydrodigitoxigenin.** Problem of gitoxigenin. W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1933, 99, 693—699).—After hydrolysis ( $\text{NaOH}$  in aq.  $\text{C}_5\text{H}_5\text{N}$ ) anhydrodihydrodigitoxigenin (Windaus and Stein, A., 1929, 71) is oxidised by 5%  $\text{KMnO}_4$  to hydroxydihydrodigitoxigenin (I), m.p. 193—196°, which differs from dihydrogitoxigenin and is further oxidised by  $\text{CrO}_3$  to a monobasic diketo-lactonic acid (II),  $\text{C}_{23}\text{H}_{32}\text{O}_6$ , sintering above



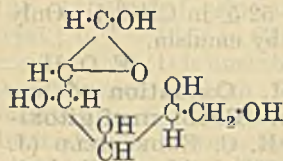
192°, m.p. 196—200°, different from the isomeric acid obtained in the oxidation of dihydrogitoxigenin (A., 1930, 1413). Reduction of (II) with  $\text{H}_2$ - $\text{PtO}_2$  in  $\text{EtOAc}$  affords a neutral hydroxydilactone (III),  $\text{C}_{23}\text{H}_{34}\text{O}_5$ , m.p. 145°, resolidifying and remelting at 232—234°. The position of the second  $\text{OH}$  group in gitoxigenin is still in doubt. It cannot be that previously assigned (*loc. cit.* and *ibid.*, 749, 1187) nor can it be a primary alcohol group on  $\text{C}_1$ , since certain reactions differ from those of dihydrostrophanthidol, which contains such a  $\text{OH}$  group (A., 1930, 1413), and which is dehydrated by  $\text{HCl}$  (*d* 1-19) at 0° to monoanhydrodihydrostrophanthidol, m.p. 175—176°. J. W. B.

[Solanine.] IX. [*Solanum tuberosum* solanine (*t*-solanine)]. G. ODDO and G. CARONNA (Gazzetta, 1932, 62, 1108—1118; cf. A., 1929, 299).—The  $\text{Ac}$  derivative of *t*-solanine, considered by Zemlén and Gerecs (A., 1929, 51) to be a trianhydro- $\text{Ac}_{13}$  compound, is a polyacetylsolanine acetate. With  $\text{KOH}$ - $\text{MeOH}$  or  $\text{MeONa}$  it yields *t*-solanino and  $\text{MeOAc}$ , and with  $\text{HCl}$ - $\text{EtOH}$  *t*-solanidine, more probably  $\text{C}_{25}\text{H}_{39}\text{ON}$  (A., 1912, i, 798) than  $\text{C}_{26}\text{H}_{41}\text{ON}$  (Zemlén, *loc. cit.*). Acetylation of *t*-solanine under conditions unfavourable to salt-formation produces acetyl-*t*-solanine, m.p. 120°, which with  $\text{HBr}$ - $\text{AcOH}$

gives the following products (I) rhamnose tetraacetate; (II) *anhydrobromonona-acetyldihydrosolanidineglucosogalactoside*, m.p. 130°, whence glucose, and, with KOH-EtOH or NaOMe, galactose and *anhydrosolanidineglucoside*, m.p. 167°, also obtained, m.p. 178°, from (III), which is *anhydropenta-acetylsolanidineglucoside hydrobromide*, m.p. 115° (decomp.).

E. W. W.

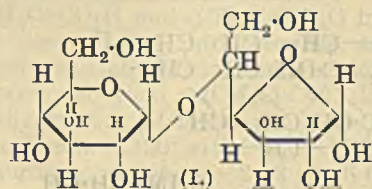
**Plant synthesis of carbohydrates and polysaccharides.** H. HIBBERT (Canad. J. Res., 1933, 8, 103—104).—The formation of polysaccharides from monosaccharide in the plant may occur by inter- or intra-mol. addition of an OH group to the ethyleneoxide ring of the equilibrium



form of glucose and fructose (annexed formula) or its anhydride (cf. this vol., 373).

H. A. P.

**Structure of starch.** R. SUTRA (Compt. rend., 1932, 195, 1282—1284).—The  $\alpha$ - and  $\beta$ -maltose octa-acetates obtained by acetylating starch (this vol., 261) are regarded as derivatives of the disaccharide, *maltose* (I). Starch is represented as a chain of these mols.



with oxide linkings, differing from cryst. dextrins which are maltose anhydrides. In accordance with this view bromomaltose acetate is obtained from starch in poor yield and from cryst. dextrin almost quantitatively by the action of AcBr. The structure of starch differs from that of glycogen which, on acetylation, gives a glucose derivative.

A. C.

**Absence of fatty acids associated with potato starch.** L. LEHRMAN and E. KABAT (J. Amer. Chem. Soc., 1933, 55, 850).—Potato starch does not contain fatty acids associated with it, since extraction with light petroleum gives only 0.02% of extractive and hydrolysis affords approx. 0.02% of "fat by hydrolysis."

H. B.

**Inulin. III. Depolymerisation of inulin.** E. BERNER (Ber., 1933, 66, [B], 397—400).—Mainly a reply to Pringsheim and Weiss (this vol., 149). The author's method of determining minute amounts of ash in inulin and the adsorptive power of inulin for EtOH are described in detail.

H. W.

**Thermal decomposition of inulin.** E. BERNER (Kongl. Norske Vidensk. Selskab, 1933, 5, 167—170; cf. A., 1930, 1025).—When inulin is heated with glycerol (I) at 140° it gives, not simpler fructosans (cf. A., 1928, 276), but their glycerol ethers. The process is favoured by a large excess of (I) and prolongation of the reaction time. There is thus obtained glycerol  $\alpha$ (?)-monofructoside, isolated as a somewhat impure hexa-acetate, b.p. 230°/high vac., converted by Me<sub>2</sub>SO<sub>4</sub> and NaOH into the Me<sub>6</sub> ether, b.p. 125°/0.02 mm.,  $[\alpha] +20.8^\circ$  in CHCl<sub>3</sub>. The product obtained by Schlubach and Elsner (A., 1932, 1022) by use of (·CH<sub>2</sub>·OH)<sub>2</sub> (II) cannot be obtained free from (II), and is probably similar in constitution.

H. A. P.

**Microscopical detection of glycogen and galactogen and their separation.** F. MAY and F. KORDOWICH (Z. Biol., 1932, 93, 233—238).—Glycogen (I) and galactogen (II) give positive tests with Best's reagent. The red coloration with I in KI solution is shown by (I) only. In mixtures, (I) can be destroyed by fermentation with ptyalin and the residual (II) determined by Best's method.

A. G. P.

**Glycogen and galactogen (animal sinistrin) content of *Helix pomatia*.** II. Galactogen content of eggs of *H. pomatia*. III. F. MAY (Z. Biol., 1932, 4, 319—324, 325—330).—II. The isolation of a starch (galactogen) derived entirely from galactose units is described.

III. Galactogen is the only polysaccharide present in the eggs of *H. pomatia*.

A. G. P.

**Cellulose from the viewpoint of organic chemistry.** J. BÖESEKEN (Chem. Weekblad, 1933, 30, 20—24).—A review. Cellulose is a poly- $\beta$ -glucose consisting of long chains of pyranose groups linked by O at the first and fourth C atoms. The no. of such groups in the mol. is about 100. The chains form parallel bundles, with the first C atom of one glucose group adjacent to the fourth C atom of the neighbouring glucose group.

H. F. G.

**Cellulose. XLVII. Relation between cellulose and cellulose-dextrins. II. Crystallisation of cellulose nitrate.** K. HESS, C. TROGUS, and K. DZIENGEL (Annalen, 1933, 501, 49—84).—Limit-dextrin 2 (I), obtained by hydrolysis (MeOH-NaOH at 20°) of its acetate (A., 1932, 47) and subsequent pptn. from a solution in 2N-NaOH, shows the same Röntgen diagram as does hydrocellulose. Pptn. of limit-dextrin nitrate (II) [methods of prep. from (I) and HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>-AcOH described] and of fibrous cellulose nitrate (III) from 1—2% solutions in COMe<sub>2</sub> with H<sub>2</sub>O, gives products which show three (not sharp) interference rings; slow pptn. from solutions in COMe<sub>2</sub> by light petroleum at 30° affords products showing sharp and identical Röntgen diagrams. These results also indicate that a second modification of (III) exists. The formation of additive compounds of (II) and COMe<sub>2</sub>, 4-methylcyclohexanone, and cyclohexanone is demonstrated by the methods previously described (*ibid.*, 568, 802); one form only is isolated in each case, and this is identical with the corresponding ketone-cellulose nitrate I compound (in the first two cases) [in the last case, one form only is isolated from (II) or (III) (cf. *loc. cit.*)]. The total double refraction of (III) and its additive compounds is negative; that of the compound of (II) with cyclohexanone is positive (the other two are negative). Some variation is found in the difference between the  $n$  of the solvent and solution for (II) and various specimens of (III) in COMe<sub>2</sub>, and (II) shows a higher sp. rotation (in COMe<sub>2</sub>, cyclohexanone, and 4-methylcyclohexanone) than any of the samples of (III) examined. Stabilised (II) is also more sol. in MeOH-COME<sub>2</sub> than stabilised (III). Some of the possible causes of these slight differences in physical properties are discussed. The same foreign substance (isolation described) appears to be formed during the prep. of (II) as with (III) (*ibid.*, 222).

H. B.

**Partial fission of animal cellulose.** L. ZECHMEISTER and G. TÓTH (Z. physiol. Chem., 1933, 215, 267—276).—Acid hydrolysis of tunicin from *Phallusia mammillaris* (A., 1893, i, 380, 497), followed by treatment with various concns. of EtOH, yields a dextrin fraction and fractions containing one or more of cellobiose, -triose (I), -tetraose (II), and -hexaose (III). Comparison of the properties of (I), (II), and (III) and of their acetates with the corresponding derivatives from vegetable cellulose (A., 1931, 716) indicates that the structures of the two celluloses have a common basis. F. O. H.

**Cellulose methylene ether.** F. C. WOOD (J.S.C.I., 1933, 52, 33—34r; cf. A., 1931, 1401).—Schenk's work on the action of AcOH-Ac<sub>2</sub>O-Pr<sub>2</sub> formal mixtures on cellulose (A., 1932, 1117) is criticised. His analytical figures do not correspond with the supposed compound (C<sub>6</sub>H<sub>9</sub>O<sub>5</sub>)<sub>2</sub>CH<sub>2</sub>. No significance can be attached to the val. 7—8% CH<sub>2</sub>O in the products, other than that this represents an equilibrium val. which is also obtained by the action of a H<sub>2</sub>SO<sub>4</sub>-paraformaldehyde mixture on cellulose. The analysis of methylenated cellulose is conducted by a modified Beltzer method.

**Compounds of high mol. wt. II. Butyl ethers of cellulose.** A. NOWAKOWSKI (Rocz. Chem., 1933, 13, 49—56).—Alkaline suspensions of cellulose react with Bu<sup>n</sup>Cl to yield ethers, m.p. 171—226°, containing 2.1—2.7 Bu groups per 6 C atoms, possessing a high degree of plasticity, and sol. in C<sub>6</sub>H<sub>6</sub>, but not in MeOH. R. T.

**Determination of tetramethylammonium.** J. J. BIKERMAN (Z. anal. Chem., 1932, 90, 335—337).—NMe<sub>4</sub> compounds can be determined by heating with 50% aq. NaOH in a Ni retort, finally to dark redness, and absorbing the NMe<sub>3</sub> produced in standard H<sub>2</sub>SO<sub>4</sub>. F. L. U.

**Quaternary ammonium salts from dimethyl-halogenoalkylamines. II. Polymerisation of dimethyl-γ-halogenopropylamines.** C. F. GIBBS, E. R. LITTMANN, and C. S. MARVEL (J. Amer. Chem. Soc., 1933, 55, 753—757).—Dimethyl-γ-phenoxypropylamine (I), b.p. 130—132°/20 mm. (*chloroplatinate*, m.p. 147°), from γ-phenoxypropyl bromide and EtOH-NHMe<sub>2</sub>, is converted by Knorr and Roth's method (A., 1906, i, 457) into dimethyl-γ-chloropropylamine (II). The polymeride (III) formed when (II) is heated at 100° (bath) for 36 hr. is basic and contains some non-ionic Cl. These facts are not explicable by Knorr and Roth's structure (*loc. cit.*), but are accounted for by the suggested structure {Cl(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>[(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>]<sub>n-2</sub>(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>}Cl<sub>n-1</sub>, for (III); the ratio of non-ionic to ionic Cl indicates that n=12—13 (M about 1500), whilst titration with acid gives M=about 4000. (I) and conc. HBr give *dimethyl-γ-bromopropylamine*, b.p. 51°/15 mm., 34—35°/6 mm. (*hydrobromide*; *chloroplatinate*, decomp. 125—130°), which when kept (alone; in EtOH or Et<sub>2</sub>O) or heated at 100° (bath), passes into a *polymeride* (IV), m.p. 225—240° (decomp.). (IV) is slightly basic and contains varying amounts of Br (according to method of prep.), some non-ionic Br, and some unsaturated material (Br-H<sub>2</sub>O; KMnO<sub>4</sub>) (probably formed by loss of HBr from the γ-bromo-

propyl group), indicating that it is a mixture of two types of polymerides, viz., as (III) and {CH<sub>2</sub>:CH-CH<sub>2</sub>-NMe<sub>2</sub>[(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>]<sub>n</sub>(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>}Br<sub>n+1</sub>. H. B.

**Local anaesthetics derived from dialkylamino-propanediols. II. Esters of piperidinopropanediol.** E. W. SCOTT and T. H. RIDER (J. Amer. Chem. Soc., 1933, 55, 804—805).—γ-Piperidinopropane-β-di-ol diphenylcarbamate hydrochloride is a better local anaesthetic than the *di-α-naphthylcarbamate hydrochloride*, m.p. 202—203°, the *di-p-tolylcarbamate hydrochloride*, m.p. 223—225°, and the dibenzoate and di-p-aminobenzoate hydrochlorides. H. B.

**Formation of nitrate, ammonia, and fatty acids from α-amino-acids and nitrate from ammonium carbonate by oxidation with potassium permanganate.** B. SJOLLEMA and J. W. DIENSKE (Rec. trav. chim., 1933, 52, 229—233).—Oxidation of various NH<sub>2</sub>-acids with KMnO<sub>4</sub> as previously described (A., 1931, 943) gives varying amounts of nitrate (calc. as HNO<sub>3</sub>) (10—52%), NH<sub>3</sub> (11—39%), and fatty acids. AcOH (72 mol.-%) is obtained from alanine, Pr<sup>n</sup>CO<sub>2</sub>H (46%) from valine, AcOH (12%) and isovaleric acid (37%) from leucine, α-methylbutyric acid (43%) from isoleucine, and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (8.6%) from serine. Except in the last case oxidation occurs at C<sub>α</sub> and CO<sub>2</sub> is eliminated; the α-CO-acid is probably an intermediate. Similar oxidation of NH<sub>4</sub> lactate gives HNO<sub>3</sub>=4% of the original N; HNO<sub>3</sub> is not produced from (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> alone, but in presence of glucose (and related substances) (1—3 mg. per mg. of N) about 1% of N is oxidised to HNO<sub>3</sub>. H. B.

**Equilibria in the formol titration.** M. LEVY (J. Biol. Chem., 1933, 99, 767—779).—Theoretical considerations and titrations indicate that only NH<sub>2</sub>-acid anions react significantly with CH<sub>2</sub>O and that two types of new anions are formed, due to the reaction with one or two mols. of CH<sub>2</sub>O. Contrary to Harris (A., 1925, i, 450), the theory of Sørensen (A., 1908, i, 115) is upheld. The importance of variations in the dielectric const. of the solvent produced by addition of CH<sub>2</sub>O is refuted (A., 1929, 648).

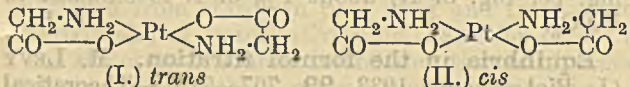
F. O. H.  
**Oxidative deamination of amino-acids by methylglyoxal.** B. KISCH (Biochem. Z., 1933, 257, 334—336).—Glycine is very readily and serine a little less readily deaminised by AcCHO, the optimum p<sub>H</sub> being 11 (similar to that using resorcinol or hydroxyquinol as catalyst). Glycyl-glycine and -tyrosine are only slightly deaminised and alanine scarcely at all. The deamination of glycine is an oxidative process and depends on the rate of aeration, almost disappearing on excluding O<sub>2</sub>. P. W. C.

**Preparation of glycine.** I. V. KULIKOV and E. A. SLASTENINA (J. Gen. Chem. Russ., 1932, 2, 777—782).—A 55% yield of pure glycine is obtained from CH<sub>2</sub>Cl-CO<sub>2</sub>H and NH<sub>3</sub> (A., 1928, 49), the product being purified by extraction with MeOH and washing with H<sub>2</sub>O (cf. A., 1931, 1042). G. A. R. K.

**Geometrically isomeric platinodiglycines.** A. A. GRÜNBERG and B. W. PTIZYN (J. pr. Chem., 1933, [ii], 136, 143—158).—Interaction of K<sub>2</sub>PtCl<sub>4</sub>

and  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  in  $\text{H}_2\text{O}$  gives a ppt. of  $[\text{PtB}_2]$  (I) ( $\text{B} = \text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2$ ) (cf. A., 1912, i, 243), whilst a more sol. *isomeride* (II) and the yellow salt  $\text{K}[\text{PtCl}_2\text{B}]$  remain in solution. Both (I) and (II) are non-ionised. The latter is shown to be the *cis*-compound by the  $\text{CS}(\text{NH}_2)_2$  method, but (I) gives misleading results, as it is insol. in the cold, and at the b.p. gives  $[\text{Pt}\{\text{CS}(\text{NH}_2)_2\}_4]\text{Cl}_2$ . The *trans* structure of (I) is, however, definitely proved by the formation of the cryst. compound  $[\text{PtCl}_2\text{B}_2]$  (III) with boiling dil. or conc.  $\text{HCl}$ ; this is a dibasic acid, and is readily converted by  $\text{CS}(\text{NH}_2)_2$  into the compound  $[\text{PtB}_2\{\text{CS}(\text{NH}_2)_2\}_2]\text{Cl}_2$ . In  $\text{H}_2\text{O}$  (III) gives  $\text{AgCl}$  only slowly in the cold, but more rapidly on warming with  $\text{AgNO}_3$ . Its Na salt in dil. aq. solution at the b.p. regenerates (I). With cold dil.  $\text{NH}_3$  (III) gives a yellow solution which becomes colourless on warming and on subsequent cooling deposits the compound *trans*- $[\text{Pt}(\text{NH}_3)_2\text{B}_2]$  (IV), which with  $\text{HCl}$  gives *trans*- $[\text{Pt}(\text{NH}_3)_2\text{B}_2]\text{Cl}_2$  (*chloroplatinite*), converted by  $\text{CS}(\text{NH}_2)_2$  into *trans*- $[\text{Pt}(\text{NH}_3)_2\{\text{CS}(\text{NH}_2)_2\}_2]\text{Cl}_2$ . Prolonged heating of (IV) with conc.  $\text{HCl}$  gives *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ .

The action of conc.  $\text{HCl}$  on (II) gives a little (III) (impurity) and a yellow solution which contains the corresponding *cis*-dichloride, for it gives the salt *cis*- $[\text{Pt}(\text{NH}_3)_2\text{B}_2]\text{Cl}_2$  with warm  $\text{NH}_3$  [this is shown to have the *cis*-configuration by its behaviour towards  $\text{CS}(\text{NH}_2)_2$  and a colourless salt with  $(\text{CH}_2 \cdot \text{NH}_2)_2$  (isolated as the salt  $[\text{Pt en B}_2]\text{PtCl}_4$ ). The solution of (III) in  $\text{HCl}$  gives  $[\text{Pt en}_2]\text{Cl}_2$  with  $(\text{CH}_2 \cdot \text{NH}_2)_2$  under the same conditions. The formulæ:



are therefore assigned to the stereoisomeric platinodiglycines.

H. A. P.

#### Constitution of monosodium *d*-glutamate.

CHAO-LUN TSENG and E. JU-HWA CHU (Sci. Quart., Pekin, 1932, 3, 1—5).—Na *d*-glutamate is probably  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{Na}$ , since at  $150$ — $160^\circ$  (2.5 hr.) it gives Na *l*-pyrrolidonecarboxylate.

CH. ABS.

**Diamino-acid, canavanin. II.** M. KITAGAWA and H. YAMADA (J. Biochem. Japan, 1932, 16, 339—349).—Canavanin (A., 1930, 121, 384),  $\text{C}_5\text{H}_{12}\text{O}_3\text{N}_4$ , m.p.  $182$ — $183^\circ$  (decomp.) [flavinate,  $\text{C}_5\text{H}_{12}\text{O}_3\text{N}_4 \cdot (\text{C}_{10}\text{H}_6\text{O}_8\text{N}_2\text{S})_2$ , m.p.  $210$ — $215^\circ$  (decomp.); picrate, m.p.  $163$ — $164^\circ$  (decomp.); Cu salt,  $(\text{C}_5\text{H}_{11}\text{O}_2\text{N}_4)_2\text{Cu}$ , m.p.  $205$ — $207^\circ$  (decomp.); *M* ester dihydrochloride, m.p.  $166$ — $167^\circ$  (decomp.);  $\text{Bz}_2$  derivative, m.p.  $86^\circ$  (decomp.); sulphate, m.p.  $172^\circ$  (decomp.)], is not a ureide, but probably a guanidine derivative. Hydrolysis by canavanase (optimum  $p_{\text{H}}$  7.7) yields carbamide and canalin,  $\text{C}_4\text{H}_{10}\text{O}_3\text{N}_2$ , m.p.  $214^\circ$  [dipicrate, m.p.  $192$ — $193^\circ$  (decomp.); dihydrochloride, m.p.  $166^\circ$  (decomp.);  $\text{Bz}_2$  derivative, m.p.  $99^\circ$  (decomp.); Cu salt,  $\text{C}_8\text{H}_{18}\text{O}_6\text{N}_4\text{Cu}$ ].

F. O. H.

Use of cysteine cuprous mercaptide in the determination of cystine. H. B. VICKERY and A. WHITE (J. Biol. Chem., 1933, 99, 701—715).—After hydrolysis of the protein [containing  $> 20$  mg. of

cystine (I)] with  $8N$ - $\text{H}_2\text{SO}_4$  in presence of Sn, cysteine  $\text{Cu}^{\text{I}}$  mercaptide is pptd. by adding an aq. suspension of  $\text{Cu}_2\text{O}$  to the diluted hydrolysate;  $10N$ - $\text{NaOH}$  is then added at  $10^\circ$  until  $p_{\text{H}}$  4—5 (Congo-red) is reached, the ppt. removed, washed, and Cu pptd. by  $\text{H}_2\text{S}$  in very dil.  $\text{HCl}$  suspension. The filtrate and washings from the  $\text{CuS}$  are conc. in vac., sulphate is removed by cold saturated  $\text{Ba}(\text{OH})_2$ , and the combined filtrate and washing again conc. The (I) content of the protein is then found by determination of org. S by Denis' method (A., 1911, ii, 66). The results agree with those obtained by the Folin-Marenzi, Sullivan, or Okuda methods. The average recovery of (I) added to casein (a) after hydrolysis, (b) before hydrolysis, and (c) to the hydrolysate freed from cysteine (II), was 92.2, 92.8, and 94.6%, respectively. From pure (II), by dissolving out from excess  $\text{Cu}_2\text{O}$  with  $8N$ - $\text{H}_2\text{SO}_4$ , cysteine  $\text{Cu}^{\text{I}}$  mercaptide (III) [corresponding with 98% of the (II)] was isolated, the N, S, Cu, and  $\text{H}_2\text{O}$  content corresponding with  $\text{C}_3\text{H}_6\text{O}_2\text{NSCu} \cdot \text{CuSO}_4 \cdot 2\text{H}_2\text{O}$ , whereas after neutralisation the fundamental compound in the ppt. appears to be the  $\text{Cu}^{\text{I}}$  salt of (III),  $\text{C}_3\text{H}_6\text{O}_2\text{NSCu}_2$ . From the ppt. only 80% of the original (I) [after aeration of the (II)] could be recovered, some decomp. ( $\text{NH}_3$  and probably  $\text{AcCO}_2\text{H}$ ) occurring. By this method 0.41% of (I) was found in horse hæmoglobin, corresponding closely with 1 mol. of (I) per mol. of mol. wt. 66,400.

J. W. B.

**White mercury fulminate.** A. DANSI (Annali Chim. Appl., 1933, 23, 29—33).—This may be obtained by treating 25 g. of  $\text{EtOH}$  (95%) at  $50^\circ$  with a solution of 2.5 g. of  $\text{Hg}$  and 0.05—0.7 g. of  $\text{Cu}$  in 25 g. of  $\text{HNO}_3$  ( $d$  1.4), the product being purer (98.4—99.5%) than in absence of  $\text{Cu}$ . The effect of  $\text{Cu}$  is not due to intermediate formation of  $\text{Cu}$  fulminate. Ni, Zn, Co, or Cd in place of  $\text{Cu}$  yields a grey fulminate.

T. H. P.

**Semicarbazone formation and incomplete dissociation of a salt of the ammonium type.** P. D. BARTLETT (J. Amer. Chem. Soc., 1933, 55, 741—749; cf. A., 1932, 916).—The relationship between the rate of reaction of furfuraldehyde and semicarbazide (I) (under the catalytic influence of  $\text{AcOH}$ ) (cf. *loc. cit.*) and the concn. of  $\text{AcOH}$  is linear only below  $0.05M$ . The velocity coeff. falls rapidly above this concn. A similar relationship is found for (I) and  $\text{AcCO}_2\text{H}$ . The results are explicable by the incomplete dissociation of semicarbazide acetate (II) in aq. solution. The dissociation const. of (II) into mols. is approx. 0.12 at  $0^\circ$  and  $25^\circ$ . The effects of the incomplete dissociation of (II) on semicarbazone formation and the mechanism of the reaction are discussed.

H. B.

**Biuret reaction. III. Biuret reaction of amino-acid amides.** M. M. RISING and P. S. YANG (J. Biol. Chem., 1933, 99, 755—765).—The biuret reaction of  $\alpha$ - $\text{NH}_2$ -acid amides occurs in the absence of alkali-producing internal salts  $[\text{Cu}(\text{amino-acid amide})_2] \cdot x\text{H}_2\text{O}$ . Thus by addition of aq.  $\text{Cu}(\text{OAc})_2$  either with or without  $\text{KOH}$  to the appropriate  $\text{NH}_2$ -acid amide (prep., A., 1931, 1150) are obtained: *Cu* dl-leucinamide (I), m.p.  $248$ — $250^\circ$  (decomp.) (cf. Bergell and Brugsch, A., 1910, i, 546); *Cu* l-asparag-

ine, decomp., 302—304°; *Cu glycynamide*, decomp., 205—207°; and *Cu d-alaninamide*, decomp. 227—231°. In agreement with the structures containing bound internal ions assigned, these derivatives are non-conductors in aq. solution, but electrolysis of (I) in presence of KOH causes migration of a coloured anion. The structures of these derivatives support the theory (A., 1931, 77) that four basic N atoms are involved in the biuret reaction. The min. no. of acid H atoms is two (in strongly basic compounds), but with more weakly basic mols. containing acid groups, four acid H atoms take part, alkali salt formation with two of these being a fundamental preliminary.

J. W. B.

**Nitroalkylguanidines. Rearrangement and preparation by nitration.** T. L. DAVIS and R. C. ELDERFIELD (J. Amer. Chem. Soc., 1933, 55, 731—740).—*N*-methyl-, *N*-butyl-, and *NN*-dimethylguanidine (as sulphates) are converted by  $\text{KNO}_3$  and conc.  $\text{H}_2\text{SO}_4$  into the corresponding *N'*- $\text{NO}_2$ -derivatives. *NN'*-Diethyl- and *NN'N''*-trimethylguanidine (I) could not be nitrated, indicating that nitration occurs only when the alkylguanidines contain a free  $\text{NH}_2$ -group. The nitrates of *N*-methyl-, *N*-*n*-butyl-, *N*-*n*-heptyl-, and *NN*-dimethylguanidine with conc.  $\text{H}_2\text{SO}_4$  also give the *N'*-nitro-*N*-alkylguanidines; *NN'*-dimethylguanidine and (I) are similarly recovered unchanged. The formation of these last  $\text{NO}_2$ -derivatives is considered not to involve dehydration. Nitroguanidine (II) is not produced from guanidine nitrate,  $\text{H}_3\text{PO}_4$ , and  $\text{P}_2\text{O}_5$  after 30 hr. at room temp. or 30 min. at 65°; after 48 hr. at room temp., 82% of (II) results (probably owing to the intermediate production of  $\text{HNO}_3$  or nitrophosphoric acid). *N'*-Nitro-*N*-alkylguanidines decompose in hot aq. solution to  $\text{NH}_2\cdot\text{NO}_2$  and alkylcyanamides (III); (III) then undergoes hydrolysis (to the carbamide) or polymerisation (to trialkylisomelamine). Decomp. in presence of an aq. alkylamine at  $p_{\text{H}}$  about 6-13 at 175° gives 40—50% of *NN'*-dialkylguanidine, also formed (in 40% yield) with the trialkylisomelamine (40%) when the reaction is carried out at the b.p./about 1.6 atm. in  $\text{CO}_2$ . The basicity of guanidine and its derivatives is considered to be a property of the mol. and not of a particular N atom. *N'*-Nitro-*N*-*n*-heptylguanidine, m.p. 115°, and *NN'*-*di-n*-heptyl- and -*di-n*-butyl-guanidine picrates, m.p. 278° (decomp.), and 122.5°, respectively, appear to be new. Tribenzylisomelamine has m.p. 146—147°, re-solidifying with m.p. 157—158° (decomp.).

H. B.

**Glucononitrile.** A. WOHL and O. WOLLENBERG (Annalen, 1933, 500, 281—286).—Glucononitrile (I), m.p. 146—148°, is obtained in 54—55% yield from glucose,  $\text{NH}_2\cdot\text{OH}\cdot\text{AcOH}$  (convenient method of prep. described) and  $\text{Ac}_2\text{O}\cdot\text{AcOH}$  at 100° (bath). Arabinose is formed when a 10% aq. solution of (I) is heated at 85° in  $\text{CO}_2$ .

H. B.

**Rapid determination of cyanogen and mercury in mercury oxycyanide.** A. ANGELETTI (Annali Chim. Appl., 1933, 23, 38—41).—When a complex cyanide is boiled with yellow  $\text{HgO}$ , all the CN yields  $\text{Hg}(\text{CN})_2$ ,  $\text{HgO}$ , and treatment of the latter with KI proceeds:  $\text{Hg}(\text{CN})_2, \text{HgO} + 8\text{KI} + \text{H}_2\text{O} = 2\text{K}_2\text{HgI}_4 +$

$2\text{KCN} + 2\text{KOH}$ , the Hg being wholly present in the sol. complex compound. The CN may then be determined by distilling the acidified solution, according to Bellucci and Ricca's procedure (A., 1924, ii, 791) and the Hg by Cattelain's modification (A., 1930, 1148) of Vanino and Treubert's process. T. H. P.

**Absorption spectrum and photochemical decomposition of diazomethane.** F. W. KIRKBRIDE and R. G. W. NORRISH.—See this vol., 359.

**Action of carbon monoxide on organo-magnesium compounds.** F. G. FISCHER and O. STOFFERS (Annalen, 1933, 500, 253—270).—Mg aryl and *tert*-alkyl bromides heated with CO under pressure react thus:  $2\text{MgRBr} + 2\text{CO} \rightarrow >\text{CR}\cdot\text{OMgBr}$  (or  $\text{R}\cdot\text{CO}\cdot\text{MgBr}$ )  $\rightarrow$   $(\cdot\text{CR}\cdot\text{OMgBr}) \rightarrow \text{OH}\cdot\text{CHR}\cdot\text{COR}$  [which may undergo autoxidation to  $(\cdot\text{COR})_2$ ]. Thus,  $\text{MgPhBr}$  at 75—85° gives 90% of benzoin and a little benzil; *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  at 150°/100 atm. affords *p*-toluin and *p*-tolil;  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$  at 160°/180 atm. yields 63% of  $\alpha$ -naphthil;  $\text{MgBu}^t\text{Br}$  furnishes hexamethylacetoin. Elimination of HBr occurs when  $\text{CEt}_2\text{Br}$  is treated with Mg.  $\text{CPh}_3\cdot\text{MgCl}$  and  $\text{CPh}_3$  do not react with CO at 160°/140 atm. With Mg alkyl and aralkyl halides,  $\text{CH}_2\text{R}\cdot\text{MgHal}$ , reaction occurs thus:  $\text{CH}_2\text{R}\cdot\text{MgX} + \text{CO} \rightarrow \text{CH}_2\text{R}\cdot\text{C}\cdot\text{OMgX}$  (or  $\text{CH}_2\text{R}\cdot\text{CO}\cdot\text{MgX}$ )  $\xrightarrow{\text{OH}\cdot\text{R}\cdot\text{MgX}}$   $(\text{CH}_2\text{R})_2\text{C}(\text{MgX})\cdot\text{OMgX} \rightarrow \text{CHR}\cdot\text{CH}\cdot\text{CH}_2\text{R}$ . Thus,  $\text{MgEtBr}$  at 110° gives 25% of  $\Delta^2$ -pentene;  $\text{MgBuCl}$  at 125° affords 65% of  $\Delta^2$ -nonene; Mg *iso*amyl bromide at 100° yields 70% of  $\beta$ -*dimethyl*- $\Delta^2$ -nonene, b.p. 57—63°/13 mm.;  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  at 120° furnishes PhMe,  $(\cdot\text{CH}_2\text{Ph})_2$ ,  $\text{CH}_2\text{Ph}\cdot\text{OH}$ , and 60% of  $\alpha\gamma$ -diphenylpropene. In these cases, small amounts of higher-boiling by-products (unsaturated alcohols) are also formed. Mg *cyclohexyl* bromide undergoes both types of reaction; with CO at 135°, 25% of *cyclohexylmethyl*-enecyclohexane and 45% of dodecahydro-benzoin and -benzil, m.p. 38°, are produced. Mg  $\beta$ -decahydronaphthyl bromide affords an unsaturated hydrocarbon, b.p. 145°/3 mm., m.p. 93—98°, and compounds, m.p. 128—130° and 151°. Reaction is not observed between CO and Mg pyrrol bromide at 100°/90 atm., *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$  (145°/90 atm.),  $(\cdot\text{C}\cdot\text{MgBr})_2$  (145°/90 atm.),  $\text{ZnPhBr}$  (in PhMe at 130°/100 atm.), or  $\text{AlEt}_3$  (250°/150 atm.). The reactions are catalysed by NaOEt or, better,  $\text{Mg}(\text{OEt})_2$  or  $\text{RO}\cdot\text{MgX}$ . Solutions of  $\text{MgEtI} + \text{OEt}\cdot\text{MgI}$  in  $\text{Et}_2\text{O}$  have higher conductivities than  $\text{MgEtI}$ .

H. B.

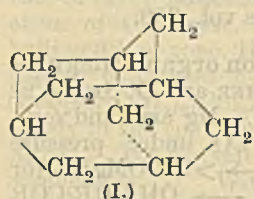
**Germanium tetraiodide and its action on hexamethylenetetramine and caffeine.** T. KARANTASSIS and L. CAPATOS (Bull. Soc. chim., 1933, [iv], 53, 115—116).—On mixing  $\text{GeI}_4$  and  $(\text{CH}_2)_6\text{N}_4$  in  $\text{CHCl}_3$  a white cryst. ppt. with a slight yellowish tinge,  $\text{GeI}_4, 4(\text{CH}_2)_6\text{N}_4$ , is obtained. Caffeine gives a green microcryst. powder,  $\text{GeI}_4, 4\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ . It decomposes slowly on exposure to air, liberating I and giving a yellow powder with a white efflorescence.

M. S. B.

**Carbon rings with a large number of carbon atoms.** L. RUZICKA (Bull. Soc. chim. Belg., 1932, 41, 565—587).—An account of the properties and

structure of natural and synthetic C ring compounds containing up to 34 C atoms. O. J. W.

**Adamantane, a new hydrocarbon extracted from petroleum.** S. LANDA and V. MACHÁČEK (Coll. Czech. Chem. Comm., 1933, 5, 1—5).—The naphtha, b.p. 150—250°, of petroleum from Hodonin and Gbely contains about 30% of material which is volatile in steam (100°) and has a terpene-like odour.



(I.) (I) is unaffected by X-rays, CrO<sub>3</sub>, alkaline KMnO<sub>4</sub>, and conc. HNO<sub>3</sub>, and is responsible for the above terpene-like odour. H. B.

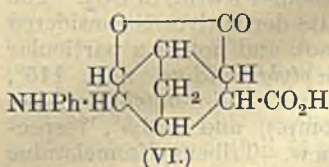
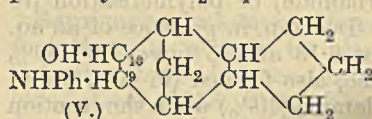
**Molecular rearrangements in the cyclohexane series; passage into the cyclopentane series.** M. TIFFENEAU (Compt. rend., 1932, 195, 1284—1286; cf. LÉVY and SFRAS, A., 1932, 395).—2-Iodo-1-methylcyclohexanol is dehalogenated by AgNO<sub>3</sub> with the formation of 90% of 2-methylcyclohexanone (I) and 10% of cyclopentyl Me ketone (A., 1932, 744). 2-Methyl-Δ<sup>1</sup>-cyclohexene oxide, b.p. 137—139°, isomerises at 220—230°/atm. pressure into equal parts of (I) and, probably, 1-methylcyclopentane-1-aldehyde (semicarbazone, m.p. 160—161°) by rupture of the oxide ring at the Me-C atom followed by a shortening to the 5-ring. 4-Methyl-Δ<sup>1</sup>-cyclohexene oxide similarly isomerises to a mixture of 3-methylcyclopentane-1-aldehyde and 4-methylcyclohexanone. A. C.

**Graduated additive powers of unsaturated ring systems. II.** K. ALDER and G. STEIN [with W. FRIEDRICHSEN] (Annalen, 1933, 501, 1—48).—Contrary to the previous statement (A., 1931, 489), dicyclohexadiene (dicyclooctene) (and related compounds) and cyclohexene form adducts with PhN<sub>3</sub>; reaction is, however, very slow. Two types of adducts (dihydro-1:2:3-triazoles) are obtained: (a) from dicycloheptenes and dicyclooctenes; (b) from monocyclic olefines. Thermal decomp. occurs thus: (a)  $\cdot\dot{C}-N\equiv N \rightarrow N_2 + \cdot\dot{C}-NPh$  (II) (often accompanied by an anil); (b)  $\cdot\dot{C}-N\equiv N \rightarrow N_2 + \cdot\dot{C}-NPh$  (III)  $\rightarrow N_2 + \cdot\dot{C}-NPh$ , which occurs at a much lower temp. than (a). Hydrolytic fission of these types by dil. acid occurs thus: (a) (I)  $\rightarrow \cdot\dot{C}-OH$  [also formed from (II) and dil. acid]; (b) (III)  $\rightarrow N_2 + NH_2Ph + \cdot\dot{C}-O$  (e.g., the adduct from PhN<sub>3</sub> and cyclopentene affords cyclopentanone).

Me propenyl ketone and PhN<sub>3</sub> give (after 12—14 days at room temp.) an adduct (IV), C<sub>11</sub>H<sub>13</sub>ON<sub>3</sub>, m.p. 106—107° (decomp.), which when heated to 140° affords N<sub>2</sub>, the anil of CH<sub>2</sub>Ac<sub>2</sub>, and a small amount of a substance, b.p. about 240°/16 mm. (IV) and dil.

H<sub>2</sub>SO<sub>4</sub> give CH<sub>2</sub>Ac<sub>2</sub>. Styryl Me ketone and PhN<sub>3</sub> afford (after 12 weeks) an adduct, C<sub>16</sub>H<sub>15</sub>ON<sub>3</sub>, m.p. 111°, whilst isoprene furnishes (after several months) an adduct, C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>, m.p. 72°. The diacetate, m.p. 155°, of dioximinodicyclopentadiene (Thiele, A., 1900, i, 298) and PhN<sub>3</sub> in EtOAc give an adduct, C<sub>20</sub>H<sub>19</sub>O<sub>4</sub>N<sub>5</sub>, m.p. 214°. Similarly, 3:6-endomethylene-Δ<sup>1</sup>- and 3:6-endoxo-3:6-dimethyl-Δ<sup>4</sup>-tetrahydrophthalic anhydrides, γ-fenchene, and dimeric Δ<sup>1,3</sup>-cyclohexadiene afford 1:1-adducts, m.p. 154°, 210° (decomp.), 177°, and 154—155°, respectively. Dicycloheptene derivatives containing the endo-CMe<sub>2</sub> group (as in bornylene and apobornylene) do not form adducts with PhN<sub>3</sub>. The adduct, C<sub>16</sub>H<sub>15</sub>O<sub>3</sub>N<sub>3</sub>, m.p. 232°, from PhN<sub>3</sub> and 3:6-endoethylene-Δ<sup>4</sup>-tetrahydrophthalic anhydride is converted by successive treatment with dil. KOH and 50% AcOH into an anilino-lactone, C<sub>16</sub>H<sub>17</sub>O<sub>4</sub>N, m.p. 227°. Me dicyclopentadiene-3:7-dicarboxylate and PhN<sub>3</sub> in EtOAc give an adduct, C<sub>20</sub>H<sub>21</sub>O<sub>4</sub>N<sub>3</sub>, m.p. 145° (decomp.), and a compound, C<sub>20</sub>H<sub>21</sub>O<sub>4</sub>N, m.p. 163°. Successive treatment of the adduct, C<sub>18</sub>H<sub>17</sub>O<sub>3</sub>N<sub>3</sub>, decomp. 208°, from 3:6-endoisopropylideneimethylene-Δ<sup>4</sup>-tetrahydrophthalic anhydride and PhN<sub>3</sub> with dil. NaOH and dil. AcOH affords an amino-lactone, m.p. 223°, whilst the adduct, C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>N<sub>6</sub>, m.p. 203—204°, from PhN<sub>3</sub> (2 mols.) and Me 3:6-endomethylene-3:6-dihydrophthalate (1 mol.) is converted by dil. AcOH into a compound, C<sub>23</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub>, m.p. 179°. The adduct from 3:6-endoxo-Δ<sup>4</sup>-tetrahydrophthalic anhydride and PhN<sub>3</sub> is similarly converted into an amino-lactone, C<sub>14</sub>H<sub>13</sub>O<sub>5</sub>N, m.p. 180° (with charring); treatment with conc. HCl gives a chloro-base, C<sub>14</sub>H<sub>14</sub>O<sub>5</sub>NCl, m.p. 234°.

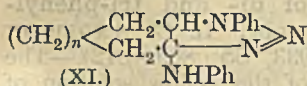
Reduction (H<sub>2</sub>, colloidal Pd, EtOH) of the adduct (A., 1931, 473) from α-dicyclopentadiene and PhN<sub>3</sub> gives a dihydro-derivative, m.p. 129—130°, decomposed by dil. H<sub>2</sub>SO<sub>4</sub> to the anilino-alcohol (V), m.p.



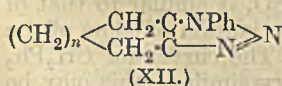
134° [picrate, m.p. 187—188° (decomp.); Ac<sub>2</sub> derivative, m.p. 151°], and thermally to the corresponding 9:10-phenylimino-derivative, m.p. 62° [converted by dil. H<sub>2</sub>SO<sub>4</sub> into (V)], and a smaller amount of the anil of an aldehyde (semicarbazone, C<sub>11</sub>H<sub>17</sub>ON<sub>3</sub>, m.p. 159—160°). The adduct (ibid., 489) from PhN<sub>3</sub> and 3:6-endomethylene-Δ<sup>4</sup>-tetrahydrophthalic anhydride with dil. NaOH and dil. AcOH gives the lactonic acid (VI), m.p. 236° [(mono) Me ester (VII) (CH<sub>2</sub>N<sub>2</sub>), m.p. 204° (Ac derivative, m.p. 159°)]. Thermal decomp. of the adduct, m.p. 138—139°, from PhN<sub>3</sub> and Me 3:6-endomethylene-Δ<sup>4</sup>-tetrahydrophthalate affords Me 4:5-phenylimino-3:6-endomethylenehexahydrophthalate, m.p. 86°, hydrolysed (dil. HCl or H<sub>2</sub>SO<sub>4</sub>) to (VII). The adduct (loc. cit.) from PhN<sub>3</sub> and santene is converted by dil. H<sub>2</sub>SO<sub>4</sub> into 2-anilino-1:2-dimethyl-3:6-endomethylene-cyclohexanol, b.p. 192°/16 mm. (hydrochloride, m.p. 195—196°; picrate, m.p. 163°), by dil. HCl into the -cyclohexyl chloride, m.p. 64° (picrate, m.p. 121°), and by

picric acid in  $C_6H_6$  into a *picrate*,  $C_{21}H_{22}O_7N_4$ , m.p. 117°.

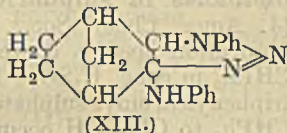
The *adduct* (VIII), m.p. 53°, from  $PhN_3$  and *cyclopentene* is hydrolysed (dil.  $H_2SO_4$ ) to *cyclopentanone*, whilst thermal decomp. gives *cyclopentanoneanil* (IX), b.p. 129—131°/19 mm. The *adduct*, m.p. 222° (decomp.), from *cyclopentene* and  $p-C_6H_4Br \cdot N_3$  undergoes thermal decomp. to *cyclopentanone-p-bromoanil* (X), b.p. 173°/20 mm. The *adduct*, m.p. 76—77°, from  $PhN_3$  and *cycloheptene* is, however, hydrolysed (dil.  $H_2SO_4$ ) to *hexahydrobenzaldehyde*; thermal decomp. gives *cycloheptanoneanil*, b.p. 155°/16 mm. The *adduct* from  $PhN_3$  and *cyclooctene* has m.p. 87°. (VIII) or (IX) and  $PhN_3$  at 100° afford the *dihydrotriazole* (XI,  $n=1$ ), m.p. 192° (decomp.), converted by  $H_2C_2O_4 \cdot 2H_2O$  in EtOAc into *2-anilino-cyclopentanone*, m.p. 64° [*semicarbazone*, m.p. 216°; *Ac* derivative, m.p. 83°; *hydrochloride*, m.p. 146° (decomp.)], which is oxidised ( $KMnO_4-COMe_2$ ) to *glutaranilic acid*, m.p. 128°. (IX) and  $p-C_6H_4Br \cdot N_3$  similarly afford a *compound*,  $C_{17}H_{17}N_4Br$ , m.p. 208° (decomp.), whilst an *isomeric*, m.p. 182° (decomp.),



(XI.)



(XII.)



(XIII.)

is obtained from (X) and  $PhN_3$ . *cycloHexanoneanil* (or *cyclohexene*) and  $PhN_3$  at 100° give the *dihydrotriazole* (XI,  $n=2$ ), m.p. 187° (decomp.), converted by  $H_2C_2O_4$  (as above) into the *triazole* (XII,  $n=2$ ), m.p. 117—118°. *cycloHeptanoneanil* similarly affords the *dihydrotriazole* (XI,  $n=3$ ), m.p. 194° (decomp.), convertible into the *triazole* (XII,  $n=3$ ), b.p. 270°/16 mm., m.p. 118° (also formed during the initial condensation), whilst *cyclooctanoneanil* and  $PhN_3$  at 100° give the *triazole* (XII,  $n=4$ ), b.p. 240°/20 mm., m.p. 83°. *Norcamphoranil*, b.p. 157°/20 mm., similarly affords the *triazole* (XIII), m.p. 238°, convertible by  $H_2C_2O_4$  in EtOAc into *2-anilino-3:6-endomethylenecyclohexanone*, m.p. 98° (*semicarbazone*, m.p. 190°). *2:5-endoEthylenecyclohexanoneanil*, b.p. 168—171°/20 mm., and  $PhN_3$  at 100° give a *compound*,  $C_{20}H_{22}N_4$ , m.p. 259°. *Camphoranil* and *6:6-dimethyl-2:5-endoethylenecyclohexanoneanil*, b.p. 170—172°/20 mm., m.p. 83°, do not react with  $PhN_3$  at 150°. H. B.

**New type of reaction between unsaturated hydrocarbons and sulphuric acid. I. cyclo-Hexene and sulphuric acid.** S. NAMETKIN and L. ABAKUMUVSKAJA (Ber., 1933, 66, [B], 358—360).—Gradual addition of *cyclohexene* to  $H_2SO_4$  ( $d$  1.84) at 2—5° results in the separation of an oily layer from which are obtained (i) a saturated *hydrocarbon*  $C_{12}H_{22}$ , b.p. 216—219°/739 mm., which could not be normally dehydrogenated, the only isolable product being a little  $C_{10}H_{18}$ ; (ii) a saturated *hydrocarbon*  $C_{18}H_{32}$ , b.p. 145—147°/1.5—2 mm.; (iii) an unsaturated *hydrocarbon*  $C_{24}H_{40}$ , b.p. 200—203°/1.5—2 mm., apparently containing one double linking. Dilution of the acid layer (see above) with  $H_2O$

causes the separation of a highly unsaturated, unstable liquid. H. W.

**Structure of the benzene nucleus.** B. L. VANZETTI (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 77—79; Chem. Zentr., 1932, ii, 3075).

**Körner's benzene formula and modern theory.** E. MACCIOTTA (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 114—117; Chem. Zentr., 1932, ii, 3075).

**Electronic theory and substitution in benzene.** E. MACCIOTTA (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 110—113; Chem. Zentr., 1932, ii, 3075).—The  $C_6H_6$  ring is regarded as a closed negative ring of C atoms neutralising one another and all negative towards the outer zone of positive H. Positive substituents give stable compounds and induce a polarity leading to *m*-substitution, whilst negative substituents cause a weakening at the point of attack, leading to *o*- and *p*-substitution. A. A. E.

**Mechanism of the Friedel-Crafts reaction.** E. WERTYPOROCH and T. FIRLA (Annalen, 1933, 500, 287—295; cf. A., 1931, 1150).—Partly an account of work previously reviewed (this vol., 127). The following is new. The amounts of  $PhEt$ ,  $C_6H_4Et_2$ , and  $C_6Et_6$  (I) formed from varying quantities of  $EtCl$  (Br),  $C_6H_6$ , and  $AlCl_3$  (Br<sub>3</sub>) are determined; production of (I) is favoured by  $AlCl_3$ . (I) is obtained in about 42% yield from  $C_6H_6$  (0.25 mol.),  $EtCl$  (1.5 mol.), and  $AlCl_3$  (0.1 mol.); increase in the amount of  $AlCl_3$  causes less (I) and more  $C_6H_2Et_4$  to be formed.  $C_6H_6$  (1 c.c.),  $Pr^{\beta}Cl$  (10 c.c.), and  $AlCl_3$  (1.3 g.) afford 0.2 g. of a *tetraisopropylbenzene*, m.p. 117—118°, whilst  $C_6H_4Pr_2$  (2 c.c.),  $PrCl$  (50 c.c.), and  $AlCl_3$  (0.74 g.) give 0.3 g. of *hexapropylbenzene*, m.p. 101°.  $PrCl$  is converted by large amounts of  $AlCl_3$  into  $HCl$ ,  $Pr^{\beta}Cl$ , and condensation products, b.p. 120—127° ( $M$  405) and 160—170° ( $M$  470). H. B.

**Decomposition of iodobenzene dichloride.**

VII. Action of solutions of iodobenzene dichloride in several liquids on Zerevitinov's reagent.

VIII. Analogies between the action of equimolecular solutions of chlorine, iodine, iodine chloride, and iodine trichloride, with the same reagent. E. V. ZAPPI and H. DEGIORGI (Bull. Soc. chim., 1932, [iv], 51, 1605—1611; cf. A., 1932, 1120).— $PhICl_2$  (I) in  $C_6H_6$ ,  $CHCl_3$ , or  $C_5H_5N$  with  $MgMeI$  in amyl ether gives 20.5, 21.1, or 50.9% yields, respectively, of  $C_2H_6$ , the order of increasing yield being that of increasing  $\epsilon$  and dipole moment.  $Cl_2$  in  $C_6H_6$  or  $CHCl_3$  gives 20.7 or 17.0% yields of  $C_2H_6$ , respectively, I in  $C_5H_5N$  49.2,  $ICl$  in  $CHCl_3$  or  $C_5H_5N$  20.8 or 46.2, and  $ICl_3$  (0.5 mol.) in  $CHCl_3$  or  $C_5H_5N$  20.9 or 46.5%, respectively. (I) is polar, since it lowers the  $\epsilon$  of  $C_6H_6$  and  $CHCl_3$ . These results lead to the belief that (I) is ionised in solution to  $PhICl^+$  and  $Cl^-$ , and that the reaction proceeds thus:  $2Cl^- + 2MgMeI \rightarrow 2MgClI + C_2H_6$ . This explains why the yield of  $C_2H_6$  never exceeds 50%. R. S. C.

**Coupling action of the Grignard reagent. IV. Benzylidene chloride and benzotrichloride.** R. C. FUSON and W. E. ROSS (J. Amer. Chem. Soc., 1933, 55, 720—723; cf. A., 1927, 46).— $CHPhCl_2$  and  $2MgMeI$  in  $Et_2O$  give  $\alpha$ -stilbene dichloride (I);  $CHPhCl_2 + 2MgMeI \rightarrow (I) + C_2H_6 + 2MgClI$ .  $CHPhCl_2$

and MgPhBr give (I), Ph<sub>2</sub>, and CHPh<sub>3</sub>, but no (·CHPh<sub>2</sub>)<sub>2</sub> (cf. Reychler, A., 1906, i, 821). CPhCl<sub>3</sub> and 0.2*M*-MgMeCl afford toluene tetrachloride (II); with 2*M*-MgMeCl, a mixture (22% yield) of *cis*- (1 pt.) and *trans*- (5 pts.) -αα'-dichlorostilbenes results. The same mixture is obtained from (II) and 2*M*-MgMeCl, indicating that (II) is first produced in the above reaction.

H. B.

Physical constants of *o*- and *m*-nitrotoluene. (MME.) HENNAUT-ROLAND (Bull. Soc. chim. Belg., 1933, 42, 80—84).—New determinations are made of the crit. solution temp. in isopentane,  $n^{15}$  (various H and He lines), and of  $d_4$ ,  $\eta$ ,  $\theta$ , and  $\gamma$  at various temp. of *o*- and *m*-nitrotoluenes.

H. A. P.

Nitro-compounds obtained by direct nitration of toluene in preparation of T.N.T. P. DE BEULE (Bull. Soc. chim. Belg., 1933, 42, 27—79).—The various stages in the nitration of PhMe to the (NO<sub>2</sub>)<sub>3</sub> stage are critically re-examined, and a table shows the behaviour of every intermediate product on further nitration. Contrary to previous lit., *m*-nitrotoluene gives, amongst other isomerides, 3 : 5-dinitrotoluene on direct nitration, and this is further nitrated with difficulty to 2 : 3 : 5- and 2 : 4 : 5-trinitrotoluenes. A colorimetric method for the detection and determination of 3 : 5-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub> is described. New m.p. are given for highly purified specimens of *o*-, *m*-, and *p*-mono-, 2 : 4-, 2 : 6-, 2 : 3-, 2 : 5-, 3 : 4-, and 3 : 5-di-, and 2 : 4 : 6-, 2 : 4 : 5-, 2 : 3 : 4-, and 2 : 3 : 6-tri-nitrotoluenes.

H. A. P.

Photo-sensitive nitro-compounds. I. N. N. VOROSCHCOV and K. A. GRIBOV. II. *pp'*-Dinitrophenyl disulphide; 1-nitronaphthalene-2-sulphonic acid. N. N. VOROSCHCOV and V. V. KOSLOV (J. Gen. Chem. Russ., 1932, 2, 929—938, 939—962).—I. Several nitronaphthalenesulphonic acids are photo-sensitive and darken on exposure to light, especially in the form of wool dyeings. Of the isomeric 1-nitronaphthalene acids, the 1 : 8 is the most sensitive, the 1 : 7 and the 1 : 6 are about equally sensitive, but the latter assumes a darker shade; the 1 : 5 acid is merely bleached on exposure. Their salts and the corresponding sulphinic acids and sulphonamides behave in the same way, showing that the nature of the S-containing group is unimportant. 1 : 6-Dinitronaphthalene-4 : 8-disulphonic acid is very sensitive, whilst the parent C acid is not; 1-C<sub>10</sub>H<sub>7</sub>·NO<sub>2</sub> itself is slightly sensitive. The darkening is attributed to the reduction of the NO<sub>2</sub> group; it is assisted by the addition of aromatic amines and can then be utilised for photographic reproduction.

1-Nitronaphthalene-7-sulphonic acid, obtained by reduction of NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·SO<sub>2</sub>Cl with Na<sub>2</sub>SO<sub>3</sub>, blackens without melting at 150—155°. The 1 : 6-acid was similarly prepared and does not melt. 1 : 7-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>NH<sub>2</sub> has m.p. 227—228° and the 1 : 6 compound m.p. 187.5—188°. The 1 : 7-anilide has m.p. 176—177°, the 1 : 6-anilide m.p. 173—174°.

II. The oxidation of crude *pp'*-dinitrophenyl disulphide (I), prepared from *p*-C<sub>6</sub>H<sub>4</sub>Cl·NO<sub>2</sub> and Na<sub>2</sub>S, with HNO<sub>3</sub> leads to *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H with *pp'*-dinitrophenylsulphone, m.p. 255°, not 282° (A., 1908, i, 631), and H<sub>2</sub>SO<sub>4</sub>. The two latter products are due to the presence in (I) of an isomeride, m.p. 134°,

probably (C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>)<sub>2</sub>S·S; pure (I), m.p. 182°, gives no sulphone on oxidation.

α-Naphthylamine-2-sulphonic acid was diazotised and treated with Cu-bronze, Cu<sub>2</sub>O, or CuSO<sub>4</sub>·Cu<sub>2</sub>SO<sub>3</sub> under a variety of conditions, giving 1-nitronaphthalene-2-sulphonic acid (monohydrate, m.p. 104.7°; chloride, m.p. 120.5°; amide, m.p. 214.3°) in yields up to 40%, with 2 : 4-dinitronaphthol and 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>3</sub>H.

The photo-sensitivity of the three nitrobenzenesulphonic acids decreases in the order *o* > *p* > *m*, but all are much less sensitive than 1 : 8-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·SO<sub>3</sub>H; *oo'*-dinitrodiphenyl disulphide is as sensitive as the corresponding acid and therefore the juxtaposition of S, not SO<sub>3</sub>H, and NO<sub>2</sub> is the determining factor. (I) is not photo-sensitive; (II) is as sensitive as the 1 : 8-acid, especially its salts with aromatic amines.

G. A. R. K.

Aryl chlorosulphinates and aryl sulphites. M. BATTEGAY and L. DENIVELLE (Compt. rend., 1932, 195, 1291—1292; cf. A., 1931, 473).—A claim for priority against Carré and Libermann (this vol., 48).

A. C.

Colour of solutions of di- and tri-phenylmethanes in sulphuric acid. L. C. ANDERSON (J. Amer. Chem. Soc., 1933, 55, 809—812).—The absorption spectra curve of the yellow solution of CHPh<sub>3</sub> in conc. H<sub>2</sub>SO<sub>4</sub> + Me<sub>2</sub>SO<sub>4</sub> is similar to that of triphenylcarbinyl sulphate; oxidation of some of the CHPh<sub>3</sub> to CPh<sub>3</sub>·OH occurs. The curves for CH<sub>2</sub>Ph<sub>2</sub> (I) and (·CHPh<sub>2</sub>)<sub>2</sub> (II) are very similar; this may be due to oxidation of (I) to a derivative of (II) or fission of (II) to a derivative of (I).

H. B.

Velocity of liberation of hydrocarbons by the action of indene on aliphatic organo-magnesium compounds. Method of measuring the attraction between alkyl radicals and the magnesium group. D. IVANOV and I. ABDUOLOV.—See this vol., 356.

Hydrogenation of naphthalene. A. M. POPOV (Ukrain. Chem. J., 1932, 7, [Tech.], 41—56).—C<sub>10</sub>H<sub>8</sub> undergoes hydrogenation in presence of Ni and other catalysts at 180—200°/200 atm. (max.). The C<sub>10</sub>H<sub>8</sub> should previously be purified by treatment with < 1% of Na.

R. T.

1-Methyl- and 1 : 7-dimethyl-4-isopropyl-naphthalene. W. S. RAPSON and W. F. SHORT (J.C.S., 1933, 128—130).—(2-Cymylmethyl)methylmalonic acid, m.p. 170°, passes at 180° into β-2-cymylisobutyric acid (I), b.p. 190—195°/14 mm., the Me ester, b.p. 142—148°/8 mm., of which is reduced to γ-2-cymylisobutyl alcohol, converted through the bromide and cyanide into γ-2-cymyl-β-methylbutyric acid, b.p. 182—188°/9 mm., the acid chloride, b.p. 150—151°/8 mm., of which readily cyclises with AlCl<sub>3</sub> to 1-keto-3 : 5-dimethyl-8-isopropyl-1 : 2 : 3 : 4-tetrahydronaphthalene (II), b.p. 150—155°/8 mm. With Na and EtOH at 110°, (II) affords a mixture dehydrogenated by S at 180—230° to 1 : 7-dimethyl-4-isopropyl-naphthalene, m.p. 60° (picrate, m.p. 92°). Hydrolysis followed by decarboxylation of Et 2-cymylmethylmalonate affords β-2-cymylpropionic acid, m.p. 85°, converted (as above) into 1-methyl-4-isopropyl-naphthalene (A., 1922, i, 1001).

J. L. D.



**Preparation and properties of octachloronaphthalene.** I. V. SCHVEMBERGER and V. GORDON (J. Gen. Chem. Russ., 1932, 2, 921—928).—Octachloronaphthalene (I) is best obtained by chlorination of  $C_{10}H_8$  in presence of Fe. with or without I; it can also be obtained by prolonged heating of Na  $\alpha$ -naphthylamine-3 : 6 : 8-trisulphonate with  $PCl_5$  at 200—225°. It has m.p. 197.5—198°, b.p. 440—442°/754 mm., 258—260°/2.5 mm., is attacked by alcoholic but not by aq. alkalis, and oxidised by  $HNO_3$  to hexachloronaphthaquinone, m.p. 222.5°, and tetrachlorophthalic acid, m.p. 254.3—254.7° (corr.). Further chlorination of (I) leads to decachlorohydroindene, m.p. 138°. G. A. R. K.

**Synthesis of chrysene and certain derivatives.** G. R. RAMAGE and R. ROBINSON (Nature, 1933, 131, 205).—Dehydration of  $\beta\beta'$ -diphenyladipic acid with hot 85%  $H_2SO_4$  gives *cis*- and *trans*-diketohexahydrochrysene. Reduction of the *cis*-compound (Clemmensen) yields a hexahydrochrysene, reduced by Se to chrysene. The prep. of a norketohydroxycetrin is foreshadowed. L. S. T.

**Constitution of  $\beta$ -carotene; 2 : 6-dimethylnaphthalene from the polyene chain.** R. KUHN and A. WINTERSTEIN (Ber., 1933, 66, [B], 429—432).—Thermal decomp. of  $\beta$ -carotene (I) at 170—190°/1 mm. leads to 2 : 6-dimethylnaphthalene (II). For other reasons and since (II) is also obtained from *trans*-crocetin  $Me_2$  ester which does not contain a ring, the possibility that (I) contains two dissimilar rings is not adopted, and (II) is regarded as derived from 12 C atoms of the polyene chain. H. W.

**Colour and structure of amides.** (MME.) RAMART-LUCAS and (MLE.) WOHL (Compt. rend., 1933, 196, 120—122).—Ultra-violet absorption curves show that the amides  $NHAcAr$  ( $Ar=Ph$ , *o*- and *p*-tolyl) have all the same constitution. The curve for  $NHAcR$  ( $R=Ph$ , *p*-tolyl) differs from that of  $NAcRMe$ ; the former exists in solution as an equilibrium mixture of the  $\cdot CO\cdot NHR$  and  $\cdot C(OH)\cdot NR$  forms (cf. Hantzsch, A., 1931, 608). H. B.

**2 : 4 : 6-Trichloroaniline.** F. D. CHATTAWAY and H. IRVING (J.C.S., 1933, 142—143).— $NH_2Ph\cdot HCl$  in anhyd.  $CHCl_3$  with  $Cl_2$  gives 2 : 4 : 6-trichloroaniline (I) (*picrate*, m.p. 81.5—82.5°; *phthalanil*, m.p. 175—176°; *dichloroacetyl* derivative, m.p. 184—184.5°;  $Ac_2$  derivative, m.p. 81—82°) (yield 80%). The alleged mol. compound of (I) with  $AcCl$  is probably the  $Ac_2$  derivative. A. A. L.

**Phenylmethylethylbetaines and the geometrical stereoisomerism of organic quinequivalent nitrogen compounds.** (MME.) M. GUAISNET-PILAUD (Compt. rend., 1932, 195, 1286—1289).—The quaternary iodide from  $NPhMe_2$  and  $CH_2I\cdot CO_2Et$  gives a single betaine hydrate if treated with excess of  $Ag_2O$  (A., 1930, 1563). Under the same conditions ( $NPhMeEt\cdot CH_2\cdot CO_2Et$ )I affords a mixture of a *betaine monohydrate* (I), m.p. 175.5°, and *dihydrate* (II), m.p. 79—79.5°, fractionated by EtOH. Both give the same *chloroplatinate* ( $+2H_2O$ ), m.p. 134°, with dehydration (anhyd. form, decomp. 155°). (I) is changed to (II) by exposure to moist air, but they differ chemically in that (I) affords a *H oxalate*, m.p.

124.5°, whilst (II) gives an *oxalate*, m.p. 166°, and a *H oxalate* ( $+H_2O$ ), m.p. 69.5°. A. C.

**Reduction of Schiff bases. III. Condensations of *sec*-aromatic amines with formaldehyde in acid solution; nuclear or *N*-methylations by formaldehyde.** E. C. WAGNER (J. Amer. Chem. Soc., 1933, 55, 724—731).—When methyl-, ethyl-, *n*-propyl-, *n*-butyl-, and *isoamyl*-anilines are treated with aq. 35%  $CH_2O$  (1 equiv.) in dil. HCl below or at 20° and the solutions treated (within 5 min.) by Zn dust (usually at  $< 25^\circ$ ), *N*-methylation occurs; the corresponding *tert*-bases are isolated in 55—88% yield. When the initial condensation is allowed to proceed until solids separate, *hydrochlorides* of the (probable) composition  $[p\text{-}NR\cdot C_6H_4\cdot CH_2(HCl)]_n$  result (probably by rearrangement of the unit  $NPhR\cdot CH_2$ ). These are reduced by Zn dust and dil.  $H_2SO_4$  at 70—85° to *N*-alkyl-*p*-toluidines in 54—80% yield. The *hydrochlorides* of *N*-*n*-propyl-, b.p. 237.3—238.8°, *n*-butyl-, and *isoamyl*-, b.p. 267—268°, *p*-toluidines have m.p. 155°, 148—149°, and 146°, respectively. The hydrochloride of  $NPhMePr^a$  has m.p. 120—122° (lit. 106°). 4 : 4'-Tetra-alkyldiaminodiphenylmethanes are often produced as by-products in the condensations. H. B.

**Synthesis of organic bases with triple linking.** C. MANNICH and F. T. CHANG (Ber., 1933, 66, [B], 418—420).—Synthesis is effected in dioxan at 100° according to the scheme  $CPh:CH + CH_2O + NHR_2 = CPh:C\cdot CH_2\cdot NR_2 + H_2O$ . The following compounds are described:  $\gamma$ -diethylamino- $\alpha$ -phenyl- $\Delta^a$ -propinene, b.p. 137°/18 mm. (*hydrochloride*, m.p. 136—137°), hydrogenated to  $\gamma$ -diethylamino- $\alpha$ -phenylpropane (hygroscopic *hydrochloride*, m.p. 119—120°);  $\gamma$ -dimethylamino- $\alpha$ -phenyl- $\Delta^a$ -propinene, b.p. 128°/18 mm. (*hydrochloride*, m.p. 156°; *methiodide*, decomp. 240°), which with Br in  $CHCl_3$  affords a non-cryst. *dibromide* (*sulphate*, m.p. 126°), but does not yield a *tetrabromide*; it is hydrogenated to  $\gamma$ -dimethylamino- $\alpha$ -phenyl- $\Delta^a$ -propene (*hydrochloride*, m.p. 147°; *hydrobromide*, m.p. 148°, adding  $Br_2$  to form  $\alpha\beta$ -*dibromo*- $\gamma$ -dimethylaminopropane *hydrobromide*, m.p. 137°) or further to  $\gamma$ -dimethylamino- $\alpha$ -phenylpropane (*methiodide*, m.p. 176°); with  $H_2SO_4\cdot H_2O$  (3 : 1 vol.) it yields  $\omega$ -dimethylaminopropiophenone (*hydrochloride*, m.p. 160°);  $\gamma$ -diethylamino- $\alpha$ -*p*-nitrophenyl- $\Delta^a$ -propinene (*hydrochloride*, m.p. 215°), hydrogenated to  $\gamma$ -diethylamino- $\alpha$ -*p*-aminophenylpropane (*p*-nitrobenzoyl derivative, m.p. 129°) and reduced by Sn and HCl to  $\gamma$ -diethylamino- $\alpha$ -*p*-aminophenyl- $\Delta^a$ -propinene (*Bz* compound, m.p. 108°);  $\gamma$ -piperidino- $\alpha$ -phenyl- $\Delta^a$ -propinene, b.p. 175—180°/18 mm. (*hydrochloride*, m.p. 216°);  $\gamma$ -diethylamino- $\alpha$ -*p*-anisyl- $\Delta^a$ -propinene, b.p. 169—172°/15 mm. (*hydrochloride*, m.p. 168°);  $\gamma$ -piperidino- $\alpha$ -*p*-anisyl- $\Delta^a$ -propinene (*hydrochloride*, m.p. 196°);  $\gamma$ -dimethylamino- $\alpha$ -*o*-aminophenyl- $\Delta^a$ -propinene, b.p. about 166°/1 mm. (*p*-nitrobenzoyl derivative, m.p. 102°). H. W.

**Nitroamines.** V. E. MACCIOTTA (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 84—87; Chem. Zentr., 1932, ii, 3083).—*o*- and *p*- $C_6H_4(NH_2)_2$  with  $HNO_3$  do not yield the nitroamines; *o*- $C_6H_4(NH_2)_2$  gives

6-nitro-1:2:3-benzotriazole, m.p. 210°, whilst the *p*-compound gives a black substance resembling aniline-black. A. A. E.

Stereochemistry of 2:2'-disubstituted diphenyls. III. Optical resolution of *o*-(2-dimethylaminophenyl)phenyltrimethylammonium iodide. (Miss) F. R. SHAW and E. E. TURNER (J.C.S., 1933, 135—140; cf. A., 1932, 1125).—Improved preps. are described for 2:2'-dinitro-, -diamino-, and -bisdimethylamino-diphenyl, m.p. 72—73° (hydriodide, m.p. 256—257°; chloroplatinate). The last-named gives dl-*o*-(2-dimethylaminophenyl)phenyltrimethylammonium iodide, m.p. 190—192° (decomp., bath initially at 180°), which gives d-*o*-(2-dimethylaminophenyl)trimethylammonium d-camphor-10-sulphonate, m.p. 189—190°,  $[\alpha]_{D}^{20} +60.6^\circ$  [iodide, m.p. 190—192° (decomp.),  $[\alpha]_{D}^{20} +50.5^\circ$ ]. The optical isomerides are similarly obtained. Rates of racemisation in H<sub>2</sub>O at 99.5° are recorded. The iodides are not racemised by HCl at room temp. A. A. L.

Diphenyl series. III. Nitration of 2:4'-derivatives. IV. Nitro-compounds of 2:4'-dihalogenodiphenyl derivatives. C. FINZI and A. MANGINI (Gazzetta, 1932, 62, 1184—1192, 1193—1203; cf. A., 1932, 1025).—III. HNO<sub>3</sub> (*d* 1.46) nitrates 2:4'-diacetamidodiphenyl to the 3'-NO<sub>2</sub>-derivative (I), m.p. 216°, the constitution of which is determined by hydrolysis to 3'-nitro-2:4'-diaminodiphenyl (II), m.p. 144° (from which 3-nitrodiphenyl is obtained, and, by partial diazotisation, 3-nitro-4-aminodiphenyl), and by reduction of (II) to 2:3':4'-triaminodiphenyl, which as an *o*-diamine condenses with phenanthraquinone to 2-*o*-aminophenylphenanthraquinone, m.p. 235°. Nitration of (I) with EtNO<sub>3</sub> does not give the 4:3'-(NO<sub>2</sub>)<sub>2</sub>-compound (cf. *loc. cit.*), but 5:3'-dinitro-2:4'-diacetamidodiphenyl, m.p. 205—206°, hydrolysed to 5:3'-dinitro-2:4'-diaminodiphenyl (III), m.p. 242—243°, the structure of which is determined by conversion into 3:3'-dinitrodiphenyl, and [the tetra-amine obtained from (III) having given only an impure phenanthraquinone, and not having combined with benzil] by the formation of 2-iodo-3:5'-dinitro-4'-piperidylidiphenyl, m.p. 125°, from the I<sub>2</sub>-derivative (see below).

IV. The following are prepared from the NH<sub>2</sub>-compounds: 2:4'-dichloro-, m.p. 122°, 2:4'-di-bromo-, m.p. 137—137.5°, and 2:4'-di-iodo-, m.p. 134°, -4-nitrodiphenyl; 2:4'-dichloro-, m.p. 91°, 2:4'-dibromo-, m.p. 90°, and 2:4'-di-iodo-, m.p. 112°, -3'-nitrodiphenyl; 2:4'-di-iodo-4:3'-dinitrodiphenyl, m.p. 156°; 2-iodo-3:4'-dinitro-4-acetamidodiphenyl, m.p. 237—238°; 2:4'-dichloro-, m.p. 172°, 2:4'-di-iodo-, m.p. 206°, -5:3'-dinitrodiphenyl; 4'-acetamido-2-cyanodiphenyl, m.p. 172° (whence 4'-amino-diphenyl-2-carboxylic acid, m.p. 215—216°); 4'-amino-2-cyanodiphenyl, m.p. 117°.

Diphenyl-2:4'-dicarboxylic acid with EtNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> yields *mono*- and *di-nitro*-derivatives, m.p. 262° and 293°, respectively. 2:4'-Dihydroxydiphenyl (Me<sub>2</sub> ether, m.p. 70°), which with EtNO<sub>3</sub> gives an ill-defined product, is nitrated by HNO<sub>3</sub>-AcOH to a (NO<sub>2</sub>)<sub>2</sub>-compound, m.p. 187°. E. W. W.

Reducing action of ferrous oxalate on azoxy-compounds. I. GASOPOULOS (Praktika, 1931, 6, 495—497; Chem. Zentr., 1932, ii, 3083).—Azoxybenzene is readily reduced to azobenzene by FeC<sub>2</sub>O<sub>4</sub> in 72% yield. 3:3'-Diamino-4:4'-dimethyl-, m.p. 202—203°, 4:4'-dimethoxy-, m.p. 161—162°, and 4:4'-diethoxy-azobenzene, m.p. 161°, were similarly prepared. A. A. E.

Stereoisomerism of azoxybenzenes. IV. Dipole moments and configuration. K. A. GEHRCKENS and E. MÜLLER (Annalen, 1933, 500, 296—306; cf. A., 1932, 734).—The dipole moments of “*n*”- and *iso*-azoxybenzenes indicate that these are *trans*- and *cis*-forms, respectively. The following vals. (all  $\times 10^{-18}$  e.s.u.) are recorded: “*n*”-, 1.70, and *iso*-, 4.67, -azoxybenzene; “*n*”-, 1.73, and *iso*-, 4.36, -*o*-azoxytoluene; “*n*”-, 1.73, and *iso*-, 5.06, -*p*-azoxytoluene; “*n*”-, 2.41, and *iso*-, 6.17, -*o*-azoxy-anisoles. The vals. for the *p*-bromoazoxybenzenes, m.p. 73° and 94°, are 2.60 and 0.90, respectively, indicating that both of these are *trans*-forms. H. B.

Dinaphthyl bases. II. Reduction of 1:1'-azoxy- and 1:1'-azo-naphthalenes. Isolation of 1:1'-hydrazonaphthalene. W. M. CUMMING and G. HOWIE (J.C.S., 1933, 133—135; cf. A., 1932, 376).—Neutral reduction of *s*-1:1'-azoxynaphthalene, or alkaline reduction of *s*- and *as*-azoxy- (I) and azo-naphthalenes (II), m.p. 188° (sublimes 170°) (improved prep.), gives 1:1'-hydrazonaphthalene, m.p. 153° [decomp. giving (II) and  $\alpha$ -naphthylamine], which undergoes the benzidine conversion in acid, neutral, and alkaline solution. The substance previously described as hydrazonaphthalene (J.C.S., 1923, 123, 2464) is dinaphthylene. Preps. of naphthidine, dinaphthylene, and dinaphthyleneimine from the above substances are described. A. A. L.

Fluorenone. II. A. C. SIRCAR and K. C. BHATTACHARYYA (J. Indian Chem. Soc., 1932, 9, 522—526).—The tinctorial properties (on wool and cotton) of the *bisazo*-compounds obtained by coupling diazotised 2:7-diaminofluorenone with PhOH, *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, salicylic acid,  $\beta$ -C<sub>10</sub>H<sub>7</sub>-OH, 2-hydroxy-3-naphthoic,  $\alpha$ -naphthylamine-4-sulphonic,  $\alpha$ -naphthol-4-sulphonic, *R*-, *G*-, Cleve's, Laurent's, *H*-, Schaffer's, and chromotropic acids, and NPhMe<sub>2</sub> are described. J. W. B.

[Diazo-compounds.] IV. Catalytic effect of alizarin on the decomposition of diazo-compounds. V. Stabilisation of diazotates. G. ODDO and R. INDOVINA (Gazzetta, 1932, 62, 1119—1138, 1138—1144; cf. A., 1891, 553; 1895, i, 514; 1897, i, 341).—IV. The velocity of decomp. of diazonium salts from NH<sub>2</sub>Ph, *o*-, *m*-, and *p*-toluidine, 1:2:4-, 1:3:4-, and 1:4:5-xylydine, and 1:2:5:4- $\psi$ -cumidine in presence of NaOH in varying concn. is increased on addition of alizarin. Comparative velocities of decomp. are tabulated.

V. Solutions of diazonium salts treated with a small quantity of NaOH give, after partial decomp., a solution of a Na salt, stable at room temp. and on exposure to light. Addition of more NaOH renders the salt less stable, and of HCl regenerates the diazonium salt. E. W. W.

**Diazonium dichloriodides.** A. ALGERINO (Gazzetta, 1932, 62, 1145—1150).—The following, of type  $\text{ArN}_2\text{ICl}_2$ , are prepared from the amine diazotised in HCl and treated with  $\text{ICl}_3$ : benzene-, *o*-, *m*-, and *p*-toluene-, *o*-nitrobenzene-, m.p. 125° (decomp.), and *m*- and *p*-nitrobenzene-diazonium dichloriodides. Action of  $\text{NH}_3$  on the last three yields the corresponding azoimides. E. W. W.

**Oxidising action of isomeric diazonium hydroxides.** Z. E. JOLLES [with E. BUSONI] (Gazzetta, 1932, 62, 1150—1160; cf. A., 1932, 155).— $\text{PhN}_2\text{OH}$  oxidises various reducing agents; alkaline  $\text{FeSO}_4$  is oxidised by *p*-nitro- and *p*-bromo-benzene-, *p*-toluene-, phenetole-, and  $\alpha$ - and  $\beta$ -naphthalene-diazonium hydroxides. From  $\text{PhN}_2\text{OH}$  the products are  $\text{C}_6\text{H}_6$ ,  $\text{Ph}_2$ , and  $\text{PhN}_3$ ; the other diazonium compounds give corresponding products. E. W. W.

**Action of thionyl chloride on phenol.** P. CARRÉ and D. LIBERMANN (Compt. rend., 1933, 196, 275—277).— $\text{PhOH}$  and  $\text{SOCl}_2$ , best in the mol. proportions 3:2, give first HCl and then  $\text{SO}_2$  (about 1 mol.);  $\text{Et}_2\text{O}$  then ppts. *tri-p*-hydroxyphenylsulphonium chloride (I), solid, hygroscopic, which with  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$  gives the  $\text{Bz}_3$  derivative (chloroplatinate, m.p. 165—168°), but with  $\text{BzCl}$  in aq. NaOH, *tri-p*-benzoyloxyphenylsulphonium hydroxide, m.p. (anhyd.) 128°, (+ $\text{H}_2\text{O}$ ) 35°. The primary reaction product, when boiled with  $\text{H}_2\text{O}$ , gives  $\text{H}_2\text{SO}_4$  by oxidation of the  $\text{SO}_2$  liberated, and, when distilled in vac., yields di-*p*-hydroxyphenyl sulphide and a mixture of *o*- and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ . The following reaction mechanism is considered proved:  $\text{PhOH} + \text{SOCl}_2 \rightarrow \text{HCl} + \text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{SOCl}$  (II); (II)  $\rightarrow \text{HCl} + \text{O}\cdot\text{C}_6\text{H}_4\cdot\text{SO}$  (III); (III) +  $\text{SOCl}_2 + 2\text{PhOH} \rightarrow 2\text{HCl} + \text{SO}_2 + \text{O}\cdot\text{C}_6\text{H}_4\cdot\text{S}(\text{C}_6\text{H}_4\cdot\text{OH})_2$  (IV); (IV) + HCl  $\rightarrow$  (I). Condensation takes place mainly in the *p*-, but also in the *o*-position. When  $\text{PhOH}$  (1 mol.),  $\text{SOCl}_2$  (1 mol.), and  $\text{C}_5\text{H}_5\text{N}$  (1 mol.) react in dry  $\text{Et}_2\text{O}$ , and the product, after removal of the base, is distilled in vac., much  $\text{Ph}_2\text{S}$  and some Ph chlorosulphite (chlorosulphinates) are formed. The last-named compound decomposes when distilled in vac., if a trace of  $\text{C}_5\text{H}_5\text{N}$  is present (cf. A., 1931, 473; this vol., 48). R. S. C.

**Intramolecular rearrangement of phenyl ethers with aluminium chloride.** R. A. SMITH (J. Amer. Chem. Soc., 1933, 55, 849).—A 65% yield of a mixture of 4- and 6-isopropyl-*m*-cresols is obtained from *m*-tolyl  $\text{Pr}^i$  ether (1 mol.) and  $\text{AlCl}_3$  (1 mol.). H. B.

**Betti condensation. Effect of substituents on stability and optical rotation of the resulting amines.** F. E. RAY and W. A. MOOMAW (J. Amer. Chem. Soc., 1933, 55, 749—752).— $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$  (1 mol.), *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$  (2 mols.), and  $\text{NH}_3$  in EtOH (cf. Betti, A., 1901, i, 81, 611) give the *m*-chlorobenzylidene derivative, m.p. 109°, of dl-*m*-chlorophenyl-2-hydroxy- $\alpha$ -naphthylmethylamine (I), m.p. 124—125° (hydrochloride, decomp. 220—230°), resolved by *l*-malic acid into *d*-, m.p. 126° (not sharp),  $[\alpha]_D^{25} +79.5^\circ$  in  $\text{Et}_2\text{O}$ , and *l*-, m.p. 122°,  $[\alpha]_D^{25} -55.5^\circ$  in  $\text{Et}_2\text{O}$ , forms. dl-*o*-Chlorophenyl- (II), m.p. 129—130° (hydrochloride, decomp. 185—190°; *o*-chlorobenzylidene derivative, m.p. 173°) (resolved similarly

into *d*-,  $[\alpha]_D^{25} +89.8^\circ$  in  $\text{Et}_2\text{O}$ , and *l*-,  $[\alpha]_D^{25} -83.7^\circ$  in  $\text{Et}_2\text{O}$ , forms), and dl-*p*-chlorophenyl- (III), m.p. 120° (hydrochloride, decomp. 190—195°; *p*-chlorobenzylidene derivative, m.p. 150°), -2-hydroxy- $\alpha$ -naphthylmethylamines are similarly prepared. (III) could not be resolved (probably owing to its instability). The stability (towards alkali) is (III) < (II) < (I) < phenyl-2-hydroxy- $\alpha$ -naphthylmethylamine (IV), whilst the order of optical activity is (II) > (I) > (IV) > (III) (?). The above condensation with  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  gives chiefly nitrohydrobenzamides. H. B.

**Structure of the hydrogen sulphite compound of nitroso- $\beta$ -naphthol.** S. V. BOGDANOV (J. Gen. Chem. Russ., 1932, 2, 770—776; cf. A., 1932, 842).—On boiling the H sulphite compound of nitroso- $\beta$ -naphthol (I) with  $\text{NH}_2\text{OH}$  in presence of AcOH (not HCl), the dioxime of 1:2-diketo-1:2:3:4-tetrahydronaphthalene-4-sulphonic acid (II) is formed; it readily loses the  $\text{SO}_3\text{H}$  group with alkalis, yielding 1:2-naphthaquinonedioxime (III) at low temp. and its anhydride (IV) at high temp. Boiling (II) with HCl gives  $\text{NH}_4$  2-nitroso- $\alpha$ -naphthol-4-sulphonate (V); this supports the suggestion (*loc. cit.*) that (II) is probably the intermediate compound in the formation of (V) from (I) and  $\text{NH}_2\text{OH}$  in HCl; some (III) and (IV) are also produced.

G. A. R. K.

**Pyrocatechol compounds of alkaline earths.** R. SCHOLDER and M. WOLF (Z. anorg. Chem., 1933, 210, 184—194).—The following compounds are described ( $\text{A} = \cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot$ ):  $\text{Ca}(\text{AH})_2\cdot 3.5\text{H}_2\text{O}$ ;  $\text{Sr}(\text{AH})_2\cdot 4.5\text{H}_2\text{O}$ ;  $\text{Ba}(\text{AH})_2\cdot 6\text{H}_2\text{O}$ ;  $\text{Sr}(\text{AH})_2\cdot 2\text{AH}_2\cdot 5\text{H}_2\text{O}$ ;  $\text{Ba}(\text{AH})_2\cdot 2\text{AH}_2\cdot 5\text{H}_2\text{O}$ ;  $\text{CaA}_2\cdot \text{H}_2\text{O}$ ;  $\text{SrA}_2\cdot 3.5\text{H}_2\text{O}$ ;  $\text{BaA}_2\cdot 0.5\text{H}_2\text{O}$ ;  $[\text{CaA}_2]\text{K}_2\cdot 2\text{H}_2\text{O}$ ;  $[\text{CaA}_3]\text{K}_4\cdot 6\text{H}_2\text{O}$ ;  $[\text{CaA}_3]\text{Na}_4\cdot 8\text{H}_2\text{O}$ ;  $[\text{Ca}_2\text{A}_5]\text{K}_6\cdot 10\text{H}_2\text{O}$ ;  $[\text{Ca}_2\text{A}_5]\text{Na}_6\cdot 24\text{H}_2\text{O}$ ;  $8\text{CaA}_2\cdot 7\text{K}_2\text{A}_7\cdot 28\text{H}_2\text{O}$ ;  $[\text{Ca}_2\text{A}_7]\text{Na}_9\cdot 5\text{H}_2\text{O}$ . Their constitution is discussed. F. L. U.

**Oxidation in presence of absorbent charcoal.** A. GANDINI (Gazzetta, 1933, 63, 9—12).—Quinol in  $\text{Et}_2\text{O}$  solution in contact with Norit is oxidised by  $\text{O}_2$  at atm. pressure first to quinhydrone and then to benzoquinone. Thymoquinol reacts similarly, but pyrocatechol does not. Buchu-camphor gives  $\gamma$ -acetyl- $\alpha$ -isopropyl-*n*-butyric acid (A., 1923, i, 474). Under similar conditions but without C negative results are obtained. E. E. J. M.

**2-Aminoresorcinol and its derivatives.** M. V. LICHOSCHERSTOV and V. E. SHABOTINSKAJA (J. Gen. Chem. Russ., 1932, 2, 761—769).—Reduction of 2-nitroresorcinol with Sn and HCl affords the double salt of 2-aminoresorcinol (I) with  $\text{SnCl}_2$ ,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot \text{NH}_2\cdot \text{HCl}\cdot \text{SnCl}_2$ , m.p. 240° (decomp.), whilst  $\text{SnCl}_2\cdot \text{H}_2\text{O}$  in HCl gives the hydrochloride of (I), m.p. 240—243° (decomp.), from which (I) can be liberated with  $\text{Na}_2\text{CO}_3$  in presence of  $\text{NaHSO}_3$ , m.p. 159—160° ( $\text{Ac}_3$  derivative, m.p. 164—165°). (I) with Br in AcOH gives 4:6-dibromo-2-aminoresorcinol (II), m.p. 214—216°, and can be coupled with diazo-compounds. When diazotised in aq. solution in presence of excess of HCl with  $\text{NaNO}_2$  or with amyl nitrite in EtOH, (I) gives principally a colourless 4-nitro-2-diazoresorcinol (III) together with a dark brown isomere (IV), which is the sole product on

diazotisation in AcOH. (III) on warming with conc. H halides gives colourless explosive salts, of true diazonium structure, readily hydrolysed back to (III) and giving an intense colour with alkalis. The following structures are suggested for (III) and (IV), although the quinone-oxime structures tautomeric with these are also possible :



(II) gives on diazotisation a reddish-brown *diazo compound*, probably an inner anhydride. Both (III) and (IV) are reduced by SnCl<sub>2</sub> to 4-amino-1:3-dihydroxy-2-phenylhydrazine hydrochloride, giving hydrazones with aldehydes. G. A. R. K.

**cis-trans-Isomerism of isoeugenol.** C. JUNGE (Riechstoffind., 1932, 7, 112; Chem. Zentr., 1932, ii, 2818—2819).—Acetylation of technical isoeugenol affords the *trans-acetate*, m.p. 79° (whence *trans-isoeugenol*, m.p. 34°, stable in absence of air). Fractional distillation of the isoeugenol from the non-cryst. technical acetate, followed by benzoylation, gives *cis-isoeugenol benzoate*, m.p. 68° (whence *cis-isoeugenol*, b.p. 115°/5 mm.,  $n_D^{20}$  1.57002). With FeCl<sub>3</sub> *cis-isoeugenol* (*phenylurethane*, m.p. 118°) gives an olive-green and *trans-isoeugenol* (*phenylurethane*, m.p. 152°) a yellowish-green colour. A. A. E.

**Naphthols. II. Chlorination of 1:5-dihydroxynaphthalene.** A. S. WHEELER and W. J. MATTOX (J. Amer. Chem. Soc., 1933, 55, 686—690).—1:5-C<sub>10</sub>H<sub>6</sub>(OAc)<sub>2</sub> and Cl<sub>2</sub> in CCl<sub>4</sub> containing I at room temp. give the *monoacetate* (I), decomp. 158—160° (after turning green), of 4:8-dichloro-1:5-dihydroxynaphthalene, m.p. 194° (*diacetate*, m.p. 143°; *dibenzoate*, m.p. 179°; *monobenzoate*, m.p. 157—158°); at 80°, 4:4:8-trichloro-5-acetoxy-3:4-dihydro- $\alpha$ -naphthol (II), m.p. 174°, also obtained by further chlorination of (I), results. (I) and (II) are oxidised (CrO<sub>3</sub>, AcOH) to 8-chloro-5-acetoxy-1:4-naphthaquinone (III), m.p. 143° [2-anilino-, m.p. 172°, 2-o-amino-anilino-, m.p. 271° (decomp.), 2-p-hydroxyanilino-, m.p. 226° (decomp.), and 2-p-toluidino-, m.p. 169° derivatives], chlorinated in AcOH to the 2:8-Cl<sub>2</sub>-derivative, m.p. 158—159°. 8-Chloro-5-hydroxy-1:4-naphthaquinone, m.p. 112°, from (III) and EtOH-HCl, is reduced (SnCl<sub>2</sub>) to 8-chloro-1:4:5-trihydroxynaphthalene, m.p. 115—120° (decomp.) (*triacetate*, m.p. 147°; *tribenzoate*, m.p. 210°), whilst (III) is reduced (Zn, dil. H<sub>2</sub>SO<sub>4</sub>) to 8-chloro-1:4-dihydroxy-5-acetoxy-naphthalene, m.p. 173° (decomp.) (*dibenzoate*, m.p. 216°). H. B.

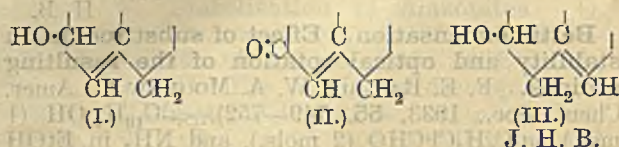
**9:10-Dihydroxy-9:10-di- $\alpha$ -naphthyl-9:10-dihydrophenanthrene and 2:2'-di- $\alpha$ -naphthoyldiphenyl.** T. W. JEZIEWSKI [with W. MARUSZEWSKA] (Rocz. Chem., 1933, 13, 44—48).—9:10-Dihydroxy-9:10-di- $\alpha$ -naphthyl-9:10-dihydrophenanthrene, m.p. 263—264°, prepared from phenanthrene and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·MgI, yields 2:2'-di- $\alpha$ -naphthoyldiphenyl, m.p. 204.5—205°, on oxidation with CrO<sub>3</sub> in boiling AcOH. R. T.

**Production of arylmercapto-compounds (hydroxythiophenols).** IMPERIAL CHEM. INDUSTRIES and K. W. PALMER.—See B., 1933, 183.

**Dehydrogenations in the coniferyl series. I. Dehydrodieugenol and dehydrodiisoeugenol.** H. ERDTMAN (Biochem. Z., 1933, 258, 172—180; cf. A., 1908, i, 783).—Dehydrodieugenol (I) (*di-p-nitrobenzoate*, m.p. 172—173°), best prepared by oxidation of eugenol with FeCl<sub>3</sub>, yields tetrahydrodehydrodieugenol, identical with the dehydrodicerulignol of Fichter and Christen (A., 1925, i, 813), on catalytic hydrogenation with PtO<sub>2</sub>. It also yields a *Me<sub>2</sub> ether*, b.p. 240—242°/6 mm., which, on oxidation with KMnO<sub>4</sub>, gives diveratric acid and on treatment with O<sub>3</sub> an *ozonide* which gives CH<sub>2</sub>O on decomp. with H<sub>2</sub>O. The *p-nitrobenzoates* of eugenol and (?)cresol have m.p. 78—80° and 117—119°, respectively. Dehydrodiisoeugenol (II) (*p-nitrobenzoate*, m.p. 157—158°) prepared from isoeugenol by oxidation with FeCl<sub>3</sub> yields a *Me ether*, m.p. 126°, which gives veratric acid on oxidation. *isoEugenol p-nitrobenzoate* has m.p. 123—124°. These results and theoretical considerations show that (I) is 3:3'-diallyl-5:5'-dimethoxy-6:6'-dihydroxydiphenyl, whilst in (II), which contains no CO group, 2 mols. of isoeugenol are linked through the O of the OH of one mol. and the propenyl group of the other. W. McC.

**Constitution of cholesterol. IX. Bromo-derivatives of cholesterol.** F. PIRRONE (Gazzetta, 1932, 62, 1101—1108).—By crystallisation from COMe<sub>2</sub>, the bromination product of cholesterol (cf. A., 1932, 54) yields products for which the following constitutions are suggested: 6:7-dibromocholesterol (I), m.p. 106—107°, 7:7'-dibromo-6:6'-dihydrodicholesterol, m.p. 112—114°, and 7-bromo-6:7:6':7'-tetrahydrodicholesterol, m.p. 74—76°. (I) is reduced to cholesterol, with HCN gives a *dicyanocholesterol*, m.p. 102—103°, and with AgNO<sub>3</sub> a hydroxycholesterol, m.p. 100—105°, and a *product*, m.p. 234—235°. E. W. W.

**Relation of cholestenone to cholesterol. Cholestenone, the ketone of allocholesterol.** K. BONSTEDT (Z. physiol. Chem., 1933, 214, 173—176).—Oxidation of allocholesterol (I) with CrO<sub>3</sub> in AcOH gives cholestenone (II) and oxycholestenone. Since (II) is thus related to (I) which is  $\alpha\beta$ -unsaturated, cholesterol (III) probably has the double linking in the  $\beta\gamma$ -position.



J. H. B.

[Preparation of] ergosterol from ergot. A. V. TRUFANOV (Khim. Farm. Prom., 1932, 132—133).—The ground ergot (2 kg.) is refluxed with abs. EtOH (3 litres for 6 hr., 2.5 for 3 hr.) and then Et<sub>2</sub>O (3 litres for 6 hr.). The Et<sub>2</sub>O is removed, and the fat dissolved in the combined EtOH, conc., and saponified (4—6 hr., 100 g. KOH). After concn. to 300 c.c. the mixture is kept cool for 24 hr., diluted with H<sub>2</sub>O, extracted with Et<sub>2</sub>O (washed with H<sub>2</sub>O, acidified with

HCl, dried, and distilled). The residue is recryst. from light petroleum (once) and EtOH (twice).

CH. ABS.

**Constitution of ergosterol.** C. K. CHUANG (Annalen, 1933, 500, 270—280).—Alternative structures (Rosenheim—King—Wieland—Dane formulation) are suggested for ergosterol from data already published. Ergostane (Reindel and Walter, A., 1928, 295) is oxidised (CrO<sub>3</sub>-AcOH at 80°) to *norallocholanolic acid*, C<sub>23</sub>H<sub>38</sub>O<sub>2</sub>, m.p. 170° (*Me* ester, m.p. 79·5°), which is also obtained by similar oxidation of the carbinol from *Me allocholanate* (Windaus *et al.*, A., 1926, 723) and MgPhBr.

H. B.

**Phytosterols. II. Sterols of rice oil.** C. ANTONIANI (Atti R. Accad. Lincei, 1932, [vi], 16, 510—514).—Rice husk yields a sterol, C<sub>27</sub>H<sub>46</sub>O, m.p. 143° (corr.), [α]<sub>D</sub> -42·8°, forming an *acetate*, m.p. 135·5° (corr.), [α]<sub>D</sub> -41·7° [*dibromide*, m.p. 133° (corr.)], and a *dihydro-derivative*, m.p. 145·5°, [α]<sub>D</sub> +20·9°. The phytosterols *B*, *C*, and *D* of Nabenhauer and Anderson (B., 1927, 48) are mixtures of the sterol with its dihydro-compound (cf. Weinlagen, A., 1918, i, 56).

T. H. P.

**Action of dehydrating agents on β-phenylethyl alcohol.** L. PALFRAY, S. SABETAY, and (MLLE.) D. SONTAG (Compt. rend., 1932, 195, 1392—1394; cf. A., 1929, 440).—Mixtures of β-phenylethyl alcohol with various dehydrating agents were distilled at 250° or refluxed. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> gives β-phenylethyl *oxalate*, m.p. 51—51·5°, b.p. 221—223°/2—3 mm., Ac<sub>2</sub>O the *acetate*. *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O gives styrene, which is also obtained in varying amounts by using calcined alum, anhyd. CuSO<sub>4</sub>, dry NaOH, K<sub>2</sub>CO<sub>3</sub>, BaO, and CaO+Ca(OH)<sub>2</sub>, and is, in some cases, accompanied by unidentified liquids. SOCl<sub>2</sub> gives β-phenylethyl chloride and mercaptan, and Br the bromide. Conc. aq. NaOH or KOH, and Na<sub>2</sub>CO<sub>3</sub> are without action. NaHSO<sub>4</sub> affords β-phenylethyl ether (72%), b.p. 180·5°/15 mm. (cf. A., 1929, 695).

A. C.

**Velocity of rearrangement of phenylvinyl-carbinol esters.** J. MEISENHEIMER, W. SCHMIDT, and G. SCHÄFER (Annalen, 1933, 501, 131—150).—The rearrangement of α-phenylallyl (I) into cinnamyl (II) *p*-nitrobenzoate at the b.p. of xylene (in absence of solvent) is influenced by numerous factors. Some of these are: the specimen of (I) used, the nature of the vessel (Pt, quartz, glass) in which the change is carried out, the presence of air, and the decomposition products formed [*p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (III) can be isolated] during the heating. The change is accelerated by addition of 0·847 mol.-% of (III). Rearrangement occurs to the extent of 7% after 15 hr. in Et<sub>2</sub>O at 137° [and is independent of the concn. (0·05-1*M*)], and 6% after 24 hr. in C<sub>6</sub>H<sub>12</sub>; addition of (III) has little effect. The conversion of α-phenylallyl 3:4:5-tribromobenzoate (IV), m.p. 75·6° (corr.), into cinnamyl 3:4:5-tribromobenzoate (V), m.p. 103·5° (corr.), at about 137° (in absence of solvent) in high vac. is catalysed by 3:4:5-C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>·CO<sub>2</sub>H. The velocity of rearrangement in various solvents is (qualitatively) proportional to the dielectric const. of the solvent. The f.-p. diagram of (IV) and (V) shows that these exist in different modifications; the f.-p. diagram of (I) and (II) is given. α-Phenylallyl, m.p. 124° (from

COMe<sub>2</sub>) and 115° (from C<sub>6</sub>H<sub>6</sub>), and *cinnamyl*, m.p. 143·2° (corr.), *anthraquinone-2-carboxylates* are described.

H. B.

**Mechanism of reduction by sodium amalgam and alcohol. I. Reduction of aromatic ketones to hydrols.** W. E. BACHMANN (J. Amer. Chem. Soc., 1933, 55, 770—774).—COPh<sub>2</sub>, 4-methyl-, 4:4'-dimethyl-, 4-phenyl-, and 4:4'-diphenyl-benzophenones, and fluorenone are reduced by 2% Na-Hg (which has practically no action on EtOH) and a little EtOH in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> to the corresponding hydrols in almost quant. yield. Reduction occurs thus: (i) 2COPh<sub>2</sub>+2Na → 2CPh<sub>2</sub>·ONa ⇌ (CPh<sub>2</sub>·ONa)<sub>2</sub>; (ii) 2CPh<sub>2</sub>·ONa+2EtOH → COPh<sub>2</sub>+CHPh<sub>2</sub>·OH+2NaOEt; the regenerated COPh<sub>2</sub> is then reduced in the same manner. Reduction can also be accomplished in two stages, viz., (i) by Na-Hg in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub>, (ii) subsequent addition of EtOH. Reduction of COPh<sub>2</sub> by Li-Hg and K-Hg occurs similarly.

H. B.

**Heteropolarity. XIX. Phenoxy-, phenylthiol-, and phenylseleno-groups as auxochromes in triphenylcarbenium salts.** W. DILTNEY [with F. HARENBERG] (J. pr. Chem., 1933, [ii], 136, 49—74).—Comparison of the absorption max. and colours of solutions of mono-, di-, and tri-*p*-methoxy-, -phenoxy-, -methylthiol- (Brand, *et al.*, A., 1925, i, 397), -phenylthiol-, and -phenylseleno-triphenylcarbenium perchlorates in AcOH-HClO<sub>4</sub> and conc. H<sub>2</sub>SO<sub>4</sub> shows that the bathochromic effect of the substituents is SePh>SPh, SMe>OPh, OMe; the third substituent exerts a hypsochromic effect in all cases. Anisylxy is slightly more bathochromic than OPh and introduction of a third anisylxy-group has, surprisingly, a bathochromic effect. The *p*-OMe·C<sub>6</sub>H<sub>4</sub>·S group is only very slightly more bathochromic than SPh. The stability of the perchlorates (in AcOH-HClO<sub>4</sub>) towards hydrolysis by 75% EtOH decreases in the order OPh, SPh, SePh; the phenylselenotriphenylcarbenium perchlorates could not be isolated. The introduction of OPh into the 4- and 4:4'-positions of COPh<sub>2</sub> has approx. the same effect on the colour as OMe; the SPh group has, however, a pronounced bathochromic effect. A reply is made to Burawoy (this vol., 62).

*p*-OEt·C<sub>6</sub>H<sub>4</sub>·OPh, COCl<sub>2</sub>, and AlCl<sub>3</sub> in CS<sub>2</sub> give 4:4'-*di-p*-ethoxyphenoxybenzophenone, m.p. 167°. 4:4'-*Dianisylxy*benzophenone, m.p. 198—199°, prepared similarly from *p*-OMe·C<sub>6</sub>H<sub>4</sub>·OPh (I) or from *p*-OMe·C<sub>6</sub>H<sub>4</sub>·ONa and 4:4'-dibromobenzophenone (II), is demethylated (AlCl<sub>3</sub>-C<sub>6</sub>H<sub>6</sub>) to 4:4'-*di-p*-hydroxyphenoxybenzophenone, m.p. 214° (*Ac*<sub>2</sub> derivative, m.p. 177—178°). (I), BzCl, and AlCl<sub>3</sub> in CS<sub>2</sub> afford 4-*anisylxy*benzophenone, m.p. 104—105°, demethylated (AlCl<sub>3</sub>) to 4-*p*-hydroxyphenoxybenzophenone, m.p. 109°. NaOPh, (II), and Cu-bronze at 210° give 4:4'-*diphenoxy*benzophenone (III), m.p. 147°; 4:4'-*diphenylthiol*- (IV), m.p. 139°, 4:4'-*di-p*-ethoxyphenylthiol-, m.p. 170—171°, and 4:4'-*dianisylthiol*-, m.p. 121—122°, -benzophenones are similarly prepared using NaSPh, *p*-OEt·C<sub>6</sub>H<sub>4</sub>·SNa, and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·SNa, respectively. 4:4'-Dihydroxybenzophenone and *p*-C<sub>6</sub>H<sub>4</sub>Br·NO<sub>2</sub> give (Ullmann method) 4:4'-*di-p*-nitrophenoxybenzophenone, m.p. 150—151°. MgPhBr

and (III) give impure 4:4'-diphenoxytriphenylcarbinol (*perchlorate*, decomp. 130—132°), whilst 4:4':4''-triphenoxytriphenylcarbinol (*perchlorate*, m.p. 236—238°) is prepared from (III) and Mg *p*-phenoxyphenyl bromide. 4-Phenylthiolbenzophenone and MgPhBr give the corresponding carbinol (unstable perchlorate) and a little 4-phenylthioltriphenylmethane, m.p. 118—119°, whilst MgPhBr and (IV) afford 4:4'-diphenylthioltriphenylcarbinol [*perchlorate*, m.p. about 190° (decomp.)]. Mg *p*-phenylthiolphenyl bromide and (IV) yield 4:4':4''-triphenylthioltriphenylcarbinol [*perchlorate*, m.p. 145° (slow decomp. from 140°)], reduced (Zn dust, AcOH) to 4:4':4''-triphenylthioltriphenylmethane, m.p. 105—106°.

Presence of conjugated double linkings in abietic acid. B. ARBUSOV (J. Gen. Chem. Russ., 1932, 2, 806—813).—Abietic acid (I) and maleic anhydride combine when heated in C<sub>6</sub>H<sub>6</sub> to a compound C<sub>24</sub>H<sub>32</sub>O<sub>5</sub> (II) (cf. A., 1932, 1254), m.p. 226.5—227°, [α]<sub>D</sub><sup>20</sup> -28.93 in MeOH, giving with alkalis the corresponding tribasic acid, which when heated reverts to (II) without melting. (II) affords a 60% yield of retene when heated with Se to 300—320°; this cannot be due to the dehydrogenation of (I), formed by the fission of (II) into its components, since (II) does not decompose below 390°, when it gives off succinic anhydride. It is suggested that the formation of retene from (II) is analogous to the elimination of Me on C<sub>12</sub> and would be expected if the double linkings in (I) occupy the positions 7:8 and 13:14 or 6:7 and 5:13; some other combinations are possible, but positions 5:6 and 7:8, and 5:13 and 14:8 appear to be excluded. (II) is oxidised by KMnO<sub>4</sub> to a compound C<sub>24</sub>H<sub>34</sub>O<sub>7</sub>, m.p. 191—192°, probably a δ-lactone. (II) is also formed from some primary resin acids from *P. insignis* and *P. Pithyusa* and from abietic acid prepared by vac. distillation of colophony, although some samples (*e.g.*, from French colophony) did not react. G. A. R. K.

Acid benzoates of zinc and cadmium. P. PFEIFFER and Y. NAKATSUKA (J. pr. Chem., 1933, [ii], 136, 241—248).—The following salts are prepared: H<sub>2</sub>[Zn(OBz)<sub>4</sub>], +2H<sub>2</sub>O, giving Zn(OBz)<sub>2</sub>, +Et<sub>2</sub>O and +H<sub>2</sub>O; H<sub>2</sub>[Cd(OBz)<sub>4</sub>], +2H<sub>2</sub>O, giving Cd(OBz)<sub>2</sub>, +H<sub>2</sub>O, Et<sub>2</sub>O, +H<sub>2</sub>O, EtOH, and +1.5H<sub>2</sub>O (1H<sub>2</sub>O lost at 160°); Ca[Cd(OBz)<sub>4</sub>], and Ba[Cd(OBz)<sub>4</sub>], +3H<sub>2</sub>O (lost at 160°). The prep. of Cd(OBz)<sub>2</sub>, +H<sub>2</sub>O is modified. Attempts to prepare acid salts led to Cd(O·CO·C<sub>6</sub>H<sub>4</sub>Cl-*m* and -*p*)<sub>2</sub>·2H<sub>2</sub>O, Cd salicylate, +3H<sub>2</sub>O (lost on heating), and Cd(O·CO·C<sub>6</sub>H<sub>4</sub>OH-*p*)<sub>2</sub>, +7.5(?)H<sub>2</sub>O and +4H<sub>2</sub>O.

R. S. C.

Mechanism of the Perkin reaction. D. A. BRODSKI (J. Gen. Chem. Russ., 1932, 2, 814—820).—Ac<sub>2</sub>O reacts with Na, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub> forming the corresponding acetates; Kalnin's suggestion (A., 1929, 63), that in Perkin's reaction acetates can be replaced by indifferent org. or inorg. compounds, which assist in the enolisation of the Ac<sub>2</sub>O, is criticised. C<sub>6</sub>H<sub>5</sub>N and piperidine acetates can be employed in place of NaOAc, and piperidine *p*-nitrophenylacetate condenses with PhCHO in the absence of Ac<sub>2</sub>O. Contrary to Kalnin's observation (*loc. cit.*), the yield

of cinnamic acid is not affected by the presence of an excess of NaOAc, whilst the diminution of the yield on the addition of AcOH shows that benzylidene diacetate cannot be an intermediate product in the reaction (A., 1898, i, 109). CH<sub>2</sub>Cl·CO<sub>2</sub>Na and Ac<sub>2</sub>O do not yield (CH<sub>2</sub>Cl·CO)<sub>2</sub>O; the formation of α-chlorocinnamic acid from these and PhCHO cannot, therefore, be due to this cause as suggested by Michael (A., 1901, i, 358). G. A. R. K.

γ-Hydroxy-α-phenylbutyric acid and its lactone. P. CARRÉ and D. LIBERMANN (Compt. rend., 1933, 196, 117—118).—The Na derivative of CH<sub>2</sub>Ph·CN reacts with CH<sub>2</sub>Cl·CH<sub>2</sub>·OH in Et<sub>2</sub>O to give 40—45% of γ-hydroxy-α-phenylbutyronitrile, b.p. 188—190°/10 mm. (phenylurethane, m.p. 89°), hydrolysed by 20% Ba(OH)<sub>2</sub> to γ-hydroxy-α-phenylbutyric acid (I), m.p. 99—100°. (I) could not be etherified or benzoylated, nor could a phenylurethane be obtained, owing to the ready formation of the lactone, b.p. 203—205°/30 mm., which is also obtained when an aq. solution of (I) is heated to 50—60°. H. B.

Preparation of 3:4-dimethoxycinnamic acid. A. OLIVERIO (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 117—118; Chem. Zentr., 1932, ii, 3087).—Veratraldehyde and malonic acid in 87% EtOH-NH<sub>3</sub> afford 88%, and in AcOH 92%, of 3:4-dimethoxycinnamic acid, m.p. 181°. A. A. E.

Stereochemistry of diphenyls. XXVII. Comparison of the racemisation of 6:6'-difluoro- and 6:6'-dimethoxy-diphenic acids. W. M. STANLEY, E. McMAHON, and R. ADAMS. XXVIII. Preparation and properties of 2:2'-difluoro-6:6'-dinisro-5:5'-dimethyldiphenyl-3:3'-dicarboxylic acid. E. C. KLEIDERER and R. ADAMS (J. Amer. Chem. Soc., 1933, 55, 706—716, 716—719).—XXVII. 6:6'-Dimethoxydiphenic acid, m.p. 293—294° (lit. 288—290°) [brucine salt, m.p. 198—199° (corr.) (lit. 268°); amide, m.p. 273—274°], is resolved by quinine (cf. Kenner and Turner, A., 1928, 1244) into *d*-, m.p. 291—292°, [α]<sub>D</sub><sup>20</sup> +108.5° in COMe<sub>2</sub> [diquinine salt, m.p. 98—100° (corr.) (lit. about 60°); Me ester, m.p. 98—99°; amide, m.p. 230—231° (corr.)], and *l*-forms (I), m.p. 291—292°, [α]<sub>D</sub><sup>20</sup> -114.9° in COMe<sub>2</sub> [diquinine salt, m.p. 178—179° (corr.) (lit. 172—173°); Me ester (II), m.p. 101—102°; amide (III), m.p. 230—231° (corr.)]. (I) and (II) racemise at about the same rate [which is faster than that of (III)]. 2-Iodo-3-aminobenzoic acid [by reduction (SnCl<sub>2</sub>, conc. HCl, and a little EtOH) of the 3-NO<sub>2</sub>-acid] is diazotised in 48% HF and the resulting solution kept at 30±2° for 2 days, whereby 2-iodo-3-fluorobenzoic acid, m.p. 152—153° (corr.) [Me (IV), b.p. 127—128°/4 mm., and Et (V), b.p. 148—150°/6 mm., esters], results. (IV) and Cu powder at 180—240° give the Me ester, m.p. 116—117°, of 6:6'-difluorodiphenic acid, m.p. 308—311° (corr.) (after previous shrinking and softening) [Et ester, m.p. 105—107°, prepared from (V)]; the acid is resolved by quinine into *d*-, m.p. 305—306° (corr.), [α]<sub>D</sub><sup>20</sup> +16.8° in 95% EtOH [quinine salt, m.p. 163—165° (corr.)], and *l*-forms, m.p. 305—306° (corr.), [α]<sub>D</sub><sup>20</sup> -22.5° in 95% EtOH [quinine salt, m.p. 221—222° (corr.)]. These active acids racemise readily in 0.1N-NaOH at 100° (bath), less readily in boiling

EtOH, AcOH, and Ac<sub>2</sub>O, and slowly in 0.1*N*-NaOH at 20° and EtOH-conc. HCl; the rates are much faster than those of (I).

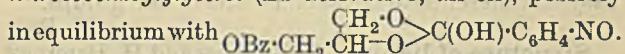
XXVIII. 5-Bromo-4-fluoro-5-nitro-*m*-xylene and dil. HNO<sub>3</sub> at 150° give 5-bromo-4-fluoro-6-nitro-*m*-toluic acid, m.p. 249—251° (corr.) [*Me* (VI), m.p. 88—89° (corr.), and *Et*, m.p. 65—66° (corr.), esters], the constitution of which is inferred from the similar production of 6-nitro-*m*-toluic acid from 4-nitro-*m*-xylene. (VI) and Cu-bronze at 220—225° give the *Me* ester, m.p. 191—193° (corr.), of 2:2'-difluoro-6:6'-dinitro-5:5'-dimethyldiphenyl-3:3'-dicarboxylic acid, m.p. (block) 301—304°, m.p. (tube) 318—320° (corr.; decomp.), resolved by strychnine into *d*-, m.p. 297—301° (corr.; decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +15° in MeOH [strychnine salt, m.p. 190—193° (corr.; decomp.)], and *l*-forms, m.p. 298—300° (corr.; decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -17° in MeOH [strychnine salt, m.p. 224—228° (corr.; decomp.)], which are not racemised appreciably in boiling EtOH, AcOH, cyclohexanone, or 0.1*N*-NaOH, in agreement with the relatively large size of the 6:6'-NO<sub>2</sub>-groups. H. B.

Depside esters of dihydroxy phenols, and polydepsides. T. CURRIE and A. RUSSELL (J.C.S., 1933, 140—142; cf. A., 1932, 1030).—Na vanilloxide in COMe<sub>2</sub> with 3:3':4'-trimethoxy-*p*-dibenzoyl chloride gives 3:3':3'':4'-tetramethoxy-*pp*-tribenzaldehyde, m.p. 159° (nomenclature, *loc. cit.*). The following are similarly obtained: 3:3':3'':4'':5'-pentamethoxy-*ppp*-tetra-, m.p. 249°, 3:4'-dimethoxy-*pp*-tri-, m.p. 152°, and *tris*-(3:3':3'':4'-tetramethoxy-*pp*-tribenzoyl)-2:3:4'-trihydroxy-benzaldehyde, m.p. 263° (decomp.), *quinol bis*-(3:3':4'-trimethoxy-*p*-dibenzoyl), m.p. 229°, -(3':4'-dimethoxy-*p*-dibenzoyl), m.p. 230°, and -(3:4'-dimethoxy-*pp*-tribenzoyl) ethers, m.p. 278—279°, *resorcinol bis*-(3':4'-dimethoxy-*p*-dibenzoyl), m.p. 194°, and -(4'-methoxy-*p*-dibenzoyl) ethers, m.p. 154°, and *pyrocatechol bis*-(3':4'-dimethoxy-*p*-dibenzoyl) ether, m.p. 175°. The above aldehydes with KMnO<sub>4</sub> by an improved method give 3:3':3'':4'-tetramethoxy-*pp*-tri-, m.p. 251—252° [chloride, m.p. 171° (decomp.)], 3:3':3'':4'':5'-pentamethoxy-*ppp*-tetra-, m.p. 327°, and 3:4'-dimethoxy-*pp*-tri-benzoic acid, m.p. 233° (chloride, m.p. 155°). A. A. L.

Formation of an intermediate in the action of phosphorus pentachloride on aldehydes. S. C. J. OLIVIER and A. P. WEBER (Rec. trav. chim., 1933, 52, 169—174).—2:6-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·CHO (I) (1 mol.) and PCl<sub>5</sub> (1 mol.) give at first *di-α*:2:6-trichlorobenzyl ether (II), m.p. 180—185° [yield 5—6 g. from 10 g. of (I)], converted (almost quant.) by PCl<sub>5</sub> (1 mol.) at 170° into 2:6-dichlorobenzylidene chloride (III), b.p. about 155° (bath)/12 mm. (II) is not obtained when mixtures of (I) and (III) are heated, whilst (III) results in almost quant. yield from equimol. amounts of (I) and PCl<sub>5</sub> in ¼ hr. at 160°. (II), which is considered to be an intermediate in the reaction between (I) and PCl<sub>5</sub>, gives (I) and (III) when it is fused and then kept at 100° for 2 min. H. B.

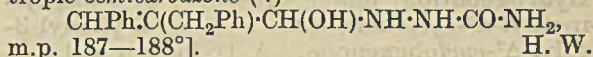
Photochemical reactions of *o*-nitrobenzylidene acetals. VII. (αβ-*o*-Nitrobenzylideneglycerol.) I. TANASESCU and E. MACOVSKI (Bull. Soc. chim., 1932, [iv], 51, 1556—1565; cf. this vol., 275).—

Hibbert's technique applied to the condensation of *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO (I) and glycerol gives only αβ-*o*-nitrobenzylideneglycerol (II), b.p. 224—226°/15 mm., and a small distillation residue, also obtained when pure (II) is distilled. The constitution of (II) is proved by methylation (MeI-Ag<sub>2</sub>O) to the α'-*Me* ether, b.p. 203—208°/11 mm., hydrolysed by dil. HCl to glycerol α-*Me* ether and re-formed therefrom by (I) in 20% H<sub>2</sub>SO<sub>4</sub> at 120°. (II) with BzCl gives α-benzoyl-α'β-*o*-nitrobenzylideneglycerol, two isomeric forms, m.p. 125—126° (III) and an oil (IV), respectively. Illumination of (III) in C<sub>6</sub>H<sub>6</sub> usually gives an isomeride, m.p. 120—121° after softening at 115—116°, considered to be probably α-benzoyl-α'-*o*-nitrosobenzoylglycerol (*Bz* derivative, an oil), possibly in equilibrium with



Illumination of (IV) gives an oily isomeride, sometimes obtained also from (III) probably by way of (IV). R. S. C.

Homologues of cinnamaldehyde. II. α-Phenyl- and α-benzyl-cinnamaldehyde. P. SCHORIGIN, V. ISSAGULIANZ, and I. MATSCHINSKAJA (Ber., 1933, 66, [B], 389—393; cf. A., 1931, 485).—PhCHO and CH<sub>2</sub>Ph·CHO in EtOH-H<sub>2</sub>O in presence of NaOH afford (*a*) α-phenylcinnamaldehyde (I), m.p. 94—95° (phototropic semicarbazone, m.p. 188.5—189.5°); (*b*) a very sparingly sol. compound, m.p. 187—199°, probably polymeric αβγ-triphenylglutardialdehyde, which does not give the typical aldehyde reactions, yields PhCHO, possibly CH<sub>2</sub>Ph·CHO, and (I) when heated in vac., and gives PhCHO under the action of NaOH; (*c*) αβγ-triphenylvalerolactone, m.p. 151—162° (*Na* and *Ag* δ-hydroxy-αβγ-triphenylvalerate). Similarly, PhCHO and CH<sub>2</sub>Ph·CH<sub>2</sub>·CHO give α-benzylcinnamaldehyde, m.p. 53—54°, with odour of CHPh·CH·CHO and jasmine [non-phototropic semicarbazone (?)]



Phototropic and thermotropic anils from 5-bromosalicylaldehyde. C. M. BREWSTER and L. H. MILLAM (J. Amer. Chem. Soc., 1933, 55, 763—766).—The following are prepared from 5-bromosalicylaldehyde (convenient prep. given) and the requisite amines usually in EtOH and occasionally by direct fusion only: 5-bromosalicylidene-*o*-, m.p. 86.5° (using EtOH) and 165° (no solvent), and -*p*-, m.p. 163.5°, -*toluidines*; -α-naphthylamine (I), m.p. 109.5°; -*p*-phenetidine, m.p. 156°; -*o*-, m.p. 110°, and -*p*-, m.p. 156°, -*anisidines*; -*p*-aminoazobenzene (II) yellowish-brown and red forms, m.p. 212°; -2-amino-5-azotoluene, m.p. 212°; -*o*-, m.p. 192.5°, and -*p*-, m.p. 239°, -aminophenols; -*p*-xylylidine, m.p. 67°; -*m*-4-xylylidine, m.p. 131.5°; -*p*-aminobenzoic acid, m.p. 282°; -*m*- (III), m.p. 169°, and -*p*-, m.p. 207°, -nitroanilines; -*o*-, m.p. 88°, -*m*-, m.p. 127.5°, and -*p*-, m.p. 158°, -chloroanilines; -*o*- (IV), m.p. 78°, and -*p*- (V), m.p. 178°, -bromoanilines; -2:4-, m.p. 148°, and 2:5-, m.p. 139°, -dichloroanilines; *di*-5-bromosalicylidene-*p*-phenylenediamine, m.p. 277°, -*m*-toluylenediamine, m.p. 188°, -*di*anisidine (VI), m.p. 279°, -*o*-tolidine, m.p. 242°, and -benzidine, m.p. 345°. Salicylidene-*p*-toluidine (VII), m.p. 95°, and the above

anils [except (II), (III), (IV), and (VI)] are thermotropic, whilst (I), (V), and (VII) are phototropic. All m.p. are corr. H. B.

**Differentiation of *O*- and *N*-methyl groups.** P. PFEIFFER and E. OCHIAI (J. pr. Chem., 1933, [ii], 136, 125—128).—Piperonal (1 mol.) and  $\text{AlBr}_3$  (3 mols.) in  $\text{C}_6\text{H}_6$  at  $100^\circ$  (bath) give 49% of 3:4-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$  and 8.5% of anthracene (formed from  $\text{C}_6\text{H}_6$ , the intermediately formed  $\text{CH}_2\text{Br}_2$ , and  $\text{AlBr}_3$  with subsequent atm. oxidation of the dihydroanthracene).  $\text{NPhMe}_2$  is unaffected by  $\text{AlBr}_3$  in  $\text{C}_6\text{H}_6$ , whilst  $p\text{-NMe}_2\text{C}_6\text{H}_4\cdot\text{CHO}$  affords  $p$ -dimethylaminotriphenylmethane. Since *OMe*-compounds are demethylated by  $\text{AlBr}_3$  in  $\text{C}_6\text{H}_6$  (A., 1928, 420), it is easy to differentiate between *O*- and *N*-Me groups.

H. B.

**Structure of lignin.** F. BRAUNS and H. HIBBERT (Pulp and Paper Canada, 1933, 34, 187—188).—A synopsis of recent work on the empirical formula of spruce lignin, indicating  $\text{C}_{47}\text{H}_{52}\text{O}_{16}$ . This is supported by analytical data on "MeOH lignin" and "glycol lignin," and their Me derivatives.

H. A. H.

**Asymmetric syntheses. II. Action of optically active nitrates on cyclic ketones.** R. L. SHREINER and E. A. PARKER (J. Amer. Chem. Soc., 1933, 55, 766—770; cf. this vol., 159).—*d*- $\beta$ -Octyl nitrate, prepared by a modification of Chapman and Smith's method (J.C.S., 1867, 20, 581), 4-methylcyclohexanone, and  $\text{KOEt}$  in  $\text{EtOH-Et}_2\text{O}$  give the *d*-*K* salt (I),  $[\alpha]_D^{25} +9.02^\circ$ , of 2-nitro-4-methylcyclohexanone; *l*- $\beta$ -octyl nitrate (II) similarly affords the *l*-*K* salt (III),  $[\alpha]_D^{25} -4^\circ$ , whilst *dl*- $\beta$ -octyl nitrate yields the inactive *K* salt. The rapid racemisation of (I) and (III) indicates that the new asymmetric centre is at  $\text{C}_2$ . *cycloHexanone* and (II) similarly give an impure salt,  $[\alpha]_D^{25} -6.72^\circ$ .

H. B.

**Hydrogenation, under pressure, of 5-phenyl-3-methyl- $\Delta^2$ -cyclohexenone and of 5-phenyl-3-*p*-tolyl- $\Delta^2$ -cyclohexenone.** A. D. PETROV and L. I. ANZUS [with A. O. SAYELJEV and E. W. IKONEN] (Ber., 1933, 66, [B], 420—423).—5-Phenyl-3-methyl- $\Delta^2$ -cyclohexenone is converted by  $\text{H}_2$  at  $225\text{--}245^\circ$  into 3-cyclohexylmethylcyclohexane, b.p.  $243\text{--}243.5^\circ/\text{atm. press.}$  *p*-Tolyl styryl ketone and  $\text{COMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  in presence of  $\text{NaOEt}$  afford 6-carbethoxy-5-phenyl-3-*p*-tolyl- $\Delta^2$ -cyclohexenone, m.p.  $133\text{--}134^\circ$ , hydrolysed to 5-phenyl-3-*p*-tolyl- $\Delta^2$ -cyclohexenone (I), m.p.  $106^\circ$ . (I) is hydrogenated with some difficulty at  $220\text{--}240^\circ$ , yielding mainly 1-cyclohexyl-3-*p*-methylcyclohexylbenzene, b.p.  $194\text{--}198^\circ/8\text{ mm.}$ , with a little completely hydrogenated substance,  $\text{C}_{15}\text{H}_{34}$ , and cracked products. H. W.

**Derivatives of diphenyl.** C. F. H. ALLEN and W. L. BALL (Canad. J. Res., 1932, 7, 643—645).—*p*-Phenylphenacyl bromide and  $\text{KOAc}$  in hot 60%  $\text{EtOH}$  give the acetate (I), m.p.  $111^\circ$ , hydrolysed by  $\text{EtOH}$  containing a little  $\text{H}_2\text{SO}_4$  (not by other methods) to *p*-phenylphenacylcarbinol, m.p.  $123\text{--}128^\circ$  [*phenylurethane*, m.p.  $186\text{--}187^\circ$ ; 2:4-dinitrophenylhydrazone, m.p.  $222\text{--}223^\circ$  (decomp.)]. *p*-Phenylacetophenone,  $\text{PhCHO}$ , and  $\text{KOH}$  in hot  $\text{EtOH}$  give benzylidene-*p*-phenylacetophenone, m.p.  $156^\circ$ , the dibromide (II), m.p.  $189^\circ$ , of which is hydrolysed to *p*-phenylbenzoyl-

benzoylmethane,  $p\text{-C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Bz}$ , m.p.  $112^\circ$  [*Cu* derivative, m.p.  $290^\circ$  (decomp.)]; this with  $\text{NH}_2\text{OH}$  in  $\text{AcOH}$  gives 5-phenyl-3-*p*-diphenylisooxazole, m.p.  $182\text{--}183^\circ$ , the constitution of which is proved by exclusion, since (II) with  $\text{NH}_2\text{OH}$  gives 3-phenyl-5-*p*-diphenylisooxazole, m.p.  $195^\circ$ .

R. S. C.

**Molecular re-arrangements of  $\alpha$ -glycols. VIII. Reduction of  $\alpha\beta$ -dinaphthyl ketone (an attempt to compare the electro-negativities of  $\alpha$ - and  $\beta$ -naphthyl radicals). IX. Conclusion (the pinacolin rearrangement as a method of establishing relative electro-negativities of organic radicals). M. MIGITA (Bull. Chem. Soc. Japan, 1933, 8, 22—27, 27—35; cf. this vol., 271).—VIII. Reduction of  $\alpha\beta$ -dinaphthyl ketone (I) and  $\alpha$ -naphthyl-*p*-diphenyl ketone (II) with  $\text{Zn}$  dust and  $\text{AcOH}$  is anomalous, probably owing to steric factors. At  $25^\circ$   $\alpha\beta$ -dinaphthylcarbinol, m.p.  $112\text{--}113^\circ$ , and  $\alpha$ -naphthyl-*p*-diphenylcarbinol, m.p.  $131^\circ$ , but, when boiled,  $\alpha\beta$ -dinaphthylmethane, m.p.  $96^\circ$ , and  $\alpha$ -naphthyl-*p*-diphenylmethane, m.p.  $146^\circ$ , are formed. (I) is unchanged in  $\text{EtOH}$  by sunlight, and with  $\text{Mg}$  and  $\text{MgI}_2$  in  $\text{Et}_2\text{O-C}_6\text{H}_6$  gives a red solution (probably containing ketyl), from which only resins were obtained. (II), m.p.  $140\text{--}141^\circ$ , is prepared from  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CN}$  and the Grignard reagent from *p*-bromodiphenyl (m.p.  $90\text{--}91^\circ$ ; modified prep.).**

IX. A discussion of results and theories already published.

R. S. C.

**Grignard reaction in synthesis of ketones. I. Deoxybenzoin.** S. S. JENKINS (J. Amer. Chem. Soc., 1933, 55, 703—706).—Prolonged interaction of  $\text{NH}_2\text{Bz}$  and  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  (3—4 equivs.) gives a 77% yield of deoxybenzoin;  $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$  similarly affords *m*-chlorophenyl benzyl ketone (72%), m.p.  $62^\circ$  (all m.p. are corr.) (*anti-oxime*, m.p.  $120^\circ$ , rearranged by  $\text{PCl}_5$  in  $\text{Et}_2\text{O}$  to phenylacet-*m*-chloroanilide, m.p.  $95^\circ$ ), whilst *p*-anisamide (I) yields anisyl benzyl ketone (74%), m.p.  $77^\circ$  (*anti-oxime*, m.p.  $118.5^\circ$ , rearranged to phenylacet-*p*-anisidide).  $\text{Mg}$  *o*-chlorobenzyl bromide and (I) give anisyl *o*-chlorobenzyl ketone (55%), m.p.  $97.5^\circ$  (cf. Buck and Ide, A., 1931, 732) (*anti-oxime*, m.p.  $99^\circ$ , rearranged to *o*-chlorophenylacet-*p*-anisidide, m.p.  $166^\circ$ ), whilst  $\text{Mg}$  *p*-chlorobenzyl bromide and (I) furnish anisyl *p*-chlorobenzyl ketone (66%), m.p.  $137.5^\circ$  (*anti-oxime*, m.p.  $138.5^\circ$ , rearranged to *p*-chlorophenylacet-*p*-anisidide, m.p.  $184^\circ$ ). The above anilides are also prepared from the requisite acids (or chlorides) and anilines.

H. B.

**Thermal interconversion of mixed benzoin.** J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1933, 55, 855).—When benzanisoin is heated at  $125\text{--}130^\circ$  for 3 hr., some anisbenzoin is produced.

H. B.

**Spontaneous resolution of 4-methoxy-*ms*-methyldeoxybenzoin.**  $\text{CHPhMe}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ . (MME.) BRUZAU (Compt. rend., 1933, 196, 122—124).—4-Methoxy-*ms*-methyldeoxybenzoin [*anisyl*  $\alpha$ -phenylethyl ketone], prepared by Ney's method (A., 1882, 1197), from  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$  and  $\text{CHPhMe}\cdot\text{CO}\cdot\text{NH}_2$ , or from  $\text{PhOMe}$ ,  $\text{CHPhMe}\cdot\text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$ , when cryst. from  $\text{EtOH}$  gives



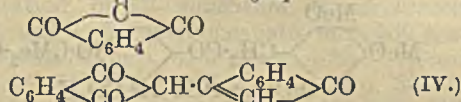
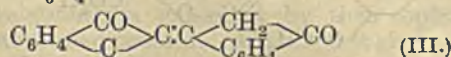
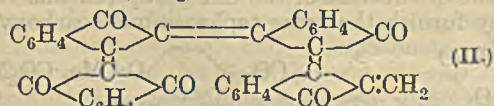
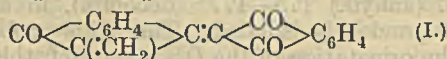
material of m.p. 58—60°, 78—80° (prisms), or 54—80°. The prisms are optically active forms of the ketone and are separable by hand. *p*-Tolyl  $\alpha$ -phenylethyl ketone, m.p. 46—47°, and Ph  $\alpha$ -phenylethyl ketone do not show similar properties.

H. B.

**Reaction between  $\alpha\beta$ -unsaturated ketones and organic magnesium compounds. Unsaturated mesitylenic ketones.** E. P. KOHLER and C. E. BARNES (J. Amer. Chem. Soc., 1933, 55, 690—695).—2 : 4 : 6-Trimethylphenyl  $\alpha\beta$ -dibromo- $\beta$ -phenylethyl ketone, m.p. 126—127°, is treated with MeOH-NaOMe, the reaction mixture acidified (HCl), and the solution boiled, whereby *benzoyl*-2 : 4 : 6-trimethylbenzoylmethane (I), m.p. 79°, is obtained. MgPhBr and (I) give 2 : 4 : 6-trimethylphenyl  $\beta$ -hydroxy- $\beta\beta$ -diphenylethyl ketone, m.p. 75°, which is dehydrated by warm dil. HCl to 2 : 4 : 6-trimethylphenyl  $\beta$ -phenylstyryl ketone (II), m.p. 104°. Contrary to the previous statement (A., 1907, i, 1050), MgPhBr and (II) afford 2 : 4 : 6-trimethylphenyl  $\beta\beta$ -triphenylethyl ketone, m.p. 194—195°, also obtained from CPh<sub>3</sub>Cl and the enolate C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>C(C<sub>6</sub>H<sub>5</sub>)OMgBr (from acetomesitylene and MgEtBr). MgMeI and (II) in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> (not in Et<sub>2</sub>O) yield 2 : 4 : 6-trimethylphenyl  $\beta\beta$ -diphenylpropyl ketone, m.p. 87°, synthesised from MgPhBr and 2 : 4 : 6-trimethylphenyl  $\beta$ -methylstyryl ketone (III), m.p. 84°, which is prepared [as (II)] from (I) and MgMeI. MgEtBr and (II) give 2 : 4 : 6-trimethylphenyl  $\beta\beta$ -diphenylbutyl ketone, m.p. 106°, whilst MgMeI and (III) afford 2 : 4 : 6-trimethylphenyl  $\beta$ -phenylisobutyl ketone, m.p. 184—185°.

H. B.

**Derivatives of di-indone. III. Action of di-indone on aldehydes in alcoholic [alkali].** M. V. IONESCU and H. SLUSANSCHI (Bull. Soc. chim., 1932, [iv], 51, 1551—1556; cf. this vol., 162).—Di-indone does not react with MeCHO in EtOH-NaOH or EtOH-NaOEt, but with CH<sub>2</sub>O gives, in both cases, a substance, C<sub>19</sub>H<sub>10</sub>O<sub>3</sub>, probably *methylenedi-indone* (I), m.p. 218°. It dissolves slowly in cold, rapidly in hot, NaOH or EtOH-NH<sub>3</sub> to give pink and orange-red solutions, respectively. With boiling AcOH it gives a purplish-black substance, C<sub>37</sub>H<sub>18</sub>O<sub>5</sub>, m.p. 280° (decomp.), probably *methylenearhydrobisdi-indone* (II), unchanged by NH<sub>3</sub>, but decomposed by alcoholic alkali to a deep blue solution. With boiling EtOH-NaOEt (I) affords a bright yellow, cryst. substance, C<sub>27</sub>H<sub>14</sub>O<sub>4</sub>, m.p. 335°, possibly *anhydrotri-indandione*



(III) (giving slowly a pale yellow solution in alcoholic alkali), and an amorphous, pale yellow substance,

D D

C<sub>18</sub>H<sub>10</sub>O<sub>3</sub>, possibly an isomeride (IV) of di-indone (giving a greenish-blue solution in alkali). (I) is unchanged by NaOEt and does not condense with indandione in presence of NaOEt. It bears no relation to the alkaline condensation products from bisdi-indone.

R. S. C.

#### Migration of acyl groups in polyhydric phenols.

F. MAUTHNER (J. pr. Chem., 1933, [ii], 136, 205—212).—1-Acetylpyrogallol Me<sub>2</sub> ether with AlCl<sub>3</sub> in PhNO<sub>2</sub> gives 2-hydroxy-3 : 4-dimethoxyacetophenone. Acetylresorcinol Me ether (from resorcinol Me ether and AcCl at 100°; b.p. 125—126°/11 mm.) gives similarly paeonol, m.p. 50° (*p*-nitrophenylhydrazone, m.p. 238—239°), volatile in steam, and isopaeonol, involatile in steam. Acetylresorcinol Me ether yields only acetylevernone, and 2-methoxydiacetylquinol, m.p. 95—96°, gives 2 : 5-dihydroxy-4-methoxyacetophenone, m.p. 165—166° [*p*-nitrophenylhydrazone, m.p. 255—256° (decomp.)], yielding with Me<sub>2</sub>SO<sub>4</sub> in NaOH-H<sub>2</sub>O-EtOH 2 : 4 : 5-trimethoxy- and 2-hydroxy-4 : 5-dimethoxyacetophenone, m.p. 111—112°. Acetylguaiacol is scarcely changed at room temp., and 3 : 5-diacetoxybenzoic acid, m.p. 156—157°, is stable to AlCl<sub>3</sub> at 70°.

R. S. C.

#### Synthesis of 2 : 3 : 5-trihydroxyacetophenone.

F. MAUTHNER (J. pr. Chem., 1933, [ii], 136, 213—216).—The Ac<sub>3</sub> derivative of hydroxyquinol (I) with AlCl<sub>3</sub> in PhNO<sub>2</sub> at room temp. gives a small amount of a substance, m.p. 182—183°, and 2 : 3 : 5-trihydroxyacetophenone, m.p. 206—207° [*p*-nitrophenylhydrazone, m.p. 241—242° (decomp.)]; Ac<sub>3</sub> derivative, m.p. 106—107°, giving on methylation the known Me<sub>3</sub> ether, and also obtained in poor yield from (I) by the Hoesch synthesis.

R. S. C.

**Manufacture of condensation products from polyhydric alcohols and cyclic ketones.** I. G. FARBENIND. A.-G.—See B., 1933, 182.

**Anodic oxidation of benzene.** R. M. ARCHIBALD.—See this vol., 358.

**Constitution and reactivity. V. Nitration and bromination of aminoanthraquinones. VI. Replacement of the sulphonic acid group in chloroanthraquinonesulphonic acids by chlorine.** K. LAUER (J. pr. Chem., 1933, [ii], 136, 1—4, 5—8).—V. Nitration of 1- and 2-aminoanthraquinones with 1.05 equiv. of NaNO<sub>3</sub> in abs. H<sub>2</sub>SO<sub>4</sub> at 5° gives mixtures of 2- and 4-, and 1- and 3-NO<sub>2</sub>-derivatives, respectively, unaccompanied by (NO<sub>2</sub>)<sub>2</sub>-compounds. Substituents in the 1-NH<sub>2</sub> group increase the proportion of 4-NO<sub>2</sub>-compound in the order of increasing acidity, viz., CH<sub>2</sub> < CO<sub>2</sub>Alk < Ac < Bz < CO<sub>2</sub>·CH<sub>2</sub>Cl < CO·CO<sub>2</sub>H < SO<sub>2</sub>·NC<sub>7</sub>H<sub>7</sub>. Parallel results are obtained by bromination with 1.05 equiv. Br in PhNO<sub>2</sub> at 30°. Vals. of the differences of the heats of activation, q<sub>1:2</sub>—q<sub>1:4</sub>, and q<sub>2:3</sub>—q<sub>2:1</sub> (cf. this vol., 69) for the bromination and nitration of the aminoanthraquinones and their *N*-substituted derivatives are given.

VI. A kinetic study of the replacement of SO<sub>3</sub>H by Cl in the chloroanthraquinonesulphonic acids using the method previously employed for the anthraquinonedisulphonic acids (*loc. cit.*) indicates that replacement of the first SO<sub>3</sub>H group by Cl reverses

the reactivity of the remaining one. Thus whilst in the disulphonic acids the reactivity of the first  $\text{SO}_3\text{H}$  in different isomeric pairs is in the order  $1:5 > 1:8$ ;  $1:7 > 1:6$ ;  $2:6 > 2:7$ , in the chloro-sulphonic acids this order is reversed. Vals. of  $K \times 10^3$  at  $94^\circ$ ,  $104^\circ$ , and  $114^\circ$ , and of  $q$  and  $\alpha \times 10^{-10}$  are given.

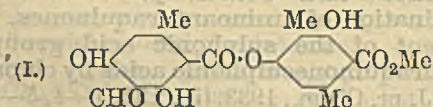
H. A. P.

**Amination by ammonolysis** [of 2-chloro-anthraquinone]. III. Effect of inorganic salts. P. H. GROGGINS and A. J. STIRTON (Ind. Eng. Chem., 1933, 25, 169—175; cf. this vol., 277).—In the prep. of 2-amino- from 2-chloro-anthraquinone by ammonolysis the side reactions of hydrolysis to 2-hydroxy-anthraquinone and *sec.*-amine formation are not markedly affected by  $\text{NH}_4$  salts, but are strongly inhibited by small amounts of oxidising agents, particularly  $\text{KClO}_3$ .  $\text{KClO}_3$  needs narrowly defined conditions for max. action, but equally good results are obtained over a wider range of conditions by the combined action of  $\text{KClO}_3$  and  $\text{NH}_4\text{NO}_3$ . Addition of Cu salts to this binary mixture enables the amination to be carried out at  $160^\circ$  instead of  $190$ — $200^\circ$ , but does not result in any marked improvement in purity or yield of product. Excess of oxidising agent and undue prolongation of the reaction are to be avoided, as they lead to the production of 1:2-diamino- and 2-amino-1-hydroxy-anthraquinones. Reducing agents, e.g., sulphites and  $\text{N}_2\text{H}_4$ , diminish the yield and purity of 2-aminoanthraquinone. Using a large excess of  $\text{NH}_3$  and small additions of  $\text{KClO}_3$  and  $\text{NH}_4\text{NO}_3$ , 2-aminoanthraquinone can be prepared on a semi-technical scale in a yield of 97% of theory of material of 97.5% purity. This affords a cheaper route than that from the -2-sulphonic acid.

H. A. P.

**Manufacture of chlorocycanoanthraquinones.** I. G. FARBERIND. A.-G.—See B., 1933, 183.

**Lichen acids.** IV. Atranorin. F. H. CURD, A. ROBERTSON, and R. J. STEPHENSON (J.C.S., 1933, 130—133; cf. A., 1932, 850).—Atranorin, regarded as (I), extracted by an improved process has the

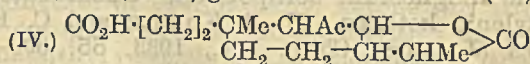


formula  $\text{C}_{19}\text{H}_{18}\text{O}_8 \cdot \text{H}_2\text{O}$ , but when extracted with  $\text{CHCl}_3$  it contains Cl. The latter product gives an O- $\text{Me}_3$  ether (II), m.p.  $123^\circ$ , an O- $\text{Me}_2$  ether, m.p.  $136^\circ$ , and a substance containing Cl, m.p.  $106$ — $107^\circ$  (*semicarbazone*, m.p.  $208^\circ$ ). (II) is hydrolysed to Me isorhizonate. Me orsellinate in  $\text{Et}_2\text{O}$  with  $\text{ZnCl}_2$  and HCN gives Me hæmotommate and isohæmotommate, m.p.  $130^\circ$ .

A. A. L.

**Bitter substances.** IV. Bitter substances of elecampane. K. F. W. HANSEN (J. pr. Chem., 1933, [ii], 136, 176—192).—Tetrahydroalantolactone (I) is converted by  $\text{NaOEt}$  in  $\text{EtOH}$  at  $170$ — $180^\circ$  into an *isomeride*, m.p.  $60$ — $61^\circ$ ; the formation of other hydrocarbons in addition to eudalene by complete reduction to hydrocarbon and subsequent dehydrogenation does not therefore disprove the formula previously assigned (cf. A., 1931, 734; Ruzicka and Pieth, *ibid.*, 1301). The action of  $\text{MgPhBr}$  on (I) is

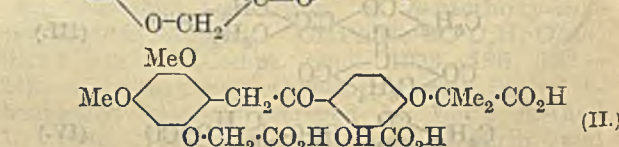
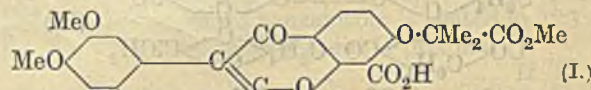
accompanied by loss of  $\text{H}_2\text{O}$  from the carbinol to give the substance  $\text{C}_{27}\text{H}_{34}\text{O}$ , m.p.  $161^\circ$ , which does not add Br or  $\text{H}_2$  (Pd), and gives indefinite products with  $\text{O}_3$ , and  $\text{COPh}_2$  only with  $\text{CrO}_3$ -AcOH. Ozonisation of the crude mixture of dihydro-alanto- (II) and *iso*-alanto-lactones (III), decomp. of the ozonide, and oxidation of the product with  $\text{KMnO}_4$  in  $\text{COMe}_2$  (cf. A., 1931, 1301) gives a *ketolactonic acid* (IV), m.p.



$190$ — $191^\circ$  [*Me* ester, b.p.  $190$ — $210^\circ/1$  mm. ( $\text{CH}_2\text{N}_2$ ); this did not give a cryst. semicarbazone]. The annexed formula is therefore assigned to (II). The product of isomerisation of (III) by addition and removal of HCl (cf. A., 1931, 1065) also gave (IV) on similar treatment. The adducts from  $\text{CH}_2\text{N}_2$  and alanto- and *iso*alanto-lactones (cf. A., 1931, 734) give with  $\text{H}_2$ -PtO<sub>2</sub> different resinous products (*picrates*, m.p.  $158$ — $159^\circ$  and  $167$ — $168^\circ$ , respectively), and hence presumably are not hydrogenated in ring B. Similarly, on elimination of  $\text{N}_2$  by heating in  $\text{CO}_2$  at their m.p. they give *substances*,  $\text{C}_{16}\text{H}_{22}\text{O}_2$ , m.p.  $119$ — $120^\circ$ , and amorphous, which give yellow colorations with  $\text{C}(\text{NO}_2)_4$  but do not take up  $\text{H}_2$ , and on oxidation give only succinic and not the expected *cyclopropane-carboxylic acid*. Treatment of *iso*alantolactone with KCN in aq. EtOH at the b.p. and alkaline hydrolysis of the resulting nitrile gives *dihydroisoalantolactone-carboxylic acid*, m.p.  $174^\circ$ , which readily gives 30% of theory of CO with warm  $\text{H}_2\text{SO}_4$ ; this, however, is no criterion of the *tert.* nature of the  $\text{CO}_2\text{H}$  group, as (I) does the same. The  $\text{CO}_2\text{H}$  group is actually primary, and therefore attached at  $\text{C}_{15}$ , as is shown by the ease of hydrolysis of its Me ester. An impure carboxylic acid similarly prepared from an "80—90%" alantolactone also gave no evidence of the presence of a *tert.*  $\text{CO}_2\text{H}$  group. The second double linking in both alanto- and *iso*alanto-lactones is therefore at  $\text{C}_{13-15}$  [formula (II)].

H. A. P.

**Tephrosin.** III. Acidic derivatives of tephrosin. E. P. CLARK (J. Amer. Chem. Soc., 1933, 55, 759—762).—Oxidation of tephrosin by the method previously described (A., 1931, 491) gives an isomeric *tephrosindicarboxylic acid* (+ $3\text{H}_2\text{O}$ ), m.p.  $127$ — $128^\circ$ , m.p. (anhyd.)  $175$ — $177^\circ$  (decomp.), in addition to that previously isolated. The acids probably differ in the orientation of the OH group (cf. this vol., 69): they furnish the same tephrosinmonocarboxylic acid



(A., 1932, 950) and are both esterified (and dehydrated) by  $\text{MeOH-HCl}$  to the *Me* ester (I), m.p.  $220$ — $221^\circ$ ,

which is hydrolysed (10% EtOH-KOH) to the *tricarboxylic acid* (II), m.p. 178—179°. Tephrosic acid (A., 1932, 950) is probably 4:5-dimethoxy-2-2':4'-dihydroxyphenylacetylphenoxyacetic acid.

H. B.

**Grayanotoxin**, the poisonous constituent of the leaves of *Leucothoe grayana*, Max. I. M. YAMASHITA (Sci. Rep. Tôhoku, 1932, 21, 537—544).—The following facts, some of them contrary to the statements of Kubo (A., 1912, ii, 281), concerning the sternutatory substance, grayanotoxin, are reported: m.p. 233—238.5°,  $[\alpha]_D^{25} - 3.15^\circ$  in AcOH; it is  $C_{23}H_{40}O_7$  or  $C_{22}H_{36}O_7$ , gives a  $Ac_3$ , m.p. 211.5—212.5°, and a  $Bz_3$  derivative, m.p. 201—201.5°, contains an Ac group, but no CO,  $CO_2H$ , or phenolic OH group, and is saturated (Br,  $H_2$ -Pt black); it is not a glucoside or saponin. Its isolation is modified.

R. S. C.

**Rottlerin**. A. HOFFMANN and L. FARI (Arch. Pharm., 1933, 271, 97—101).—Analyses of hexaacetylröttlerin, m.p. 212°, *tetrahydroröttlerin*, m.p. 200—201°, from röttlerin ( $H_2$ , Pd-C), and *hexaacetyltetrahydroröttlerin*, m.p. 183—185°, indicate that röttlerin has the formula  $C_{31}H_{30}O_8$  and not the usually accepted  $C_{33}H_{30}O_9$  and that it contains two double linkings.

S. C.

**Menthone series. X. Complete optical resolution of *dl*-neomenthol by means of *l*-menthol.** J. READ and W. J. GRUBB. XI. **Diagnosis and characterisation of the stereoisomeric menthols.** J. READ, W. J. GRUBB, and D. MALCOLM (J.C.S., 1933, 167—170, 170—173).—X. By successive application to *dl*-neomenthol of *l*- and *d*-menthoxyacetyl chloride, *l*- and *d*-neomenthol,  $[\alpha]_D \mp 8.65^\circ$ , have been obtained, purified through *l*-neomenthyl *p*-nitrobenzoate, m.p. 95°,  $[\alpha]_D^{25} - 17.9^\circ$ , the pure *l*-neomenthol having  $[\alpha]_D^{25} - 8.82^\circ$ . *l*-Neomenthyl 3:5-dinitrobenzoate, m.p. 153°,  $[\alpha]_D^{25} - 23.9^\circ$ ; *d*-(I), m.p. 116° (decomp.),  $[\alpha]_D^{25} + 8.9^\circ$ , and *l*-camphor-10-sulphonate, m.p. 92° (decomp.),  $[\alpha]_D^{25} - 50.3^\circ$ , and *l*-, m.p. 64°,  $[\alpha]_D^{25} - 81.1^\circ$ , and *d*-menthoxyacetate, m.p. 28.5°,  $[\alpha]_D^{25} + 32.0^\circ$ , of *l*-neomenthol have been prepared. (Of these only (I) shows anomalous rotatory dispersion.) Separation of *dl*-neo- and *dl*-iso- from *dl*-menthol is described and the crystallographic examination of *dl*-neomenthol (*dl*-neomenthyl *p*-nitrobenzoate, m.p. 78.5°; 3:5-dinitrobenzoate, m.p. 130°; and  $\beta$ -naphthoate, m.p. 98°) is given.

XI. The m.p. and optical rotatory powers of the following *l*-menthyl, *l*-neomenthyl, and *d*-isomenthyl derivatives are summarised: *d*- and *l*-camphor-10-sulphonate, *d*- and *l*-menthoxyacetate, *p*-nitrobenzoate, 3:5-dinitrobenzoate, and  $\beta$ -naphthoate. The use of these esters in the diagnosis and separation of the stereoisomeric menthols is reviewed, and certain numerical relationships exhibited by their optical rotatory powers are discussed. A method is given for the purification of *dl*-isomenthol (*p*-nitrobenzoate, m.p. 64.5°, and 3:5-dinitrobenzoate, m.p. 130°), and pure *d*-isomenthol, m.p. 82.5°,  $[\alpha]_D^{25} + 25.9^\circ$  (*p*-nitrobenzoate, m.p. 54°,  $[\alpha]_D^{25} + 24.9^\circ$ ; *d*-, m.p. 30—31°,  $[\alpha]_D^{25} + 35.4^\circ$ , and *l*-camphor-10-sulphonate, m.p. 33—34°,  $[\alpha]_D^{25} - 20.7^\circ$ ), has been obtained from *l*-piperitone. *l*-Menthyl 1- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m.p. 96—

97°,  $[\alpha]_D^{25} - 109.2^\circ$ ; *dl*-menthyl *p*-nitrobenzoate, m.p. 91°, 3:5-dinitrobenzoate, m.p. 121°, and  $\beta$ -naphthoate, m.p. 70°, are described. F. R. S.

**Phenylcamphor and its derivatives. II. 4-*p*-Nitrophenylcamphor and 4-*p*-aminophenylcamphor.** S. NAMETKIN and A. KITSCHKIN (J. pr. Chem., 1933, [ii], 136, 137—142).—4-Phenylcamphor is converted by  $HNO_3$  (*d* 1.5) at  $-12^\circ$  to  $-6^\circ$  into the *p*- $NO_2$ -derivative, m.p. 150—151°, which is identified by oxidation by  $KMnO_4$  to *p*-nitrobenzoic acid with intermediate formation

of a dilactone, probably  $\begin{array}{c} O-C(C_6H_4 \cdot NO_2) \cdot O \\ | \quad \quad \quad | \\ CO-CMe \quad \quad \quad CO \end{array}$ , m.p.

155—157°. Reduction of the  $NO_2$ -compound gives 4-*p*-aminophenylcamphor, m.p. 144—144.5° (*Bz* derivative, m.p. 208—209°), a colourless base which forms red salts, and as an indicator gives the same end-point as phenolphthalein. Slow decomp. of the corresponding diazonium salt in presence of  $CuSO_4$  gives 4-*p*-hydroxyphenylcamphor, m.p. 122—124°.

H. A. P.

**Stability of the oxide linking in tetrahydrofuran derivatives.** R. PAUL (Compt. rend., 1932, 195, 1289—1291; cf. A., 1932, 166).—2-Tetrahydrofurfuryl alcohol (I) is converted by  $HBr$  at  $110^\circ$  into a mixture of  $\alpha$ -dibromopentane- $\beta$ -ol and  $\alpha\beta$ -tribromopentane (II) which is completely converted into (II) by  $PBr_5$ . Ring fission of (I) is effected by autoclaving with  $Ac_2O-ZnCl_2$  at  $200^\circ$ , affording  $\alpha\beta\epsilon$ -pentanetriol triacetate (55%). Treatment of the reaction product of tetrahydrofurfuryl bromide and  $Mg$  with  $H_2O$  gives tetrahydrofuran, b.p.  $80^\circ/761$  mm.,  $d_4^{25} 0.853$ ,  $n_D^{25} 1.40595$ . When the  $Mg$  compound is heated at  $110$ — $115^\circ$  ring fission between O and the *sec*-C atom occurs, and treatment with  $H_2O$  gives  $\Delta^8$ -pentenol, b.p.  $139^\circ/760$  mm., in 50% yield (*allophanate*, m.p. 148°). A. C.

**Preparation of furan from furoic acid.** H. GILMAN and M. B. LOUSINIAN (Rec. trav. chim., 1933, 52, 156—159).—Furoic acid heated with a little  $CuO$  or  $CuSO_4$  (anhyd. or  $+5H_2O$ ) in crude tar bases (b.p.  $>250^\circ$ ) at  $170$ — $220^\circ$  gives 85% of furan. H. B.

**Orientation in the furan nucleus. IV. Equivalence of the  $\alpha$ -positions and of the  $\beta$ -positions in furan.** H. GILMAN, R. R. BURTNER, and R. J. VANDERWAL (Rec. trav. chim., 1933, 52, 151—155).—The chloride, b.p.  $109$ — $112^\circ/4$  mm., m.p. 69—70°, from  $Et(2)H$  furan-2:5-dicarboxylate (I) is reduced ( $H_2$ , Pd- $BaSO_4$ , xylene) and then hydrolysed ( $6N-HCl$ ), thus giving 5-aldehydo-2-furoic acid, m.p.  $200^\circ$  (decomp.), decarboxylated (quinoline and  $Cu$ -bronze at  $210$ — $220^\circ$ ) to furfuraldehyde. Furoic acid prepared by oxidation of this is identical with that obtained by successive decarboxylation and hydrolysis of (I), thus showing the equivalence of the 2- and 5-positions. The chloride, b.p.  $149$ — $151^\circ/18$  mm., from  $EtH$  2:5-dimethylfuran-3:4-dicarboxylate (II) is similarly reduced to 3-aldehydo-2:5-dimethyl-4-furoic acid, m.p.  $176^\circ$ , which on successive decarboxylation and oxidation gives the same 2:5-dimethyl-3-furoic acid as is obtained by successive decarboxylation and hydrolysis of (II), thus showing the equivalence of the

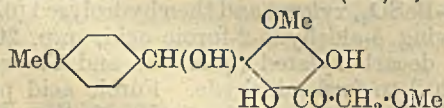
3- and 4-positions. Furan is considered to be a dynamic equilibrium mixture of several forms. H. B.

**Orientation in the furan nucleus.** H. GILMAN and R. R. BURTRER (J. Amer. Chem. Soc., 1933, 55, 859—860).—3-Methylfuran gives a 2-chloromercuri-derivative, m.p. 142°, and with fuming HNO<sub>3</sub> affords 2-nitro-3-methylfuran. H. B.

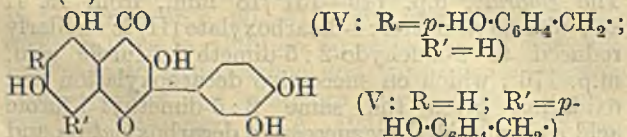
[Existence of isomeric 2:4-dinitrophenylhydrazones.] E. SIMON (Ber., 1933, 66, [B], 320).—In reply to Brederick (this vol., 154), it is pointed out that the existence of two forms of the 2:4-dinitrophenylhydrazones of furfuraldehyde and 2-methylfurfuraldehyde has been observed by the author (A., 1932, 763). H. W.

**Halogen-substitution products of furfuraldehyde.** H. SCHEBLER, J. JESCHKE, and W. BEISER (J. pr. Chem., 1933, [ii], 136, 232—240).—Furfurylidene diacetate (I) and Br in CHCl<sub>3</sub> give oily (?) open-chain compounds and a 10% yield of 5-bromofurfuraldehyde, m.p. 85°, b.p. 112°/16 mm. [oxime, m.p. 101°; semicarbazone, m.p. 215° (decomp.); phenylhydrazone, m.p. 80—85°], giving *s*-bromopyromucic acid by the Cannizzaro reaction. The prep. of tetraiodofuran is modified. The triacetomercuri-derivative of (I) with HCl, best in AcOH—EtOH, gives the trichloromercuri-derivative, and with I in Et<sub>2</sub>O 5-iodofurfuraldehyde, m.p. 110°, and (?) di-iodofurfuraldehyde, sinters from 130°. R. S. C.

**Constitution of fukugetin and garcinin.** M. MURAKAMI (Proc. Imp. Acad. Tokyo, 1932, 8, 500—502).—Fukugetin (I) and garcinin (II), both C<sub>22</sub>H<sub>16</sub>O<sub>8</sub>·2H<sub>2</sub>O, are obtained in 0.9 and 0.45% yield, respectively, from the bark of *Garcinia spicata* by extraction with MeOH, and therefore occur free and not as glucosides. (II) and (I) with Me<sub>2</sub>SO<sub>4</sub> give cryst. Me<sub>2</sub> ethers, decomp. 141—142° (lit. oils), +1 and 1.5H<sub>2</sub>O, respectively; both ethers contain three OH groups (Zerevitinov) and, when oxidised, give some anisic acid; with boiling KOH—EtOH they give veratric acid (20% yield), anisic acid (poor yield), and a phenol (III), C<sub>15</sub>H<sub>8</sub>O(OH)<sub>3</sub>(OMe)<sub>3</sub>, giving with Me<sub>2</sub>SO<sub>4</sub> a non-phenolic compound, C<sub>15</sub>H<sub>8</sub>O(OH)(OMe)<sub>5</sub>, m.p. 161—163°, which is oxidised by KMnO<sub>4</sub> to anisic acid. (III) must contain the nucleus of phloroglucinol [which, with proto-catechuic acid, is obtained from (I) and (II) by KOH-fusion], and the anisyl residue must be attached to the nucleus by a CH<sub>2</sub> group, since it is obtained as a secondary oxidation product on alkali-treatment; the last OH must be in a side-chain. (III) is, therefore,



Two flavonols, (IV) and (V), can be derived from the demethylation product of (III). These may be (I) and (II).



R. S. C.

**Carbohydrates and polysaccharides. XLIII.** Cyclic acetal and ketal formation from  $\alpha$ -phenylglycerol as further examples of the "ring partition principle." (MISS) M. E. PLATT and H. HIBBERT (Canad. J. Res., 1932, 7, 629—642).— $\alpha$ -Phenylglycerol (I) condenses with COMe<sub>2</sub> (II) to give the two possible 5-membered ring-compounds only, and with *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO (III) to give the 6-membered ring (two stereoisomeric forms) and a mixture of 5-membered ring-compounds. Cinnamyl alcohol with BzO<sub>2</sub>H in CHCl<sub>3</sub> at 0° gives (I), b.p. 184—186°/5 mm., m.p. 98—99° (lit. an oil), and with MeI and Ag<sub>2</sub>O in Et<sub>2</sub>O affords cinnamyl Me ether, b.p. 94—96°/8 mm., oxidised by KMnO<sub>4</sub> in aq. COMe<sub>2</sub> to  $\alpha$ -phenylglycerol  $\gamma$ -Me ether (IV), m.p. 54°, b.p. 159°/8 mm.  $\alpha$ -Phenylallyl alcohol with MeI and Ag<sub>2</sub>O in Et<sub>2</sub>O gives the Me ether, b.p. 77.5—78.5°/14—15 mm., oxidised by KMnO<sub>4</sub> to  $\alpha$ -phenylglycerol  $\alpha$ -Me ether (V), m.p. 68°. (I), (II), and anhyd. CuSO<sub>4</sub> at 60° give a mixture of isopropylidene derivatives, separable into fractions (a), b.p. 151—154°/11 mm., and (b), b.p. 154—157°/11 mm. Fraction (a), when methylated, gives a nearly pure ether, b.p. 115—117°/5—6 mm., which is hydrolysed to (V) by MeOH containing a drop of conc. HCl. Fraction (b) yields similarly an impure ether, b.p. 111—114°/5—6 mm., yielding some (IV) when hydrolysed. (V) and (II) in presence of anhyd. CuSO<sub>4</sub> give  $\beta\gamma$ -isopropylidene- $\alpha$ -phenylglycerol  $\alpha$ -Me ether, b.p. 117—120°/7 mm., proved to be homogeneous by reconversion into pure (V) by hydrolysis. (IV) gives similarly  $\alpha\beta$ -isopropylidene- $\alpha$ -phenylglycerol  $\gamma$ -Me ether, b.p. 115—117°/7—8 mm., hydrolysed to pure (IV). (V) and (III) in presence of a drop of 40% H<sub>2</sub>SO<sub>4</sub> give two stereoisomeric forms of  $\beta\gamma$ -*p*-nitrobenzylidene- $\alpha$ -phenylglycerol  $\alpha$ -Me ether, m.p. 79—80° and 57—58°, respectively. (IV) gives similarly  $\alpha\beta$ -*p*-nitrobenzylidene- $\alpha$ -phenylglycerol  $\gamma$ -Me ether, an oil (cannot be distilled). (I) and (III) give a cryst. and an oily compound; the former, m.p. about 120—122° (*Bz* derivative, m.p. 141—143°), is a mixture of stereoisomeric  $\alpha\gamma$ -*p*-nitrobenzylidene- $\alpha$ -phenylglycerols (VI), since it yields, when methylated, a mixture, m.p. 90—97°, of  $\beta$ -Me ethers (separable into forms, m.p. 96° and 113—115°, respectively), which is rather slowly hydrolysed by EtOH—HCl to  $\alpha$ -phenylglycerol  $\beta$ -Me ether, b.p. 153—156°/5—6 mm., m.p. 44°. The last-named ether with (III) gives a mixture of *p*-nitrobenzylidene derivatives, m.p. 91—97°. The oily portion of (VI) gives an oily mixture of Me ethers which, when hydrolysed, gives a small amount of (IV); it yields oily acyl derivatives and with CPh<sub>3</sub>Cl in dry C<sub>5</sub>H<sub>5</sub>N an oil, which gives an oil when methylated. R. S. C.

**Cyclic and polymeric compounds from reactions of ethylene mercaptan with polymethylene halides.** N. B. TUCKER and E. E. REID (J. Amer. Chem. Soc., 1933, 55, 775—781).—CH<sub>2</sub>Cl<sub>2</sub> (1 mol.) and (·CH<sub>2</sub>·SH)<sub>2</sub> (I) (1 mol.) in EtOH—NaOEt give 26% of 1:3-dithiolan, m.p. —51°, and 0.2% of the cyclic tetrasulphide, (CH<sub>2</sub>)<sub>2</sub> < S·(CH<sub>2</sub>)<sub>n</sub>·S > (CH<sub>2</sub>)<sub>2</sub> (II, n=1), m.p. 121°. (I) and *s*-C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> similarly give 46% of 1:4-dithian (III), whilst trimethylene

dibromide affords the cyclic *disulphide*,  $\begin{matrix} \text{CH}_2\cdot\text{S} \\ \text{CH}_2\cdot\text{S} \end{matrix} > (\text{CH}_2)_n$  (IV,  $n=3$ ), m.p. 47°, and 1% of the *tetrasulphide* (II,  $n=3$ ), m.p. 122°. Tetra- and penta-methylene dibromides give traces of the *tetrasulphides* (II,  $n=4$  and 5, respectively), m.p. 73° and 89°, respectively, whilst hexamethylene dibromide affords a trace of the *disulphide* (IV,  $n=6$ ), m.p. 65°. In all the above experiments large amounts of polymeric material (mixtures which are partly separable by extraction with various solvents) of the probable composition  $[(\text{CH}_2)_2\cdot\text{S}\cdot(\text{CH}_2)_n\cdot\text{S}]_x$  are produced. The polymeric material formed during the prep. of (I) is separated into fractions, m.p. 30—40° to 118—121°, some of which contain  $\cdot\text{S}\cdot\text{S}\cdot$  groupings. All the polymerides give (III) when heated with  $s\text{-C}_2\text{H}_4\text{Br}_2$ ; (III) is also produced from most of the polymerides by heating in a current of dry HCl and from  $(\text{CH}_2)_2\text{S}(\text{Bu})_2$  and  $s\text{-C}_2\text{H}_4\text{Br}_2$ . H. B.

**Theory of the ease of ring formation of cyclic imines.** H. FREUNDLICH and G. SALOMON (Ber., 1933, 66, [B], 355—357).—Ruzicka's theory of the ease of formation of C rings (A., 1926, 727) is directly applicable to the production of cyclic imines from halogenoalkylamines (Freundlich and Kroepelin, A., 1926, 1010). Ph, attached to the same C atom as halogen, enormously enhances the ease of ring formation. H. W.

**Action of ultra-violet light on pyridine. II. Reactions of photopyridine with naphthylamine- and aminonaphthol-sulphonic acids and with alkalis.** H. FREYTAG (J. pr. Chem., 1933, [ii], 136, 193—201; cf. A., 1932, 1149).—Photopyridine on filter-paper gives with acid solutions of naphthylamine- and aminonaphthol-sulphonic acids in concn. > 1:10,000 immediate colorations, which have a brown ground colour with  $\alpha$ - and a red with  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$  derivatives. The colours are weakened by alkali, but can usually be restored by acids. The compounds formed show characteristic fluorescence in filtered ultra-violet light. Alcoholic solutions of the acids give colorations only as the EtOH evaporates. Alkali prevents formation of the colour.  $\beta$ -Naphthylamine-7-sulphonic acid does not give a colour under any conditions. Photopyridine gives with NaOH, KOH, or  $\text{Ca}(\text{OH})_2$ , but not with  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{HPO}_4$ , aq.  $\text{NH}_3$ , or Na borate, a transient purple colour, removed by acid, and fluorescing purplish-violet in ultra-violet light. R. S. C.

**Photochemical oxidation of  $\alpha$ -picoline.** H. JOHN and G. BEHMEL (Ber., 1933, 66, [B], 426—427).—Irradiation of a solution of  $\alpha$ -picoline in  $\text{C}_6\text{H}_6$  in presence of anthraquinone (I) yields 5.3% of picolinic acid and about 10% of dark resin, sol. in  $N\text{-NaOH}$ , sparingly sol. in  $2N\text{-HCl}$ , which does not give a ppt. with picric acid in EtOH. 97.5% of (I) is recovered. H. W.

**N-Alkylated 1:5-aminoketones and their conversion into piperidine derivatives.** C. MANNICH and K. T. LESSE (Arch. Pharm., 1933, 271, 92—97).— $\beta$ -Dimethylamino- $\alpha\alpha$ -dimethylpropaldehyde (I) (cf. A., 1932, 503) and  $\text{COMe}_2$  condense in presence of NaOEt giving  $\alpha$ -dimethylamino- $\beta\beta$ -dimethyl- $\Delta^7$ -hexen- $\epsilon$ -one, b.p. 100—105°/11 mm. [hydrochloride, m.p.

147°; *methiodide*, m.p. 172°; *oxime*, m.p. 69°; *oxime hydrochloride*, m.p. 177° (decomp.); *semicarbazone*, m.p. 134°; *semicarbazone hydrochloride*, m.p. 165°], hydrogenated (Pd-C) to  $\alpha$ -dimethylamino- $\beta\beta$ -dimethylhexan- $\epsilon$ -one, b.p. 92°/13 mm. [hydrochloride (II), m.p. 100—101°; *chloroaurate*, m.p. 118.5°; *methiodide*, m.p. 133°; *oxime*, m.p. 58.5° (*hydrochloride*); *semicarbazone*, m.p. 128° (*hydrochloride*, m.p. 163°)].  $\alpha$ -Dimethylamino- $\beta\beta$ -dimethylhexan- $\epsilon$ -ol, b.p. 98°/12 mm. (*chloroaurate*, m.p. 116°; *p-nitrobenzoate hydrochloride*, m.p. 162°), is obtained by reducing (II) with Na-Hg in AcOH, and when treated with  $\text{SOCl}_2$  affords 1:1:2:5:5-pentamethylpiperidinium chloride, m.p. 260° (*picrate*, m.p. 201°), which when heated decomposes into MeCl and 1:2:5:5-tetramethylpiperidine, b.p. 147—148° (*hydrochloride*, m.p. 221°). The following were prepared from (I) and CPhMe:  $\alpha$ -dimethylamino- $\epsilon$ -phenyl- $\beta\beta$ -dimethyl- $\Delta^7$ -penten- $\epsilon$ -one, b.p. 159—161°/0.8 mm. [*hydrochloride*, m.p. 162—163°; *oxime hydrochloride*, m.p. 178° (decomp.); *semicarbazone hydrochloride*, m.p. 195°], with a compound,  $\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}$ , m.p. 102—103°, from (I) with 2 mols. CPhMe;  $\alpha$ -dimethylamino- $\epsilon$ -phenyl- $\beta\beta$ -dimethylpentan- $\epsilon$ -one, b.p. 165—170°/10 mm. [*hydrochloride*, m.p. 149—150°; *semicarbazone hydrochloride*, m.p. 176° (decomp.)];  $\alpha$ -dimethylamino- $\epsilon$ -phenyl- $\beta\beta$ -dimethylpentan- $\epsilon$ -ol, m.p. 41°, b.p. 168—170°/15 mm. (*benzoate hydrochloride*, m.p. 91—92°);  $\epsilon$ -chloro- $\alpha$ -dimethylamino- $\epsilon$ -phenyl- $\beta\beta$ -dimethylpentane hydrochloride, m.p. 150°; 2-phenyl-1:1:5:5-tetramethylpiperidinium chloride, m.p. above 250° (*chloroaurate*, m.p. 118°); 2-phenyl-1:5:5-trimethylpiperidine, b.p. 145—147°/12 mm. [*hydrochloride*, m.p. 148° (decomp.)].  $\alpha$ -N-Piperidino- $\beta\beta$ -dimethyl- $\Delta^7$ -hexen- $\epsilon$ -one, b.p. 140—142°/12 mm. (*nitrate*, m.p. 105°), is obtained in a similar manner from  $\beta$ -piperidino- $\alpha\alpha$ -dimethylpropaldehyde and  $\text{COMe}_2$ . S. C.

**Piperidine derivatives. XII. Local anæsthetics derived from reduction products of 3-acetylpyridine.** F. M. STRONG and S. M. MOELVAIN (J. Amer. Chem. Soc., 1933, 55, 816—822).—Et nicotinoacetate (*hydrochloride*, m.p. 156—157.5°), from Et nicotinate, EtOAc, and NaOEt, is hydrolysed (10% HCl) to 3-acetylpyridine, b.p. 90—92°/5 mm., m.p. 13—14° (*hydrochloride*, m.p. 176—177.5°), which is reduced ( $\text{H}_2$ , PtO<sub>2</sub>, H<sub>2</sub>O) to 3- $\alpha$ -hydroxyethylpyridine (I), b.p. 123—125°/5 mm. [*hydrochloride*, m.p. 92—93°; *benzoate hydrochloride*, m.p. 175—176°; *p-nitrobenzoate hydrochloride*, m.p. 199—200°, reduced (Fe, dil. HCl) to the *p-aminobenzoate*, b.p. 227—230°/4 mm., m.p. 100—101°]. Reduction ( $\text{H}_2$ , PtO<sub>2</sub>, dil. HCl) of (I) affords 3-ethylpiperidine (II) and two diastereoisomeric 3- $\alpha$ -hydroxyethylpiperidines, m.p. 58—61° and 103—104° (III) (*hydrochloride*, m.p. 152—153°). Successive treatment of (III) with the appropriate aralkyl or alkyl halide (in dioxan) and BzCl gives 1-benzyl-, m.p. 199—200°, 1- $\beta$ -phenylethyl-, m.p. 196—198°, 1- $\gamma$ -phenylpropyl-, m.p. 158—159°, 1- $\epsilon$ -phenylamyl-, m.p. 141—142°, and 1-n-hexyl-, m.p. 142—144°, - $\alpha$ -3-piperidylethyl benzoate hydrochlorides.  $\gamma$ -Chloropropyl benzoate and (II) give  $\gamma$ -3-ethylpiperidinopropyl benzoate hydrochloride, m.p. 164—165°. Pharmacological data for most of the above ester hydrochlorides are given. H. B.

Condensation of piperidinoacetonitrile with resorcinol and phloroglucinol. M. YAMASHITA (Sci. Rep. Tôhoku, 1932, 21, 545—548).—Piperidinoacetonitrile with  $ZnCl_2$ , HCl, and resorcinol or phloroglucinol in AcOH gives the hydrochlorides, decomp. 243—245° and 244—245°, respectively, of piperidino-methyl 2:4-dihydroxy- and 2:4:6-trihydroxy-phenyl ketone. The free bases or their picrates could not be obtained. R. S. C.

Indole group. I. Synthesis of 3-phenyloxindole. M. BAKUNIN and D. PECCERILLO (Gazzetta, 1933, 63, 3—8).— $\alpha$ -Phenyl-*o*-nitrocinnamic acid when boiled for 12 hr. with a conc. solution of 10 times its wt. of  $Ba(OH)_2$  gives 3-phenyldioxindole (A., 1912, i, 50), which with gaseous HCl gives a substance  $C_{14}H_{10}O_2NEt$ , m.p. 166°. The mechanism of the reaction is discussed. E. E. J. M.

Constitution of bisdiethylanilineisatin and of the green colouring matter obtained by oxidation. C. CANDEA (Gazzetta, 1933, 63, 75—80).—Condensation of isatin with  $NPhEt_2$  in presence of  $ZnCl_2$  gives bisdiethylanilineisatin [(4-diethyl-3:3-bis-aminophenyl)oxindole],  $(NH \langle \begin{smallmatrix} C_6H_4 \\ CO \end{smallmatrix} \rangle C(C_6H_4 \cdot NEt_2)_2)_2$ , which is colourless and gives on oxidation with  $PbO_2$  a green colouring matter, probably  $NH_2 \cdot C_6H_4 \cdot C(C_6H_4 \cdot NEt_2)_2OH$  (A., 1886, 154).

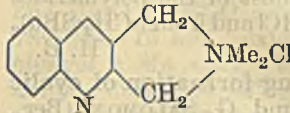
E. E. J. M.

Synthesis of 8-ethoxyquinoline-5-sulphonic acid. N. N. ORLOV and G. M. BOGDANOV (J. Appl. Chem., Russia, 1932, 5, 803—808).—Quinoline-8-sulphonic acid, obtained (yield 90%) from  $C_9H_7N$  and fuming (18%)  $H_2SO_4$  at 180°, is treated with solid NaOH, and 8-hydroxyquinoline (yield 64%) distilled in steam. On esterification with EtBr it yields 8-ethoxyquinoline, b.p. 220° (yield 68%), which is sulphonated with fuming  $H_2SO_4$ , the mixture being cooled. CH. ABS.

Quinoline derivatives. XLI. Derivatives of  $\beta$ -2-phenyl-4-quinolylaminoacetic acid. H. JOHN and G. BEHMEL (J. pr. Chem., 1933, [ii], 136, 121—124; cf. this vol., 165).—The acid chloride hydrochloride (impure), m.p. 272°, diethylamide, m.p. 149°,  $\beta$ -hydroxyethylamide, m.p. 210°, and  $\beta$ -chloroethyl ester, m.p. 104°, are prepared. H. B.

Synthesis of quinoline derivatives with basic side-chains. C. MANNICH and B. REICHERT (Arch. Pharm., 1933, 271, 116—127).—Me  $\beta$ -dimethylaminoethyl ketone, PhCHO, and NaOEt give  $\alpha$ -dimethylamino- $\epsilon$ -phenyl- $\Delta^5$ -penten- $\gamma$ -one (hydrochloride, m.p. 158°), also obtained from  $NHMe_2$ , paraformaldehyde, and benzylideneacetone, but in presence of HBr,  $\alpha$ -dimethylamino- $\beta$ -benzylidenebutan- $\gamma$ -one (hydrochloride, m.p. 148°) is obtained, whereas *o*- $NO_2 \cdot C_6H_4 \cdot CHO$  with either catalyst furnishes  $\alpha$ -dimethylamino- $\beta$ -(*o*-nitrobenzylidene)butan- $\gamma$ -one (I), m.p. 134° (decomp.) [hydrochloride, m.p. 158°,  $+H_2O$ , m.p. 122.5°; phenylhydrazone hydrochloride,  $+H_2O$ , m.p. 217° (decomp.); semicarbazone, m.p. 165° (decomp.)]. The latter is reduced by  $SnCl_2$  to 2-methyl-3-dimethylaminomethylquinoline, m.p. 56° [dihydrobromide, m.p. 250° (decomp.)], the methiodide, m.p. 233° (decomp.), of which is reduced to  $NMe_3$  and

2:3-dimethylquinoline with Na-Hg, whilst hydrogenation (Pd-C) produces the isoxime of  $\alpha$ -dimethylamino- $\beta$ -(*o*-hydroxylaminobenzylidene)butan- $\gamma$ -one, m.p. 102.5°,  $+3H_2O$ , m.p. 69° [hydrochloride, m.p. 214°; methiodide, m.p. 223° (decomp.)], which is extraordinarily resistant to acids or alkalis, but is converted by acylating agents into esters of 2-hydroxy-methyl-3-dimethylaminomethylquinoline, m.p. 73° [hydrochloride (II), m.p. 219° (decomp.); methiodide m.p. 202° (decomp.); *O*-benzoate *N*-hydrochloride, m.p. 188°; *O*-acetate *N*-hydrochloride, m.p. 191°]. 2-Chloromethyl-3-dimethylaminomethylquinoline dihydrochloride, m.p. 197° (decomp.), obtained from (II) and  $SOCl_2$ , immediately undergoes intramol. alkylation on treatment with dil. KOH with the formation of the chloride of the tricyclic base (annexed formula), m.p. 126°. 2-Dimethylaminomethyl-6-(*o*-nitrobenzylidene)cyclohexanone hydrobromide, m.p. 182°, is reduced by  $SnCl_2$  to 1:2:3:4-tetrahydro-4-methyleneacridine, m.p. 167° (hydrochloride, m.p. 230°), from which 4-methylacridine is obtained by distillation with Zn. The above compounds have no particular pharmacological action. S. C.



Preparation of anti-malarials. J. N. RAY, G. S. AHLUWALIA, and B. D. KOCHHAR (J. pr. Chem., 1933, [ii], 136, 117—119).—1-Hydroxy- $\beta$ -naphthyl *o*-nitrostyryl ketone, m.p. 218°, from 2-acetyl- $\alpha$ -naphthol, *o*- $NO_2 \cdot C_6H_4 \cdot CHO$ , and EtOH-NaOH, is reduced ( $SnCl_2$ -conc. HCl in EtOH-EtOAc) to 2-1'-hydroxy- $\beta$ -naphthylquinoline, m.p. 150°. The following are similarly prepared: 1-hydroxy- $\beta$ -naphthyl 2-nitro-4:5-methylenedioxy-styryl, m.p. 205°, and 2-nitro-4:5-dimethoxystyryl, m.p. 245°, ketones; 1-methoxy- $\beta$ -naphthyl *o*-nitrostyryl, m.p. 127°, and 2-nitro-4:5-dimethoxystyryl, m.p. 202°, ketones; 2-1'-methoxy-, m.p. 105°, 6:7-methylenedioxy-2-1'-hydroxy-, m.p. 235°, and 6:7-dimethoxy-2-1'-methoxy-, m.p. 170°, - $\beta$ -naphthylquinolines. H. B.

Occurrence of phenanthridine in coal tar. J. SIELISCH and R. SANDKE (Ber., 1933, 66, [B], 433—434).—The presence of phenanthridine (I) in the mixture of bases from anthracene oil is established. The amended data are recorded: (I) m.p. 106°, b.p. 349°/760 mm. ( $HgCl_2$  compound, m.p. 195—207° after softening at 190°; methiodide, m.p. 204.5°). H. W.

Activation of complex salts in aqueous solution. III. P. PFEIFFER and Y. NAKATSUKA (Ber., 1933, 66, [B], 415—418; cf. A., 1932, 578).—The following salts have been prepared:  $[Ni \text{ phen}_3]Br_2 \cdot 7H_2O$ ;  $[Ni \text{ phen}_3](NO_3)_2 \cdot 9H_2O$ ;  $[Ni \text{ phen}_3]SO_4 \cdot 9H_2O$ ;  $[Ni \text{ phen}_3](O \cdot SO_2 \cdot C_{10}H_{15}O)_2 \cdot 7H_2O$  (phen=phenanthroline). In  $H_2O$  they are activated in the opposite sense by  $NH_4$  camphorsulphonate and  $NH_4$   $\alpha$ -bromo- $\pi$ -camphorsulphonate, respectively. *l*-Nicotine also causes activation. Attempts to separate an optically active  $[Ni \text{ phen}_3]$  salt from the solution by KBr, HBr, or  $NaNO_3$  were fruitless. With tridipyridyl compounds the optical effect is < with phenanthroline salts. Activation of Co and Mn phenanthroline salts is recorded. H. W.

**Mechanism of the condensation between amines, formaldehyde, and ketones.** K. BODENDORF and G. KORALEWSKI (Arch. Pharm., 1933, 271, 101—116).—A study of the reactions between  $\text{NHMe}_2$  or piperidine with  $\text{CH}_2\text{O}$  and a series of ketones shows that neither dimethylaminomethyl alcohol (*picrate*, m.p. 91°; *hydrochloride*) nor piperidinomethyl alcohol (*hydrochloride*, m.p. 105—110°) is an intermediate product in the prep. of  $\gamma$ -ketotrialkylamines.  $\gamma$ -Ketobutanol and 2-hydroxymethylcyclohexanone react immediately with *sec.* amines, but not with amine salts, to form the corresponding ketoamines, whereas 1-phenyl-2:3-dimethyl-4-hydroxymethyl-5-pyrazolone, m.p. 159—160° (*Bz* derivative, m.p. 126°), and  $\gamma$ -phenyl- $\beta$ -propen- $\alpha$ -ol (I) fail to react, although 1-phenyl-2:3-dimethyl-5-pyrazolone reacts normally with  $\text{CH}_2\text{O}$  and  $\text{NHMe}_2$ . The latter reacts with Ph vinyl ketone giving  $\omega$ -dimethylamino-propiofenone, whilst (I) reacts abnormally with piperidine forming a *substance*, m.p. 74° (*picrate*, m.p. 178—179°), and not the expected  $\omega$ -piperidino- $\alpha$ -phenylallylene. Benzoylacetone and Et acetoacetate react with  $\text{CH}_2\text{O}$  and  $\text{NHMe}_2$  to give the corresponding bismethylene derivatives. The mechanism of the condensation is explained by assuming the formation of a loose 4-membered, semi-acetal ring complex between  $\text{CH}_2\text{O}$  and the enol modification of the ketone, which then reacts with the *sec.* amine, the ring opening in the process. S. C.

**Molecular compound from pyrimidone and diallylbarbituric acid.** P. PFEIFFER and E. OCHIAI (J. pr. Chem., 1933, [iii], 136, 129—132).—The compound  $\text{C}_{13}\text{H}_{17}\text{ON}_3\cdot\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$ , m.p. 131° (softens at 92.5°), is prepared by interaction of pyrimidone with diallylbarbituric acid in  $\text{COMe}_2$ . By the thermal method of Rheinboldt (cf. A., 1926, i, 25) it is shown to be a definite compound, but to be decomposed on fusion with separation of one of its constituents.

H. A. P.

**Crystalline organic thio-salts of As, Mo, Sn, Te, W, and Ge.** L. DEBUQUET and L. VELLUZ (Bull. Soc. chim., 1932, [iv], 51, 1565—1571).—The following compounds have been prepared by the prolonged action of  $\text{H}_2\text{S}$  on the solution obtained by boiling the metal oxide with piperidine or piperazine hydrate:  $\text{MoS}_3\cdot\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$ ,  $\text{MoS}_3\cdot 2\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$ ,  $2\text{WS}_3\cdot 2\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$ ,  $\text{WS}_3\cdot 2\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$ ,  $\text{As}_2\text{S}_3\cdot\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$ ,  $\text{As}_2\text{S}_5\cdot 3\text{C}_4\text{H}_{10}\text{N}_2\cdot 3\text{H}_2\text{S}$ ,  $\text{As}_2\text{S}_3\cdot 2\text{C}_4\text{H}_{11}\text{N}\cdot\text{H}_2\text{S}$ ,  $\text{SnS}_2\cdot\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$ ,  $\text{TeS}_2\cdot\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$ ,  $\text{GeS}_2\cdot\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{S}$ .

E. S. H.

**Stereoisomeric 2:3:4:6-tetramethylpiperazines.** IV. F. B. KIPPING (J.C.S., 1933, 143—144).—It is suggested that  $\gamma$ -2:3:5:6-tetramethylpiperazine has the constitution previously assigned (cf. A., 1931, 851; 1932, 754), since it has not been resolved;  $\alpha$ -2:3:5:6-tetramethylpiperazine has also resisted resolution. The following have been prepared: *d*-camphor-10-sulphonate, m.p. 248—251°, 258—260°,  $[\alpha]_{5461} +14.9^\circ$ , and *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m.p. 256—257°,  $[\alpha]_{5461} +62.5^\circ$ , of  $\gamma$ -2:3:5:6-tetramethylpiperazine; *di*-*d*-camphor-10-sulphonate, m.p. 261°,  $[\alpha]_{5461} +20.0^\circ$ , and *d*-tartrate, m.p. 164—165°,  $[\alpha]_{5461} +20.3^\circ$ , of  $\gamma$ -2:3:4:5:6-

pentamethylpiperazine;  $\gamma$ -2:3:4:5:6-pentamethylpiperazine-*d*-methylenecamphor, m.p. 123°,  $[\alpha]_{5461} +509^\circ$  (which gives with Br the *dihydrobromide*, m.p. 268—270°, of the base), and its *d*-camphor-10-sulphonate, m.p. 263—264°,  $[\alpha]_{5461} +266^\circ$  and *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m.p. 257°,  $[\alpha]_{5461} +278^\circ$ ; *d*-camphor-10-sulphonate, m.p. 213—215° (decomp.)  $[\alpha]_{5461} +15.2^\circ$ , and *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m.p. 207°  $[\alpha]_{5461} +68.5^\circ$ , of 1-nitroso- $\gamma$ -2:3:4:5:6-pentamethylpiperazine; *d*-camphor-10-sulphonate, m.p. 208—211°,  $[\alpha]_{5461} +28.4^\circ$ , *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m.p. 204—205°,  $[\alpha]_{5461} +63.6^\circ$ , *d*- $\alpha$ -chlorocamphor- $\pi$ -sulphonate, m.p. 215—216°,  $[\alpha]_{5461} +49.5^\circ$ , and *d*-tartrate, m.p. 174—175°,  $[\alpha]_{5461} +9.7^\circ$ , of *p*-toluenesulphonyl- $\gamma$ -2:3:4:5:6-pentamethylpiperazine; *mono*-, m.p. 113—114°,  $[\alpha]_{5461} +17.4^\circ$ , and *di*-*d*-camphor-10-sulphonate, m.p. >320°,  $[\alpha]_{5461} +23.8^\circ$ , *mono*-, m.p. 230—231°,  $[\alpha]_{5461} +73.0^\circ$ , and *di*-*d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m.p. >320°,  $[\alpha]_{5461} +89.7^\circ$ , of  $\alpha$ -2:3:5:6-tetramethylpiperazine; and  $\alpha$ -2:3:5:6-tetramethylpiperazine-*di*-*d*-methylenecamphor, m.p. 320°,  $[\alpha]_{5461} +822^\circ$ .

F. R. S.

**Action of bromine on 2-nitrofluorene.** L. GUGLIAMELLI and M. R. FRANCO (Anal. Farm. Biochim., 1932, 3, 1—23; Chem. Zentr., 1932, ii, 2820).—9-Bromo-2-nitrofluorene is accompanied, when the quantity of solvent (AcOH) is restricted, by 2-bromo-7-nitro- and (?) 5-bromo-2-nitro- (m.p. 100—110°) -fluorene. The mobility of the Br atom in 9-bromo-2-nitrofluorene was demonstrated by condensation with amines. 2-Nitro-9-piperidino-, m.p. 311°, and 9-phenylmethylamino-, m.p. 147°, -fluorene, and piperazine derivatives,  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}_3$ , m.p. 225—230°, and  $\text{C}_{30}\text{H}_{24}\text{O}_4\text{N}_4$ , m.p. 230°, are described.

A. A. E.

**Reaction of 2:4-dichloroquinazoline with sodium azide.** R. STOLLÉ and F. HANUSCH (J. pr. Chem., 1933, [ii], 136, 120).—2-Chloro-4-ethoxyquinazoline and  $\text{NaN}_3$  in EtOH give 4-ethoxy-1:2-tetrazolo-1:2-dihydroquinazoline, m.p. 165°, hydrolysed by 2*N*-NaOH to the same OH-derivative as is obtained from azidotetrazolodihydroquinazoline (I) (this vol., 404) and NaOEt. (I) is, therefore, 4-azido-1:2-tetrazolo-1:2-dihydroquinazoline.

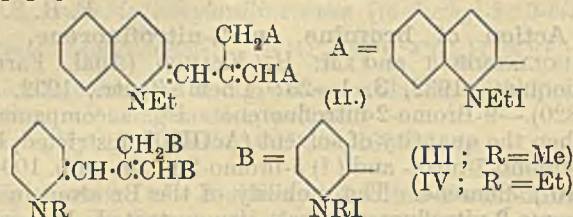
H. B.

**Constitution of bases obtained from protein.** IV. F. WREDE, E. BRUCH, and G. FEUERREGEL (Z. physiol. Chem., 1933, 214, 63—70; cf. A., 1932, 624).—Electrolytic reduction in 20%  $\text{H}_2\text{SO}_4$  of prolyl-leucine anhydride gave 5-isobutyl-1':2'-pyrrolidino-1:2-piperazine,  $\text{NH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2 > \text{CH}_2$ , b.p. 110°/15 mm. (*chloraurate*, m.p. 197°), identical with the base  $\text{C}_{11}\text{H}_{23}\text{N}_2$  from protein. *dl*-Valine and bromoisohexoyl bromide give a mixture of racemic bromoisohexoylvalines, m.p. 185°, which in 25% aq.  $\text{NH}_3$  affords racemic leucylvaline (I), m.p. 272—274°. The Et ester hydrochloride of (I) with  $\text{NH}_3$  in MeOH gives leucylvaline anhydride (II), m.p. 277°. Electrolytic reduction of (II) yields 2-isopropyl-5-isobutylpiperazine (*chloraurate*, blackens at 245° without melting). Similarly, racemic bromoisovalerylphenylalanine, m.p. 147° (obtained from bromoisohexoylvaline and

phenylalanine), gives racemic *valylphenylalanine*, m.p. 235° (decomp.), which was converted into the *anhydride* (III), m.p. 247—248°. Reduction of (III) gave 2-benzyl-5-isopropylpiperazine [chloroaurate, sinters at about 230° (decomp.)]. By corresponding stages the Pr derivative was obtained: *bromovaleryl bromide*, b.p. 186° (decomp.), racemic *bromovalerylphenylalanine*, m.p. 116°, racemic *norvalylphenylalanine*, m.p. 241°, *anhydride*, m.p. 238°, 2-benzyl-5-propylpiperazine (chloroaurate, black mass at 240°).

J. H. B.

**Cyanine dyes. V. Lepidyl-, quinaldyl-, and picolyl-carbocyanines.** T. OGATA (Proc. Imp. Acad. Tokyo, 1932, 8, 503—506; cf. this vol., 285).—Lepidine ethiodide (0.002 mol.) and CH(OEt)<sub>3</sub> (I) (0.004 mol.) in AcOH or EtCO<sub>2</sub>H (0.3 c.c.) at 165° give a 67% yield of neocyanine ethiodide, the yield being poorer in other solvents and 0 in non-acidic solution. (I), quinaldine ethiodide, and succinic acid at 170° give similarly the *dye* (II), m.p. 244.5° (decomp.), in 4% yield. (I),  $\alpha$ -picoline methiodide, and anhyd. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at 175—178° give a 4% yield of the *dye* (III),



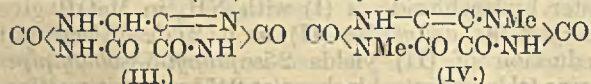
m.p. 244°, whilst  $\alpha$ -picoline ethiodide at 185° gives the *dye* (IV), m.p. 227°, in 23% yield. The dyes are photographic sensitizers, the sensitivity max. for (II) and (III) being 740 and 640 m $\mu$ , respectively.

R. S. C.

**Condensation of aldehydes with hydrazones.** A. GIACALONE (Gazzetta, 1933, 63, 20—22).—PhCHO condenses with 1 mol. of its *p*-tolylhydrazone in presence of ZnCl<sub>2</sub>, giving a compound C<sub>42</sub>H<sub>36</sub>N<sub>4</sub>, m.p. 245°, which does not react with Ac<sub>2</sub>O. Alternative formulæ are suggested.

E. E. J. M.

**Condensation of hydantoins with parabanic acids.** H. BILTZ, F. LACHMANN, and (in part) R. LEMBERG (J. pr. Chem., 1933, [ii], 136, 217—231).—Parabanic acid (I) and hydantoin (II) at 160° give 1:5-dehydro-5:5'-dihydantyl, m.p. 222° [Na (+4H<sub>2</sub>O)], m.p. about 140° (decomp.), K, and NH<sub>4</sub>, m.p. 240° (decomp.), salts, probably (III), since it is oxidised by HNO<sub>3</sub>, CrO<sub>3</sub>, or H<sub>2</sub>O<sub>2</sub>-AcOH to (I) (1 mol. only) and reduced by HI-PH<sub>4</sub>I to (II) (1 mol. only). CH<sub>2</sub>N<sub>2</sub> gives the 3:1':3'-Me<sub>2</sub> derivative, m.p. 175—176°, stable to acids, Ac<sub>2</sub>O, and Zeisel HI, slowly hydrolysed by alkali to NH<sub>3</sub> and NH<sub>2</sub>Me, and oxidised by HNO<sub>3</sub> to dimethylparabanic acid. (III) with boiling Ac<sub>2</sub>O gives the 2(?2'):1':3'-Ac<sub>2</sub> derivative, m.p. 95—96°, which with boiling EtOH gives the (?1)':3'-Ac<sub>2</sub> derivative, m.p. 152°, hydrolysed by EtOH-HCl to (III). 1-Methylhydantoin and 1-

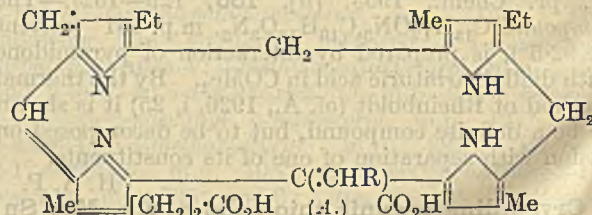


methylparabanic acid at 220° gives 1(?3):3'-dimethyl-5:5'-dihydantylidene (IV), m.p. 273° [Ac

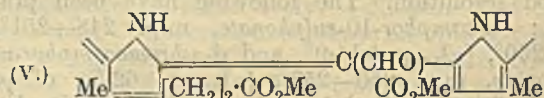
derivative (V), m.p. 213°, hydrolysed by EtOH-HCl; Et<sub>2</sub> derivative, m.p. 126—127°], giving with CH<sub>2</sub>N<sub>2</sub> 1:3:1':3'-tetramethyl-5:5'-dihydantylidene, m.p. 217—218° (OMe test negative), also obtained from (V) and CH<sub>2</sub>N<sub>2</sub>, oxidised by H<sub>2</sub>O<sub>2</sub> or Br-H<sub>2</sub>O to dimethylparabanic acid (2 mols.), and giving with Cl<sub>2</sub>-MeOH 5:5'-dimethoxy-1:3:1':3'-tetramethyl-5:5'-dihydantylidene, m.p. 182°. Other Me derivatives of (I) and (II) do not condense. The prep. of 3-methylhydantoin is modified. R. S. C.

**Chlorophyll. XXX. Pyrrohodin and derivatives.** H. FISCHER and P. PRATESI. XXXI. Chlorin e<sub>4</sub>, chloroporphyrin e<sub>5</sub>, and isophæoporphyrin a<sub>5</sub>. H. FISCHER, J. HECKMAIER, and E. PLÖTZ (Annalen, 1933, 500, 203—215, 215—252).—XXX. Pyrrohodin (A., 1928, 1383) (Fe and Cu salts; oxime) [now prepared by dehydration of pyrroporphyrin (I) with oleum] and Br in Et<sub>2</sub>O-AcOH give  $\beta$ -bromopyrrohodin, which with MeOH-KOH in C<sub>5</sub>H<sub>5</sub>N affords pyrroverdin. Bromopyrroporphyrin XV is dehydrated by oleum to bromopyrrohodin XV, decomp. >250° (Fe and Cu salts) (which reacts difficultly or not at all with NH<sub>2</sub>OH), and is converted by MeOH-KOH at 130—135° into (I). Acetylpyrroporphyrin (oxime) is similarly dehydrated (to the not isolated verdin) only with difficulty.

XXXI. Successive treatment of chlorin e (A, R=CO<sub>2</sub>H) with HI-AcOH in N<sub>2</sub> at 50° and NaOAc gives chloroporphyrin e<sub>6</sub> (II) and a little chloroporphyrin e<sub>5</sub> (III) [Cu salt; impure Ac derivative; (mono)Me ester (Bz derivative), esterified (Me<sub>2</sub>SO<sub>4</sub>) to (V) (below)]; (III) is probably formed from (II) by



oxidation with I. (II) heated in N<sub>2</sub> or treated with HCO<sub>2</sub>H gives chloroporphyrin e<sub>4</sub> (IV). Chlorin e, which is isomeric with (II), is decarboxylated by boiling with C<sub>5</sub>H<sub>5</sub>N to chlorin e<sub>4</sub> (A, R=H), m.p. 250°, decomp. 270—280° [Me<sub>2</sub> ester, m.p. 166° (crystallographic data by STEINMETZ)], which is isomeric with, and convertible (HI-AcOH) into, (IV). The Me<sub>2</sub> ester of (IV) is converted by I in AcOH into the above Me ester of (III), whilst (III) is reduced by HI-AcOH at 50° to (IV). These results suggest that (III) is  $\gamma$ -hydroxymethylrhodoporphyrin rather than  $\gamma$ -formylrhodoporphyrin (A., 1931, 744); the question is undecided but the latter formulation is favoured by spectroscopic data, analytical data, and the following results. (III) affords two different Me<sub>2</sub> esters when treated with CH<sub>2</sub>N<sub>2</sub> and MeOH-HCl, which can be formulated as (V) and (VI), respectively.



Thus, (V) (which may react in the oxymethylene form) is reduced (HI-AcOH) to rhodoporphyrin,



whilst (VI) similarly gives (IV). The *hæmin* (*Cu* salt) of (V) affords rhodoporphyrin when freed from *Fe* by  $\text{HBr}-\text{AcOH}$  [but gives (III) using conc.  $\text{H}_2\text{SO}_4$ ] and reacts with  $\text{NH}_2\text{OH}$  (shown spectroscopically), whilst the *hæmin* (*Cu* salt) of (VI) gives ( $\text{HBr}-\text{AcOH}$ ) (III) and does not react with  $\text{NH}_2\text{OH}$ . (V), unlike (VI), yields rhodoporphyrin *Me*<sub>2</sub> ester when heated to 270°.

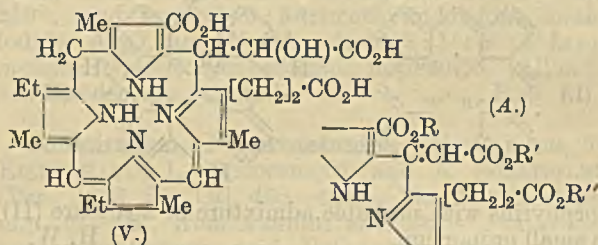
The constitution of phæoporphyrin *a*<sub>6</sub> (VII) is discussed (cf. A., 1931, 1431; 1932, 757). Reduction ( $\text{HI}-\text{AcOH}$  at 65°) of native phæophorbide gives (probably) the unstable isophæoporphyrin *a*<sub>5</sub> (VIII), which passes readily into phæoporphyrin *a*<sub>5</sub> (IX) and with  $\text{NH}_2\text{OH}$  affords the oxime of (IX); (VIII) cannot therefore be identical with the protophæoporphyrin *a*<sub>5</sub> of Stoll and Wiedemann (A., 1932, 1265). (IX) reacts with  $\text{NH}_2\text{OH}$  at a much faster rate than (VII). Benzoylation or addition of  $\text{HCN}$  to phæoporphyrin *a*<sub>6</sub> *Me* *Et* ester *Et* ether (X) could not be accomplished; the *Me*<sub>2</sub> ester *Et* ether and  $\text{MeOH}-\text{conc. HCl}$  give (probably) isophæoporphyrin *a*<sub>7</sub> (spectrum). The change undergone by several chlorophyll porphyrins on treatment with alkali can easily be confused with the phase test. Treatment of phæoporphyrin *a*<sub>5</sub> *Me*<sub>2</sub> ester in  $\text{C}_5\text{H}_5\text{N}$  with 30%  $\text{MeOH}-\text{KOH}$  causes the ester to pass into the alkali, giving a greenish-yellow solution (which gradually turns brownish-red), from which the unchanged ester can be recovered; (X), phæoporphyrin *a*<sub>5</sub> *Me* ester (XI), and phylloerythrin ester show a similar colour reaction. (XI) and benzoquinone in  $\text{EtOH}-\text{C}_5\text{H}_5\text{N}$  give phæoporphyrin *a*<sub>7</sub> as the main product. The following substances (all of which give a negative phase test) are allomerised by  $\text{EtOH}-\text{benzoquinone}$  in  $\text{N}_2$  [subsequent reduction ( $\text{HI}-\text{AcOH}$ ) gives small amounts of (VII) (cf. A., 1932, 756)]: methylchlorophyllide *a*, the phyllin from methylchlorophyllide *a*+*b*, phæophytin *a*+*b* and its phyllin, phæophorbide *a* and *a*+*b*, and the phyllins of native phæophorbide *a* and of methylphæophorbide *a*. Allomerisation of methylchlorophyllide *a*+*b* with  $\text{O}_2$  in  $\text{EtOH}$  gives (after reduction) phæoporphyrin *a*<sub>7</sub>, whilst reduction of the product formed by the action of  $\text{O}_2$  on allomerised ( $\text{EtOH}-\text{benzoquinone}$  in  $\text{N}_2$ ) ethylchlorophyllide affords (X). Methylchlorophyllide and  $\text{MeOH}-\text{benzoquinone}$  in absence of air give (after reduction) phæoporphyrin *a*<sub>6</sub> *Me*<sub>2</sub> ester *Me* ether, m.p. 259°. The *Cu* salt of phæoporphyrin *a*<sub>6</sub> *Me* *Et* ester *Me* ether has m.p. 192° (not sharp).

H. B.

**Chlorophyll series.** IX. Transformations establishing the nature of the nucleus. J. B. CONANT and C. F. BAILEY. X. Esters of chlorin *e*. J. B. CONANT and K. F. ARMSTRONG. XI. Position of the [carbo]methoxyl group. J. B. CONANT and E. M. DIETZ (J. Amer. Chem. Soc., 1933, 55, 795—800, 829—839, 839—849).—IX. Chlorin *f* is a dihydroporphyrin, since it is dehydrogenated by alkaline  $\text{K}_3\text{Fe}(\text{CN})_6$  or by  $\text{O}_2$  and 10%  $\text{NaOH}$  containing  $\text{MgO}$  and  $\text{ZnO}$  to isorhodoporphyrin (I),  $\text{C}_{32}\text{H}_{34}\text{O}_4\text{N}_4$  [*Me*<sub>2</sub> ester (II), m.p. (block) 264° (softens at 261°)], which is identical with the porphyrin previously obtained (A., 1931, 369) as a by-product

during the pyrolysis of phæopurpurin 7, and with the  $\psi$ -verdoporphyrin of Fischer *et al.* (A., 1931, 1431). It follows, therefore, that the nucleus of the phæophorbides and chlorophyll *a* is a dihydroporphyrin ring. Reduction of (I) with  $\text{HI}-\text{AcOH}$  and oxidation (air) of the resulting leuco-compound gives rhodoporphyrin, also formed [with pyrroporphyrin (III)] from (II), 25%  $\text{MeOH}-\text{KOH}$ ,  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{MgO}$ , and  $\text{ZnO}$  at 185—190°. (I) and boiling anthracene afford (III) and an unidentified porphyrin. Chlorin *e* is considered to be a dihydroisorhodoporphyrin with a lactic [glycollic?] acid residue on one of the bridge C atoms [see Part X], since it is oxidised by  $\text{K}_3\text{Mo}(\text{CN})_8$  to  $\text{CO}_2$  and chlorin *k* (IV) (cf. A., 1931, 1075). Reduction of (IV) with  $\text{HI}-\text{AcOH}$  and oxidation of the resulting leuco-compound gives chloroporphyrin *e*<sub>4</sub> and another porphyrin (or mixture). Rhodin *g* is oxidised [ $\text{K}_3\text{Mo}(\text{CN})_8$ ] to rhodin *n*,  $\text{C}_{33}\text{H}_{32}\text{O}_5\text{N}_4$ , which contains a CO group, since its (mono)*Me* ester, sinters at 140—150°, gives a semicarbazone.

X. The *Me*<sub>3</sub> esters prepared by esterification ( $\text{CH}_2\text{N}_2$ ;  $\text{Me}_2\text{SO}_4$ ;  $\text{MeOH}-\text{HCl}$ ) of chlorin *e* (V) are identical, since they give the same *Cu* salt, m.p. 218—220°; the *Zn* salts from the esters prepared as quoted have m.p. 237—238°, 243—245°, and 236—237°, respectively, but depression does not occur with any two. The *Cu* salt of chlorin *e* *Et*<sub>3</sub> ester has m.p. 154—155°. Hydrolysis of chlorin *e* *Me*<sub>3</sub> ester (VI) (*A*,  $\text{R}=\text{R}'=\text{R}''=\text{Me}$ ) with cold  $\text{MeOH}-\text{KOH}-\text{C}_5\text{H}_5\text{N}$  in  $\text{N}_2$  regenerates (V), whilst partial hydrolysis (similar conditions) gives chlorin *e*  $\alpha$ -*Me* ester (*A*,  $\text{R}=\text{R}''=\text{H}$ ,  $\text{R}'=\text{Me}$ ), which is esterified by  $\text{CH}_2\text{N}_2$  to (VI) and by diazoethane to the  $\alpha$ -*Me* *Et*<sub>2</sub> ester, m.p. 152° [*Cu* salt, m.p. (block) 166.5—167°], is converted by heating with  $\text{Ph}_2$  at 215° in  $\text{N}_2$  into (by loss of 1 mol. of



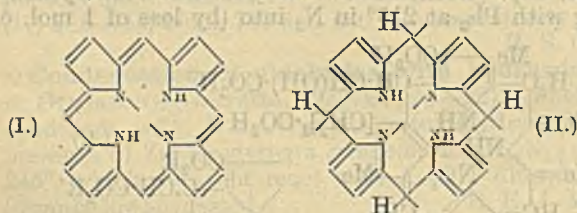
$\text{CO}_2$ ) the *Me* ester of pyrochlorin *e* carboxylic acid [*Me*<sub>2</sub> ester, m.p. (block) 206—208°], and when oxidised [ $\text{K}_3\text{Mo}(\text{CN})_8$ ] does not give  $\text{CO}_2$ , but affords a chlorin,  $\text{C}_{35}\text{H}_{36}\text{O}_6\text{N}_4$  (*Me* ester, m.p. 260—262°). Partial methylation ( $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ ) of (V) affords chlorin *e*  $\beta$ -*Me* ester (VII) (*A*,  $\text{R}=\text{Me}$ ,  $\text{R}'=\text{R}''=\text{H}$ ), which is esterified by  $\text{CH}_2\text{N}_2$  to (VI) and by diazoethane to the  $\beta$ -*Me* *Et*<sub>2</sub> ester, m.p. 155—157° (*Cu* salt, m.p. 187—189°). (VII) when heated with  $\text{Ph}_2$  at 245—265° in  $\text{N}_2$  gives chloroporphyrin *e*<sub>4</sub> *Me* ester and an unidentified porphyrin *Me* ester, whilst oxidation [ $\text{K}_3\text{Mo}(\text{CN})_8$ ] affords  $\text{CO}_2$  and a product which appears to form an insol. complex with the reagent. Hydrolysis of (VI) with cold 12%  $\text{HCl}$  yields chlorin *e* *Me*<sub>2</sub> ester (*A*,  $\text{R}=\text{R}'=\text{Me}$ ,  $\text{R}''=\text{H}$ ), sinters >230° (block), which is not oxidised by  $\text{K}_3\text{Mo}(\text{CN})_8$  and gives only a little  $\text{CO}_2$  when heated with  $\text{Ph}_2$ . The group  $>\text{C}\cdot\text{CH}\cdot\text{CO}_2\text{R}'$  in *A* is probably interconverted into  $>\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{R}'$  in solution.

XI. Pure methylphæophorbide *a* (VIII),  $\text{C}_{36}\text{H}_{38}\text{O}_5\text{N}_4$

(details of prep. given), does not give phæopurpurin 7 when oxidised [ $K_3Mo(CN)_8$ ]; that previously isolated (A., 1931, 1075) arises from an impurity in (VIII). Oxidative hydrolysis of (VIII) with  $O_3$  and dil. MeOH-KOH in cold aq.  $C_5H_5N$  gives chlorin g (mono)Me ester (IX),  $C_{35}H_{38}O_7N_4$ , which is stable in solution and converted by  $CH_2N_2$  and diazoethane into dimethyl- and diethyl-phæopurpurin 7 (X), respectively. Pyrolysis of (IX) in boiling  $Ph_2$  and  $N_2$  affords mainly isorhodoporphyrin, whilst (X) and  $C_5H_5N-Na_2CO_3$  give isorhodoporphyrin Et<sub>2</sub> ester, m.p. 240–241°. These results show that the  $CO_2Me$  group in (IX) is part of the bridge grouping, and thus confirm the position of the Me group in chlorophyll *a* assigned by Fischer *et al.* (A., 1931, 1432). Phæopurpurin 7 (prep. from various sources described) and boiling  $Ph_2$  give CO,  $CO_2$ , and chlorin *f* Me ester; it contains a  $CO_2Me$  group attached to a pyrrole ring, and its precursor appears to be a second form of chlorophyll *a* (designated  $a_2$ ; structure suggested). Chlorophyll *a* ( $a_1$ ) is best represented by the alternative formula previously suggested (A., 1931, 1075). Stoll and Wiedemann's formulæ (A., 1932, 1265) for chlorophylls *a* and *b* are unlikely; contrary to these authors, hydrolysis of phæoporphoride *a* gives chlorin *e* even in presence of a reducing agent. Contrary to Fischer *et al.* (*ibid.*, 1263), the conversion of phæopurpurin 7 into 18 has not been observed.

H. B.

**Constitution of the porphyrins.** E. CLAR and F. HAUROWITZ (Ber., 1933, 66, [B], 331–334).—The absorption spectra of tetramethylhæmatoporphyrin in MeOH and of mesoporphyrin in HCl-EtOH and  $NH_3$ -EtOH indicate the constitution (I) for the



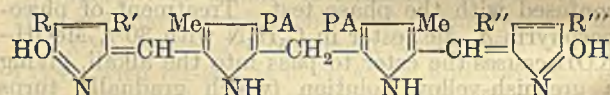
porphyrins with probable admixture of structure (II) in small proportion.

H. W.

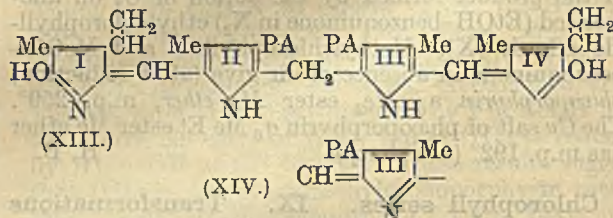
**Constitution of bile pigment. X. Constitution of bilirubin.** Syntheses of neo- and iso-neo-xanthobilirubic acid. W. SIEDEL and H. FISCHER (Z. physiol. Chem., 1933, 214, 145–172; cf. this vol., 76).—With Br in AcOH, 2-aldehydro-4-methyl-3-ethylpyrrole-5-carboxylic acid (I), decomp. 199° (obtained by hydrolysis of the Et ester), yields 5-bromo-2-aldehydro-4-methyl-3-ethylpyrrole (II), m.p. 115° (aldazine, m.p. 200°), and 5:5'-dibromo-4:4'-dimethyl-3:3'-diethylpyrromethene (III), m.p. 184° (Cu salt). (II) combines with opopyrrolecarboxylic acid in presence of HBr to form the hydrobromide (IV), not melted at 300°, of 5-bromo-4:3'-dimethyl-3-ethyl-4'-β-carboxyethylpyrromethene (picrate, m.p. 199°). Heated to 180° with NaOMe, (IV) gives xanthobilirubic acid, under reflux neo-xanthobilirubic acid Me ether (V), m.p. 160° (Me ester, m.p. 70°). Hydrogenation of (V) with HI-AcOH gives neobilirubic acid (VI), the benzylidene derivative (VII), m.p. 276°, of which showed no depression with the

analytical compound, m.p. 248°. With 10% NaOMe at 150°, neo-xanthobilirubic acid (VIII), m.p. 244–246°, was obtained directly. It showed no depression with the analytical compound, m.p. 227°. The suspicion that the analytical acid is a mixture was confirmed by a resorcinol fusion of the *s*-mesobilirubin of Fischer and Adler (A., 1931, 1420), which gave isoneoxanthobilirubic acid (IX), m.p. 242°, which when mixed with (VIII) gave the m.p. of the analytical acid. (IX) was converted into isoneobilirubic acid [benzylidene compound, m.p. 273°, gave no depression with the analytical product, but m.p. 246–247° with (VII)]. Neo-xanthobilirubic acid forms a Me ester, m.p. 174°, (IX) a Me ester (X), m.p. 205°. The analytical ester, m.p. 190–191°, recryst. from MeOH-EtOH gave a final product of m.p. 203°, identical with (X). Thus all products obtained from analytical neo-xanthobilirubic acid must be mixtures of three isomerides (two symmetrical and one unsymmetrical). Similarly, analytical "xanthobilirubic acid" contains two isomerides, xanthobilirubic acid, m.p. 287° (Me ester, m.p. 212°), and isoxanthobilirubic acid, m.p. 289° (Me ester, m.p. 189°).

The known mesobilirubins have the following constitution:



For mesobilirubin-XIIIα (XI)  $R=R''=Me$ ,  $R'=R'''=Et$ ; for -IIIα  $R'=R''=Me$ ,  $R=R'''=Et$ ; for -IXα  $R=R''=Me$ ,  $R'=R'''=Et$  ( $\alpha$  denotes ring opening at the  $\alpha$ -methine bridge); PA =  $\cdot CH_2 \cdot CH_2 \cdot CO_2H$ . (XI) is obtained by the various methods given and is identical with Fischer and Adler's product. Treatment of the Me ether of neo-xanthobilirubic acid with  $CH_2O$  and HCl gives the Me<sub>2</sub> ether hydrochloride of (XI), m.p. 295° [free base (XII), m.p. 193°, Me<sub>2</sub> ester of diether, m.p. 144°]. The Gmelin reaction of (XI) remains at the green phase, which is ascribed to the lack of a quinonoid form. Hydrolysis of (XII) with  $AlCl_3$  in cyclohexane affords (XI). Bilirubin (XIII) and uteroverdin (XIV) are formulated:



Ring closure to a furan ring by loss of  $H_2$  between the OH and vinyl groups of ring IV is not excluded.

J. H. B.

Reactions of 2:4-dichloroquinazoline and 2:3-dichloroquinoxaline with sodium azide. R. STOLLÉ and F. HANUSCH (J. pr. Chem., 1933, 136, 9–14).—Interaction of 4-chloro-1:2-dihydro-1:2-tetrazolophthalazine (A., 1932, 1266) with  $N_2H_4$  at 130° gives the 4-hydrazino-compound, m.p. 287° (CHPh. derivative, m.p. 300°), converted by  $HN_3$  into the 4-azido-compound (*loc. cit.*). With 2:4-

dichloroquinazoline  $\text{NaN}_3$  gives 4(or 1)-*azidodihydro*-1 : 2(or 3 : 4)-*tetrazoloquinazoline*, m.p. 145° (decomp.), which, when heated with  $\text{NaOEt}$  in  $\text{EtOH}$ , gives the 4( or 1)-*OH*-compound, m.p. 243° (decomp.). Similarly, from 2 : 3-dichloroquinoxaline, 3-*azido*-, m.p. 265° (decomp.), and 3-*hydroxy*-1 : 2-*dihydro*-1 : 2-*tetrazoloquinoxaline*, m.p. 288° (decomp.), are formed.  $\text{NN}'$ -Diphenyloximinochloride is converted by anhyd.  $\text{N}_2\text{H}_4$  in light petroleum into the *dihydrazide*,  $\text{NH}_2\cdot\text{NH}\cdot\text{C}(\text{NPh})\cdot\text{C}(\text{NPh})\cdot\text{NH}\cdot\text{NH}_2$ , m.p. 156° (decomp.) [ $(\text{CMe}_2)_2$ -derivative, m.p. 203°], which with  $\text{NaN}_3$  gives 1 : 1'-diphenyl-5 : 5'-ditetrazolyl.

H. A. P.

**Derivatives of 2 : 3-pyridinethioindoxyl [3-hydroxy-4 : 5-pyridothiophen].** A. E. TSCHITSCHIBABIN and N. N. VOROSCHOV, jun. (Ber., 1933, 66, [B], 364—372).—2-Pyridylthiolacetic acid (I), m.p. 127—133° (slight decomp.) [hydrochloride, m.p. 168—170° (decomp.)], is transformed by  $\text{Ac}_2\text{O}$  at 100—145° into the "3-hydroxy-4 : 5-pyridylthiophen" (II), m.p. 180.5—181.5°, of Koenigs and Geisler (A., 1925, i, 166), which on account of the ready hydrolysis by  $\text{H}_2\text{O}$  to (I) and for other reasons (see below) cannot have the constitution ascribed to it. 3 : 5-Dibromo-2-aminopyridine is converted by diazotisation in conc.  $\text{HCl}$  into 3 : 5-dibromo-2-hydroxy- and 2-chloro-3 : 5-dibromo-pyridine (III), m.p. 43—44° (III),  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and  $\text{NaOAc}$  at 180—190° afford 3 : 5-dibromo-2-pyridylthiolacetic acid, m.p. 145—148°, transformed by  $\text{Ac}_2\text{O}$  at 100—130° into a compound  $\text{C}_7\text{H}_7\text{ONBr}_2\text{S}$ , decomp. 222—224°, closely analogous to (II) but not re-converted into the initial material (in this case the production of a "pyridylthiophen" is impossible). 3-Pyridylthiolacetic acid, m.p. 170—173°, obtained by diazotisation of 3-aminopyridine followed by coupling with  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  in presence of  $\text{K}_2\text{CO}_3$  and  $\text{NaOAc}$ , is unchanged by  $\text{Ac}_2\text{O}$  under the conditions described above. 2-Thiopyridine-3-carboxylic acid, from the 2-chloro-acid and  $\text{KHS}$ , is transformed by  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  and  $\text{Na}_2\text{CO}_3$  in boiling  $\text{H}_2\text{O}$  into 3-carboxy-2-pyridylthiolacetic acid (IV), m.p. about 220°, whilst  $\text{Me}$  2-chloropyridine-3-carboxylate and  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  at 110° yield 3-carbomethoxy-2-pyridylthiolacetic acid (V), m.p. 82—83°. (IV) and (V) are converted by  $\text{CH}_2\text{N}_2$  in  $\text{MeOH}$  into  $\text{Me}$  3-carbomethoxy-2-pyridylthiolacetate (VI), m.p. 100—100.5°. Treatment of (VI) with  $\text{NaOMe}$  in  $\text{MeOH}$  affords  $\text{Me}$  3-hydroxy-4 : 5-pyridylthiophen-2-carboxylate, m.p. 160—161°, transformed by  $\text{CH}_2\text{N}_2$  into  $\text{Me}$  3-methoxy-4 : 5-pyridylthiophen-2-carboxylate, m.p. 98—99°. Treatment of (IV) or (VI) with boiling  $\text{HCl}$  doubtless yields 3-hydroxy-4 : 5-pyridothiophen, since the solutions in  $\text{KOH}$  are oxidised by  $\text{K}_3\text{Fe}(\text{CN})_6$  or air to an insol. violet dye which gives a colourless vat with alkaline  $\text{Na}_2\text{S}_2\text{O}_4$ .

2-Chloropyridine-3-carboxylic acid and  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  yield small amounts of two compounds, m.p. 257° and 145—148°, respectively. 2-Chloro-3-nitropyridine and  $\text{KSH}$  in  $\text{EtOH}$  yield 3 : 3'-dinitro-2 : 2'-dipyridyl disulphide, m.p. 202—205°. 2-Methylthiopyridine methiodide appears to be formed by the action of  $\text{MeI}$  on (I).

H. W.

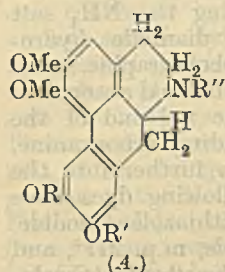
**Tricarboyanines.** (MISS) N. I. FISHER and (MISS) F. M. HAMER (J.C.S., 1933, 189—193).—Tri-

carboyanines, in which the 2 heterocyclic nuclei are joined by a 7-C unsaturated chain, may be prepared by adding an  $\text{EtOH}$  solution of a heterocyclic  $\text{NH}_4$  salt containing a reactive  $\text{Me}$  group to one of 2 : 4-dinitrophenylpyridinium chloride (which has been previously heated with alkali so as to liberate glutacetaldehyde) or preferably by heating the  $\text{NH}_4$  salt solution with glutacetaldehyde dianilide hydrochloride and alkali. These are photographic sensitizers and the max. of the sharply defined absorption band lies 190—205  $\text{m}\mu$  nearer the red end of the spectrum than that of the corresponding carboyanine, making it possible to photograph further into the infra-red than formerly. The following dyes have been prepared : from 1-methylbenzthiazole ethiodide, 2 : 2'-diethylthiotricarboyanine iodide, m.p. 211°, and from the methochloride, 2 : 2'-dimethylthiotricarboyanine chloride, m.p. 154°; from 1-methyl- $\alpha$ -naphthathiazole ethiodide, 2 : 2'-diethyl-5 : 6 : 5' : 6'-dibenzthiotricarboyanine iodide, m.p. 191°, and from the methochloride, 2 : 2'-dimethyl-5 : 6 : 5' : 6'-dibenzthiotricarboyanine chloride, m.p. 166°; from 2-methyl- $\beta$ -naphthathiazole ethiodide, 2 : 2'-diethyl-3 : 4 : 3' : 4'-dibenzthiotricarboyanine iodide, m.p. 183°, and from the methochloride, 2 : 2'-dimethyl-3 : 4 : 3' : 4'-dibenzthiotricarboyanine chloride, m.p. 181°; from 2-methylthiazoline ethiodide, 3 : 3'-diethyl-, m.p. 192°, and from the methiodide, 3 : 3'-dimethyl-thiazolinotricarboyanine iodide, m.p. 213°; from 1-methylbenzselena-azole ethiodide, 2 : 2'-diethyl-, m.p. 225°, and from the methiodide, 2 : 2'-dimethyl-selenotricarboyanine iodide, m.p. 198°; from *p*-toluquinaldine ethiodide, 6 : 6'-dimethyl-1 : 1'-diethyl-2 : 2'-tricarboyanine iodide, m.p. 248°; from quinaldine ethiodide (in small yield) 1 : 1'-diethyl-2 : 2'-tricarboyanine iodide, m.p. 219°; and from 2 : 3 : 3-trimethylindolenine methiodide,  $\text{Ac}_2\text{O}$ , and  $\text{NaOAc}$ , 1 : 3 : 3 : 1' : 3' : 3'-hexamethylindotricarboyanine iodide, m.p. 207°. (All m.p. are also decomp. points.)

F. R. S.

**Constitution of laurotetanine.** G. BARGER, T. EISENBRAND, L. EISENBRAND, and E. SCHLITTLER (Ber., 1933, 66, [B], 450—461).—Vanillin  $\text{Et}$  ether, m.p. 64—65°, from vanillin and  $\text{Et}_2\text{SO}_4$ , is transformed by hippuric acid,  $\text{NaOAc}$ , and  $\text{Ac}_2\text{O}$  at 100° into the *azlactone* of 3-methoxy-4-ethoxybenzylidenehippuric acid, m.p. 162—163°, converted by boiling 10%  $\text{NaOH}$  into 3-methoxy-4-ethoxyphenylpyruvic acid (I), m.p. 190—191° (decomp.). Oxidation of (I) with  $\text{NaOH}\cdot\text{H}_2\text{O}_2$  affords 3-methoxy-4-ethoxyphenylacetic acid, m.p. 183—185° (decomp.), whence 6-nitro-3-methoxy-4-ethoxyphenylacetic acid (II), m.p. 169—170°. *iso*Vanillin  $\text{Et}$  ether, m.p. 52—53°, similarly yields successively the *azlactone* of 4-methoxy-3-ethoxybenzylidenehippuric acid, m.p. 180—181°, 4-methoxy-3-ethoxyphenylpyruvic acid, m.p. 155°, 4-methoxy-3-ethoxyphenylacetic acid, m.p. 72° (+ $\text{H}_2\text{O}$ ), m.p. 67—68°, and 6-nitro-4-methoxy-3-ethoxyphenylacetic acid, m.p. 185—186°. 6-Nitro-3-methoxy-4-ethoxyphenylacet- $\beta$ -3' : 4'-dimethoxyphenylethylamide, m.p. 152—153°, obtained under defined conditions from the chloride of (II) and homoveratrylamine (prep. described), is transformed by  $\text{P}_2\text{O}_5$  in boiling  $\text{PhMe}$  into 6 : 7-dimethoxy-1-6'-nitro-3'-methoxy-4'-ethoxybenzyl-3 : 4-dihydroisquinoline, m.p. 139—140°. The

corresponding *ethiodide*, m.p. 203—204° (decomp.), is reduced by Zn dust and HCl to 6 : 7-dimethoxy-1-6'-amino-3'-methoxy-4'-ethoxybenzyl-2-ethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline dihydrochloride, m.p. about 185° (decomp.) after becoming pink at 173°, transformed by successive treatment with NaNO<sub>2</sub> in 2*N*-H<sub>2</sub>SO<sub>4</sub>-



MeOH and Zn dust and HCl into 2 : 5 : 6-trimethoxy-3-ethoxy-*N*-ethylnoraporphine (III) (cf. A, R=R'=Et, R''=Me), isolated as the *hydriodide*, decomp. 210°. In similar sequence are prepared: 6-nitro-4-methoxy-3-ethoxyphenylacet-β-3' : 4'-dimethoxyphenylethylamide, m.p. 160°, 6 : 7-dimethoxy-1-6'-nitro-4'-methoxy-3'-ethoxybenzyl-3 : 4-dihydroisoquinoline, m.p. 174—175°, and its *ethiodide*, m.p. 207° (decomp.), 6 : 7-dimethoxy-1-6'-amino-4'-methoxy-3'-ethoxybenzyl-*N*-ethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline dihydrochloride (+H<sub>2</sub>O), m.p. 178° (decomp.), and 3 : 5 : 6-trimethoxy-2-ethoxy-*N*-ethylnoraporphine (IV), (A : R=Me, R'=R''=Et), isolated as the *hydriodide*, decomp. 205—210°. Ethylation of laurotetanine affords non-cryst. *ON*-diethyl-laurotetanine (V), isolated as the *hydriodide*, m.p. 210° (decomp.). The Hofmann degradation of (IV) leads to 3 : 5 : 6-trimethoxy-2-ethoxy-8-vinylphenanthrene, m.p. 142° after softening at 141° [oxidised by KMnO<sub>4</sub> to a compound, m.p. (indef.) 213°], identical with that derived similarly from (V), whereas (III) affords 2 : 5 : 6-trimethoxy-3-ethoxy-8-vinylphenanthrene, m.p. 141° after softening at 139°, oxidised to 2 : 5 : 6-trimethoxy-3-ethoxyphenanthrene-8-carboxylic acid, m.p. 209°. Laurotetanine has therefore the constitution A (R=Me, R'=H, R''=Et). ClCO<sub>2</sub>Et and (V) give an optically inactive compound C<sub>26</sub>H<sub>33</sub>O<sub>6</sub>N, m.p. 129—130°, identical with that derived from (IV). Similarly, (V) and (IV) are transformed by BzCl into the optically inactive substance C<sub>30</sub>H<sub>33</sub>O<sub>5</sub>N, m.p. 138° after softening at 136°, thus confirming the above structure.

H. W.

**Alkylation of hydrocupreine.** K. H. SLOTTA and R. BEHNISCH (Ber., 1933, 66, [B], 360—364).—Higher alkyl ethers are prepared by treatment of hydrocupreine (I) with the requisite alkyl *p*-toluenesulphonate in boiling EtOH in presence of KOH. Use of higher temp. or pressure or of a large excess of ester diminishes the yield owing to formation of quaternary salts. The ethers are isolated as the monosulphates from which the amorphous base is readily obtained pure, although its m.p. is frequently some degrees lower than that of the cryst. compound. The following *-hydrocupreines* are described: *n*-propyl-, m.p. (amorph.) 136°, (cryst.) 142° (*sulphate*, m.p. 251°; *hydrochloride*, m.p. 247°); *n*-butyl-, m.p. (amorph.) 147° (*sulphate*, m.p. 244°); *isoamyl*-, m.p. (amorph.) 152° (*sulphate*, m.p. 238°); *n*-hexyl-, m.p. (amorph.) 145° (*dihydrochloride*, m.p. 184°). (I) and C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·O·CH<sub>2</sub>·CH<sub>2</sub>Cl, when reaction is interrupted as soon as the mixture becomes gelatinous, afford β-chloroethylhydrocupreine, m.p. (amorph.) 154°, (cryst.) 156° (*sulphate*, m.p. 218°), whereas prolongation of the change appears to lead to the β-hydroxyethyl compound. *isoAmyl*, b.p. 156°/0.06 mm., and

*n*-hexyl, b.p. 145—150° (bath)/0.05 mm., *p*-toluenesulphonates are described.  
H. W.

**Structure of strychnine and brucine.** III. **Decomposition of strychnine and strychnidine methochlorides by hydrogen in the presence of palladium.** O. ACHMATOWICZ (Rocz. Chem., 1933, 13, 25—36).—Strychnine methochloride with H<sub>2</sub> (Pd) gives chano-Nb-methylhydrostrychnine (I), C<sub>22</sub>H<sub>26</sub>O<sub>2</sub>N<sub>2</sub>, m.p. 145°, the dihydro-derivative of (I) (II), m.p. 201°, and dihydrostrychnine methochloride (III), +2H<sub>2</sub>O, m.p. 250°. (III) does not react with H<sub>2</sub> or with KOMe; dihydrostrychnine cannot be obtained from it by thermal decomp. KOH and (III) yield dihydro-methylstrychnine, m.p. 274—276°. Electro-reduction of (I) or (II) yields dihydro-chano-Nb-methylhydrostrychnidine (IV), C<sub>22</sub>H<sub>30</sub>ON<sub>2</sub>, m.p. 176° (*methiodide* and *methochloride*, uncrystallisable). Catalytic reduction of strychnidine methochloride yields chiefly (IV), together with dihydrostrychnidine and salts of strychnidine-X (V), m.p. 233—235° (*methiodide*, m.p. 290°), a new isomeride of strychnidine. The *methochloride* of (V), m.p. 292°, yields *methoxy*-, m.p. 143—145°, and *hydroxymethoxy-methyl*dihydrostrychnidine-X, m.p. 304—305°, when heated with NaOMe in MeOH solution.  
R. T.

**Solanine.** IX. [*Solanum*] *tuberosum* solanine. G. ODDO and G. CARONNA.—See this vol., 379.

**Synthesis of glucoalkaloids.** M. POLONOVSKI, M. POLONOVSKI, and A. LEMETRE (J. Pharm. Chim., 1933, [viii], 17, 145—154).—By passing dry HCl into a solution of β-tetra-acetylglucosidyl bromide and the alkaloid in dry COMe<sub>2</sub> and subsequent hydrolysis are obtained the *glucosides* of quinine, m.p. 138°, [α]<sub>D</sub><sup>19</sup> -120° in H<sub>2</sub>O (*sulphate*, m.p. 110°; *picrate*, m.p. 128°; *chloroaurate*, m.p. 109°); atropine, m.p. 97—98°, [α]<sub>D</sub><sup>19</sup> -4.24° in EtOH (*hydrobromide*, m.p. 126°; *picrate*, m.p. 162°); hyoscyamine, m.p. 86°, [α]<sub>D</sub><sup>19</sup> -11.7° in EtOH (*hydrobromide*, m.p. 115—116°; *picrate*, m.p. 122°), and of genatropine as its tartrate, m.p. 111°, [α]<sub>D</sub><sup>19</sup> +6.60° (*picrate*, m.p. 117—118°) (none of the salts was analysed). Conversion of the OH group into a glucoside has no effect on the physiological action of these alkaloids, nor on their bactericidal action on *Staphylococci*.  
J. W. B.

**Nitration and bromination of heterocyclic arsenic compounds.** G. A. RAZUVAIEV and M. M. KOTON (J. Gen. Chem. Russ., 1932, 2, 889—892).—Diphenylene chloroarsine (I) in AcOH is oxidised by HNO<sub>3</sub> to the *nitrate* of the corresponding arsenic acid, m.p. 156—157°, giving an intense blue colour with NHPh<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>, but in presence of conc. H<sub>2</sub>SO<sub>4</sub> a yellow *dinitro-acid* (probably the *mm'*), m.p. >320°, is formed by simultaneous nitration and oxidation. Similarly, chlorophenoxarsine (II) gives, respectively, the *nitrate* of phenoxarsinic acid, m.p. 170°, and the *dinitro-acid*, decomp. above 275° without melting. On bromination (I) and (II) behave like the acyclic arsines, adding Br<sub>2</sub>, the As<sup>V</sup> derivative being immediately hydrolysed to the arsenic acid. 10-Acetyl-9 : 10-dihydrophenarsazine (III) on nitration gives a mixture of NO<sub>2</sub>-, brown, m.p. 225°, and (NO<sub>2</sub>)<sub>2</sub>-derivatives, yellow, both of which are As<sup>III</sup> derivatives; they are accompanied by phenarsazinic acid.

Bromination of (III) leads to fission of the heterocyclic ring. G. A. R. K.

**Reaction of iodine monochloride with organic mercury compounds.** F. C. WHITMORE and M. A. THORPE (J. Amer. Chem. Soc., 1933, 55, 782—786).—Hg dianisyl and ICl in CCl<sub>4</sub> (or H<sub>2</sub>O) give 95% of *p*-C<sub>6</sub>H<sub>4</sub>I·OMe, also formed similarly from *p*-OMe·C<sub>6</sub>H<sub>4</sub>·HgCl. β-C<sub>10</sub>H<sub>7</sub>·HgCl affords (in 95% EtOH) 95% of 2-C<sub>10</sub>H<sub>7</sub>I and *p*-C<sub>6</sub>H<sub>4</sub>Me·HgCl yields (best in aq. NaCl) 92% of *p*-C<sub>6</sub>H<sub>4</sub>MeI. HgPh<sub>2</sub> gives (in CCl<sub>4</sub> or H<sub>2</sub>O) 78% of PhI, whilst CH<sub>2</sub>Ph·CH<sub>2</sub>·HgCl furnishes about 30% of CH<sub>2</sub>Ph·CH<sub>2</sub>I (I) and 35% of CH<sub>2</sub>Ph·CH<sub>2</sub>Cl (II). (II) is produced from (I) and ICl, but not from (I) and HgCl<sub>2</sub>. H. B.

**Abnormal reactions of organometallic compounds. Cinnamyl chloride and magnesium. Grignard reagent from halogenated tertiary amines.** S. A. HARRIS (Iowa State Coll. J. Sci., 1932, 6, 425—428).—The Grignard reagent from cinnamyl chloride in Et<sub>2</sub>O and Mg behaves as if its structure is CHPh(MgCl)·CH·CH<sub>2</sub>. Dicinnamyl and liquid hydrocarbons, one of which is CHPh·CH·CH<sub>2</sub>·CHPh·CH·CH<sub>2</sub>, are also formed.

3-Bromo- and 3:5-dibromo-pyridine do not form Grignard reagents in the cold; at higher temp. tars are formed, and during the reaction Michler's ketone gives a colour reaction. 2-Iodopyridine reacts with Mg to give a green solution and an insol. tar; the solution gives no colour reaction with Michler's ketone, but if the ketone is added immediately to the solution and tar a positive reaction is obtained. *o*-C<sub>6</sub>H<sub>4</sub>I·NMe<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>Br·NMe<sub>2</sub> give high yields of Grignard reagents in presence of I. CH. ABS.

**Organic selenium compounds. II. New type of aromatic selenium halide.** D. G. FOSTER (J. Amer. Chem. Soc., 1933, 55, 822—829).—SePhEt (from PhSe·MgBr and EtBr) (cf. A., 1928, 655) and Br give SePhEtBr<sub>2</sub> (I), m.p. 86° (cf. Edwards *et al.*, A., 1928, 1147), also prepared from Br and the reaction product from SePhBr, EtBr, Mg, and a little Mg-Cu couple in Et<sub>2</sub>O, which decomposes slowly at room temp. and fairly rapidly in boiling Et<sub>2</sub>O to SePhBr and EtBr. A by-product in the prep. of (I) is *Se Ph tribromide* (II), m.p. 105—106°, also obtained from SePhBr and Br in Et<sub>2</sub>O·CS<sub>2</sub>, and from PhSeO<sub>2</sub>H, conc. HBr, and aq. NH<sub>4</sub>Br. (II) and Cl<sub>2</sub> in Et<sub>2</sub>O give *Se Ph trichloride* (III), m.p. 133—134° (decomp.), also formed from SePhBr and Cl<sub>2</sub> in Et<sub>2</sub>O, by saturation of a saturated aq. solution of PhSeO<sub>2</sub>H with HCl, and by thermal decomp. of SePhEtCl<sub>2</sub> and subsequent treatment (of the SePhCl) with Cl<sub>2</sub>. SePhI<sub>3</sub> could not be prepared, probably owing to its instability. (II) and (III) are not hydrolysed by H<sub>2</sub>O [(III) changes into an oil], but with aq. NaOH give PhSeO<sub>2</sub>H. The methods of prep. and reactions of (II) and (III) indicate that they are salts of the hypothetical PhSe(OH)<sub>3</sub> (which has basic properties). H. B.

**Phenylmethylselenetene mercuri-iodide.** M. P. BALFE and H. PHILLIPS (J.C.S., 1933, 127—128).—*dl*-Phenylmethylselenetene bromide and K mercuritri-iodide give *dl*-phenylmethylselenetene mercuritri-iodide, m.p. 90°, and a mol. compound (I), m.p. 140°, of selenetene mercuri-tri-iodide (1 mol.) and -tetra-

iodide (3 mols.) (cf. Pope and Neville, J.C.S., 1902, 81, 1552). *d*-Phenylmethylselenetene *d*-bromocamphorsulphonate, m.p. 174°, [α]<sub>D</sub><sup>20</sup> +61.2°, obtained from the *dl*-salt, affords with PtCl<sub>4</sub> the chloroplatin-ate (+EtOH), m.p. 95°, [α]<sub>D</sub><sup>20</sup> +11.8°, and with K mercuritri-iodide or HgI<sub>2</sub> and KI, optically inactive (I), m.p. 135°. The racemisation is to be attributed to the instability of the selenetene ion. F. R. S.

**Organic compounds of selenium. III. Action of selenium oxychloride on esters of salicylic acid.** R. E. NELSON, R. A. SCHROEDER, and W. R. BUNTING (J. Amer. Chem. Soc., 1933, 55, 801—803).—SeOCl<sub>2</sub> (1 mol.) and *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>R (2 mols.) give 4:4'-dihydroxy-3:3'-dicarbalk(aryl)oxydiphenyl selenide dichlorides, which are reduced (Zn dust in CHCl<sub>3</sub>) to the selenides (which add 2Br and 2I), and hydrolysed by aq. NaHCO<sub>3</sub> to the dihydroxides. The following are described: 4:4'-*dihydroxy-3:3'-dicarbomethoxydiphenyl selenide*, m.p. 158° (dichloride, m.p. 176°; dibromide, m.p. 143°; di-iodide, m.p. 150°; dihydroxide, m.p. 137°); -3:3'-*dicarbomethoxydiphenyl selenide*, m.p. 88° (dichloride, m.p. 165°; dibromide, m.p. 147°; di-iodide, m.p. 140°; dihydroxide, m.p. 107°); -3:3'-*dicarbopropoxydiphenyl selenide*, unstable viscous oil (dichloride, m.p. 130°; dibromide, m.p. 110°; di-iodide, m.p. 78°; dihydroxide, m.p. 63°); -3:3'-*dicarboisopropoxydiphenyl selenide*, m.p. 81° (dichloride, m.p. 173°; dibromide, m.p. 159°; di-iodide, m.p. 96°; dihydroxide, m.p. 83°); -3:3'-*dicarbobutoxydiphenyl selenide*, unstable viscous oil (dichloride, m.p. 133°; dibromide, m.p. 95°; di-iodide, m.p. 65°; dihydroxide, m.p. 57°); -3:3'-*dicarboamyloxydiphenyl selenide*, an unstable viscous oil (dichloride, m.p. 138°; dibromide, m.p. 121°; di-iodide, a viscous oil; dihydroxide, m.p. 97°); -3:3'-*dicarbophenoxydiphenyl selenide*, m.p. 138° (dichloride, m.p. 185°; dibromide, m.p. 160°; di-iodide, m.p. 120°; dihydroxide, m.p. 122°). H. B.

**Optical activity and coagulation of the degradation products of caseinogen. II.** B. JIRGENSONS (Biochem. Z., 1933, 257, 427—436).—The optical activity and coagulation of the peptones obtained by degradation of caseinogen on heating for 3 hr. at 130—140° in glycerol are investigated. In acid solution, coagulation is effected most readily with SO<sub>4</sub>' and CNS', in feebly alkaline solution by Cl' and Br'. Optimal coagulation at *p*<sub>H</sub> 4.3 is obtained by MeOH, EtOH, and Pr<sup>o</sup>OH, respectively, in concns. of 5.8, 3.6, and 2.1 mols. per litre, at *p*<sub>H</sub> 6.9 in concns. of 3.5, 3.0, and 2.6, and at *p*<sub>H</sub> 7.4 in concns. of 2.2, 2.8, and 3.4 mols. per litre. P. W. C.

**Highly-sensitive specific colour reaction of tyrosine on *p*-substituted phenols. Tyrosine content of various proteins, particularly of collagen and gelatin.** O. GERNGROSS, K. VOSS, and H. HERFELD (Ber., 1933, 66, [B], 435—442).—When 1 c.c. of 1% tyrosine is boiled with 1 drop of 1% 2-nitroso- $\alpha$ -naphthol in EtOH and 1—2 drops of HNO<sub>3</sub> (*d* 1.4) are added to the hot solution a dark purple colour is developed which is distinct in dilution 1:10<sup>6</sup>. The colour is gradually bleached on exposure to light, and Beer's law is not followed, so that quant. measurement is based on the limit of visibility with increasing dilution. Reaction is not given by any

known natural  $\text{NH}_2$ -acid except tyrosine. Positive results are given by *N*-benzoyltyrosine, tyrosol, tyramine, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$ , *p*- $\text{C}_6\text{H}_4\text{Et}\cdot\text{OH}$ , 1:3:4- and 1:2:4-xyleneol, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ , *p*-chloro- and *p*-bromo-*m*-cresol, chloroxylenol, *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$ , *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ , *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , phenolphthalein,  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$  and "folliculin," whilst negative results are recorded for *ON*-dibenzoyl- and *o*-nitro-tyrosine, 3:4-dihydroxyphenylalanine, adrenaline, thyroxine,  $\text{PhOH}$ , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ , *o*- and *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$ , 1:3:5-, 1:4:5- and 1:2:3-xyleneol, isopseudocumol, *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , trichlorophenol, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SH}$ , *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\text{Bz}$ , resacetophenone, *p*-methylcyclohexanol, decahydro- $\beta$ -naphthol,  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ , vanillin, *o*-vanillin, coniferin, fisetin, tannin, eugenol, thymol, terpineol, and *p*-benzoquinone. Examination of gelatins and collagens discloses the presence of tyrosine except in such as have been treated with  $\text{HNO}_2$  or  $\text{ClO}_2$ . Whether it is present as an actual component of the protein or only as an accompaniment is regarded as an open question. H. W.

**Apparatus for the study of the destruction of organic matter.** E. KAHANE (Bull. Soc. chim., 1933, [iv], 53, 95—97).—An all-glass apparatus is described for the oxidation of org. matter by  $\text{HClO}_4$ - $\text{HNO}_3$  and collection of volatile products. The acid mixture is preferable to  $\text{HClO}_4$  alone. R. S. C.

**Determination of organic nitrogen in the presence of nitrates by Kjeldahl's method.** R. CAMBIER and L. LEROUX (Compt. rend., 1932, 195, 1280—1282).—The  $\text{NO}_3^-$  is removed as  $\text{HNO}_3$  by vac. distillation of the solution with  $\text{H}_2\text{SO}_4$  at 30—40°, and finally at 100°. The residual liquid gives accurate vals. for org. N by ordinary Kjeldahl procedure. A. C.

**Determination of halogens in organic substances by the ammonia-sodium method. Determination of fluorine in organic compounds.** F. GOVAERT (Compt. rend., 1932, 195, 1278—1280).—Trifluorotoluene,  $\text{CF}_3\cdot\text{CO}_2\text{Et}$ , and  $\text{PhF}$ , with non-reactive F, are accurately analysed for F by this method (cf. this vol., 80). A. C.

**Determination of fluorine in organic compounds by a lamp method.** G. CADENBACH (Angew. Chem., 1933, 46, 130).—The substance is volatilised in a stream of  $\text{H}_2$  through a strongly heated Ag tube and burnt under a Ag funnel. HF is detected by  $\text{Ca}(\text{OAc})_2$  or  $\text{La}(\text{OAc})_3$  and determined by 0.2*N*-KOH. S. C.

**Iodometric determination of mercury in organic compounds.** J. OPIENSKA-BLAUTH (Przemysł Chem., 1933, 17, 14—18).—Rupp's iodometric method (A., 1901, ii, 348) gives results which are, according to the compound under analysis, either high, owing to combination of I with the org. part of the mol., or low, as a result of partial hydrolysis of the complex. In the case of Hg salicylate satisfactory results are given only by very pure samples. R. T.

**Micro-determination of alcohol in alcohol-air mixtures.** M. NICLOUX (Compt. rend. Soc. Biol.,

1931, 107, 527—529; Chem. Zentr., 1932, ii, 2083—2084).—The EtOH is retained by bubbling the air through  $\text{H}_2\text{O}$ , and determined by distillation in a Schloesing-Aubin apparatus. A. A. E.

**Determination of thymol.** C. V. BORDEIANU (Z. anal. Chem., 1933, 91, 421—425).—Errors of 10—70% are involved in the usual iodometric determination of thymol. By mercurating thymol to the dimercuriacetate with excess of  $\text{Hg}(\text{OAc})_2$  in 50% aq. AcOH, diluting with  $\text{H}_2\text{O}$ , and determining  $\text{Hg}^{2+}$  in the filtrate with  $\text{NH}_4\text{CNS}$ , a mean accuracy of 0.6% can be attained. F. L. U.

**Micro-determination of picrolonic acid by means of acridine.** H. SCHIEDEWITZ (Z. physiol. Chem., 1933, 214, 177—178).—The picrolonate is dissolved in 20 c.c. of hot  $\text{H}_2\text{O}$  with addition of 1 c.c. of dil. HCl and treated with 15 c.c. of 0.3% acridine in aq. HCl. The acridine salt is separated by filtration and weighed. J. H. B.

**Tannin spot-tests.** J. H. HOCH (J. Amer. Pharm. Assoc., 1933, 22, 121—124).—The sensitivity of the reaction of tannin with 33 reagents has been examined. The reactions of a group of 8, being the most sensitive, with aq. dilutions of 7 drugs indicate that the sensitivity of the reaction is not affected by either the time (5—30 min.) or temp. of maceration or the filtration of the extract. E. H. S.

**Reactions and determination of ephedrine.** J. A. SÁNCHEZ (Semana méd., 1932, II, 1183—1185).—NaOH and I in KI afford  $\text{CHI}_3$ . Evaporation with NaOH and  $\text{KMnO}_4$ , then heating with EtOH and  $\text{H}_2\text{SO}_4$ , gives an odour of BzOEt. Distillation with  $\text{KMnO}_4$  gives PhCHO. Bouchardat's, Wavelet's, Walser's, Sánchez' (molybdic), and Bertrand's (silicotungstic) reagents, and  $\text{Br}-\text{H}_2\text{O}$ , react. Distillation with NaOH or CaO and Zn gives PhCHO and  $\text{NHMeEt}$ .  $\text{NaNO}_2$  and HCl give white nitrosoephedrine. Nitration, reduction with Zn, and treatment with  $\text{NaNO}_2$  gives a diazo-compound which in alkaline solution gives with PhOH yellow, resorcinol dark orange,  $\beta$ -naphthol red, phloroglucinol dark orange, thymol intense red. For the determination, 10 c.c. (0.1% solution) are heated with NaOH solution (3 c.c.) and 0.1*N*-I (30 c.c.) for 30 min. to 60°; the solution is then cooled and titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  (1 c.c. I=0.0020625 g. ephedrine,  $\pm 0.5\%$ ). CH. ABS.

**Separation of alkaloids by means of buffer mixtures.** S. ELGAZIN (Khim. Farm. Prom., 1932, 128—131).—A solution of harmine and harmaline (1 kg. of hydrochlorides in 10 kg.  $\text{H}_2\text{O}$  at 80—85°) is filtered through animal C and treated with NaOAc (3 kg.), which ppts. 80% of the harmine; the operation is repeated on the mother-liquor. For the separation of strychnine from brucine 1 pt. is dissolved in 10 pts. of 10%  $\text{NH}_4\text{Cl}$  and treated with 10% aq.  $\text{NH}_3$  at 80—85° until all the strychnine is pptd., brucine being pptd. from the cooled mother-liquor with NaOH. CH. ABS.

**Micro-chemical reaction of scopolamine.** Z. F. KLAN (Časopis Českoslov. Lék., 1932, 12, 91—94; Chem. Zentr., 1932, ii, 2085).— $\text{AuCl}_3$  forms cryst. reaction products. A. A. E.

## Biochemistry.

**Components of the atmosphere and synthetic gases in relation to animal life.** J. W. HERSHEY (Nature, 1933, 131, 238—239).—A discussion of results previously obtained (*ibid.*, 1928, 122, 684).

L. S. T.

**Solubility and tendency to dissociate in ammonium sulphate solutions of carbon monoxide-hæmoglobin.** S. P. L. SØRENSEN and M. SØRENSEN (Biochem. Z., 1933, 258, 16—47; cf. A., 1931, 245).—Methods for preparing highly purified, stable CO-hæmoglobin (I) (unchanged after 18 months) from horse-blood, for analysing (I), and for determining the  $p_H$  of its solutions are described. Each g. of the hydrate of (I) contains 0.353 g. of  $H_2O$ . The effect of the concn. of  $(NH_4)_2SO_4$  added to solutions of (I) on the equilibrium (II) between dissolved and pptd. (I) is in accordance with the equation given by Green (A., 1932, 73). The curve showing the effect of  $[H^+]$  ( $p_H$  4.39—7.64) on (II) exhibits two min., one at  $p_H$  6.6 and another at 5.4. The latter probably corresponds with a sparingly sol. sulphate containing 12—13  $H_2SO_4$  per mol. of (I). Min. at these points are also found on the curve showing the ionisation in acid and alkaline solutions of (I). The tendency of (I) to dissociate in solution is indicated by the effect of the concn. of (I) on (II). This tendency is very slight when the concn. is high, but increases considerably with dilution. (I) cannot be fractionated by freezing or by crystallisation.

W. McC.

**Hæmoglobin content of normal serum.** P. MÜLLER (Klin. Woch., 1932, 11, 1352—1353; Chem. Zentr., 1932, ii, 2482).—Normal serum always contains hæmoglobin (7—20 mg. per 100 c.c.), the amount depending on the coagulation velocity etc. The yellow colour of non-icteric serum is largely dependent on this hæmoglobin content.

A. A. E.

**Constitution of hæmocyanin and hæmoerythrin by means of their ultra-violet absorption spectra.** J. ROCHE and P. DUBOULOZ (Compt. rend., 1933, 196, 646—648).—Application of Laporta's method (Bol. Soc. Ital. Biol. sper., 1932, 7, 630) to hæmoerythrin (I) affords an Fe-free protein and a *cryst. hæmoferrin* (II), rich in Fe and an ultra-violet absorption spectrum (band at 2950 Å.) closely similar to that of hæmocuprin (III), similarly obtained from hæmocyanin (IV) (Schmitz, A., 1931, 497, 753; Laporta, *loc. cit.*; the specimens prepared by these two methods also give almost identical spectra and are probably identical). Hence (I) and (IV) probably consist of a protein combined with the metal complexes (II) or (III), which possess very similar constitutions. The ultra-violet absorption spectra of oxyhæmocyanin (absorption between 3800 and 3000 Å.; band at 3450 Å.) and oxyhæmoerythrin are also very similar, reduction causing considerable diminution in intensity and disappearance of the 3450 Å. band in the former case.

J. W. B.

**Mol. wts. of the blood-pigments of the invertebrates.** T. SVEDBERG (Nature, 1933, 131, 325; cf. A., 1932, 1151).—Five forms of the erythrocrucorin type of respiratory protein differing with regard to sedimentation const. have been found in

the blood of invertebrates and two in the blood-corpuses. Each of the five forms is characteristic of one of the following groups: oligochaete worms, polychaete worms (I), gastropods (II), crustaceans (III), and insects (IV), whilst the two forms of the second type occur in the erythrocytes of the capitellide and glyceride worms. Only one sedimentation const. has been observed for the chlorocruorin type of respiratory protein, whilst the hæmocyanin type has six const. representing the groups (II), cephalopods (two const.), xiphosurans, and (III) (three const.). Several species within a group have the same sedimentation const., and hence, probably, the same mol. wt., to within 2%. Among (I) six species of six different families have a sedimentation const. of  $57.5 \times 10^{-13}$  corresponding with a mol. wt. of  $285 \times 10^4$ ; among (II) eleven species of seven different families have a const. of  $99.5 \times 10^{-13}$  (mol. wt.  $5 \times 10^6$ ), whilst in (III) five species of three families have a const. of  $23.0 \times 10^{-13}$ . The lowest const. for a respiratory pigment in blood is that of the erythrocrucorin of (IV); it is approx. one half that of the hæmoglobin of vertebrates and corresponds with a comparatively low mol. wt. The respiratory proteins of invertebrates possessing red corpuses give low sedimentation const. The constancy of the mol. wts. of the respiratory blood-proteins within various animal groups is discussed in relation to variation of the chemical composition of the blood-pigment.

L. S. T.

**Globins. II. Hæmatins, globins, and the specificity of hæmatin pigments.** J. ROCHE (Bull. Soc. Chim. biol., 1933, 15, 110—129).—The spectroscopic characteristics of artificial compounds of various hæmatins with the globins (I) of muscle- (II) and blood-pigments (III) and the relative affinity of muscle-hæmoglobin for  $O_2$  and CO indicate that the globin is responsible for the differences in the oxy- and carboxy-hæmoglobins of various animals. The protohæmatins of (II) and (III) are identical, whilst the "span" relationship (A., 1924, i, 1362) applies equally to both. The protein of chlorocruorin is not identical with the (I) of (II) or (III), but can combine with hæmatins. The hæmatin of helicorubin yields the same product as protohæmatin when combined with (I). A hæmoglobin is formed by the combination of (I) with cytochrome c (A., 1925, i, 1112). The functions of the hæmatins and globins are discussed.

F. O. H.

**Determination of protein in blood-serum by oxidation.** P. BOULANGER and H. WAREMBOURG (Compt. rend. Soc. Biol., 1931, 106, 958—960; Chem. Zentr., 1932, ii, 3446).—Oxidation with  $KMnO_4$  and with  $CrO_3 + H_2SO_4$  (iodometric) gives concordant vals.

A. A. E.

**Analysis of whole blood. IV. Glutathione.** S. R. BENEDICT and G. GOTTSCHALL (J. Biol. Chem., 1933, 99, 729—740).—The blood is deproteinised with tungstomolybdic acid (A., 1929, 1189) and the filtrate treated with aq. NaOAc and aq.  $NaHSO_3$  followed by arsenophosphotungstic acid (A., 1922, ii, 405). A blue colour slowly develops and, 10—30 min. after

mixing, comparison is made with standards similarly prepared. Methionine does not interfere. F. O. H.

**Occurrence of acetylcholine in ox-blood.** I. VOGELFANGER (Z. physiol. Chem., 1933, 214, 109—110).—When the reaction was prevented from becoming alkaline during evaporation of the EtOH extract acetylcholine was isolated from ox-blood.

J. H. B.

**Volumetric micro-determination of uric acid in urine and blood.** S. RUSZNYÁK and E. HATZ (Biochem. Z., 1933, 257, 420—426).—The method, which depends on the titration until colourless with 0.01—0.005*M*-K<sub>2</sub>Fe(CN)<sub>6</sub> of the blue solution obtained by the usual Folin-Wu reagents, is described and a table indicates its accuracy.

P. W. C.

**Relation between sodium chloride and residual nitrogen.** E. KERPEL-FRONIUS (Z. ges. exp. Med., 1932, 85, 235—247).—Excess excretion of N compounds reduces the urinary concn. of Cl; when oliguria supervenes there is Cl<sup>-</sup> retention and hyperchloremia (I). During experimental exsiccosis in animals there may occur a sudden fall in the concentrating power of the kidney. In infants suffering from dehydration the (I) is not renal in origin, but is due to H<sub>2</sub>O loss without corresponding reduction in Cl<sup>-</sup>. In (I) the blood has an increased osmotic pressure. The increase in non-protein-N of the blood in (I) is not a compensatory osmotic process, but is dependent on dehydration. Tissue alterations of osmotic pressure run parallel with those of the blood.

NUTR. ABS.

**Colorimetric determination of free cholesterol in blood-serum.** A. GRIGAUT (Compt. rend. Soc. Biol., 1933, 112, 34—36).—A modification of the author's method for determination of cholesterol (I) permits its use for determination of esterified (I), free (I) being determined by difference.

NUTR. ABS.

**Direct determination of free cholesterol in the blood without precipitation.** O. KANNER (Compt. rend. Soc. Biol., 1931, 108, 383—384; Chem. Zentr., 1932, ii, 2998).—Blood (2 c.c.) is diluted (to 15 c.c.) with 60% EtOH containing 0.5% NaOH and vigorously shaken 12 times with light petroleum. The petroleum layer is washed with 15 c.c. H<sub>2</sub>O, and cholesterol in the residue on evaporation is determined colorimetrically (Liebermann).

A. A. E.

**Plasma-protein, cholesterol, and [corpuscle] sedimentation rate in various kinds of animals.** B. SWEDIN (Biochem. Z., 1933, 257, 411—419).—The readily Et<sub>2</sub>O-sol. cholesterol, the protein, and the sedimentation rate for ox, horse, dog, goat, hedgehog, and rabbit are determined. The cholesterol vals. showed fair agreement for all the animals except rabbit, but no relationship could be detected between the sedimentation rate and the amount of plasma-protein.

P. W. C.

**Influence of intravenous injection of diastase on the blood-sugar of normal and depancreatized animals.** G. MANSFELD (Biochem. Z., 1933, 257, 333).—An erroneous statement attributed to the author by Wilson and Strieck (A., 1932, 1054) is disclaimed.

P. W. C.

**Action of hydrocyanic acid on the optical properties of blood-sugar.** J. THOMAS and E. J. BIGWOOD (Bull. Soc. Chim. biol., 1933, 15, 75—83).—The variation with  $p_H$  of  $[\alpha]$  of dialysates of the blood of rabbits or dogs (A., 1931, 858) is almost completely eliminated by addition of HCN. This is due to formation of the cyanohydrin of glucose; NH<sub>2</sub>-acids and lactic acid play a secondary and far less significant part.

F. O. H.

**Silica in the organism, and siliceous particles of the blood.** L. LEMATTE and E. KAHANE (Compt. rend., 1933, 196, 575—578).—SiO<sub>2</sub> of the order of 1 mg. may be determined in org. matter to within 0.1—0.2 mg. by the authors' method (A., 1931, 926, 1201). Smaller quantities are detected qualitatively as gelatinous solubilised SiO<sub>2</sub>. Ox, horse, pig, dog, and human fibrins contain 0—1 mg. of SiO<sub>2</sub> per 100 g.; these vals. are much < those recorded in the literature. In addition, fibrin also contains traces of insol. SiO<sub>2</sub>.

A. C.

**Phosphorus fractions in blood of the growing organism.** C. BOMSKOV and H. NISSEN (Z. ges. exp. Med., 1932, 85, 142—147).—Figures are given for the P fractions of the blood of rabbits and dogs at various ages. As adult life approaches there is a fall in all the fractions except the acid-insol., which shows a tendency to rise.

NUTR. ABS.

**Determination of blood- and urine-sulphur.** A. LESURE and A. THOMAS (J. Pharm. Chim., 1933, [viii], 17, 114—130).—In the benzidine method, LiOH is used for neutralisation in place of NaOH, allowing phosphates to be removed by filtration. This is considered indispensable in determination of SO<sub>4</sub><sup>2-</sup> and advantageous in the case of ethereal sulphates.

H. G. R.

**Blood-iodine.** I. I. NITZESCU and E. BINDER (Compt. rend. Soc. Biol., 1931, 108, 279—280; Chem. Zentr., 1932, ii, 2481).—Blood-I is normally 8.7—9.4 ( $\times 10^{-6}$  g.-%) (Jan.—Mar.), 11.7—12.3 (June—Dec.); in goitre it is 4—5.

A. A. E.

**Antigenic properties of cholesterol and its derivatives.** A. J. WEIL and F. BESSER (Z. Immunität., 1932, 76, 76—82; Chem. Zentr., 1932, ii, 3428).—Various cholesterol derivatives with pig serum were used to immunise rabbits. The antibodies have a high structure specificity. Oxy-cholesterol (Lifschutz), dihydrocholesterol, and cholesterol are antigenic, whilst cholesteryl oxide (Westfalen), dibromide, acetate, and palmitate do not give antibodies.

A. A. E.

**Adsorption and elution of the Forssman heterogenetic antigen.** E. BRUNIUS (Biochem. Z., 1933, 258, 207—220; cf. Rudy, A., 1932, 1153).—Forssman heterogenetic antigen (from guinea-pig and horse kidney) is readily adsorbed by kaolin (I), Al(OH)<sub>3</sub> (II), colloidal Fe(OH)<sub>3</sub> (III), and animal C (IV), but cannot be removed from the adsorbent by elution [with physiological NaCl, even for long periods, dil. AcOH, aq. NH<sub>3</sub> for (I), H<sub>2</sub>O, Na<sub>2</sub>HPO<sub>4</sub> for (II) and (III), NaCl, octyl alcohol, 96% EtOH, C<sub>6</sub>H<sub>6</sub>, 0.001*N*-HCl, 0.001*N*-NaOH for (IV)]. Adsorption with (III) is most effective at high temp. (70°).

W. McC.



**Specificity of antibodies towards lipins. Sterols.** E. BERGER and H. SCHOLER (Z. Immunität., 1932, 76, 16—35; Chem. Zentr., 1932, ii, 3428).—Various sterols (non-irradiated and irradiated) were injected with pig's serum into rabbits. The sera were highly sp., reacted only with the homologous antigens, and permitted the serological differentiation of irradiated and non-irradiated ergosterol. Even small impurities are detectable. A. A. E.

**Effect of heparin and germanin on immunoreactions.** F. KLOPSTOCK (Z. Immunität., 1932, 75, 348—354; Chem. Zentr., 1932, ii, 3112).—A discussion. A. A. E.

**Specific combination of arsanil-protein and arsanilic acid with immune serum.** F. HAUROWITZ and F. BREINL (Z. physiol. Chem., 1933, 214, 111—120; cf. A., 1930, 1608).—The ppt. from arsanil-azoprotein and homologous anti-serum contains the more antigen the greater is its concn. in the fluid, unsp. adsorption being excluded. The inhibitory action of arsanilic acid on the pptn. is lost when  $As^V$  is replaced by  $Sb^V$  or  $As^{III}$  or by conversion of the primary into the secondary arsinic acid (replacement of OH by the  $NPhMe_2$  radical). The binding of the anti-serum by the arsanilic acid is directly proved by compensation dialysis (cf. Marrack and Smith, A., 1932, 184). J. H. B.

**Kinetics of hæmolysis in colloidal silicic acid-complement systems.** E. PONDER (Proc. Roy. Soc., 1933, B, 112, 298—315).—Previously described methods (A., 1932, 413) have been applied to systems containing ox red blood-cells sensitised by silicic acid (I), and guinea-pig complement. The systems are characterised by "hæmolytic zones." The cells absorb some of the sensitising agent, and if the free (I) is removed, the complement acts as a simple hæmolysin. The "zones" are accounted for by a reaction between the free (I) and part of the complement, whereby the latter is inactivated. A. C.

**Phosphorescence in human tissues. I. Proof of the phosphorescence in normal human tissues and its measurement.** S. HOSHIJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 20, 109—113).—By a modified Becquerel phosphoroscope, phosphorescence has been detected in human bones, teeth, cartilage, nails, and tendons, but not in various other organs. Calcined bone and tooth, but not bone or cartilage decalcified by dil.  $HNO_3$ , show phosphorescence. The phosphorescence with most tissues lasts about 0.2 sec. (excitation time 0.04 sec.), but with calcined bone and tooth it lasts about 15 sec. The phosphorescence spectrum has been photographed and measured. W. O. K.

**Sulphur and cystine content of egg-membrane of Chinese hens.** P. P. T. SAH and C. S. CHEN (Sci. Rep. Nat. Tsing Hua Univ., 1932, A, 1, 285—287).—The egg-membrane contained 80.5% protein and 2.83% S. S was present only as cystine. H. G. R.

**Identification of l-(+)-norleucine as constituent of proteins of the spinal marrow and peripheral nerves.** E. ABDERHALDEN and K. HEYNS (Z. physiol. Chem., 1933, 214, 262—266).—l-(+)-

Norleucine (I) was obtained from peripheral nerve hydrolysate and was identified by conversion into the corresponding  $\alpha$ -bromo-fatty acid, then into the trimethylamino-acid (*chloroaurate*, m.p. 137°). The smaller amount of (I) obtained from spinal marrow was identified by means of the *benzenesulphonyl*, m.p. 113°, and *formyl*, m.p. 114—116°, derivatives. The *phenyl-carbimido*-, m.p. 133°, and *phenylhydantoin*, m.p. 110—111°, derivatives of (I) were also prepared. J. H. B.

**Distribution of lipin-phosphorus in the adrenals of mammals.** A. LEULIER and L. REVOL (Compt. rend. Soc. Biol., 1931, 106, 667—668; Chem. Zentr., 1932, ii, 2990).

**Arginine. III. Arginine content of vertebrate and invertebrate muscle.** A. ARNOLD and J. M. LUCK (J. Biol. Chem., 1933, 99, 677—691).—Arginine (free or as phosphate) is present in small amounts in the thigh muscles of rats and rabbits, but is absent from the muscles of pigeons, cats, frogs, and gopher snakes. Amongst the invertebrates the highest content occurs in the *Crustacea*, a high content occurring in the cephalopod *Paroctopus apollyon*. It is present in the *Echinodermata*, *Platyhelminthes*, and *Phoronidea*, but absent from the *Cœlenterata*, marine *Annelida*, *Echiuroidea*, and *Sipunculoidea* (cf. A., 1932, 532). F. O. H.

**am-Hexose which occurs in the organism.** Y. KOTAKE and M. NISHAGAKI.—See this vol., 378.

**Mineral content of cartilage.** W. SILBER (Biochem. Z., 1933, 257, 363—370).—Air-dried cartilage of rabbit's ear has a 4% ash content containing Na 22, K 12, Ca 3, Mg 2,  $SO_4$  40,  $P_2O_5$  7, and Cl 15%. Aq. extraction for 3 weeks removes 90% of the ash together with 10% of the org. substances. P. W. C.

**Copper, iron, and manganese content of fish.** T. B. PARKS and E. R. ROSE (J. Nutrition, 1933, 6, 95—98).—20 species of fresh- and salt- $H_2O$  fish contained 1.4—4.1 mg. Cu, 3.4—9.6 mg. Fe, and 0.1—0.5 mg. of Mn per kg. of moist material. About 12% more Fe was found in salt- than in fresh- $H_2O$  fish, and about 75% more Fe in fish with dark- than in fish with light-coloured tissue. E. B. H.

**Red dye of the lobster shell.** H. WILLSTAEDT (Biochem. Z., 1933, 258, 301—303; cf. Verne, A., 1920, i, 680).—The dye is obtained (not quite pure) by extraction with EtOH and  $CS_2$ , evaporation of the solvent, dissolution in EtOH, pptn. with alkali hydroxide, dissolution in dil.  $H_2SO_4$ , and extraction with  $Et_2O$ . The product does not crystallise or yield a cryst. Me derivative with  $CH_2N_2$ , but this treatment produces a cryst. *by-product*,  $C_{29}H_{41} \cdot CO_2Me$ . The dye resembles carotene. W. McC.

**Diastase content of cerebrospinal fluid.** A. MARCHIONINI and B. OTTENSTEIN (Klin. Woch., 1932, 11, 1345—1348; Chem. Zentr., 1932, ii, 2482).—A mixture of the fluid (0.1 c.c.),  $H_2O$  (2 c.c.), 0.3% glycogen solution (9.1 c.c.), 1.1% NaCl solution (0.1 c.c.), and  $N/15-KH_2PO_4 + N/15-Na_2HPO_4$ ,  $pH$  6.8, (0.3 c.c.) is kept for 2 hr. at 40° and cooled. The reducing val. is determined (Hagedorn-Jensen) without deproteinisation, and that of the fluid alone is

subtracted from it. In non-syphilitic disease the val. is 11—40 mg. per 100 c.c., and in syphilis 0—10 mg. A. A. E.

**Mechanism of salivary secretion.** V. E. HENDERSON and M. H. ROEPKE (J. Pharm. Exp. Ther., 1933, 47, 193—207).—Stimulation of the chorda tympani leads to the peripheral production of a substance which decreases the contractility of the frog's heart. This effect is overcome by atropine. The active principle is destroyed by alkali and is insol. in Et<sub>2</sub>O. It is thought to be acetylcholine. A. L.

**Gastric lipase.** H. LICHTENBERG (Klin. Woch., 1932, 11, 2117).—Whereas the gastric lipase of older children and adults shows an optimum  $p_{\text{H}}$  about 5, the activity at this  $p_{\text{H}}$  being five times that at 7, the gastric lipase of infants may show equal activities at  $p_{\text{H}}$  5 and 7. When sugar solution is taken there are equal activities at  $p_{\text{H}}$  5 and 7, but when 1% "plasmon" solution is taken there is an inhibition at  $p_{\text{H}}$  7. The addition of proteins and peptides to the gastric contents of infants results in an inhibition of activity at  $p_{\text{H}}$  7. Apparently the fasting gastric secretion of achlorhydric individuals shows  $p_{\text{H}}$  characteristics similar to those of infants. NUTR. ABS.

**Lactic acid of gastric juice.** L. NORPOTH and E. KADEN (Arch. exp. Path. Pharm., 1933, 169, 414—428).—The gastric juice (I) of a no. of hospital cases contained 0.006—0.025% of lactic acid (II). The highest vals. occurred with gastric diseases. An increase of (II) in the blood induced by injection of adrenaline is not accompanied by an increase of (II) in (I) and, whilst the level of (II) in the blood approximates to that in (I), the (II) of (I) is not due to a simple process of diffusion, but probably to glycolysis in the cells of the stomach tissue. F. O. H.

**Gastric secretion of normal Chinese.** H. C. CHANG and H. L. CHANG (Chinese J. Physiol., 1932, 6, 321—331).—The vol., acidity, and total Cl' of the gastric juice of 200 normal Chinese, fasting and after histamine stimulation, showed little deviation from the normal Occidental standard except in the incidence of achlorhydria, this being 4% of the fasting cases examined. A. L.

**Gastric acidity with special reference to the pars pylorica and pyloric mucosa.** J. T. PRIESTLEY and F. C. MANN (Arch. Surg., 1932, 25, 395—403). NUTR. ABS.

**Effect of acetylcholine on gastric acidity and its relationship to degree of acidity.** P. MERKLEN, J. WARTER, and J. KABAKER (Compt. rend. Soc. Biol., 1932, 111, 1013—1015).—Injections of 0.2 g. of acetylcholine increased the acidity of the gastric juice of a- and hypo-chlorhydric, but lowered that of hyper-chlorhydric, i.e., those with free acid > 0.2% HCl. NUTR. ABS.

**Gastro-intestinal  $p_{\text{H}}$  in rats.** I. EASTMAN and E. G. MILLER, jun. (Proc. Soc. Exp. Biol. Med., 1932, 30, 332—334).—The  $p_{\text{H}}$  vals. of the gastro-intestinal tract of rats fed on a normal diet were on the average: stomach, 3.6; small intestine, upper third, 5.9; middle third, 6.3; lower third, 6.8; caecum, 6.2; colon, 6.6. The vals. were slightly higher in young rats. Diets of suet, potato, or lard had no distinct effect on the

reaction, but rachitogenic diets increased intestinal alkalinity slightly. NUTR. ABS.

**Chemical differentiation of nervous and hormonal pancreatic secretion.** T. F. ZUCKER, P. G. NEWBURGER, and B. N. BERG (Proc. Soc. Exp. Biol. Med., 1932, 30, 166—167).—The secretion of pancreatic juice is continuous even when secretin is eliminated by complete removal of the intestine. The inhibiting and stimulating effects of atropine and pilocarpine (I), respectively, indicate that the flow is influenced by the parasympathetic nervous system. A comparison of secretin juice with spontaneous or (I) juice shows that the latter is richer in enzymes and other solids with the exception of HCO<sub>3</sub>'. NUTR. ABS.

**Reaction of human milk.** W. PARTRIDGE (Analyst, 1933, 58, 88—89).—In agreement with Richmond, the acidity usually varies from 2.0 to 5.5 "dairy" degrees. Analyses of 15 samples of human milk are given. T. McL.

**Composition and heat of combustion of Danish cow's milk.** A. C. ANDERSEN, P. LANGMACK, and J. E. WINTHER (Proc. World's Dairy Cong., 1931, ii, 122—123).—For mixed milks,  $P=1.597+0.446F\pm 0.11$ ;  $D=7.627+1.346F\pm 0.12$ ;  $R=6.03/0.1F\pm 0.13$ ;  $C=300+113.5F\pm 8$ , where  $P$  is the protein,  $D$  the dry substance,  $F$  the fat, and  $R$  the fat- and N-free dry substance (%), and  $C$  is g.-cal. per kg. of milk. CH. ABS.

**Effect of dietary fat on the fat of cow's milk.** E. J. SHEEHY (Proc. World's Dairy Cong., 1931, i, 76—94).—Cottonseed, olive, and soya-bean oils (> 30 oz. daily) had no effect. Cod-liver oil (6—8 oz.) and linseed oil (15 oz.) had a depressant effect. CH. ABS.

**Source of the primary catalase of cow's milk.** A. ZEILINGER (Biochem. Z., 1933, 257, 450—462).—Milk-catalase is partly derived from the animal (primary) and partly from its bacterial content. Daily determination in cows showed an unmistakable parallelism between blood- and primary milk-catalase. The amount of primary milk-catalase also varies directly with the fat content of the milk and inversely with its  $d$  and with the amount of fat-free dry substance of the milk. P. W. C.

**Osmotic pressure and milk secretion.** W. E. PETERSEN and T. V. RIGOR (Proc. Soc. Exp. Biol. Med., 1932, 30, 259—264). NUTR. ABS.

**Biological relationship between cow's, goat's, and human caseinogens.** A. F. ANDERSON, O. M. SCHLOSS, and H. C. STUART (Amer. J. Dis. Child., 1932, 44, 1178—1186).—Cow's (I), human (II), and goat's caseinogens sensitise against each other. Anti-cow's-caseinogen sera gave positive pptn. reactions to (II), and animals that were passively sensitised to (I) exhibited evidence of anaphylaxis when given (II) intravenously. In each case the converse was equally true. NUTR. ABS.

**Effect of heat on antigenic properties of milk.** J. H. LEWIS and H. C. HAYDEN (Amer. J. Dis. Child., 1932, 44, 1211—1220).—The serological reactivity of raw (I) and pasteurised (II) milks was > that of evaporated milk (III) and a manufactured sample of

"hypo-allergic fat-free" milk (IV), known as Smaco 303. The caseinogen from (I) and (II) reacted in a higher dilution with all antisera than that derived from (III) and (IV). The reverse is true for the whey-proteins. Although the isolated whey-proteins are extremely heat-labile, showing a decrease in antigenic reactivity even at 60°, caseinogen from (I) is relatively heat-stable, no change occurring in its reactivity until the temp. exceeds 100°. With (I) little change occurs in its antigenic reactivity until the temp. exceeds 110°. There is some evidence that immunisation with heated milks produces antisera that appear to be sp. for the heated antigens.

NUTR. ABS.

Presence in the bile of an enzyme which dehydrogenates stearic acid. G. QUAGLIARIELLO (Atti R. Accad. Lincei, 1932, [vi], 16, 387—389).—Bile brought to  $p_H$  7.5 by mixed phosphates, saturated with PhMe, and shaken in  $O_2$  absorbs  $O_2$ . In presence of Na stearate, the absorption is increased.

T. H. P.

Changes in the secretion and composition of bile during alimentation. S. LEITES and W. JUSSIN (Arch. exp. Path. Pharm., 1933, 169, 365—384).—The feeding of glucose (I), peptone, flesh (II), nuclein (III), or hempseed oil (IV) or linseed oil (V) to dogs with biliary fistulæ has no influence on the quantity of bile secreted, whilst with butter (VI) there is a decrease. The abs. and relative contents of bile acids are increased with (II) and decreased with (VI); with (III), (IV), and (V) the concn. is slightly increased, whilst with (I) the concn. increases during the first 3 hr. and then decreases for the following 2 hr. In no instance is the concn. of cholesterol or of lipin-P affected.

F. O. H.

Changes in the bile-calcium and -potassium after alimentation. S. LEITES and A. KOSLOWA (Arch. exp. Path. Pharm., 1933, 169, 385—391).—In dogs with biliary fistulæ the bile-Ca is relatively const., whilst the K level varies considerably. Lesions or inflammation of the gall-bladder or -duct result in an increase of the Ca and, to a greater extent, of the K level. Various types of alimentation have no action on the Ca and K levels.

F. O. H.

Simultaneous study of constituents of urine and sweat. H. H. MOSHER (J. Biol. Chem., 1933, 99, 781—790).—The composition of human sweat (I) qualitatively resembles that of the urine (II) from the same subject. (II) is the more conc. solution containing 3—5 times the amount of total solids and 5—9 times the amount of org. matter. The uric acid-N content of (I) is 0.2—0.5 and the creatinine-N 0.2—0.8 mg. per 100 c.c., whilst the  $p_H$  is 5.02—5.71.

F. O. H.

Total analysis of unknown urinary substances. K. HAGENGUTH (Biochem. Z., 1933, 257, 484—491).—A table summarises the urea content, the total N, C, and vacate O before and after removal of urea and after pptn. also with phosphotungstic acid (I) of five samples of human and rabbit urine. The results suggest that the urinary residue contains substances extremely rich in O and that after pptn. with (I) a mixture of N-containing and N-free substances still remains.

P. W. C.

Detection of  $\beta$ -hydroxybutyric acid in urine and other physiological liquids. J. KHOURI (J. Pharm. Chim., 1933, [viii], 17, 161—165).—The detection of  $\beta$ -hydroxybutyric acid in urine (after removal of ketones by boiling with a few drops of  $H_3PO_4$ ) is effected by its oxidation with  $Na_2O_2$  (avoiding excess) in the cold and detection of  $COMe_2$  so formed by Frommer's reaction with salicylaldehyde. Preliminary purification and removal of glucose by usual methods are necessary unless the sample is free from sugars and colouring matter.

J. W. B.

Lead in urine. T. C. BOYD and H. D. GANGULY (Indian J. Med. Res., 1932, 19, 75—80).—Urine of Indians was free from Pb.

CH. ABS.

Examination of urinary ash and uric acid in Wood's light after incomplete ashing. Detection of uric acid. A. HADJIOLOFF and T. KRESTEFF (Compt. rend. Soc. Biol., 1931, 106, 663—664; Chem. Zentr., 1932, ii, 3128).—A bluish fluorescence, differing from that of fresh urine, is observed after incomplete ashing. Uric acid, slowly ignited until decomp. begins, shows a similar fluorescence. The blue fluorescence becomes yellowish-green on addition of KOH. The test is more sensitive and sp. than the murexide reaction.

A. A. E.

Examination of human and vertebrate animal urine in Wood's light. A. HADJIOLOFF and T. KRESTEFF (Compt. rend. Soc. Biol., 1931, 106, 662; Chem. Zentr., 1932, ii, 3128).—Fluorescence cannot be due entirely to urochrome or urobilin.

A. A. E.

Organic fraction of urinary phosphorus. B. S. WALKER and E. W. WALKER (J. Lab. Clin. Med., 1932, 18, 164—166).—An improved method for the determination of org. P in urine is described. The normal output of org. P per 24 hr. is 6—13 mg. (mean 9 mg.). In leucæmia the output is high (up to 23 mg.).

NUTR. ABS.

Excretion of creatinine by the frog's kidney. R. HÖBER (Pflüger's Archiv, 1932, 230, 327—330; Chem. Zentr., 1932, ii, 3115).

Excretion of lipin-insoluble acid dyes through the frog's kidney. R. HÖBER and A. MEIROWSKY (Pflüger's Archiv, 1932, 230, 331—343; Chem. Zentr., 1932, ii, 3115).

Detection of hæmatophorphyrin in, and extraction from, fæces. R. GOIFFON and J. WALTZ (Compt. rend. Soc. Biol., 1931, 108, 663—664; Chem. Zentr., 1932, ii, 3447).—Garrod's procedure is applied to the separation of hæmato- and coproporphyrin and to the determination by means of fluorescence in  $CHCl_3$  solution.

A. A. E.

Correlative regulation of organic and inorganic constituents of venous blood in disease. Parallel determination of lactic acid, ketones, phenols, carbon dioxide, sodium, chlorine (potassium, calcium, phosphorus), and  $p_H$ . R. STURM (Arch. exp. Path. Pharm., 1933, 169, 633—654).—The following mean figures have been found per 100 c.c. of venous blood from healthy individuals: lactic acid 12.66 mg., ketones 7.58 mg. (calc. as  $COMe_2$ ), phenols 39 m.-mol., combined  $HCO_3$  21 m.-equiv., and  $p_H$  7.38. When blood from pathological

cases is abnormally acid, increase of org. anions (lactic acid and ketone) is mainly responsible, whilst when the change is of the opposite type, it is usually due to increase in the concn. of Na<sup>+</sup>. W. O. K.

**Physico-chemical and clinical studies of cholesterol metabolism.** W. SCHEMENSKY and J. MRUGOWSKY (*Z. ges. exp. Med.*, 1932, 85, 329—368).—There is very little correlation between serum-cholesterol (I) and rise of blood-pressure; any that exists is to be attributed to the greater age of the patients with hyperpiesia. With increasing age there is a rise in the average (I). In 20 patients with arteriosclerosis the (I) was raised in 11; the rise is attributed to relative impermeability of the vessels through which (I) leaves the blood. Residence at high altitude produced an increase, possibly the result of splenic action. In infectious diseases there is a fall in (I) at the height of infection and a rise during convalescence. The initial fall is attributed to (I) being fixed by toxins. In diabetes the level of the (I) is related in great part but not entirely to general fat metabolism. In nephritis there was no correlation between (I) and blood-pressure or ability to excrete water or concentrate solids. In patients with neoplasms the level of (I) varies, and it is suggested that the rate of tumour growth is the deciding factor.

NUTR. ABS.

**Antibody to ovalbumin in the blood of allergic subjects.** P. WORINGER (*Ann. Inst. Pasteur*, 1933, 270—281).—Two antibodies (A and B) to ovalbumin have been characterised, only one of which (A) is characteristic of congenital allergy. The optimal zones for the fixation of complement by A and B differ widely. An approx. idea of the content of A of a serum is obtained as follows. Egg-white is added in proportions varying from 1 : 500 to 1 : 5 × 10<sup>6</sup> and the mixtures are injected in a normal subject. The following day an injection of egg-white is given and the limits are noted within which an urticarial reaction is produced. There is no fundamental difference between allergy and immunity.

P. G. M.

**Anæmia. I. Gas metabolism in muscles in experimental anæmia. II. Lactic acid metabolism in muscle in experimental anæmia. III. Resynthesis of lactic acid in anæmic patients.** H. SAITO (*Tôhoku J. Exp. Med.*, 1932, 19, 296—307, 308—325, 326—336).—I. In anæmic dogs the O<sub>2</sub> unsaturation of arterial blood entering the gastrocnemius muscle is increased and that of venous blood is normal.

II. In anæmic and normal dogs the venous blood leaving a muscle contains less sugar (I) and more lactic acid (II) than arterial blood. In NHPh-NH<sub>2</sub> or blood-letting anæmia the arterial and venous (II) are high. In such dogs muscular work causes a less pronounced rise in O<sub>2</sub> consumption and blood-flow and a less pronounced fall in blood-(I) than in normal animals.

III. The blood-(II) in human anæmia is at the upper level of normal limits, and the blood-(I) is normal. Intravenous injection of Na lactate (3 g.) causes a less pronounced but more prolonged rise in blood-(II) than the normal.

CH. ABS.

**Consumption of oxygen by anæmic blood.** K. SIMIDU (*Japan. J. Med. Sci., Biochem.*, 1932, 267—281).—The O<sub>2</sub> consumption of the blood-corpuseles, intact or hæmolysed, of anæmic rabbits is > that of normals. The content of the deproteinised corpuscles in cysteine and cystine, as measured by I titration before and after reduction, is markedly greater in anæmic than in normal rabbit's blood. This difference probably accounts for the change in O<sub>2</sub> consumption. W. O. K.

**Test for liver extract [for use in pernicious anæmia].** C. W. EDMUNDS, H. H. BRUECKNER, and A. I. FRITZELL (*J. Amer. Pharm. Assoc.*, 1933, 22, 91—99).—The method is based on the measurement of the reticulocyte count of pigeon's blood. It is yet only qual. E. H. S.

**Intensity of augmented adrenaline liberation elicited by asphyxiating the non-anæsthetised dog.** H. SAITO, T. INABA, and W. TAKAHASHI (*Tôhoku J. Exp. Med.*, 1932, 19, 421—439).—Asphyxia in dogs causes hyperglycæmia and increased liberation of adrenaline. The former is partly and the latter entirely inhibited by previous splanchnicotomy.

CH. ABS.

**Magnesium and cancer in Indochina.** J. BABLET and H. BADER (*Bull. Assoc. Franç. Cancer*, 1932, 21, 570—573).—In regions where cancer is prevalent the soil and surface H<sub>2</sub>O are poor in Mg.

NUTR. ABS.

**Lactic acid content of normal and carcinomatous tissue.** R. BIERICH and A. ROSENBOHM (*Z. physiol. Chem.*, 1933, 214, 271—280).—The anaërobic glycolysis of normal and cancerous tissue is of the same order. Cancerous tissue and rat's brain tissue both show an aërobic lactic acid (I) content higher than the normal. The rate of formation of (I) is not greater in carcinomatous than in normal tissue. The lessened respiration in the diseased tissue chiefly affects resynthesis, and hence produces an accumulation of (I). J. H. B.

**Action of complex-formers and X-rays on the partition of lead in organs and tumours.** E. FLINT, P. L. GÜNTHER, and F. EICHHOLTZ (*Arch. exp. Path. Pharm.*, 1933, 169, 618—624).—The partition of an active Pb isotope (I) (from radioactive Th) in normal and sarcomatous rats is not influenced by simultaneous administration of complex-formers. The fate of (I) may be closely followed by the use of multiple inoculation sarcoma (A., 1931, 976). X-Irradiation of tumours (II) does not lead to an increased deposition of (I); in old rats the Ca content of (II) increases, whilst the Pb decreases. Thus the division of Pb is not parallel with the increase in the Ca level.

F. O. H.

**Biochemistry of Rous chick sarcoma. II.** V. MORÁVEK (*Z. Krebsforsch.*, 1932, 35, 492—508, 509—522, 626—640; 36, 386—398; *Chem. Zentr.*, 1932, ii, 3120).—Sarcomatous tissue contains less dry substance and ash than normal tissue. Fowl muscle contains about 100 mg., Rous sarcoma tissue about 300 mg. Na per 100 g. Organs of normal and sarcomatous fowls contain similar amounts of K. The K content of the sarcoma is low (46, normally 300, mg. per 100 g.). Rous sarcoma contains >200, and

surrounding muscle 65, mg. Ca per 100 g. Blood-serum-Ca is rather high, and blood-Ca rather low, in sarcomatous animals. A. A. E.

**Inorganic elements in malignant tumours (Rous chick sarcoma).** V. MORÁVEK (Biochem. Z., 1933, 258, 340—346).—In advanced stages of the sarcoma (I) the surface tension,  $[H^+]$ ,  $H_2O$  content, and contents of inorg. elements (K, Na, Ca, Mg, Cl, S, P) differ, often very greatly, from those of healthy tissue (II) from the same chicks and from those of the tissue of healthy chicks (III), and in the case of some of these factors (II) also differs from (III). The tissue in the immediate neighbourhood of the tumour also has abnormal composition. W. McC.

**Extraction of specific substances from mouse sarcoma *in vitro*.** P. MENDELEEV (Compt. rend. Soc. Biol., 1932, 107, 901—902; Chem. Zentr., 1932, ii, 3120).—An extract of comminuted mouse sarcoma with Locke solution containing agar, when injected into a growing tumour, arrests its growth or reduces it. A. A. E.

**Calcium and phosphorus content of the blood in children with caries-free and carious teeth.** I. JUNDELL and H. MAGNUSSON (Acta paediat., 1932, 14, 13—18).—In children free from caries serum-P varied between 4.2 and 6.2 mg. per 100 c.c. (average 5.01) and serum-Ca between 9.6 and 12.0 mg. per 100 c.c. (average 10.55), and for those with very advanced caries P was between 4.1 and 5.3 mg. (average 4.71) and Ca between 8.9 and 11.0 mg. (average 9.92). The differences are not significant. NUTR. ABS.

**Theory of dental caries; chemical procedures for determining immunity and susceptibility.** W. D. PRICE (Dental Cosmos, 1932, 74, 1139—1156).—In persons immune to caries Ca and P tend to deposit into the tooth structure from the saliva; in susceptible persons the movement of P, and even Ca, is zero or reversed. The Ca and P in diet can be reinforced sufficiently to control caries by use of sources of vitamins and of ash-forming elements. CH. ABS.

**Mottled enamel and brown stain.** J. F. McINTOSH, G. MONTELIUS, and Y. C. MA (Chinese Med. J., 1932, 1099—1103).—The stained and mottled enamel of human teeth, frequently found in North China, contains the normal amount of org. material and of Ca and P, so that decalcification is apparently not involved in its formation. The brown stain does not contain Fe, and therefore does not arise from hæmoglobin. W. O. K.

**Lysine excretion in the urine in cystinuria.** F. A. HOPPE-SEYLER (Z. physiol. Chem., 1933, 214, 267—270).—From an evaporated urine of cystinuria there was isolated 5- $\delta$ -carbamidobutylhydantoin (I),

$NH_2 \cdot CO \cdot NH \cdot [CH_2]_4 \cdot CH \cdot CO \cdot NH \cdot CO \cdot NH$ , m.p. 198—200°, decomp. 202—205°, affording with  $HNO_2$  5- $\delta$ -aminobutylhydantoin,

$NH_2 \cdot [CH_2]_4 \cdot CH \cdot CO \cdot NH \cdot CO \cdot NH$  [chloroplatinate, m.p. 234—238° (decomp.); hydrochloride, m.p. 198—200°; chloroaurate, m.p. 189—190° (decomp.)]. (I) is probably an artefact, since it is obtained on evaporation

of a mixture of *d*-lysine sulphate,  $Ba(CNO)_2$ , and aq.  $H_2SO_4$ . J. H. B.

**Occupation and insulin action in diabetes.** F. BRAUCH (Deut. Arch. klin. Med., 1932, 174, 352—365).—Of 13 diabetics 10 showed a lower blood-sugar level, diminished urinary excretion of sugar, and a greater response to insulin during bodily work as compared with rest. NUTR. ABS.

**Protein, fat, and enzyme chemistry in relation to diabetes.** W. DYES (Chem.-Ztg., 1933, 57, 133).—A brief summary of recent work on the source of ketonic substances in diabetes. P. G. M.

**Ketogenic-antiketogenic relation in the treatment of infantile diabetes.** F. PUCHULU (Semana méd., 1932, ii, 1260—1265).—A diet with a high ketogenic:antiketogenic quotient does not disturb development in children. A const. ketosis is dangerous even in absence of glycosuria. CH. ABS.

**Serum-proteins and -lipins in infantile eczema.** H. K. FABER and D. M. BROWN (Proc. Soc. Exp. Biol. Med., 1932, 30, 335—336).—There is an increase in serum-albumin, albumin:globulin ratio, total protein, protein osmotic pressure, and cholesterol; there is a doubtfully significant decrease in serum-globulin and no change in lipin-P. NUTR. ABS.

**Blood-glutathione in fever.** H. WAELSCH and E. WEINBERGER (Arch. exp. Path. Pharm., 1933, 169, 625—632).—Fever experimentally induced in man leads to an increase in the I-reducing titre (I) of the blood, the extent of which is dependent on the initial val. of (I). That the increase appears to be limited indicates that the greater part of (I) is due to glutathione (II) and ergothioneine. Injection of (II) into normal or febrile rabbits has no action on the body-temp. F. O. H.

**Blood-, tissue-, and urine-protein in kidney diseases.** E. G. SCHENCK and H. SCHLÜTER (Arch. exp. Path. Pharm., 1933, 169, 343—364).—The constitution of human urine-proteins (I) is different from that of the blood-proteins (II), whilst that of (II) differs from day to day. With kidney disease the kidney- and liver-proteins differ from those of the normal organs both in constitution (III) and distribution (IV). The (III) and (IV) of (I) are changed by administration of urea or protein. The quotient albumin/globulin is of no diagnostic val. F. O. H.

**Glycogen-storing [liver] disease.** L. SCHALL (Münch. med. Woch., 1932, 79, 2078—2080).—Observations are made of an obscure condition involving greatly enlarged liver with abnormally high glycogen content, slight hypoglycæmia, and defective glycogen mobilisation with adrenaline. NUTR. ABS.

**Intermediary fructose metabolism in experimental liver damage.** H. STEINITZ (Z. ges. exp. Med., 1932, 82, 180—190; Chem. Zentr., 1932, ii, 2990).— $CHCl_3$ , but not  $N_2H_4$ ,  $H_2SO_4$ , pulegone, or cocaine, intensifies and prolongs fructosæmia after ingestion of fructose. A. A. E.

**Metabolism of the fatty liver. I. Respiration and respiratory quotient.** R. MEIER and E. THOENES. **II. Formation and utilisation of lactic acid.** E. THOENES (Arch. exp. Path. Pharm.,

1933, 169, 655—666, 667—676).—I. The  $O_2$  consumption of sections of liver from guinea-pigs poisoned with P or  $CHCl_3$  and showing fatty degeneration is 40—50% > that of normal starving animals, whilst the R.Q. is markedly < normal. Addition of glucose to Ringer's solution in the case of the fatty livers does not alter the  $O_2$  consumption or the R.Q.

II. Sections of livers from animals poisoned with P probably produce smaller quantities of lactic acid than similar normal liver sections. The isolated liver cell does not appear to vary from the normal in its power to convert lactic acid into carbohydrate.

W. O. K.

**Mastitis and carbohydrate deficiency.** F. WIEDMANN (Z. Unters. Lebensm., 1933, 65, 186—198).—A sufficiency of carbohydrates is important for the production of fat and lactose by the cow, and a deficiency causes a fall in these constituents in the milk, and increases in Cl content and (Trommsdorff) sediment-val. In extreme cases the milk loses its emulsifying properties, and contains blood corpuscles.

J. G.

**X-Ray irradiation in mongolism and its effect on blood-cholesterol level.** A. MADER and E. BINGENHEIMER (Jahrb. Kinderheilk., 1933, 133, 9—20).—The blood-cholesterol is ordinarily much lower in mongolism than normal and is increased on X-ray irradiation.

NUTR. ABS.

**Ammonium chloride decalcification as modified by calcium intake. Relation between generalised osteoporosis and ostitis fibrosa.** H. L. JAFFE, A. BODANSKY, and J. P. CHANDLER (J. Exp. Med., 1932, 56, 823—834).—Dogs receiving an adequate Ca diet and  $NH_4Cl$  showed less decalcification than those receiving a low-Ca diet with or without  $NH_4Cl$ .

CH. ABS.

**Viosterol in experimental fibrous osteitis.** A. J. ABELOFF and I. P. SOBEL (Arch. Pathol., 1932, 14, 471—490).—Lesions of fibrous osteitis, produced in young guinea-pigs by repeated injections of parathormone, were not significantly affected by the administration of vitamin-D.

NUTR. ABS.

**Phosphorus metabolism in general diseases of the bones.** M. LABBÉ and M. FABRYKANT (Compt. rend. Soc. Biol., 1931, 103, 381—382; Chem. Zentr., 1932, ii, 2483).—In osteomalacia and Recklinghausen's disease the blood-P (all fractions except -lipin) is low; in Paget's disease normal vals. are obtained.

A. A. E.

**Chemical diagnosis of pregnancy.** E. O. MANOILOV (Compt. rend. Soc. Biol., 1931, 106, 913—915; Chem. Zentr., 1932, ii, 3447).—Colour reactions given by serum with diuretin and Nile-blue solutions are attributed to differences in acidity, or to the presence in pregnancy serum of an enzyme which decomposes Nile-blue.

A. A. E.

**Metabolism after oral administration of glucose to non-pregnant, pregnant, and carcinomatous women.** GUTHMANN, GENTZSCH, GOEBEL, and GRÜTZMACHER (Arch. Gyn., 1932, 150, 78—125; Chem. Zentr., 1932, ii, 3115).—The effects of X-irradiation and of administration of glucose on the basal metabolism are described. In pregnancy the blood-

sugar reached a higher level and remained high longer than in non-pregnant women.

A. A. E.

**Arsenic content of the blood of women. Influence of menstrual cycle, pregnancy, and carcinoma.** H. GUTHMANN and H. GRASS (Arch. Gynäkol., 1932, 152, 127—140).—The average As content of woman's blood in the inter-menstrual period is 63.8 ( $\times 10^{-8}$  g. per 100 c.c.) (range 20.5—113.4) with little variation in the individual. During menstruation there is a 50% increase to an average of 92.5. During pregnancy the increase is still greater, reaching its max. (average 220) between the 5th and 6th months. In the later months of pregnancy there is a gradual fall, but at full term the val. is still above the inter-menstrual val. Carcinomatous subjects have a blood-As content approximating to that found during menstruation. The increase in blood-As may be related to growth processes and cell proliferation.

NUTR. ABS.

**Mechanism of the glycosuria of starvation and of under-nourishment.** M. SAKAUCHI (J. Biochem. Japan, 1932, 16, 259—316).—Moderate starvation in rabbits often produces a glycosuria (I) due to a decrease both in insulin secretion and in the kidney threshold val. With more severe starvation this phenomenon does not occur, whilst administration of glucose orally is followed by a very slight hyperglycæmia (II) and intravenously by a prolonged (II) together with (I). Hence severe starvation decreases intestinal absorption of sugar, a decrease which is accompanied by a lowering of the  $O_2$ -consumption.

F. O. H.

**Serum-proteins in infancy and in childhood. Effects of malnutrition and of acute and chronic infections on serum-proteins in infancy and in childhood.** C. H. WEBB (Amer. J. Dis. Child., 1932, 44, 1239—1248).—Normal infants up to 6 months showed low vals. for total protein (I) and particularly for serum-globulin (II), but in older children (2 years and upwards) the vals. for (I) were at the same level as those in the adult. There was no regular relation between the state of nutrition and serum-albumin (III) content, and acute infections were found to produce only comparatively mild and temporary changes in (I). During chronic infections the alterations in the vals. of (I) varied with the type of infection. The most pronounced changes were seen in (a) chronic osteomyelitis, which gave high vals. for (II), and (b) renal involvement, especially nephrosis, which was accompanied by lowered (III) and lowered total (I), but increased (II).

NUTR. ABS.

**Vitamin therapy in pulmonary tuberculosis. II. Activated ergosterol hypercalcæmia.** P. D. CRIMM (Amer. Rev. Tuberc., 1932, 26, 112—123).—A cumulative effect on serum-Ca (probably by mobilisation of Ca from the osseous system) is accompanied at first by a brief rise in P concn., and then a gradual fall. After return of Ca to normal, a repetition of the same (massive) dosage produces hypercalcæmia for a longer period. Disagreeable conditions of calcio-toxæmia are alleviated by intravenous injection of  $NaHCO_3$ . Activated ergosterol increases the Ca, and often the P, in pleural fluid.

CH. ABS.

**Transmineralisation in the lymphatic glands.** P. REINEMER (Biochem. Z., 1933, 257, 442—449).—Investigation of normal and tuberculous guinea-pig lymphatic glands shows that the K, Ca, Cl, and often the H<sub>2</sub>O contents were increased in the pathological glands, and that the Ca content further increased, whereas the K and Cl contents decreased on caseation. Investigation of human glands gave less uniform results. P. W. C.

**Chemistry and nutrition.** W. R. SIBBALD (Chem. and Ind., 1933, 173—178).—A review.

**Action of methylene-blue on cell respiration.** W. FLEISCHMANN and S. KANN (Biochem. Z., 1933, 257, 293—300).—Respiration of the retina *in vitro* is considerably increased by methylene-blue (I). If the oxidation of fructose in neutral PO<sub>4</sub>''' solution by atm. O<sub>2</sub> is partly inhibited by KCN, it is increased again by addition of (I), whereas the normal rate of oxidation without KCN is unaffected. The system fructose phosphate-(I) is discussed as a model double respiratory system, a CN'-sensitive Fe respiration and a CN'-insensitive system depending on the oxidation-reduction powers of (I). P. W. C.

**Energetics of the mammalian heart.** H. GREMELS (Arch. exp. Path. Pharm., 1933, 169, 689—723).—In a heart-lung prep., the efficiency of the conversion of the energy of oxidation into mechanical energy increases as the rate of mechanical work done becomes greater when this is brought about through increasing the min. vol., but it remains const. when the increase in mechanical work is the result of high aortic pressure. Adrenaline decreases the O<sub>2</sub> uptake specifically and independently of the heart frequency and decreases the mechanical efficiency. Strophanthin and lanadigin decrease the O<sub>2</sub> uptake, whilst the mechanical work remains const. or even increases. W. O. K.

**Metabolism of cartilage and callus-tissue.** G. KUWABARA (J. Biochem. Japan, 1932, 16, 389—402).—Cartilage (I) and callus-tissue (II) contain no oxidase, whilst the dehydrogenase activity (III) of (I) is > that of bone (IV). The epiphyseal (I) of rachitic rabbits has a sub-normal (III). Glycolysis by way of hexose phosphate formation provides energy during the formation of (I), (II), and (IV). The val. of (III) is greatest in (II) when calcification is most rapid, whilst with both (I) and (II) advanced development is accompanied by a decrease in (III). F. O. H.

**Influence of calcium on cartilage-phosphatase.** G. KUWABARA (J. Biochem. Japan, 1932, 16, 403—406).—The phosphatase of callus-tissue, unlike that of the kidney, is activated by Ca salts. Mg salts are ineffective. F. O. H.

**Metabolism of the developing egg of the sea-urchin.** J. RUNNSTRÖM (Biochem. Z., 1933, 258, 257—279).—In the eggs of the sea-urchin, on fertilisation under aerobic (I) and anaerobic (II) conditions production of acid occurs. Such production also occurs in a hypertonic medium, and is then greater under (II) than under (I). There is a close connexion between the respiration of the eggs and the synthetic processes which occur in them. The production of

hexose monophosphate (but not that of lactic acid) is an important factor in the process of development, but normal aerobic fertilisation causes no change in the phosphate fraction or lactic acid content. Under (I), in hypertonic and still more in hypotonic media, changes occur in that fraction. Extracts of both fertilised and unfertilised eggs contain cozymase. W. McC.

**Diffusion of atmospheric oxygen into oil-covered water.** Development of eggs of *Rana fusca* and *Triton taeniatus* in mineral oil. S. LALLEMAND (Bull. Soc. Chim. biol., 1933, 15, 91—109).—When covered by a layer (10—40 mm.) of pure paraffin oil, O<sub>2</sub>-free H<sub>2</sub>O attains equilibrium with the atm. O<sub>2</sub> in approx. 50 hr. With less pure oils, periods of 150—200 hr. are necessary owing to the greater oxidation of the protective oil. An anaerobic condition of the aq. layer is maintained only for the first 3—4 hr. The eggs of *R. fusca* and *T. taeniatus* develop normally when immersed in oil of various degrees of purity or in oil-covered H<sub>2</sub>O. F. O. H.

**Nutrition of flesh fly larvæ, *Lucilia sericata* (Meig).** I. Adequacy of sterile synthetic diets. A. E. MICHELbacher, W. M. HOSKINS, and W. B. HERMS (J. Exp. Zool., 1932, 64, 109—128)

NUTR. ABS.

**Fat metabolism.** P. E. VERKADE, M. ELZAS, J. VAN DER LEE, H. H. DE WOLFF, A. VERKADE-SANDBERGEN, and D. VAN DER SANDE (Z. physiol. Chem., 1933, 215, 225—257).—The use of "intarvin" and of a prep. containing undecic and tridecic acids in the treatment of diabetes is discussed (cf. A., 1930, 1206). When normal fat in the diet of diabetics is replaced by glyceryl triundecate (I), the disordered fat catabolism is partly corrected. Absorption of (I) in the alimentary tract is practically complete, whilst ketonuria and acidosis of the blood are decreased. The lactic acid excretion is unchanged, and no pyruvic acid appears in the urine. Ingestion of 100 g. of (I) is followed by the excretion of approx. 4 g. of nonane- $\alpha$ -dicarboxylic acid. The possibility of an  $\omega$ -oxidation occurring in fat catabolism is discussed. F. O. H.

**Diet and blood-cholesterol in normal women.** R. OKEY and D. STEWART (J. Biol. Chem., 1933, 99, 717—727).—Variations in the free and total cholesterol (I) of the blood were followed in women fed on diets of low (II) and moderate content (III) of (I). Substitution of (III) by (II) to which was added an amount of (I) equiv. to the deficiency, resulted in slightly lower blood vals. Increased intake of (I) produced an increased level of esterified (I) in the blood. With (III) there was little difference from the menstrual variations in (I) due to (II). F. O. H.

**Diurnal cycle in the liver.** I. Periodicity of the cycle, with analysis of chemical constituents involved. G. M. HIGGINS, J. BERKSON, and E. FLOCK (Amer. J. Physiol., 1932, 102, 673—682).—The changes in the liver of the white rat after a 2-hr. feeding and drinking period include the actual wt. of the liver, as well as the increase or decrease in the amount of H<sub>2</sub>O, glycogen, protein, and fat for a 2-day period after a single feeding. NUTR. ABS.

**Chemical rôle of normal liver in intermediary metabolism.** S. J. THANNHAUSER (Klin. Woch., 1933, 12, 49—54).—Nucleic acids are broken down in the liver by enzymes which split off  $\text{PO}_4'''$  and  $\text{NH}_2$  groups, leaving oxypurine glucosides. Deamination of  $\text{NH}_2$ -acids takes place in other organs besides the liver, and actually with greatest rapidity in the kidney. This is presumably to facilitate the excretion of fixed acids as  $\text{NH}_4$  salts. Excess  $\text{NH}_3$  is also converted by the liver into urea. In conjunction with  $\text{CO}_2$ , it is linked up with ornithine to form citrulline, which takes up a further mol. of  $\text{NH}_3$  to form arginine. This is then hydrolysed by arginase into the original ornithine and urea. The liver is the principal site of production of sugar from non-carbohydrate material. The hæmin of the blood cannot be directly converted by the liver into the bilirubin of the bile, since they are related to ætioporphyrins of different structure. A rupture and re-closure of the pyrrole ring must therefore be assumed.

NUTR. ABS.

**Energy of urea synthesis.** H. BORSOOK and G. KEIGHLEY (Science, 1933, 77, 114).—The synthesis of urea from  $\text{NH}_3$  and  $\text{CO}_2$  by liver slices is accompanied by a definite increase in  $\text{O}_2$  consumption: one  $\text{O}_2$  appears to be used for each  $\text{CO}(\text{NH}_2)_2$  synthesised. Similar results were obtained with glucose and *dl*-lactate and with and without ornithine.

L. S. T.

**Partition of nitrogenous constituents of urine and its physiological significance. II. Minimal specific excretion of endogenous nitrogen during growth.** E. F. TERROINE, G. BOY, M. CHAMPAGNE, and G. MOUROT (Bull. Soc. Chim. biol., 1933, 15, 42—62).—The total endogenous excretion of N in pigs is proportional to the energy production (A., 1927, 276). When restricted to a protein-free diet, creatine (I) tends to disappear completely from the urine, whilst with growth the excretion of  $\text{NH}_3$ ,  $\text{NH}_2$ -acid, and allantoin-N decreases parallel with the total N. During growth the proportion of excreted (I) to body-wt. is fairly const., the increase in muscle counterbalancing the decrease of functional activity.

F. O. H.

**Origin of creatine. VII.** K. THOMAS, A. T. MILHORAT, and F. TECHNER (Z. physiol. Chem., 1933, 214, 121—137; cf. A., 1932, 422).—The tolerance of the rabbit for  $\epsilon$ -guanidohexoic acid (I) (*picrate*, m.p. 152°; *picrolonate*, m.p. 236°),  $\epsilon$ -methylguanidohexoic acid (II) (*picrolonate*, m.p. 249—251°),  $\gamma$ -methylguanidobutyric acid (III) (*picrolonate*, m.p. 252—255°), and  $\delta$ -methylarginine (IV) [*diflavianate*, m.p. 231° (decomp.); *picrolonate* +  $1.5\text{H}_2\text{O}$ , m.p. 227—228°], taken *per os* is about the same as for creatine. A human patient with progressive muscular dystrophy can tolerate 3—5 times as much of (I) as of creatine, of (II) and (III) about the same amount. Glycine and  $\gamma$ -aminobutyric acid increase the creatinuria in muscular dystrophy; glutamic and hydantoic acids are without effect. In recovery of (IV) from the urine a small amount of *N*-methyl-2-amino-piperidone was isolated.

J. H. B.

Is the capacity to break down exogenous creatine a specific function of the sexually

mature organism? O. MÜHLBOCK and C. KAUFMANN (Arch. Gynäkol., 1932, 151, 706—709).—The excretion of creatine and creatinine after intravenous injection of 0.3—1 g. of creatine into women (a) during menstruation, (b) between menstrual periods, (c) with the ovaries removed or functionless by previous operation or disease, (d) after the menopause was inconst., creatinuria being sometimes present and sometimes absent.

NUTR. ABS.

**Effect of administration of tryptophan on the weight and the carbon and nitrogen excretion of the adult animal.** G. FONTÈS and L. THIVOLLE (Compt. rend. Soc. Biol., 1931, 106, 590—591; Chem. Zentr., 1932, ii, 2986).—In dogs the N excretion was unchanged, but the C excretion increased.

A. A. E.

**Effect of administration of histidine on the weight and the carbon and nitrogen excretion of the adult animal.** G. FONTÈS and L. THIVOLLE (Compt. rend. Soc. Biol., 1931, 106, 590—591; Chem. Zentr., 1932, ii, 2986).—No effect was observed.

A. A. E.

**Effect of simultaneous administration of tryptophan and histidine on the weight and the carbon and nitrogen excretion of the adult animal.** G. FONTÈS and L. THIVOLLE (Compt. rend. Soc. Biol., 1931, 106, 593—595; Chem. Zentr., 1932, ii, 2987).—The C excretion is const.; the N excretion is const. or diminished.

A. A. E.

**Variation in the protein intake of sheep in relation to wool growth.** A. H. H. FRASER and J. A. F. ROBERTS (J. Agric. Sci., 1933, 23, 97—107).—Wool characteristics (fineness, length, fibre-wt.) were not significantly different from sheep receiving high- and low-protein diets. The synthesis of cystine is suggested as a special function of the wool follicle.

A. G. P.

**Covering of nitrogen and sulphur balances by cystine at the level of endogenous protein metabolism.** E. F. TERROINE, P. MEZINCESCO, and S. VALLA (Compt. rend., 1933, 196, 502—504).—Ingestion of cystine slightly reduces the negative N balance of pigs on a carbohydrate diet at the level of min. expenditure of N; the S balance becomes positive simultaneously. There is therefore no parallelism between N and S metabolism.

A. C.

**Comparative excretion of neutral sulphur in endogenous and exogenous nitrogen metabolism, and its significance.** O. V. AMANN and G. MOUROT (Compt. rend., 1933, 196, 504—506).—The urinary N (I) and neutral S (II) of pigs are 4.85 g. and 0.137 g. daily, respectively, on a carbohydrate diet containing only 1.65 g. of protein-N per day. If the latter is increased to 30.7 g., (I) rises to 14.93 g., whilst (II) is almost stationary. On a protein diet, however (100 g. of protein-N and 5.63 g. of S per day), (I) is 70.96 and (II) shows a distinct rise to 0.427 g. There appears to be no essential difference between endogenous and exogenous protein metabolism, although, in the latter, production of neutral S is lower.

A. C.

**Effect of age on metabolism, especially on sulphate excretion in urine.** M. MÜHLMANN



(Deut. Arch. klin. Med., 1932, 174, 432—443).—A fall in the urinary excretion of  $\text{SO}_4$  occurs with advancing age. NUTR. ABS.

**Influence of thiol on the formation of aberrant disorganised overgrowths in the regenerating right chela of the hermit crab (*Pagurus longicarpus*).** F. S. HAMMETT and D. W. HAMMETT (Protoplasma, 1932, 17, 321—358).—The growth and differentiation of overgrowths are accelerated by  $\cdot\text{SH}$  and retarded by  $\cdot\text{SO}$ . The  $\text{SH}$  group is specifically responsible for the formation of certain typical emergent disorganised growths. A. G. P.

**Chemical basis of nerve stimulation.** H. WINTERSTEIN (Naturwiss., 1933, 21, 21—23).— $\text{NH}_3$  is produced at the rate of  $13.5 \times 10^{-6}$  g. per g. of nerve tissue per hr. The average increase in  $\text{NH}_3$  production by the action of reflex stimuli is 24%. Its production is a vital process in nerve metabolism. P. G. M.

**Ammonia formation in mammalian nerve.** K. HALTER (Biochem. Z., 1933, 257, 313—324).—Rabbit's isolated surviving sciatic nerve eliminates  $4-5 \times 10^{-6}$  g. of  $\text{NH}_3$  per g. per hr. Temp. does not but electric stimulation does lead to the formation of a considerably increased amount of  $\text{NH}_3$ . Mechanical stimulation also increases and asphyxiation decreases  $\text{NH}_3$  formation. When the nerve is still connected with the central nervous system,  $\text{NH}_3$  formation in the first 0.5—1.5 hr. is  $13.56 \times 10^{-6}$  g. per g. per hr., 2—3 times as great as in the isolated prep. Reflex stimulation by mechanical means increases the  $\text{NH}_3$  formation by 24% of the resting val. Urethane narcosis of the animals and asphyxiation of the nerves cause considerable decrease. P. W. C.

**Formation of carbon dioxide and ammonia by non-medullated mammalian nerves.** H. ROSENBAUM and K. HALTER (Biochem. Z., 1933, 257, 325—332).—Repetition of former work (A., 1932, 770) confirms the fact that for ox splenic nerve at body temp. the  $\text{CO}_2$  elimination is much  $<$  would correspond with the  $\text{O}_2$  absorption, leading to a R.Q. of 0.335, whereas the R.Q. at room temp. is 0.78. The excess utilisation is probably involved in dehydrogenation processes. The formation of  $\text{NH}_3$  at room temp. is of the same order as for medullated nerves and is dependent on the temp., being increased at body temp. P. W. C.

**Dependence of the oxygen utilisation of the intercostal nerves of the ox on the oxygen tension.** A. PRAGER (Biochem. Z., 1933, 257, 301—306).—The  $\text{O}_2$  utilisation of a nerve (diam. 1.9 mm.) reaches a limiting val. at 15—18%  $\text{O}_2$  and decreases below this val. approx. proportionally with the  $\text{O}_2$  tension. P. W. C.

**Elimination of carbon dioxide by nerves under reflex stimulation.** J. VON LEDEBUR (Biochem. Z., 1933, 257, 310—312).—Reflex stimulation of mammalian nerve under physiological conditions does not increase the elimination of  $\text{CO}_2$ . P. W. C.

**Sugar metabolism of non-medullated mammalian nerves.** H. ROSENBAUM (Biochem. Z., 1933, 257, 307—309).—The previously discovered (A., 1932, 770) increased utilisation of  $\text{O}_2$  by ox splenic

nerves on addition of glucose is confirmed. The excess utilisation is greatest in the first hr., the mean val. being four times that of medullated nerve under the same conditions, and then rapidly falls away. P. W. C.

**Specific dynamic action of food. II. Gas exchange after administration of carbohydrates in different animals.** U. LOMBROSO and S. DI FRISCO (Arch. internat. Pharmacodyn., 1932, 44, 50—66).—Sucrose (3—4 g.) given in  $\text{H}_2\text{O}$  by mouth had no appreciable effect on the gas exchange of pigeons or rats. In dogs orally given sucrose or intraperitoneally given glucose raised the metabolism by as much as 30%. NUTR. ABS.

**Absorption rates of galactose and mannose.** C. E. BURGET, R. LLOYD, and P. MOORE (Proc. Soc. Exp. Biol. Med., 1932, 30, 368—370).—Using closed jejunal loops in dogs and unanæsthetised rats the relative rates of absorption of galactose and mannose were: in dogs, 108:49; in rats, 115:64. Mannose were: accurately determined by the Shaffer-Hartman method. NUTR. ABS.

**Metabolism of lactose. II. Blood-sugar during lactation.** L. B. WINTER (J. Physiol., 1933, 77, 100—103).—Analysis of combined blood samples from nursing women showing lactosuria gave no evidence of the presence of either lactose or galactose. There is therefore no renal threshold for lactose. NUTR. ABS.

**Effect of glucosamine on metabolism in the pigeon.** D. C. ZUMMO (Arch. Internat. Pharmacodyn., 1932, 44, 40—49).—Oral administration of 3—4 g. of glucosamine to pigeons caused the  $\text{O}_2$  consumption to fall by as much as 30%. It returned to normal in about 2 hr. Subcutaneous or intramuscular injections of smaller doses into pigeons or rats also caused the  $\text{O}_2$  consumption to fall, and it did not return to normal in 4—5 hr. NUTR. ABS.

**Lactic acid formation in liver cells.** M. OKUYAMA (J. Biochem. Japan, 1932, 16, 237—258).—Isolated liver cells (A., 1932, 428) neither consume  $\text{O}_2$  nor form lactic acid (I) owing to the absence of hexose degradation. With unwashed cells the effect of various dyes on the  $\text{O}_2$  consumption is parallel to that on the glycolysis, but not to that on the formation of (I). On keeping, the formation of (I) rapidly decreases owing to decomp. of glyoxalase (II) coenzyme (III), whilst the  $\text{O}_2$  consumption is only slightly changed. The liver-(II) is more stable than (III). F. O. H.

**Resynthesis of lactic acid in man.** S. DIETRICH and M. ZEYEN (Z. klin. Med., 1932, 120, 517—548; Chem. Zentr., 1932, ii, 2991).—Injection of Na *r*-lactate proportionally increases the  $\text{O}_2$  demand and the  $\text{CO}_2$  produced. 2% is excreted by the kidneys; 20.9% is burnt. In liver diseases and diabetes the quantity burnt is greater. A. A. E.

**Bile acids and carbohydrate metabolism. XXIII. Influence of bile acids and of adrenaline on experimental glycocholia.** T. TANAKA (J. Biochem. Japan, 1932, 16, 407—416).—The glycocholia induced in dogs with biliary fistulae by intravenous injection of glucose is reduced by simultaneous

administration of cholic acid (I) and increased by that of adrenaline (II). Unilateral splanchnicotomy increases the action of (I), but reduces that of (II). The differences between glycosuria and glycocholia are discussed. F. O. H.

**Glutathione, iodoacetic acid, and glucose metabolism.** J. H. QUASTEL (*Nature*, 1933, 131, 206; cf. this vol., 314).—The toxicity of  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  (I) *in vivo* is diminished or eliminated by admixture with  $\text{Na}_2\text{S}_2\text{O}_3$  (II). One mol. of (I) combines with 1 of (II). The inhibitory action of small amounts of (I) on the oxidation of glucose by brain tissue is decreased or inhibited by the addition of glutathione (III), cysteine, or (II) to the tissue. There is a direct action between the S compounds and (I). (III) markedly affects the relationship between fermentation and the respiration of yeast in the presence of glucose. The toxicity of (I) towards biological processes appears to be connected with its power to combine readily with SH compounds, and (III) plays a part in processes inhibited by (I). L. S. T.

**Resistance of glucoseureide to urease and other enzyme action; non-absorbability of glucoseureide from the jejunum.** F. A. CAJORI (*Proc. Soc. Exp. Biol. Med.*, 1932, 30, 184—186).—Glucoseureide (I) was not attacked by urease or by yeast. (I) was not hydrolysed or absorbed when placed in Thiry-Vella loops, and when injected into the blood it was excreted unchanged almost quantitatively in the urine. NUTR. ABS.

**Relative fatigue recovery values of different carbohydrate mixtures.** D. A. LAIRD (*J. Ind. Hygiene*, 1933, 15, 89—97).—In the acceleration of the recovery from mental and physical fatigue, ingestion of milk (I) containing 70% maltose (II) is superior to (I) containing the carbohydrate equiv. as 20% (I) + 48% sucrose, which, in turn, is superior to milk alone. The phenomenon is explained by the greater rates of absorption and assimilation of (II). F. O. H.

**Glucose and the moulting of crustaceans.** A. DRILHON (*Compt. rend.*, 1933, 196, 506—508).—The blood-glucose (I) of crabs rises during moulting, then falls and rises again in the adult stage, but to a lower level. (I) is slightly higher in females than in males. The total glucose of crabs is approx. const. at 3.4—3.6 g. per kg., at all stages of development and in both sexes. A. C.

**Phosphorus [in the blood] and moulting of crustaceans.** A. DRILHON (*Compt. rend.*, 1933, 196, 725—726).—Although the total P in the blood of *Maia* remains const. at all stages of the animals' development (the quantity in the blood of the female being twice that of the male), the proportion of org. P increases rapidly after moulting at the expense of inorg. P, and, in adults, may then represent 84% of the total P. J. W. B.

**Natural phosphates in cattle-feeding.** H. VELU (*Rev. vet. et J. Méd. vet. et Zootech.*, 1932, Nov.).—Experiments on sheep show the toxic effects of (a) prolonged addition of small doses of natural phosphate to the ration (3% of the grain ration for 2 years); (b) providing  $\text{H}_2\text{O}$  containing  $\text{PO}_4'''$ . NUTR. ABS.

**Mechanism of adaptation to varying salinity in the common eel; osmotic regulation in fishes.** A. KEYS (*Proc. Roy. Soc.*, 1933, B, 112, 184—199).— $\text{H}_2\text{O}$  swallowing plays an essential rôle in the adaptation of eels to sea- $\text{H}_2\text{O}$  (I), but not in fresh  $\text{H}_2\text{O}$  (II). Transference of eels from (II) to (I) causes a loss in wt. due to a passive outward flow of  $\text{H}_2\text{O}$  which is counteracted after about 10 hr. by an active process, delayed by narcosis, in which  $\text{H}_2\text{O}$  is taken up, adaptation being complete in 2 days. The change from (I) to (II) results in the reverse order of wt. change. In adaptation to (I), osmotic regulation is effected by the gills which excrete excess salt due to ingested (I), whilst the kidney is responsible for adaptation to (II). The euryhaline teleost is considered a typical fresh- $\text{H}_2\text{O}$  fish in (II) and typically marine in (I). A. C.

**Increased permeability [of larvæ] to acetic acid in narcosis.** M. A. VAN HERWERDEN (*Protosplasma*, 1932, 17, 358—375).—The permeability of the tail membranes of larvæ of *Rana temporaria* and *R. esculenta* to AcOH increases and that to neutral-red and other dyes decreases during narcosis. A. G. P.

**Cellular toxicity of ethyl alcohol.** S. LALLEMAND (*Bull. Soc. Chim. biol.*, 1933, 15, 84—90).—Fresh eggs of hens, when exposed to air saturated with EtOH at 18° for periods of 9 hr. or more, are rendered sterile. The rate of penetration of EtOH vapour through the shell agrees approx. with Graham's law of diffusion, the toxic action occurring when the concn. within the egg reaches approx. 0.4%. F. O. H.

**Influence of narcotics on the sugar-excretion threshold.** Y. IWANAGA (*J. Biochem. Japan*, 1932, 16, 417—431).—Administration of morphine,  $\text{Et}_2\text{O}$ , or  $\text{CHCl}_3$  to dogs produces an increase of blood-sugar and a lowering of the kidney threshold val. The sympathetic origin of the hyperglycæmia (I) is demonstrated by its inhibition following bilateral splanchnicotomy (II) or injection of ergotamine. (I) due to adrenaline is not influenced by (II), but in such animals it is partly inhibited by narcotics. F. O. H.

**Optically active hydantoins as hypnotics.** H. SOBOTKA, S. M. PECK, and J. KAHN (*J. Pharm. Exp. Ther.*, 1933, 47, 209—215).—*l*-Phenylethylhydantoin (I) is as effective as *r*- but 1.25—1.5 times as active as the *d*-isomere (II) in regard to the min. effective and lethal doses. The toxicity of (II) is, however, only one third that of *r*- as judged by the incidence of nirvanol disease after oral administration in humans. The curative effect therefore does not depend on the appearance of the nirvanol disease. It is suggested that the mechanism of the drug eruption may be explained on the assumption that the (I) is a "spontaneous haptene." A. L.

**Piperidinopropanediol diphenylurethane hydrochloride—a new local anæsthetic.** T. H. RIDER (*J. Pharm. Exp. Ther.*, 1933, 47, 255—267).—The hydrochloride ("diothane"), m.p. 195—196°, gives unstable saturated aq. solutions containing 1.3%; > 1.0% aq. solutions are stable below  $p_H$  5.6; above this val., the free base is pptd. The aq. solutions may be sterilised without loss of activity and have considerable antiseptic power. With rapid

intravenous injection diothane is thrice as toxic as, but on subcutaneous injection less toxic than, novocaine. On mucous membrane the anæsthetic activity is twice that of cocaine; when injected it is thrice as active as novocaine.

A. L.

**Biological assay of analgesics and their mixtures.** III. E. HESSE and H. REICHEL (Arch. exp. Path. Pharm., 1933, 169, 453—458).

F. O. H.

**Complex constant of the reaction between novocaine and caffeine.** R. LABES and H. RUTENBECK (Arch. exp. Path. Pharm., 1933, 169, 557—575).—Caffeine (I) and novocaine hydrochloride (II) form a 1:1 complex, the complex const. being 20—30. Hence the retardation by high concns. of (II) of the rigor in frog's muscle due to (I) depends on this phenomenon, whilst the action of (II) at low concns. must depend on a sp. action of (II). A parallelism appears to exist between the affinity for adsorption and that for complex-formation when these affinities are correlated with the constitution.

F. O. H.

**Application quotient and the pharmacological differentiation of similarly acting drugs.** P. PULEWKA (Arch. exp. Path. Pharm., 1933, 169, 482—497).—The ratio between the doses of a drug necessary to cause death, anæsthesia, mydriasis, etc. when administered to the same animal by two different routes is termed the "application quotient." Its use in differentiating similarly acting drugs is exemplified by various mydriatics and local anæsthetics.

F. O. H.

**Purification of visceral extracts. New method of toxicological examination for alkaloids.** J. A. PINTO (Anal. Asoc. Quím. Argentina, 1932, 20, 168—175).—The extract of the macerated viscera (100 g.), obtained with dil.  $H_2SO_4$ , is neutralised, KOAc (8 g.) is added, and then a solution of an equal amount of  $SnCl_4$ . This pptn. is repeated, and alkaloids are extracted from the filtrate and washings in the usual way. 90—98% of alkaloid is recovered. R. K. C.

**Pharmacology of *Clerodendron*.** H. C. HON (Chinese J. Physiol., 1932, 6, 353—356).—A variety of Huang-teng from South China, identified as *Clerodendron commersonii*, Spreng., contained only a trace of alkaloids, the amounts being too small to cause any physiological effect. No other active principle was present.

A. L.

**Toxic action and elimination of nicotine.** I. Toxic action of nicotine and oxynicotine. II. Elimination and cutaneous absorption of nicotine and caffeine. N. SABATUCCI (Atti R. Accad. Lincei, 1932, [vi], 16, 520—523, 524—527).—I. For a frog of 20 g., the min. dose of nicotine causing complete paralysis and recovery after a few hr. is 1.2 mg. and the min. lethal dose 3 mg. With oxynicotine the min. lethal dose is 15 mg. The toxic action of nicotine thus depends, at least partly, on the chemical function blocked by the O in oxynicotine.

II. If a frog (20 g.) is placed in 200 c.c. of  $H_2O$  immediately after subcutaneous injection of nicotine, the min. lethal dose falls to 1.5 mg., but such dose remains at 3 mg. if the animal is placed in 200 c.c.

of  $H_2O$  containing the alkaloid. Similar differences are found with caffeine. T. H. P.

**Tar in cigarette smoke and its possible effects.** W. D. McNALLY (Amer. J. Cancer, 1932, 16, 1502—1514).—The tar contains nicotine, phenols,  $C_5H_5N$  bases, and  $NH_3$ . Physiological effects are discussed.

CH. ABS.

**Tobacco tar: alleged carcinogenic action.** E. BOGEN and R. N. LOOMIS (Amer. J. Cancer, 1932, 16, 1515—1521).—Tobacco tar did not produce cancer when painted on the skin of mice and rabbits over periods in which gas tar produced cancer.

CH. ABS.

[Pharmacological effect of] milk. N. J. MODI (Arch. internat. Pharmacodyn. Théor., 1932, 43, 111—121).—Frog hearts were perfused with Ringer to which were added different quantities of milk, raw, heated, or dried, or milk derivatives, casein, whey, lactose, or alcohol extract of milk. Whole milk in all cases acted as a powerful stimulant.

NUTR. ABS.

**2-Amino-1-hydroxyhydrindene, an ephedrine-like substance.** W. AUGSTEIN (Arch. exp. Path. Pharm., 1933, 169, 114—118).—The action of the compound (I) on the frog's heart and on the blood-vessels, and intestinal and bronchial muscles of homeotherms, resembles that of ephedrine (II). The toxicities for guinea-pigs and rats are equal, but for mice that of (I) is < that of (II). (I) is rapidly absorbed from the intestine.

F. O. H.

**Rôle of the augmented adrenaline secretion in dogs after guanidine on the fluctuation of the blood-sugar concentration simultaneously occurring.** H. TADA (Tôhoku J. Exp. Med., 1932, 20, 1—13).—Contrary to results obtained with normal dogs, intravenous administration of guanidine hydrochloride (I) to doubly splanchnotomised animals brought about a lowering of the blood-sugar level. Simultaneous administration of (I) and adrenaline was followed by an effect which resembled in degree and duration the algebraic sum of the results obtained from the separate administration of these two substances.

NUTR. ABS.

**Effect of acetylcholine on the carbohydrate metabolism. Blood-sugar; muscle-glycogen.** H. ERNOULD (Compt. rend. Soc. Biol., 1931, 108, 434—435, 436—440; Chem. Zentr., 1932, ii, 2483).—In normal rabbits acetylcholine (2.5 mg., subcutaneous) produces slight hyperglycæmia. In vagotomised and nephrectomised rabbits with high blood-sugar following ingestion of glucose (0.6 g. per kg.) the same quantity of acetylcholine produces hypoglycæmia.

In cats after destruction of the brain and spinal cord glycogen is not regenerated in fatigued muscle; it is regenerated, however, when acetylcholine is injected into such animals. This formation of glycogen is independent of the secretion of insulin.

A. A. E.

**Carbamylcholine. III. Action on gastric and uterine muscle. Habituation or accumulation.** W. VELTEN (Arch. exp. Path. Pharm., 1933, 169, 223—237).—Carbamylcholine chloride (A., 1932, 301) increases the tonus of and excites single contractions in the gastric musculature which are accompanied

by an increased secretion of gastric juice. It produces a contraction of the isolated uterus (cat, pig), and whilst intravenous injection of large doses increases the blood-sugar of rabbits, that of small doses has no effect. Repeated dosage is attended neither by accumulative action nor by habituation. F. O. H.

**Physiological-chemical analysis of the depressor action of organ extracts. II.** K. FELIX and A. VON PUTZER-REYBEGG (Arch. exp. Path. Pharm., 1933, 169, 214—222).—The compound  $C_4H_{12}N_6$  from mesentery (A., 1932, 414) [*disflavinate* (I), sinters 226—227°, decomp. 230—231°; *dipicrate*, m.p. 196—197° (decomp.); *dichloroaurate*, m.p. 204°] has a marked depressor activity on the atropinised cat, that of (I) being significant with  $2.5-5 \times 10^{-6}$  g. F. O. H.

**Assay of antipyretics. Comparison of an optically active antipyretic with its racemate.** W. HEUBNER and W. SILBER (Arch. exp. Path. Pharm., 1933, 169, 530—536).—Selected mice, kept at a const. external temp., or rabbits in which fever has been induced by subcutaneous injection of bacteria-rich hay infusions, are suitable subjects for the testing of antipyretics. The two optical isomerides of 1-(3-methyl- $\Delta^1$ -cyclohexenylphenyl)-2:3-dimethylpyrazolone are equal in their blood-temp. lowering action. Bis-*p*-phenetylphenylacetamidine exhibits neither antipyretic nor methaemoglobin-forming activity. F. O. H.

**Action of condiments on the movement of the intestinal villi and glucose absorption.** E. VON KOKAS and G. VON LUDÁNY (Arch. exp. Path. Pharm., 1933, 169, 140—145).—Pimento, garlic, pepper, paprika, onion, cinnamon, and caraway accelerate the movement of the villi of the isolated or *in situ* dog's or pigeon's intestine. The rate of absorption of glucose is also increased to an approx. proportional degree. These two factors lead to an increased val. of the nourishing power of a diet on addition of condiments. F. O. H.

**Toxic effects of large amounts of sugar in the blood.** C. EVANS (J. Physiol., 1933, 77, 189—193).—Nine rabbits were injected intravenously with 4.5—30 g. of sugar in 10—15% solution. Blood-sugar vals. were obtained up to 1.90%. No pathological effects could be attributed to the raised blood-sugar content. NUTR. ABS.

**Pharmacology of soaps.** J. MANGER (Arch. exp. Path. Pharm., 1933, 169, 268—274).—Aq. Na oleate (I), but not Ringer's solution, removes the effects of poisoning by quinine from the isolated frog's heart. With the normal heart, dil. aq. (I), palmitate, or stearate is more harmful than more conc. solutions. This phenomenon is contrary to the behaviour of soaps in hæmolysis, to their toxicity to tadpoles, and to their action on frog's ciliated epithelium. The growth-accelerating properties of (I) on implants of fowl embryonic tissue are not observed with plants (lupin and wheat). F. O. H.

**Avoidance and termination of pregnancy in white rats by means of fission products of fats.** B. A. KUDRJASHOV (Arch. exp. Path. Pharm., 1933, 169, 275—289).—In rats fed on a diet containing

lard which has been exposed to the air for 12—18 months, egg-implantation fails or an absorption of the embryos occurs. The fertilised egg is not killed prior to implantation. Rancid lard on saponification and extraction with org. solvents yields two fractions which, on administration to pregnant rats on a normal diet, result in termination of pregnancy, especially between the 6th and 9th day. Sterility due to the action of fatty degradation products is not identical with that due to lack of vitamin-E. F. O. H.

**Spermicidal powers of chemical contraceptives. V. Comparison of human and guinea-pig sperms.** J. R. BAKER (J. Hyg., 1932, 32, 550—556). CH. ABS.

**Experimental variation of the toxicity of digitalis. I. Influence of hypertonic solutions and of experimental uræmia.** R. KOHN and B. C. COSTOPANAGIOTIS (Arch. exp. Path. Pharm., 1933, 169, 146—163).—Intravenous injection of hypertonic aq. NaCl, urea, or glucose into cats produces definite changes in the blood-pressure (I) without injuring the circulatory system. Injection of such solutions simultaneously with or followed by continuous or single dosage of digitalis extract (II) produces similar changes in (I) and, even with 60—70% of the normal min. lethal dose of (II), death. This effect is due to osmotic changes in the blood and tissues due to the hypertonic solution; thus uræmia resulting from  $HgCl_2$ -poisoning or ligation of the ureters has the same action. F. O. H.

**Glucosides acting on the heart. I. Elimination of strophanthin under various conditions.** L. LENDE (Arch. exp. Path. Pharm., 1933, 169, 392—413).—Injection of 70—80% of the lethal dose of strophanthin (I), followed by slow continuous injection at the rate of 0.006 and 0.03 mg. per kg. per hr. into cats (II) and rabbits (III), respectively, just fails to cause death. Hence the rate of elimination or detoxication of (I) is five times as great in (III) as in (II). Experimentally induced fever in (III) increases the rate of elimination by 20—30%, whilst it is decreased by thyroidectomy and increased by administration of thyroxine. F. O. H.

**Pharmacology of *Adonis vernalis*.** R. A. HATCHER and H. B. HAAG (J. Pharm. Exp. Ther., 1933, 47, 217—232).—The average activity of four specimens of *Adonis* (I), as tested by the method of Hatcher and Broody, was < that of good quality digitalis (II). The fatal dose was 100—140 mg., the leaves being more active than the stems. A mixture of the leafy portions deteriorated 35% in 9 months. The infusion, the tincture, and the fluid extract were absorbed irregularly from the gastro-intestinal tract of the cat. (I) is an active emetic, its action being similar to that of (II). The active principles of (I) are sol. in  $H_2O$  and 70% EtOH, and a  $CHCl_3$  extract of the infusion gives a substance resembling digisol, the purified extract being half as active as cryst. digitoxin. The results indicate that (I) might be used in cases of cardiac disease if (II) were not available. A. L.

**Nitrobenzene poisoning.** W. BONDE (Pharm. Zentr., 1933, 74, 113—114).—An account of a fatal case. S. C.

**Infiltration of fat into the liver.** A. LOEWY and G. CRONHEIM (*Biochem. Z.*, 1933, 257, 267—288).—The body-wt. of starving guinea-pigs decreases less on keeping at reduced pressure than at normal air pressure. The liver decreases relatively far more than the body-wt. In fed guinea-pigs, keeping at reduced pressure leads to fatty liver, the lipin-sol. P being found chiefly in the  $\text{COMe}_2$  fraction, but in starving guinea-pigs has not this action, and the  $\text{Et}_2\text{O}$ -sol. P is increased relative to the total P. Similar experiments with rabbits, hens, and geese are reported and differences noted. P. W. C.

**Influence of rarefaction of air on the glutathione content of the liver.** S. L. MALOWAN (*Biochem. Z.*, 1933, 257, 437—441).—Seasonal variation of the glutathione content (I) of rat's and guinea-pig's liver could not be detected. (I) increases on keeping the animals at diminished pressure, during surgical shock, and in certain diseases. P. W. C.

**Effect of magnesium salts on content of reduced glutathione in the organs of the dog.** R. WOLFF and S. MANJEAN (*Compt. rend. Soc. Biol.*, 1932, 111, 779—781).—The livers of dogs which had been receiving 2 g. daily of  $\text{MgSO}_4$  contained larger amounts of reduced glutathione than did livers of control dogs. NUTR. ABS.

**Properties and biological action of complex salts of the alkaline earths.** K. MULLI and F. STAUDENATH (*Arch. exp. Path. Pharm.*, 1933, 169, 605—617).—The toxicities of Mg salts and Na citrate (I) are mutually decreased on their admixture, due to the formation in the blood of (I)—Ca citrate complexes. Determinations of the max. effect of this phenomenon, together with those of conductivity etc., indicate that in aq. solution complex salt formation occurs with 36% of (I) and 25% of  $\text{MgSO}_4$ , 20.6% of  $\text{MgCl}_2$ , 29.6% of  $\text{MgBr}_2$ , or 26% of  $\text{Mg}(\text{NO}_3)_2$ . F. O. H.

**Microscopic study of tissues of the albino rat following the ingestion of aluminium salts.** E. SCOTT and M. K. HELZ (*Amer. J. Hyg.*, 1932, 16, 865—870).—No deleterious effects were caused by Al salts ( $\rightarrow$  3.6% of feed). CH. ABS.

**Cobalt-proteins of serum and liver and their distribution in the organism. Affinity between proteins and their parent organs.** P. MASCHERPA and L. CALLEGARI (*Arch. exp. Path. Pharm.*, 1933, 169, 206—213).—Subcutaneous injection into rabbits of small amounts of Co in combination with liver-protein (I) results in a greater accumulation of Co in (I) than in the serum-protein (II). Administration of the Co compound with (I) leads to a lower content of Co in the urine and a greater content in the faeces than that of the compound with (II). The theory that this partition is due to the natural affinity of the protein for its parent organ is discussed. F. O. H.

**Spectro-analytical detection of bismuth in tissue and determination of mercury in urine.** R. PROBST (*Arch. exp. Path. Pharm.*, 1933, 169, 119—129).—Very small amounts of Bi are detectable by means of a method using a high-frequency current. Determination of amounts  $> 16 \times 10^{-6}$  g. of Hg is also possible; with urine 50 c.c. are required. With gum-tissue localised occurrence of traces of both Bi

and Cu was established, those parts free from Bi being also free from Cu. F. O. H.

**[Physiological] action of copper.** S. ODA and T. OSUKA (*Z. ges. exp. Med.*, 1932, 82, 128—142; *Chem. Zentr.*, 1932, ii, 2990).—Parenteral or enteral administration of Cu produces general metabolic changes similar to those produced by Fe. A. A. E.

**Distribution of arsenic in the organism after cutaneous resorption of therapeutic doses.** L. FUCHS (*Deut. Z. ges. gerichtl. Med.*, 1932, 19, 280—284; *Chem. Zentr.*, 1932, ii, 2497).—As ( $\rightarrow$  0.1 mg. per 100 g.) was found chiefly in the liver and kidneys, but also in the brain and heart. In bones (lower leg) 6 mg. per 100 g. was found. A. A. E.

**Microchemical determination of lead in organic material [urine].** A. NECKE and H. MÜLLER (*Arch. Pharm.*, 1933, 271, 81—92).—Separation of 0.1 mg. Pb from 500 c.c. of urine cannot be effected electrolytically, but it may be pptd. together with  $\text{PO}_4'''$  with  $\text{CaCl}_2$  and  $\text{NH}_3$ , as  $\text{PbC}_2\text{O}_4$  or as PbS, especially in presence of added  $\text{CuSO}_4$ . Titrimetric methods based on separation of  $\text{PbO}_2$  or  $\text{PbCrO}_4$  are inaccurate for  $< 0.1$  mg. Pb. Nephelometric methods with  $\text{PbSO}_3$  (Badham and Taylor, *Rep. of Dir.-Gen. of Public Health, N.S.W.*, 1925) and PbS (Danckwortt and Uhde, *A.*, 1927, i, 277) are more satisfactory, but not entirely so, neither are the usual colorimetric methods based on pptn. as PbS or the blue colour produced by  $\text{PbO}_2$  on tetramethyldiaminodiphenylmethane (I). The most satisfactory method is as follows: 1 litre of slightly acid urine is pptd. with  $\text{K}_2\text{C}_2\text{O}_4$  and  $\text{CaCl}_2$ , the ppt. ignited, and dissolved in  $\text{HNO}_3$  with addition of 15 mg.  $\text{CuSO}_4$  or  $\text{FeSO}_4$ , and metals are pptd. with  $\text{H}_2\text{S}$ . The sulphide ppt. is treated successively with  $\text{EtOH}-\text{H}_2\text{SO}_4$  and KCN solution and the residue dissolved in  $\text{HNO}_3$ . Pb is finally separated electrolytically as  $\text{PbO}_2$  and the latter determined colorimetrically with (I). The error is  $< \pm 0.02$  mg. Pb. S. C.

**Effect of thallium on metabolism.** M. KOJIMA-KIOTO (*Arch. Gynäkol.*, 1932, 152, 82—88).—Administration of Tl acetate to rats resulted during the first three weeks in a deterioration of the hair and disturbance of the sexual cycle. A qual. increase in the oxidative powers of the organism was indicated by a diminution of the urinary quotients C : N, vacate-O ( $\text{KMnO}_4$  val.) : N, and vacate-O : C. NUTR. ABS.

**Action of intravenous injection of sodium hydrogen carbonate on kidney-fat in the dog.** C. ACHARD, J. VERNE, M. BARIETY, and E. HADJIGEORGES (*Compt. rend. Soc. Biol.*, 1933, 112, 30—31).—When  $\text{NaHCO}_3$  is intravenously injected into dogs, the alkaline reserve is increased, the total blood-lipins, cholesterol, fatty acid, and lipæmic index show slight variations (usually a decrease), but the kidney-fat does not appear to be altered in spite of the alkalosis. NUTR. ABS.

**Pharmacology of inorganic thiocyanates.** E. G. JAHR (*Arch. exp. Path. Pharm.*, 1933, 169, 429—452).—The properties of the Li (I), Na (II),  $\text{NH}_4$  (III), and Ca (IV) salts were investigated in rabbits, dogs, cats, and guinea-pigs. Those of (I), (II), and (III) are

similar, being characteristic of  $\text{SCN}^-$ , whilst those of (IV) are modified by  $\text{Ca}^{++}$ . F. O. H.

**Pharmacology of metaphosphoric acids.** B. BEHRENS and K. SEELKOPF (*Arch. exp. Path. Pharm.*, 1933, **169**, 238—245).—Moderate amounts of Na hexametaphosphate (I) or of  $\text{Na}_4\text{P}_2\text{O}_7$  (II) cause no marked injury when fed to mice. Trimetaphosphate (III) occasionally leads to a loss in body-wt. When introduced by stomach-tube to mice or intravenously to rabbits, (II) is more toxic than (I) or (III). The action on blood-pressure and -coagulation indicates that the toxicity of (I) and (II) on intravenous injection is due to pptn. of Ca in the organism and that (I) and (II) are finally converted into non-toxic orthophosphate. F. O. H.

**Blood of rabbits in experimental sodium fluoride poisoning.** M. VALJAVEC (*Z. ges. exp. Med.*, 1932, **85**, 382—386).—Acute NaF poisoning causes a fall in serum-Ca and -P, a reduction in white cells, especially lymphocytes, and a shift of polymorphs to the left, but no const. changes in red cells or hæmoglobin. Chronic NaF poisoning causes a fall in serum-Ca, great variations in P, normal or increased numbers of white cells, and a fall in red cells and hæmoglobin. NUTR. ABS.

**Iodine tolerance in sheep and lambs.** S. WEISER and E. VÉGHELYI (*Fortschr. Landw.*, 1932, **7**, 289—291; *Chem. Zentr.*, 1932, ii, 3437).—Sheep receiving daily 4 mg. I as KI had normal body-wt.; the wool yield (normal quality) was 3.14 (control 2.84) kg. per animal, and its I content ( $1372 \times 10^{-6}$  g. per 100 g.) 87 times the normal val. The milk contained  $97 \times 10^{-6}$  g. per 100 g. (control 3.4) and the cheese prepared from it  $948 (3.5) \times 10^{-6}$  g. per 100 g. The wt. of the lambs was (average) 17.17 kg. (15.70 kg.). Long administration of much higher doses (40 mg. daily) had no injurious effect. A. A. E.

**Iodine metabolism in man. I. Blood-iodine and urinary excretion of iodine after single intravenous injection of inorganic iodine in cases with normal thyroids.** A. W. ELMER (*Deut. Arch. klin. Med.*, 1932, **174**, 390—398).—After determination of the fasting blood-I level, intravenous injections of  $1300 \times 10^{-6}$  g. I as KI were given and blood- and urinary I determined at intervals for 24 hr. Blood-I fell rapidly from about 40 to  $19 \times 10^{-6}$  g. on the average, in 4 hr. and was normal at 24 hr. Percentage urinary excretion was 13—17 in the first 6 hr. and 21—30 in 24 hr. After injection of 2 mg. of thyroxine giving the same amount of I, only 13% was excreted in the urine in 24 hr. NUTR. ABS.

**Effect of high altitudes on total iodine content of the thyroid.** A. RABBENO and E. VALLESI (*Arch. internat. Pharmacodyn. Thé.*, 1932, **43**, 448—460).—The I content of guinea-pig thyroids rises for 2 weeks, returning to normal at the end of the third week when the animals are taken to high altitudes (3000 m.). NUTR. ABS.

**Changes in blood metabolism under quartz lamp irradiation.** I. TEPLOV and R. MESCHERITSKAJA (*Deut. Arch. klin. Med.*, 1932, **174**, 399—414).—Systematic irradiation of healthy animals,

and of healthy and diseased men, resulted in an increased destruction of red cells, as shown by a greater excretion of urobilin in the faeces, accompanied by increased erythropoiesis with resultant reticulocytosis. The hæmoglobin content of the red cells generally was unchanged. NUTR. ABS.

**Biological action of homogeneous and heterogeneous X-rays.** C. M. SCOTT (*Proc. Roy. Soc.*, 1933, **B**, **112**, 365—383).—The responses of the allantois of the chick to homogeneous and heterogeneous X-rays are identical. There is no antagonism between components of different  $\lambda$  in mixed radiation, controverting the findings of Moppett (*A.*, 1931, 122).

**Hypoglycaemia after X-irradiation of the pancreas.** A. TERBRÜGGEN and H. HEINLEIN (*Klin. Woch.*, 1932, **11**, 1139—1142; *Chem. Zentr.*, 1932, ii, 3267).—The hypoglycaemia produced was accompanied by unchanged or hypertrophic islets and degeneration of the other pancreatic tissue. In lethal hypoglycaemia there was complete disappearance of glycogen from the liver, musculature, and other organs. The symptoms were prevented by injection of glucose. A. A. E.

**Chemical nature of enzymes.** J. B. SUMNER (*J. Nutrition*, 1933, **6**, 103—112).—A review. E. B. H.

**Discontinuity of hydration processes. II. Enzyme action.** J. V. EYRE and W. A. DAVIS (*J. Inst. Brew.*, 1933, **39**, 103—125).—A no. of enzymic processes are analysed and the hydrolysis-time curves are shown to be composed of a series of parabolas of the type  $x = Bt \pm Ct^2$ , which show abrupt changes at definite points. This holds good up to > 90% hydrolysis. The fact that the "drag" or retarding force is const. (as evidenced by the parabolic nature of the curves) indicates that the deflexion from the straight-line path is not due only to accumulation of the products of the reaction. The hydrogenation of oils in the presence of a Ni catalyst appears to be governed by similar laws. P. G. M.

**Yellow oxidation enzyme.** O. WARBURG and W. CHRISTIAN (*Biochem. Z.*, 1933, **257**, 492).—The cryst. pigment derived from the oxidation enzyme (this vol., 313) sublimes in high vac. unchanged, m.p. 329°, C 60.98, H 5.04, N 21.4%, S, ash, and halogen nil, agreeing best with the formula  $(\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_2)_n$  or  $(\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_2)_n$ . P. W. C.

**Energy relationships in biological dehydrogenations.** W. FRANKE (*Biochem. Z.*, 1933, **258**, 280—300).—A discussion of the relationship between free and total energy and heat of reaction of org. substances based on recent data concerning compounds and reactions (particularly dehydrogenations) of biological importance. W. McC.

**Specificity of dehydrogenases.** T. THUNBERG (*Biochem. Z.*, 1933, **258**, 48—64; cf. *A.*, 1920, i, 784).—The specificity of succinodehydrogenase is not abs., since it activates the H of pyrotartaric acid (I) as well as of succinic (II) and methylsuccinic acids. (I) is probably converted thus into mesaconic acid. Alkylsuccinic acids ( $\text{Me}_2$ ,  $\text{MeEt}$ ,  $\text{Et}_2$ ) are very slightly or not at all affected. Oxalic and malonic acids fix

the enzyme and reduce its effect on (II), but glutaric, adipic, alkylmalonic (Me<sub>2</sub>, Et, Et<sub>2</sub>, allyl), the alkylsuccinic acids, and (I) produce little or no such result. The H of *d*-malic acid is scarcely or not at all activated by malic dehydrogenase. W. McC.

**Determination of diffusion coefficients of substances of high mol. wt. Diffusion of catalase.** K. ZELE (Biochem. Z., 1933, 258, 347—359; cf. A., 1929, 587).—Since the mol. wt. of hæmoglobin determined by the method of Northrop and Anson agrees with the accepted val., Einstein's formula (Ann. Physik, 1906, 19, 371) is valid, in this case at least. The method cannot be applied to the determination of the mol. wt. of catalase because it decomposes on the filter. This decomp. is a species of dissociation, study of which throws light on the nature of the enzyme. W. McC.

**Determination of liquefying power of diastase.** J. J. WILLAMAN, E. W. CLARK, and O. B. HAGER (Biochem. Z., 1933, 258, 94—101).—The procedure of Józsa and Gore (B., 1930, 389) is improved by modifying the pipette in a manner described and by using CH<sub>2</sub>O as inhibitor of the enzyme action. A formula for calculating liquefying power is also given. W. McC.

**Adsorption of malt-amylase on starch.** O. HOLMBERG (Biochem. Z., 1933, 258, 134—140; cf. Arkiv Kemi, Min., Geol., 1932, 11B, No. 4, 1).—For the selective adsorption (I) on starch of  $\alpha$ -amylase from malt extracts the starch should be finely powdered. The extracts, which should be prepared with 40—50% EtOH, must contain low concn. of maltose. Low concn. of enzyme gives much better results than does high. The extent of (I) is much greater at low (0°) than at higher (20°) temp. Within the range  $p_H$  7.65—4.7 the [H<sup>+</sup>] has no effect on (I). W. McC.

**Amylases of malt and barley.** K. MYRBÄCK and S. MYRBÄCK (Biochem. Z., 1933, 258, 158—171; cf. A., 1930, 955; 1931, 1089).—The diastatic power of Swedish brewer's barley (50 samples) is between 50 and 250; its content of free and total amylase (I) varies from year to year, the order of richness of the samples remaining unchanged. Barleys rich in protein are often but not always rich in (I). On malting, the free (I) increases two- to four-fold, but the total (I) increases by <30%. As regards the effect of [H<sup>+</sup>] on them, the two amylases of malt and that of barley do not differ. W. McC.

**Relation between amount of enzyme and its reaction velocity.** N. TAKETOMI and T. HORIKOSHI (Waseda Appl. Chem. Soc. Bull., 1932, 18, 4—6).—The velocity of hydrolysis of sucrose by invertase of *Aspergillus oryzae* is not proportional to quantity or (quantity)<sup>2</sup> of enzyme. CH. ABS.

**Invertase action as a heterogeneous reaction.** T. A. WHITE.—See this vol., 357.

**Action of formaldehyde on emulsin and invertase.** M. MASCRÉ and R. PARIS (Compt. rend., 1933, 196, 438—440).—The hydrolytic effect of emulsin is retarded in media containing 0.65—3.25% CH<sub>2</sub>O. The enzyme recovered after 4 days is only slightly less active than that recovered from the

usual aq. medium. The retardation occurs mainly during the second hr., but is not due to fixation of CH<sub>2</sub>O by the enzyme, although there is an immediate liberation of acid which changes the reaction of the medium from  $p_H$  6.8 to 5.6. The inhibition is probably a physical phenomenon, and is less marked in 70% EtOH. Invertase is similarly affected. P. G. M.

**Emulsin. IX.** B. HELFERICH, H. HEYNE, and R. GOOTZ (Z. physiol. Chem., 1933, 214, 139—144; cf. A., 1932, 1063).—The ratio of the activities of emulsin heated at 45° for varying lengths of time and at different  $p_H$  towards phenol- $\beta$ -*d*-glucoside and phenol- $\beta$ -*d*-galactoside is const.; hence one enzyme only,  $\beta$ -glucosidase, probably effects both fissions. On the other hand, the  $\alpha$ -mannosidase is obviously different, since it is much more stable to heat and is attacked only moderately at 70°. J. H. B.

**Emulsin. X.** B. HELFERICH, H. APPEL, and R. GOOTZ.—See this vol., 379.

**Glycolytic degradation of carbohydrates.** R. NILSSON (Biochem. Z., 1933, 258, 198—206; cf. A., 1932, 192).—None of the hexose phosphates so far isolated has properties which indicate that it is an intermediate product in glycolysis. All results so far obtained are best explained by supposing that, during the process, the polysaccharides are first converted into hexose phosphate (I), but that in the further degradation an equilibrium is set up between the normal and the active forms of the hexose produced, this equilibrium greatly favouring the normal form. Probably (I) is an enolic form. Thus are also explained the production of glyceraldehyde phosphate (II) and of the compound C<sub>3</sub>H<sub>6</sub>O<sub>3</sub> (possibly AcCHO, H<sub>2</sub>O) especially since 2 mols. of (II) yield hexose diphosphate (A., 1932, 364). On the assumption that an activator for galactose (III) similar to Meyerhof's hexokinase exists, the production of Harden and Young's ester from (III) is also explained. W. McC.

**Fermentation of methylglyoxal.** C. NEUBERG and M. KOBEL (Biochem. Z., 1933, 258, 365—370; cf. A., 1931, 662; 1932, 1235).—Yeast converts the H sulphite compound of AcCHO, in presence of O<sub>2</sub>, first into AcCO<sub>2</sub>H and then into MeCHO. W. McC.

**Glyoxalase and its co-enzyme. I.** M. ARIYAMA and Y. KOBAYASHI (J. Biochem. Japan, 1932, 16, 317—337).—Contrary to Giršavičius (A., 1930, 814; 1931, 1455; 1932, 650), the destruction of AcCHO by liver extracts is not due to its reaction with proteins or NH<sub>2</sub>-acids present in the enzyme sample. The rate of decrease in glyoxalase (I) in liver during starvation varies with different species of animals. Enzyme preps. on keeping decrease both in (I) and in co-enzyme. Formation of lactic acid from AcCHO by blood-(I) proceeds quantitatively (cf. A., 1931, 1455). F. O. H.

**Specificity of kidney-phosphatases.** E. WALDSCHMIDT-LEITZ and F. KÖHLER (Biochem. Z., 1933, 258, 360—364; cf. Levene and Dillon, A., 1931, 123).—The phosphatase of pig-kidney hydrolyses glycerophosphate, PhH<sub>2</sub>PO<sub>4</sub>, hexose diphosphate, and adenosinephosphoric acid. The results give no support to

the view of Uzawa (A., 1932, 650) that a phosphodiesterase exists, but it seems that a sp. phosphamidase is responsible for the hydrolysis of  $\text{NH}_2$ -acids (creatine-phosphoric acid), even although the enzymic hydrolyses of both phosphoric esters and phosphoric amides are inhibited in the same way by SH compounds.

W. McC.

**Activation by magnesium of phosphatases at low concentration.** I. C. HOMMERBERG (Biochem. Z., 1933, 258, 154—157; cf. Jenner and Kay, A., 1931, 1456).—During the hydrolysis of  $\text{PhH}_2\text{PO}_4$  (Na salt) by low concn. of phosphatase in presence of  $\text{MgCl}_2$  the activating effect of the Mg and its effect on the spontaneous decomp. of the ester are in some degree additive.

W. McC.

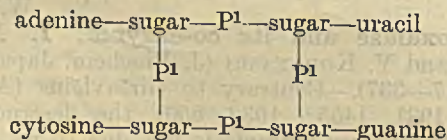
**Monophosphatases of animal organs and blood.** W. HORI (J. Biochem. Japan, 1932, 16, 433—445).—With Na glycerophosphate as substrate, the following  $p_{\text{H}}$  optima were obtained: pig's kidney, 8.8; rabbit's kidney, 8.7; defibrinated, hæmolyzed, and dialysed rabbit's blood, 4; hæmolyzed erythrocytes (I), 5; serum, 8.7; leucocytes, 8.8. The action of papain or trypsin on (I) decreased the optimum to approx.  $p_{\text{H}}$  4, that of a hæmolyzing snake venom to approx.  $p_{\text{H}}$  3, whilst that of 1%  $\text{CaCl}_2$  produced a marked increase.

F. O. H.

**Pyrophosphatase and its activator.** H. TAKAHASHI (J. Biochem. Japan, 1932, 16, 447—461).—Three monophosphatases exist with  $p_{\text{H}}$  optima at 3 (from taka-diestase or kidney), 5.6 (from rice-bran), and 8.8—10 (from kidney). There are also at least three pyrophosphatases,  $p_{\text{H}}$  optima for the hydrolysis of  $\text{Ph}_2\text{H}_2\text{P}_2\text{O}_7$  occurring at 4, 5, and 8.7 (cf. A., 1932, 305).

F. O. H.

**Enzymic dephosphorylation of nucleic acid.** H. TAKAHASHI (J. Biochem. Japan, 1932, 16, 463—481).—Neither monophosphatases (I) nor pyrophosphatases hydrolyse yeast-nucleic acid (II), whilst diphosphatases (III) in presence of (I) produce rapid diphosphorylation. By the use of a suitable type of (III) the hydrolysis can be carried out in both acid and alkaline media. The four  $\text{H}_3\text{PO}_4$  residues in (II) are therefore of the diester type and the following formula [where  $\text{P}^1 = \text{O} \cdot \text{P}(\text{O})(\text{OH}) \cdot \text{O}$ ] for (II) is advanced.



F. O. H.

**Enzymic scission of lysochitin and lecithin. Isomeride of lecithin.** A. CONTARDI and A. ERCOLI.—See this vol., 374.

**Action of esterase.** III. E. A. SYM (Biochem. Z., 1933, 258, 304—324; cf. A., 1930, 1475; 1931, 520).—In both one- and two-phase systems the  $\text{H}_2\text{O}$  content (I) of preps. (II) containing esterase has a powerful activating effect (III) on the enzyme, (III) being proportional to (I) for low (I). In two-phase systems containing little  $\text{H}_2\text{O}$  (but not in one-phase systems or in two-phase systems rich in  $\text{H}_2\text{O}$ ) the rate of action of the ground (II) increases greatly with

increase in the fineness of grinding. (II) withstand temp. up to  $75^\circ$  without loss of activity, and activity lost at higher temp. ( $90$ — $120^\circ$ ) returns after some weeks. In two-phase systems the  $p_{\text{H}}$  optimum (within the range 4.4—8.5) is 6.8.

W. McC.

**Problem of the identity of pancreas-lipase and pancreas-esterase.** G. LO MONACO (Arch. Int. Pharm. Thér., 1932, 42, 387—399; Chem. Zentr., 1932, ii, 3424).—In pancreatic extracts thermal inactivation of lipase is strictly parallel with that of esterase; for pancreatic juice different results were obtained with different animals (dog).

A. A. E.

**Effect of certain chemicals on the hydrolytic activity of Ricinus and pancreatic lipase.** R. H. CLARK and R. M. ARCHIBALD (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 87—92).—Over long periods of time I may act as an accelerator, whilst most of the other substances tested act as inhibitors. Br acts similarly to I, but larger concns. are required and the return of the activity of the lipase is slower. HCl is a marked and lactic acid a complete inhibitor.  $\text{CH}_2\text{O}$  inhibited, although some aldehydes activated at low concns. and inhibited at higher. *Ricinus* lipase was more sensitive than pancreatic.

H. G. R.

**Histochemistry of enzymes.** III. Proteinases of *Drosera rotundifolia*. H. HOLTER and K. LINDERSTRØM-LANG (Z. physiol. Chem., 1933, 214, 223—240; cf. A., 1932, 427).—The micro-method was used to investigate the activity of the proteinases using edestin as substrate. *Drosera* leaves contain two proteinases, one present in the gland secretion, optimum  $p_{\text{H}}$  3.2, and the other as endo-enzyme in the leaf tissue, optimum  $p_{\text{H}}$  4.3. The secretion proteinase probably differs from animal pepsin.

J. H. B.

**Rennin.** A. HEIDUSCHKA and W. SCHMIDT (Biochem. Z., 1933, 257, 463—466).—All relishes and spices modify the action of rennin on milk, either inhibiting coagulation by basicity or accelerating through acidity, viscosity, and dispersion. PhOH and tannic acid are exceptions, inhibiting although acidic. The substances also modify the degree of fineness of coagulation.

P. W. C.

**Action of papain on barley and malt and extracts of these.** Ageing of amylase solutions. H. LÜERS and R. LECHNER (Woch. Brau., 1933, 50, 33—38).—When papain acts on macerated barley, an increase occurs in the saccharifying amylase (I), but no significant development of liquefying amylase (II) can be detected. When malt is treated in a similar way, the increase in (I) is less marked, and again no development of (II) takes place. The protease apparently liberates the (I) from an insol. combination with protein, but is unable to effect any change in its type. When papain activated with HCN is employed, smaller increases of saccharifying power are observed, apparently due to the inhibiting action of HCN on (I), and again no development of (II) is detected. Barley or malt preps. kept aseptically for many days at  $0^\circ$ , room temp., and  $35^\circ$  show no development of (I) or (II), but malt-macerates kept for more than 100 days, in contrast to the fresh material, are able to carry the hydrolysis of starch beyond the point at which colour is developed with I.

W. O. K.



**Degradation of ovalbumin with papain.** T. SVEDBERG and I. B. ERIKSON (Biochem. Z., 1933, 258, 1—3).—The sedimentation const. of ovalbumin (ultra-centrifuge) decreases following treatment with papain activated with HCN. W. McC.

**Action of gastric juice and pancreatic juice on trypsin coated with fatty acid.** BOURCET and RAYMOND-HAMET (Bull. Acad. Méd., 1931, [iii], 105, 690—691; Chem. Zentr., 1932, ii, 2476).—"Enzypan" loses only 25% of its potency after 24 hr. treatment with human gastric juice. Pancreatic juice completely hydrolyses the fatty acid. A. A. E.

**Enzyme content of pancreas-substitute preparations.** E. WALDSCHMIDT-LEITZ and W. SCHÄFFNER (Klin. Woch., 1932, 11, 1175—1176; Chem. Zentr., 1932, ii, 2475).—Tests with commercial preps. are reported. A. A. E.

**Destruction spectrum of urease.** F. KUBOWITZ and E. HAAS (Biochem. Z., 1933, 257, 337—343).—Dil. solutions of urease are irradiated with ultra-violet light of known intensity (196—366 m $\mu$ ) and the decrease of urease activity is followed. The absorption coeffs. calc. from the destruction closely correspond with those directly measured. P. W. C.

**Uricolysis. III.** W. SCHULER and W. REINDEL (Z. physiol. Chem., 1933, 215, 258—266).—Amongst artificial oxidising agents, alkaline KMnO<sub>4</sub> and mol. O<sub>2</sub> in presence of alkaline MnO<sub>2</sub> react with uric acid (I) in a manner practically identical with that occurring during enzymic uricolysis (cf. A., 1929, 217; 1932, 882). With both reagents hydroxyacetylenediurein-carboxylic acid (II) (A., 1932, 864) is formed. Decomp. of (II) yields CO<sub>2</sub> and allantoin (III). During the formation of uroxyanic acid or carbonyl-diurea from (I), (II) is not formed, nor does the conversion of (II) into (III) by NH<sub>2</sub>Ph yield iso-allantoin at any stage. The optical inactivity of enzymically produced (III) and the relation of the intermediate products of enzymic to those of catalytic oxidation of (I) indicate that the *in vivo* formation of (III) from (I) is through (II). F. O. H.

**Purification of cocarboxylase. Its occurrence in the animal organism.** E. AUHAGEN (Biochem. Z., 1933, 258, 330—339; cf. A., 1932, 967).—Methods for preparing dry, stable, active  $\alpha$ -ketozymase and for determining cocarboxylase (I) are described. (I) obtained in 10% yield in a form 200 times as active as yeast extract contains cozymase (II) (which it is impracticable to remove) in the proportion 1:10, is free from S, and is adsorbed by Al(OH)<sub>3</sub> and animal C. The P content suggests that it is a nucleotide like (II). Uranyl acetate ppts. it, but it becomes progressively less easy to ppt. with various reagents as its purity increases. It is destroyed, although not so rapidly as (II), during the autolysis of yeast. The liver, kidney, and heart of the pig and the blood (but not the muscle) of the guinea-pig contain small amounts of it or of a substance having similar effects. W. McC.

**Yeast asparaginase.** W. GRASSMANN and O. MAYR (Z. physiol. Chem., 1933, 214, 185—210).—Yeast asparaginase (I) is extremely sensitive to acid. It is best prepared by autolysis at weakly alkaline reaction in presence of PhMe or (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and

is purified by adsorption on kaolin and elution. It is not sensitive to enzyme poisons such as HCN, H<sub>2</sub>S, and P<sub>2</sub>O<sub>7</sub><sup>4-</sup>, which may therefore be used to suppress peptidases. Glutathione inhibits slightly, 0.1% solutions of Fe<sup>III</sup> and Ni<sup>II</sup> scarcely at all, of Cu<sup>II</sup> considerably, and of Ag and Hg<sup>II</sup> completely. (I) is a highly sp. amidase. Substitution in or removal of the NH<sub>2</sub>-group of asparagine prevents the hydrolysis. The four isomeric hydroxyasparagines are inactive. Replacement of CO<sub>2</sub>H by Me inhibits fission. Aspartic acid diamide is hydrolysed, but much more slowly and only at the amido-linking  $\beta$  to the free NH<sub>2</sub> group. Glutamine is not hydrolysed by (I), but is slowly attacked by fresh yeast autolysate. (I) activity seems to demand the group,  $\cdot\text{CO}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ .

The following substrates, amongst others, were prepared: aspartic acid diamide, m.p. 141° (acetate, m.p. 144—145°),  $\beta$ -aminobutyramide (sulphate, m.p. 238°; hydrochloride, m.p. 142°), bromopropionyl-l-asparagine, m.p. 154°, [ $\alpha$ ]<sub>D</sub> +18.5° in EtOH, dl-asparagylglycine, m.p. 147°, fumaryl-l-dialanine, m.p. 265° (decomp.) (Et ester, m.p. 211.5°, [ $\alpha$ ]<sub>D</sub> +88.3° in EtOH), dl-asparagyl-l-dialanine, m.p. 213° (decomp.). J. H. B.

**Specificity of the electric charge of yeast cells.** E. A. MOLDAVSKAJA (Biochem. Z., 1933, 257, 480—483).—Pretreatment of yeast cells with gelatin enables them to migrate to the cathode both in solutions containing 0.005N-HCl and on addition of 0.005% AlCl<sub>3</sub>. P. W. C.

**Determination of hydrogen-ion concentration in living yeast and bacterial cells.** M. GUTSTEIN (Protoplasma, 1932, 17, 454—470).—Colour changes shown by certain indicators absorbed from nutrient solutions by living cells suggest that cells of particular species have an internal  $p_H$  which is fixed within narrow limits and is different from that of the nutrient. A. G. P.

**Growth of yeast.** T. PHILIPSON (Biochem. Z., 1933, 258, 244—250; cf. A., 1932, 550).—The material (I) from green peas which promotes the growth of yeast consists of at least two components. It is sol. in H<sub>2</sub>O and EtOH-Et<sub>2</sub>O mixture, but insol. in Et<sub>2</sub>O. Inositol, mannitol, and dulcitol do not increase the growth-promoting effects of (I). (I), but not its components separately, promotes growth in various strains of yeast. W. McC.

**Effect of inositol, of bios II, and of both together in the culture medium, on the reproduction of twelve kinds of yeast.** H. STANTIAL (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 163—164).—Yeasts, the growth of which is greatly increased by media containing both bios I and II, are: Wildier's yeast, *S. cerevisiae*, *S. validus*, *Sch. octosporus*, baker's and brewer's yeasts. Growth of *S.* and *Zyg. mandschuricus* is increased by bios II only. *S. pastorianus* is unsuited for determination of bios. H. G. R.

**Fractionation of bios II.** W. L. MILLER, E. V. EASTCOTT, and E. M. SPARLING (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 165—169).—Large-scale prep. of relatively pure bios II from malt combings is described. The product is easily fractionated into bios IIa and IIb by shaking with C in acid solution.

There is no reason to assume more than one IIa and one IIb. H. G. R.

**Yeast cozymase.** K. MYRBÄCK, H. VON EULER, and H. HELLSTROM (Z. physiol. Chem., 1933, 214, 184; cf. this vol., 95).—The priority of Dhéré (A., 1905, ii, 783) is recognised. J. H. B.

**Synthetic hexose phosphates. II.** K. JOSEPHSON and S. RORFE (Biochem. Z., 1933, 258, 147—153; cf. A., 1930, 1166; 1929, 1044).— $\gamma$ -Acetyl- $\zeta$ -triphenylmethyl- $\alpha\beta$ -isopropylidene-glucose, treated with  $\text{POCl}_3$  in  $\text{C}_5\text{H}_5\text{N}$ , yields the  $\varepsilon$ -phosphate (Ba salt), which, on hydrolysis with  $\text{H}_2\text{SO}_4$ , yields glucose  $\varepsilon$ -phosphate [Ba salt,  $[\alpha]_D^{20} +15.8$ ; strychnine salt, m.p. about  $160^\circ$  (decomp.)]. The behaviour of the phosphate on fermentation indicates that it cannot occur as an intermediate product in the fermentation of glucose to EtOH and  $\text{CO}_2$ . W. McC.

**Putrefactive products of beer yeast.** K. NISHIDA (Bull. Chem. Soc. Japan, 1933, 8, 14—22).—8 kg. of dried beer yeast, when putrefied in  $\text{H}_2\text{O}$  at  $10$ – $28^\circ$ , yielded  $\text{CH}_3\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$  (7.2 g. of hydrochloride), adenine (11.5 g. of nitrate), hypoxanthine (13.7 g. of hydrochloride), histamine (9.1 g. of hydrochloride), tyramine (12.4 g. of hydrochloride), putrescine (1.1 g. of hydrochloride), cadaverine (4.1 g. of hydrochloride), leucine (324.9 g.), and  $\text{NH}_3$  (128.74 g.). R. S. C.

**Cytochrome spectra of brewer's yeasts.** H. FINK and E. BERWALD (Biochem. Z., 1933, 258, 141—146; cf. A., 1932, 1167).—Yeasts having two-banded cytochrome spectra are converted into those having four-banded cytochrome spectra by long-continued cultivation in air in large shallow dishes containing shallow layers of nutrient media (preferably containing sucrose). The converted yeast sometimes reverts to the original type on further propagation. W. McC.

**Influence of oxygen on alcoholic fermentation.** A. J. KLUYVER and J. C. HOGERHEIDE (Compt. rend., 1933, 196, 443—445).—When a large excess of  $\text{O}_2$  is present relative to the amount of yeast, fermentation is partly inhibited as indicated by Meyerhof, but the reverse holds good, as shown by Windisch, when the  $\text{O}_2$  is kept const. at a lower level. P. G. M.

**Influence of iron on aerobic alcoholic fermentation.** A. MALKOV (Ukrain. Chem. J., 1932, 7, [Sci.], 75—83).—The fermentation of sucrose by yeast is stimulated by the presence of 0.6—4.8 mg. of  $\text{Fe}^{II}$  per 100 c.c. of medium; higher concns. (9.6 mg. per 100 c.c.) retard fermentation. The quality of yeast grown in media containing Fe is normal, whilst the yield is higher, as is also assimilation of N and of P. R. T.

**Acceleration by arsenate of fermentation by yeast.** A. HARDEN (Biochem. Z., 1933, 258, 65—68).—The accelerating effect of  $\text{Na}_2\text{HAsO}_4$  on the fermentation of hexose diphosphate (I) by zymisin is  $>$  that of  $\text{K}_2\text{HPO}_4$ , although the effect of the two substances acting simultaneously is  $<$  the calc. val. The results support the view that arsenate accelerates the direct fermentation of (I). W. McC.

**Method of action of Euler's Z-factor.** K. MYRBÄCK and H. LARSSON (Biochem. Z., 1933, 258, 118—133; cf. A., 1925, i, 209). The factor, which

is very stable and is not destroyed by long boiling, greatly activates aerobic and anaerobic fermentation by certain fresh and dried yeasts. The smaller is the amount of yeast the greater is the effect of the factor, which, however, has little effect on the respiration. As regards respiration, fermenting power, effect of hexose phosphate, effect of KCN, and period of induction, differences, sometimes great, are found between the different kinds of yeast. W. McC.

**Large-scale laboratory cultivation of moulds.** W. H. PETERSEN, L. M. PRUESS, H. J. GORCICA, and H. C. GREENE (Ind. Eng. Chem., 1933, 25, 213—215).—A steriliser-incubator is described capable of growing 9 sq. m. of mould mycelium in pure culture. E. B. H.

**Resorption of potassium by *Penicillium glaucum* growing in Raulin's solution with increasing additions of potassium chloride.** P. BRETIN, P. MANCEAU, and J. REY (Compt. rend. Soc. Biol., 1931, 106, 652—653; Chem. Zentr., 1932, ii, 2981).

**Behaviour of *Penicillium glaucum* growing in Raulin-type solutions with increasing additions of aluminium chloride.** P. MANCEAU (Compt. rend. Soc. Biol., 1931, 106, 654—655; Chem. Zentr., 1932, ii, 2981—2982).—No effect on the sugar metabolism was observed. A. A. E.

**Action of certain fungi on solutions of aldoses and other carbohydrates. VI. Formation of oxalic acid from *d*-gluconic acid.** A. ANGELETTI and D. PONTE (Annali Chim. Appl., 1933, 23, 33—37).—When grown in solutions of Ca *d*-gluconate, *Penicillium crustaceum* (L.), Fries, yields  $\text{CaC}_2\text{O}_4$  and a little  $\text{CaCO}_3$ . In Na citrate solution, this mould gives  $\text{Na}_2\text{CO}_3$  in small quantity, but no  $\text{H}_2\text{C}_2\text{O}_4$ , whilst *P. luteum-purpurogenum*, st. 2A, does not attack the citrate. Hence the  $\text{H}_2\text{C}_2\text{O}_4$  is formed from *d*-gluconic acid directly. T. H. P.

**Oxygen requirements of *Neurospora sitophila* for formation of perithecia and growth of mycelium.** F. E. DENNY (Contr. Boyce Thompson Inst., 1933, 5, 95—102).—Perithecia were produced in atm. containing  $< 1\%$  of  $\text{O}_2$ . The growth-rate of mycelium was not retarded until the  $\text{O}_2$  concn. was reduced to 0.1%, and ceased only in the presence of alkaline pyrogallol.  $\text{CO}_2$  up to 30% did not retard mycelial growth. A. G. P.

**Susceptibility of *Bilharzia miracidia* to different salts and different  $p_{\text{H}}$ .** A. HASAN (J. Egypt. Med. Assoc., 1933, 16, 229—231).—Slight acidity ( $p_{\text{H}}$ ) killed them in 30 min. Salt solutions at 0.5—0.9% are effective in 4 hr. H. G. R.

***Pseudomonas Lindneri-Kluyver* (*Termobacterium mobile*, Lindner).** Aerobic and anaerobic fermentation. Alcohol formation. K. SCHREDER, R. BRUNNER, and R. HAMPE (Woch. Brau., 1933, 50, 43—48).—The bacterium (I) ferments sugar in inorg. media, producing EtOH and lactic acid (II) under both anaerobic (III) and aerobic conditions (IV). The fermentation  $\text{CO}_2$  production is the same for (III) and (IV), whilst the production of EtOH and that of (II) are respectively smaller and greater with (IV) than with (III). With (IV) addition of EtOH has no significant effect on the fermentation,

although a small additional amount of EtOH is metabolised by (I). The amount of (I) added to the culture influences to a certain extent the respiration and the formation of (II) and EtOH. Max. assimilation occurs with (IV) following the addition of EtOH. This assimilation continues, although at a reduced rate, to the end of the fermentation.

F. O. H.

**Assimilation of carbonic acid.** F. M. MULLER (Chem. Weekblad, 1933, 30, 202—207).—Under the action of light, red S bacteria are able to reduce  $\text{CO}_2$  to  $\text{CH}_2\text{O}$  in presence of various H donors. They contain pigments related to carotene and xanthophyll, and a parallel exists between the reduction of  $\text{CO}_2$  by these organisms and assimilation in green plants, from which it is concluded that reduction of  $\text{CO}_2$  depends on the presence of a H donor, in this case  $\text{H}_2\text{O}$ . Carotenoids are absent from green S bacteria, and the latter reduce  $\text{CO}_2$  only in presence of  $\text{H}_2\text{S}$ . The presence of carotenoids in photosynthesis is connected with the occurrence of less active donors than  $\text{H}_2\text{S}$ . From a consideration of the energy relationships, it follows that four light quanta are absorbed per mol.  $\text{CO}_2$  assimilated, and the reduction to  $\text{CH}_2\text{O}$  takes place in two stages by way of  $\text{HCO}_2\text{H}$ . Accepting the fact that both chlorophyll and carotene are loosely combined in the chloroplast with protein, it is suggested that  $\text{CO}_2$  becomes attached to Mg in chlorophyll and  $\text{H}_2\text{O}$  to a double linking in carotene. The absorption of light quanta causes an electronic disturbance in the chlorophyll, which is passed on through the protein to the carotene forming + and - poles at the absorbed  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , respectively.  $\text{H}^+$  and  $\text{OH}^-$  ions are subsequently discharged at these poles, giving  $\text{HCO}_2\text{H}$  and  $\text{H}_2\text{O}_2$  and finally  $\text{CH}_2\text{O}$  and  $\text{O}_2$ .

S. C.

**Influence of inorganic salts on the multiplication of *Gonococcus*.** C. P. MILLER, jun., A. B. HASTINGS, and R. CASTLES (J. Bact., 1932, 24, 439—455).—In the effects on the growth of *Gonococcus* Na and K were interchangeable and non-toxic even at high concns. Ca and Mg were non-essential and inhibited growth in concns. > 30 millimols. per litre. The toxic action of Ca, but not that of Mg, was prevented by addition of citrate or oxalate. The growth range of the organism was  $p_{\text{H}}$  6.0—8.2 with optimum 7.0—7.6. Substitution of  $\text{Cl}^-$  for  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  in the media did not affect growth. Nutrients must be well buffered with  $\text{HCO}_3^-$  or phosphates.

A. G. P.

**Effects of various neutral salts on the growth of bacteria. I—III. Sodium and potassium salts.** G. KOBAYASHI (Japan. Z. Mikrobiol. Path., 1932, 26, 1—15, 16—31, 32—42).—Experiments with *S. aureus*, *B. pyogenes*, *Eb. typhi*, *Es. coli*, and *V. aquatilis* are described.

CH. ABS.

**Production of hydroxylamine by the reduction of nitrates and nitrites by various pure cultures of bacteria.** G. A. LINDSEY and C. M. RHINES (J. Bact., 1932, 24, 489—492).—Organisms of diverse types produce  $\text{NH}_2\text{OH}$  from  $\text{NO}_3^-$  and  $\text{NO}_2^-$ .

A. G. P.

**Carbohydrate common to the group of acid-fast organisms, including the tubercle bacilli.**

A. BRANCH (Tubercle, 1932, 13, 481—488).—The common (precipitin) carbohydrate is not related to the pathogenicity or virulence of acid-fast bacilli.

CH. ABS.

**Influence of silica on the growth of the tubercle bacillus.** R. M. PRICE (Canad. J. Res., 1932, 7, 617—621).—0.01 mg. of  $\text{SiO}_2$  (colloidal or as Na silicate) per c.c. of Dorset's egg medium increases the growth of the tubercle bacillus *in vitro*.

R. S. C.

(a) Non-specific complement fixation reaction due to ion antagonism. (b) Mechanism of complement fixation. A. HAMBLETON (Canad. J. Res., 1932, 7, 583—595, 596—605).—(a) The complement fixation test for tuberculosis gives a non-sp. (falsely positive) reaction with Petroff's whole bacillus antigen (but not with the "fat-free" antigen), if the plain saline solution be replaced by a solution containing the following salts in the molar concns. stated: NaCl 0.152,  $\text{CaCl}_2$  0.0005—0.0025 (optimum 0.0008), and  $\text{MgCl}_2$  0.0002—0.001 (optimum 0.0003). It is considered that the antagonistic effects of Na and Ca ions produce at the surface of the antigen particles a state of unstable equilibrium which leads to agglutination and hence complement fixation.

(b) Complement fixation is not due to sp. chemical affinity; it is produced by modification of the physical properties of the tuberculo-antigen, either by immune serum or by non-sp. means.

R. S. C.

**Composition of the active principle of tuberculin. XV. Precipitated purified tuberculin protein suitable for the preparation of a standard tuberculin.** F. B. SEIBERT and B. MUNDAY (Amer. Rev. Tuberc., 1932, 25, 724—737).—The protein is obtained by growth on a non-protein synthetic medium, ultrafiltration, and one pptn. with  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ . This protein is relatively stable and its potency varies almost within the range of experimental error of the skin test. Pptn. with  $(\text{NH}_4)_2\text{SO}_4$  affords a pure product, but is tedious.

CH. ABS.

**Toxicity of toxins after treatment with aluminium hydroxide or tapioca.** S. SCHMIDT (Compt. rend. Soc. Biol., 1932, 107, 330—332; Chem. Zentr., 1932, ii, 3429).—Diphtheria and tetanus toxins can be detoxicated, with preservation of antigenic properties, by treatment with  $\text{Al}(\text{OH})_3$  (Willstätter) or tapioca powder, thus permitting hyperimmunisation.  $\text{Al}(\text{OH})_3$  added to the anatoxin stimulates the formation of antibodies.

A. A. E.

**Adsorption of bacteriophage with kaolin and infusorial earth.** M. L. RAKIETEN and G. A. HUNT (Amer. J. Hyg., 1932, 16, 823—831).—Prep. of protein-free phage of high titre was not accomplished.

CH. ABS.

**Photodynamic action of methylene-blue on bacteriophage.** J. R. PERDRAU and C. TODD (Proc. Roy. Soc., 1933, B, 112, 277—287; cf. Clifton, A., 1931, 1461).—Phages for two staphylococci and a dysentery strain are inactivated by methylene-blue (optimal concn. 1 in 100,000) in the presence of light and  $\text{O}_2$ , both of which are necessary. The phages are not reactivated by reducing agents; they are rendered resistant to inactivation by previous union with living bacteria, not necessarily homologous.

A. C.

**Photodynamic action of methylene-blue on certain viruses.** J. R. PERDRAU and C. TODD (Proc. Roy. Soc., 1933, B, 112, 288—298).—Similar phenomena of sensitivity of several viruses to methylene-blue are observed (cf. preceding abstract). Some are protected by living cells from infected animals. The photodynamic action appears to be an oxidative process. A. C.

**Bacterial detoxification.** R. S. HARRIS and J. W. M. BUNKER (Proc. Amer. Acad. Arts Sci., 1932, 67, No. 5, 147—168).—The action of Na ricinoleate (I) is due to mol. structure as well as surface tension effects. (I), tri(hydroxyethyl)amine ricinoleate (II), and ephedrine ricinoleate afforded evidence of detoxification of tubercle bacillus. (II), but not Me ricinoleate, detoxified *S. aureus*. CH. ABS.

**Effect of organic substances on the toxic action of hypochlorite in *B. coli*.** A. ROUSLACROIX, L. BOYER, and J. BOIRON (Compt. rend. Soc. Biol., 1931, 108, 102—104; Chem. Zentr., 1932, ii, 2478).—Peptone and sewage rich in org. matter diminish the disinfective action of NaOCl; glucose and urea do not affect it. A. A. E.

**Action of iodopyridone derivatives on streptococci.** A. BINZ and H. MAIER-BODE (Biochem. Z., 1933, 257, 351—360).—A table shows the disinfecting power against streptococci of a large no. of C<sub>5</sub>H<sub>5</sub>N derivatives. 4- and 2-Hydroxy- and 5-iodo-4-hydroxy-pyridine are inactive, but 5-iodo-2-hydroxy-pyridine in 0.5% solution has the disinfecting power of PhOH, whilst the more sol. Na salt is less active. Iodopyridones in considerable doses are often non-toxic (cf. A., 1932, 1060). P. W. C.

**Oligodynamic action of silver on bacteria and bacteriophage.** E. WOLLMAN and (MME.) E. WOLLMAN (Compt. rend. Soc. Biol., 1931, 108, 111—113; Chem. Zentr., 1932, ii, 2477).—The action increases with rise of temp. Bacteriophages are more resistant than bacteria. A. A. E.

**Effect of adrenaline on liver- and muscle-glycogen.** I. I. NITZESCU and N. MUNTEANU (Compt. rend. Soc. Biol., 1931, 108, 294—296; Chem. Zentr., 1932, ii, 2481).—Hyperglycæmia following injection of adrenaline into the portal vein is produced by mobilised liver-glycogen, and hyperlactacidæmia by that of muscle-glycogen. A. A. E.

**Effect of adrenalectomy on sugar tolerance.** E. HILL and A. E. KOEHLER (Proc. Soc. Exp. Biol. Med., 1932, 30, 244—247).—Removal of the adrenals lowers sugar tolerance. NUTR. ABS.

**Basal metabolism in thyroidectomised, bilaterally adrenalectomised, and castrated rabbits.** T. KAIWA (Tôhoku J. Exp. Med., 1932, 10, 440—444).—Thyroidectomy, with castration and/or adrenalectomy, causes a fall in the basal metabolism of rabbits. CH. ABS.

**Influence of thyroxine on tissue oxidation.** G. MYHRMAN (Acta med. Scand., 1932, 79, 323—330).—Thyroxine does not increase the oxidation intensity of tissue pulp as shown by methylene-blue technique. NUTR. ABS.

**Effect of thyroxine on blood-cholesterol and -lipin.** C. I. PARHON and I. ORNSTEIN (Compt. rend. Soc. Biol., 1931, 108, 303—304; Chem. Zentr., 1932, ii, 2481).—Intramuscular injection of thyroxine (1 mg. every other day) diminishes the blood-cholesterol, -fatty acid, and -total fat in old age. A. A. E.

**Effect of thymus preparations on experimental hyperparathyroidism.** H. G. SCHOLTZ (Z. ges. exp. Med., 1932, 85, 547—558).—Administration of thymus extract to rats led to a fall in serum-Ca. Simultaneous administration of thymus extract and parathormone prevented a rise in serum-Ca and decalcification of bones. Splenic extract did not prevent parathormone hypercalcæmia. NUTR. ABS.

**Effect of splenectomy and splenic extracts on blood-sugar in the dog.** N. FIESSINGER and R. CATTAN (Compt. rend. Soc. Biol., 1933, 112, 53—55).—Splenectomised dogs show a tendency to high normal fasting blood-sugar levels, prolonged but not intensified alimentary hyperglycæmia, and diminished sensitivity to insulin, although their hyperglycæmic response to adrenaline is unchanged. Injection of a purified extract of spleen causes a transient hypoglycæmia in splenectomised, but not in normal, dogs. This action occurs even in the absence of the pancreas, but the active agent is thought not to be insulin. NUTR. ABS.

**Conversion of urinary folliculin into an ether-extractable form.** B. ZONDEK (Klin. Woch., 1932, 11, 812; Chem. Zentr., 1932, ii, 3265).—A claim for priority. A. A. E.

**Effect of hormones on blood-sugar regulation.** L. ELEK (Z. ges. exp. Med., 1932, 85, 227—234).—The blood-sugar curve (I) after oral administration of glucose is the same in the pregnant and non-pregnant woman; glycosuria is more frequent in the former. A second dose of glucose 1—1½ hr. after the first often leads to the Staub effect [second peak in (I)] both in the pregnant and non-pregnant. Previous administration of folliculin leads to a rise in the height of (I) in the female rabbit and a fall in the male, increases the hypoglycæmic effect of insulin, and reduces the hyperglycæmic effect of adrenaline. Anterior pituitary extract increases the hyperglycæmic effect of the adrenaline. NUTR. ABS.

**Relation between mouse- and rat-unit of the cestrus-producing hormone.** H. KREITMAIR (Arch. exp. Path. Pharm., 1933, 169, 576—584).—The ratio mouse unit : rat unit for any cestrin prep. depends on the medium in which the prep. is suspended or dissolved. Thus for aq. sols (with lecithin as protective agent) the ratio is 1 : 1, whilst for solutions in oil it is 1 : 4. F. O. H.

**Purification of the gonadotropic hormone (prolan).** B. ZONDEK, H. SCHEIBLER, and W. KRABBE (Biochem. Z., 1933, 258, 102—105).—Fresh pregnancy-urine (or such urine preserved with Et<sub>2</sub>O) is treated with EtOH, the ppt. is extracted with Et<sub>2</sub>O, and the insol. portion is dissolved in H<sub>2</sub>O. To the aq. solution phosphomolybdic acid is added and the ppt. produced, after separation in the centrifuge, is treated with Ba(OH)<sub>2</sub>, excess of which is then

removed by  $\text{CO}_2$ . The filtrate from the  $\text{BaCO}_3$  is then evaporated in a vac. Further purification is achieved by dialysis, which yields a product having activity of  $10^6$  rat units per g. 100% of the hormone is thus extracted. The crystals obtained by Claus and those described by Lejwa (this vol., 194) are probably not pure hormone. W. McC.

**Gonad-stimulating principle of the anterior lobe of the pituitary.** H. B. VAN DYKE and Z. WALLEN-LAWRENCE (J. Pharm. Exp. Ther., 1933, 47, 163—181).—The gonad-stimulating principle retains its activity for 5 months if kept in aq. solution at  $p_{\text{H}}$  3.7—6.4. At  $p_{\text{H}}$  7.5, the solutions are stable for at least  $2\frac{1}{2}$  months. Boiling in aq. solution at  $p_{\text{H}}$  4.9—5.4 causes inactivation, but no deterioration is caused at acid  $p_{\text{H}}$  by 0.25% *m*-cresol after 6 weeks. Filtration through Berkefeld candles does not remove the hormone. The posterior lobe pressor principle is removed by treatment of the dry pituitary body with aq. 0.02N- $\text{NH}_3$  for 24 hr. at room temp. After bringing to  $p_{\text{H}}$  5.0 with AcOH, the solution is centrifuged and EtOH added until the concn. is 35%; from the supernatant liquid the gonad-stimulating principle is pptd. by adding EtOH until concn. is 70%. Gonad-stimulating powders are free from Mn.

A. L.

**Growth-promoting action of anterior pituitary extracts.** H. LUCKE and R. HÜCKEL (Arch. exp. Path. Pharm., 1933, 169, 290—297).—Continuous intramuscular injection of anterior pituitary extract into rats produces a rate of growth, but in only a few cases a final wt., > normal. The changes occurring in the articular cartilage of the tibial epiphysis are typical of the sp. arthritis of acromegaly in man.

F. O. H.

**Thyreotropic hormone of the anterior pituitary gland.** H. HORSTERS (Arch. exp. Path. Pharm., 1933, 169, 537—556).—Injection of the hormone into normal persons produces a decrease in the blood-sugar and -pressure. In cases of deficient glycogen metabolism this action is enhanced and, as with insulin, the assimilation of carbohydrate and phosphate is improved. The hormone, the mechanism of which involves the central nervous system, appears to be concerned with the genesis of "pituitary diabetes."

F. O. H.

**Isoelectric point of insulin.** Electrical properties of adsorbed and crystalline insulin. O. WINTERSTEINER and H. A. ABRAMSON (J. Biol. Chem., 1933, 99, 741—753).—Insulin (I) has a fairly const. solubility of 0.0004% in *M*/30-acetate buffer of  $p_{\text{H}}$  4.8—6.5. In the same media, nephelometric determination of flocculation gives a max. of  $p_{\text{H}}$  5.4, whilst electrophoresis of (I) adsorbed on quartz particles or pptd. in an amorphous form indicates an isoelectric point of  $p_{\text{H}}$  5.3—5.35 (cf. A., 1932, 1292). Suspended crystals of (I) have a zero mobility at  $p_{\text{H}}$  5.0. The difference in the surface behaviour of adsorbed and cryst. (I) is discussed. F. O. H.

**Reduction of toxicity of insulin.** E. M. WALTER (Z. ges. exp. Med., 1932, 85, 495—500).—The addition of physiological saline, serum, or 5% red-cell suspensions lessened the hypoglycaemic action of insulin in rabbits. The greatest effect was produced when an

insulin and red-cell mixture was kept in a thermostat for 1 hr. before injection. NUTR. ABS.

**Observations on various insulin mixtures administered per os.** E. S. GAIS (Proc. Soc. Exp. Biol. Med., 1932, 30, 216—218).—To prevent enzymic destruction of insulin administered by mouth, an extract from *Ascaris lumbricoides*, containing an anti-protease which prevents the destruction of insulin by peptic and tryptic proteases *in vitro*, has been mixed with it. When administered to fasting rabbits by stomach tube, this mixture caused no hypoglycaemia. Whether the hormone was unabsorbed or destroyed was not ascertained. NUTR. ABS.

**Ketosis in the pancreatic and phloridzin diabetes of hypophysectomised dogs.** C. T. RIETTI (J. Physiol., 1932, 77, 92—96).—The removal of the pituitary body in the fasting dog reduces phloridzin glycosuria and results in a fatal hypoglycaemia (I), which is prevented by a diet of meat or sugar but not of fat. Removal of the thyroid or the posterior lobe of the pituitary body or lesions of the tuber cinereum do not produce this (I), which is therefore attributed to removal of the anterior lobe of the pituitary. Analysis shows that, following hypophysectomy, the capacity to form blood-sugar at the expense of endogenous protein is diminished, as also is ketosis. NUTR. ABS.

**Changes in phosphate fractions and glycogen of muscle in fasted cats and in diabetes without and after insulin.** V. M. VESSELKINA (Z. ges. exp. Med., 1932, 85, 463—476).—Starvation led to a fall in hexose phosphate (I), creatine phosphate, and glycogen (II), a rise in adenyl phosphate (III), and no change in total P (IV). In depancreatized animals there was a fall in (I) and (II), a rise in (III) and lipin-P, and no change in (IV). In depancreatized animals treated with insulin (V) there was a return of all the P fractions to normal, but the (II) remained low. During hypoglycaemia there was a rise in (I) above normal and a fall in (III). The fall in muscle-(II) after administration of (V) is not to be interpreted as evidence against the glycogenetic function of (V); the fall is probably due to increased formation of (I). (V) apparently regulates the initial stage of carbohydrate and P metabolism in muscle.

NUTR. ABS.

**Biochemical and physiological action of carotene and vitamin-A.** H. VON EULER (Ergeb. Physiol., 1932, 34, 361—405).—A review.

**Carotenoids.** P. KARRER (Ergeb. Physiol., 1932, 34, 812—847).—A review.

**Vitamin of growth. IV.  $\gamma$ -Carotene.** R. KUHN and H. BROCKMANN (Ber., 1933, 66, [B], 407—410).—Fractional adsorption of purified carotene by activated  $\text{Al}_2\text{O}_3$  followed by elution with MeOH-light petroleum permits the isolation, as most readily adsorbed material, of  $\gamma$ -carotene (I),  $\text{C}_{40}\text{H}_{56}$ , m.p.  $178^\circ$  (vac., corr.), which is optically inactive. It differs from other carotenes in absorbing  $12\text{H}_2$  and yielding  $\text{COMe}$ , when degraded with  $\text{O}_3$ . In absorption spectrum and adsorptive behaviour it occupies a position intermediate between  $\beta$ -carotene and lycopene. The

constitution  $\text{CH}_2 \begin{matrix} \diagup \text{CH}_2 \cdot \text{CMe}_2 \\ \diagdown \text{CH}_2 \cdot \text{CMe}_2 \end{matrix} \text{C} \cdot [\text{CH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}]_2 \cdot \text{CH} \cdot \text{CH} \cdot [\text{CH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}]_2 \cdot \text{CH} \cdot \text{CMe} \cdot [\text{CH}_2]_2 \cdot \text{CH} \cdot \text{CMe}_2$  is suggested. The growth-promoting action of (I) is approx. the same as that of  $\alpha$ - or  $\beta$ -carotene. Activity appears to depend not on the no. of double linkings, but on the presence of at least one C ring of the ionone type. H. W.

Carotene derivative giving with antimony trichloride an absorption band at 610–630  $\mu$ . M. VAN EEKELLEN and A. EMMERIE (Nature, 1933, 131, 275).—The prep. of a carotene derivative which gives a strong absorption band at 610–630  $\mu$  with  $\text{SbCl}_3$ , and has no growth-promoting power, is described. L. S. T.

Inhibitor of the antimony trichloride test for vitamin-A in cod-liver oil. A. EMMERIE (Nature, 1933, 131, 364).—After saponification cod-liver oil gives a stronger Carr-Price reaction in the unsaponifiable fraction. The inhibitor  $\text{C}_{27}\text{H}_{36}\text{O}_3$  (I) is a pale yellow viscous substance, b.p.  $203^\circ/1$  mm., mol. wt. 332. In the catalytic hydrogenation with Pt 4H per mol. are absorbed, yielding a product with no inhibiting power. (I) readily absorbs Br and gives an orange-yellow colour with  $\text{C}(\text{NO}_2)_4$ , but the inhibiting power is not due entirely to unsaturation. L. S. T.

Colpokeratosis method of demonstrating the action of vitamin-A. E. KLUSMANN and P. E. SIMOLA (Biochem. Z., 1933, 258, 194–197).—A-Avitaminosis in castrated female rats and in guinea-pigs results in colpokeratosis (I), which is readily and rapidly cured by administration of vitamin-A. Since (I) does not accompany scurvy in guinea-pigs or B- or D-avitaminosis in rats, a sp. and sensitive method (which can be used when the growth method fails) of testing for vitamin-A potency is provided. (I) is not cured by giving xanthophyll although the latter is resorbed by rats and stored in their livers. W. McC.

Carotene and vitamin-A. H. GOLDBLATT and H. M. BARNETT (Proc. Soc. Exp. Biol. Med., 1932, 30, 201–204).—The whole of the vitamin-A activity of carrot oil was due to carotene and not to the presence of vitamin-A. The dose of carotene which appeared to be equal to one Sherman unit of vitamin-A was  $0.5 \times 10^{-6}$  g. NUTR. ABS.

Relation between vitamin-A potency and carotene content of green plant tissue. W. C. RUSSELL, M. W. TAYLOR, and D. F. CHICHESTER (Proc. Soc. Exp. Biol. Med., 1932, 30, 376–377).—Lucerne had a higher vitamin-A potency than could be accounted for by its carotene content. NUTR. ABS.

Vitamin-A content of yellow-tissued and white-tissued apples. M. T. POTTER (J. Nutrition, 1933, 6, 99–102).—There is practically no difference in the vitamin-A content of the varieties of apples tested. E. B. H.

Comparison of apricots and their carotene equivalent as sources of vitamin-A. A. F. MORGAN and E. O. MADSEN (J. Nutrition, 1933, 6, 83–93).—The vitamin-A vals. corresponded approx. with the carotene contents of the apricots. E. B. H.

Vitamin-A content of the blood of cows and oxen. M. LUNDBORG (Biochem. Z., 1933, 258, 325–329; cf. A., 1931, 644, 988).—The method previously described gives quant. results when applied to the determination of vitamin-A in dil. cow- and ox-blood. In cow's blood (which contains three times as much vitamin-A as does ox-blood) all the vitamin is found in the serum, but defibrinated ox-blood has two thirds as much vitamin-A as has the serum. W. McC.

Growth-promoting action of xanthophyll. M. RYDBOM (Biochem. Z., 1933, 258, 239–243).—Daily doses of 0.015 mg. of xanthophyll (I) do not promote growth in rats receiving diet free from vitamin-A even when the treatment is begun before the special diet is commenced. In guinea-pigs receiving a diet almost free from the vitamin, daily doses first of 0.225 and then of 0.300 mg. of (I) promote growth almost to the same extent as do daily doses of 0.0225 and 0.030 mg. of carotene. W. McC.

Vitamins and immunity. Complement content [of blood-serum] and production of hæmolyisin in A- and B-avitaminosis. P. E. SIMOLA and E. BRUNTUS (Biochem. Z., 1933, 258, 228–238).—As regards the complement content (I) of their blood-serum and their power to produce immune hæmolyisin (II) guinea-pigs suffering from A- and C-avitaminosis do not differ appreciably from healthy guinea-pigs. Administration of vitamin-D (irradiated ergosterol) to the diseased guinea-pigs does not affect either (I) or (II). It is probable that the lowered resistance to infection which accompanies avitaminosis is due simply to lowered vitality. W. McC.

Avitaminosis. XIII. Effect of vitamin-A deficiency and vitamin-D deficiency on differential leucocyte count of the albino rat. XII. Influence of vitamin-B deficiency on differential leucocyte count of the albino rat during lactation. B. SURE and K. S. BUCHANAN (Proc. Soc. Exp. Biol. Med., 1932, 30, 173–174, 174–175). NUTR. ABS.

The B-vitamins. H. SIMONNET (Z. Vitaminforsch., 1933, 2, 28–47).—A review.

Vitamin-B<sub>2</sub> values of pasteurised milk, evaporated milk, and eggs. E. N. TODHUNTER (J. Amer. Dietet. Assoc., 1932, 8, 42–46).—The materials are good sources of vitamin-B<sub>2</sub>. NUTR. ABS.

Muscle-phosphate during B-avitaminosis. S. NAGAI (J. Biochem. Japan, 1932, 16, 351–358).—In rats (I) and pigeons (II) suffering from B-avitaminosis, the muscle-acid-sol. and -inorg.  $\text{PO}_4$  are normal, whilst the  $\text{P}_2\text{O}_7$  level in certain muscles [heart in (I), leg in (II)] is decreased. The phosphagen and hexose monophosphate+adenylic acid contents are subnormal in all muscles. F. O. H.

Adrenal phosphate during B-avitaminosis. S. NAGAI (J. Biochem. Japan, 1932, 16, 377–382).—In fowls suffering from B-avitaminosis, the adrenals hypertrophy, the abs. content of acid-sol.  $\text{PO}_4$  increases, whilst the abs. and relative content of inorg.  $\text{PO}_4$  remains const. and decreases respectively. The abs. contents of  $\text{P}_2\text{O}_7$  and hexose phosphate+adenylic acid also increase. F. O. H.

**Phosphatase and phosphatase action during B-avitaminosis.** S. NAGAI (J. Biochem. Japan, 1932, 16, 359—370).—In pigeons suffering from B-avitaminosis, the phosphorylating activities of the tissues of the heart (I), kidney (II), liver (III), and pectoral muscle (IV) are increased by 14.6—77.7%, whilst that of the brain-tissue (V) remains normal. The phosphatase activities of (IV) and (V) are increased, that of (III) is decreased, whilst those of (I) and (II) are unchanged. F. O. H.

**Glutathione and B-avitaminosis.** S. NAGAI (J. Biochem. Japan, 1932, 16, 371—375).—The oxidised form of glutathione (I) occurs in the heart (II) but not in the liver (III) or leg-muscles (IV) of normal rats. During B-avitaminosis the content of reduced (I) is markedly lowered in (II), (III), and (IV) of rats and in (II) and (IV) of pigeons, whilst in (III) of pigeons it is increased. F. O. H.

**Co-enzyme content of the adrenals of fowls during B-avitaminosis.** S. NAGAI (J. Biochem. Japan, 1932, 16, 383—387).—The adrenals of fowls suffering from B-avitaminosis have a higher content of the co-enzyme accelerating the anaerobic decomp. of hexose phosphate than those of normal birds. That this increase is associated with the accompanying symptom of hypertrophy of the adrenal cortex is indicated by the delay of the onset of the disease on feeding adrenal cortex. F. O. H.

**Rôle of avitaminosis-B and of alimentary equilibrium in the utilisation of lactose by the rat.** R. LECOQ (Compt. rend., 1933, 196, 565—567).—Rats maintained on strictly equilibrated diets free from vitamin-B complex, and containing (a) 72% of sucrose, (b) 72%, (c) 38%, and (d) 55% of lactose survive for 20—40 days, 10—25 days, 3—5 months, and >6 months, respectively. Addition of 5% of vitamin-B complex causes increase in wt. on diets (a), (c), (d), but not on (b). As in the case of the pigeon (A., 1929, 726), utilisation of lactose is determined not only by the presence of vitamins-B, but also by the alimentary equilibrium. A. C.

**Relation of the vitamin-B complex to renal enlargement caused by cystine and protein in the diet of the rat.** B. B. LONGWELL, R. M. HILL, and R. C. LEWIS (J. Nutrition, 1932, 5, 539—550).—The kidneys of rats on a diet deficient in the vitamin-B complex were slightly larger than those of rats receiving a whole yeast extract. This difference was augmented by the addition of cystine to the diet, or by increasing the caseinogen. NUTR. ABS.

**Experimental cataract in vitamin-B<sub>2</sub> deficiency.** C. S. O'BRIEN (Arch. Ophthalmol., 1932, 8, 880—887).—Cataracts were noted in young rats fed on diets deficient in vitamin-B<sub>2</sub>, in which vitamin-B<sub>1</sub> was supplied in the form of an EtOH extract of rice polishings. NUTR. ABS.

**Avitaminosis and intoxication. I. Experimental polyneuritis and chemical intoxication by metals and metalloids. II. Experimental scurvy and chemical intoxication by metals and metalloids.** M. MITOLO (Atti R. Accad. Lincei, 1932, [vi], 16, 451—455, 528—531).—I. Ingestion of a mixture of salts of metals and metalloids in doses

non-poisonous to normal animals enhances nutritional deficiency in pigeons suffering from experimental polyneuritis, the injurious effect of the salts being also increased.

II. Ingestion by guinea-pigs suffering from avitaminosis-C of a mixture of salts of metals and metalloids in doses non-toxic to normal animals accelerates and intensifies the effects of the deficiency.

T. H. P.

**Identification of vitamin-C.** A. SZENT-GYÖRGYI (Nature, 1933, 131, 225—226).—A lecture. L. S. T.

**Hexuronic (ascorbic) acid as the antiscorbutic factor and its chemical determination.** T. W. BIRCH, L. J. HARRIS, and S. N. RAY (Nature, 1933, 131, 273—274).—Evidence is produced which is considered to establish the identity of vitamin-C and hexuronic acid. L. S. T.

**Hexuronic (ascorbic acid) as the antiscorbutic factor and its chemical determination.** W. J. DANN (Nature, 1933, 131, 274; cf. preceding abstract).—Zilva's data (A., 1932, 1294) are analysed and shown not to be contrary to the view that hexuronic acid and vitamin-C are identical. L. S. T.

**Indophenol-reducing capacity of lemon juice and its fractions in relation to vitamin-C activity.** S. S. ZILVA (Nature, 1933, 131, 363).—A criticism of Dann's interpretation (preceding abstract) of the author's previous results. L. S. T.

**Vitamin-C and ascorbic acid.** A. L. BACHARACH (Nature, 1933, 131, 364).—The view that vitamin-C and ascorbic acid are identical is supported. L. S. T.

**Reducing power of plant foodstuffs and its relation to vitamin-C. VI. Purification of the reducing substance from [potatoes and] hipberries and its identity with vitamin-C.** J. TILLMANS, P. HIRSCH, and R. VAUBEL (Z. Unters. Lebensm., 1933, 65, 145—168).—Determinations of the reduction val. (A., 1932, 310, 658), solids, ash, and "apparent equiv. wt." indicate that extraction of the reducing substance from potato is most complete after 2.5 hr. in a mixture containing 60% COMe<sub>2</sub> and 40% 0.05N-H<sub>2</sub>SO<sub>4</sub>. Various physical and chemical methods of purification are described for hipberries. The best procedure is extraction with H<sub>3</sub>PO<sub>4</sub> in CO<sub>2</sub>, followed by evaporation, pptn. in succession with COMe<sub>2</sub> and Pb(OAc)<sub>2</sub> (excess being removed with H<sub>2</sub>S), evaporation, extraction with MeOH, pptn. with Et<sub>2</sub>O, and extraction with H<sub>2</sub>O of the residue after a final evaporation. Pptn. with Pb(OAc)<sub>2</sub> and COMe<sub>2</sub> is repeated, and an evaporated extract of the residue in light petroleum is finally extracted at -5° with COMe<sub>2</sub> and then with Et<sub>2</sub>O, all operations being carried out in an atm. of N<sub>2</sub>. The residue is recryst. from MeOH and gives a yield of 0.0016%, the substance being very similar to "hexuronic acid" (this vol., 196). Feeding experiments on guinea-pigs show that 0.5 mg. per day suffices to prevent scurvy. J. G.

**Vitamin-C. Addendum.** H. VON EULER and E. KLUSMANN (Svensk Kem. Tidskr., 1932, 44, 310).—With 2:6-dichlorophenol-indophenol the ad-

renal glands of scorbutic guinea-pigs give a titration val. of 0.6—0.9 (see this vol., 325), whereas those of normal animals give 1.2—3, a val. which is still further increased by injection of vitamin-C.

F. O. H.

**Scorbutic dental changes and their modification by synthetic vitamin-C preparations.** G. WESTIN (Z. Vitaminforsch., 1933, 2, 1—24).—A study of histo-pathological changes in teeth of guinea-pigs after administration of orange-juice, narcotine derivatives, or glycuronic acid (I) in experiments of prophylactic or curative type lasting 10—31 days or 3—10 days, respectively [with A. RYGH and O. RYGH]. (I), narcotine, and narcotine irradiated or treated with germinating seeds, had no action.  $\beta$ -Gnoscopine, anhydrohydrastininephthalide, nor-narcotine, and dimethylnornarcotine showed slight antiscorbutic action. Methylnornarcotine showed action in daily doses of 10—30 (prophylactic) and  $100 \times 10^{-6}$  g. (curative), and a synthetic preparation was active in doses of 1—3  $\times 10^{-6}$  g. (curative). Simultaneous administration of (I) was without effect. R. K. C.

**Preservation of vitamins of the fodder of cattle.**

A. I. VIRTANEN (Biochem. Z., 1933, 258, 251—256).—Fodder for farm animals (cows, calves, horses, pigs, poultry) loses most or all of its vitamin-C on storage (for 5—10 months), whereas such fodder maintained at  $p_{\text{H}}$  3—4 during storage by admixture of acid (HCl, H<sub>2</sub>SO<sub>4</sub>) loses only 40—60% during that time. Similarly, whilst the carotene content of the fodder stored in the customary ways decreases by as much as 55% this content in the acidified fodder either remains unchanged or increases on keeping for 1½—5 months.

W. McC.

**Determination of vitamin-C standard and the requirement of healthy individuals by measurement of the strength of skin capillaries.** G. F. GÖTHLIN (Skand. Arch. Physiol., 1931, 61, 225—270; Chem. Zentr., 1932, ii, 2989).—A scorbutic diet produces a marked fall in the strength of skin capillaries; the condition disappears on administration of fresh orange juice. The protective dose is calc.

A. A. E.

**Products obtained by heating vitamin-D and their hydro-derivatives.** P. BUSSE (Z. physiol. Chem., 1933, 214, 211—222).—The product obtained by heating vitamin-D at 180—190° for 4 hr. consists of a mol. compound, m.p. 122—124°, of pyrocalciferol (I) and an isomeride, isopyrovitamin (II), m.p. 112—115°,  $[\alpha]_{\text{D}}^{20} +332^\circ$  (acetate, m.p. 113—115°,  $[\alpha]_{\text{D}}^{20} +333^\circ$ ). (II) is reduced by Na in EtOH to dihydroisopyrovitamin (III), m.p. 129—130°,  $[\alpha]_{\text{D}}^{20} +11.85^\circ$  (acetate, m.p. 145—146°,  $[\alpha]_{\text{D}}^{20} +30.2^\circ$ ). Catalytic hydrogenation (spongy Pt in Et<sub>2</sub>O—EtOH) of the acetate of (III) and hydrolysis gives hexahydroisopyrovitamin, sinters 68—80°,  $[\alpha]_{\text{D}}^{20} -6.9^\circ$  (2:6-dinitro-p-toluate, m.p. 164—165°,  $[\alpha]_{\text{D}}^{20} +1.37^\circ$ ). Reduction of (I) with Na in EtOH gives dihydropyrocalciferol (IV), m.p. 121—122°,  $[\alpha]_{\text{D}}^{20} +70.3^\circ$  (acetate, m.p. 131—133°,  $[\alpha]_{\text{D}}^{20} +44.7^\circ$ ), and when heated for 11 hr. at 190°, epidihydropyrocalciferol (V), m.p. 138—139°,  $[\alpha]_{\text{D}}^{20} +54.3^\circ$  (acetate, m.p. 98—99°,  $[\alpha]_{\text{D}}^{20} +35.6^\circ$ ). Catalytic reduction of the acetate of (IV) and hydrolysis affords hexahydropyrocalciferol (VI), m.p. 130—131°,  $[\alpha]_{\text{D}}^{20}$

+34.35°. Catalytic reduction of (V) or heating (VI) gives hexahydroepiprocalciferol, m.p. 137°,  $[\alpha]_{\text{D}}^{20} +30.15^\circ$  (m-dinitrobenzoate, m.p. 197—198°,  $[\alpha]_{\text{D}}^{20} +20.9^\circ$ ): all rotations in CHCl<sub>3</sub>. (I) and (II) are antirachitically inactive in 10<sup>-6</sup> g. dose and less toxic than vitamin-D. J. H. B.

**Origin of vitamin-D in the organism.** F. VENULET and F. GOEBEL (Compt. rend. Soc. Biol., 1932, 111, 1026—1028).—Vitamin-D (I) was absent from the faeces of rats fed either on normal diet or on McCollum's diet (3143). Ultra-violet irradiation caused (I) to appear in the faeces of the normally fed rats but not in the faeces of those fed on rachitogenic diet. The dried flesh of the rachitic rats contained the precursor of (I), but not (I) itself. NUTR. ABS.

**Vitamin-D and the blood-phosphate curve.** C. BOMSKOV and G. RATH (Z. ges. exp. Med., 1932, 85, 400—404).—Na  $\beta$ -glycerophosphate was injected subcutaneously into rabbits given vitamin-D or treated with ultra-violet light. In both cases the resulting increases of blood-phosphate were < in similarly injected but otherwise untreated control animals. NUTR. ABS.

**Comparison of bone-ash of rachitic rats treated with viosterol and with phosphate ion.** C. A. LILLY (Proc. Soc. Exp. Biol. Med., 1932, 30, 175—176).—Addition of phosphate or of vitamin-D to Steenbock's low-phosphate, rachitogenic diet raised the bone ash of young rats consuming the diet. NUTR. ABS.

**Effect of irradiated ergosterol on the parathyroidectomised rat.** T. VON SPRETER (Z. ges. exp. Med., 1932, 85, 19—45).—Irradiated ergosterol (I), in daily amounts of 150 rat units, exerted no influence on the progress of the symptoms in parathyroidectomised rats. A daily dose of 500 units, while producing no symptoms of overdosage, prolonged the life of the animals and prevented the development of such defects in the enamel and dentine of the teeth as were found in animals receiving the lower amounts of (I). NUTR. ABS.

**Effect of viosterol on excretion of lead.** F. B. FLINN and A. R. SMITH (Proc. Soc. Exp. Biol. Med., 1932, 30, 367—368).—Large doses of viosterol (I) caused an increased elimination of Pb in cats. In two cases the elimination was 10 and 30 times as great as during the period previous to the administration of (I). Only a slightly increased elimination was produced in guinea-pigs, due possibly to their relatively greater resistance to (I). (I) had no protective action against Pb poisoning in the case of four guinea-pigs. NUTR. ABS.

**Relation between hormones and vitamins, with special reference to the thymus and irradiated ergosterol.** M. COPPO (Arch. internat. Pharmacodyn. et Thérap., 1932, 43, 123—185).—Young rabbits, from which the thymus had been recently removed, received daily doses of 0.25 c.c. of a 1% solution of irradiated ergosterol (I), and survived, whilst intact controls, receiving the same toxic doses, died. Far larger doses were needed to kill the former. X-Ray examination of the bones of such rabbits revealed typical decalcificatory lesions, following extirpation of the thymus. Dosage with (I) in



no way prevented the development of these, although intact controls similarly dosed showed enhanced calcification of the bone. Extirpation of the thymus did not affect the rise in blood-sugar or -phosphate, observed to occur in normal animals, following administration of (I).  
NUTR. ABS.

**Activated ergosterol.** D. BEALL and J. BIELY (Trans. Roy. Soc. Canada, 1932, [iii], 26, III, 57—60).—1/40 c.c. of viosterol, having a potency of 250D, is as effective as 1 c.c. of cod-liver oil (112 units per g.) in prevention of rickets.  
H. G. R.

**Unirradiated ergosterol and vascular sclerosis.** T. GORDONOFF and S. ZURUKZOGU (Z. Vitaminforsch., 1933, 2, 25—28).—Sclerotic patches in the aorta with lesions in the media were observed in rabbits fed with ergosterol and exposed either to alpine sunlight or an ultra-violet lamp.  
R. K. C.

**A thermodynamic law of life.** K. STERN (Ber. deut. bot. Ges., 1933, 51, 44—52).—In order to maintain the living organism, the "chemical potential" (Gibbs) of the essential nutrients must lie within certain well-defined limits, otherwise the nutrient becomes non-effective however great the amount supplied.  
A. G. P.

**Plant growth substances. IV. Phytohormone of cell elongation. Isolation of auxin from human urine.** F. KÖGL, A. J. HAAGEN-SMIT, and H. ERXLBEN (Z. physiol. Chem., 1933, 214, 241—261).—Cryst. *auxin*, m.p. 196°, activity 50 million units per mg., and its *lactone*, m.p. 172—173°, activity 35 million units per mg., were obtained from normal and mixed human urine. Lactonisation was accomplished by treatment with HCl in MeOH prior to distillation. The activity was followed by means of the Went technique (bending of oat coleoptile). Substances showing the Went reaction obtained from various sources appear to be identical.  
J. H. B.

**Auxin; its occurrence in the plant and animal kingdoms.** F. KÖGL (Naturwiss., 1933, 21, 17—21).—Precise details are given for extracting auxin from urine (see preceding abstract). Auxin has  $[\alpha]_D^{20}$   $-3.18^\circ$  and its *lactone*, m.p. 173°,  $[\alpha]_D^{20}$   $-3.42^\circ$ , activity 50 million units per mg. The following *derivatives* have been prepared; dihydro-, m.p. 199°; tri(dinitrobenzoyl)-, m.p. 169°; Me ester, m.p. 150°; dihydroauxin-lactone,  $C_{18}H_{32}O_4$ , m.p. 191°; *p*-phenylphenacyl ester,  $C_{32}H_{42}O_6$ , m.p. 166°;  $\psi$ -auxin,  $C_{18}H_{32}O_5$  (inactive). The auxin content of urine during pregnancy is normal.  
P. G. M.

**Plant respiration. IV. Relation of the respiration of potatoes to the concentration of sugars and to the accumulation of a depressant at low temperatures. (i) Effect of temperature-history on the respiration/sugar relation. (ii) Form of the normal respiration/sugar relation and the mechanism of depression.** J. BARKER (Proc. Roy. Soc., 1933, B, 112, 316—335, 336—358).—The effect of varying sugar concn. on the respiration rate (I) of potatoes has been studied, and curves are given, showing the R/S relation at different temp. In addition to the direct retardation of (I) at low temp., a sp. temp. effect is observed as a result of

which (I) is also dependent on the temp. history of the potato. Thus exposure to cold causes the accumulation of a (I)-depressing substance, max. at  $-1^\circ$  and approx. nil at  $8^\circ$ . The development and operation of the effect of this substance, however, have a temp. coeff. in the opposite sense, being observed maximally at the higher temp. ( $10^\circ$ ) and negligibly at  $-1^\circ$ .  
A. C.

**Large respirometer.** W. B. BALCH (Science, 1933, 77, 116—117).  
L. S. T.

**Starch formation in cane leaves.** W. E. COLLINGH and V. J. KONINGSBERGER (Arch. Suikerind. Ned.-Indië, 1932, 40, Meded. No. 19, 1325—1340).—In  $CO_2$  assimilation by the leaves of the cane variety POJ 2878 much starch is formed and is stored in the starch sheath surrounding the vascular bundles. This is much less marked in the leaves of some other varieties, viz., Striped Lahaina, or in those of sorghum. An excised leaf of cane which is caused to absorb sugar solution (sucrose, maltose, glucose, or fructose) converts part of the sugar into starch.  
J. P. O.

**Maturity of sugar cane. II. Life history of "Hayaue" plant canes. III. Sucrose accumulation in the sugar cane. IV. Significance of water in "maturity." S. OZAWA and S. KOMATSU. V. Utilisation of solar energy in the cane. S. OZAWA. VI. Changes in chemical composition of cane stalks deprived of their leaves. S. OZAWA and Y. MAKINO (Mem. Coll. Sci. Kyoto, 1933, A, No. 1, 125 pp.).—II. Variations in the  $H_2O$  and chlorophyll contents of leaves with age and climatic conditions are recorded. In the expressed sap of the canes high titratable acidity and low  $p_H$  are especially marked in the upper sections, where active transformation of sugars into org. acids occurs. Variations with age of the total solids and non-reducing sugars of the sap and of fibre in the cane are of a similar character. Non-reducing and reducing sugars show an approx. inverse relationship.**

III. The sprouting of stem cuttings of cane involves the utilisation of stored sucrose. Shoots developing from over-mature crowns left in the soil withdraw very little reserve sucrose from the parent plant. Tasselling and side-shoot production necessitate the consumption of stored sucrose, to an extent which depends on the general activity of the cane.

IV. In the early stages of maturity canes from poorly drained soils contained a higher proportion of reducing sugars than those from more porous soils. Irrigation may increase sugar yields by curtailing vegetative growth and in this respect is more effective than drainage.

V. A mathematical discussion of the photosynthesis and metabolism of carbohydrates.

VI. Removal of all but the tip leaves of canes causes, in the expressed sap, a decrease of total solids and sp. rotation to vals. which remain approx. const. until new leaves have developed and are actively functioning. Subsequently these vals. rise to the normal. Growth of the cane continues slowly in the absence of leaves, stored carbohydrate serving as an energy source. During this period the reducing sugar content of the sap is not greatly reduced.  
A. G. P.

**Relation between water content, chlorophyll content, and the rate of photosynthesis in some tropical plants at different temperatures.** R. H. DASTUR and B. L. DESAI (Ann. Bot., 1933, 47, 69—88).—The "assimilation no." ( $W$ ), *i.e.*, ratio of  $H_2O$  content : rate of assimilation, in plants increases with rising temp. up to a max. point and subsequently declines. Willstätter's "assimilation no." ( $CH$ ), *i.e.*, ratio of chlorophyll content :  $CO_2$  assimilated, showed no such regularity with temp. changes. The assimilation of  $CO_2$  is more closely related to the  $H_2O$  content than to the chlorophyll content of leaves. A. G. P.

**Fat metabolism of leaves. II. Fats and phosphatides of the runner bean (*Phaseolus multiflorus*).** R. C. JORDAN and A. C. CHIBNALL (Ann. Bot., 1933, 47, 163—186).—All organs of the plant contain lecithin and kephalin, in amounts which decrease in order from the cotyledons to the pinnate leaves. Cotyledons and embryo axes also contain a small amount of Mg phosphatide. On germination the proportion of this compound increases rapidly until the prophylls begin to expand, when there is a steady transition to the Ca salt which is the principal phosphatide of the mature prophylls and pinnate leaves. The transition of the (fat-sol.) Mg salt to the Ca salt coincides with the onset of chlorophyll synthesis. The disappearance of phosphatides from the cotyledons during germination is more rapid than the appearance of phosphatides in the growing organs. Evidence is advanced that glyceride fatty acids in mature pinnate leaves can function as food reserves, but that phosphatides form integral parts of the protoplasm. Waxes and unsaponifiable materials in plants are probably the end-products of metabolism. A. G. P.

**Metabolism of certain sea-weeds.** P. HAAS and T. G. HILL (Ann. Bot., 1933, 47, 55—67).—Examination of a no. of sea-weeds shows the contents of fats and fat-like substances and also the saturation of the fats to increase with the degree of emergence of the plants. The unsaponifiable residue of the fatty matter increases with the depth of immersion. The sugar content of marine algae is small, but sugar alcohols (mannitol, sorbitol, dulcitol) are of general distribution. These compounds are probably the secondary products of sugars.  $NH_3$  is present in all but certain exposed algae. In exposed plants of high zones the amide-N content is usually  $>$  the  $NH_2$ -N. The reverse is the case in plants bathed with or frequently immersed in  $H_2O$ .  $NMe_3$  occurs in several species; an octapeptide of glutamic acid is found in *Phaeophyceae* of the higher zones and a pentapeptide in other species. A. G. P.

**Synthesis of protein by green plants.** L. LOOSE and W. H. PEARSALL (Nature, 1933, 131, 362—363).—In *Chlorella* the velocity of protein synthesis is approx. five times as great in the light as in the dark. If sufficient carbohydrate be present, the final equilibrium is similar in both cases. L. S. T.

**Formation of tubers and other storage organs. Influence on translocation of the period of light and the supply of potassium.** M. A. H. TINKER and F. V. DARBISHIRE (Ann. Bot., 1933, 47, 27—53).—Accumulation of carbohydrates in certain tubers

varied with the period of exposure of the plants to light. Replacement of K by Na in nutrient solutions did not effect as much change in growth habit as did variations in light exposure. K-deficient plants wilted at higher levels of  $H_2O$  supply than those receiving adequate K. In dahlias the total dry-matter production was markedly reduced by K deficiency. The rate of formation and translocation of starches was influenced by the K supply.

A. G. P.

**Effect of chemical treatment of dormant potato tubers on the conductivity of the tissue and on the leaching of electrolytes from the tissue.** J. D. GUTHRIE (Contr. Boyce Thompson Inst., 1933, 5, 83—94).—Treatment of potato tubers with  $CH_2Cl \cdot CH_2 \cdot OH$  increased by small but significant amounts the conductivity of the tissue and the ease of leaching of electrolytes from it. KCNS produced similar but smaller changes. The action of thiourea was less definite. A. G. P.

**Absorption and accumulation of solutes by living plant cells. IV. Surface effects with storage tissue: quantitative interpretation with respect to respiration and salt absorption.** F. C. STEWARD (Protoplasma, 1932, 17, 436—453).—High respiration rates in potato discs exposed to air occur only in a surface zone of cells which is deeper than in the case of discs exposed to salt solutions. Salt absorption is confined to cells exhibiting high respiration rates and from which there is a marked disappearance of starch. A. G. P.

**Plant buffer systems in relation to the absorption of bases by plants.** T. C. DUNNE (Hilgardia, 1932, 7, No. 5, 207—234).—Examination of the expressed sap of frozen and thawed tissues indicates that org. acids, amides,  $NH_2$ -acids, sugars, and phosphates are the principal buffering agents present. Low supplies of K and P to the plant result in a decreased  $p_H$  and increased buffer power in the sap, probably due to relative increases in the proportions of org. acids, amides, and  $NH_2$ -acids. Plants grown with low Ca supplies are not necessarily injured nor do they show more acid saps. Under these conditions more K is absorbed and serves as a base in the buffer system. Treatment with  $CaCO_3$  may produce an injurious alkalinity in the sap of certain plants. In buckwheat treatment with  $CaCO_3$  reduced the oxalate content of the sap. Much of the oxalate in buckwheat is in an insol. form. A. G. P.

**Antagonism. I. Effect of the presence of salts of univalent, bivalent, and tervalent cations on the intake of calcium and ammonium ions by potato tuber tissue.** G. F. ASPREY (Proc. Roy. Soc., 1933, B, 112, 451—472).—Absorption of  $Ca^{++}$  and  $NH_4^+$  from aq. solutions of  $CaCl_2$  and  $NH_4Cl$ , respectively, is at first rapid (for 3 and 10 hr., respectively), and then proceeds slowly. The similar initial rates of absorption are due to their dependence during this period on physical properties (*e.g.*, mobility) of the ions, which are similar. Experiments with added NaCl,  $MgCl_2$ , and  $LaCl_3$  show that the antagonistic action of an ion to absorption varies directly as the valency and concn. of the added ion. Mixtures of  $CaCl_2$  and  $NH_4Cl$  exhibit mutual antagon-

ism. 0.02*N* and more conc. solutions of  $\text{AlCl}_3$  have an anomalous effect, causing considerable initial reduction in absorption of  $\text{NH}_4^+$ , which increases for 9 hr., and then decreases again.  $\text{LiCl}$  increases the absorption of  $\text{NH}_4^+$ , possibly due to the exosmosis induced by  $\text{Li}$  salts. The intake of  $\text{Cl}^-$  is not greatly affected by  $\text{Na}$  or  $\text{K}$ , but is reduced by  $\text{Li}$ . The increased absorption of  $\text{NH}_4^+$  and  $\text{Cl}^-$  caused by sucrose may be due to an increase in tissue respiration. The "antagonism" of an ion may be regarded as due to a balance between its sp. effect on the tissue and ionic competition for absorption. A. C.

**Growth and differentiation. IV. Distribution of some solutes in the tissues of *Kleinia articulata*.** D. THODAY and H. EVANS (Ann. Bot., 1933, 47, 1—20).—In the stem tissues of *K. articulata*  $\text{Ca}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NO}_3^-$ , and malate are the predominant ions with  $\text{PO}_4^{---}$ ,  $\text{SO}_4^{--}$ ,  $\text{Cl}^-$  in small amounts. The proportions of  $\text{Mg}^{++}$ ,  $\text{Al}^{+++}$ ,  $\text{NH}_4^+$ , and  $\text{Fe}^{+++}$  are small. The amount of  $\text{Ca}^{++}$  is nearly equiv. to that of  $\text{Na}^+ + \text{K}^+$ . In the separated zones of the stem the ratio  $\text{Ca}^{++} : (\text{Na}^+ + \text{K}^+)$  averages 4:1 in the pith and 1:4 in the cortex. No  $\text{Ca}^{++}$  was detectable in the outer cortex. The cortex contains approx. two thirds of the total  $\text{K}^+$  and the pith two thirds of the total  $\text{Ca}^{++}$ . There is a general distribution of  $\text{NO}_3^-$  in stems with a tendency to decrease towards the outer cortex and in the centre of the pith. Largest amounts occur in the bundle zone. Inulin and  $\text{PO}_4^{---}$  accumulate in the bundle zone in which the sugar concn. is low.  $\text{Cl}^-$  is evenly distributed throughout the tissues.  $\text{SO}_4^{--}$  is less in the pith than in the cortex or bundle zone.  $\text{Sol. Mg}^{++}$  occurs mainly in the pith centre where  $\text{Ca}^{++}$  is low. In cortex and pith the relative excess of bases indicates high proportions of malates. Diurnal changes in acidity occur in those parts of the stem in which malic acid and  $\text{K}$  are associated. A. G. P.

**Initiation and stimulation of roots from exposure of plants to carbon monoxide.** P. W. ZIMMERMANN, W. CROCKER, and A. E. HITCHCOCK (Contr. Boyce Thompson Inst., 1933, 5, 1—17).—Exposure of a no. of plants to an atm. containing 1% of  $\text{CO}$  induced root production from young stems and in other cases stimulated the growth of pre-existing root primordia on older parts of stems. Root hairs were more abundant on  $\text{CO}$ -treated plants and cuttings of tobacco plants rooted much more rapidly after exposure to  $\text{CO}$ . A. G. P.

**Water-permeability of protoplasm.** B. HUBER (Ber. deut. bot. Ges., 1933, 51, 53—64).—Plasmolysis by neutral salt solutions of the mesophyll cells of *Vallisneria* is much less rapid than in those of the epidermis. This effect is not the result of differences in cell size, but of differences in the permeability of the protoplasm to  $\text{H}_2\text{O}$ . A. G. P.

**Artificial nutrition of cultivated plants. I. Nutrient media of stable  $p_{\text{H}}$ .** C. ZINZADZÉ (Ann. Agron., 1932, 2, 809—853).—Nutrient media are stabilised with respect to  $p_{\text{H}}$  by the use of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ . Addition to the media of active  $\text{C}$  improved the growth of plants by the adsorption of toxic material which tends to accumulate in the medium. A. G. P.

**Health condition of cultivated plants in relation to their nutrition.** F. LABROUSSE (Ann. agron., 1932, 2, 774—808).—The influence of physical and chemical soil conditions, of unbalanced nutrition, and of the absence of certain essential nutrients, on the distribution of plant disease and the susceptibility of plants to infection is discussed. An extensive bibliography is appended. A. G. P.

**Nitrate storage by higher marine algæ.** S. SUNESON (Z. physiol. Chem., 1933, 214, 105—108).—Many species were tested for nitrate ( $\text{NHPb}_2$  reaction).  $\text{NO}_3^-$  is present in some green, but absent from most brown, algæ. The red species show the greatest differences. J. H. B.

**Fixation of nitrogen by the bacteria of legumes.** H. BURGEVIN (Compt. rend., 1933, 196, 441—443).—Soya beans grown in soil inoculated with *B. radicola*, Beij., are more able to utilise  $\text{N}$  both from the air and as  $\text{NH}_4\text{NO}_3$  than those grown in soil not inoculated. The foliage is greener, the plants are healthier, and the harvest is better, typical nodules being formed on the roots. P. G. M.

**Legume-bacteria and plants. XII. Utilisation by non-leguminous plants of the nitrogen compounds from the root-nodules of leguminous plants.** A. I. VIRTANEN, S. VON HAUSEN, and H. KARSTRÖM (Biochem. Z., 1933, 258, 106—117; cf. A., 1931, 1101).—The org. compounds which diffuse from root-nodules produced by inoculation in otherwise sterile leguminous plants (clover, peas) grown from seed in a  $\text{N}$ -free medium consist almost entirely of  $\text{NH}_2$ -acids. Non-leguminous plants (barley) grow very well while utilising these compounds as their sole source of  $\text{N}$ , and it is very probable that under natural conditions such utilisation occurs to a great extent. The view that higher plants utilise only inorg. compounds for their  $\text{N}$  supply is thus controverted. Org.  $\text{N}$  compounds (aspartic acid, asparagine, caseinogen hydrolysates, urea, alanine) exhibit great differences as regards their capability to serve as  $\text{N}$  sources for red clover, peas, and barley. Aspartic acid is an excellent  $\text{N}$  source for leguminous plants but is not so for the Gramineæ. W. McC.

**After-ripening of *Rhodotypos kerrioides* seeds.** F. FLEMION (Contr. Boyce Thompson Inst., 1933, 5, 143—159).—During the after-ripening period there is an increase in catalase, peroxidase, and lipase activity, in  $\text{H}_2\text{O}$ -absorbing power, and in the contents of  $\text{N}$  sol. in 80%  $\text{EtOH}$ , titratable acid, and sucrose, and a steady decrease in  $\text{Et}_2\text{O}$ -sol. constituents. A. G. P.

**Is elementary nitrogen absorbed by nodules on the roots of Leguminosæ in the assimilation of atmospheric nitrogen?** G. J. A. GALESTIN (Chem. Weekblad, 1933, 30, 207—209).—An apparatus is described in which a limited supply of air or other gas can be circulated over approx. 500 g. of nodules. Experiments with detached nodules from *Lupinus luteus* show that no absorption of  $\text{N}_2$  takes place. S. C.

**Drying and fermentation of tobacco. II Relationship of enzyme content (peroxidase oxygenase, catalase) of tobacco and the dis-**

appearance of nicotine during fermentation. L. BARTA (Biochem. Z., 1933, 257, 406—410).—In tobacco poor in peroxidase and oxygenase, loss of nicotine (I) by fermentation does not occur and in tobaccos rich in these enzymes there is no relationship between the enzyme content and loss of (I). There is, however, a definite relationship between the catalase content and the loss of (I) by fermentation.

P. W. C.

Biological introduction to the cellulose symposium [Delft, May 1932]. G. VAN ITERSSEN (Chem. Weekblad, 1933, 30, 2—19).—A survey of the production of cellulose in plants, and of the structure, optical and mechanical properties, swelling, and chemical behaviour of cellulose. An extensive bibliography is given.

H. F. G.

Robinoside in the flowers of *Vinca minor*, L. (*alba*). J. RABATÉ (Bull. Soc. Chim. biol., 1933, 15, 130—134).—The flowers of *V. minor*, L. (*alba*), but not of the blue variety or of *V. major*, L., contain 0.4% of robinoside (A., 1926, 1183).

F. O. H.

Starch and alkaloid content of leaves. M. JANICSEK (Mezőg.-Kutat., 1932, 5, 283—292; Chem. Zentr., 1932, ii, 3277).—For the determination of starch the leaves are freed from colouring matter and reducing substances by extraction with EtOH and the residual starch is determined colorimetrically with I. The alkaloid content of leaves of *Datura stramonium* and *D. metel* increases relatively at night, since starch is then saccharified and passes to other parts of the plant.

A. A. E.

Physico-chemical heterogeneity of plastids. A. MAIGE (Compt. rend., 1933, 196, 424—426).—Starch grains are entirely evolved in the plastid vacuoles in the unilocular type, but the plastid walls exhibit a variable permeability to sugars over different portions of their surfaces, which explains the formation of starch mainly by the plastid cap.

P. G. M.

Chinese "dragon eyes." P. P. T. SAH and T. W. LI (Sci. Rep. Nat. Tsing Hua Univ., 1932, A, 1, 277—283).—The dried fruit (*Euphoria longana*, Lam.) contains no vitamin-A or -B. An analysis of the fresh fruit is given.

H. G. R.

Chinese peanuts and peanut oils. P. P. T. SAH, K. PING, T. S. MA, and J. CHOW (Sci. Rep. Nat. Tsing Hua Univ., 1932, A, 1, 289—294).—Analyses are given.

H. G. R.

Sativic and tetrabromostearic acids derived from lumbang oil and their significance in relation to naturally occurring linoleic acid. D. M. BIROSEL (Univ. Philippines Nat. Appl. Sci. Bull., 1932, 2, 103—117).—Only two isomeric sativic acids have been obtained by oxidation of the free fatty acids from lumbang oil and of linoleic acid from  $\alpha$ -linoleic acid tetrabromide. The compounds usually designated  $\beta$ - and  $\delta$ -linoleic acid are, respectively, almost pure Me ester and a mixture of the acid and ester.

CH. ABS.

Phosphatide content of apples, pears, plums, and peaches. B. REWALD and A. SCHWIEGER

(Biochem. Z., 1933, 257, 289—292).—No characteristic differences could be detected between the phosphatide contents of peel and pulp with any of the fruits, the contents ranging from 0.03% in peach to 0.009% in apple pulp and from 0.066% in plum to 0.011% in apple peel. The highest vals. (0.41%) were obtained in the pips (plum). In pulp, the total crude fat is highest in plum (0.37%) and lowest in pear (0.11%), whilst in peel it is highest in peach (1.57%) and lowest in pear (0.54%).

P. W. C.

Change of colour of *Boletus strobilaceus*, Scop. G. BERTRAND (Biochem. Z., 1933, 258, 76—78; cf. A., 1902, i, 220).—The fungus yields a cryst. phenolic substance, strobilomycol, which is easily attacked by laccase with production of a red and then a black colour.

W. McC.

Effects of sulphur deficiency on metabolism in tomato. G. T. NIGHTINGALE, L. G. SCHEMMERHORN, and W. R. ROBBINS (Plant Physiol., 1932, 7, 565—595).—Tomatoes grown in S-deficient media slowly developed symptoms resembling those of N starvation except that stem growth of a thin and woody character continued. The carbohydrate content of these plants was very high and they contained more  $\text{NO}_3^-$  than corresponding plants in a complete nutrient. This results from a retardation of the normal  $\text{NO}_3^-$ -reducing and carbohydrate-oxidising processes. Starch digestion and sugar translocation took place freely in S-deficient plants (I). The latter were further characterised by thick cell walls containing a high proportion of fibre and lignin, reduced amounts of protoplasm, and a much reduced content of -SH compounds in the meristematic tissue. Proteolysis, normally associated with decreased carbohydrate contents, was active in (I). Whereas the org. S of normal plants existed mainly as insol. protein complexes, that of (I) was largely  $\text{H}_2\text{O}$ -sol. and contained little or no cystine, cysteine, or glutathione. In tomato the reduction  $\text{SO}_4^{2-} \rightarrow \text{SO}_3^{2-} \rightarrow \cdot\text{SH}$  and of  $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NH}_3$  occurred in the relatively alkaline phloem-regions of roots and tops. In apple, narcissus, and asparagus  $\text{NO}_3^-$  reduction is confined chiefly to fibrous roots and  $\text{SO}_4^{2-}$  reduction mainly to the tops and only to a small extent in roots.

A. G. P.

Determination of protein by sulpho-chromic oxidation. A. BOUTROUX (Bull. Soc. Chim. biol., 1932, 14, 1343—1349).—The method is satisfactory for purified proteins, but cannot be used directly on sera owing to interference of lipins.

A. L.

Micro-Kjeldahl method. S. BALACHOVSKI and B. BRUNS (Biochem. Z., 1932, 256, 292).—An apparatus is described which permits the  $\text{NH}_3$  to be distilled off by evaporating to dryness in vac., the vol. of distillate being always the same.

P. W. C.

Alternative reagent for the determination of galactose. V. J. HARDING, T. F. NICHOLSON, and G. A. GRANT (J. Biol. Chem., 1933, 99, 625—628).—*Saccharomyces marxianus*, being, in contrast to galac yeast, without action on maltose, can be used for the determination of galactose mixed with certain other sugars in urines and Folin-Wu blood-filtrates. The technique of the method is described.

A. L.

