

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

MAY, 1934.

### General, Physical, and Inorganic Chemistry.

**Fine structure of the Balmer lines.** W. V. HOUSTON and Y. M. HSIEH (Physical Rev., 1934, [ii], 45, 263—272).—A new method of treating interferometer patterns of doublets, involving measurements of the intensities of min. between the members of the doublet and between successive orders of interference, is applied to the Balmer series. The separations of the centres of gravity for the lines  $H_{\beta, \gamma, \delta, \epsilon}$  are much < the calc. vals., and explanations of the discrepancy are discussed. N. M. B.

**Mathematical representation of the energy levels of the secondary spectrum of hydrogen.** I. SANDEMAN (Proc. Roy. Soc. Edin., 1932—1933, 53, 347—353).—Assuming certain vals. for the coeffs. of the higher powers of  $J(J+1)$ , where  $J$  is the quantum no., it is proposed to write the energy term form for the rotational spectra of diat. mols. as  $F(J)=[B_e J(J+1)]/[1+u^2 J(J+1)]$ , where  $u=2B_e/\omega_e$ ,  $B_e$  is a const., and  $\omega_e$  is the equilibrium val. of the vibration frequency. The expression fits the simpler states of  $H_2$ , and is equiv. to Kratzer's potential energy expression. An extension is suggested for states to which the simple form is not applicable. N. M. B.

**Polarisation effect in helium D terms. Dipole and quadrupole effects.** E. A. HYLLERAAS (Z. Physik, 1934, 88, 108—113).—Theoretical. A. B. D. C.

**Spectrum of the carbon arc in the red region.** H. BIRKENBELL (Z. Physik, 1934, 88, 1—13).—The region 6000—9000 Å. has been photographed and analysed. A. B. D. C.

**Rydberg's potential energy function and transition probabilities.** N. R. TAWDE (Current Sci., 1934, 2, 293—294).—Band intensity measurements on the  $N_2$  spectrum agree far better with the Condon parabola of max. probabilities based on Rydberg's function than with Morse's function, confirming Johnson and Dunstan's conclusions (A., 1933, 884). D. R. D.

**Intensities in the spectrum of O II.** K. G. EMELEUS (Proc. Nat. Acad. Sci., 1934, 20, 115—117).—In order to explain the absence of the multiplets  $\lambda\lambda$  4956, 4406, and 2419 and the presence of 4950 in the negative glow of a cold-cathode discharge with low c.d., spectra from other sources were examined. The possibility of simultaneous dissociation, ionisation, and excitation of the  $O_2$  mol. by electron impact is considered. N. M. B.

**Anomalous dispersion for the doublet H, K of ionised calcium.** L. PUCCIANI (Atti R. Accad.

Lincei, 1934, [vi], 19, 13—15).—Anomalous dispersion measurements show that the intensity of the  $1S-2P_1$  line of  $Ca^+$  is double that of the  $1S-2P_2$  line. O. J. W.

**Arc spectrum of chromium under reduced pressure.** H. WERRES (Z. wiss. Phot., 1934, 32, 278—282).—The spectra in air and under reduced pressure are mapped from 2900 to 4400 Å. The "vac." lines, although close to those of the solar spectrum, do not entirely correspond with them. J. L.

**Multiplets in the spectrum of Cu III.** B. V. R. RAO (Z. Physik, 1934, 88, 135—138). A. B. D. C.

**Paschen-Back effect. I. L-S coupling; the  $3p^3D$  multiplets of Zn and Cd.** J. B. GREEN and D. E. GRAY (Physical Rev., 1934, [ii], 45, 273—276).—Observed frequencies and intensities are in good agreement with those calc. by Darwin's method. N. M. B.

**Absorption of light by adsorbed bromine.** J. F. H. CUSTERS and J. H. DE BOER (Physica, 1934, 1, 265—270; cf. A., 1933, 656).—Br adsorbed on  $CaF_2$  at low pressures gives absorption max. at 2670, 2520 Å., attributed to dissociation into two normal and into one normal and one excited atom, respectively. The energy difference between the max. corresponds with that between the  $2P_{3/2}$  and the  $2P_{1/2}$  states of Br. The displacement of these two bands towards the ultra-violet represents an energy of 1.9 e.v. H. J. E.

**Nuclear moment of indium.** F. PASCHEN and I. S. CAMPBELL (Naturwiss., 1934, 22, 136—137).—Fine structure of lines in the In  $\pi$  spectrum leads to the conclusion that the nuclear moment of In is  $9/2$ , in agreement with Jackson (A., 1933, 200). There is no evidence of any new isotope of In. A. J. M.

**Nuclear moment of tellurium and selenium isotopes.** S. RAFAŁOWSKI (Acta. phys. polon., 1933, 2, 119—123; Chem. Zentr., 1933, ii, 3096—3097).—Hyperfine structure in the line spectra of Te and Se has been measured. The isotopes have zero nuclear moment. H. J. E.

**Absorption spectra due to excitation of inner electrons. VI. The Cs spectrum between 1020 and 600 Å. due to excitation of the  $(5p)^6$  shell (Cs I<sup>b</sup>).** H. BEUTLER and K. GUGGENHEIMER (Z. Physik, 1934, 88, 25—42). A. B. D. C.

**Regularities in the spectrum Ce III.** V. D. DABHOLKAR (Current Sci., 1934, 2, 286).—A note (cf. this vol., 2). D. R. D.

**Arc spectrum of osmium.** W. ALBERTSON (Physical Rev., 1934, [ii], 45, 304—308).—Complete classifications as transitions between 137 terms of Os I are tabulated for > 1050 lines, and  $J$  vals. are assigned. The normal state of Os is  $5d^6s^2(^5D_4)$ ; the ionisation potential is approx. 8.7 volts.

N. M. B.

**Illumination of rarified gases by high-frequency currents.** F. ESCLANGON (Ann. Physique, 1934, [xi], 1, 267—406).—The gases are contained in discharge tubes at the centre of a solenoid carrying a high-frequency current of wave-length range 50—150 m. Two stages of illumination are found, one for weak excitation, and a brilliant one appearing only for intense excitation and low pressure. Variations of the field components show that the first is due primarily to the electrostatic field, and the second to induced currents. The induced field alone is incapable of exciting the discharge, but can sustain the second stage when initiated. Data are given for  $O_2$ , and for Ne, Ar, He,  $H_2$ , and  $N_2$ . Spectroscopic observations, and the excitation, by high-frequency currents, of at. jets, and Doppler broadening are discussed.

N. M. B.

**Theory of positive column with moving striations.** M. J. DRUYVESTEYN (Physica, 1934, 1, 273—280).—Theoretical.

H. J. E.

**K series of aluminium and magnesium.** H. KARLSSON and M. SIEGBAHN (Z. Physik, 1934, 88, 76—82).

A. B. D. C.

**Weak lines in  $K\beta$  spectra of molybdenum, rhodium, and silver.** H. HULUBEL and (MLLE.) Y. CAUCHOIS (Compt. rend., 1934, 198, 1222—1223).—Seven lines,  $\beta_0, \beta_{4-9}$ , of each of these elements have been measured, of which two,  $\beta_8$  and  $\beta_9$ , are new (cf. A., 1933, 548, 881).

C. A. S.

**Probability of double ionisation in the X-ray range.** F. WISSHAK (Physikal. Z., 1934, 35, 301—302).—Examination of the  $K\alpha_1$  and  $K\alpha_2$  lines of Cu shows that the probability of double ionisation for a potential of 30 kv. is  $2 \times 10^{-5}$ .

A. J. M.

**Ionisation in nitrogen at high pressures.** S. CHYLINSKI (Physical Rev., 1934, [ii], 45, 309—313; cf. Broxon, A., 1932, 3; Compton, *ibid.*, 556).—The ionisation-pressure relation for  $\gamma$ - and residual rays was investigated up to 120 atm., and a series of saturation characteristics up to 109 atm. for the intensity range 7—1200 ions per c.c. per sec. per atm. was determined.

N. M. B.

**Ionisation functions of the inert gases.** H. FUNK (Physikal. Z., 1934, 35, 302—303).—The at.-ray method (A., 1930, 268) has been applied to the inert gases. Max. ionisation occurred at potentials of 120, 130, and 85 volts for He, Ne, and Ar, respectively.

A. J. M.

**Self energy of the electron.** G. WATAGHIN (Z. Physik, 1934, 88, 92—97).—Theoretical.

A. B. D. C.

**Electron affinities.** P. P. SUTTON and J. E. MAYER (J. Chem. Physics, 1934, 2, 145—146).—The electron affinity of an electronegative gas  $X_2$  can be found from the equilibrium const. of the reaction  $X \rightarrow X + e^-$ , when the gas comes in contact with

a hot metallic surface, obtained from the surface temp., gas pressure, and ratio of the currents carried by the ions and electrons. Results for  $I_2$  are in good agreement with those calc. from the lattice energies of the alkali iodides.

N. M. B.

**New transition produced by electron impact in helium.** R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1934, 2, 491).—A line has been observed in the electron spectrum in He corresponding with an energy loss of 59.2 volts. It is not due to three successive transitions  $1'S_0-2'P_0$  corresponding with energy loss of 63.3 volts.

H. S. P.

**Emission of electrons under the influence of chemical action. II. General conclusions and a further study of the case of carbonyl chloride.** A. K. DENISOFF and O. W. RICHARDSON (Proc. Roy. Soc., 1934, A, 144, 46—75; cf. A., 1931, 994).—The energy distribution of the electrons emitted in the reaction between  $K_2Na$  and twenty-two gases has been studied. The results can be interpreted by the equation  $E_m = E_c - \phi$ , where  $E_m$  is the max. energy of the emitted electrons,  $E_c$  is the energy of the corresponding chemical reaction responsible for  $E_m$ , and  $\phi$  is the work function of the metal. This relation is general, and is similar to the fundamental law of photoelectricity.

L. L. B.

**Electron and positron.** W. H. FURRY and J. R. OPPENHEIMER (Physical Rev., 1934, [ii], 45, 245—262).—Mathematical. Dirac's interpretation of the negative kinetic energy states in his theory of the electron is developed to give a consistent theory of electrons and positrons.

N. M. B.

**Production of positive electrons.** J. CHADWICK; P. M. S. BLACKETT, and G. P. S. OCCHIALINI (Proc. Roy. Soc., 1934, A, 144, 235—248).—The emission of positive electrons (positrons) has been observed from a Pb target exposed to the  $\gamma$ -rays of Th-C'', from a source of the active deposit, and from a Pb target exposed to the radiations ( $\gamma$ -rays and neutrons) emitted by Be, B, and F when bombarded by Po  $\alpha$ -particles. The observations of the energies of the positrons ejected by the  $\gamma$ -rays of Th-C'' support the view that an electron and a positron of equal mass are produced simultaneously by the interaction of a  $\gamma$ -ray and an atom. They are probably produced in the electric field outside, rather than inside, the nucleus.

L. L. B.

**Physical properties of the positron. Annihilation of matter and radiation of dematerialisation.** J. THIBAUD (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 36—52).—A full account of work already noted (cf. A., 1933, 993; this vol., 4, 126, 341).

J. W. S.

**Emission of alkali atoms from various ammonia catalysts.** A. K. BREWER (J. Chem. Physics, 1934, 2, 116—118).—The rate of emission of alkali as positive ions and neutral atoms is measured (cf. A., 1931, 1106; this vol., 233). When the temp. of the catalyst is first raised to the emission point, the no. of emitted atoms far exceeds that of ions, but falls to a negligible val. after several min. heating. Atom emission is much more persistent from catalysts containing  $Al_2O_3$ , and the temp. for equiv. ion

currents is higher. Both atom and ion emission increase when sintering occurs, since the alkali can diffuse more readily to the surface. Factors determining the ratio of atoms to ions are discussed.

N. M. B.

**Slow ions and neutral rays.** A. ROSTAGNI (*Z. Physik*, 1934, **88**, 55—75).—Formation of neutral rays by  $A^+$  and  $H_2^+$  was studied for grazing incidence at a metal target with velocities between 100 and 600 volts, and the effective cross-section of  $A^+$ ,  $Ne^+$ , and  $He^+$  was determined for transference of charge when passing through the same gas at velocities between 600 and 6 volts. The efficiency of  $H_2$ ,  $A$ ,  $Ne$ , and  $He$  for releasing electrons from metal surfaces at velocities from 600 to 6 volts was obtained for the ionic and neutral rays.

A. B. D. C.

**Distribution of initial velocities of positive ions from tungsten.** G. J. MUELLER (*Physical Rev.*, 1934, [ii], **45**, 314—319).—Data and curves for eighteen temp. (1300—3000° abs.) are given; distribution is Maxwellian.

N. M. B.

**Optical investigation of mercury atom beams.** S. YEN (*Helv. phys. Acta*, 1933, **6**, 250—252; *Chem. Zentr.*, 1933, ii, 3392).—The resonance radiation from a beam of Hg atoms illuminated with  $\lambda$  2536 Å., and the effect of a magnetic field perpendicular to the beam, have been studied.

H. J. E.

**Curves for collisions between neutrons and protons.** G. MONOD-HERZEN (*J. Phys. Radium*, 1934, [vii], **5**, 95—96; cf. Auger, this vol., 235).—The distribution of slow and swift protons as a function of their direction with that of the incident neutron is determined from an examination of 6000 photographs. The curve for swift protons is symmetrical with a max. at 54°, and for slow protons it is asymmetrical with a max. at 70°.

N. M. B.

**At. wts. of iodine, carbon, and sodium. Ratio of iodine pentoxide to sodium carbonate.** G. P. BAXTER and A. H. HALE (*J. Amer. Chem. Soc.*, 1934, **56**, 615—617).—By assuming two of the at. wts. involved the third is calc. for several possible vals. of each element. It is concluded that the at. wt. of I is  $\approx$  126.92 and that of C is probably  $>$  12.00.

E. S. H.

**Discussion on heavy hydrogen.** (Proc. Roy. Soc., 1134, **A**, **144**, 1—28).—(LORD) RUTHERFORD discussed the history of the discovery of heavy hydrogen and its probable constitution: two protons and an electron, or a neutron and a proton. Also the question as to whether the fields of force near the  $H^1$  and  $H^2$  nuclei are the same. The use of  $H^2$  nuclei as swift projectiles for the study of the transmutation of the elements was mentioned.

N. V. SIDGWICK discussed the at. vol. of  $H^2$ , and the equilibrium const. for the reactions in which it takes part.

F. W. ASTON pointed out what a very small discrepancy of at. wts. and masses enabled the discovery to be made.

P. HARTECK demonstrated the differences in v.p. and f.p. between  $H_2O$  and  $H_2^2O$ , and discussed the prep. of  $H_2^2O$  by the electrolysis of alkaline solutions with Ni electrodes.

F. SODDY criticised the extension of the term "isotope" to  $H^2$ , and other supposed examples revealed only by band spectra. "Isotope" is a term applied to the individuals of a group of two or more chemically identical elements existing together in const. natural proportion and separable only by a few physical methods which depend directly on the masses of the mols. Aston's work on the non-radioactive elements and his discovery of the whole-no. rule give the best proof of this conception, particularly the constancy of the natural ratio.  $H^2$  does not appear to be in sufficient proportion to give concordance between the chemically and physically determined at. wts. The marked difference of chemical character discovered for  $H^2$  destroys the basis of the prediction. In the determination of the combining ratio of  $H_2$  to  $O_2$ , differences in purification would lead to differences in at. wt. determinations which have not been observed. The case under discussion appears more analogous to the separation of a pair of homologues, e.g., Zr and Hf, than isotopes.

M. PÓLÁNYI discussed the catalysed (Pt-black) interchange between the  $H^2$  and the  $H^1$  in  $H_2O$ . The results throw light on the nature of overvoltage and point to its cause being the transition of the H ion to its at. form adsorbed on the Pt. The generally assumed view that  $H^2$  will react more slowly than  $H^1$  is not always correct.

E. K. RIDEAL described work carried out by L. and A. Farkas on the equilibrium  $H_2^1 + H_2^2 \rightleftharpoons 2H^1H^2$  by a thermal conductivity method. The equilibrium const. does not change much above room temp. and up to 600°, and lies between 3 and 4. The two possible mechanisms for the reaction (1)  $H_2^1 + H_2^2 \rightleftharpoons 2H^1H^2$ , and (2)  $H^1 + H_2^2 \rightleftharpoons H^1H^2 + H^2$ ,  $H^2 + H_2^1 \rightleftharpoons H^1H^2 + H^1$ , are discussed. The kinetics of the  $H_2^2 + H_2O$  reaction have been investigated, also the diffusion of the isotopes through Pd.  $H^1$  passes through more rapidly than  $H^2$ . The gas evolved on dissolving Zn in dil  $H_2SO_4$  (30%  $H^1$ - $H^2$  water) has  $H^1 : H^2 = 3.5$ .

R. H. FOWLER discussed the separation of  $H^1$  and  $H^2$  by electrolysis.

R. P. BELL described measurements carried out with J. H. Wolfenden. The nature of the cathode metal, the temp., and the c.d. exert no appreciable influence on the efficiency of separation of  $H^1$  and  $H^2$  by electrolysis, as expressed by the factor  $\alpha$  in the equation  $l \log H^2 = \alpha d \log H^1$ .

J. D. BERNAL. The cell measurements (X-ray) of a crystal of ice from 91%  $H_2^2O$  show a definite small difference from those of ordinary ice determined under the same experimental conditions. The apparent mol. vol. of  $H_2^2O$  is slightly  $>$  that of  $H_2^1O$ , whilst the apparent mol. vol. of heavy ice is slightly  $<$  that of ordinary ice. The reason for this difference is discussed.

W. JEVONS discussed recent spectroscopic investigations on  $H^2$ .

L. L. B.

**Isotopic ratio in oxygen.** W. R. SMYTHE (*Physical Rev.*, 1934, [ii], **45**, 299—303).—An improved mass-spectrometer is described (cf. A., 1932, 668). The ratio  $O^{16} : O^{18}$  in  $O_2$  prepared by the

decomp. of  $\text{PbO}_2$  is  $503 \pm 10$ . The divergence from available vals. is attributed to the method of prep.

N. M. B.

**Measurements of pressure dependence of ionisation currents.** P. KRAUS (Z. Physik, 1934, 88, 99—102).—These measurements should be corr. for change in capacity of the ionisation chamber with pressure.

A. B. D. C.

**Physical relationship between the "Röntgen" ( $r$ ) and the so-called radium dosage "mgeh/cm."** R. JAEGER (Physikal. Z., 1934, 35, 273—275).—The relationship between the "Röntgen" ( $r$ ) and the radium dosage unit mgeh/cm. (mg. Ra element-hr. at a distance of 1 cm. from the prep.) has been derived using the Eve const. (no. of ion-pairs produced per c.c. in free air by the  $\gamma$ -radiation from 1 Curie of Ra-C at a distance of 1 cm. from the prep.). If this is  $4.28 \times 10^9$  at n.t.p., 1 mgeh/cm. =  $7.35r$ ; this depends to a certain extent on the filtration adopted.

A. J. M.

**Mobility of radioactive atoms on the surface of solids.** H. JĘDRZEJOWSKI (Acta phys. polon., 1933, 2, 137—142; Chem. Zentr., 1933, ii, 3091—3092).—A deposit of Po on one part of a Pt foil was found (photographically) to be almost uniformly distributed over the Pt surface after heating to  $910^\circ$ . An evaporation process is excluded, and surface diffusion must have occurred. No such diffusion occurs on Au up to  $1000^\circ$ .

H. J. E.

**Distribution of Ra-A, -B, and -C in radioactive equilibrium with radon in a spherical vessel.** W. MUND and A. LUYCKX (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 24—29).—Theoretical.

J. W. S.

**Diffusion of Th-C''.** (MLLE.) C. CHAMIÉ (J. Phys. Radium, 1934, [vii], 5, 54—56; cf. this vol., 5).—Curves for the diffusion of Th-C'', obtained by the recoil method from Th-C and received on an uncharged plate, show that the amount diffusing in air is very small, and decreases rapidly with the distance between the receiver and the source. Diffusion conditions differ widely from those of emanations.

N. M. B.

**Activation by diffusion.** P. LANGEVIN (J. Phys. Radium, 1934, [vii], 5, 57—60).—Mathematical. The results of Chamie (see preceding abstract) lead to a hyperbolic law of variation of activation as a function of the distance between the receiver and the source.

N. M. B.

**Penetrating radiation from potassium.** F. D. GREEVES (Proc. Roy. Irish Acad., 1933, A, 41, 129—136).—Using an arrangement of counter, screens, and small source, and having regard to the background effect varying with meteorological conditions, the  $\beta$  and fast  $\gamma$  radiations from K were examined. The absorption coeff. of the  $\gamma$  radiation in Pb was  $0.60 \text{ cm.}^{-1}$ .

N. M. B.

**Absolute energy measurement in the  $\beta$  spectrum of active thorium deposit.** R. ARNOULT (J. Phys. Radium, 1934, [vii], 5, 67—70).—A focalisation method gives for the most intense ray the val.  $HR=1381.5$  gauss cm. corresponding with an energy  $146.88$  electron kv.

N. M. B.

**Scattering of hard gamma-rays by lead, and the annihilation of positive electrons.** E. J. WILLIAMS (Nature, 1934, 133, 415).—An experiment which supports the hypothesis that the nuclear scattering of hard  $\gamma$ -rays by heavy elements is due to the annihilation of positive electrons produced by the  $\gamma$ -rays is described.

L. S. T.

**Absorption of penetrating  $\gamma$ -rays.** W. GENTNER (J. Phys. Radium, 1934, [vii], 5, 49—53; cf. this vol., 5).—The absorption in Pb of  $\gamma$ -rays of wavelengths 4.7, 5.9, 6.6, 7.9, and 9.3 Å. was measured. Comparison of the experimental and theoretical absorption curves gives the nuclear absorption as a function of the wave-length.

N. M. B.

**Scattering of hard  $\gamma$ -rays.** L. MEITNER (Naturwiss., 1934, 22, 174).—Scattering of  $\gamma$ -rays with no change of wave-length should occur at electrons with negative energy in the presence of an at. nucleus.

A. J. M.

**Neutron.** A. BRAMLEY (Science, 1934, 79, 160).—A discussion.

L. S. T.

**Photographic detection of spontaneous neutron emission.** S. PIENKOWSKI and J. STARKIEWICZ (Acta phys. polon., 1933, 2, 105—110; Chem. Zentr., 1933, ii, 3090—3091).—No emission from Sb, Bi, and La was detectable photographically.

H. J. E.

**Angular distribution of protons ejected by neutrons.** N. A. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 179—181).—The angular distribution of protons ejected by a parallel beam of neutrons (from Rn+Be) from a paraffin plate inside a Wilson chamber is in better agreement with the results of Curie (Physical Rev., 1933, [ii], 44, 463) than with those of Auger and Monod-Herzen (A., 1933, 551). The greater angle scattering observed by Dunning and Pegram (Physical Rev., 1933, [ii], 43, 497) may be due to C of the paraffin.

J. W. S.

**Photographic method, and artificial disintegration of atoms.** (MLLE.) M. BLAU (J. Phys. Radium, 1934, [vii], 5, 61—66).—A photographic plate is sensitive to H-rays, and shows trajectories, from the lengths of which the speed of the rays can be found. Velocity distributions of H-rays from at. disintegrations, and excited by neutrons, are thus investigated. Results are given for H-rays from disintegration of Al, and for transmutation neutrons of Be.

N. M. B.

**Artificial production of a new kind of radioelement.** F. JOLIOU and I. CURIE (Nature, 1934, 133, 201—202; cf. this vol., 234, 343).—The transmutation of B, Mg, and Al  $\alpha$ -particles gives rise to new radio-elements emitting positrons. *E.g.*, for B, there occurs the nuclear reaction  ${}_5\text{B}^{10} + {}_2\text{He}^4 = {}_7\text{N}^{13} + {}_0\text{e}^1$ , where  ${}_7\text{N}^{13}$  is the radioactive nucleus disintegrating with emission of positrons, giving a stable nucleus  ${}_6\text{C}^{13}$ . With Al and Mg the radioactive nuclei would be  ${}_{15}\text{P}^{30}$  and  ${}_{14}\text{Si}^{27}$ , respectively, produced in the ratio of  $10^{-7}$  or  $10^{-6}$  of the no. of  $\alpha$ -particles. A Po prep. of 100 millicuries gives approx.  $10^5$  atoms of the new radioactive elements. The  $\text{NH}_3$  obtained by heating irradiated BN with NaOH carries the activity with it, as does the  $\text{H}_2$  liberated

by action of HCl on irradiated Al. Pptn. of the activity in this case with Zr phosphate indicates that the radio-element is an isotope of P.

L. S. T.

**Artificial radioactivity discovered by Curie and Joliot.** L. MEITNER (Naturwiss., 1934, 22, 172—174).—The artificial radioactivity (*i.e.*, nuclear disintegration continuing after removal of bombarding particles) discovered by Curie and Joliot (see above) has now been directly observed in the Wilson cloud chamber. Photographs of the process are given. Positive electrons were found to be emitted from Al 9 min. after shutting off the Po  $\alpha$ -rays, and from B 12 min. after. No negative electrons were produced, so that the reaction discussed by Curie and Joliot,  $\text{Si}_{28}^{30} = \text{Si}_{28}^{29} + e^+ + e^-$ , does not occur. A. J. M.

**Nuclear spin and maintenance of rotation impulse for nuclear processes.** H. RÄTHER (Naturwiss., 1934, 22, 151).—By considering the nuclear processes:  $\text{H}^2 + \text{Li}^6 = 2\text{He}^4$ ,  $\text{H}^1 + \text{Li}^7 = 2\text{He}^4$ ;  $\text{H}^2 + \text{Li}^7 = 2\text{He}^4 + n^1$ ,  $\text{B}^{11} + \text{He}^4 = \text{N}^{14} + n^1$ ,  $\text{Be}^9 + \text{He}^4 = \text{C}^{12} + n^1$ , it is shown that the application of the law of maintenance of rotation impulse to nuclear processes agrees with the calculation of nuclear spin from spectroscopic data. The last three processes indicate that the neutron has a nuclear spin involving  $\frac{1}{2}$ . A. J. M.

**Transmutation effects observed with heavy hydrogen.** M. L. OLIPHANT, P. HARTECK, and (LORD) RUTHERFORD (Nature, 1934, 133, 413).—When  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  in which  $\text{H}^1$  has been largely displaced by  $\text{H}^2$  are bombarded by an intense beam of protons no marked differences from  $\text{H}^1$  compounds are observed. When ions of  $\text{H}^2$  are used, however, there is a large emission of fast protons detectable even at energies of 20,000 volts. The proton group has a range of 14.3 cm., corresponding with an energy of emission of  $3 \times 10^6$  volts. There is also a short-range group of singly-charged particles of approx. 1.6 cm. range and numerically equal to the 14-cm. group. A large no. of neutrons, max. energy approx.  $3 \times 10^6$  volts, also result, but the reaction by which they are produced is probably less frequent than that which produces the protons. An interpretation of the results is put forward and the possible reactions  $\text{H}_2^+ + \text{H}_2^+ \rightarrow \text{H}_1^+ + \text{H}_1^+$  or  $\text{H}_2^+ + \text{H}_2^+ \rightarrow \text{H}_2^+ + n^0$  are discussed. L. S. T.

**Ranges of disintegration particles from lithium and boron by bombardment with rapid protons.** F. KIRCHNER and H. NEUBER (Physikal. Z., 1934, 35, 292—293; cf. A., 1933, 1098).—The ranges of the disintegration particles from Li and B were determined by a cloud-chamber method. For Li, particles of ranges 7, 9, and 12 mm. were found in the short-range group, whilst the range of the long-range group was 18.4 cm. The total no. of short-range particles was about twice that of the long-range. For B, the previous observations have been confirmed. There was a group with a max. at 22 mm., and another at 45 mm. A. J. M.

**Atomic disintegration of metallic sodium.** A. KÖNIG (Naturwiss., 1934, 22, 150—151).—A thin layer of Na on Au, protected from atm. oxidation by

a layer of Ag, was bombarded with Po  $\alpha$ -rays. The emitted protons fall into four groups. A. J. M.

**Disintegration of deuterons by high-speed protons and the instability of the deuteron.** G. N. LEWIS, M. S. LIVINGSTON, M. C. HENDERSON, and E. O. LAWRENCE (Physical Rev., 1934, [ii], 45, 242—244).—A comparison of the effect of proton bombardment on pairs of targets containing H and  $\text{H}^2$  in the form of  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{OH}^2)_2$  gave an excess of long-range protons from the targets containing  $\text{H}^2$ , and attributed to disintegration of the deuteron by the bombarding protons. The range of protons requires a neutron mass of approx. 1. N. M. B.

**The deuteron and disintegration.** H. J. WALKER (Phil. Mag., 1934, [vii], 17, 793—800).—A neutron-proton combination (the deuteron) may be a stable nuclear sub-unit for elements up to S. Two deuterons should unite to form an  $\alpha$ -particle. Nuclear structures are suggested and correlated with results on disintegration. H. J. E.

**Interpretation of the relation between cosmic and atomic quantities.** K. SITTE and W. GLASER (Z. Physik, 1934, 88, 103—107).—Theoretical. A. B. D. C.

**New hard component of the cosmic ultra-radiation.** A. CORLIN (Nature, 1934, 133, 419; cf. this vol., 128). L. S. T.

**Cosmic rays under 600 metres of water.** W. KOLHÖRSTER (Nature, 1934, 133, 419).—Measurements in the Stassfurt salt-mine show that the hardest cosmic rays penetrate also to 600 m. of  $\text{H}_2\text{O}$ . The apparent mass absorption coeff. is  $< 5 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1}$  with an upper limit  $1.8 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1}$  (cf. A., 1933, 1100). L. S. T.

**Stellar atmospheres with and without oxygen.** P. SWINGS (Bull. Acad. roy. Belg., 1934, [v], 20, 137—139).—Possible classification of stars according to their  $\text{O}_2$  spectra is discussed. J. W. S.

**Absence of molecular hydrogen bands in the spectra of sun-spots.** P. SWINGS (Bull. Acad. roy. Belg., 1934, [v], 20, 132—136).—It is shown theoretically that the concn. of mol.  $\text{H}_2$  in sun-spots may be too low for the absorption bands to appear in the astronomical spectral region. J. W. S.

**Free paths and transport phenomena in gases and the quantum theory of collisions. II. Determination of the laws of force between atoms and molecules.** H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1934, A, 144, 188—205; cf. A., 1933, 1101).—The form and magnitude of the interaction energy between two He atoms are considered in terms of observations of the viscosity of He at different temp. The interaction between a He atom and ion is discussed with reference to the mobility of He ions in He. Free paths are calc. for various laws of force between gas atoms. L. L. B.

**Relativistic theory of atoms with many electrons.** J. SOLOMON (Compt. rend., 1934, 198, 1023—1025; cf. A., 1933, 660). C. A. S.

**Materialisation of polarised æther.** V. POSEJ-PAL (Compt. rend., 1934, 198, 914—916; cf. this vol., 236). C. A. S.

**Interaction of two helium nuclei.** W. M. ELSASSER (*J. Phys. Radium*, 1934, [vii], 5, 71—74; cf. this vol., 6).—Mathematical. N. M. B.

**The atom as a system quantised in time and space.** G. BECK (*Helv. phys. Acta*, 1933, 6, 309—314; *Chem. Zentr.*, 1933, ii, 2634).—Theoretical. H. J. E.

**Velocity of light.** M. E. J. G. DE BRAY (*Nature*, 1934, 133, 464). L. S. T.

**Wave equation of photon.** Y. MIMURA and T. MAEKAWA (*J. Sci. Hiroshima Univ.*, 1934, A, 4, 41—45).—Mathematical.

**Vector model for almost-closed shells.** M. H. JOHNSON, jun. (*Proc. Nat. Acad. Sci.*, 1934, 20, 117—120).—Mathematical. The formulation of the properties of a group of equiv. electrons in terms of the corresponding holes, or electrons missing from a partly filled shell, is examined. N. M. B.

**Atmospheric water vapour band 6324 Å. in the solar spectrum.** V. N. KONDRATEEV and D. I. EROPKIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 1, 170—175).—235 new lines have been measured over an interval of 170 Å. around 6300 Å. in the spectra of the sun near the horizon. By comparison with the same spectral region for the sun higher in the sky some of these lines have been identified as due to terrestrial H<sub>2</sub>O vapour, and three others as new lines of the O<sub>2</sub> band  $\alpha$ . From measurements of the 6324 Å. H<sub>2</sub>O band of the 3, 1, 1 vibration state, vals. of the fine structure const., and moments of inertia of the H<sub>2</sub>O mol. are calc. The valency angle and O-H distance are 104.18° and 1.016 × 10<sup>-8</sup> cm., respectively. J. W. S.

**Band spectrum of aluminium deuteride.** W. HOLST and E. HULTHÉN (*Nature*, 1934, 133, 496).—Preliminary results for the spectra of AlH<sup>1</sup> and AlH<sup>2</sup> are given. The application of the data to the question of isotopes is discussed. L. S. T.

**Spectrum of MgF.** F. A. JENKINS and R. GRINFELD (*Physical Rev.*, 1934, [ii], 45, 229—233).—Consts. for the <sup>2</sup>Σ, <sup>2</sup>Σ and <sup>2</sup>Π, <sup>2</sup>Σ systems are evaluated from measurements of the band heads and of the partly resolved rotational structure. The isotope effect of Mg is observed in the +1 sequence of <sup>2</sup>Σ, <sup>2</sup>Σ bands. N. M. B.

**Absorption [spectrum] of liquid oxygen.** R. GUILLIEN (*Compt. rend.*, 1934, 198, 1223—1225; cf. A., 1931, 404; this vol., 123).—The spectrum between  $\lambda$  3500 and 8400 Å. has been examined using thicknesses of liquid O<sub>2</sub> up to 109 cm. A new band with max. at  $\lambda$  7307 was found. C. A. S.

**Line spectrum of chromic oxide and absorption spectra of chromium glasses.** G. JOOS and K. SCHNETZLER (*Z. physikal. Chem.*, 1934, B, 24, 389—392).—Cr<sub>2</sub>O<sub>3</sub> at -190° exhibits five ill-defined absorption lines characteristic of the lattice. B<sub>2</sub>O<sub>3</sub> glass with 1% Cr<sub>2</sub>O<sub>3</sub> shows the same lines, but if alkali is added, the lines disappear, and the spectrum, despite the low temp., then resembles that of an aq. solution of a Cr salt, indicating the absence of periodicity in the structure of the glass. R. C.

**Absorption [spectrum] of chromyl chloride.** M. KANTZER (*Compt. rend.*, 1934, 198, 1226—1227; cf. A., 1933, 791).—103 lines between  $\lambda$  5894 and 5050.5 Å. have been measured, and classified as affected by varying temp. (0—270°) and pressure. C. A. S.

**Absorption band spectra of polyatomic molecules in solution. I. Absorption due to the double linkings O:C:OH, O:C:H, :C:C, ·N:N·, and :C:N·.** S. KATO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, 23, 256—263).—The two absorption bands attributed to the groups :C:O etc. in polyat. mols. are shifted towards the red relative to the absorption of the CO mol., whilst the difference between the threshold frequencies of the bands is approx. equal to the difference between the <sup>3</sup>Π and <sup>1</sup>Π levels of the CO mol. R. S.

**Infra-red absorption spectra of phosphine.** L. W. FUNG and E. F. BARKER (*Physical Rev.*, 1934, [ii], 45, 238—241).—Data are given for the 10 μ absorption region showing three bands with centres at 1121, 992, and 990 cm.<sup>-1</sup> The 4.3 μ band centre is at 2327 cm.<sup>-1</sup> Weak bands were observed at 2.9 μ (3428 cm.<sup>-1</sup>) and 2.2 μ (4541 cm.<sup>-1</sup>). Doubling found in corresponding NH<sub>3</sub> bands is not shown; hence the P atom cannot pass readily through the plane of the three H atoms. The perpendicular type bands have intense central max., indicating that PH<sub>3</sub> behaves like a spherical top. N. M. B.

**Vibrational energy level system of the linear molecule HCN.** A. ADEL and E. F. BARKER (*Physical Rev.*, 1934, [ii], 45, 277—279).—The complete vibrational energy level scheme of the normal HCN mol., determined with the help of the newly-discovered rotation-vibration bands in the infra-red (cf. this vol., 129), is in good agreement with theory. The fundamental frequencies of the isotopic mol. H<sup>2</sup>CN are predicted from those found for HCN. N. M. B.

**Infra-red absorption spectrum of some cyclic and chain organic compounds.** R. FREYMAN and A. NAHERNIAC (*J. Phys. Radium*, 1934, [vii], 5, 75—84).—A recording spectrometer for the region 0.8—1.2 μ is described, by means of which data are obtained for the absorption bands of C<sub>6</sub>H<sub>6</sub>, PhI, PhBr, PhCl, PhNO<sub>2</sub>, PhMe, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeOH, cyclohexane, C<sub>6</sub>H<sub>14</sub>, and CHCl·CCl<sub>2</sub>. A new classification system of the C<sub>6</sub>H<sub>6</sub> bands is proposed, and the mol. structure is discussed. N. M. B.

**Smekal-Raman effect and molecular structure.** K. W. F. KOHLRAUSCH (*Naturwiss.*, 1934, 22, 181—189, 196—204).—A review.

**Raman spectrum of nitric acid.** H. ANDERHOLD and H. E. WEISS (*Z. Physik*, 1934, 88, 83—91).—The variation of the Raman spectrum of HNO<sub>3</sub> with concn. is not entirely due to dissociation, but to the formation of OH·NO<sub>2</sub> in the conc. acid; the frequency characteristic of  $\dot{N}O_3$  is absent from the pure acid spectrum. A. B. D. C.

**Raman frequencies of the ammonium group.** I. R. RAO and C. S. RAO (*Z. Physik*, 1934, 88, 127—134).—NH<sub>4</sub>Cl, NH<sub>4</sub>NO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were investigated in the cryst. form and in solution; the

Raman displacements for the  $\text{NH}_4$  group are 3117, 3169 (?), 3220  $\text{cm}^{-1}$  for crystals, and 3157, 3221, 3275 (?)  $\text{cm}^{-1}$  for solutions. A. B. D. C.

**Changes in the Raman spectrum of sulphuric acid on dilution.** L. A. WOODWARD and R. G. HORNER (Proc. Roy. Soc., 1934, A, 144, 129—143).—Microphotometer curves of the Raman spectra of  $\text{H}_2\text{SO}_4$  are given for the concn. range 100—10%. The frequencies 910, 978, and 1121  $\text{cm}^{-1}$  (characteristic of the  $\text{H}_2\text{SO}_4$  mol. and present in the pure acid) rapidly vanish on dilution, whilst the frequency 1036 (characteristic of the  $\text{HSO}_4'$  ion) appears and increases in intensity. At 50% acid the frequency 982 (characteristic of the  $\text{SO}_4''$  ion) appears and becomes stronger. The behaviour of the continuous background supports the view that it consists mainly of a true continuous Raman effect due to vibrations of mol. complexes. L. L. B.

**Raman spectrum of arsenic trifluoride and the molecular constants of  $\text{AsF}_3$ ,  $\text{AsCl}_3$ , and  $\text{PCl}_3$ .** D. M. YOST and J. E. SHERBORNE (J. Chem. Physics, 1934, 2, 125—127).—The Raman spectrum of  $\text{AsF}_3$  consists of four lines with frequencies  $\omega_1(1)$ , 707;  $\omega_2(1)$ , 341;  $\omega_3(2)$ , 644; and  $\omega_4(2)$ , 274  $\text{cm}^{-1}$ . The selection rules require a pyramidal mol. Electron diffraction data for  $\text{AsF}_3$ ,  $\text{AsCl}_3$ , and  $\text{PCl}_3$  are used to establish linking angles. Entropies are calc., and free energies of formation of liquid and gaseous  $\text{AsCl}_3$  are —65,190 and —62,718 g.-cal., respectively, at 25° ( $\pm 500$ —1400 g.-cal.). N. M. B.

**Raman spectrum of lead tetramethyl.** A. B. F. DUNCAN and J. W. MURRAY (J. Chem. Physics, 1934, 2, 146).—The lines 135, 458, 472, 766, 930, 1155, 1169, 2921, and 3000 were found and provisionally assigned. N. M. B.

**Raman spectra of ring compounds. II. Poly-substituted benzene compounds.** J. W. MURRAY and D. H. ANDREWS (J. Chem. Physics, 1934, 2, 119—124; cf. this vol., 10).—Data are given for  $\text{PhF}$ , 1:2:4- $\text{C}_6\text{H}_3\text{Cl}_3$ , 1:2:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$ ,  $\text{C}_6\text{HCl}_5$ ,  $\text{C}_6\text{Cl}_6$ , and  $\text{C}_6\text{Me}_6$ . Relations to the vibrations of the  $\text{C}_6\text{H}_6$  ring are discussed. N. M. B.

**Raman effect. II. Raman effect of phenylacetates, phenylpropionates, cinnamates, phthalates, salicylates, and phenylmethylcarbinol.** K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1934, 9, 88—108; cf. this vol., 130).—Data refer to the Me, Et, and Pr<sup>s</sup> esters and  $\text{CHPhMe}\cdot\text{OH}$ . The frequency 3060  $\text{cm}^{-1}$  of the C-H linking in the  $\text{C}_6\text{H}_6$  ring is influenced little by groups or atoms other than those adjacent to the C in the ring, and is raised by neighbouring double linkings. The intensities of the lines attributed to the C-O linking are enhanced by the proximity of the C:C linking, and the frequency 1720  $\text{cm}^{-1}$  is diminished to 1672  $\text{cm}^{-1}$  by  $\cdot\text{OH}$ , e.g., in the salicylates. The  $\text{C}_6\text{H}_6$  ring frequencies 615 and 1000  $\text{cm}^{-1}$  are absent from the di-derivatives, but other frequencies appear. The frequency of the  $\cdot\text{C}\cdot\text{O}\cdot\text{CH}_2\cdot$  grouping is 845  $\text{cm}^{-1}$ . J. G. A. G.

**Raman effect. XXX. Raman spectra of aliphatic ketones and aldehydes.** K. W. F. KÖHLRAUSCH and F. KÖPFL (Z. physikal. Chem., 1934,

B, 24, 370—388; cf. this vol., 346).—The frequencies 510 and 1390 are assigned to the group H·CO and the frequency 590  $\text{cm}^{-1}$  to the Me·CO group in addition to the CO frequency and the internal vibrations of the Me group. In compounds R·CO·X, where R is alkyl and X represents H, Cl, Me, OH, OMe, or OEt, the CO frequency  $\sim 1700$   $\text{cm}^{-1}$  is independent of the length of the R chain when this is straight, and the effect of branching in the  $\alpha$  position is small compared with that of varying X. Examination of the frequencies of R, where this group is not branched in the  $\alpha$  position, has shown that when R = isoamyl, two forms of mol. probably exist, owing to free rotation about the axis of the CH·CH<sub>2</sub> linking.

R. C.

**Application of the Raman effect. II. Conjugate ethylenic and benzenic double linking in the hydroaromatic ring.** T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 274—287).—Progressive substitution of ethylenic compounds is accompanied by an increase in the mean Raman frequency associated with the double linking (I). These frequencies can be separately identified in compounds containing two non-conjugated (I), but when (I) are conjugated, the frequencies are diminished. Measurements of the Raman spectra of dihydronaphthalene and indene show that conjugation of a (I) in the hydroaromatic nucleus with a benzenic (I) produces a still greater diminution in the frequency. R. S.

**Molecular scattering of light in liquids: fluctuations in orientation of homopolar and heteropolar molecules.** A. ROUSSET (Compt. rend., 1934, 198, 1227—1229).—An explanation of the more extensive continuous background on each side of the exciting line in the light scattered by a homopolar liquid (e.g.,  $\text{CS}_2$ ,  $\text{C}_6\text{H}_6$ ) than in that scattered by a heteropolar liquid (e.g.,  $\text{PhNO}_2$ ,  $\text{AcOH}$ ) is based on the stronger orientation of, and consequent smaller amplitude of vibrations induced in, heteropolar as compared with homopolar mols. The inference as regards gases is shown to be in conformity with recent results for compressed  $\text{O}_2$  (cf. A., 1929, 985; 1933, 998; this vol., 10). C. A. S.

**Phenomena of metachromasis.** L. LISON (Bull. Acad. roy. Belg., 1933, [v], 19, 1332—1341).—Metachromatic colouring matters all contain at least one not entirely substituted  $\text{NH}_2$  group. Such compounds only are capable of forming an imine base or of existing in two tautomeric forms, (a) of "normal" colour and (b) of colour near that of the imine base and probably directly related to it chemically. J. W. S.

**Variation of properties of zinc oxide as a result of mechanical treatment.** A. KUTZELNIGG (Monatsh., 1934, 64, 61—73).—The changes of colour and luminescence of ZnO brought about by pressure vary with the method of prep.; the most sensitive to pressure is the sublimed form and the least sensitive that prepared in the wet way. When the compressed product is powdered and ignited, it regains its original colour, but luminescence is regained incompletely. Light has no influence on the colour change. E. S. H.

**Fluorescence of zinc oxide at the temperature of liquid air.** A. KUTZELNIGG (*Monatsh.*, 1934, 64, 74—75).—The fluorescence of ZnO, prepared in different ways, is increased strongly at low temp.

E. S. H.

**Indications and reproducibility of fluorescence phenomena in solids and application to determinations of concentration.** J. EISENBRAND and G. SIEWERT (*Arch. Pharm.*, 1934, 272, 428—440).—The distribution of spectral intensity may be used to classify the fluorescence of solids, since it is almost independent of the size of the powder particles. The intensity of the fluorescence depends on the size and surface of the particles; consequently determinations of concn. in mixtures are uncertain.

H. S. P.

**Luminescence of pharmaceutical zinc oxide.** J. EISENBRAND and G. SIEWERT (*Arch. Pharm.*, 1934, 272, 440—451).—Luminescence produced by Hg radiation decreases with the size of particle, as measured by sedimentation and the adsorption of Congo-red.

H. S. P.

**Emission of Lenard phosphors in the red and infra-red.** E. LOES (*Ann. Physik*, 1934, [v], 19, 489—500).—The emission of various phosphors in the red and infra-red was photographed up to 950  $\mu$ . The long-wave bands were similar in structure to those found already in the visible and ultra-violet. Many emission bands were found in the infra-red. The temp. displacement of these bands is like that of the visible bands.

A. J. M.

**Photo-electric effect of crystalline semiconductors. I. Argentite, achantite, and cuprite.** G. ATHANASIU (*J. Phys. Radium*, 1934, [vii], 5, 85—94).—Photo-electric sensitivity for radiations in the range 0.4—1.4  $\mu$  was measured; max. were shown at 1.15, 1.2, and 0.64  $\mu$  for argentite (I), achantite (II), and cuprite, respectively. The influence of an auxiliary potential on the val. and sense of the photo-electric effect was investigated for (I). Evidence is given of residual phenomena supporting the theory of electrolytic decomp. of the crystal under the influence of the current. For (I) and (II), the radiation giving the max. photo-electric effect coincides with that inducing max. photo-conductivity at low temp.

N. M. B.

**Ionising power of compounds of light elements.** A. DORABIALSKA (*Rocz. Chem.*, 1934, 14, 105—114).—The ionising power of a no. of compounds has been measured, using piezoelectric quartz in a large ionising chamber, with a paraffin screen. Compounds of Se, Y, La, As, Sb, Bi, F, Nb, and Ta give rise to feeble currents, whilst Sb and compounds of Li, Ca, Al, Si, and Ti are inactive.

R. T.

**Mobility of metallic ions in alkali halide crystals.** S. A. ARZYBYSHEV and A. S. TOPORETSZ (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 1, 176—178).—When a potential is applied between two metal plates in contact with opposite faces of a NaCl crystal at a high temp., a coloured layer forms on the side in contact with the positively-charged plate, the thickness of the layer formed at const. temp. being proportional to the time of application of the potential. The effect is attributed to distortion of the crystal lattice

by diffusing Cu ions, and it is deduced that at 700° the mobility of Cu<sup>++</sup> ions is about 130  $\mu$  per sec.

J. W. S.

**Variation with time of current in semi-conducting material with low voltage.** G. DECHÊNE (*Compt. rend.*, 1934, 198, 1021—1023; cf. A., 1930, 129; 1933, 884).—With yellow HgO, PbCl<sub>2</sub>, ZnO, or effloresced Na<sub>2</sub>CO<sub>3</sub> as semi-conducting material and Hg electrodes, the counter-e.m.f. increases slowly with increase in the d.c.; with low voltage resistance increases with time at the anode, and decreases at the cathode, but on reversal shows an increase followed by a decrease.

C. A. S.

**Electrical conductivity of Cu-Pd alloys with disordered and ordered atomic distributions at low temperatures (with an appendix on Cu<sub>3</sub>Pt).** H. J. SEEMANN (*Z. Physik*, 1934, 88, 14—24).—Measurements of the resistance of Cu-Pd alloys containing 38—53 at.-% Pd at room, liquid N<sub>2</sub>, and liquid H<sub>2</sub> temp. show that although the resistance of the ordered atom alloy is < that of the disordered at room temp., the resistance of the ordered decreases less rapidly with fall in temp.

A. B. D. C.

**Resistance of manganese arsenide.** L. F. BATES (*Phil. Mag.*, 1934, [vii], 17, 783—793; cf. A., 1933, 1109).—The resistance of Mn<sub>3</sub>As<sub>2</sub> changes abruptly at a temp. between 30° and 50°, depending on the previous heat-treatment. The relation between this change and changes in the energy of spontaneous magnetisation is discussed.

H. J. E.

**Electromagnetic waves of 1.1 cm. wave-length and the absorption spectrum of ammonia.** C. E. CLEETON and N. H. WILLIAMS (*Physical Rev.*, 1934, [ii], 45, 234—237).—Using magnetron-type oscillators as the source of continuous short-wave radiation, the absorption spectrum of NH<sub>3</sub> was mapped for the wave-length region 1—4 cm. The absorption max. was at 1.25 cm. The calc. effective collision diameter of the mol. is 8.8 × 10<sup>-8</sup> cm.

N. M. B.

**Resonance frequency of oscillatory circuits with leaky condenser, and its bearing on the measurement of the dielectric constant of ionised gas.** S. S. BANERJEE (*Phil. Mag.*, 1934, [vii], 17, 834—843).—The apparent increase in the dielectric const. is due to the conductivity of the ionised gas.

H. J. E.

**Determination of dipole moments in solution.** S. SUGDEN (*Nature*, 1934, 133, 415—416).—When mol. polarisation  $P_2$  is plotted against vol. polarisability  $(\epsilon-1)/(\epsilon+2)$  for solutions of PhCN, PhNO<sub>2</sub>, and PhCl in non-polar solvents, the points for each substance all lie near a straight line through the entire range of solutions to the pure liquid. The measured polarisation appears to be < the true val. of  $P_2$ , which should be obtained by extrapolating the curve to  $(\epsilon-1)/(\epsilon+2)=0$ . Vals. for  $\mu$  obtained from the curve are given. The dipole moments calc. from  $\propto P_2$  in a solvent may be erroneous when the dipole moment is large.

L. S. T.

**Two types of dielectric polarisation.** S. O. MORGAN (*Trans. Electrochem. Soc.*, 1934, 65, 185—192).—Dielectric polarisation of the Debye type (I),



due to orientation of dipoles, usually occurs at high frequencies, but it may be found at low frequencies with highly viscous materials. Polarisation of the Maxwell-Wagner type (II), due to heterogeneity, is generally to be sought at low frequencies, but it may occur at high frequencies if either component of the dielectric has a high conductance. The two types may be distinguished, however, by their being affected by temp. in opposite senses. Data at various temp. show that anomalous dispersion in glycerol is attributable to (I), but that in "halowax" and paper to (II).

H. J. T. E.

**Dipole moment of associated molecules and validity of mass law for association.** I. SAKURADA (Z. physikal. Chem., 1934, B, 24, 437—444).—Assuming that when an associating liquid is dissolved in a non-polar solvent the associated mols. are either all double mols. or all triple mols. and that the mass law is valid for the association, equations are derived permitting the calculation from the orientation polarisation of the solute of the dipole moment of the polymerised mols. and the dissociation const. The equations have been verified from existing data. PhCl, EtOAc, MeOAc, and CHCl<sub>3</sub> are stated to form dipole-free double mols., whilst PhNO<sub>2</sub> forms dipole-free triple mols.

R. C.

**Dielectric constant studies. IV. Moments of some inorganic compounds.** (Miss) M. G. MALONE and A. L. FERGUSON (J. Chem. Physics, 1934, 2, 99—104; cf. this vol., 363).—The dipole moments of SbCl<sub>3</sub>, SbBr<sub>3</sub>, SbI<sub>3</sub>, AsBr<sub>3</sub>, AsI<sub>3</sub>, AsF<sub>3</sub>, PI<sub>3</sub>, and LiClO<sub>4</sub> have been determined in various solvents. The vals. agree fairly well with those derived from a consideration of the electronegativity of the elements.

N. M. B.

**Electric moment of dioxan.** C. H. SCHWINGEL and E. W. GREENE (J. Amer. Chem. Soc., 1934, 56, 653—654).—Data recorded for dielectric const. and polarisation of 1:4-dioxan vapour at temp. between 337° and 487° abs. indicate zero electric moment.

E. S. H.

**Dielectric measurements with dipole liquids.** J. L. SNOEK (Physikal. Z., 1934, 35, 196—203).—The dipole contribution to the vol. polarisation has been determined for different concns. of the following substances in various solvents (CCl<sub>4</sub>, C<sub>6</sub>H<sub>14</sub>, or C<sub>6</sub>H<sub>6</sub>): MeNO<sub>2</sub>, PhNO<sub>2</sub>, C<sub>5</sub>H<sub>11</sub>NO<sub>2</sub>, EtNO<sub>2</sub>, EtOAc, PhF, MeCN, CH<sub>2</sub>Cl·CN, CHCl<sub>2</sub>·CN, CCl<sub>3</sub>·CN, pyrazine, 2:5- and 2:6-di- and tetra-methylpyrazine, 2-methyl- and 2:3-dimethyl-quinoxaline, C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

A. J. M.

**Dipole moments of acetic anhydride and of some fatty acids.** A. PIEKARA and B. PIEKARA (Compt. rend., 1934, 198, 1018—1020).—The mol. polarisation,  $P_{\infty}$ , of Ac<sub>2</sub>O, deduced from several concns. in CS<sub>2</sub> solution, is 196.5 at 5° and 187.5 at 25°; dipole moment,  $\mu$ ,  $2.82 \times 10^{-18}$ , or from temp. variation of  $P_{\infty}$ ,  $2.46 \times 10^{-18}$ .  $P$  of AcOH and EtCO<sub>2</sub>H in C<sub>6</sub>H<sub>14</sub> at 10° and 30° show increases with both concn. and temp., but  $P_{\infty}$  is independent of temp. (cf. A., 1930, 523, 824; 1933, 888, 1240).

C. A. S.

**Derivatives of normal pentane and normal heptane. III. Dipole moments of the bromoethoxy- and the dibromo-derivatives.** M. L.

SHERRILL, M. E. SMITH, and D. D. THOMPSON (J. Amer. Chem. Soc., 1934, 56, 611—614; cf. A., 1930, 888).—Data are recorded for b.p.,  $d$ ,  $n$ , dielectric const., and electric moment of six bromoethoxy- and five Br<sub>2</sub>-derivatives.

E. S. H.

**Polarity of chemical compounds. V. K. HIGASHI** (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 16—17; cf. A., 1933, 1230).—The dipole moment of (·CH<sub>2</sub>Cl)<sub>2</sub> dissolved in C<sub>6</sub>H<sub>6</sub> (I) and in amylene (II) has been measured at different temp. The abnormally high, almost const. moment in (I) is attributed to the influence of the (I) ring itself. Data from the (II) solution show normal behaviour and are considered to be trustworthy in view of its small moment, 0.37, in (I). The moment of CH<sub>2</sub>Cl·CH<sub>2</sub>Br is 1.52 and  $1.17 \times 10^{-18}$  e.s.u. in (I) and C<sub>6</sub>H<sub>14</sub> solution, respectively, at 25°.

R. S.

**Dielectric constants of polar solutions. J. WYMAN, jun.** (J. Amer. Chem. Soc., 1934, 56, 536—544).—Data are recorded for solutions of NH<sub>3</sub>-acids and polypeptides in H<sub>2</sub>O, aq. EtOH, aq. CO(NH<sub>2</sub>)<sub>2</sub>, and other solvents. In all cases the dielectric const. is a nearly additive property of the solutions. A theoretical interpretation is advanced.

E. S. H.

**Volumes of substances in the free state and in solution. I. I. SASLAVSKI** (J. Gen. Chem. Russ., 1933, 3, 897—903).—The apparent mol. vol. (I) of non-electrolytes diminishes on dissolution; that of electrolytes may increase or diminish, according to the nature of the individual salt. These effects are due chiefly to change in vol. of the solvent. Certain periodic variations in the magnitude of the effect obtained are found for salts of the same anion with cations of increasing at. no. Where the cation is const. (Na<sup>+</sup>), and the anion is varied, the % diminution in (I) increases in the series I' = ClO<sub>3</sub>' < BrO<sub>3</sub>' < NO<sub>3</sub>' < OAc' < Br' = N<sub>3</sub>' < Cl' < NO<sub>2</sub>' < HCO<sub>2</sub>' < MoO<sub>4</sub>' < WO<sub>4</sub>' < SO<sub>4</sub>' < SeO<sub>4</sub>' < CO<sub>3</sub>' < PO<sub>4</sub>' < AsO<sub>4</sub>' < OH' < S'.

R. T.

**Physical properties and chemical constitution. I. Esters of normal dibasic acids and of substituted malonic acids. A. I. VOGEL** (J.C.S., 1934, 333—341).—Data are given for  $n_{D, D, F, G}$  at 20°, mol. refraction coeffs., parachors, and dispersion, and for the density and surface tension over a temp. range for the Me and Et esters of malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids, and for the Me esters of substituted malonic and of cyclic 1:1-dicarboxylic acids. The vals. for an increment of CH<sub>2</sub> for the mol. refraction coeffs. for the mol. refractivities of the C, D, F, and G lines agree with available data, but the mean difference for the parachor is 40.3, giving at. parachors C=11.5, H=14.4, calc. from existing data on the normal hydrocarbons.

N. M. B.

**Molecular refractions and dispersions in the ultra-violet of salts and of ions in water solution. G. S. FORBES and H. B. ELKINS** (J. Amer. Chem. Soc., 1934, 56, 516—521).—Data have been determined for KCl, KBr, KI, KNO<sub>3</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SeO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, LiClO<sub>4</sub>, NaClO<sub>4</sub>, NaClO<sub>3</sub>, NaBrO<sub>3</sub>, NaIO<sub>3</sub>, LiIO<sub>3</sub>, LaCl<sub>3</sub>, AgClO<sub>4</sub>, TiClO<sub>4</sub>, TlNO<sub>3</sub>, Hg<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, Hg(ClO<sub>4</sub>)<sub>2</sub>, Pb(ClO<sub>4</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, and CdSO<sub>4</sub>.

E. S. H.

**Analysis of the dispersion curves of substituted propionic acids.** P. A. LEVENE and A. ROTHEN (J. Amer. Chem. Soc., 1934, 56, 746).—Data are recorded for four pairs of optically active, configuratively related derivatives. The partial rotations of the significant chromophoric group and of the rest of the mol. remain the same in sign. E. S. H.

**Polarimetric researches on narcotine.** PARISELLE (Compt. rend., 1934, 198, 928—930).—For Hg  $\lambda$  5461 in aq. HCl solution  $M[\alpha]$  of narcotine increases with excess of HCl to  $+240^\circ$ ; in  $\text{CHCl}_3$  with HCl to  $+650^\circ$ , but alone in  $\text{CHCl}_3$  it is  $-1006^\circ$ . In aq. NaOH  $M[\alpha]$  is  $+273^\circ$ , diminishing on addition of HCl until with formation of the normal hydrochloride of the Na salt it is  $-587^\circ$ . Further addition of HCl causes mutarotation,  $M[\alpha]$  after 48 hr. becoming  $+230^\circ$ . The changes of sign are attributed to rotation of the meconic group around its linking with the isoquinoline nucleus. C. A. S.

**Absolute configuration of optically active compounds.** W. KUHN and K. BEIN (Z. physikal. Chem., 1934, B, 54, 335—369; cf. A., 1933, 211).—By means of models the optically active behaviour of compounds of the type of pentaerythritoldipyrvic acid and  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$  (I) in absorption bands in the near ultra-violet and visible has been calc. The fundamental assumption is that the coupling forces which are effective between various parts of the mol. in optical oscillations can be deduced, at least as far as sign is concerned, from the polarisability of the various parts of the mol. and the vibrational scattering moments in the adjoining parts. This affords a semi-quant. explanation of the observed behaviour of (I). Relations are deduced permitting the calculation of the anisotropy factor of an absorption band having a scattering moment of any form. With asymmetric compounds the optical activity of which is due to nonsymmetrical arrangement of like symmetrical parts, the absorption bands are resolved into parts the anisotropy factors of which for a given band differ in magnitude and at times in sign. This has been detected with the two absorption regions of (I) in the visible, and from comparison of the optical properties of (I) with those of a model, it has been possible to deduce the abs. configuration of the isomeride which is levorotatory in Na-D light. These conclusions have been confirmed by measurements of the absorption, rotation, and circular dichroism at 2600—9000 Å. R. C.

**Solvent action. VIII. Rotatory powers of the *l*-menthyl esters of *o*-nitro-, 2:4-dinitro-, and *p*-nitro-benzoic acids in relation to the solvent, concentration, temperature, and wavelength of light.** A. McLEAN (J.C.S., 1934, 351—360; cf. A., 1933, 1110).—Solutions of the first two groups of esters in benzenoid solvents show rotatory powers varying inversely as the dipole moment of the solvent, the relation being quant. for solvents of weak or medium polarity, and becoming qual. with strongly polar solvents, indicating solvent influence through dipole association between solvent and solute. No regularity is observed for the effect of solvents on the rotation of the *p*-nitro-ester. For non-polar solvents, an explanation of the effects of concn. and temp. on

rotatory power is advanced in terms of dipole association. For the series of related solvents, the consts. in three-const. Drude equations are calc. from dispersion data; for approx. const. solute concn., the dispersion const.  $\lambda^2$  increases with the polarity of the solvent. An explanation in terms of dipole association is given. N. M. B.

**Stereochemical structure. VI. The isomeric (–)menthyl  $\alpha$ -naphthylglycollates.** R. ROGER and E. R. L. GOW (J.C.S., 1934, 130—137).—The dispersions of (–)- $\alpha$ -naphthylglycollic acid and (–)-menthyl (–)- $\alpha$ -naphthylglycollate (I) are normal and slightly complex, whilst that of the (+)- $\alpha$ -naphthylglycollate (II) is normal and definitely complex. The dispersion of (–)menthyl *dl*-naphthylglycollate (purified by treatment of the  $\text{Et}_2\text{O}$  solution with C) is normal and almost simple, and identical with that found for equimol. mixtures of (I) and (II), for (I) and (II) superimposed in separate tubes, and may be calc. by superposition of the vals. from (I) and (II). This and other examples of superposability are discussed, and it is concluded that it is not related to the formation of *dl*-compounds. A. A. L.

**Kasolite.** J. MELON (Bull. Acad. roy. Belg., 1934, [v], 20, 178—182).—The orientation of the optical axes of kasolite ( $3\text{PbO}\cdot 3\text{UO}_2\cdot 3\text{SiO}_2\cdot 4\text{H}_2\text{O}$ ) has been measured. The crystal is strongly birefringent. J. W. S.

**Magnetic rotation of hydrogen selenide.** R. DE MALLEMANN and P. GABIANO (Compt. rend., 1934, 198, 1030—1031).—Verdet's const. is  $61 \times 10^{-6}$  ( $\lambda$  5780), and the mol. rotation  $40 \times 10^{-5}$ ; the resultant at. rotation of Se is  $36 \times 10^{-5}$ . C. A. S.

**Kerr effect with benzene derivatives.** G. OTTERBEIN (Physikal. Z., 1934, 35, 249—265).—The determination of the Kerr effect in dil. solutions is discussed, and a mixture formula is derived. A simple apparatus, employing the Brace compensation method, for determining the Kerr const. in dil. solutions is described. Observations with  $\text{C}_{10}\text{H}_8$  and 1- and 2- $\text{C}_{10}\text{H}_7\text{Cl}$  show that a simple addition of polarisation tensors does not always lead to correct results. A. J. M.

**Spectroscopy and valency. II. Periodic groups of non-hydride diatomic molecules.** C. H. D. CLARK (Proc. Leeds Phil. Soc., 1934, 2, 502—512; cf. A., 1932, 901).—A system of classification of diat. mols. is suggested which emphasises the relations between mols. of similar kinds. The spectroscopic features of the mols. which should occupy gaps in the table can be forecast. H. S. P.

**Primary and secondary valencies of nitrogen as deduced from the crystal structure of hexamethylenetetramine.** R. REINICKE (Z. Krist., 1934, 87, 417—422).—The author's theory of tetrahedral domains (cf. A., 1931, 1001; 1932, 563; 1933, 450) is shown to give a satisfactory explanation of the mol. and crystal structure of  $(\text{CH}_2)_6\text{N}_4$ . C. A. S.

**Theory of the structure of ethylene. Structure of ethane.** W. G. PENNEY (Proc. Roy. Soc., 1934, A, 144, 166—187).—Two methods, that of electron pairs and that of mol. orbits, used to determine the structure of the  $\text{C}_2\text{H}_4$  mol. give consistent results. The

most stable arrangement has all six nuclei coplanar, with a large HCH angle (about  $130^\circ$ ). Similar calculations on the  $C_2H_6$  mol. show that it is only the H-H repulsions which prevent free rotation of the Me group about the C-C axis. L. L. B.

**Hydrazoic acid.** E. C. FRANKLIN (J. Amer. Chem. Soc., 1934, 56, 568—571).—Numerous reactions of  $HN_3$  are consistent with the constitution H·N·N·N. E. S. H.

**Molecular structure of carbon suboxide.** H. BOERSCH (Naturwiss., 1934, 22, 172).— $C_3O_2$  is probably  $O=C \begin{array}{c} \diagup C \diagdown \\ \diagdown O \diagup \end{array} C$ ;  $a=1.2$ ,  $b=1.3$ ,  $c=1.2$ ,  $d=1.51$ ,  $e=1.13$ ,  $f=1.3 \text{ \AA}$ . A. J. M.

**Comparative chemistry. III. Binary compounds of hydrogen. IV. Binary compounds of halogens. V. Didactic importance.** I. N. LONGINESCU (Bul. Chim. Soc. Romana Ştiinţe, 1932, 35, 21—24, 45—51, 103—106).—Theoretical. Four kinds of combination are suggested. R. T.

**Apparent molecular association of some aliphatic acids.** G. BROUGHTON (Trans. Faraday Soc., 1934, 30, 367—372).—The apparent mol. association of a no. of aliphatic acids has been determined cryoscopically in cyclohexane (I).  $HCO_2H$  and  $AcOH$  have an association factor  $> 2$  because their solutions in (I) deviate from ideal. More ideal solutions might have been expected with a lengthening chain, but  $C_{15}H_{31} \cdot CO_2H$  and  $C_{13}H_{27} \cdot CO_2H$  deviate from Raoult's law to an extent  $> C_5H_{11} \cdot CO_2H$ ,  $C_7H_{15} \cdot CO_2H$ , and  $C_{11}H_{23} \cdot CO_2H$ , the last having a min. deviation. Lateral adhesion between chains may take place when these are long. M. S. B.

**Affinity. III.** T. DE DONDER (Bull. Acad. roy. Belg., 1933, [v], 19, 1364—1376; cf. A., 1933, 1232; this vol., 133).—Theoretical. J. W. S.

**Chemical formulæ of compounds containing hydrogen and oxygen isotopes.** R. A. GORTNER (Science, 1934, 79, 203—204). L. S. T.

**Naming hydrogen isotopes.** W. A. BOUGHTON (Science, 1934, 79, 159—160). L. S. T.

**Natural classification of chemical elements and compounds.** F. M. SCHEMJAKIN (Uspekhi Khim., 1933, 2, 630—642).—A review. CH. ABS.

**Law of multiple proportions.** A. ROSE (Science, 1934, 79, 206; cf. this vol., 234). L. S. T.

**Magnetic susceptibility of liquid ozone and of mixtures thereof with liquid oxygen.** P. LAINÉ (Compt. rend., 1934, 198, 918—919; cf. A., 1933, 449).—By similar methods the magnetic susceptibility of  $O_3$  at temp. near that of liquid air is determined to be about  $1.5 \times 10^{-7}$  and its thermal variation to be  $< 1/3$  of that required by the Curie law. By maintaining a vac. above an agitated mixture of liquid  $O_2$  and  $O_3$ , liquid  $O_2$  containing  $< 0.01\%$   $O_3$  can be obtained. C. A. S.

**Magnetism of  $B_2H_6$ .** L. FARKAS and H. SACHSSE (Trans. Faraday Soc., 1934, 30, 331—333).—The conversion of para- into ortho- $H_2$  in presence of  $B_2H_6$  at different temp. has been studied. The reaction velocity coeffs. and collision efficiencies

indicate that the observed conversion is not caused by the paramagnetism of  $B_2H_6$ . At  $195^\circ$  abs. there is no conversion, hence the ground level of  $B_2H_6$  must be diamagnetic. It is suggested that the para- $H_2$  conversion effected by  $B_2H_6$  in the homogeneous reaction must be due to exchange of the para- $H_2$  with part of the H of  $B_2H_6$ . M. S. B.

**Magnetic study of hydrated thoria.** F. BOURION and (Mlle.) D. BEAU (Compt. rend., 1934, 198, 916—918).—The magnetic susceptibility varies linearly with the content of  $H_2O$ , indicating a mixture and not a true hydroxide (cf. A., 1923, ii, 25; 1929, 20). C. A. S.

**Diamagnetism of nitroso-compounds.** E. B. WILSON, jun. (J. Amer. Chem. Soc., 1934, 56, 747).— $NOCl$ ,  $PhNO$ , and  $p-NMe_2 \cdot C_6H_4 \cdot NO$  are diamagnetic. It is inferred that these compounds are in singlet states. E. S. H.

**Paramagnetism of rare-earth ions.** C. J. RODDEN (J. Amer. Chem. Soc., 1934, 56, 648—649).—Magnetic susceptibilities at room temp. are recorded for  $Pr_2(SO_4)_3 \cdot 8H_2O$ ,  $Nd_2(SO_4)_3 \cdot 8H_2O$ ,  $Nd_2O_3$ ,  $NdFe(CN)_6 \cdot 4H_2O$ ,  $Sm_2(SO_4)_3 \cdot 8H_2O$ ,  $Sm_2O_3$ , and  $Yb_2(SO_4)_3 \cdot 8H_2O$ . The results are discussed in the light of Van Vleck's theory of paramagnetism. E. S. H.

**Energetics of ferromagnetic materials.** R. GANS (Magnetismus, Leipziger Vorträge, 1933, 91—110; Chem. Zentr., 1933, ii, 2651).—A review of the energy relations in ferromagnetic phenomena. H. J. E.

**Ferromagnetism in the oxide obtained by dehydration of gamma ferric oxide hydrate.** L. A. WELO and O. BAUDISCH (Phil. Mag., 1934, [vii], 17, 753—768; cf. A., 1932, 709).—Dehydration of paramagnetic  $\gamma-Fe_2O_3 \cdot H_2O$  was studied by measurements of the magnetic properties of the ferromagnetic  $\gamma-Fe_2O_3$  formed. Dehydration is slow at  $180^\circ$ , and rapid at  $240^\circ$ , whilst at  $285^\circ$   $\gamma-Fe_2O_3$  forms paramagnetic  $\alpha-Fe_2O_3$ . From X-ray measurements the crystals of  $\gamma-Fe_2O_3$  are very small initially. They grow, and simultaneously change their magnetic characteristics, above  $180^\circ$ . Colloidal  $\gamma-Fe_2O_3$  shows a similar dependence of permeability and susceptibility on particle size. H. J. E.

**Shape of molecules.** N. V. SIDGWICK (Proc. Roy. Inst., 1934, 28, 35—45).—A lecture.

**Parachor of sulphur hexafluoride and the single electron linking.** A. H. SPONG (Chem. and Ind., 1934, 312).—The parachor of  $SF_6$  cannot be considered as sufficient evidence for the structure (I) suggested by Pearson and Robinson (this vol., 132); (I) is improbable owing to the singlet linkings involved, and, on certain assumptions, the ordinary symmetrical non-polar structure would lead to the parachor 147.0 [actual val. 143.3; val. calc. for (I) 148.6]. D. R. D.

**Dissociation of diatomic molecules with  $p-p$  binding.** H. LESSHELM and R. SAMUEL (Z. Physik, 1934, 88, 276).—Corrections to an earlier paper (cf. A., 1933, 996).

**Relation between internuclear distances and linking force constants.** R. M. BADGER (J. Chem.

Physics, 1934, 2, 128—131).—For diat. mol. the relation between linking force const.  $k_0$  and inter-nuclear distance  $r_e$  is  $k_0(r_e - d_{ij})^2 = 1.86 \times 10^5$ , where  $d_{ij}$  is a const. depending only on the rows in the periodic table in which the two elements comprising the mol. are located. The expression holds for the normal and, with a few possible exceptions, all excited states. Uses, and an extension to polyat. mol., are discussed. N. M. B.

Energies of the atomic linkings in methane, ethane, methyl and ethyl alcohols. F. D. ROSSINI (J. Chem. Physics, 1934, 2, 145).—Data on heats of combustion show that the energy of breaking a C-H linking in the R-CH<sub>3</sub> mol., and forming R-CH<sub>2</sub>-OH is appreciably affected by the nature of R, and that the energies of the at. linkings in these and homologous compounds are not additive. N. M. B.

Connexion between chemical constitution and K-X-ray absorption spectra. XIV. K-X-Ray absorption spectra of stereoisomerides. II. O. STELLING (Z. physikal. Chem., 1934, B, 24, 407—428; cf. this vol., 133).—The Cl absorption spectrum of org. Cl-compounds, which consists of two edges similar to those of inorg. Cl-compounds with non-ionic Cl, has been studied. With saturated CH<sub>4</sub> derivatives the short-wave edge shifts towards shorter waves with increase in the no. of Cl atoms attached to the central C atom. In Cl<sub>1</sub>-substituted C<sub>2</sub>H<sub>4</sub> derivatives the short-wave edge of the Cl is influenced principally by the group in the *cis* position to the Cl, CO<sub>2</sub>H shifting the edge to considerably shorter wave-lengths, whilst Me causes a slight shift in the opposite direction; the *trans* group is of little moment. Of isomeric  $\alpha\beta$ -Cl<sub>2</sub>-substituted C<sub>2</sub>H<sub>4</sub> derivatives the isomeride with Cl in the *cis* position has the hardest short-wave edge. With C<sub>6</sub>H<sub>6</sub> derivatives the hard edge becomes increasingly soft in the order  $o < m < p$ . The position of the long-wave edge is the same for all saturated compounds, but different from that of the corresponding edge of Cl linked to C:C. Nuclear-substituted C<sub>6</sub>H<sub>6</sub> derivatives give the same edge as C<sub>2</sub>H<sub>4</sub> derivatives. R. C.

Liquid crystals. (SIR) W. BRAGG (Proc. Roy. Inst., 1934, 28, 57—92).—A lecture.

Liquid crystals obtained by rapid evaporation of an aqueous solution. P. GAUBERT (Compt. rend., 1934, 198, 951—953; cf. this vol., 18).—Both liquid and solid crystals of tartrazine are hydrated. The birefringence of its smectic state is  $<$  that of calcite, and  $>$  that of its nematic state. Certain dyes, e.g., Na alizarinsulphonate, increase the stability of the nematic constitution. A solution of brilliant-crocoine gives rise to a viscous birefringent liquid. C. A. S.

Comparative X-ray and optical investigations with the anisotropic and isotropic melts of *p*-azoxyanisole. W. KAST (Ann. Physik, 1934, [v], 19, 571—581).—X-Ray photographs of diffraction of monochromatic rays at the liquid cryst. and normal liquid phases of *p*-azoxyanisole (I) show that in both cases only one ring is obtained, and that the variation of intensity in the rings is the same. The difference between the two phases must lie in the different

structures of the mol. aggregates, being isotropic in the case of the normal melt, and anisotropic in that of the liquid cryst. The solid cryst. phase of (I) shows a very high val. of the double refraction, like the liquid-cryst. phase. A. J. M.

Crystallisation of melts. J. MEYER and W. PFAFF (Z. anorg. Chem., 1934, 217, 257—271).—By careful filtration through fine sintered glass filters crystallisation nuclei can be removed from fused salol, thymol, C<sub>6</sub>H<sub>5</sub>, *o*- and *m*-cresol, C<sub>6</sub>H<sub>5</sub>Me, and guaiacol so that the supercooled melt no longer shows a readiness to crystallise, even on freezing and introducing some of the solid into the supercooled liquid and remelting. The nuclei apparently consist of foreign particles removable by filtration. For this reason no conclusions can be reached by means of crystallisation experiments regarding the polymorphic relations of the crystallising substances, as has hitherto been done erroneously for *allocinnamic acid*. M. S. B.

Modification of form of crystals grown in solutions containing foreign materials. L. ROYER (Compt. rend., 1934, 198, 949—951).

C. A. S.

Manner of separation of small quantities of foreign substances in crystallising salts. O. HAJN, H. KÄDING, and R. MUMBRAUER (Z. Krist., 1934, 87, 387—416; cf. A., 1931, 1225, 1230; 1932, 359).—Photographs, taken at intervals, of the same crystal as it grows in a solution containing, in addition to the main substance, a suitable radioactive isotope, e.g., Th-B, Ra-X, or Po, show the distribution of the latter. C. A. S.

Differences in lattice constant between single crystals and polycrystalline materials. P. WIEST (Metallwirtsch., 1933, 12, 255; Chem. Zentr., 1933, ii, 2499).—Phillips and Brick's results (A., 1933, 1234) have been confirmed for Ag-Cu alloys. Lattice const. are not functions of the grain size, but of the mechanical and thermal treatment.

H. J. E.

Primary crystallisation of metals. Influence of temperature gradients on the orientation of zinc single crystals. V. D. KUZNETZOV and D. D. SARATOVKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 248—255).—Crystal orientation from Zn melts in glass tubes (0.3—0.5 cm. diameter) has been correlated with conditions of cooling; both single and poly-crystals form, depending on conditions. Single crystals are oriented with the hexagonal axis perpendicular to the greatest temp. gradient, influenced by the no. of crystallisation centres. H. J. E.

Change of shape of alternately twisted cadmium crystals. W. FAHRENHORST and H. EKSTEIN (Z. Metallk., 1933, 25, 306—308).—When a round, single-crystal Cd wire is subjected to 100,000 alternate twists of  $\pm 5^\circ$  the cross-section becomes distorted (S-shaped), two sharp ruffles appearing at opposite ends of a diameter. A crystallographic analysis of the stresses causing this change of shape is given.

A. R. P.

Influence of the shaping process on the crystal orientation in [metal] wires. G. VON VARGHA

and G. WASSERMANN (Z. Metallk., 1933, 25, 310—313).  
A. R. P.

**Lattice constants of cubic space-centred  $\beta$ -tungsten.** M. C. NEUBURGER (Z. anorg. Chem., 1934, 217, 154—156).—The longer-known cubic space-centred modification of W is formed from the more recently discovered modification (A., 1931, 805) above 600—650°, and therefore the latter is more suitably described as  $\alpha$ -W and the cubic space-centred form as  $\beta$ -W. The following vals. for the lattice const. of  $\beta$ -W have been determined:  $a$  3.1589 $\pm$ 0.0004 Å. at 20°, in good agreement with previous determinations, the shortest at. distance 2.7357 Å., at. radius 1.368 Å., no. of atoms in unit cell 2, and  $d_{\text{calc}}$ . 19.24 at 20° (cf. A., 1933, 665).  
M. S. B.

**Nomenclature [of the two modifications of tungsten].** F. EBERT and H. HARTMANN (Z. anorg. Chem., 1934, 217, 156).—Since the new modification of W has already been described in the literature as  $\beta$ -W, confusion would be avoided by retaining the name  $\alpha$ -W for the cubic space-centred form, contrary to Neuburger's suggestion (cf. preceding abstract).  
M. S. B.

**Structure of cold-worked threads of silver chloride, and their recrystallisation.** V. CAGLIOTTI (Atti R. Accad. Lincei, 1933, [vi], 18, 570—574).—X-Ray investigation shows that in cold-worked AgCl threads the crystallites are oriented partly along the (111) axis, but mainly along the (100) axis. The latter arrangement is still more marked in the recryst. structure after heat-treatment at 250°.  
O. J. W.

**Fibrous structure in ionic lattices.** G. R. LEVI and M. TABEL (Atti R. Accad. Lincei, 1933, [vi], 18, 574—579).—Threads of AgCl and AgBr formed under pressures of 3.4—3.5 atm. show a marked fibrous structure. AgCl is oriented along the (111) and AgBr along the (100) axis. TlCl, TlBr, and AgI threads show no fibrous structure.  
O. J. W.

**Crystal hydrates. I. Structure of magnesium chloride and bromide hexahydrates.** K. R. ANDRESS and J. GUNDERMANN (Z. Krist., 1934, 87, 345—369).—These are monoclinic, with 2 mols. in the unit cell, and respectively  $a$  9.90,  $b$  7.15,  $c$  6.10,  $\beta$  94°, and  $a$  10.25,  $b$  7.40,  $c$  6.30,  $\beta$  93° 30'; space-group  $C_{2h}^2$ — $C/2m$ . The 6H<sub>2</sub>O are arranged octahedrally around a Mg atom, each such group is surrounded by eight halogen atoms, six in the same plane with the Mg, of which four are distant therefrom 4.7<sub>5</sub>, and two 4.8<sub>5</sub> Å., whilst two are vertically above and below the Mg and distant 4.1<sub>5</sub> Å.; these last two are the two in direct connexion with that Mg atom.  
C. A. S.

**Crystal structure of anhydrous zinc sulphate.** K. SCHIFF (Z. Krist., 1934, 87, 379—386).—ZnSO<sub>4</sub> is rhombic,  $a$  8.58<sub>1</sub>,  $b$  6.73<sub>7</sub>,  $c$  4.76 Å., with 4 mols. in the unit cell.  
C. A. S.

**Calcium sulphate hemihydrate and soluble anhydrite.** P. GALLITELLI [with W. BÜSSEM] (Periodico Mineralogia, 1933, 4, 1—42; Chem. Zentr., 1933, ii, 3391).—The hemihydrate is monoclinic ( $a$  11.94,  $b$  6.83,  $c$  12.70 Å., 12 mols. CaSO<sub>4</sub>·0.5H<sub>2</sub>O in unit cell; space-group  $C_{2h}^2$ ). Anhydrite made by dehydration of the hemihydrate has the same structure,

characterised by chains of CaSO<sub>4</sub> mols. along the  $c$  axis, between which the H<sub>2</sub>O mols. are accommodated.  
H. J. E.

**Structure of the trithionate group (S<sub>3</sub>O<sub>6</sub>)<sup>-2</sup>.** W. H. ZACHARIASEN (J. Chem. Physics, 1934, 2, 109—111; cf. A., 1932, 903).—The group structure is found from the crystal lattice of the K compound; two of the S atoms form four linkings each, three with O atoms and one with S, and are directed to the corners of a tetrahedron. The third S atom forms only two linkings, both with S atoms; the angle is 103°. The S—O distance is 1.50, and S—S 2.15 Å.  
N. M. B.

**Crystal structure of barium nickelocyanide.** H. BRASSEUR, A. DE RASSENFOSSE, and J. PIÉARD (Compt. rend., 1934, 198, 1048—1050).—BaNi(CN)<sub>4</sub> crystallises with 4H<sub>2</sub>O, not 3 (cf. A., 1871, 389), is monoclinic,  $d^{20}$  2.383. X-Ray examination gives  $a$  11.89,  $b$  14.08,  $c$  6.54 Å.,  $\beta$  103° 42', with 4 mols. in the unit cell, identical with the structure of BaPt(CN)<sub>4</sub>·4H<sub>2</sub>O. [Ni(CN)<sub>4</sub>]<sup>'</sup> is therefore planar with the Ni in the centre of a square formed by 4(CN) (cf. A., 1933, 1107).  
C. A. S.

**Structure and formula of 12-phosphotungstic acid.** J. F. KEGGIN (Proc. Roy. Soc., 1934, A, 144, 75—100).—The structure of the mol. of 12-phosphotungstic acid, H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] $\cdot$  $n$ H<sub>2</sub>O, has been found by X-ray analysis, using the powder method. The anion consists of a central PO<sub>4</sub> tetrahedral group surrounded by 12 WO<sub>6</sub> octahedral groups, linked by shared O atoms. The positions of the atoms are given. The symmetry is  $T_d$ . In the partly dehydrated acid ( $n=5$ ) the anions pack together with cubic symmetry ( $O_h$ ), the edge of the unit cube being 12.14 $\pm$ 0.005 Å. There are 2 mols. of acid per unit cell. Most of the chemical evidence supports this formula.  
L. L. B.

**Crystal structure of thallic dimethyl halides.** H. M. POWELL and (MISS) D. M. CROWFOOT (Z. Krist., 1934, 87, 370—378).—TlMe<sub>2</sub>Cl,  $d_x^3$  3.445, TlMe<sub>2</sub>Br,  $d_x^3$  3.790, and TlMe<sub>2</sub>I,  $d_x^3$  3.909, are tetragonal. The unit cells are body-centred tetragonal,  $a$  4.29, 4.47, 4.78;  $c$  14.01, 13.78, 13.43 Å., respectively, and contain 2 mols.  
C. A. S.

**Polymorphic phenomena and crystal structure.** T. F. W. BARTH (Amer. J. Sci., 1934, [v], 27, 273—286).—Polymorphic manifestations are classified. Potash feldspar is trimorphous. A structural relation between orthoclase and microcline is suggested.  
C. W. G.

**Crystal structure of 1 : 3 : 5-triphenylbenzene.** K. S. KRISHNAN and S. BANERJEE (Nature, 1934, 133, 497).—The magnetic susceptibilities along the  $a$ ,  $b$ , and  $c$  axes support the view (this vol., 134) that the C<sub>6</sub> rings are inclined to the (001) plane at an angle of 24°. The optical const. also support this orientation.  
L. S. T.

**Films of cellulose nitrate and their polymorphism.** J. J. TRELAT (J. Chim. phys., 1934, 31, 125—137).—Films of cellulose nitrate (I) containing 13% N and prepared with COMe<sub>2</sub> (II) and EtOAc (III) exhibit X-ray diagrams characteristic of two different cryst. forms, one of which disappears rapidly and the other more slowly as drying proceeds. (I) with < 13% N is amorphous. Butyl and amyl

acetate alone and mixed with  $\text{COMe}_2$  afford (I) of the ordinary structure, showing that (I) probably forms cryst. additive products with (II) and (III). Dissolution and re-formation of the film reproduce the same series of phenomena. Experiments with stretched films show that the swelling and contraction are due to addition and removal of solvent mols. perpendicularly from the direction of the C chains.

J. G. A. G.

**Electron diffraction by cellulosic films.** J. J. TRILLAT (Compt. rend., 1934, 198, 1025—1027).—When 20—25-kv. electrons pass through films of cellulose nitrate (13% N), acetate, propionate, and butyrate, the diagrams show that the film when freshly prepared is usually amorphous, but that microcrystals appear in a few hr., and that in a few days the whole film is cryst. The cellulosic chains lie parallel and flat in the film with equiv. atoms at the nodes of a monoclinic network with  $a$  7.10,  $b$  4.68,  $c$  2.5 or 5.0 Å.

C. A. S.

**Diffraction of rapid electrons by talc.** G. AMINOFF and B. BROOME (Arkiv Kemi, Min., Geol., 1934, 11 B, No. 25, 5 pp.).—Talc is hexagonal or pseudohexagonal, with  $a$  5.25 Å.

D. R. D.

**General proof of certain fundamental equations in the theory of metallic conduction.** H. JONES and C. ZENER (Proc. Roy. Soc., 1934, A, 144, 101—117).

**Magneto-caloric effect in superconducting tin.** K. MENDELSSOHN and J. R. MOORE (Nature, 1934, 133, 413).—Measurements of the adiabatic magnetisation and demagnetisation of superconducting Sn at 2.5—4.0° abs. show a cooling effect on magnetisation and heating on demagnetisation.

L. S. T.

**Piezoelectric properties of Rochelle salt.** P. D. SHULBAS-SOROKINA (J. Tech. Phys., U.S.S.R., 1931, 1, 756—760).—The val. of the modulus is 10 times that given by Valasek (Physical Rev., 1924, 24, 560).

CH. ABS.

**Discontinuities of resistance associated with the Barkhausen effect.** C. W. HEAPS (Physical Rev., 1934, [ii], 45, 320—323).—A Ni wire under bending stress shows a jump of magnetoresistance associated with the magnetisation jump.

N. M. B.

**Light absorption by metals.** A. SMAKULA (Z. Physik, 1934, 88, 114—126; cf. A., 1933, 1226).—Chemically related metals show similar absorption curves.

A. B. D. C.

**Elastic behaviour and elastic constants of zinc single crystals.** A. W. HANSON (Physical Rev., 1934, [ii], 45, 324—331).—For each crystal orientation there is a limited region of proportionality between an initially increasing stress and the corresponding strain, and this is a min. for crystals of 45° orientation. Elastic hysteresis occurs for bending, but not for torsion. Elastic consts., differing appreciably, are given for two grades of 99.99+ % pure Zn. The behaviour of the single-crystal form is definite, but variable for the polycryst. and technical forms.

N. M. B.

**Is liquid benzene allotropic?** E. COHEN and J. S. BUY (Proc. K. Akad. Wetensch. Amsterdam,

1934, 37, 55—61).—From a consideration of published work it is inferred that no allotropic change occurs between 0° and 70° (cf. this vol., 353).

E. S. H.

**Magneto-thermo-electrical effects in nickel and iron: theoretical interpretations.** A. PERRIER and (MLLE.) T. KOUSMINE (Compt. rend., 1934, 198, 920—921; cf. this vol., 353).—The thermo-electric anisotropies ( $\Delta E_{\parallel} - \Delta E_{\perp}$ ) of Ni and Fe are, respectively, 43.7 and  $14.8 \times 10^{-8}$  volt per degree; Both  $\Delta E_{\parallel}$  and  $\Delta E_{\perp}$  are intrinsic properties of the metal independent of contact potential.

C. A. S.

**Thermal power generated by twisting zinc and cadmium wires.** G. TAMMANN and G. BANDEL (Ann. Physik, 1934, [v], 19, 582—584).—The differences between Zn and Cd and other metals as regards the thermal power produced by twisting are discussed.

A. J. M.

**Superconductivity.** I. C. J. GORTER and H. CASIMIR (Physica, 1934, 1, 306—320).—Theoretical.

H. J. E.

**Intensity determinations for the explanation of the depolymerising action of ultrasonic waves.** A. SZALAY (Physikal. Z., 1934, 35, 293—296).—Highly polymerised substances, such as starch, in aq. solution, are hydrolysed when exposed to ultrasonic waves. By comparing the energy imparted to the system by direct heating and that imparted by the waves, it was found that the effect of placing the solution in the ultrasonic beam was the same as heating it to 100°.

A. J. M.

**Softening of vitreous substances.** E. RENCKER (Compt. rend., 1934, 198, 934—936; cf. B., 1934, 351).—Differential cooling curves for  $\text{B}_2\text{O}_3$ ,  $\text{HPO}_3$ , etc. show that at the transformation or softening point there is merely a change in the sp. heat; this coincides with the change in the coeff. of dilatation (cf. B., 1921, 347; A., 1928, 354; 1930, 862).

C. A. S.

**Para-ortho conversion of deuterium.** A. FARKAS, L. FARKAS, and P. HARTECK (Science, 1934, 79, 204).—The thermo-conductivity method shows the para-ortho conversion of  $\text{H}_2^2$  at 78°, 53°, and 20.4° abs., changes in readings relative to normal  $\text{H}_2^2$  being in the ratio 3 : 11 : 30, respectively. This agrees with the Bose-Einstein statistics if the nuclear spin of the deuteron is one which gives excess concn. of 3.3, 11.1, and 31.2%, respectively, of ortho- $\text{H}_2^2$  at these temp. relative to normal  $\text{H}_2^2$ . The velocity coeff. of reconversion of ortho- $\text{H}_2^2$  by  $\text{O}_2$  (0.57 litre per mol. per min.) at room temp. is  $\frac{1}{16}$  that of para- $\text{H}_2^2$ .

L. S. T.

**Ortho- and para-states of hydrogen of mass 2. Temperature variation of heats of rotation of  $\text{H}_2^2$ .** H. MOTZ and F. PATAT (Monatsh., 1934, 64, 17—20).—Theoretical. The equilibrium proportions of ortho- and para- $\text{H}_2^2$  are calc. for the range 10—110° abs.

E. S. H.

**International Bureau of Physico-chemical Standards. Physical constants of twenty organic compounds.** J. TIMMERMANS and (MLLE.) Y. DELCOURT (J. Chim. phys., 1934, 31, 85—124).—The following data for b.p./760 mm., m.p., and  $d^{15}$  have been determined: MeI 42.50°, —66.45°, 2.29300,

Pr<sup>α</sup>I 102.45°, -101.3°, 1.75840, Pr<sup>β</sup>I 89.45°, -90.1°, 1.71371, CCl<sub>2</sub>Me<sub>2</sub> 70.5°, -34.4°, 1.09843, Bu<sup>α</sup>I 130.40°, -103.0°, 1.62366, Bu<sup>β</sup>I 121.0°, -93.5°, 1.61176, Bu<sup>β</sup>Br 91.20°, -111.9°, 1.26808, *sec.*-BuI 120.0°, -104.0°, 1.60584, Bu<sup>γ</sup>Cl 50.7°, -27.1°, 0.84739, Bu<sup>γ</sup>Br 73.25°, -16.2°, 1.22861, PrOH 97.15°, vitreous in liquid air, 0.80749, Pr<sup>α</sup>OH 82.40°, -89.5°, 0.78916, Bu<sup>α</sup>OH 82.50°, 25.55°, *d*<sup>20</sup> 0.78670, Pr<sup>α</sup>CO<sub>2</sub>H 154.70°, -46.1°, 0.95296, Et malonate 199.30°, -51.5°, 1.06040, EtCN 97.20°, -91.9°, 0.78673, Pr<sup>α</sup>CN 117.9°, -111.9°, 0.79544, Pr<sup>β</sup>CN 103.85°, -71.5°, 0.77511, Bu<sup>α</sup>CN 141.30°, -96.0°, 0.80350, Bu<sup>β</sup>CN 130.5°, -100.85°, 0.79490. The data include the relation between b.p. and pressure, coeffs. of dilatation,  $\tau_{\lambda}^{\lambda}$ , viscosity coeffs., and surface tensions. Earlier data are tabulated. J. G. A. G.

Exact measurement of the specific heat of solid substances at higher temperatures. XIII. Specific heats of vanadium, niobium, tantalum, and molybdenum from 0° to 1500°. F. M. JAEGER and W. A. VEENSTRA. XIV. Specific heats and thermal retardation phenomena of beryllium. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 61—66, 67—76).—XIII. The following true sp. heats have been determined: V 0.11846 + 0.313734 × 10<sup>-4</sup>t - 0.675396 × 10<sup>-8</sup>t<sup>2</sup> + 0.14184 × 10<sup>-11</sup>t<sup>3</sup>; Nb 0.06430 + 0.772766 × 10<sup>-5</sup>t + 0.234774 × 10<sup>-8</sup>t<sup>2</sup>; Ta 0.033218 + 0.4198 × 10<sup>-5</sup>t + 0.3295 × 10<sup>-9</sup>t<sup>2</sup>; Mo 0.061046 + 0.0616043 × 10<sup>-4</sup>t + 0.0345454 × 10<sup>-8</sup>t<sup>2</sup>.

XIV. The apparent sp. heat of cast Be varies with the thermal treatment. When Be is reduced to fine powder const. vals. are obtained at a given temp. represented by  $c_p = 0.414032 + 0.719894 \times 10^{-3}t - 0.2221422 \times 10^{-6}t^2 - 0.1436704 \times 10^{-9}t^3 + 0.156547 \times 10^{-11}t^4$ . E. S. H.

Does the fusion of crystalline substances depend on the previous and subsequent history? M. LE BLANC and E. MÖBIUS (Ber. Verh. Sachs. Akad. Wiss., math.-phys. Kl., 1933, 85, 75—96; Chem. Zentr., 1933, ii, 3106).—Samples of pure C<sub>6</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> exhibit a rise of sp. heat just below the m.p., due to residual impurities. The sp. heat of liquid C<sub>6</sub>H<sub>6</sub> has a min. val. (for the range 5.15—30°) at 18°. A change in mol. state is excluded by the const. val. of  $C_p - C_v$ , and the min. val. is attributed to residual orientation in the liquid. C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> has a similar min. H. J. E.

Heat conduction in a solid in contact with a well-stirred liquid. A. N. LOWAN (Phil. Mag., 1934, [vii], 17, 849—854).—Theoretical. H. J. E.

Thermodynamic properties of helium gas. J. R. ROEBUCK and H. OSTERBERG (Physical Rev., 1934, [ii], 45, 332—340).—Joule-Thomson coeffs. (cf. A., 1932, 218) and *pv* data are used to calculate variation of sp. heat with pressure, sp. vol., coeff. of vol. expansion, elastic coeff., coeff. of free expansion  $\eta$ , and intrinsic energy variation with vol,  $\lambda$ . Simple relationships exist between  $\eta$  and  $\lambda$ .  $\eta$  is independent of pressure *p* and  $\lambda$  is proportional to *p*<sup>2</sup> except at low temp. Both  $\eta$  and  $\lambda$  are zero at about -70°, and are positive below and negative above this temp. The pressure and temp. behaviour of  $\eta$  and  $\lambda$  is explained kinetically. N. M. B.

V.p. of fluorine. W. H. CLAUSSEN (J. Amer. Chem. Soc., 1934, 56, 614—615).—The v.p. (6.3—75.2 cm.) is given by  $\log_{10} P(\text{cm.}) = -462.66/T + 8.7202 - 0.016567T$ . F<sub>2</sub> has b.p. 85.21 ± 0.1° abs., calc. heat of vaporisation 1560 g.-cal. per mol.

E. S. H.

Vapour pressure of benzanthrone and of quinizarin. W. WENZEL and H. PIRAK (Coll. Czech. Chem. Comm., 1934, 6, 54—59).—Data, by the gas saturation method, are recorded for the ranges: benzanthrone 180° (0.17 mm.) to 280° (6.10 mm.) and quinizarin 200° (1.15 mm.) to 260° (11.0 mm.).

J. G. A. G.

Saturation pressure of radium emanation at low temperatures. L. WERTENSTEIN (Acta phys. polon., 1933, 2, 131—136; Chem. Zentr., 1933, ii, 3107).—At the b.p. of liquid O<sub>2</sub> the v.p. was 0.05 bar. H. J. E.

Low-pressure data of state of nitric oxide and of nitrous oxide between their b.p. and room temperature. H. L. JOHNSTON and H. R. WEIMER (J. Amer. Chem. Soc., 1934, 56, 625—630).—Apparatus and technique are described. Data of state have been determined for NO between 122° and 308° abs., and for N<sub>2</sub>O between 197° and 298° abs., and the second virial coeffs. have been calc. for each gas. The data for both gases are represented by  $PV_m = RT + BP$ , where  $B = 20 + 5881.5/T - 5.7639 \times 10^6/T^2 + 8.4301 \times 10^{10}/T^4 - 9.2783 \times 10^{14}/T^6$  c.c. per mol. for NO and  $B = 32 - 5611.5/T + 3.9424 \times 10^6/T^2 - 3.9145 \times 10^{11}/T^4 + 3.0747 \times 10^{15}/T^6$  for N<sub>2</sub>O. E. S. H.

Nernst's form of the equation for free energy. H. SCHIMOLKE (Z. Physik, 1934, 88, 139—142).—Nernst's expression for free energy is shown to lead to exact results. A. B. D. C.

Dependence of the coefficient *a* of van der Waals' equation on temperature. IV. K. JABŁCZYŃSKI (Rocz. Chem., 1934, 14, 93—97).—Van der Waals' equation is formulated  $[p + f_1(w)/w^2 - f_2(w)T/w^2](w - b) = RT$ , where *w* is the vol. of 1 mol. of gas. R. T.

Physical researches in the neighbourhood of absolute zero. F. HENNING (Chem.-Ztg., 1934, 58, 308—309).—A review.

Dilatation of fused silica. L. DUNOYER (Compt. rend., 1934, 198, 909—911, 1132—1134).—The method used depends on determining the form of the meridian line of a tube of the material when a definite temp. difference is maintained between two opposite generatrices of the tube. Applied to glass and fused SiO<sub>2</sub> it gave as the coeff. for temp. approx. between 0° and 40° 6.9 × 10<sup>-6</sup> and -6.6 × 10<sup>-8</sup>, respectively.

C. A. S.

Viscosity of *n*-heptadecane, tetra-*n*-butylmethane [ $\zeta$ -di-*n*-butylnonane], and cycloheptadecane. P. KARRER and C. FERRI (Helv. Chim. Acta, 1934, 17, 358—362).—The prep. of the above compounds is described. The viscosity ( $\eta$ ) of the first two in the fused condition at 30° has been determined, and also the sp.  $\eta$  of solutions of all three in C<sub>6</sub>H<sub>6</sub> at two different concns. The results indicate that the space configuration of the mol. has a great influence on the  $\eta$ .  $\eta$  measurements can be used only for the deter-

mination of mol. wts. in homologous series of completely analogous structure. M. S. B.

**Application of Batschinski's formula to the viscosity of fused salts at high temperatures.** M. P. VOLAROVITSCH (Bull. Acad. Sci. U.R.S.S., 1933, 1431—1437).—For  $\text{KNO}_3$  between  $348^\circ$  and  $542^\circ$ , Batschinski's formula  $v=0.50315+0.000958\phi$  (A., 1913, ii, 928) gives results  $\pm 0.98\%$  from the observed vals.; with Dantuma's interpolation formula (A., 1928, 1208), the mean deviation is  $\pm 0.94\%$ . For  $\text{NaCl}$  at  $816$ — $997^\circ$ ,  $v=0.6066+0.000672\phi$ . As Batschinski's formula holds only for non-associated liquids, fused  $\text{KNO}_3$  and  $\text{NaCl}$  must be non-associated. For associated liquids the  $\eta$ - $t$  relation is in accordance with Lasarev's form of Le Chatelier's formula,  $\log \log \eta/\eta_0 = a - bt$ . T. H. P.

**Effect of magnetic field on the inner friction of oxygen.** H. SACK [with H. ENGELHARDT] (Magnetismus. Leipziger Vortrage, 1933, 25—35; Chem. Zentr., 1933, ii, 3105).—The diminution in the inner friction by a field is  $< 0.4\%$  for  $\text{O}_2$  and air and  $< 0.01\%$  for  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$ . The effect is independent of pressure from 30 to 760 mm., and reaches a saturation val. with a field of 6000—8000 Oersteds. H. J. E.

**Transport phenomena in degenerate gases.** A. GANGULI and P. MITRA (Current Sci., 1934, 2, 295). D. R. D.

**System aluminium-barium.** E. ALBERTI (Z. Metallk., 1934, 26, 6—9).—The system contains a compound with  $> 50\%$  Ba which forms a simple eutectiferous series with pure Al, the eutectic containing 2% Ba and melting at  $651^\circ$ . The liquidus rises sharply from this point, and reaches  $1013^\circ$  at 36.5% Ba; alloys with  $> 5\%$  Ba could not be prepared. A. R. P.

**System copper-silicon.** K. SAUTNER (Forschungsarb. Metallkunde Röntgenmetallogr., No. 9, 30 pp.; Chem. Zentr., 1933, ii, 2226—2227).—Over the range 0—13% Si, thermal and X-ray data reveal six intermediary phases:  $\alpha$  (Si 5.2%), cubic face-centred,  $a$  3.60 Å.;  $\beta$  (Si 5.99%), hexagonal,  $a$  2.40,  $c$  3.91 Å., with 16 atoms per unit cell;  $\zeta$  (Si 7.6%), stable at  $> 760^\circ$ ,  $a$  2.58,  $c$  3.91 Å., identical with Westgren's  $\beta$ -phase;  $\gamma$  ( $\text{Cu}_3\text{Si}$ , Si 8.12%), m.p.  $815^\circ$ ,  $a$  6.21 Å.; 20 atoms per unit cell;  $d$  7.95;  $\delta$ , lattice consts. not determined;  $\eta$  ( $\text{Cu}_3\text{Si}$ , Si 12.8%), stable at high temp., cubic body-centred;  $a$  9.69 Å., with 19 mols. per unit cell;  $\epsilon$  ( $\text{Cu}_{20}\text{Si}_8$ , Si 12.26%), tetragonal body-centred,  $a$  9.21 Å.,  $a:c$  0.87, with 76 atoms in the unit cell. A. A. E.

**Manganese-silicon equilibrium diagram.** R. VOGEL and H. BEDARFF (Arch. Eisenhüttenw., 1933—1934, 7, 423—425).—A re-investigation of this system up to 35% Si by thermal analysis and micrographic observations shows it to be much more complex than found by Doerinckel (A., 1906, ii, 676). The existence of  $\text{MnSi}$  (m.p.  $1275^\circ$ ) and a eutectic ( $E_2$ ) at 30% Si and  $1235^\circ$  have been confirmed, but the second constituent of  $E_2$  is  $\text{Mn}_5\text{Si}_3$  (m.p.  $1280^\circ$ ) and not  $\text{Mn}_2\text{Si}$ , which does not exist.  $\text{Mn}_5\text{Si}_3$  reacts with Mn-rich liquid at  $1075^\circ$ , forming the compound  $\text{Mn}_3\text{Si}$ , which can retain up to 1% Mn in solid solution.

$\text{Mn}_3\text{Si}$  forms a eutectic with  $\beta$ -Mn saturated with Si at 12% Si and  $1040^\circ$ . The  $\beta \rightleftharpoons \gamma$  transformation temp. of Mn is raised by addition of Si from  $1100^\circ$  to  $1155^\circ$  with 3% Si, and the  $\alpha \rightleftharpoons \beta$  transformation from  $770^\circ$  to  $900^\circ$  with 10% Si; with increasing Si the  $\alpha + \beta$  range becomes broader. With rise in temp. the  $\alpha$ -( $\alpha + \text{Mn}_3\text{Si}$ ) boundary is displaced towards the Si end. In the  $\beta + \text{Mn}_3\text{Si}$  field with alloys containing 9—13% Si a heat effect occurs at  $980^\circ$ , the exact cause of which has not been elucidated, although it appears to be due to the formation of  $\text{Mn}_5\text{Si}$ .

A. R. P.

**X-Ray investigation of alloys of silicon with chromium, manganese, cobalt, and nickel.** B. BORÉN (Arkiv Kemi, Min., Geol., 1934, 11 A, No. 10, 28 pp.).—The following compounds are formed in the system Cr-Si:  $\text{Cr}_3\text{Si}$ , cubic crystals with  $a$  4.555 Å. and 8 atoms in the unit cell; a phase of uncertain composition and structure, stable only at  $<$  about  $1000^\circ$ ;  $\text{CrSi}$ , cubic,  $a$  4.620 Å., space-group  $T^4$ , 8 atoms in the unit cell, structure analogous to that of  $\text{FeSi}$ ;  $\text{CrSi}_2$ , hexagonal,  $a$  4.422,  $c$  6.351 Å., space-group  $D_6^4$ . System Mn-Si:  $\text{Mn}_3\text{Si}$ , hexagonal,  $a$  6.898,  $c$  4.802 Å., 16 atoms in the unit cell;  $\text{MnSi}$ , with the  $\text{FeSi}$  structure,  $a$  4.548 Å.;  $\text{MnSi}_2$ , tetragonal,  $a$  5.513,  $c$  17.422 Å., probably 48 atoms in the unit cell. System Co-Si:  $\text{Co}_2\text{Si}$ , rhombic,  $a$  3.730,  $b$  4.908,  $c$  7.095 Å., space-group  $C_{2v}^6$  or  $V_6^h$ , 12 atoms in the unit cell;  $\text{CoSi}$ , with the  $\text{FeSi}$  structure,  $a$  4.438 Å. The investigation of the system Ni-Si is not yet completed, but  $\text{NiSi}$  has been shown to have the  $\text{FeSi}$  structure with  $a$  4.437 Å. At. co-ordinates are given. Si dissolves Co and Ni, and Cr dissolves a little Si, with contraction of the lattice. Cr and Mn are insol. in Si. D. R. D.

**Equilibrium diagram of the system nickel-zinc.** II. K. TAMARU and A. OSAWA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 13—14; cf. A., 1932, 801).—The lattice structures of the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$  solid solutions have been determined by X-ray analysis.  $\alpha$  is face-centred cubic; the parameter increases rapidly up to 20% Zn and reaches 3.592 Å. at 38.9% Zn.  $\beta$  is body-centred tetragonal,  $a$  2.724,  $c$  3.168 Å.,  $c/a$  1.163.  $\gamma$ , probably  $\text{Ni}_2\text{Zn}_{10}$ , is body-centred cubic,  $a$  8.927 Å., 52 atoms in unit cell.  $\delta$ -solid solution is face-centred tetragonal;  $a$  3.867,  $c$  3.203 Å.,  $c/a$  0.8278.  $\epsilon$  is tetragonal,  $a$  8.922,  $c$  9.254 Å.,  $c/a$  1.0372; 50 atoms in unit cell. The  $\epsilon$  phase,  $\text{Ni}_3\text{Zn}_{22}$ , contains 10.9% Ni. A peritectic reaction occurs at  $517^\circ$  between  $\gamma$  and the melt, forming  $\epsilon$ . The reaction range lies between 13.5 and 0.5% Ni. Alloys containing 10—11% Ni increase in vol. by 3% with the formation of the  $\epsilon$  phase. R. S.

**Germanium.** XV. **Germanium-copper phase diagram.** R. SCHWARZ and G. ELSTNER (Z. anorg. Chem., 1934, 217, 289—297).—The m.p. of Ge is  $940^\circ$ , which is  $<$  that given by previous investigators. Several series of mixed crystals are formed. The eutectic is at  $650^\circ$  and 65 at.-% Cu. A compound  $\text{Cu}_3\text{Ge}$ , silver-white with a bluish tinge, is formed and probably undergoes an  $\alpha$ - $\beta$  transformation at  $615^\circ$ . Alloys up to 17 at.-% Ge are golden-yellow, and the yellowish tinge persists up to 24 at.-%; above that they are greyish-white. All the alloys are resistant



to HCl, attacked by conc.  $\text{HNO}_3$  up to 25 at.-% Ge, but above that by aqua regia only; they are slowly decomposed by boiling  $\text{H}_2\text{SO}_4$ . They are harder and more brittle than Cu, and Ge-rich alloys can be powdered in a mortar.

M. S. B.

**Praseodymium-magnesium alloys.** G. CANNERI (Metallurg. ital., 1933, 25, 250—252; Chem. Zentr., 1933, ii, 2227).—Thermal and micrographical analysis indicates the existence of  $\text{PrMg}$ , m.p.  $767^\circ$ , and  $\text{Pr}_2\text{Mg}_3$ , m.p.  $798^\circ$ ;  $\text{Pr}_2\text{Mg}$  is stable only between  $528^\circ$  and  $752^\circ$ .

A. A. E.

**Recrystallisation of iron alloys with a closed  $\gamma$ -field at the A3 and A4 points.** A. HEINZEL (Arch. Eisenhüttenw., 1933—1934, 7, 479—482).—The recrystallisation during polymorphic transformation of alloys of Fe with Al, Si, V, and W in the  $\gamma$ -field has been studied. During cooling from the liquid state the no. of nuclei at the A4 transformation is independent of the amount of alloying element ( $E$ ) present; grain refinement in the  $\gamma$ -field takes place only in the range up to  $4/5$  of the saturation limit of  $E$ , and the crystallites formed at A4 become more regularly oriented with increase of  $E$ , until finally the fully oriented  $\delta$  is converted first into regularly oriented  $\gamma$ , and then into regularly oriented  $\alpha$ . The disappearance of the grain refinement is associated with the fall in the A4 temp. produced by addition of  $E$ , and therefore the recrystallisation of Fe at the A4 point is comparable with the recrystallisation of cold-worked metals. An explanation is given for the absence of recrystallisation at the A3 point and for the formation of  $\alpha$ -veining instead.

A. R. P.

**Heat effects in the austenite-martensite transformation.** H. ESSER and W. BUNGARDT (Arch. Eisenhüttenw., 1933—1934, 7, 533—536).—The heat contents of Ag, 20 : 80 Mn-Fe alloy, and steels with 0.5, 0.8, and 1.4% C between  $300^\circ$  and  $900^\circ$  have been determined with the aid of a new type of  $\text{H}_2\text{O}$  calorimeter, and from the results the heat effect at the austenite ( $A$ )-martensite transformation at  $721^\circ$  has been calc. as 13.6 g.-cal. per g. for steel with 0.5% C (I), 11.9 for steel with 0.82% C (II), and 11.4 for steel with 1.4% C (III). Magnetic measurements show that the  $A$  content of quenched (I) is always 2%, that of (II) falls from 8% after quenching at  $750^\circ$  to 6% after quenching at  $1000^\circ$ , and that of (III) rises from 6 to 25% in the same temp. range.

A. R. P.

**System Fe- $\text{Fe}_3\text{C}$ -ZrC- $\text{Fe}_3\text{Zr}_2$ .** R. VOGEL and K. LÖHBERG (Arch. Eisenhüttenw., 1933—1934, 7, 473—478).—The system is divided into two similar sections by the line Fe-ZrC, which constituents form a pseudobinary system with a eutectic at Fe 88.82, Zr 9.88, and C 1.3%,  $1460^\circ$ , and a eutectoid at Fe 99.14, Zr 0.76, and C 0.1%,  $780^\circ$ ; the solid solubility of C as ZrC in the  $\gamma$ -phase rises from 0.1 at  $780^\circ$  to 0.8% at  $1460^\circ$ . In the pseudoternary system Fe- $\text{Fe}_3\text{C}$ -ZrC ( $A$ ) there is a eutectic plane at  $1145^\circ$  in which the binary Fe-C liquid is in equilibrium with a solid solution of C,  $\text{Fe}_3\text{C}$ , and ZrC in  $\gamma$ -Fe; similarly in the pseudoternary system Fe-ZrC- $\text{Fe}_3\text{Zr}_2$  ( $B$ ) there is a eutectic plane at  $1330^\circ$  in which the binary Fe-Zr liquid is in equilibrium with a solid solution of Zr, ZrC, and  $\text{Fe}_3\text{Zr}_2$  in  $\gamma$ -Fe. In  $A$  a plane of 4-phase

equilibrium occurs at  $780^\circ$  corresponding with the decomp. of  $\gamma$  with 0.1% C and 0.8% Zr into almost pure  $\alpha$ -Fe and Zr in the presence of  $\text{Fe}_3\text{Zr}_2$ , the quantity of which remains practically const.; in  $B$  a 4-phase equilibrium occurs at  $721^\circ$  corresponding with the eutectoid temp. of pearlite. In Zr steel the separation of  $\text{Fe}_3\text{Zr}_2$  is accompanied by a reduction in hardness ( $H$ ), but with increase in the Zr content  $H$  increases; the structure of quenched Zr steels is martensitic, and the steels are much less brittle than plain martensitic steels.

A. R. P.

**Theory of alloys in the  $\gamma$ -phase.** H. JONES (Proc. Roy. Soc., 1934, A, 144, 225—234).—Large diamagnetic susceptibilities and Hall coeffs. are to be expected for alloys in the  $\gamma$ -phase. These properties are related to the crystal structure of the alloys, and to the fact that the composition within the  $\gamma$ -phase follows the Hume-Rothery electronic rule. A reason is shown to exist for the ratio 21/13 of the no. of approx. free electrons to that of atoms.

L. L. B.

**Effect of X-ray analysis on the development of physical metallurgy.** U. DEHLINGER (Arch. Eisenhüttenw., 1933—1934, 7, 523—526).—The use of X-rays in investigating the equilibrium diagrams and structure of alloys, the nature of transformations and pptns. in the solid state, and the effects of mechanical and heat-treatment on metals and alloys is briefly reviewed.

A. R. P.

**Mixtures of dipole liquids with dielectric constants independent of temperature.** A. E. VAN ARKEL and J. L. SNOEK (Physica, 1934, 1, 271—272).—A solid substance is chosen which, when suspended in the liquid, changes the dielectric const. of the solvent (due to increasing solubility) sufficiently to compensate for the normal temp. coeff. of dielectric const. A mixture of  $o\text{-C}_6\text{H}_4\text{Cl}_2$  and glyceryl triacetate with suspended  $m\text{-C}_6\text{H}_4(\text{OBz})_2$  shows this behaviour.  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  stabilises the suspension.

H. J. E.

**New table of refractive index of pure glycerol at  $20^\circ$ .** L. F. HOYT (Ind. Eng. Chem., 1934, 26, 329—332).—The measured vals. are given by:  $0-44^\circ$  glycerol,  $n_D=1.33303+0.001124x+0.05605x^2-0.07555x^3$ ;  $45-79^\circ$ ,  $n_D=1.32359+0.00149x$ ;  $80-100^\circ$ ,  $n_D=0.90799+0.0154x-0.03155x^2+0.06576x^3$ . The temp. coeff. for 99.84% glycerol is 0.000225 per  $1^\circ$  for the range  $10-20^\circ$ .

G. H. C.

**Gas analysis and confining liquids.** A. NAHOCZKY (Bányász. kohás. Lapok, 1933, 66, 332—335; Chem. Zentr., 1933, ii, 3163).—The absorption coeff. of  $\text{CO}_2$  at  $15^\circ$  in four org. liquids and in seven saturated aq. solutions and their mixtures has been measured.

H. J. E.

**Velocity of gas exsorption from liquids.** A. GUYER and B. TOBLER (Helv. Chim. Acta, 1934, 17, 257—271).—A formula has been deduced for the mean concn. of a gas at any given time in its undisturbed solution when the osmotic pressure of the gas in the solution is  $>$  the partial pressure above it. The formula has been found to be valid for  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . The results show that the rate of diffusion through the liquid is the determining factor in the velocity of exsorption, and not the rate of escape from the surface.

M. S. B.

**Chemical and physico-chemical properties of polonium. II. Diffusion coefficient of polonium in solution. Apparatus.** M. SERVIGNE (J. Chim. phys., 1934, 31, 147—161).—The rate of diffusion of Po from aq. HCl into a superimposed column of aq. HCl is deduced from the rate of discharge,  $R$ , of a superposed electroscope. With a homogeneous liquid,  $R$  is directly proportional to concn. of Po. Full details of the technique are given. The air-solution interface is a film of  $H_2O$  with underlying Po ions. J. G. A. G.

**Solubility of sulphite in presence of sodium hydroxide and  $\beta$ -naphthol.** I. M. KOGAN, A. N. PLANOVSKI, and A. N. EVDOKIMOV (Anilinokras. Prom., 1934, 4, 34—37).—The solubility of  $Na_2SO_3$  in  $H_2O$  falls from  $90^\circ$  to  $106^\circ$ , and is greatly depressed by the presence of NaOH and  $NaO \cdot C_{10}H_7$ . R. T.

**Physico-chemical analysis of systems containing diamines. V. Mutual solubility of ethylenediamine and certain  $C_6$  hydrocarbons.** A. S. BROWN. VI. Viscosity and fusion diagrams of the systems ethylenediamine-butyl alcohols. D. E. DIONISIEV (J. Gen. Chem. Russ., 1933, 3, 973—975, 976—989).—V. Solubility data are recorded for *n*- and *cyclo*-hexane at  $25^\circ$ .

VI. The viscosity isotherms suggest formation of 1:2 compounds in the case of  $Bu^oOH$  and  $Bu^sOH$  at  $0^\circ$  and  $25^\circ$ , but not at  $50^\circ$ ; the fusion diagrams indicate similar compounds with all four alcohols, m.p.  $-34^\circ$  (primary)  $-33^\circ$  (sec.),  $-21^\circ$  (tert.), and  $-31.5^\circ$  (iso). R. T.

**Relation between solubility and inverse fusion point.** J. N. BRÖNSTED (Rec. trav. chim., 1934, 53, 421—424).—Theoretical. A reply to Voogd (A., 1933, 897). H. S. P.

**Relation between solubility and inverse fusion point.** N. H. J. M. VOOGD (Rec. trav. chim., 1934, 53, 425—429).—Theoretical. A reply to Brönsted (see above). H. S. P.

**Double sulphates  $M^I_2SO_4 \cdot M^{II}SO_4 \cdot nH_2O$ . A summary.** R. M. CAVEN (J. Roy. Tech. Coll., 1934, 3, 218—222).—The solubility isotherms of the systems  $M^I_2SO_4 \cdot M^{II}SO_4 \cdot nH_2O$ , where  $M^I$  is Na, K, or  $NH_4$  and  $M^{II}$  is Mn, Co, Ni, Cu, and Zn, are compared to show the influence of the different metallic ions on the range of stability and the degree of hydration of the salts. H. S. P.

**Behaviour of the magnesium ion towards ammonia in aqueous solution.** I. H. FREDHOLM (Z. anorg. Chem., 1934, 217, 203—213).—Distribution experiments between  $CHCl_3$  and aq.  $NH_4Cl$  of const. concn. and varying  $NH_3$  and  $MgCl_2$  concn. indicate the existence of the Mg ammine ion  $[Mg(H_2O)_nNH_3]^+$ . Since the co-ordination no. of Mg is usually 6,  $n$  is probably 5. M. S. B.

**Adsorption of gases on solid surfaces at low temperatures.** C. ZICKERMANN (Z. Physik, 1934, 88, 43—54).—Absorption isotherms for  $N_2$  and A adsorbed on mica and glass between  $77.7^\circ$  and  $40.2^\circ$  abs. and  $10^{-5}$  to  $5 \times 10^{-4}$  mm. indicate that proportionality of adsorbed quantity and pressure does not hold between  $1.5$  and  $3 \times 10^{-4}$  mm.; this is

attributed to the most efficient active centres becoming saturated. A. B. D. C.

**Adsorption of carbon dioxide and hydrogen on bare and oxygen-covered silver surfaces.** L. C. DRAKE and A. F. BENTON (J. Amer. Chem. Soc., 1934, 56, 506—511).—On bare Ag,  $CO_2$  shows instantaneous physical adsorption with a heat change = 5 kg.-cal. Physical adsorption of  $H_2$  is very small even at  $-183^\circ$ , but activated adsorption occurs at  $>200^\circ$ , and is removable by evacuating at  $300^\circ$ . When the Ag surface is covered with adsorbed  $O_2$ , slow activated adsorption of  $CO_2$  occurs at  $0-200^\circ$  with an energy of activation of 4—5 kg.-cal. Ag surfaces covered by  $Ag_2O$  react with  $CO_2$  to form  $Ag_2CO_3$  at  $>56^\circ$ , with a heat of formation of 17.3 kg.-cal. and an energy of activation of 13 kg.-cal. The rate of formation of  $Ag_2CO_3$  is proportional to the pressure of  $CO_2$  and independent of the amount of  $Ag_2O$ . Activated adsorption of  $CO_2$  occurs below the equilibrium pressure of  $Ag_2CO_3$ . E. S. H.

**Adsorption at high pressures. I.** A. S. COOLIDGE. II. A. S. COOLIDGE and H. J. FURNWALT (J. Amer. Chem. Soc., 1934, 56, 534—561, 561—568).—I. Theoretical.

II. The adsorption of  $CO_2$ ,  $N_2O$ , and  $SiF_4$  by C has been investigated over a wide range of temp. and pressure, with particular attention to the region near the crit. point. The behaviour of  $CO_2$  is in agreement with the predictions of Pólányi's theory. E. S. H.

**Adsorption of hydrogen by zinc oxide, zinc chromite, and zinc oxide-molybdenum oxide.** H. S. TAYLOR and C. O. STROTHER (J. Amer. Chem. Soc., 1934, 56, 586—590).—With ZnO, van der Waals adsorption (I) is observed between liquid air temp. and  $-78^\circ$ , slow adsorption from  $0^\circ$  to  $100^\circ$ , requiring an activation energy of 5 kg.-cal., and further slow adsorption from  $100^\circ$  to  $>300^\circ$ , having an activation energy of 12 kg.-cal. Addition of  $Cr_2O_3$  increases the amount of (I), and only one form of activated adsorption is observed, beginning at  $-78^\circ$ . Adsorption is a max. at  $218^\circ$ . Addition of  $MoO_3$  renders ZnO less active. (I) occurs at liquid air temp.; no adsorption occurs between  $-78^\circ$  and  $200^\circ$ .  $H_2$  is adsorbed slowly above  $200^\circ$ , with an activation energy of 17 kg.-cal. Max. adsorption occurs at  $400^\circ$ . E. S. H.

**Gas-solid equilibria. V. Pressure-concentration equilibria between silica gel and (1) oxygen, (2) nitrogen, (3) mixtures of oxygen and nitrogen, determined isothermally at  $0^\circ$ .** B. LAMBERT and D. H. P. PEEL (Proc. Roy. Soc., 1934, A, 144, 205—225).—The adsorption of  $N_2$  and  $O_2$  by  $SiO_2$  gel at  $0^\circ$  is directly proportional to the pressure except for a very slight divergence at pressures  $<100$  mm. The pressure-concn. isothermals are completely reversible up to 1 atm. At corresponding pressures the adsorptive power of  $SiO_2$  gel for  $N_2$  is  $>$  for  $O_2$ . With mixtures of  $N_2$  and  $O_2$  at  $0^\circ$ , the adsorptive power of  $SiO_2$  gel for  $O_2$  is greater (up to 15%) in presence of  $N_2$  than with  $O_2$  alone, but the adsorptive power for  $N_2$  is less in presence of  $O_2$  than with  $N_2$  alone. The total amount of gas

adsorbed from the mixture is always slightly < the sum of the separate amounts of the pure gases absorbed singly at the same pressures. L. L. B.

**Adsorption. VII. Form of the isothermals of vapour on charcoal and its relation to hysteresis.** L. J. BURRAGE (Trans. Faraday Soc., 1934, 30, 317—325).—Adsorption isotherms have been determined for  $\text{CCl}_4$  and  $\text{MeOH}$  on charcoal A and for  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{PrOH}$ , and  $\text{HCO}_2\text{H}$  on charcoal N1. In all cases a reversible hysteresis loop has been observed and the pressure determined at which it closes. The factors influencing the form of the isotherms are discussed and Lindau's const. (A., 1932, 1084) is criticised. M. S. B.

**Relation between activity and binding power of active charcoal.** F. KRZYL [with H. WEJROCH] (Kolloid-Z., 1934, 67, 37—40).—With C from the same source and subjected to the same activation treatment, the activity towards methylene-blue,  $\text{PhOH}$ , and I runs parallel with the adsorption of  $\text{C}_6\text{H}_6$  and the heat of wetting. Such a relation does not exist between the activity or the heat of wetting and the binding power. E. S. H.

**Active charcoal. II. Constitution of the surface and the activated adsorption of water.** C. OCKRENT (J.C.S., 1934, 291—301).—Analysis of three activated ash-free charcoals has shown that, at  $500^\circ$ , C and  $\text{H}_2\text{O}$  only are present. The latter forms an adsorption layer consisting of two parts, a low-temp. and a high-temp. adsorption layer (I). (I) is the chief component, and is desorbable above  $500^\circ$  only. The total  $\text{H}_2\text{O}$  forms an approx. unimol. layer. The results indicate that the "oxide" theory of activation is untenable. Differences in adsorptive properties are associated with the presence or absence of (I), and a mechanism for its formation is suggested. (I) is an example of activated adsorption, and its desorption curve is discontinuous with temp. These discontinuities are evidence for the existence of a no. of activated energies of adsorption anticipated on theoretical grounds. M. S. B.

**Heat of adsorption of carbon monoxide on copper.** R. A. BREEBE and E. L. WILDNER (J. Amer. Chem. Soc., 1934, 56, 642—645).—Differential heats of adsorption, determined at  $0^\circ$ , show a marked decrease in the initial stages as successive small portions of the gas are adsorbed. E. S. H.

**Adsorption and diffusion phenomena of gases at points of contact of solid substances.** E. HABANN (Ann. Physik, 1934, [v], 19, 501—512; cf. A., 1931, 671; 1932, 985).—If the gas possesses electron affinity, the adsorbed gas forms a space charge, and this is shown in the p.d. For strong currents, the space charge is destroyed, and the potential falls rapidly. From observations on the decrease of potential, the amount of adsorbed gas can be calc. Part of the neutralised gas is retained by the contact spaces by adsorption forces, but some diffuses into the solid substances. A. J. M.

**Mathematical and experimental studies on repeated extraction of adsorption systems, which are in equilibrium.** I. J. VOICU (Kolloid-Z.,

1934, 66, 322—328).—After  $q$  extractions the concn.  $x^p$  of a substance in adsorption equilibrium in the solution, and the total amount  $0^p$  of the same substance are given by  $x^p = A_x(1-r)^{pq} + K$  and  $0^p = A_0(1-r)^{pq} + K_0$ , where  $A_x$ ,  $A_0$ ,  $r$ ,  $p$ ,  $K$ , and  $K_0$  are consts. These relations, derived theoretically, are verified experimentally for several adsorption systems.

E. S. H.

**Transference of surface changes to the interior of crystals. III.** D. BALAREV [with B. SREBROV] (Kolloid-Z., 1934, 66, 317—322; cf. A., 1933, 122).—Kinetic and microscopical studies of the thermal decomp. of  $\text{KClO}_3$  in presence of  $\text{MnO}_2$  are explained with reference to the mosaic structure of the  $\text{KClO}_3$  crystals. No thermal effect is produced on mixing powdered  $\text{KClO}_3$  and  $\text{MnO}_2$ . E. S. H.

**Adsorption of organic substances at the surfaces of crystals.** N. A. HELD and V. DJATSCHKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 193—198).—The adsorption of  $\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$  on  $\text{BaSO}_4$  is of an ionic type, being increased by the presence of adsorbed  $\text{Ba}^{++}$  on the surface, and decreased by  $\text{SO}_4^{--}$ . The electrokinetic potential at the surface of  $\text{BaSO}_4$  crystals has been measured for different concns. of  $\text{BaCl}_2$  and  $\text{Na}_2\text{SO}_4$  and shown to be related to the  $\text{C}_3\text{H}_7\cdot\text{CO}_2\cdot$  adsorption. Adsorbed cation appears to act as an activator of adsorption, whereas the anion has the reverse effect, this being confirmed by the relative effects of  $\text{Ba}^{++}$  and  $\text{K}^+$  on the above system. Applications to flotation problems are discussed.

J. W. S.

**Formation and properties of precipitates. I. Theory of co-precipitation.** I. M. KOLTHOFF [with R. MOLTZAU] (Chem. Weekblad, 1934, 31, 102—103; cf. A., 1932, 908).—Co-pptn. may involve adsorption, occlusion, or the formation of a chemical compound, whilst a further case is presented by the subsequent deposition of the second substance on the original ppt. The catalytic influence of  $\text{HgS}$  on the ppta. of  $\text{ZnS}$  is so pronounced that if both metals are present the Zn may be completely pptd. by  $\text{H}_2\text{S}$  from 0.1N-HCl; the presence of N-HCl is necessary for complete separation to be effected. In more dil. acid solutions the cryst.  $\text{HgS}$  which is first pptd. begins to adsorb  $\text{ZnS}$  and becomes difficult to filter if the passage of the  $\text{H}_2\text{S}$  is continued, but on ageing (24 hr.) the adsorbent power of the  $\text{HgS}$  diminishes.  $\text{HgS}$  also adsorbs  $\text{H}_2\text{S}$  strongly.  $\text{ZnS}$  adsorbs  $\text{HgS}$  from, e.g., solutions in  $\text{Na}_2\text{S}$ , whilst if a suspension of  $\text{HgS}$  in  $\text{H}_2\text{O}$  is shaken with  $\text{Na}_2\text{HgS}_2$  solution, free  $\text{Na}_2\text{S}$  appears in the solution, i.e.,  $\text{HgS}$  adsorbs  $\text{HgS}$  from such solutions, and the solubility of  $\text{HgS}$  in  $\text{Na}_2\text{S}$  solutions is a function of the surface of the solid phase. H. F. G.

**Capillary penetration of fibrous materials.** R. L. PEEK, jun., and D. A. MCLEAN (Ind. Eng. Chem. [Anal.], 1934, 6, 85—90).—The rate of capillary rise of liquids into porous materials varies inversely with the height of rise; the slope of the straight-line plot of these quantities is proportional to  $\gamma/\eta$ , where  $\gamma$  is the penetration tension (the product of the surface tension and the cosine of the contact angle) and  $\eta$  the viscosity of the liquid. The proportionality const. depends on the average pore size and on the

range of pore sizes. Results are given for the rise of several org. liquids in strips of paper. E. S. H.

**Interfacial activity of salts of the higher fatty acids and other emulsifiers.** A. LOTTERMOSER and H. WINTER (Kolloid-Z., 1934, 66, 276—288).—A ring-torsion balance for the determination of surface and interfacial (I) tensions, having a sensitivity of 0.01 dyne per cm., is described. (I) against paraffin oil of Na or K acetate, butyrate, valerate, hexoate, octoate, decaoate, laurate, myristate, palmitate, stearate, and oleate have been determined at 20° and 80° and concns. 0.01—10%. The max. lowering of (I) is almost attained in 0.2% solutions. Similar determinations with solutions of carrageen, gum arabic, tragacanth, gelatin, and saponin show that the max. lowering is attained in 0.5% solutions.

E. S. H.

**Structure and growth of thin surface layers on metals by atmospheric oxidation.** A. STEINHEIL (Ann. Physik, 1934, [v], 19, 465—483).—The properties, chemical composition, structure, and growth of thin surface layers formed on Al and Sn on exposure to air at room and higher temp. have been investigated. The layer forming on Al has a face-centred cubic lattice,  $a$  5.35 Å.; it corresponds with  $\epsilon$ -Al<sub>2</sub>O<sub>3</sub>, previously unknown. By melting the metal, oxide layers  $4 \times 10^{-5}$  cm. thick, consisting of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, are produced. Sometimes surface lattice interference occurs. This is due to single crystals of hexagonal  $\beta$ -Al<sub>2</sub>O<sub>3</sub> which possess an unusually long  $c$ -axis. When Sn foil is melted, the layer consists of SnO and SnO<sub>2</sub> in varying proportions. The rate of growth of the layer on Al has been studied.

A. J. M.

**Optical observations on the passivity of iron and steel in nitric and chromic acids.** L. TRONSTAD and C. W. BORGMANN (Trans. Faraday Soc., 1934, 30, 349—361).—The surface films on Fe and on ordinary and unstainable steels have been studied by Drude's optical method during immersion in conc. HNO<sub>3</sub>, 0.01M-CrO<sub>3</sub>, and M-K<sub>2</sub>CrO<sub>4</sub>+0.1M-KCl. The natural films are strengthened or replaced by denser films in accordance with the oxide theory of passivity. The approx. thickness of the film on steel in conc. HNO<sub>3</sub> is 100 Å., on purer Fe 25—35 Å., and on austenitic unstainable steel about 10 Å. In CrO<sub>3</sub> and K<sub>2</sub>CrO<sub>4</sub>-KCl mixtures the films are of the same order as previously obtained during anodic treatment, i.e., 30—40 Å.

M. S. B.

**Optical observations on the protective films on aluminium in nitric, chromic, and sulphuric acids.** L. TRONSTAD and T. HÖVERSTAD (Trans. Faraday Soc., 1934, 30, 362—366; cf. preceding abstract).—In CrO<sub>3</sub> and K<sub>2</sub>CrO<sub>4</sub>-KCl mixtures only small changes are observed in the optical properties of the natural oxide film. The films are not protective in conc. H<sub>2</sub>SO<sub>4</sub>, and there is alternate formation and breakdown of the protective film in conc. HNO<sub>3</sub>. The mean thickness of the natural oxide film is about 100 Å.

M. S. B.

**Physical chemistry of wetting phenomena and flotation processes.** XII. Parallelism between wetting isotherms and flotation curves. M. LIPETZ, P. REHBINDER, and M. RIMSKAJA (Kolloid-

Z., 1934, 66, 273—276; cf. this vol., 141).—The parallelism is demonstrated for the system malachite-H<sub>2</sub>O-air.

E. S. H.

**Kinetics of penetration.** VIII. Temporary accumulation. W. J. V. OSTERHOUT and S. E. KAMERLING (J. Gen. Physiol., 1934, 17, 507—516).—Aq. solutions of HCl and KOH are separated by a mixture of guaiacol and *p*-cresol, whereby a temporary accumulation of K<sup>+</sup> occurs in the HCl phase together with an increase in vol. up to a steady state. Lowering the  $p_H$  of the acid phase increases accumulation.

H. D.

**Electrolytic dissociation by the Raman effect.** II. Nitrates. I. R. RAO (Proc. Roy. Soc., 1934, A, 144, 159—165; cf. A., 1930, 1370).—Raman frequencies of nitrates in the cryst. state and in solution are given. The frequencies in the cryst. state are different for different cations, but the same for all nitrates in solution. For the same cation, the frequency in the solid state is higher than for the solution, with the exception of NH<sub>4</sub>NO<sub>3</sub> and possibly KNO<sub>3</sub>. No trace of any additional line due to undissociated mols. is found in the spectra of conc. solutions of NaNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub>. The ratio of intensity of the NO<sub>3</sub>-line of NaNO<sub>3</sub> to the concn. is const. The evidence points to the hypothesis of complete dissociation of nitrates even at high concns.

L. L. B.

**Properties of electrolytic solutions.** X. F.p. of solutions of an electrolyte in a non-polar solvent. C. A. KRAUS and R. A. VINGEE (J. Amer. Chem. Soc., 1934, 56, 511—516).—An apparatus for use between 0° and 25°, giving an accuracy of about 1% with concns. down to 10<sup>-3</sup>N, is described. F.p. curves for solutions of CHPh<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> and dioxan indicate that the f.p. const. of C<sub>6</sub>H<sub>6</sub> is 5.065° and that of dioxan is 4.63°. The f.p. curve of 0.001—0.011N-tetraisoamylammonium nitrate in dioxan deviates greatly from linearity, due probably to the association of the ion-pairs to more complex aggregates.

E. S. H.

**Derivation of distribution functions in problems of Brownian motion.** L. S. ORNSTEIN and W. R. VAN WIJK (Physica, 1934, 1, 235—254).—Theoretical.

H. J. E.

**Mechanical properties of disperse systems.** III. Effect of vibrations on the deformation of disperse, powdered substances. G. I. POKROVSKI and I. S. FEDEROV (Kolloid-Z., 1934, 66, 270—272; cf. A., 1932, 901).—A theoretically derived relation between velocity of deformation of coarsely disperse substances and the frequency and strength of vibrations is verified experimentally for sand saturated with H<sub>2</sub>O.

E. S. H.

**Chromatic, disperse two-phase systems, with special reference to their application as light filters.** E. KNUDSEN (Kolloid-Z., 1934, 66, 257—266).—The theory of the production of colour in disperse systems in which the two phases have equal  $n$  and different dispersions is treated with reference to numerous examples. The variation of colour with temp. is discussed. The least temp.-variable systems are solid-solid. Such systems can be formed

by dispersing glass in solutions of lacquers, celluloid, etc., and evaporating the solvent, by emulsifying molten colophony in molten grape sugar and subsequently cooling, or in the manufacture of glass under certain conditions. E. S. H.

**Dust and smoke.** R. WHYTLAW-GRAY (Proc. Roy. Inst., 1934, 28, 149—163).—A lecture.

**Conditions for the production of fog in the neutralisation of a volatile acid or alkali.** C. N. JACKSON and J. C. PHILIP (J.C.S., 1934, 341—346).—The view previously expressed (A., 1930, 855) as to the mechanism of the formation of the fog produced when an air-HCl stream is passed through aq. NaOH containing a trace of  $\text{NH}_3$  has been confirmed. The amount and composition of the fog have been determined and the influence of the v.p. of the aq. NaOH on its formation is considered. Similar observations and measurements have been made when an air- $\text{NH}_3$  stream is passed into HCl. Observations have also been made on the less stable fogs produced when an air- $\text{SO}_2$  stream is passed into aq. NaOH containing  $\text{NH}_3$ . M. S. B.

**Colloidal gases. II. Determination of particle size of colloidal air.** A. KRAUSE and K. KAPITANCZYK (Kolloid-Z., 1934, 66, 288—292; cf. A., 1931, 1230).—Colloidal particles of air in aq. NaOH have a radius about  $0.14 \mu$ . E. S. H.

**Viscosity of froth.** J. O. SIBREE (Trans. Faraday Soc., 1934, 30, 325—331).—A froth behaves similarly to a coarse emulsion. The viscosity ( $I$ ) varies with the velocity gradient and becomes const. above a certain val. of the latter. In the const. region ( $I$ ) is expressed by the formula  $\eta_e = \eta_0 / [1 - \sqrt[3]{(1.2\phi)}]$ , where  $\eta_e$  and  $\eta_0$  are ( $I$ ) for the froth and continuous phase, respectively, and  $\phi$  is the val. of the disperse phase in unit vol. of the froth. A curve showing the size-distribution of the bubbles is given.

M. S. B.

**Plasticity of powdered slate from Solnhofen and the thixotropic behaviour of its suspensions.** H. FREUNDLICH and F. JULIUSBURGER (Trans. Faraday Soc., 1934, 30, 333—338).—Finely-powdered slate from Solnhofen containing about 95%  $\text{CaCO}_3$  and 2% clay gives, when mixed with either sea- $\text{H}_2\text{O}$  or pure  $\text{H}_2\text{O}$ , a highly plastic thixotropic paste. Thin layers dry on a porous surface without cracking, and this property is probably necessary for the formation of the Solnhofen petrification. Finely-powdered quartz gives a thixotropic paste within a very narrow range of concn. with sea- $\text{H}_2\text{O}$  or an aq. solution if an electrolyte (e.g.,  $\text{MgCl}_2$ ). With pure  $\text{H}_2\text{O}$ , on the contrary, the Osborne-Reynolds phenomenon is observed. The conditions producing the two different phenomena are contrasted.

M. S. B.

**Residual tension in layered dielectrics, especially in colloid systems.** E. L. LEDERER [with F. DANNMEYER and J. SCHUBERT] (Kolloid-Z., 1934, 67, 63—65).—The apparatus and technique described allow the detection of small quantities of degradation products, particularly of photochemically sensitive substances. E. S. H.

**Influence of traces of  $\text{Na}_2\text{S}$  in preparation of colloidal gold by the formaldehyde method (Zsigmondy's  $\text{Au}_F$ ).** Preparation at room temperature. R. WERNICKE and R. B. LOSSON (Anal. Asoc. Quím. Argentina, 1933, 21, 149—155; cf. A., 1931, 303).—Using  $\text{Na}_2\text{S}$ , it is difficult to obtain Au sols of consistent properties at the b.p., but at room temp. optically empty ruby-red sols are obtained by using larger proportions of  $\text{Na}_2\text{S}$ .  $\text{AuCl}_3$  (100 c.c. of 0.01%) is treated with 1.4 c.c. of 0.18N- $\text{K}_2\text{CO}_3$ , and after 20 min. 0.5—0.6 c.c. of 0.02M- $\text{Na}_2\text{S}$ , and after 24 hr. 1 c.c. of 1.2%  $\text{CH}_2\text{O}$ . R. K. C.

**Influence of heat on structure formation in ferric hydroxide sols.** A. RABINERSON (Kolloid-Z., 1934, 66, 303—311).—When 4.5—10%  $\text{Fe}(\text{OH})_3$  sols are heated under various conditions, partial solidification occurs, the system returning to the liquid state subsequently at room temp. either spontaneously or after shaking. The cause of these phenomena is attributed to the increasing degree of hydrolysis of the intermicellar  $\text{FeCl}_3$ , which lowers the  $\zeta$  potential. After cooling the hydrolysis is reversed. E. S. H.

**Colloid chemistry of arsphenamine solutions: viscosity and conductivity measurements.** C. ROBINSON and C. A. MORRELL (Trans. Faraday Soc., 1934, 30, 339—349).—Viscosity ( $\eta$ ) and conductivity ( $\lambda$ ) measurements have been made on aq. arsphenamine dihydrochloride (I) in an atm. of  $\text{N}_2$ . The vals. depend on the history of the solution. After cooling for some time, both  $\eta$  and  $\lambda$  for a 0.5% solution at  $25^\circ$  are  $>$  in a solution recently heated, but both return in time to the equilibrium val., which is always reproducible after a sufficient length of time at const. temp. This slow reversible equilibrium has not hitherto been observed with other colloidal electrolytes. The increased vals. are probably to be explained by the aggregation of the cations into complex ions of high valency and mobility. In the hot solutions (I) may exist in true solution. In a 2% solution  $\lambda$  does not change in the same direction as  $\eta$ . Probably this concn. corresponds with concns. above the max. in  $\lambda$  curves for soaps or mobility curves for dyes. The existence of structural  $\eta$  could not be proved. Reproducible vals. were also observed for solutions of the  $\text{Na}_2$  salt. Equilibrium is reached rapidly. M. S. B.

**Colloid-chemical processes in the formation of colour lakes.** F. PAVELKA and F. HEISNAR (Kolloid-Z., 1934, 66, 340—351).—Experiments on the taking up of dyes by the hydroxides of Zr, Bi, Th, Sn, and Al show that an adsorption process is involved; no stoichiometric relation exists, and the concn. variation is in accordance with the usual adsorption isotherm. E. S. H.

**Colloid-chemical properties of sulphur dyes.** L. J. BELENKI (Kolloid-Z., 1934, 67, 79—87).—The leuco-solutions are highly-dispersed, negative colloids. The  $p_H$  of the bath is lowered by the presence of wool fibre. At lower  $p_H$  the dyes tend to become lyophobic; their pptn. at the surface of the fibre explains why they are not fast to rubbing. E. S. H.

**Transference of the disperse phase from one dispersion medium to another by demulsification.** II. A. JANEK and A. SCHMIDT (Kolloid-Z., 1934, 66, 296—302; cf. A., 1930, 1368).—The systems studied consist of hydrosols of Au, to a const. amount of which varying amounts of an alcohol and a third org. liquid (PhNO<sub>2</sub>, PhMe, CHCl<sub>3</sub>) are added. Demulsification occurs on cooling, and at certain mixture relations a zone is reached in which the Au is transferred from the aq. to the org.-liquid phase. In some cases the concn. of the colloidal Au is increased 300—400 times in this process. Certain resins, especially sandarac, facilitate the transference.

E. S. H.

**Electrochemistry of colloids.** W. PAULI and E. VALKÓ (Kolloid-Z., 1934, 66, 312—316).—A review of published work.

E. S. H.

**Quantitative relations in the lyotropic series.** I. Introduction. E. H. BÜCHNER. II. Lyotropic numbers and their explanation. E. M. BRUINS (Rec. trav. chim., 1934, 53, 288—291, 292—307).—I. The method of Bruins, which enables the flocculation concns. for one colloid to be calc. from those for another, is considered.

II. The method of deducing lyotropic nos. is explained, and these nos. are placed on a physical basis by means of a general coagulation theory. The flocculation vals. of salts and a simple method of determining the hydration energy are considered.

H. S. P.

**Regularities in the formation of Liesegang rings.** M. P. LAKHANI and R. N. MATHUR (Kolloid-Z., 1934, 67, 59—62).—When the concns. of gel and K<sub>2</sub>CrO<sub>4</sub> are const. the distance between successive rings is expressed by  $\log X_n = nK$ , where  $X_n$  is the distance for the  $n$ th ring. The val. of  $K$  increases with the concn.  $C$  of the AgNO<sub>3</sub> in accordance with  $K\sqrt[3]{C} = A$ , where  $A$  is a const.

E. S. H.

**Potentiometric studies of colloidal solutions.** I. Stearic acid hydrosols. M. P. U. IYER (J. Mysore Univ., 1932, 6, 188—196).—The sols were prepared by dissolving stearic acid in MeOH, adding to H<sub>2</sub>O, and boiling off the MeOH. The  $p_H$  of the intermicellar liquid is found to depend on the size of the particles, but not on the concn. of the acid. Potentiometric titration with NaOH or Ba(OH)<sub>2</sub> shows no evidence of a stoichiometric acid-alkali relation; the amount of alkali required varies with the time of contact. An adsorption theory of these phenomena is outlined.

E. S. H.

**Dependence of the state of division of dissolved fatty acid salts (soaps) in water on concentration.** G. JANDER and K. F. WITTENDORF (Angew. Chem., 1934, 47, 197—200).—The variation of the diffusion coeff. of Na decaate and laurate with concn. has been determined in presence of a large excess of NaOH and NaCl and compared with that of Bu<sup>n</sup>CO<sub>2</sub>Na. With increasing concn. soap particles of colloidal dimensions are gradually built up from the unimol. soaps obtained in solution at low temp. The bimol. stage of aggregation is of especial importance in building up the higher stages. The diffusion coeff. of 0.12*N*-Na decaate indicates an aggregation of 24 decaic acid residues with a mean mol. wt. of at least 4000.

M. S. B.

**High electrolyte sensitivity of the pasting process of potato starch and the colloid system produced thereby.** E. WIEGEL (Kolloid-Z., 1934, 67, 47—55).—Neutral salts of uni- and bi-valent cations at a concn. of 0.0001*N* lower the viscosity of the system by 40—60%, whilst the effect is detectable in 0.00001*N* solutions. At the same time the presence of electrolytes hinders the dispersion of starch granules to a sol. The influence of valency of the cation is in the direction indicated by the Schulze-Hardy rule, but is not very pronounced; H<sup>+</sup> has a stronger effect, and also promotes hydrolysis. The viscosity of starch sols is increased when the electrolyte normally present is removed.

E. S. H.

**Diffusion in silicic acid gels.** Z. V. VOLKOVA (Kolloid-Z., 1934, 66, 292—295).—The diffusion coeff.  $K$  of glucose in SiO<sub>2</sub> gels decreases linearly with increasing concn. of SiO<sub>2</sub>, and increases with the age of the gel, probably as a result of widening of the pores. The width of the pores is about 1—4  $\mu$ .

E. S. H.

**Combination of proteins with acids and bases.** (Miss) D. J. LLOYD (J. Soc. Leather Trades Chem., 1933, 17, 245—258).—The preferential adsorption of OH ions by protein from solutions at  $p_H$  7.0 is evidence of chemical combination. According to the zwitterion theory, isoelectric protein (I) should have one acid and two or more basic  $p_K$  vals. The acid  $p_K$  and one basic  $p_K$  are of the same order as those of aliphatic acids and primary aliphatic amines. At the isoelectric point, (I) carries equal and opposite charges, but there is considerable salt formation and an equilibrium between ionised and non-ionised acid groups, basic groups, and dissociated and associated salt linkings. The general titration curves of (I) can be explained on this basis.

D. W.

**Colloid-chemical hydrolysis of albumins.** I. S. J. DIJATSCHKOVSKI and V. A. LIVANSKAJA (Kolloid-Z., 1934, 67, 41—47).—When aq. solutions of proteins are shaken with C<sub>6</sub>H<sub>6</sub>, PhMe, or Et<sub>2</sub>O, the concn. of the aq. phase diminishes; the effect increases with the dilution. The hydrolysis product thus extracted is amorphous and increases in amount with the duration of hydrolysis.

E. S. H.

**Effect of deamination on combination curves of serum-albumin and -globulin.**—See this vol., 427.

**Change in the isoelectric point of collagen under the action of trypsin.** N. I. GAVRILOV and A. M. SIMSKAYA (Ovlad. Tekh. Kozh. Proiz., 1931, No. 2, 23—24).—Trypsin causes a change from  $p_H$  4.64 to  $p_H$  3.7; oropon causes a change to 3.4—4.2, depending on the duration of bating.

CH. ABS.

**Silk fibroin.** G. RASTELLI (Kolloid-Z., 1934, 67, 55—59).—The isoelectric point of fibroin is  $p_H$  4.6; the  $p_H$  of fibroin in the silk cocoon is 7.2. Fibroin has a slight solubility in H<sub>2</sub>O and reacts with AgNO<sub>3</sub>.

E. S. H.

**Simultaneous determination of the equilibrium constants of the reactions**  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ;  $2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CO}_2 + \text{CH}_4$ ;  $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ ;  $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$  by using activated nickel catalysts. J. C. GHOSH, K. M.

CHAKRAVARTY, and J. B. BAKSHI (Z. anorg. Chem., 1934, 217, 277—283).—The experimental arrangement was similar to that previously described (A., 1931, 1376), but the gas mixture was passed much more slowly over the Ni-ThO<sub>2</sub>-CoO<sub>2</sub> catalyst to ensure that the temp. of the gases should be the same as that of the furnace. The required equilibrium consts. were determined at temp. between 400° and 490°.

M. S. B.

**Table for the methanol synthesis equilibrium.** G. FRACASSO (L'Ind. Chimica, 1934, 9, 293—299).—Published vals. of the equilibrium const. for the synthesis of MeOH from CO+2H<sub>2</sub> differ widely among themselves and from the calc. vals. The discrepancies are due partly to secondary reactions and partly to errors in the theoretical treatment. All the available data are discussed and the relations between  $K_p$ , temp., and pressure are deduced. A nomographic table summarises the relations under the conditions of the industrial synthesis.

T. H. P.

**Cryoscopic determination of hydration of ions of strontium chloride.** E. ROUYER (Compt. rend., 1934, 198, 1156—1158; cf. this vol., 361).—The hydration of the ions in 0.5 and 0.25*M*. SrCl<sub>2</sub> corresponds with SrCl<sub>2</sub>.26.7H<sub>2</sub>O and SrCl<sub>2</sub>.30.3H<sub>2</sub>O, respectively.

C. A. S.

**Calculation of dissociation constants from the electrometric titration of acids.** E. SÖDERBÄCK (Arkiv Kemi, Min., Geol., 1934, 11 A, No. 8, 48 pp.).—A rigid derivation of the equations of Auerbach and Smolezyk (A., 1925, ii, 118).

D. R. D.

**Constitution of homogeneous acids and the influence of solvents on their acidity. Investigations with indicators.** A. MÜLLER (Z. anorg. Chem., 1934, 217, 113—153).—The relative acidity of acids in different org. solvents has been determined by comparing the extent of dilution necessary for the complete splitting up of an indicator salt formed from the acid and indicator base. The indicators *p*-dimethylaminoazobenzene and the less basic dicinnamylidenecyclohexanone have been used and, for single experiments, dianisylideneacetone and -cyclohexanone, and (*p*-NMe<sub>2</sub>.C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH.OH. The results are compared with those obtained by the kinetic diazo-ester method, and, although the indicator method is less sensitive, it is much simpler. The halogenated acetic acids, except the abnormal CH<sub>2</sub>Cl.CO<sub>2</sub>H, contain a great deal of active acidium salt. Aliphatic and aromatic mono- and poly-carboxylic acids are in general associated pseudo-acids, and therefore inactive towards diazo-ester and indicators. Anhyd. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is an exception. Introduction of halogen or of a triple linking causes strong activity. Aliphatic and aromatic OH-acids form complex pseudo-acids by internal salt formation. The simple sulphonic acids are homogeneous, and strongly active in solution. They readily form oxonium salts or solvates. Aminosulphonic acids are inactive. Among inorg. acids HClO<sub>4</sub>, which is the strongest, is always active, whilst HNO<sub>3</sub> is completely inactive in Et<sub>2</sub>O. Complex acids and hetero-poly-acids are, for the most part, active in the solid state, and not appreciably affected by inactivating solvents. The behaviour of

acid salts depends on the nature of the constituent acids. As a solvent AcOH has an inactivating action which is in accordance with Hantzsch's conception of it (A., 1927, 1011) as bimolar acetyl alcohol. N<sub>2</sub>CH.CO<sub>2</sub>Et is a strongly inactivating solvent on account of its unsaturation. The inactivating power of a solvent is greater in proportion to the degree of unsaturation of its mol. and to the weakness of the acid dissolved in it. The action of certain O-containing compounds, especially Et<sub>2</sub>O, cineol, and acetal, is the most marked. Acids rich in acidium salt form solvates of varying stability in solution. Strong acids form true oxonium salts or acidium solvates with Et<sub>2</sub>O and EtOH, whilst other acids give inactive "neuro-solvates."

M. S. B.

**Interhalogen compounds: dissociation of halide complexes, dissociation, hydrolysis, distribution ratios in acid solution.** J. H. FAULL, jun. (J. Amer. Chem. Soc., 1934, 56, 522—526).—The data recorded are: [IBr][Br']/[IBr<sub>2</sub>'] = 0.0027; [IBr][Cl']/[IBrCl'] = 0.023, [ICl][Cl']/[ICl<sub>2</sub>'] = 0.0060; distribution ratios between CCl<sub>4</sub> and H<sub>2</sub>O, IBr 3.9, ICl 0.34; [I<sub>2</sub>][Br<sub>2</sub>]/[IBr]<sup>2</sup> = 1.2 × 10<sup>-5</sup>, [I<sub>2</sub>][Cl<sub>2</sub>]/[ICl]<sup>2</sup> = 1.6 × 10<sup>-10</sup>. Preliminary vals. for hydrolysis consts. are given. The results diverge from the rule that properties are intermediate between those of the component halogens.

E. S. H.

**Equilibrium in the reaction Cl<sub>2</sub>+Br<sub>2</sub>=2BrCl.** H. G. VESPER and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 620—625).—In measurements of the absorption coeff. of BrCl, with wave-lengths near 0.50 μ the following vals. have been obtained at 28°:  $K = \frac{[Br_2][Cl_2]}{[BrCl]^2} = 0.107 \pm 0.002$ ,  $\alpha = 0.384 \pm 0.006$ . Equilibrium is attained after some hr. in the dark, but after 2 min. when illuminated with light of wave-length 0.365 μ. The steady state in the light is identical with the thermal equilibrium.

E. S. H.

**Formation of high-molecular inorganic compounds in hydrolysing systems.** G. JANDER and K. F. JAHR (Chem.-Ztg., 1934, 58, 247—249).—Data for aq. solutions of salts of weak bases with strong acids and of strong bases with weak acids show that salts of weak acids (e.g., Na<sub>2</sub>WO<sub>4</sub>) yield on acidification a series of definite anhydro-acid salts the anions of which are stable over a definite range of  $p_H$ , whereas the salts of weak bases [e.g., Fe(ClO<sub>4</sub>)<sub>3</sub>] give no definite complex cations, the mol. wt. of the complex increasing steadily with the  $p_H$ .

D. R. D.

**Amphoteric behaviour of metallic hydroxides. VI. Plumbites.** R. SCHOLDER and R. PATSCH (Z. anorg. Chem., 1934, 217, 214—224).—In alkaline plumbite solutions the complex ions Pb(OH)<sub>3</sub>', Pb(OH)<sub>4</sub>'', and Pb(OH)<sub>6</sub>'''', are present in proportions depending on temp. and concn., but pure cryst. hydroxoplumbites cannot be separated. Decomp. takes place and PbO is formed. Stabilisation is brought about, however, by replacement of OH by halogen X up to a proportion of 1Pb:0.5X. I is especially effective, and mixtures of the following compounds can be obtained: [Pb(OH)<sub>3</sub>]<sub>2</sub>Na; [Pb(OH)<sub>4</sub>]<sub>2</sub>Na<sub>2</sub>; [PbX(OH)<sub>3</sub>]<sub>2</sub>Na<sub>2</sub>; [Pb(OH)<sub>4</sub>]<sub>2</sub>Ba; [PbX(OH)<sub>3</sub>]<sub>2</sub>Ba; [Pb(OH)<sub>6</sub>]<sub>2</sub>BaNa<sub>2</sub>. Pure cryst. [Pb(OH)<sub>4</sub>]<sub>2</sub>Na<sub>2</sub> has been obtained in presence of hot

and very conc. aq. NaOH, but cannot be isolated from this without decomp. M. S. B.

**Hydrolysis of acetoxime.** J. E. W. RHODES (J.C.S., 323—325).—The const. for the equilibrium between  $\text{NH}_2\text{OH}$ ,  $\text{COMe}_2$ , and acetoxime in dil. aq. solution is approx.  $16 \times 10^{-6}$  in neutral solution, but increases slightly in very acid solution. H<sup>+</sup> is evidently not involved in the equilibrium const., but may have a small influence on the active masses of the reactants. M. S. B.

**Application of the van 't Hoff-Le Chatelier-Braun principle to chemical equilibria.** K. POSTHUMUS (Rec. trav. chim., 1934, 53, 308—311).—Le Chatelier's new formulation (cf. A., 1933, 783) is incorrect, even if the ideal gas laws are assumed. H. S. P.

**Thermodynamic deduction of the law of infinitely dilute gases.** D. MATURO (Rev. fac. quim. ind. agric., Univ. nac. litoral, 1932, 2, 38—49).—Starting with  $(\partial U/\partial v)_T=0$  and  $(\partial H/\partial v)_T=0$ , and assuming that in any real gas it is impossible to reach zero pressure by any finite reversible isometric process, it is shown that  $\lim P=0$ ,  $\lim MPV=kT$ . The application to the thermodynamic temp. scale and to the determination of mol. wts. is discussed. CH. ABS.

**Activity coefficients of solutions.** P. VAN RYSELBERGHE (Bull. Acad. roy. Belg., 1934, [v], 20, 234—238).—Theoretical. J. W. S.

**Solubility of strong electrolytes in concentrated solutions.** G. ÅKERLÖF and H. C. THOMAS (J. Amer. Chem. Soc., 1934, 56, 593—601).—Simple relations between the thermodynamic activities of strong electrolytes in pure or mixed aq. solutions are considered with reference to the solubility of  $\text{Ag}_2\text{SO}_4$  in  $\text{H}_2\text{SO}_4$  and several sulphate solutions. Equations are derived for calculating the composition of the solution in three-component systems containing two strong electrolytes. E. S. H.

**Equilibrium constants in terms of activities (cryoscopic). III. Dissociation of quinoline *o*-chlorophenoxide in benzene and *p*-dichlorobenzene.** H. M. GLASS, W. M. MADGIN, and (in part) F. HUNTER (J.C.S., 1934, 260—263).—The vals. of the true equilibrium const.  $K_a = a_{AB}/a_A a_B$  for the dissociation of quinoline *o*-chlorophenoxide in  $\text{C}_6\text{H}_6$  and *p*- $\text{C}_6\text{H}_4\text{Cl}_2$  are 219.8 and 36.74, respectively, at the f.p. of the solvents. Hence the molal heat of formation is —6800 g.-cal., which is the same as for pyridine *o*-chlorophenoxide (this vol., 28). This equality is ascribed to the existence of the same type of valency linking in each compound, i.e., a coordinate linking between the N atom of the base and the H atom of OH in *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ . M. S. B.

**Equations of state of water vapour.** J. KUUSI-NEN (Forsch. Ingenieurwes., 1933, A, 4, 200—201; Chem. Zentr., 1933, ii, 2654).—Equations for the heat content (*i*), entropy (*s*), and pressure (*p*) are recorded. H. J. E.

**Deliquescence and efflorescence.** A. DAMIENS (Compt. rend., 1934, 198, 1233—1235). C. A. S.

**Thermal dissociation of cadmium carbonate.** P. Y. NARAYANA and H. E. WATSON (J. Indian

Inst. Sci., 1934, 17, A, 1—6).—The dissociation pressure falls steadily with increase in the proportion of CdO present. D. R. D.

**Binary system,  $\text{MnO}\text{--}\text{SiO}_2$ .** J. WHITE, D. D. HOWAT, and R. RAY (J. Roy. Tech. Coll., 1934, 3, 231—240).—The equilibrium has been derived from thermal observations and the phase changes confirmed by use of a high-temp. microscope. H. S. P.

**Binary system  $\text{TlNO}_3\text{--}\text{Tl}_2\text{CO}_3$ .** A. S. BROUN (J. Gen. Chem. Russ., 1933, 3, 998—1000).—The fusion diagram suggests formation of the compounds  $2\text{TlNO}_3, \text{Tl}_2\text{CO}_3$ , m.p. 218°, and  $\text{TlNO}_3, \text{Tl}_2\text{CO}_3$ , m.p. 214°. R. T.

**Active oxides. LXXIII. Changes of the magnetic properties of a mixture of magnesium oxide with chromium oxide and calcium oxide with iron oxide during transformation into spinel.** H. KITTEL and G. F. HÜTTIG (Z. anorg. Chem., 1934, 217, 193—202).—Magnetic susceptibility data have been obtained for the above systems at different temp. and compared with the data previously obtained for other oxide mixtures. X-Ray spectroscopic observations have also been made on the system  $\text{CaO}\text{--}\text{Fe}_2\text{O}_3$ . M. S. B.

**Thermal analysis of picrates. II.** T. TUCHOLSKI (Rocz. Chem., 1934, 14, 125—140).—Dehydration and fusion temp., and those leading to explosion of the picrates of Be, Mg, Zn, Cd, Hg, Ca, Sr, and Ba are recorded. The following hydrates are recorded: Mg,  $4\text{H}_2\text{O}$ ; Zn,  $10\text{H}_2\text{O}$ ; Cd, 1 and  $4\text{H}_2\text{O}$ ; Hg, 1 and  $3\text{H}_2\text{O}$ ; Ca,  $8\text{H}_2\text{O}$ . Evidence is not found for the hydrates Mg,  $5\text{H}_2\text{O}$ ; Zn, 1 and  $5\text{H}_2\text{O}$ ; Cd,  $5\text{H}_2\text{O}$ ; Ca,  $3\text{H}_2\text{O}$ ; Ba, 2.5, 3, 4, and  $4.5\text{H}_2\text{O}$ , recorded by other authors. R. T.

**Phase equilibria in hydrocarbon systems. II. Methane-propane.** B. H. SAGE, W. N. LACEY, and J. G. SCHAAFSMA (Ind. Eng. Chem., 1934, 26, 214—217).—The system has been studied between 20° and 90°, and 1 and 200 atm. The results are given in full, with pressure-composition isotherms, const. composition curves on pressure-temp. and density-pressure diagrams, and isobars on the gas-liquid composition diagram. H. F. G.

**Fusion diagram of the system carbamide-diphenylamine.** W. J. NIJVELD (Rec. trav. chim., 1934, 53, 430—432).—The diagram shows an extensive region of miscibility in the fluid state. This region meets the m.p. line of  $\text{CO}(\text{NH}_2)_2$ . H. S. P.

**Binary systems. IV.** J. H. KOERS and F. E. C. SCHEFFER (Rec. trav. chim., 1934, 53, 279—287).—Systems (*a*) with a stable quadruple point, (*b*) without a quadruple point, and (*c*) the transition case are considered theoretically. The systems  $\text{CO}_2\text{--}o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ ,  $\text{CO}_2\text{--}m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ , and  $\text{C}_6\text{H}_5\text{--}p\text{-C}_6\text{H}_4\text{ClBr}$  belong to type (*a*) and the systems  $\text{CO}_2\text{--}o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  and  $\text{C}_2\text{H}_6\text{--}s\text{-C}_6\text{H}_3\text{Cl}_3$  to type (*b*). H. S. P.

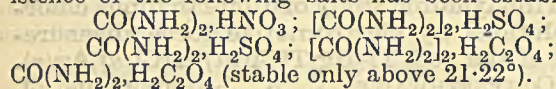
**25° isotherms of the systems  $\text{Na}_2\text{CO}_3\text{--}\text{NaHCO}_3\text{--}\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3\text{--}\text{NaHSO}_4\text{--}\text{H}_2\text{O}$ .** S. Z. MAKAROV and M. N. JAKIMOV (J. Gen. Chem. Russ., 1933, 3, 990—997).—The equilibrium relations are discussed. R. T.



**Ternary system KI-PbI<sub>2</sub>-H<sub>2</sub>O at 0° and 25°.** H. S. VAN KLOOSTER and P. A. BALON (J. Amer. Chem. Soc., 1934, 56, 591—592).—Only one double salt exists, KPbI<sub>3</sub>·2H<sub>2</sub>O. E. S. H.

**Mixed crystals in the sulphate series. II.** A. BENRATH and A. BLANKENSTEIN (Z. anorg. Chem., 1934, 217, 170—174).—Data are given for the system MnSO<sub>4</sub>-ZnSO<sub>4</sub>-H<sub>2</sub>O. M. S. B.

**Ternary systems of carbamide and acids. I.** Carbamide, nitric acid, and water. **II.** Carbamide, sulphuric acid, and water. **III.** Carbamide, oxalic acid, and water. L. H. DALMAN (J. Amer. Chem. Soc., 1934, 56, 549—553).—The existence of the following salts has been established:



E. S. H.

**Equilibria in binary and ternary systems of certain polynitro-compounds.** K. HRYNAKOWSKI and Z. KAPUŚCIŃSKI (Rocz. Chem., 1934, 14, 115—124).—Contrary to Giua's findings (A., 1914, i, 817; 1915, i, 659) no compounds are formed in the systems *m*-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> (I)-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub> (II), C<sub>6</sub>H<sub>2</sub>Me(NO<sub>2</sub>)<sub>3</sub> (III), C<sub>6</sub>H<sub>2</sub>(OH)(NO<sub>2</sub>)<sub>3</sub> (IV); (I)-(III); (II)-(IV); (III)-(IV); and (I)-(II)-(III). R. T.

**Double decomposition in the absence of a solvent. XIX.** A. P. OBUCHOV. **XX, XXI.** V. P. RADISCHTSHEV (J. Gen. Chem. Russ., 1933, 3, 787—791, 843—851, 852—864).—**XIX.** Fusion diagrams are given for the system NaI+KBr → NaBr+KI.

**XX.** The diagrams for NaCl-NaBr-NaI and KCl-KBr-KI suggest the formation of solid solutions which contain all three components.

**XXI.** Diagrams are given for the system 2NaCl+K<sub>2</sub>CO<sub>3</sub> → 2KCl+Na<sub>2</sub>CO<sub>3</sub>. R. T.

**Double decomposition in the absence of a solvent. XXII, XXIII.** O. S. DOMBROVSKAJA. **XXIV.** M. A. KLOTSCHKO (J. Gen. Chem. Russ., 1933, 3, 1007—1016, 1017—1025, 1026—1039).—**XXII.** The fusion diagrams for the systems KCl-K<sub>2</sub>SO<sub>4</sub>, KCl-LiCl, Li<sub>2</sub>SO<sub>4</sub>-LiCl, Li<sub>2</sub>SO<sub>4</sub>-KCl show no compound formation, whilst that for K<sub>2</sub>SO<sub>4</sub>-Li<sub>2</sub>SO<sub>4</sub> indicates K<sub>2</sub>SO<sub>4</sub>·Li<sub>2</sub>SO<sub>4</sub>, m.p. 716°. The equilibrium relations for the system K<sub>2</sub>SO<sub>4</sub>+2LiCl ⇌ 2KCl+Li<sub>2</sub>SO<sub>4</sub> are discussed.

**XXIII.** The diagrams for Cs<sub>2</sub>SO<sub>4</sub>+2KCl ⇌ K<sub>2</sub>SO<sub>4</sub>+2CsCl and 2RbCl+K<sub>2</sub>SO<sub>4</sub> ⇌ Rb<sub>2</sub>SO<sub>4</sub>+2KCl do not suggest compound formation.

**XXIV.** The equilibrium relations in the system 2LiCl+Na<sub>2</sub>SO<sub>4</sub> ⇌ 2NaCl+Li<sub>2</sub>SO<sub>4</sub> are discussed. R. T.

**Thermochemistry of iron.** W. A. ROTH and F. WIENERT (Arch. Eisenhüttenw., 1933—1934, 7, 455—460).—The heat of reaction with aq. HCl at room temp. of finely-divided Fe and Fe<sub>2</sub>O<sub>3</sub> [from Fe(CO)<sub>5</sub>], Fe<sub>3</sub>O<sub>4</sub> (from the reduction of Fe<sub>2</sub>O<sub>3</sub> with H<sub>2</sub> and steam at 500°), and FeO (from anhyd. FeCl<sub>2</sub> and CaO) have been determined and the following thermochemical data derived: Fe+0.5O<sub>2</sub>=FeO+64.65±0.12 kg.-cal.; 3Fe+2O<sub>2</sub>=Fe<sub>3</sub>O<sub>4</sub>+266.76±0.22 kg.-cal.; 2Fe+1.5O<sub>2</sub>=Fe<sub>2</sub>O<sub>3</sub>+195.19±0.20 kg.-cal.; FeO+Fe<sub>2</sub>O<sub>3</sub>=Fe<sub>3</sub>O<sub>4</sub>+6.94±0.33 kg.-cal.; Fe+1.5Cl<sub>2</sub>=

FeCl<sub>3</sub>+93.56±0.23 kg.-cal.; Fe<sub>2</sub>O<sub>3</sub>+3Cl<sub>2</sub>=2FeCl<sub>3</sub>+1.5O<sub>2</sub>-8.07±0.44 kg.-cal. A. R. P.

**Thermometric study of formation of inorganic complexes.** P. MONDAIN-MONVAL and R. PARIS (Compt. rend., 1934, 198, 1154—1156).—The curve obtained by plotting the temp. rise against the amount of aq. KI added to aq. HgCl<sub>2</sub> (cf. A., 1922, ii, 578) affords evidence of the formation of HgI<sub>2</sub> and K<sub>2</sub>HgI<sub>4</sub> (cf. A., 1933, 37). Similarly when aq. KCN is added to aq. NiSO<sub>4</sub>, ZnSO<sub>4</sub>, or CoSO<sub>4</sub> breaks indicate the formation of (1) M<sup>II</sup>(CN)<sub>2</sub> and (2) of K<sub>2</sub>Ni(CN)<sub>4</sub>, K<sub>2</sub>Zn(CN)<sub>4</sub>, and K<sub>3</sub>Co(CN)<sub>5</sub>, respectively (cf. A., 1910, ii, 458; 1924, ii, 704). C. A. S.

**Heat of formation of silicon carbide and the existence of siloxicon.** R. BRUNNER (Z. anorg. Chem., 1934, 217, 157—160).—The different vals. obtained for the heat of formation of SiC are discussed. It is not found possible to reconcile the val. of 39 kg.-cal. obtained dynamically (A., 1932, 341) with any of the calorimetric data. The existence of Si<sub>2</sub>C<sub>2</sub>O, as indicated by pressure data, is reaffirmed, contrary to the conclusions of Arndt and Hausmann (this vol., 42). M. S. B.

**Heats of neutralisation of the amino-acids.** G. DEVOTO (Atti R. Accad. Lincei, 1934, [vi], 19, 50—52).—The heats of neutralisation of thirteen NH<sub>2</sub>-acids are recorded. The polar character of the various acids deduced from these data agrees with the results of other methods. O. J. W.

**Conductance of aqueous solutions as a function of the concentration of potassium bromide and lanthanum chloride.** G. JONES and C. F. BICKFORD (J. Amer. Chem. Soc., 1934, 56, 602—611).—Electrical conductance and *d* of 0.00025—3.75*M*-KBr and 0.00025—1.0*M*-LaCl<sub>3</sub> have been determined at 0° and 25°. The vals. of *d* are in accordance with an equation of the form given by Root (A., 1933, 347). The equation of Jones and Dole (A., 1930, 998) is applicable to the conductance data; Shedlovsky's equation (A., 1932, 699) fits the data for KBr up to 0.1*M*, but is not applicable to LaCl<sub>3</sub>. E. S. H.

**Guaiacol solutions. I. Electrical conductivity of sodium and potassium guaiacoxides. II. Distribution of sodium and potassium guaiacoxides between guaiacol and water.** T. SHEDLOVSKY and H. H. UHLIG (J. Gen. Physiol., 1934, 17, 549—561, 563—576).—The vals. of *D* (=14.3), relative  $\eta$  (=7.23), and  $\rho$  (=1.1275) for a saturated solution of H<sub>2</sub>O in guaiacol (I) and of  $\Lambda$  for solutions of Na and K guaiacoxide (II) in (I) are used to derive  $\Lambda_\infty$  and *K*, the dissociation const., of (II) in (I) by use of the Onsager equation (A., 1927, 517). Using an average val. of  $\Lambda_\infty$ , the calc. vals. for  $\Lambda$  at various concns. agree with those obtained experimentally.

**II.** The distribution ratios for (II) between (I) and H<sub>2</sub>O are determined by analysis and vals. for *K* derived in good agreement with those obtained conductimetrically. Bjerrum's equation for the variation of *r* with concn. (A., 1927, 1028) is modified by introducing the individual vals. of the radii of the ions, giving vals. for *r* of the same order as those obtained experimentally. H. D.

**Electrochemical examination of the system  $\text{AlBr}_3\text{-KBr}$  in the solid state.** V. A. PLOTNIKOV and S. I. JAKUBSON (J. Gen. Chem. Russ., 1933, 3, 869—871).—The compound  $2\text{AlBr}_3\cdot\text{KBr}$  conducts electricity, and with Al electrodes Al is transported to the cathode. An increase in the KBr content of the electrolyte does not appreciably change the conductivity. R. T.

**Electrochemical examination of solutions of aluminium chloride and potassium chloride in nitrobenzene.** V. A. PLOTNIKOV and I. M. PODORVAN (J. Gen. Chem. Russ., 1933, 3, 782—786).—The sp. conductivity  $\kappa$  of  $\text{PhNO}_2$  solutions of  $\text{AlCl}_3$  is greatest when the concn. of  $\text{AlCl}_3$  is 14%.  $\kappa$  rises on addition of KCl, to an extent proportional to its concn.; on electrolysis of such solutions K is deposited at the cathode, at a decomp. potential of 5 volts, as compared with 4.5 volts for solutions containing KCl alone. R. T.

**Electrochemical properties of smooth films of electrolytically deposited platinum metals.** I. I. SHUKOV (J. Gen. Chem. Russ., 1933, 3, 959—962).—Pt electrodes covered with a smooth layer of Pt (I) give better results in conductivity measurements than do those covered with Pt-black (II); the overpotentials obtained on electrolysis of aq.  $\text{H}_2\text{SO}_4$  are of the same magnitude for (I) and (II). The active surface of (I) is  $> 10$  times that present before platinising. R. T.

**Superconductivity of films of tin.** E. F. BURTON (Nature, 1934, 133, 459).—Thin films of Sn cease to show superconductivity (I) when they are plated over with a film of a non-superconducting metal such as Cu or Ni. When the film of Sn increases in thickness, a point is reached at which (I) is not lost by surface plating. L. S. T.

**Persistent currents in superconductors.** K. MENDELSSOHN and J. D. BABBITT (Nature, 1934, 133, 459—460). L. S. T.

**Production of heat in superconductors by alternating currents.** H. LONDON (Nature, 1934, 133, 497—498). L. S. T.

**The antimony electrode.** A. HOLMQUIST (Svensk Kem. Tidskr., 1934, 46, 2—10).—The potential attained in an acid solution of given  $p_{\text{H}}$  depends on whether the electrode is massive or powdered Sb, and varies with the nature of the acid, the greatest differences being observed between HCl and  $\text{HClO}_4$ . The variations with different types of electrode are considered to be due to variable  $\text{O}_2$  content of the solution. The oxidation-reduction potential for  $\text{Sb}^{\text{III}}\text{-Sb}^{\text{V}}$  was measured in 3.8*N*-HCl, and data are given for the distribution of  $\text{SbCl}_3$  between aq. HCl and  $\text{Et}_2\text{O}$ . R. P. B.

**Effect of electrical leakage on the electromotive behaviour of the glass electrode.** C. MORTON (J.C.S., 1934, 256—260).—Correct indications of the electromotive behaviour are obtained only by use of the quadrant electrometer or the electrometer triode valve. Other instruments distort the e.m.f.- $p_{\text{H}}$  graph to an extent depending on input impedances, but give satisfactory results in routine work provided

that the conditions obtaining during calibration are maintained const. by control of temp. and humidity. M. S. B.

**Cell lead|lead sulphate|cupric sulphate|copper.** (MLLE.) M. QUINTIN and A. LEBETRE (Compt. rend., 1934, 198, 1140—1141).—Comparison of the normal potentials of the cells  $\text{Pb}(\text{amalgam two phases})|\text{PbSO}_4(\text{s})|\text{CuSO}_4(\text{c})|\text{Cu}(\text{amalgam two phases})$  for  $c=0.105\text{--}0.00105$ , and  $\text{Cu}(\text{amalgam two phases})|\text{CuSO}_4(\text{c})|\text{Hg}_2\text{SO}_4(\text{s})|\text{Hg}$  shows that the irregularities in the latter when  $c$  is  $< 0.003M$  are determined by the solubility of  $\text{Hg}_2\text{SO}_4$ . Similar irregularities occur in the former if  $c$  is  $< 0.001M$  (cf. A., 1933, 781). C. A. S.

**Thermodynamic study of dilute thalious chloride solutions by electromotive force measurements of the cell  $\text{Tl-Hg}|\text{TlCl}(m)|\text{AgCl}(s), \text{Ag}(s)$ .** I. A. COWPERTHWAIT, V. K. LA MER, and J. BARKSDALE (J. Amer. Chem. Soc., 1934, 56, 544—549).—Data for the cell at 25° are:  $E^\circ 0.55833$ ,  $dE^\circ/dT 6.646 \times 10^{-4}$ ,  $-\Delta F^\circ 12,877$  g.-cal.,  $-\Delta H^\circ 8307$  g.-cal. The curve obtained by plotting the logarithms of the activity coeffs. of TlCl against the square root of concn. is discussed in relation to the Debye-Hückel theory. E. S. H.

**Thermodynamics of aqueous sodium sulphate solutions from electromotive force measurements.** H. S. HARNED and J. C. HECKER (J. Amer. Chem. Soc., 1934, 56, 650—653).—Activity coeffs., relative partial mol. heat contents, and sp. heats of  $\text{Na}_2\text{SO}_4$  have been calc. from e.m.f. determinations of the cells  $\text{Pb}(\text{Hg})|\text{PbSO}_4(\text{s})|\text{Na}_2\text{SO}_4(m)|\text{Na}_2\text{Hg}|\text{Na}_2\text{SO}_4(0.05)|\text{PbSO}_4(\text{s})|\text{Pb}(\text{Hg})$  at 5° intervals from 0° to 40°. E. S. H.

**Electrometric measurements in solutions of quinine salts.** H. L. PEDERSEN (Dansk Tidsskr. Farm. 1934, 8, 17—39).—On adding  $> 1$  equiv. of acid to a solution of a pure quinine salt and then titrating with NaOH, the potential curve (measured with a quinhydrone electrode) has two points of inflexion, one (weak) corresponding with the di-acid salt, and one (strong) corresponding with the mono-acid salt. The  $p_{\text{H}}$  corresponding with the di-salt can be obtained from measurements with pure salt, and the amount of NaOH necessary to change the  $p_{\text{H}}$  from this val. to the mono-salt point of inflexion gives the amount of quinine present. If quinine is written  $\text{B}_1\cdot\text{B}_2$ , the acid dissociation consts. for the processes  $\text{B}_1\text{H}^+\cdot\text{B}_2\text{H}^+ \rightarrow \text{B}_1\text{H}^+\cdot\text{B}_2 + \text{H}^+$  and  $\text{B}_1\text{H}^+\cdot\text{B}_2 \rightarrow \text{B}_1\cdot\text{B}_2 + \text{H}^+$  are  $4.3 \times 10^{-5}$  and about  $2 \times 10^{-11}$ , respectively. R. P. B.

**Electrolytic reduction potentials of organic compounds. XI. Reduction potentials of nitranilines.** M. SHIKATA and E. TAGUCHI (Mem. Coll. Agric. Kyoto, 1934, No. 29, 1—17).—The electrolytic reduction potentials,  $P$ , of  $10^{-3}\text{--}10^{-5}M$ . *o*-(I), *m*-(II), and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (III) determined polarographically with the dropping Hg cathode become more negative with increase of  $p_{\text{H}}$  from 1 to 10 and are independent of  $p_{\text{H}}$  in the range 10—13. Consistent with the weak basicity of the compounds, vals. of  $P$  for the ionic and the mol. forms are observed. The  $P$  of the ionic forms in 0.1*N*-HCl at 25° are (I)

-0.121, (II) -0.104, (III) -0.117 volt, which are more positive than  $P$  for  $\text{PbNO}_2$  (IV), whilst for the mol. forms at  $p_H$  7 the vals. are (I) -0.553, (II) -0.425, and (III) -0.507, which, excepting the val. for (II), are more negative than  $P$  for (IV). These results are related to the authors' negativity rule (cf. A., 1932, 231) and the theory of induced alternating polarity.  
J. G. A. G.

**Electromotive behaviour of organic derivatives of arsenic and arsenious acids.** H. ERLÉNMEYER and H. ARNI (Helv. Chim. Acta, 1934, 17, 308-311).—The potential of the oxidation-reduction system atoxyl acid  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$  and its reduction product  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_2\cdot 2\text{H}_2\text{O}$  has been determined at various concns. in 6*N*-HCl, 0.1*N*-HCl, and 0.0667*M*- $\text{KH}_2\text{PO}_4$ .  
M. S. B.

**Oxidation-reduction properties of "evolved carbohydrates" in absence of oxygen.** See this vol., 550.

**Capacity of non-polarisable electrode with a.c.** N. THON (Compt. rend., 1934, 198, 1219-1221).—By means of an arrangement similar to that of Jones and Josephs (cf. A., 1928, 595) it is shown that the capacity,  $C$ , of Hg electrodes in 0.5*M*- $\text{HgNO}_3$  varies as  $1/\omega^2$  if the frequency,  $\nu$ , is  $> 4200$  per sec. ( $\omega = \text{pulsatance}, = 2\pi\nu$ ); in 0.1*M*- $\text{HgNO}_3$  between  $1/\omega^2$  and  $1/\omega$ , approaching  $1/\sqrt{\omega}$  as the concn. of Hg diminishes; and in 2*M*- $\text{KNO}_3$  as  $1/\sqrt{\omega}$ . This disagrees with previous results (cf. A., 1873, 348; 1903, ii, 707).  $C$  appears to increase with depolarisation (cf. A., 1932, 24).  
C. A. S.

**Arced gases.** B. W. BRADFORD and G. I. FINCH (J.C.S., 1934, 360-365).—Apparatus is described for examining pre-arc'd jets of gases or mixtures, and for studying the interaction of two such jets, for preheating, and for determining the homogeneous and heterogeneous ignition temp. of various mixed arc'd and unarc'd gases. Arc'd jets of CO and  $\text{O}_2$  both showed strong afterglows, and a bright characteristic glow appeared on mixing. No  $\text{CO}_2$  was formed by direct combination of CO and  $\text{O}_2$ . Pre-arc'ing of  $\text{H}_2$  alone caused no appreciable formation of steam in mixed  $\text{H}_2$  and  $\text{O}_2$  jets, arc'ing of  $\text{O}_2$  being also necessary. Moist arc'd  $\text{H}_2$  gave the reactions of at. H. Arc'ing or otherwise of preheated jets had no effect on the ignition temp. of the mixed streams. It is concluded that H does not act as a promoter.  
N. M. B.

**Influence of pressure on the spontaneous inflammation of hydrocarbons.** H. F. COWARD (Nature, 1934, 133, 463-464).—Unpublished pressure-temp. curves by Dixon for the lag on ignition of  $\text{C}_5\text{H}_{12}$  vapour heated to a given temp. and issuing into the atm. at the same temp. show a break at 60 cm. pressure and are of the same general character as those obtained by Neumann and Estrovich (this vol., 259).  
L. S. T.

**Movement of flame in firedamp explosions.**—See B., 1934, 307.

**Combustion of carbon monoxide.** A. H. W. ATEN, jun. (Rec. trav. chim., 1934, 53, 269-278).—The theory is advanced that reactions in flames are due to ions. The extinction of flames by an electric

field, the influence of  $\text{H}_2\text{O}$  vapour and composition of the gas mixture on flame velocity, and the effect of pressure and composition of the mixture on ignition temp. are considered.  
H. S. P.

**Kinetics of the thermal reaction of gaseous alkyl iodides with hydrogen iodide.** R. A. OGG, jun. (J. Amer. Chem. Soc., 1934, 56, 526-536).—The reactions  $\text{RI} + \text{HI} \rightarrow \text{RH} + \text{I}_2$ , where R is Me, Et, or  $\text{Pr}^n$ , are homogeneous, free from appreciable side reactions, and proceed almost to completion at 250-320° and 3-360 mm. The order of reaction is complex, and appears to be controlled by two concurrent mechanisms—a bimol. reaction of RI with HI, and a unimol. dissociation of RI. The consts. for both reactions have been determined with the three materials. The unimol. coeff. for MeI and EtI falls at low pressures in accordance with the collision theories.  
E. S. H.

**Spontaneous inflammability of fatty oils.**—See B., 1934, 333.

**Wave theory of periodic reactions.** I. F. M. SCHEMJAKIN, V. K. NIKIFOROV, and P. F. MICHALEV. II. P. F. MICHALEV and F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1933, 3, 798-801, 1001-1004).—I. The expression  $\lambda v = \text{const.}$ , where  $\lambda$  is the distance between Liesegang rings forming from  $\text{AgNO}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  in gelatin, and  $\text{Pb}(\text{NO}_3)_2$  and KI in agar, and  $v$  is the velocity of propagation, is experimentally verified.

II.  $\lambda v = \text{const.}$  is verified for  $\text{MnCl}_2$  and  $(\text{NH}_4)_2\text{S}$ , and  $\text{Na}_2\text{HPO}_4$  and  $\text{CaCl}_2$  in gelatin (I), and for  $\text{AgNO}_3$  and  $\text{Na}_2\text{HASO}_4$  in (I) and in agar (II). If a drop of aq. KI is placed on (I) or (II) containing  $\text{HgCl}_2$ , a yellow ring appears, travels down the test-tube, and finally disappears at the bottom. This phenomenon is due to the successive reactions:  $\text{HgCl}_2 + 2\text{KI} \rightarrow \text{HgI}_2 + 2\text{KCl}$ ;  $\text{HgI}_2 + 2\text{KI} \rightarrow \text{K}_2\text{HgI}_4$ .  
R. T.

**Kinetics of thermal cis-trans isomerisation.** III. G. B. KISTAKOWSKY and W. R. SMITH (J. Amer. Chem. Soc., 1934, 56, 638-642; cf. A., 1931, 1239).—Semi-quant. experiments with  $\text{Me}_2$  citrate at 280-360° and 500-30 mm. show that the reaction is similar to that previously described for  $\text{Me}_2$  maleate. The activation energy increases with rise of temp., reaching about 25,000 g.-cal. at the highest temp. studied. The isomerisation of *iso*-stilbene (I) is a unimol. reaction, having an activation energy of 43,000 g.-cal., which does not fall with pressure down to 4 mm.  $\leq 12$  oscillators must participate in the isomerisation process. In the gaseous system stilbene  $\rightarrow$  (I) the equilibrium consts. near 600 Å. are about 0.07, from which 3000 g.-cal. is the calc. approx. heat of reaction.  
E. S. H.

**Polymerisation processes.** I. Kinetic investigations of aqueous solutions of formaldehyde. M. WADANO, C. TROGUS, and K. HESS (Ber., 1934, 67, [B], 174-190).—The kinetics of the establishment of the equilibrium  $3(\text{CH}_2\text{O}, \text{H}_2\text{O}) \rightleftharpoons \text{C}_3\text{H}_5\text{O}_3, \text{H}_2\text{O} + 2\text{H}_2\text{O}$  (cf. Auerbach *et al.*, A., 1905, i, 859; 1908, i, 131) have been studied by the interferometer method controlled by cryoscopic determination of mol. wt. Reaction is balanced with reverse

change of a higher order. With  $> 3\%$   $\text{CH}_2\text{O}$  the change is unimol., the reverse action being negligible. The temp. coeff. of the velocity coeff. is 2.7 per  $10^\circ$ .  $\text{OH}^-$  is 10 times as powerful as  $\text{H}^+$  as catalyst. Substances (e.g.,  $\text{MeOH}$ ) which diminish the ionic product of  $\text{H}_2\text{O}$  diminish the velocity coeff. markedly, whereas neutral salts have no observable effect. The energy of activation of the depolymerisation of  $\text{CH}_2\text{O}$  is practically identical with that of ester hydrolysis and mutarotation, but differs from that of glucoside fission. As in the case of depolymerisation, the velocity coeffs. pass through a min. at  $p_{\text{H}}$  3—7 for mutarotation,  $p_{\text{H}}$  3.8—4.6 for ester hydrolysis, and  $p_{\text{H}}$  5.8—6.2 for amide hydrolysis. In all these cases within the region of moderate  $[\text{H}^+]$  and  $[\text{OH}^-]$  the reaction coeff. is directly proportional to the concn. of the ions; in contrast, fission of the glucosidic anion is accelerated only by  $\text{H}^+$ . It is therefore established that the O linkings in polymeric  $\text{CH}_2\text{O}$  are of the same character as in esters, amides, and semi-acetals and that the mechanism of polymerisation and depolymerisation of  $\text{CH}_2\text{O}$  in  $\text{H}_2\text{O}$  is similar to that of the rupture and formation of such linkings. The acidic and basic dissociation consts. of  $\text{CH}_2(\text{OH})_2$  are determined. In dil. solution the following equilibria are assumed,  $\text{CH}_2(\text{OH})_2 \rightleftharpoons \text{CH}_2^+\cdot\text{OH} + 3\text{OH}^-$  (I);  $\text{CH}_2(\text{OH})_2 \rightleftharpoons \text{CH}_2^+\cdot\text{O} + 3\text{H}^+ + 3\text{OH}^-$  (II);  $\text{CH}_2(\text{OH})_2 \rightleftharpoons \text{OH}\cdot\text{CH}_2\cdot\text{O} + 3\text{H}^+$  (III). (I), (II), and (III) are favoured at  $p_{\text{H}} < 2.6$ ,  $2.6-4.5$ , and  $> 4.5$ , respectively. In conc. solution the following equilibria also exist:  $(\text{OH}\cdot\text{CH}_2\cdot\text{O})_2\text{CH}_2$  (IV)  $\rightleftharpoons \text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2^+ + \text{OH}^-$ ; (IV)  $\rightleftharpoons \text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O} + \text{H}^+$ ; (IV)  $\rightleftharpoons \text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}^- + \text{OH}^- + \text{H}^+$ . It is estimated that the energy of formation of the C·O linking in polymerised  $\text{CH}_2\text{O}$  is 1/4 to 1/5 that of the normal C·O union.

H. W.

**Acid hydrolysis of ethyl malonate.** (MLLE.) M. G. TER HORST (Rec. trav. chim., 1934, 53, 312—324).—When Et malonate is hydrolysed in a mixture of EtOH and  $\text{H}_2\text{O}$ , the ratio of the coeffs. of the two consecutive reactions is 1.59, whilst in  $\text{H}_2\text{O}$  the ratio is 1.57. The agreement between these two vals. shows that the ratio is independent of the medium, and is due to the structure of the acid. The ratio for the esterification of malonic acid is 2.34. H. S. P.

**Rate of hydrolysis of bromoacetic acid in relation to its degree of ionisation.** H. M. DAWSON and N. B. DYSON (Proc. Leeds Phil. Soc., 1934, 2, 495—498).—The reduced rate of hydrolysis of  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$  (I) in presence of strong acid is due to the gradual elimination of the reaction between (I) and  $\text{CH}_2\text{Br}\cdot\text{CO}_2^-$  with increase of  $[\text{H}^+]$ . H. S. P.

**Mutarotation of  $\alpha$ -D-glucose in deuterium water.** E. PASCU (J. Amer. Chem. Soc., 1934, 56, 745—746).—The velocity in  $\text{H}_2\text{O}$  at  $20^\circ$  is identical with that observed in  $\text{H}_2\text{O}$  at  $10^\circ$ . For the equilibrium solution in  $\text{H}_2\text{O}$   $[\alpha]_{\text{D}}^{20}$  is  $+52.14^\circ$ , as compared with  $52.06^\circ$  in  $\text{H}_2\text{O}$ . E. S. H.

**Mutarotation of  $\beta$ -D-ribose and  $\beta$ -L-ribose.** F. P. PHELPS, H. S. ISBELL, and W. PIGMAN (J. Amer. Chem. Soc., 1934, 56, 747—748).—Measurements at  $20^\circ$  and  $1^\circ$  show that mutarotation takes place rapidly,

the direction of change being reversed after a few min., so that the initial and final rotations do not differ greatly. E. S. H.

**Decomposition of malic acid by sulphuric acid.** R. E. DERIGHT (J. Amer. Chem. Soc., 1934, 56, 618—620).—The rate of decomp. increases up to a certain point as  $\text{H}_2\text{O}$  is removed, and then decreases. The max. resembles that observed in the similar reactions of  $\text{HCO}_2\text{H}$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , and citric acid. The temp. coeff. at  $35-45^\circ$  for 100%  $\text{H}_2\text{SO}_4$  is 3.75.

E. S. H.

**Kinetics of the decomposition of trichloroacetates in various solvents.** F. H. VERHOEK (J. Amer. Chem. Soc., 1934, 56, 571—577).—The velocities of decomp. of  $\text{NH}_2\text{Ph}\cdot\text{CCl}_3\cdot\text{CO}_2\text{H}$  in  $\text{H}_2\text{O}$ , EtOH, and  $\text{NH}_2\text{Ph}$ , and of  $\text{CCl}_3\cdot\text{CO}_2\text{Na}$  and  $(\text{CCl}_3\cdot\text{CO}_2)_2\text{Ba}$  in  $\text{H}_2\text{O}$  and EtOH at  $70^\circ$  increase in the order given. The decomp. in  $\text{H}_2\text{O}$  and of the Na salt in EtOH are first-order reactions, but departures are observed in the remaining reactions, probably due to changes in the degree of dissociation. The reaction velocity depends on  $[\text{CCl}_3\cdot\text{CO}_2^-]$ . Temp. coeffs. in several solvents indicate that the stability of this ion is determined by the nature and extent of solvation. The formation of  $\text{Cl}^-$  in aq. and EtOH solutions of  $\text{CCl}_3\cdot\text{CO}_2^-$  is due to oxidation of  $\text{CHCl}_3$  produced by decomp. E. S. H.

**Application of the ebullioscope to precise determination of coefficients of esterification.** W. SWIENTOSLAWSKI (Rocz. Chem., 1934, 14, 98—104).—Using an ebullioscopic method, which permits the elimination of a no. of sources of error inherent in the analytical methods, slightly higher vals. are obtained for velocity of formation of EtOAc.

R. T.

**Reaction of organic halides with piperidine. IV. Bromo-esters.**—See this vol., 532.

**Determination of enzyme dissociation constants.**—See this vol., 558.

**Influence of the surface of the oxidiser ( $\text{I}_2\text{O}_5$ ) on the velocity of oxidation of carbon monoxide.** ASTAPENJA, VAPNIK, and ZELKIN (J. Gen. Chem. Russ., 1933, 3, 839—842).—The optimum temp. of oxidation of CO by  $\text{I}_2\text{O}_5$  varies with the degree of subdivision of the latter. R. T.

**Measurement of reaction rates at high temperatures.** J. H. CHESTERS and C. W. PARMELEE (J. Amer. Ceram. Soc., 1934, 17, 50—59).—The reactions quartz  $\rightarrow$  cristobalite and  $\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow$  spinel were studied by measuring continuously the firing expansion ( $1300-1500^\circ$ ) of test-pieces moulded at 10,000 lb. per sq. in. The products were identified by X-ray and microscopical examination, and the amounts present also calc. from the changes in  $d$ . Medina quartzite was completely converted into cristobalite after 2 hr. at  $1500^\circ$ ; addition of 2% of CaO increased the rate, and a further addition of 1.5% of  $\text{Na}_2\text{O} + 1.5\%$  of  $\text{Fe}_2\text{O}_3$  completed the change after 2 hr. at  $1400^\circ$ . A mixture of electrically fused MgO (grain size 0.15—0.06 mm.) and  $\text{Al}_2\text{O}_3$  (3.59—0.15 mm.) contained 25% of  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  after 2 hr. at  $1500^\circ$ ; addition of 2% of  $\text{B}_2\text{O}_3$  increased the amount to 75%. A mixture containing only fine particles

(0.06 mm.) was completely converted after 10 min. at 1450°. Test-pieces moulded under high pressure increased in porosity during firing. J. A. S.

**Rate of displacement of copper from solutions of its sulphate by cadmium and zinc.** C. V. KING and M. M. BURGER (Trans. Electrochem. Soc., 1934, 65, 115—122).—Rates of dissolution of cylindrical specimens of pure Zn and Cd in dil.  $\text{CuSO}_4$  solutions increase continuously with speed of rotation and show no sign of approaching a max. (cf. Centnerszwer, A., 1932, 1003). Observed differences in rates of dissolution of Zn and Cd in a given  $\text{CuSO}_4$  solution and of Cd in  $\text{CuSO}_4$  solutions of various concns. are attributed to differences in adhesion and physical character of the replaced Cu. H. J. T. E.

**Theory of corrosion. II. Rusting of iron on the film theory of passivity.**—See B., 1934, 324.

**Corrosion of zinc in chloride solutions.**—See B., 1934, 325.

**Mechanism of detonation in lead azide crystals.** T. C. SUTTON (Nature, 1934, 133, 463).—The unit cell of  $\text{PbN}_6$ , space-group  $Q_6^3$ , contains 24 mols., arranged in eight groups each containing  $3\text{PbN}_6$ . The criterion for detonation is closely related to cryst. structure, and thermal decomp. appears to be due to the activation of 1 mol. of  $\text{PbN}_6$ , whilst detonation requires the simultaneous activation of all three constituents of one of the complex groups ( $\text{PbN}_6$ )<sub>3</sub>. L. S. T.

**Detonation of explosives.**—See B., 1934, 350.

**Preservation of hydrogen peroxide.**—See B., 1934, 318.

**Induced oxidation of cyanide.** B. K. HARNED and C. J. DEERE (J. Biol. Chem., 1934, 104, 727—736).—Oxidation of  $\text{NaCN}$ , yielding  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{NH}_3$ , is induced by oxygenation of alkaline glucose solutions, utilising about 0.5 of the extra  $\text{O}_2$  absorbed. H. G. R.

**Catalysis of ethyl diazoacetate in very dilute solutions of organic acids.** M. DUBOUX and P. MATAVULJ (Helv. Chim. Acta, 1934, 17, 245—257).—In very dil. org. acid solutions the velocity coeff. of hydrolysis of  $\text{N}_2\text{CH}\cdot\text{CO}_2\text{Et}$  is not strictly proportional to  $[\text{H}^+]$  as determined by conductometric methods. The accepted val. 38.5 for  $k_{\text{H}}$  in the equation  $k=k_{\text{H}}[\text{H}^+]$  becomes 36.7 in 0.001*M*-acid and 35.5 in 0.0005*M*-acid. This diminution of  $k_{\text{H}}$  with concn. of acid is comparable with the behaviour observed in the inversion of sucrose in presence of org. acids. M. S. B.

**Oxidation of sucrose to oxalic acid by the method of Naumann, Moeser, and Lindenbaum.** W. DOMINIK and J. JANCZAK (Rocz. Chem., 1934, 14, 141—151).—70% yields of  $\text{H}_2\text{C}_2\text{O}_4$  (I) are obtained from sucrose and  $\text{HNO}_3$  ( $d$  1.4) at 70°, using 0.006 g.  $\text{NH}_4\text{VO}_3$  (II) per 100 c.c. as catalyst. The velocity of reaction can be increased by taking higher concns. of (II), which, however, also catalyses oxidation of (I). Satisfactory yields of (I) are also obtained at higher temp., using less conc.  $\text{HNO}_3$ . The yields of (I) are not increased by conducting the reaction in an atm. of  $\text{CO}_2$ . The intermediate products of oxidation are also convertible into (I), so that the

mother-liquors from crystallisation of (I) can be further utilised. Reduction of  $\text{HNO}_3$  does not proceed further than to NO. The vol. of the reaction mixture can be reduced by adding only a fraction of the necessary quantity of  $\text{HNO}_3$ , and introducing  $\text{NO}_2$  during the reaction. R. T.

**Oxidation of carbon monoxide with a silver catalyst.** A. F. BENTON and R. T. BELL (J. Amer. Chem. Soc., 1934, 56, 501—505).—Experiments with reduced Ag at 80—140° show that the rate of reaction is proportional to the pressure of CO, independent of the  $\text{CO}_2$  pressure, and independent of  $\text{O}_2$  pressure when CO is in excess. The average energy of activation is 13.3 kg.-cal. The facts are consistent with measurements showing a very small adsorption of CO, no adsorption of  $\text{CO}_2$ , and a slow, irreversible, activated adsorption of  $\text{O}_2$ . The observed rates are  $\times 1/30$  of those calc., assuming that reaction occurs at every collision of CO with adsorbed  $\text{O}_2$ , in which the joint energy exceeds the energy of activation. E. S. H.

**Oxidation of phosphine in presence of tungsten and molybdenum.** H. W. MELVILLE and H. L. ROXBURGH (J.C.S., 1934, 264—272; cf. A., 1933, 790).—The oxidation of  $\text{PH}_3$  in presence of Mo and W filaments at pressures below the explosion limit appears to take place almost wholly on the surface. A faint glow indicates the presence of a trace of homogeneous reaction, but this is not measurable. Experiments with  $\text{SiO}_2$  and Pyrex filaments were also unsuccessful, and the presence of P did not induce the reaction to leave the surface. The causes of the difference in the reaction of  $\text{O}_2$  with P and with  $\text{PH}_3$  are discussed. The catalytic decomp. of  $\text{PH}_3$  and  $\text{NH}_3$  is inhibited by the simultaneous bombardment of the filament with at. H. M. S. B.

**Regeneration of vanadium catalysts.**—See B., 1934, 273.

**Effect of catalysts on the reaction between olefines and hydrogen sulphide.**—See B., 1934, 265.

**Mechanical activation at the surface of an electrode.** K. M. GORBUNOVA and A. T. VAHRAMJAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 127—129).—A study of the deposition of metal on a Ag cathode in  $\text{AgNO}_3$  solution, with a highly polished and with a scratched surface. In the latter case deposition tends to take place around the scratch, owing to an increased no. of active centres.

W. R. A.

**Relation between oxygen overvoltage and catalysis.** A. D. GARRISON and J. F. LILLY (Trans. Electrochem. Soc., 1934, 65, 171—184).—At a polished metal surface in 0.1*N*- $\text{NaOH}$  a steady representative val. of the O overvoltage ( $\eta$ ) at given c.d. (I) can be obtained by approach from either higher or lower c.d., and for given metal  $\eta=\eta_0+kI$ , where  $k$  has the same val. for all metals examined. For different metals the overvoltage at zero c.d.  $\eta_0$  increases in the order: Ni, Co, Fe, Ir, Pt, Au. When the same metal surfaces are cathodically polarised while air is bubbled around them, the single potential is also a linear function of  $I$ , and the slope

of this line ( $k_0$ ) is taken as a measure of the catalytic effect of the given metal on the ionisation of  $O_2$ . For the various metals  $k_0$  increases in the reverse order to that for  $\eta_0$ , and  $\log k_0$  is a linear function of  $\eta_0$ . The behaviour of Au at low cathodic c.d. is anomalous.

H. J. T. E.

**Electrodeposition of metallic niobium, and its separation from tantalum.** N. A. IZGARISCHEV and A. F. PREDE (J. Gen. Chem. Russ., 1933, 3, 831—838).—Mixtures of  $Ta_2O_5$  and  $Nb_2O_5$  are fused with  $K_2S_2O_7$ , and the melt is dissolved in 40% KOH, or in saturated aq.  $H_2C_2O_4$  or citric acid. On electrolysis of these solutions, Nb is deposited quantitatively on the cathode, in the form of a bright, smooth, adherent coating. The industrial possibilities of Nb plating are discussed.

R. T.

**Electrodeposition of cuprous oxide film.**—See B., 1934, 330.

**Chlorine in the lead storage battery.**—See B., 1934, 330.

**Electrodeposition of aluminium from non-aqueous solutions.**—See B., 1934, 326.

**Electrolysis of ether solutions of the Grignard compound.**—See this vol., 517.

**Electro-organic oxidations in concentrated aqueous organic salt solutions. Stability of the sulphonate solvents and the oxidation of benzaldehyde and benzyl alcohol.** R. H. MCKEE and J. R. HEARD, jun. (Trans. Electrochem. Soc., 1934, 65, 135—139).—Conc. aq. solutions of Na salts of aromatic sulphonates are not appreciably oxidised at Pt or Ni anodes except when strongly acidified, and act as solvents for many substances insol. in  $H_2O$ , which can thus be subjected to anodic oxidation more effectively than if in suspension. PhCHO is very sol. in these solvents, especially in the presence of BzOH, and in alkaline solutions is readily oxidised anodically to BzOH without tar formation, especially in the presence of CuO as catalyst. In such solutions there is some direct production of BzOH by the Cannizzaro reaction, and the  $CH_2Ph\cdot OH$  simultaneously produced is probably the effective anodic depolariser.  $CH_2Ph\cdot OH$  is very sol. in these solvents and is readily anodically oxidised to PhCHO and BzOH, especially in the presence of hydroxides of Ni or Co as catalysts. With free NaOH in the solution BzOH is the main product; with  $Na_2CO_3$ , PhCHO. The efficiency of these oxidations under various conditions has been investigated.

H. J. T. E.

**Electro-organic oxidations in concentrated aqueous organic salt solutions. Reactions with toluene, oleic acid, benzoin, and other substances.** R. H. MCKEE and J. R. HEARD, jun. (Trans. Electrochem. Soc., 1934, 65, 161—170; cf. preceding abstract).—In alkaline solutions of Na salts of aromatic sulphonates benzoin is oxidised efficiently to BzOH at a Ni anode. The efficiency of anodic oxidation of oleic acid is lower in slightly acid than in alkaline solutions, but the reverse is true with more unsaturated linseed fatty acids. Anodic oxidation of quinol and anodic halogenation of PhMe in these solvents were also investigated.

H. J. T. E.

**Chemical reactivity and light absorption. I.** N. R. DHAR and A. K. BHATTACHARYYA (J. Indian Chem. Soc., 1934, 11, 33—43).—It is suggested that the presence of a second reactant sensitises mols. to radiation of longer wave-length. Examples are quoted.

R. S.

**Correlation of the photosyntheses of phosgene and hydrogen chloride.** G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 579—583).—Kinetic investigations show that the active form of Cl involved in the chain processes of the two reactions is the same and is probably  $Cl_3$ . The calc. heat of dissociation of the reaction  $Cl_3 \rightarrow Cl_2 + Cl$  is  $5.0 \pm 1.0$  kg.-cal.

E. S. H.

**Photolysis of nitrogen oxides:  $N_2O_5$ ,  $N_2O_4$ , and  $NO_2$ .** H. H. HOLMES and F. DANIELS (J. Amer. Chem. Soc., 1934, 56, 630—637).—Absorption coeffs. have been determined from 436 to 265  $m\mu$ .  $N_2O_5$  is decomposed by light of 280 and 265  $m\mu$  with a quantum efficiency 0.6.  $N_2O_4$  is decomposed at 265  $m\mu$  with a quantum efficiency 0.4;  $\lambda\lambda$  366 and 313  $m\mu$  are absorbed, but give no measurable decomp.  $NO_2$  is decomposed by 313, 366, 405, and 436  $m\mu$ . He, A,  $N_2$ ,  $O_2$ ,  $H_2$ ,  $CO_2$ , and  $N_2O$  decrease the photo-decomp., but are more effective in reducing the fluorescence of  $NO_2$ . Photo-decomp. in  $CCl_4$  solution is slight.

E. S. H.

**Effect, on the latent image, of post-heating and of melting the gelatin.** A. J. REARDON and H. P. GRIGGS (J. Opt. Soc. Amer., 1934, 24, 85—90).—Exposed plates, half of which were bathed in  $H_2O$  at  $45^\circ$  for 5 sec. and dried, were heated for const. time in an oven saturated with  $H_2O$  vapour, or for varying times at  $70^\circ$ . The results on development show that, for the bathed plates, a continuous decrease of the latent image is caused by increased heating, but with the unbathed plates an increase occurs up to about 30 min. heating at  $70^\circ$ , after which a rapid decrease sets in. The bathing treatment causes more immediate fluidity of the gelatin. The rate of decrease is the greater the greater is the initial exposure to light. The crystal-cracking hypothesis of the latent image is supported on the ground that heating causes increased cracking until the fluidity of the gelatin is sufficient to start filling the cracks, forming a less developable gelatin—Ag—AgBr surface.

J. L.

**Formation of histamine by irradiation of histidine.**—See this vol., 534.

**Photochemical addition of chlorine to cinnamic acid.** A. BERTHOUD and D. PORRET (Helv. Chim. Acta, 1934, 17, 237—245).—The above reaction follows the same laws as the photobromination of cinnamic acid (A., 1927, 528; 1930, 718). The velocity is practically independent of the concn. of acid, proportional to  $[Cl_2]$  for total absorption of light and to  $[Cl_2]^{1.5}$  for feeble absorption. It is also proportional to  $I^{1/2}$ . The quantum yield differs with experimental conditions. It was 2.4 in one case. The thermal coeff. ( $25$ — $35^\circ$ ) is 1.5. The life of a reaction chain is  $< 0.02$  sec.

M. S. B.

**Photochemical reduction of methyl-red by phenylhydrazine using chlorophyll solution as photosensitiser.** J. C. GHOSH and S. B. SEN-

GUPTA (J. Indian Chem. Soc., 1934, 11, 65—77).—The reaction velocity, after an induction period, is of zero order with respect to Me-red (I) and  $\text{NHPh}\cdot\text{NH}_2$  (II) in  $\text{MeOH}$  or  $\text{C}_6\text{H}_6$  solution when  $\lambda=5460 \text{ \AA}$ .;  $\gamma$  is approx. 1. When  $\lambda=4358 \text{ \AA}$ ., the same holds in  $\text{MeOH}$ , but in  $\text{C}_6\text{H}_6$  the velocity is unimol. with respect to (I) and (II), and  $\gamma=0.05$ . Using  $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$  in  $\text{MeOH}$ ,  $\gamma=0.013$ , and the rate is unimol. with respect to (I). In this case there is a measurable dark reaction. A mechanism based on the formation of an activated complex of chlorophyll and (I) is advanced. R. S.

**Kinetics of photosynthesis and allied processes.** E. C. C. BALY and L. B. MORGAN (Nature, 1934, 133, 414).—Theoretical. L. S. T.

**Influence of the intensity of irradiation on the ionic yield in reactions produced by alpha particles.** W. MUND (Bull. Soc. chim. Belg., 1934, 43, 100—110).—Theoretical. The general case is considered, followed by the case of a gas exposed to  $\alpha$ -rays from a capsule of Rn within the gas, and that of a mixture of a gas with Rn. D. R. D.

**Mechanism of reactions provoked by  $\alpha$ -rays in gases.** W. MUND (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 30—35).—Theoretical. J. W. S.

**Effect of lead content on the colouring of sodium and potassium chlorides when irradiated with radium radiations.** O. HAHN and H. J. BORN (Naturwiss., 1934, 22, 137—138).—Two processes occur when  $\text{NaCl}$  and  $\text{KCl}$  crystals containing Pb are irradiated with Ra radiations. Pb-free  $\text{NaCl}$  is coloured amber-yellow, but with increasing quantities of Pb an unstable yellow colour is first produced, which later changes to a stable blue colour. The stability of the primary yellow colour decreases with increasing Pb content. Pb-free  $\text{KCl}$  is coloured reddish-violet by Ra irradiation, but with increasing Pb content the colour becomes increasingly unstable, and a stable rose colour is produced. The effect of the addition of Pb to these crystals on the colour on irradiation is the same as that of pressure or temp. A. J. M.

**Influence of the intensity of irradiation, pressure, mercury vapour, and nature of the walls on the radiochemical decomposition of ammonia.** A. LUYCKX (Bull. Soc. chim. Belg., 1934, 43, 117—159).—Experimental determinations of the ionic yield,  $M/I$ , using both central irradiation and admixture with Rn, are recorded.  $M/I$  decreases with increase of pressure, except for very low intensities, when the reverse is true. In  $\text{Na}_2\text{O}$ -glass vessels  $M/I$  increases with the size of the vessel.  $M/I$  is not affected by the presence of Hg vapour, but at low pressures it is decreased by the presence of a Hg mirror on the walls of the vessel. Etching of the walls with HF has no measurable effect on  $M/I$ . D. R. D.

**Negative catalysis of the radiochemical decomposition of ammonia by platinised walls.** A. LUYCKX (Bull. Soc. chim. Belg., 1934, 43, 160—177).—The ionic yield is reduced by sputtering the walls of the glass vessel with Pt. The amount of adsorption by the Pt is negligible. The sphere of

activity of the Pt does not extend any appreciable distance into the gas, and it is probable that it must be actually struck by an  $\alpha$ -particle in order to exhibit its activity. Pt has no effect on the radiochemical synthesis of  $\text{NH}_3$  from its elements, but the negative catalytic effect of the Pt on the decomp. is destroyed by this process. D. R. D.

**Fractionation of hydrogen by diffusion through palladium.** V. LOMBARD and C. EICHNER (Compt. rend., 1934, 198, 932—934; cf. A., 1932, 906).— $\text{H}_2$  which has diffused once through Pd diffuses again approx. 19% more quickly than that portion of the original stream of  $\text{H}_2$  which did not diffuse. Accumulation of impurities was very improbable (cf. this vol., 156). C. A. S.

**Exchange reactions of hydrogen atoms.** N. F. HALL, E. BOWDEN, and T. O. JONES (J. Amer. Chem. Soc., 1934, 56, 750).—When 2%  $\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  dissolves substances and is subsequently distilled off, (1) no interchange of  $\text{H}^1$  with  $\text{H}^2$  occurs with  $\text{KCl}$ ,  $\text{KH}_2\text{PO}_2$ ,  $\text{KOAc}$ ,  $\text{KOBz}$ , or  $\text{H}_2$  during brief contact, (2) one third of  $\text{H}^1$  is immediately exchanged in  $(\text{CH}_2\cdot\text{OH})_2$ , (3) exchange increases with time of contact with  $\text{KOAc}$  and  $\text{H}_2$ . E. S. H.

**Preparation of distilled water.** R. KUMMER (Pharm. Ztg., 1934, 79, 355—358).

**Isotopic fractionation of water by distillation.** N. F. HALL and T. O. JONES (J. Amer. Chem. Soc., 1934, 56, 749—750).—Determinations of  $d$  and  $n$  show that considerable separation occurs in the distillation of  $\text{H}_2^{16}\text{O}$ - $\text{H}_2^{18}\text{O}$  mixtures. E. S. H.

**Preparation of beryllium.**—See B., 1934, 325.

**Boron hydrides. XVIII. Preparation of  $\text{B}_2\text{H}_6$  from boron trichloride and hydrogen.** A. STOCK, H. MARTINI, and W. SÜTTERLIN. XIX. Preparation of  $\text{B}_2\text{H}_6$  from boron tribromide and hydrogen. A. STOCK and W. SÜTTERLIN (Ber., 1934, 67, [B], 396—407, 407—411; cf. A., 1933, 34).—XVIII. The prep. of  $\text{B}_2\text{H}_6$  from  $\text{BCl}_3$  and  $\text{H}_2$  by action of an electric discharge according to Schlesinger *et al.* (A., 1932, 350) has been examined in detail. Only  $\text{B}_2\text{H}_5\text{Cl}$  appears to be formed in the region of the discharge;  $\text{B}_2\text{H}_6$  in the gaseous product arises secondarily by decomp. of  $\text{B}_2\text{H}_5\text{Cl}$  into  $\text{B}_2\text{H}_6$  and  $\text{BCl}_3$ . Complete removal of  $\text{HCl}$  formed during the reaction from  $\text{B}_2\text{H}_6$  is effected with sufficient rapidity by K.  $\text{B}_2\text{Cl}_4$  is found among the products of the reaction only, and then in very small amount, when a mixture of much  $\text{BCl}_3$  and little  $\text{H}_2$  is subjected to the electric discharge. Reaction between  $\text{B}_2\text{H}_6$  and  $\text{HCl}$  leads through  $\text{B}_2\text{H}_5\text{Cl}$  to an equilibrium between this and its decomp. products,  $\text{B}_2\text{H}_6$  and  $\text{BCl}_3$ . Small amounts of  $\text{HCl}$  and  $\text{B}_2\text{H}_6$  disappear thereby practically completely. Reaction occurs with a  $\text{B}_2\text{H}_6$ - $\text{HCl}$  mixture obtained from the prep. of  $\text{B}_2\text{H}_6$  much more rapidly than with one prepared from pure  $\text{B}_2\text{H}_6$  and  $\text{HCl}$ ; the former contains therefore a catalytic accelerator of unknown type in small amount. Hg does not affect the rate of reaction. The equilibrium  $6\text{B}_2\text{H}_5\text{Cl} \rightleftharpoons 5\text{B}_2\text{H}_6 + 2\text{BCl}_3$  has been examined quantitatively.  $\text{BBr}_3$  is better adapted than  $\text{BCl}_3$  to the prep. of  $\text{B}_2\text{H}_6$ .

XIX. Details are given of the prep. of  $\text{B}_2\text{H}_6$  from

$BBr_3$  and  $H_2$ . Advantages claimed are that the saturation of  $H_2$  with  $BBr_3$  does not require a cooling bath, that reaction in the zone of discharge occurs more smoothly and with production of less B and solid B hydrides than when  $BCl_3$  is used, and, mainly, that  $B_2H_6$  and HBr can be separated completely from one another by fractional distillation.  $BBr_3$  does not react as completely as  $BCl_3$  in the zone of discharge. H. W.

**Isolation of chlorodiborane: additions to the high-vacuum technique for chemical work with volatile substances.** A. B. BURG (J. Amer. Chem. Soc., 1934, 56, 499—501).— $B_2H_6Cl$ , prepared by reaction of  $B_2H_6$  with  $BCl_3$  followed by distilling through a U-tube at  $-150^\circ$ , has m.p.  $-142^\circ$  and v.p. 18 mm. at  $-78.5^\circ$ . Apparatus and technique for fractional condensation are described. E. S. H.

**Periodic efflorescence of alum.** F. M. SCHEM-JAKIN (J. Gen. Chem. Russ., 1933, 3, 1005—1006).—A crystal of K Cr alum exhibited numerous points around which concentric zones (15—20) of efflorescence were evident. R. T.

**Compounds of aluminium bromide with toluene, nitrobenzene, and metal bromides.** V. A. PLOTNIKOV, Z. A. JANKELEVITSCH, and I. A. SCHEKA (J. Gen. Chem. Russ., 1933, 3, 802—807).—The compound  $CuBr, AlBr_3$  (I), m.p.  $239^\circ$ , is prepared by concentrating a  $C_6H_6$  solution of  $CuBr$  and  $AlBr_3$ ; the crystals separating from an analogous PhMe solution are  $CuBr, AlBr_3, PhMe$  (II), decomposing at  $140^\circ$  to yield PhMe and  $C_6H_4MeCl$ , and dissociating into its constituents in  $H_2O$ , with partial oxidation of PhMe to PhCHO. The compound  $LiBr, 2AlBr_3, 2PhNO_2$ , m.p.  $63^\circ$ , obtained analogously from  $PhNO_2$  solutions, decomposes at  $265^\circ$ , with copious evolution of gaseous products; on electrolysis its solutions in  $C_6H_6$  or PhMe Li is deposited at the cathode. Compressed (II), but not (I), conducts electricity. R. T.

**Formation of aluminium nitride from aluminium and amines.** V. A. PLOTNIKOV and N. T. KALITA (J. Gen. Chem. Russ., 1933, 3, 872—873).—The reaction  $2AlCl_3, NH_3$  (I)  $\rightarrow 2AlCl_3, AlN + 3H_2$  takes place on adding Al to fused (I). R. T.

**Preparation and properties of gallium and gallium trichloride.** W. M. CRAIG and G. W. DRAKE (J. Amer. Chem. Soc., 1934, 56, 584—585).—The separation of traces of Ga from Pb dross is described. Ga has m.p.  $29.755^\circ$ ,  $d^{25} 5.903$ , at. vol. 11.81. Pure Ga has little tendency to supercool.  $GaCl_3$  has m.p.  $76.65^\circ$ , b.p.  $199.6^\circ$ . E. S. H.

**Combustion of graphite.** I. V. SIHVONEN (Suomen Kem., 1934, 7, B, 80—82).—A further discussion of previous work (cf. A., 1933, 1254). J. L. D.

**Solubility of silicon in hydrofluoric acid.** H. FUNK (Ber., 1934, 67, [B], 464; cf. Marchot and Funk, A., 1930, 1007).—The solubility of Si in HF is best judged by the evolution of  $H_2$ . Bedel's method (this vol., 135) of measuring loss in wt. involves  $SiO_2$  and other sol. impurities. H. W.

**Preparation of rutile.** H. RHEINBOLDT and W. WISFELD (Ber., 1934, 67, [B], 375—376).—Rutile is obtained when  $TiCl_4$  vapour and  $O_2$  are passed through a porcelain tube at about  $700^\circ$ ; oxychlorides do not appear to be formed at any stage of the reaction. H. W.

**Preparation of hydrazine sulphate by Raschig's process.** J. HENRION (Bull. Soc. chim. Belg., 1934, 43, 115—116).—The published methods for the prep. of  $N_2H_4, H_2SO_4$  from  $NH_3$ ,  $NaOCl$ , and  $H_2SO_4$  are reviewed and the following improved method is recommended.  $Cl_2$  is passed into 100 c.c. of 5% aq.  $NaOH$ , cooled in a freezing mixture, until 4 g. have been absorbed. The solution is exposed to the air for 12 hr. for all free  $Cl_2$  to evaporate (essential for a good yield). The solution is then added to a mixture of 200 c.c. of saturated aq.  $NH_3$  with 15—20 c.c. of aq. gelatin. The mixture is boiled down to half its vol. and then well cooled. 10 c.c. of conc.  $H_2SO_4$  dissolved in 50 c.c. of  $H_2O$  are added, followed by sufficient EtOH to form a slight cloudiness. On keeping, cryst.  $N_2H_4, H_2SO_4$  is obtained in  $> 70\%$  yield. D. R. D.

**Action of sodium nitrite on sodium polysulphide.** I. CHEMELNITSKAJA and V. VERCHOVSKAJA (Anilinokras. Prom., 1934, 4, 27—31).— $NaNO_2$  and  $Na_2S_x$  react as follows:  $4Na_2S_{3.5} + 6NaNO_2 + 9H_2O \rightarrow 7Na_2S_2O_3(I) + 6NH_3$ ; if  $x$  is  $> 3.5$ , the remaining S is pptd. as such, and, should  $NaOH$  be present, is also converted into (I), as follows:  $4NaOH + 3S_2 + 2NaNO_2 + H_2O \rightarrow 3Na_2S_2O_3 + 2NH_3$ . R. T.

**Dehydration and decomposition of the dithionates.** J. SCHREIBER (Ann. Chim., 1934, [xi], 1, 88—127, 129—180).—The dehydration of the dithionates of the alkali, alkaline-earth, and certain heavy metals, prepared by crystallisation at room temp., has been studied at various const. temp. and at temp. rising linearly with time. Equilibrium is attained only slowly.  $Na_2S_2O_6, 6H_2O$  yields the dihydrate at  $9.1^\circ$ ,  $Na_2S_2O_6$  at about  $70^\circ$ , and  $Na_2SO_4$  at  $245^\circ$ .  $Li_2S_2O_6, 4H_2O$  behaves similarly ( $27^\circ$ ,  $87^\circ$ , and  $195^\circ$ ).  $(NH_4)_2S_2O_6, 2/3H_2O$  (lit. 0.5 and 1.5  $H_2O$ ) yields hemihydrate ( $25^\circ$ ) and anhyd. salt ( $55^\circ$ ); no other hydrate exists. Other new hydrates described include those of Ca, Sr, Ba ( $1H_2O$ ), Mg, Mn, Ni, Zn, Cd (4 and  $2H_2O$ ), Cu, Fe, and Co ( $2H_2O$ ). The anhyd. Sr and Mg salts have been prepared. Monohydrated sulphates are obtained in many cases by thermal decomp. of heavy metal dithionates.  $PbS_2O_6, 4H_2O$  is exceptional in that it yields  $PbSO_4$  at  $45^\circ$ . No tri- or penta-hydrates could be obtained, but all the bivalent metals studied yielded tetra-hydrated dithionates. H. F. G.

**Preparation of sulphur chlorides and of arsenic trichloride.** T. D. IONESCU and A. G. SOARE (Bul. Chim. Soc. Romana Ştiinţe, 1932, 35, 25—31).—96% yields of  $SCl_2$  are obtained by passing  $Cl_2$  over dry pyrites at  $130—140^\circ$ , whilst gas-works spent oxide gives 96% yields of a product containing 35%  $S_2Cl_2$  and 64%  $SCl_2$ . Theoretical yields of  $AsCl_3$  and  $SCl_2$  are obtained analogously from realgar or orpiment. R. T.



**Ammoniates of chromium compounds.** F. EPHRAIM and C. ZAPATA (Helv. Chim. Acta, 1934, 17, 287—295).—CrCl<sub>3</sub> and CrBr<sub>3</sub> form *ammines* with similar decomp. curves. On charging both CrCl<sub>3</sub> and CrBr<sub>3</sub> with NH<sub>3</sub> the colour becomes first ash-grey, then violet, and finally bright green. In both cases at low temp. solid solutions of ammines with > 5NH<sub>3</sub> are formed. At 97° CrCl<sub>3</sub>·5NH<sub>3</sub> is reached, and breaks up to form CrCl<sub>2</sub>·3NH<sub>3</sub> at 98°. There is a gradual decomp. to CrCl<sub>2</sub>·2NH<sub>3</sub> which is complete at 250°. At 333° there is a sharp fall to CrCl<sub>2</sub>·NH<sub>3</sub>. Practically all NH<sub>3</sub> has been removed at 410°. CrBr<sub>3</sub>·5NH<sub>3</sub> decomposes to CrBr<sub>2</sub>·3NH<sub>3</sub> at 135—143°. Up to 153° CrBr<sub>2</sub>·2·5NH<sub>3</sub> appears to be gradually formed and to remain stable up to 300°. There is then further slow decomp., but 1·5NH<sub>3</sub> still remains at 400°. M. S. B.

**Ammoniates of chromates and perchlorates.** F. EPHRAIM and C. ZAPATA [with E. AMMANN] (Helv. Chim. Acta, 1934, 17, 296—308).—The following *ammines* have been prepared and the temp. of decomp. determined: Ag<sub>2</sub>CrO<sub>4</sub>·4NH<sub>3</sub> (known), decomp. 137° with reduction; CuCrO<sub>4</sub>·5NH<sub>3</sub> 44—45°, 4NH<sub>3</sub> (known) 162—164°, possibly 2NH<sub>3</sub> and 0·5NH<sub>3</sub>; ZnCrO<sub>4</sub>·5NH<sub>3</sub> 55°, 4NH<sub>3</sub> forming solid solution with ZnCrO<sub>4</sub>·3NH<sub>3</sub> from 59° to 77°, the latter then becomes stable to 150°; CdCrO<sub>4</sub>·>6NH<sub>3</sub> 23°, 6NH<sub>3</sub> 40°, 5NH<sub>3</sub> 79°, 3NH<sub>3</sub> 122—124°, 2NH<sub>3</sub> 160°, reduction, but also formation of CdCrO<sub>4</sub>·NH<sub>3</sub> at 200°; Ca(ClO<sub>4</sub>)<sub>2</sub>·6NH<sub>3</sub> 148—150°, 3NH<sub>3</sub>, which gradually loses NH<sub>3</sub> until more extensive decomp. sets in at 307°; Sr(ClO<sub>4</sub>)<sub>2</sub>·>7NH<sub>3</sub> 53°, 6NH<sub>3</sub> 102°, 4NH<sub>3</sub> 110—123°, 3NH<sub>3</sub> which gradually loses NH<sub>3</sub> as temp. rises; Ba(ClO<sub>4</sub>)<sub>2</sub>·>6NH<sub>3</sub> 63°, 6NH<sub>3</sub> 74°, 3NH<sub>3</sub> 74—122°, 2NH<sub>3</sub> 129°; Cd(ClO<sub>4</sub>)<sub>2</sub>·6NH<sub>3</sub> (known) 154·5°, 4NH<sub>3</sub> 298—301° reduction then beginning; Zn(ClO<sub>4</sub>)<sub>2</sub>·6NH<sub>3</sub> 40°, 4NH<sub>3</sub> still stable at 300°; Ni(ClO<sub>4</sub>)<sub>2</sub>·6NH<sub>3</sub> (known) stable to 264° and then explodes. M. S. B.

**Peroxides and per-acids of halogens.** L. V. PISARSHVSKI (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1121—1124).—Theoretical. R. T.

**"Red hydrogen chloride."** E. TIEDE [with H. REINICKE] (Ber., 1934, 67, [B], 492—494).—The red colour of HCl obtained from NaCl and H<sub>2</sub>SO<sub>4</sub> and frozen in vac. is due to the substance, NO·HCl, formed from minute traces of NO in H<sub>2</sub>SO<sub>4</sub>. The reaction is much more sensitive than the NHPh<sub>2</sub> test. NO is completely removed from H<sub>2</sub>SO<sub>4</sub> by partial treatment with NaCl. H. W.

**Attacking powers of binary systems of organic liquids on metals.** L. SLADOVIĆ (Monatsh., 1934, 64, 35—40).—Losses of wt. of metals in a large no. of org. liquids and their binary mixtures have been determined at 45° and 55°. No significant corrosion was observed with Fe or Al, but with Cu and the systems NH<sub>2</sub>Ph—PhOH, NH<sub>2</sub>Ph—PhNO<sub>2</sub>, and C<sub>5</sub>H<sub>5</sub>N—PhOH the corrosive effect of the mixtures is considerably > that of either component. In the system NH<sub>2</sub>Ph—C<sub>6</sub>H<sub>6</sub>, which does not form a mol. compound, the rate of corrosion is < that of the more corrosive component. E. S. H.

**Precipitation of cobalt from zinc sulphate solutions by means of zinc dust and metallic compounds.** G. HÄNSEL (Wiss. Veröff. Siemens-Konz., 1934, 13, 55—60).—The use of various metals (Cu, Bi, Cd, Ag, Hg, Pb, and Sn) as pptg. agents for Co from ZnSO<sub>4</sub> solutions used in the electrolytic prep. of Zn was investigated. The best metal was Sn, which gave the same degree of pptn. as As or Sb. The method recommended is to add Zn dust and a solution of a Sn salt. A. J. M.

**Precipitation of cobalt from zinc sulphate solutions used in the electrolytic preparation of zinc.** A. GREVEL (Wiss. Veröff. Siemens-Konz., 1934, 13, 61—71).—The course of the reaction occurring when Co is pptd. from ZnSO<sub>4</sub> solutions by the addition of Zn dust and an Sb salt was investigated. The potential developed at a Zn surface in a dil. solution of ZnSO<sub>4</sub>, alone, and after addition of various metallic salts, was measured. A cementation process takes place between the Zn and the Sb. Examination of Zn—Sb preparations by the X-ray method indicated that alloy formation also occurred. Other methods of causing the pptn. of Co were investigated; Zn—Cu couple in the presence of CuCN acts similarly to Zn—Sb. For the colorimetric detection of Co, 1 c.c. of the Co solution, 2 c.c. of eriochrome blue-black (0·02 g. per 100 c.c.), and 0·5 c.c. of NaNO<sub>2</sub> (3·5 g. per 100 c.c.) are mixed. The reagent is capable of detecting the Co in 1 c.c. of a solution containing 2 mg. per litre, in the presence of a Zn concn. 80,000 times as great. Cu, Cd, and Fe interfere. A. J. M.

**Sulphoacetato-salts of complex hexammine-, pentammine-, and tetrammine-cobaltic salts.**—See this vol., 517.

**Simple and complex metallic salts of thio-sulphatopentacyanocobaltic acid.** S. N. MAULIK (J. Indian Chem. Soc., 1934, 11, 1—4; cf. A., 1931, 1140).—The following *compounds* have been prepared: BeO·Be<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]<sub>2</sub>·2H<sub>2</sub>O, orange-red; K<sub>2</sub>Mn[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]<sub>4</sub>·4H<sub>2</sub>O, pale yellow cryst. powder; Mn<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]<sub>6</sub>·6H<sub>2</sub>O; [Cu(NH<sub>3</sub>)<sub>1</sub>]<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>], blue crystals; [Cu(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]<sub>3</sub>·3H<sub>2</sub>O, green; [Cu(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]; [Zn(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]; [Zn(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]<sub>4</sub>·4H<sub>2</sub>O; [Ni(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]<sub>3</sub>·3H<sub>2</sub>O, yellowish-green crystals; [Ni(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]<sub>6</sub>·6H<sub>2</sub>O, green; Ag<sub>4</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>], light yellow powder; Ag<sub>4</sub>[(CN)<sub>5</sub>CoS<sub>2</sub>O<sub>3</sub>]<sub>4</sub>·5NH<sub>3</sub>·6·5H<sub>2</sub>O, unstable crystals rapidly turning black. R. S.

**Varying spectrographic sensitivity of an element alone or mixed with others.** G. PICCARDI (Annali Chim. Appl., 1934, 24, 35—36).—The diminution in intensity or disappearance of the spectral lines of an element when other elements are present, observed by Gazzi (A., 1933, 581), is due to the fact that many of the lines used for analytical purposes belong to the ionised, and not to the neutral, atom. With a mixture of two elements, that with the lower ionisation potential generates a cloud of electrons which, by mass action, retard the ionisation of the other element. T. H. P.

**Theory of mean values.** H. NIKLAS and M. MILLER (Z. Pflanz. Düng., 1934, A, 33, 242—246).—A mathematical discussion. A. G. P.

**Determination of concentration of surface-active substances.** K. SCHULTZE (Kolloid-Z., 1934, 67, 26—35).—The ring method is adapted. Results are given for humic acid, medicinal soap, oleic acid, ovalbumin, and quinine sulphate. E. S. H.

**Simple micro-ashing process.** J. ERDÖS (Z. Unters. Lebensm., 1934, 67, 284—287).—A description of the method and apparatus, and the results of determination of Ca in ashed material, are given. E. C. S.

**Colorimetric determination of  $p_H$  at higher temperatures.** W. NEUMANN (Z. anal. Chem., 1934, 96, 175—183; cf. A., 1933, 1022).—Solutions of NaCl and KCl showed a  $p_H$  decrease on heating to the b.p., the extent of the change decreasing with increasing concn. of salt. J. S. A.

**Silver electrodes "of the second kind" as comparison electrodes.** W. HILTNER (Z. anal. Chem., 1934, 96, 193).—A reply to Hahn (cf. this vol., 160). J. S. A.

**Nitrazine-yellow, a new indicator.** H. WENKER (Ind. Eng. Chem., 1934, 26, 350).—Nitrazine-yellow (2':4'-dinitrobenzeneazo-2- $\alpha$ -naphthol-3:6-disulphonic acid) changes from yellow at  $p_H$  6.0 to blue at  $p_H$  7.0, and the colour change between  $p_H$  6.4 and 6.8 is very sharp. It is very suitable for test papers. A. G.

**Ter Meulen method of analysis.**—See this vol., 540.

**Indirect determination of halogen acids.** T. I. PIRTEA (Z. anal. Chem., 1934, 96, 263—266).—The  $Cl^- + Br^-$  (or  $I^-$ ) are pptd. as  $AgCl + AgBr$  ( $AgI$ ). The weighed ppt. is dissolved in hot, saturated aq.  $KBr$  ( $KI$ ) and repptd. as  $AgBr$  ( $AgI$ ) by adding  $HNO_3$  and diluting. Where  $Cl^- + Br^-$  and  $I^-$  are present, the ppt. is converted first into  $AgBr + AgI$ , then into  $AgI$ . J. S. A.

**Negative catalysis and microchemistry.** A. QUARTAROLI (Annali Chim. Appl., 1934, 24, 70—74).— $10 \times 10^{-6}$  g. of  $KClO_3$  may be determined, even in presence of  $KCl$  and  $KClO_4$ , by its negative catalytic action on the reaction between  $NO_3^-$  and  $HCO_2H$ . The alteration of pptd.  $Cu(OH)_2$  occurs in two phases, characterised by darkening and contraction, both of which are retarded by traces of  $Mg$ ,  $Ni$ , and  $Co$ , and accelerated by traces of  $H_2O_2$ . A method for determining these substances in this way is outlined. T. H. P.

**Colorimetric determination of fluorine.** E. PEYROT (Annali Chim. Appl., 1934, 24, 74—78).—A combination of Treadwell and Koch's (A., 1904, ii, 841) and of Penfield's method (A., 1879, 829; see Steiger, A., 1908, ii, 426). The powdered substance, ashed if necessary, is mixed with  $SiO_2$  and treated at about  $160^\circ$  in the Penfield apparatus with conc.  $H_2SO_4$ ; the air circulated need not be purified. The evolved gas is collected in about  $0.5N$ - $NaOH$ , which converts it into  $NaF$ , this being determined colorimetrically as described by Steiger;  $CO_2$ ,  $SO_2$ ,  $SO_3$ , and  $HCl$  do not interfere. T. H. P.

**Detection and determination of small amounts of fluorine. Application of the zirconium purpurin test.** I. M. KOLTHOFF and M. E. STANSBY (Ind. Eng. Chem. [Anal.], 1934, 6, 118—121).—The qual. test of De Boer and Basarat (A., 1926, 590) is modified, making it sensitive to 0.003 mg.  $F^-$ . Many anions interfere with the test, but by distilling as  $SiF_4$  and collecting in the  $Zr$ -purpurin reagent 0.005 mg.  $F^-$  can be detected in presence of any other ion.  $F^-$  can be determined with an accuracy of 2% by titrating with  $ZrOCl_2$ , using purpurin as indicator. A colorimetric titration procedure for determining 0.01—0.05 mg.  $F^-$  with an accuracy of 0.002 mg.  $F^-$  is described. E. S. H.

**Determination of fluorides in natural waters.** J. M. SANCHIS (Ind. Eng. Chem. [Anal.], 1934, 6, 134—135).—Modifications of the  $Zr(NO_3)_4$ -alizarin method (A., 1933, 477) are described.  $Cl^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  up to 500 p.p.m.,  $Mn^{2+}$  up to 200 p.p.m.,  $SiO_3^{2-}$  up to 50 p.p.m.,  $PO_4^{3-}$ ,  $B$ ,  $Cu^{2+}$ , and  $Fe$  up to 5 p.p.m., and  $S^{2-}$  up to 2 p.p.m. do not interfere. E. S. H.

**Determination of  $SO_4^{2-}$  in presence of rhodizonic acid as indicator.** R. B. ROSCHAL (Anilinokras. Prom., 1934, 4, 37—38).— $SO_4^{2-}$  is determined in solutions of technical sulphonic acids as follows: 2—3 g. of  $NaOAc$ , 5 c.c. of glycerol, 5 g. of  $NH_4Cl$ , 10 c.c. of  $0.5N$ - $BaCl_2$ , and 8 drops of 0.3%  $Na$  rhodizonate (I) are added to 10 c.c. of solution, and excess of  $BaCl_2$  is titrated with  $0.25N$ - $H_2SO_4$ . The solutions of (I) deteriorate rapidly, and should be freshly prepared every 24 hr. R. T.

**Colorimetric determination of ammonia in small amounts of material.** F. ALTEN, H. WEILANDT, and E. HILLE (Z. Pflanz. Düng., 1934, A, 33, 129—133).—Golub's method (B., 1927, 397) is unsatisfactory. The colour produced in ammoniacal solutions by Nessler's reagent (I) varies considerably with  $p_H$ . The sample of plant material (20—50 mg.) is digested with  $H_2SO_4$  and  $K_2SO_4$ ,  $H_2O_2$  being added during the digestion process. The product is diluted with  $H_2O$  and a portion neutralised with  $0.5N$ - $NaOH$  (thymolphthalein). A borate buffer solution is added, followed by (I). Colour comparisons are made after 1 hr. A. G. P.

**Analytical method of separating dimethylamine and ammonia.** E. KATTSCHER and M. VOROSCHLOVA (Anilinokras. Prom., 1934, 4, 39—41).—100 c.c. of  $H_2O$ , 15 c.c. of 8% aq.  $NH_3$ , and 2.5—3 c.c. of  $CS_2$  are added to 10 c.c. of the solution under analysis, and the well-shaken solution is titrated after 15 min. with  $0.2N$ - $CuSO_4$  (I), the titration being completed when a drop of solution placed beside a drop of (I) on filter-paper does not give a dark brown demarcation line. This titration gives the  $NHMe_2$  content:  $2NHMe_2 + 2CS_2 + 2NH_3 \rightarrow 2NMe_2 \cdot CS \cdot SNH_3 \rightarrow [S \cdot CS \cdot NMe_2]_2Cu$ . Total alkalinity is determined in a second 10 c.c. of solution, and the  $NH_3$  content is calc. by difference. R. T.

**Determination of phosphoric acid by the phosphomolybdate method and its use for plant ashes.** J. TISCHER (Z. Pflanz. Düng., 1934, A, 33, 192—242).—The Mo-blue colour developed in determinations of

$\text{PO}_4'''$  reaches a max. early after the addition of the reducing agent (I), and subsequently falls to a stable intensity after approx. 30 min. The max. colour is reproduced by further additions of (I). Fe salts prevent its formation. With appropriate proportions of reagents a direct proportionality between the colour produced and the  $\text{PO}_4'''$  content of test solutions (up to  $50 \times 10^{-6}$  g. P) is demonstrated. The influence of [H'] and of varying proportions of different salts on the intensity of coloration is examined. Technique for the determination of  $\text{PO}_4'''$  in plant ashes is given.

A. G. P.

**Determination of phosphoric acid with ammonium molybdate, and the application of the process in certain cases.** A. BAURLE, W. RIEDEL, and K. TAUFEL (Z. Unters. Lebensm., 1934, 67, 274—279).—Excess of  $\text{H}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  is to be avoided. Titration of the ppt. with NaOH to phenolphthalein gives consistent results, and the method can be applied to foodstuffs treated by the wet combustion method. In the prep. of melted butter (I) the phosphatides are pptd., consequently (I) does not suffer from browning.

E. C. S.

**Tabular method of reading arsenic strips.** B. D. THOMAS (Ind. Eng. Chem., 1934, 26, 356).—The lengths of the stains on As test papers vary from one set of tests to another, but the ratio between the lengths for different wts. of As remains const. A set of tables can therefore be prepared, and the correct table for any series of tests is chosen by the sum of the lengths of the stains obtained for a series of wts. of As. This is more accurate than plotting the lengths against the wts. of As.

A. G.

**Potentiometric determination of arsenates.** W. E. HANSON, S. B. SWEETSER, and H. B. FELDMAN (J. Amer. Chem. Soc., 1934, 56, 577—579).—The procedure is satisfactory when a large excess (10 times the theoretical amount) of NaOAc is used in 50 vol.-% aq. EtOH as solvent.

E. S. H.

**Determination of small quantities of carbon monoxide in medicinal oxygen and carbon dioxide.**—See B., 1934, 299.

**Determination of sodium by the uranyl method.** S. Z. MAKAROV and V. V. BUKINA (J. Gen. Chem. Russ., 1933, 3, 881—891).—15 c.c. of a reagent (I), prepared by mixing 50 c.c. of a solution containing 10 g. of  $\text{UO}_2(\text{OAc})_2$  and 6 c.c. of 30% AcOH with 50 c.c. of 60%  $\text{Zn}(\text{OAc})_2$  containing 6% of AcOH, are added to the dry residue of the solution under analysis (containing  $\geq 10$  mg. Na), the ppt. of  $\text{NaZn}(\text{UO}_2)_3(\text{OAc})_9 \cdot 6\text{H}_2\text{O}$  (II) is washed successively with several portions of (I), with 95% EtOH saturated with (II), and with  $\text{Et}_2\text{O}$ , dried, and weighed. The method gives good results for solutions containing only Na, as well as in presence of  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Mg}^{++}$ , and of  $\geq 20$  mg. K per mg. Na.

R. T.

**Manganese uranyl acetate as a reagent for the detection of sodium.** T. C. CHANG and C. L. TSENG (Sci. Quart. Nat. Univ. Peking, 1934, 4, 185—189).—Mn uranyl acetate (prep. described) detects 0.02 mg. of Na in 0.5 c.c.,  $\text{NaMn}(\text{UO}_2)_3(\text{OAc})_9 \cdot 6\text{H}_2\text{O}$  being pptd. K, Li (unless in large excess), Mg, alkaline earths, and  $\text{NH}_4$  salts do not interfere.

R. S. C.

**Analytical reactions of rubidium and caesium.** W. J. O'LEARY and J. PAPISH (Ind. Eng. Chem. [Anal.], 1934, 6, 107—111).—Rb and Cs can be separated quantitatively from K by adding luteo-phosphomolybdic acid, which does not ppt. K. Cs is quantitatively pptd. in 6N-HCl in presence of Rb by adding silicotungstic acid; when  $\text{PO}_4'''$  is present it is more satisfactory first to concentrate as platinum-chlorides, a modified method for which is worked out.

E. S. H.

**Gravimetric determination of magnesium as  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ .** J. DICK and A. RUDNER (Z. anal. Chem., 1934, 96, 245—248).—Mg is pptd. cold from conc. solution by adding  $\text{NH}_4\text{Cl}$  and excess of  $\text{Na}_2\text{HAsO}_4$ . The ppt. is dissolved in HCl, then neutralised with 2.5% aq.  $\text{NH}_3$  (phenolphthalein), and 1/3 vol. of conc. aq.  $\text{NH}_3$  is added (total 60—70 c.c.). The ppt. is filtered after 1 hr., washed with EtOH and  $\text{Et}_2\text{O}$ , and dried in an air stream. For semi-micro-determinations, the vol. should be  $\geq 5$  c.c.

J. S. A.

**Rapid semi-micro-gravimetric determination of magnesium as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  or as  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ .** L. W. WINKLER (Z. anal. Chem., 1934, 96, 241—245).— $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is pptd. from hot solution (20 c.c.) by addition of 0.5 g. of  $\text{NH}_4\text{Cl}$ , 1 c.c. 20% aq.  $\text{NH}_3$ , and 2 c.c. 10%  $\text{Na}_2\text{HPO}_4$ . After 5 min. the solution is cooled, shaken vigorously, and filtered after 15 min. The ppt. is washed with EtOH and dried in an air stream. Ca if present is first pptd. by  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ; the time of keeping is then doubled.  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  is pptd. cold and filtered after 30 min. shaking, addition of  $\text{NH}_4\text{Cl}$  being omitted after pptn. of Ca.

J. S. A.

**Precipitation of zinc sulphide and aluminium hydroxide, and gravimetric separation of zinc from aluminium.** C. MAYR (Z. anal. Chem., 1934, 96, 273—274).—Frers' claim of priority is rejected (cf. this vol., 161, and A., 1933, 478).

J. S. A.

**Separation of metals of the second analytical group.** G. L. CHABORSKI and E. PETRUSCU (Bul. Chim. Soc. Romana-Ştiinţe, 1932, 35, 33—36).—Modifications of Longinescu and Theodorescu's procedure are proposed.

R. T.

**Iodometric and potassium permanganate determinations of lead in lead acetate.**—See B., 1934, 318.

**Oxidation of thallos to thallic salts, and reduction of the latter by sodium arsenite for analytical purposes.** F. ČUTA (Chem. Listy, 1934, 28, 58—59).— $\text{TI}^{\text{I}}$  is oxidised to  $\text{TI}^{\text{III}}$  by Br, excess of Br is removed by boiling with HCl, the solution is made alkaline, and titrated with standard  $\text{Na}_3\text{AsO}_3$ . The mean error is  $\pm 0.2\%$ . In the absence of  $\text{Cl}^-$ ,  $\text{TI}^{\text{III}}$  undergoes partial reduction to  $\text{TI}^{\text{I}}$  when its solutions are heated, even if reducing agents are not present.

R. T.

**Copper [borax and microcosmic] beads.** H. RAKETT (Z. anal. Chem., 1934, 96, 192—193).— $0.1 \times 10^{-6}$  g. of Cu may be detected by means of small borax or  $\text{NaNH}_4\text{HPO}_4$  beads, with addition of a particle of Sn to effect reduction.

J. S. A.

**Detection and determination of copper in fresh waters.**—See B., 1934, 350.

**Determination of mercury in air and urine.** A. M. FRASER (J. Ind. Hygiene, 1934, 16, 67—76).—Hg in air is determined by electrolytic deposition or micrometrically, after condensation by passage through a tube immersed in liquid air (cf. Stock and Heller, A., 1926, 703). In urine, Hg is determined as HgS after wet ashing with  $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ .

H. G. R.

**Potentiometric determination of mercurous salts.** G. SPACU and P. SPACU (Z. anal. Chem., 1934, 96, 188—192).—Titration of Hg by  $\text{KIO}_3$  (cf. this vol., 270) may be performed potentiometrically, preferably in 30% EtOH. Use of 0.01N solutions is impossible, the Hg-coated Pt electrode becoming passivated.

J. S. A.

**Determination of manganese in iron and steel or in ores.**—See B., 1934, 279.

**Colour reactions of rhenium.** B. TOUGARINOFF (Bull. Soc. chim. Belg., 1934, 43, 111—114).—On adding a few drops of 5% aq.  $\text{K}_4\text{Fe}(\text{CN})_6$  and 2—3 c.c. of a solution (I) of 25 g. of cryst.  $\text{SnCl}_2$  in 100 c.c. of conc. HCl to a solution (II) containing  $\text{ReO}_4^-$  (not strongly alkaline) a brown coloration is produced. Re may be separated from metals which interfere (W, V, Mo, Nb, Cr) by distillation with conc.  $\text{H}_2\text{SO}_4$ . On adding a few drops of a saturated solution of dimethylglyoxime in EtOH and 2—5 c.c. of (I) to 1 c.c. of (II), a yellow to red colour is produced and the solution develops a green fluorescence when heated. 0.01 mg. of Re may be detected by either of these reactions.

D. R. D.

**Influence of nitric acid on the determination of iron by potassium permanganate.** D. TOTORESCU (Z. anal. Chem., 1934, 96, 183—188).— $\text{NO}_3^-$  can be totally removed only by evaporation to dryness with  $\text{H}_2\text{SO}_4$ . If  $\text{NO}_3^-$  is present, reduction with  $\text{Zn} + \text{H}_2\text{SO}_4$  gives  $\text{NH}_2\text{OH}$ , invalidating  $\text{KMnO}_4$  titration.

J. S. A.

**2-Aminopyridine in microchemical identification of some cations.** A. SÁ (Anal. Farm. Bioquim., 1933, 4, 77—80).—2-Aminopyridine gives characteristic cryst. compounds with salts of Co, Cu, Zn, and Cd and KCNS or  $\text{NH}_4\text{CNS}$ .

R. K. C.

**Indirect potentiometric determination of nickel.** G. SPACU and P. SPACU (Z. anal. Chem., 1934, 96, 270—273).—The Ni solution is treated with 0.1N-KSCN and  $\text{C}_5\text{H}_5\text{N}$ , pptg.

$[\text{Ni}(\text{SCN})_2(\text{C}_5\text{H}_5\text{N})_4]$ , which is filtered off. The filtrate is acidified with  $\text{HNO}_3$  and excess KSCN titrated back potentiometrically with  $\text{AgNO}_3$ .

J. S. A.

**Separation of the components of the ammonium sulphide group.** J. KUNZ (Helv. Chim. Acta, 1934, 17, 369—372).—An error in a previous communication (A., 1932, 827) is corr. The dark ppt. obtained by adding  $\text{Cl}_2$ - or  $\text{Br}-\text{H}_2\text{O}$  in AcOH to a Co salt solution does not give a complete separation of  $\text{Co}^{+++}$  from  $\text{Ni}^{+++}$ , but is an indication of the presence of  $\text{Co}^{+++}$ . The separation of Cr, Zn, Al, Mn, and Fe is effected by dissolving the pptd. sulphides in HCl, evaporating to dryness, oxidising  $\text{Fe}^{II}$  to  $\text{Fe}^{III}$  with  $\text{HNO}_3$ , treating with boiling  $\text{Na}_2\text{CO}_3$ , filtering, and

fusing the dried residue with  $\text{KNO}_3$  and NaOH. If only one cation is present, the colour of the melt or of the solution in  $\text{H}_2\text{O}$  gives an indication of its nature. From a colourless solution Al is pptd. by an excess of  $(\text{NH}_4)_2\text{CO}_3$  and Zn from the filtrate by  $\text{Na}_2\text{S}$ . After removing Al and Zn from a clear yellow solution, Cr is pptd. by acidifying with AcOH and adding  $\text{Pb}(\text{OAc})_2$ . A red powder in the melt or solution indicates  $\text{Fe}_2\text{O}_3$ . If the solution of the melt is coloured bluish-green by  $\text{Na}_2\text{MnO}_4$ ,  $\text{H}_2\text{O}_2$  is added and gives, on warming, pptd.  $\text{Mn}(\text{OH})_4$ , which may also contain  $\text{Fe}_2\text{O}_3$ . The latter is left behind when the  $\text{Mn}(\text{OH})_4$  is brought into solution by  $\text{K}_2\text{S}_2\text{O}_5$ . From the filtrate, freed from Mn and Fe, Al is separated as before; the filtrate is acidified with conc. HCl and  $\text{Cr}^{\text{VI}}$  reduced to  $\text{Cr}^{\text{III}}$  by  $\text{K}_2\text{S}_2\text{O}_5$ . From the green solution  $\text{Cr}(\text{OH})_3$  is pptd. by aq.  $\text{NH}_3$ . In the filtrate ZnS is pptd. by  $\text{Na}_2\text{S}$ .

M. S. B.

**Application of the potential-forming system metal/metal anion to potentiometric titrations.** E. MÜLLER and K. MEHLHORN (Z. anal. Chem., 1934, 96, 173—175; cf. this vol., 49).—Titration of, e.g.,  $\text{CrO}_4^{2-}$  using a Cr reference electrode (I) can also be effected using (I) of Pt or Au. (I) actually functions as an O electrode, measuring the change in  $\text{OH}^-$  concn., due to hydrolysis of  $\text{CrO}_4^{2-}$ . The method can therefore be used only in solutions of the same  $p_{\text{H}}$  as  $\text{K}_2\text{CrO}_4$ .

J. S. A.

**Inclusion of rarer metals in elementary qualitative analysis. I. Inclusion of tungsten and molybdenum in groups I and II.** L. E. PORTER (Ind. Eng. Chem. [Anal.], 1934, 6, 138—139).—A suitable scheme is recommended.

E. S. H.

**Volumetric determination of uranium in highly ferriferous ores.**—See B., 1934, 325.

**Detection of bismuth with alkali thiocyanates.** E. TOMMILA (Suomen Kem., 1934, 7, B, 79; cf. A., 1923, i, 1076).—A slightly acid solution (I) of < 5 mg. Bi per litre gives a visible yellow colour with KCNS. The same reaction occurs in glycerol or glycol.  $\text{HNO}_3$  affects the reaction, but not org. acids. (I) is decolorised by EtOAc and amyl alcohol, but not by  $\text{Et}_2\text{O}$  (in which the corresponding Fe compound is sol.). Molybdates produce similar colours, but the (I) is decolorised by  $\text{Et}_2\text{O}$ .

J. L. D.

**Detection of bismuth with sulphur-containing organic reagents. I. Dimercaptothiodiazole.** J. V. DUBSKÝ and A. OKÁČ (Z. anal. Chem., 1934, 96, 267—270).—Dimercaptothiodiazole (prep. given) gives with acid and alkaline Bi solutions an intense red ppt.  $[\text{Bi}(\text{C}_2\text{HNS})_2]_3$  if pptd. from alkaline solution]. Other metals of the sulphide group give white to yellow ppts., except Hg (black). Bi may be first separated as  $\text{Bi}(\text{OH})_3$ . The limit is  $1.2 \times 10^{-6}$  g. Bi. The test is not suited to spotting on filter-paper.

J. S. A.

**Determination of traces of bismuth in presence of other metals.** L. A. HADDOCK (Analyst, 1934, 59, 163—168; cf. A., 1932, 1103; 1933, 1064).—Bi is extracted with a solution of diphenylthiocarbazonone in  $\text{CHCl}_3$ , and is determined colorimetrically as iodobismuthous acid in amyl alcohol. 0.005—0.1 mg. of Bi in 1 g. of material can be determined, the only

elements which interfere being Pb and Th, and these only in amounts  $> 0.5$  mg. E. C. S.

**Detection of small amounts of tantalum and niobium.** W. R. SCHOELLER (*Z. anal. Chem.*, 1934, 96, 252—257; cf. this vol., 50).—The tannin (I) test is more sensitive than those of Rienacker and Schiff. 0.05 mg. of  $Ta_2O_5$  gives a yellow ppt. with (I) in presence of  $NH_4Cl$ . 0.02 mg.  $Nb_2O_5$  gives a red ppt. (II), as does Ti. In presence of Ti the  $NaHSO_4$  melt is dissolved in aq.  $(NH_4)_2C_2O_4$ , and (I) is added, giving (II) with Nb only. Mixtures containing Nb, Ta, Ti, and Zr are fused with  $NaHSO_4$  and pptd. with (I). The ppt. is treated with  $HNO_3 + H_2SO_4$ . Ti is detected with  $H_2O_2$ , Zr with  $Na_2HPO_4$ . The residue is fused with  $NaHSO_4$ , taken up in  $(NH_4)_2C_2O_4$ , and pptd. with (I). This ppt.  $P_1$  is re-fused and re-pptd., giving a lighter orange ppt.  $P_2$  if Ta is present. Nb gives a red ppt. when  $NH_4OAc$  and (I) are added to the filtrate. With small amounts of Ta,  $P_2$  may be only slightly lighter than  $P_1$ . J. S. A.

**Amalgamation assay of platinum.**—See B., 1934, 325.

**Thermostat for temperatures between 5° and 20°.** L. M. PIDGEON (*Canad. J. Res.*, 1934, 10, 252). J. L. D.

**Equalisation of temperature in electric ovens.** F. G. H. TATE (*Analyst*, 1934, 59, 168—170).—A fan mounted in the door maintains temp. equality to within 1° in an oven which otherwise has temp. inequalities of 20°. E. C. S.

**Electrical combustion furnace.** G. B. CRIPPA and M. GALLOTTI (*Annali Chim. Appl.*, 1934, 24, 82—86).—Eleven U-shaped heating elements, arranged side by side and separately controllable, form the bed in which the combustion tube lies. T. H. P.

**Calorimetry. Method of electrical compensation. Microcalorimetry.** A. TIAN (*J. Chim. phys.*, 1933, 30, 665—708).—Full details are given for the construction and manipulation of a microcalorimeter operating on the principle that the heat evolved during an exothermal change is absorbed by means of the Peltier effect and the heat absorbed by an endothermal change is replaced by means of the Joule effect. Heat changes of  $< 0.7$  g.-cal. per hr. lasting for 10—20 hr. are determined, and the method, applied ballistically, is satisfactory for heat changes of  $< 100$  sec. duration. Data are recorded. J. G. A. G.

**Examination of opaque objects with the aid of polarised light.** O. FEUSSNER (*Z. Metallk.*, 1933, 25, 313—314, 314). M. VON SCHWARZ (*Ibid.*, 314).—Polemical (cf. A., 1932, 606, 908). A. R. P.

**Degree of precision in measurement of the refractive index of samples of small dimensions.** A. BIOT (*Ann. Soc. Sci. Bruxelles*, 1934, B, 54, 5—13).—The min. deviation, grazing incidence, and interference methods of determining  $n$  should each require certain min. vols. of the sample to ensure definite degrees of accuracy, about  $10^{-3}$  c.c. and 0.5 c.c., respectively, for accuracies of  $1 \times 10^{-4}$  and  $1 \times 10^{-5}$ . The last method shows slight advantages for small samples. The theory is applied to the study of  $n$  for lenses. J. W. S.

**Nickel salts as light filters.** W. V. BHAGWAT (*J. Indian Chem. Soc.*, 1934, 11, 5—11).—The absorption and % transmission of solutions of  $NiCl_2$ ,  $Ni(NO_3)_2$ , and  $(NH_4)_2SO_4 \cdot NiSO_4$ , have been determined. Combinations of Ni salts with Co salts transmit only in the ultra-violet. R. S.

**Absolute colorimeter.** R. GUELKE (*J. Soc. Dyers and Col.*, 1934, 50, 77—80).—A Leitz abs. colorimeter (dipping spectrophotometer), which combines the simplicity of the ordinary colorimeter with the accuracy of the spectrophotometer, and is suitable for the determination of dyes in solution or on the fibre (including vat dyes), is described. A. J. H.

**Colorimetry.** J. GUILD (*J. Sci. Instr.*, 1934, 11, 69—78).—General principles are discussed. C. W. G.

**Interferometer microscope.** C. DUNBAR (*J. Sci. Instr.*, 1934, 11, 85—89).—Small displacements of the stage are measured by means of an interferometer system. Applications to the determination of the sizes of small particles are described. C. W. G.

**Spectrometer.** S. J. DULY (*J. Sci. Instr.*, 1934, 11, 92—94).—The instrument is intended principally for measuring  $n$ , crystal angles, and visual spectra. C. W. G.

**Industrial microscopy. IV. Crystals.** C. H. BUTCHER (*Ind. Chem.*, 1934, 10, 105—108).—The method of identification of crystals by determining  $n$  with polarised light is discussed. C. A. K.

**Constant ultra-violet output from quartz mercury arc lamps.** W. T. ANDERSON, jun. (*Rev. Sci. Instr.*, 1934, [ii], 5, 127—129).—A method of intensity control, using the Weston "Photronic" light-sensitive cell for measuring the ultra-violet emission from quartz Hg arcs, is described. N. M. B.

**Mercury-sealed, water-cooled, rotating X-ray target.** W. T. ASTBURY and R. D. PRESTON (*Nature*, 1934, 133, 460—461). L. S. T.

**Universal chamber for measuring X-ray doses without the use of lead sulphide.** R. JAEGER (*Physikal. Z.*, 1934, 35, 184—187).—The apparatus, which is considerably smaller than the usual blende chamber, is described. A spectral range of 2—0.15 Å. can be covered without changing the window. A. J. M.

**Focalisation method for X-ray crystal analysis.** A. ROCOZINSKI (*Compt. rend.*, 1934, 198, 953—955).—The substance is arranged in the form of a hoop, the plane of which is perpendicular to the beam of X-rays, the centre lying in that beam. A small Pb screen prevents direct incidence of the beam on the photographic film. The method greatly reduces the period of exposure. C. A. S.

**Optical osmometer.** C. H. DWIGHT and H. KERSTEN (*Rev. Sci. Instr.*, 1934, [ii], 5, 130—131).—The instrument makes use of an optical lever for measuring rapid changes in vol. of a solution in osmosis, and gives magnified readings at a distance. N. M. B.

**Photographic intensity measurement with moving electron beams.** F. C. POULTNEY and R.

WHIDDINGTON (Proc. Leeds Phil. Soc., 1934, 2, 492—494).—Electron streams of very different intensity may be compared by measuring the effects produced by the streams on photographic films moving at different speeds. H. S. P.

**Photo-electric spectrophotometer using dual electrostatic compensation.** L. A. WOODWARD (Proc. Roy. Soc., 1934, A, 144, 118—128).—The apparatus described is suitable for the measurement of extinction coeffs. of substances in solution, especially in the ultra-violet region. The method used is purely electrical. It is tested by a series of determinations of the mol. extinction coeff. of  $\text{KNO}_3$  in dil. solution. L. L. B.

**Radio relay circuit.** G. B. HEISEG and D. C. GERNES (Ind. Eng. Chem. [Anal.], 1934, 6, 155—156). E. S. H.

**Silver chloride electrode for use in dilute solutions.** A. S. BROWN (J. Amer. Chem. Soc., 1934, 56, 646—647).—A Pt wire is plated with Ag by electrodeposition from a solution of  $\text{KAg}(\text{CN})_2$ , and coated with AgCl by anodic treatment for 30 min. in 0.1N-HCl. The electrodes are not sensitive to light, and are reproducible to within a few hundredths of a mv., even in very dil. solutions. E. S. H.

**Comparison of vacuum and gas-filled [photo-electric] cells.** G. A. BOUTRY and J. ORCEL (Compt. rend., 1934, 198, 808—810; cf. this vol., 383).—The claim to an accuracy of 0.25% for vac. cells is doubtful. The max. potential safely applicable diminishes as the flux of light increases, but should never be > 80 volts. C. A. S.

**Technique of investigation of crystalline powders by means of electron scattering.** F. TRENDELENBURG and O. WIELAND (Wiss. Veröff. Siemens-Konz., 1934, 13, 41—47).—An arrangement for the use of the powder method with an electron beam of 50 kv. intensity is described. A. J. M.

**Sector copying process for the diminution of the diffuse background blackening in electron diffraction photographs.** F. TRENDELENBURG and E. FRANZ (Wiss. Veröff. Siemens-Konz., 1934, 13, 48—54).—By means of a sector device, the intensity of illumination of the negative in taking a positive of electron diffraction photographs is varied in different parts, so eliminating the background. A. J. M.

**Construction and performance of the magnetic electron microscope.** E. RUSKA (Z. Physik, 1934, 87, 580—602). A. B. D. C.

**Comparison of constancy of gold- and chromium-plated analytical weights.** H. V. MOYER and P. K. WINTER (Ind. Eng. Chem., 1934, 26, 238).—Cr-plated weights underwent much smaller changes than did similar weights plated with Au during use for 1 year in the same laboratory. The reason is probably the greater resistance of the Cr to scratching and abrasion, since positive errors due to corrosion of the underlying brass had occurred with some of the Au-plated weights. H. F. G.

**Preparation of sintered Pyrex glass filters.** P. L. KIRK, R. CRAIG, and R. S. SOSENFELS (Ind.

Eng. Chem. [Anal.], 1934, 6, 154—155).—Directions are given for making filters of any desired degree of porosity. E. S. H.

**Application of the automatic pipette in dispensing.** R. F. ARMBRUST (Pharm. Weekblad, 1934, 71, 300—301).—An automatic pipette for measuring conc. solutions from bottles is described. S. C.

**Retention of dichromate by glassware after exposure to potassium dichromate cleaning solution.** E. P. LAUG (Ind. Eng. Chem. [Anal.], 1934, 6, 111—112).—The amount of  $\text{Cr}_2\text{O}_7^{2-}$  retained is practically independent of the duration of contact of glass with the cleaning solution. About 50% is recovered in the wash- $\text{H}_2\text{O}$  during the first 30 min. and about 80% within 2 hr. Little difference is observed between behaviours of Pyrex and Na<sub>2</sub>O-glass. E. S. H.

**Automatic vacuum regulation.** G. F. LIEBIG, jun. (Ind. Eng. Chem. [Anal.], 1934, 6, 156). E. S. H.

**Preparation of microscopic glass spheres.** S. SKLAREW (Ind. Eng. Chem. [Anal.], 1934, 6, 152—153).—Powdered glass is blown by an air blast through a heated chamber, in which the particles melt to spherical droplets, to a settling chamber. E. S. H.

**Absorption tube.** G. E. LE WORTHY (Ind. Eng. Chem. [Anal.], 1934, 6, 139).—The tube is designed for the determination of H in analysis by combustion. E. S. H.

**Rapid method of dust sampling.** T. HATCH and E. W. THOMPSON (J. Ind. Hygiene, 1934, 16, 92—99).—Eight samples are collected on a single slide, by a modification of the Owens counter, and matched against standards under a microscope. H. G. R.

**Measurement of surface tension of liquids.** A. ACHMATOV (Kolloid-Z., 1934, 66, 266—270).—Apparatus and technique for a method, in which the pressure in a conical capillary tube is measured, are described. Results for a no. of liquids compare favourably with those obtained by the capillary rise method. E. S. H.

**Improved form of Sprengel tube.** A. D. GARDINER (Analyst, 1934, 59, 172). E. C. S.

**Objective demonstrations with rutile suspensions.** A. EHRLINGHAUS (Naturwiss., 1934, 22, 149—150).—Experimental details are given for showing the increase in mean velocity of the Brownian movement with temp., the coagulation by electrolytes, and the electrophoresis of colloidal solutions of rutile. A method of showing the rotation of the plane of polarisation of linearly polarised light, making use of scattering at colloidal particles of rutile, is described. A. J. M.

**Highly polymerised compounds. XCI. Ultra-centrifugal mol. wt. determinations in synthetic highly polymerised substances.** R. SIGNER and H. GROSS (Helv. Chim. Acta, 1934, 17, 335—351).—Mol. wts. of polystyrene and polyanethole in  $\text{CHCl}_3$  solution and of polyethylene oxide in  $\text{C}_2\text{H}_4\text{Br}_2$  have been obtained by determining sedimentation equilibria with the ultra-centrifuge. The method can be applied to substances not otherwise accessible to measure-

ment. The results also make it possible to show at what concn. swelling pressures set in. By determining the friction factor from the mol. wt. and sedimentation const. and comparing with the friction factor for spherical particles of the same mass, a dissymmetry factor is obtained. There is a parallelism between the ultra-centrifugal mol. wt. determinations and Staudinger's sp. viscosity-mol. wt. relationship. M. S. B.

**Mol.-wt. analysis in the centrifugal field.** T. SVEDBERG (*Kolloid-Z.*, 1934, 67, 2—16).—A review of much published work, describing apparatus, technique, and results for several proteins. E. S. H.

**Micromanometer.** O. STÅLHANE (*J. Sci. Instr.*, 1934, 11, 79—82).—A bubble in a tube is brought back to its original position by tilting with a micrometer screw. C. W. G.

**Sealed  $\alpha$ -ray bulbs in the study of chemical reactions produced by radon.** E. C. TRUESDALE and C. H. SHIFLETT (*Rev. Sci. Instr.*, 1934, [ii], 5, 119).—To avoid the use of a Hg seal, a method of progressively sealing off the stem of the bulb and driving the radon ahead of the seal is employed. N. M. B.

**Evaporation technique for highly refractory substances.** H. M. O'BRYAN (*Rev. Sci. Instr.*,

1934, [ii], 5, 125—126).—Pt, B, Mo, SiO<sub>2</sub>, and other substances which would react with a W filament have been evaporated in vac. in a pure graphite crucible heated by bombardment with electrons at 4000 volts from a W filament. N. M. B.

**Determination of the specific gravity of liquids with a new pycnometer.** J. M. AAS (*Fettchem. Umschau*, 1934, 41, 3—4).—A 25-c.c. bottle with a narrow neck (3.5—4 mm. diameter) is graduated in divisions of 0.01 c.c., so that the vol. of the liquid can be read to 0.002 c.c.;  $d$  is determined to  $\pm 0.0001$ , if the temp. is measured to within  $\pm 0.1^\circ$ . E. L.

**"Atmos" distillation apparatus for water.** J. J. HOFMAN (*Pharm. Weekblad*, 1934, 71, 338—339).—In a continuous, all-glass distillation apparatus the condenser jacket is fitted with a const.-level device and is also connected directly with the boiling vessel. S. C.

**Nomogram for solving percentage conversions of binary mixture components.** T. C. PATTON (*Chem. Met. Eng.*, 1934, 41, 148—149).

**Lecture experiment on gas diffusion.** A VISWANATHAN (*J. Indian Chem. Soc.*, 1934, 11, 79).—The change of pressure resulting from the different rates of diffusion of gases can be demonstrated by the use of Cartesian divers. R. S.

## Geochemistry.

**Conductivity of natural mineral waters. I. Mineral water of Vrnjačka Banja.** P. S. TUTUNDZIC (*Bull. Soc. Chim. Yougoslav.*, 1933, 4, 145—155).—The conductivity of the H<sub>2</sub>O of various springs has been determined. R. T.

**Bucharest drinking water.** D. BUTESCU (*Bul. Chim. Soc. Romana Ştiinţe*, 1932, 35, 137—170).—Analytical and other data are given. R. T.

**Analysis and physico-chemical data of the thermo-mineral water of the S. Calogero spring, Lipari.** L. IRRERA and G. LABRUTO (*Annali Chim. Appl.*, 1934, 24, 57—70).—This H<sub>2</sub>O, issuing at 58°, has  $d$  1.002,  $p_H$  7.46, residue 1.9 g. per litre, radioactivity 0, and contains mainly SO<sub>4</sub>'', CO<sub>3</sub>'', Na', Ca'', and Mg'', in amounts < in 1872 and 1907, when the temp. was higher. T. H. P.

**Analysis of water from the Mangiatorella (Calabria) spring.** B. RICCA (*Annali Chim. Appl.*, 1934, 24, 36—54).—Results are given of the chemical, physico-chemical, and bacteriological analysis of this H<sub>2</sub>O, which is classed as an oligo-mineral drinking H<sub>2</sub>O. T. H. P.

**Phytoplankton in English lakes. II. Composition of the phytoplankton in relation to dissolved substances.** W. H. PEARSALL (*J. Ecology*, 1932, 20, 241—262).—Diatoms occur when the H<sub>2</sub>O is richest in NO<sub>3</sub>', PO<sub>4</sub>'', and SiO<sub>2</sub>; green algæ and desmids occur when NO<sub>3</sub>' and PO<sub>4</sub>' are low. CH. ABS.

**Origin of iodine and bromine in oil-bearing waters.** A. P. VINOGRADOV (*Compt. rend. Acad.*

*Sci. U.R.S.S.*, 1934, 1, 214—216).—It is concluded that the deep-seated H<sub>2</sub>O of oil-bearing regions which contain large amounts of I and Br originate in fossil mud H<sub>2</sub>O of marine bottoms. J. W. S.

**Accuracy of mineralogical measurements.** M. H. HEY (*Min. Mag.*, 1934, 8, 495—500).—The accuracy to be expected from the measurement of various physical consts. and in chemical analyses is reviewed. L. J. S.

**Origin of helium in sylvine.** O. HAHN and H. J. BORN (*Naturwiss.*, 1934, 22, 138).—The high He content of sylvine is due to the action of hot H<sub>2</sub>O rich in Ra-*D* on the primary minerals, carnallite or kainite. The Ra-*D* content of sea-H<sub>2</sub>O is too low to account for it. A. J. M.

**Silica-glass from the Libyan desert.** P. A. CLAYTON and L. J. SPENCER (*Min. Mag.*, 1934, 23, 501—508).—Wind-worn lumps, up to 10 lb., of clear, pale greenish-yellow SiO<sub>2</sub>-glass, suitable for cutting as gemstones, have been found in large amount on the surface of the desert 500 miles S.W. of Cairo. Analysis [by M. H. HEY] gave SiO<sub>2</sub> 97.58, TiO<sub>2</sub> 0.21, Al<sub>2</sub>O<sub>3</sub> 1.54, Fe<sub>2</sub>O<sub>3</sub> 0.11, FeO 0.23, CaO 0.38, Na<sub>2</sub>O 0.34, H<sub>2</sub>O 0.10, NiO, MnO, MgO traces, total 100.49;  $d$  2.206,  $n_D$  1.4624. The material is compared with tektites, but its origin is obscure. L. J. S.

**Metasomatism in flint nodules in the Scawt Hill contact-zone.** C. E. TILLEY and A. R. ALDERMAN (*Min. Mag.*, 1934, 23, 513—518).—Flint nodules in the chalk of Co. Antrim have been altered by the

intrusion of dolerite, showing a progressive change from granular quartz to an assemblage of wollastonite, melilite, and alkali-pyroxene with pectolite and xenotilite, but without any change in the vol. and shape of the nodules. Analyses are given of the material at the various stages, and the nature and origin of the solutions that effected the change are discussed.

L. J. S.

**Zeolites. VI. Edingtonite.** M. H. HEY [with F. A. BANNISTER] (*Min. Mag.*, 1934, 23, 483—494).—Analysis of edingtonite from Böhlet, Sweden, gave  $\text{SiO}_2$  35.35,  $\text{Al}_2\text{O}_3$  19.98,  $\text{BaO}$  38.83,  $\text{CaO}$  0.10,  $\text{Na}_2\text{O}$  0.04,  $\text{K}_2\text{O}$  0.65,  $\text{H}_2\text{O}$  13.11=100.06,  $d$  2.777, and the orthorhombic unit cell,  $a$  9.56,  $b$  9.68,  $c$  6.53 Å., contains  $\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{30}\cdot 8\text{H}_2\text{O}$ . The rarer edingtonite from Old Kilpatrick, Scotland, is apparently tetragonal with  $a$  9.585,  $b$  9.585,  $c$  6.53 Å., but the two minerals appear to be essentially identical, the difference shown by them being due to an appreciable amount of Ca in the Scottish mineral. Optical data and v.-p. curves are given for the Böhlet mineral. By base-exchange  $\text{Ti}^{\text{I}}$  and Ag edingtonites were prepared. The K and Na base-exchange products (pseudo-edingtonites) have a unit cell about eight times as large as that of edingtonite.

L. J. S.

**Geochemistry of strontium [and barium].** W. NOLL (*Chem. Erde*, 1934, 8, 507—600).—Full details are given (cf. A., 1933, 1030). Many determinations were made of the minute amounts of Sr present in a variety of minerals and in igneous and sedimentary rocks. The average amount of both SrO and BaO in igneous rocks is about 0.05%, but Sr has a preference for alkali-rocks, whilst Ba occurs more in granitic rocks. In the minerals of sedimentary rocks Sr is associated with Ca, but more in aragonite and anhydrite than in calcite, gypsum, and dolomite.

L. J. S.

**Contact-metamorphic limestones in Spessart.** R. MOSEBACH (*Chem. Erde*, 1934, 8, 622—662).—Calc-silicate rocks and their minerals (phlogopite, chondrodite, etc.) are described. An analysis of a mineral related to picrosmine occurring as veins in the rock is given.

L. J. S.

**Ball sandstone in Thuringia.** H. JUNG (*Chem. Erde*, 1934, 8, 601—612).—Spherical concretions 2.5—3 cm. in diameter occur in the Middle Bunter sandstone at Kahla. Analysis of the balls and of the matrix show an addition of 33.03%  $(\text{Ca}, \text{Mg}, \text{Fe})\text{CO}_3$  in the balls.

L. J. S.

**Origin of sulphur deposits.** F. AHLFELD (*Chem. Erde*, 1934, 8, 613—621).— $\text{SO}_4^{''}$  in mineral oils may give  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , and the  $\text{H}_2\text{S}$  coming to the surface in contact with  $\text{O}_2$  deposits S.

L. J. S.

**Origin of volcanic sulphur from observations of the craters of volcanoes in S. Italy.** O. VON DEINES (*Naturwiss.*, 1934, 22, 129—134).—Three reactions are supposed to give rise to the S found in volcanic districts: (i)  $\text{SO}_2 + \text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}$ . The kinetics of this reaction are examined. It is also necessary to take into account the thermal dissociation of the  $\text{H}_2\text{S}$ , and the action of  $\text{SO}_2$  on the  $\text{H}_2$  thus produced. In a gas consisting of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{S}_2$ , and  $\text{H}_2$ ,  $\text{SO}_2$  remains const.,  $\text{H}_2\text{S}$  dis-

appears, and  $\text{H}_2$  increases if the temp. is raised from 700° to 1000°. The action of  $\text{H}_2$  on the sulphide magma ( $\text{FeS}_2$  or  $\text{FeS}$ ) is also considered. (ii) Hydrolysis of S can occur at  $> 100^\circ$ , forming  $\text{H}_2\text{S}$  and  $\text{H}_2\text{SO}_3$ , from which polythionic acids and their decomp. products ( $\text{S}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_4$ , etc.) are produced. (iii) The decomp. of  $\text{H}_2\text{SO}_4$  at high pressures:  $3\text{H}_2\text{SO}_3 = 2\text{H}_2\text{SO}_4 + \text{S} + \text{H}_2\text{O}$ . All the above reactions may occur at various depths.

A. J. M.

**Eruptive rocks of the Trias of Wezzan (Morocco).** J. BOURCART and G. CHOUBERT (*Compt. rend.*, 1934, 198, 960—963).—In addition to sericite schists, red sandstones, marbles, clays with foetid limestones and gypsum, dolomites, and grey limestone, there are associated with the Triassic rocks a large variety of granites (including syenites, monzonites, diorites, and gabbros), gneisses (with leptynites, and orthoamphibolites), and episyenites (with ophites and a hauyne phonolite), exhibiting two metamorphoses separated by crushing.

C. A. S.

**Basic rocks, intrusive and metamorphic, of the Kasai (Belgian Congo).** M. E. DENAEYER (*Compt. rend.*, 1934, 198, 956—958).—These include hypersthene-gabbros, dolerites passing into basalts, with spessartite and ariegites, all apparently derived from the same magma; associated with them are amphibolites, much diopside, and an orthoamphibolite containing zoisite. Mt. Musungu consists of a dark red rock made up of red garnet, magnetite, and hypersthene, with vein quartz.

C. A. S.

**Alteration of feldspars in granite sands of the Vosges.** A. S. MIHARA (*Compt. rend.*, 1934, 198, 955—956).—The white altered feldspars of the sands, etc. formed from the granite of Hohwald (Vosges) consist of 55% soda-lime feldspar, 36 phyllite (28 sericite+8 kaolinite) and 9 free  $\text{SiO}_2$ . Analyses of granite in which the feldspar was sericitised, but had not disintegrated, compared with one of the granite sand show insufficient  $\text{Al}_2\text{O}_3$  in the former for kaolinite to be present there as such; it must therefore result from sub-aërial action accompanying disintegration.

C. A. S.

**Chemical modifications of clay in typical Yugoslavian red earth and podsol.** S. NIKOLIĆ (*Bull. Soc. Chim. Yougoslav.*, 1933, 4, 157—167).—Various clays (I) are capable, in contradistinction to kaolin, of combining with both acids and alkalis. The combining power of (I) diminishes with the depth from which the sample is taken.

R. T.

**Separation of constituents of clays.** P. URBAIN (*Compt. rend.*, 1934, 198, 964—967).—Electrolytes are removed by suspension in  $\text{H}_2\text{O}$  and thrice centrifuging. The solids are then suspended in  $\text{H}_2\text{O}$  in an inverted cylindrical vessel closed by a cap, and subjected to a vertical electric field of approx. 100 volts per cm.; positive below. The negative colloids are subsequently separated from the cryst. solids (with which they have settled to the bottom) by a similar method, whilst the positive colloids remain in suspension. All trace of electrolytes is finally removed by electro dialysis, and four fractions are obtained: cryst. solids, positive colloids (metallic hydroxides), negative colloids (Al silicates), and a saline solution.

C. A. S.



**Metallogenetics of the Caucasus.** L. A. VARDANJANTZ (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1145—1162).—Four geological epochs are distinguished in connexion with the origin of various Caucasian ores.

R. T.

**Mineralogy of cassiterite and of certain other pegmatitic and pneumatolytic minerals.** B. N. ARTEMIYEV (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1125—1144).—Crystallographic, analytical, and other data are recorded for samples of cassiterite, wolframite, beryl, columbite, tantalite, and monazite from various localities of the U.S.S.R.

R. T.

**Viscosity of basalt glass at high temperatures.** II. K. KANI (Proc. Imp. Acad. Tokyo, 1934, 10, 79—82; cf. this vol., 385).—The viscosities of four glasses have been determined between 1150° and 1400°.

C. W. G.

**Thermal expansion of olivine.** S. KÔZU, J. UEDA, and S. TSURUMI (Proc. Imp. Acad. Tokyo, 1934, 10, 83—86).—Analyses and thermal expansions of an Egyptian olivine are recorded.

$Mg_2SiO_4 : (Fe^{II}Fe^{III}Mn)_2SiO_4 = 89.92 : 10.08$ .

C. W. G.

**Thermal expansion of augite.** S. KÔZU and J. UEDA (Proc. Imp. Acad. Tokyo, 1934, 10, 87—90).—Vals. for specimens from Japan, Bohemia, and Rhineland are given.

C. W. G.

**Radio-geological survey of Czechoslovakia.** W. SANTHOLZER and F. ULRICH (Nature, 1934, 133, 461).—The radioactivity of the springs of the Krkonoše (Rieser Gebirge), Jizera Mts., has been systematically determined. The  $H_2O$  of the strongest springs

contains  $10^{-11}$  g. Ra per litre. Chemical and mineralogical analyses of the neighbouring rocks have also been made. At Zaly (Heidelberg on Benecko), waters become radioactive through their long contact with phyllite ( $8.3 \times 10^{-12}$  g. Ra per g.) and orthogneisses (4 to  $7 \times 10^{-12}$  g. Ra per g.).

L. S. T.

**Soil mapping.** E. OSTENDORFF (Z. Pflanz. Düng., 1934, B, 13, 119—124).—The practical val. of soil classification and mapping is discussed.

A. G. P.

**Paleo-soils in quaternary deposits in the Saar valley.** ERHART (Compt. rend., 1934, 198, 959—960).—Three old soils are described. The lowest, 1 m. thick, is a steppe soil; the two upper, each 1.8—2 m. thick, are forest soils.

C. A. S.

**Transformation of petroleum in nature.** D. C. BARTON (J. Inst. Petroleum Tech., 1934, 20, 206—213).— $CH_4$  and petroleum may be formed simultaneously, the former from a wide range of material, the latter from a limited range.

C. W. G.

**Chemical evidence for the low-temperature history of petroleum.** B. T. BROOKS (J. Inst. Petroleum Tech., 1934, 20, 177—205).—A review and discussion.

C. W. G.

**Peaty lignites and anthracitic coals.** C. MAHADEVAN (Indian J. Physics, 1933, 8, 259—268).—The cellulose : lignin ratio decreases during the early stages of coal development, but increases again in later stages, indicating that lignin is the more resistant initially, but cellulose later. The ratio provides an index of the stage of coal development.

J. W. S.

## Organic Chemistry.

**Pyrolysis of the lower paraffins. V. Conversion of the gaseous paraffins into aromatics in baffled metal tubes and the chemical composition of the products.** A. CAMBRON and C. H. BAXLEY (Canad. J. Res., 1934, 10, 145—163; cf. B., 1934, 308).—"Recycling" of  $C_3H_8$  in baffled steel tubes (Cr 18%, Ni 8%) affords some liquid (I), but the deposit of C diminishes the utility of the tubes. The catalytic activity (II) of the alloy does not decrease on prolonged use, is variable, and depends on (II) of a surface oxide film. When 28% Cr (Ni-free) baffles are used, more (I) and a higher light oil/tar ratio result. In steel tubes (Cr 28%, Ni 0%) C is not deposited; 20% of (I) is formed at 850° under the best conditions of flow, and increase of pressure up to 1 atm. increases the yield of (I) without increasing C deposition. Pyrolysis of  $C_3H_8$  affords a product separated into olefines (mostly  $C_2H_4$ ), butadiene, light oil containing  $C_6H_6$  (64%), PhMe (14%), styrene (7.8%), xylene and cyclopentadiene in traces, and a tar which contains  $C_{10}H_8$  (25%), anthracene (12.5%), also  $C_{10}H_7Me$ ,  $C_{10}H_6Me_2$ , and phenanthrene.

J. L. D.

**Neopentyl deuteride.** F. C. WHITMORE, G. H. FLEMING, D. H. RANK, E. R. BORDNER, and K. D. LARSON (J. Amer. Chem. Soc., 1934, 56, 749).—Mg neopentyl chloride (I) and distilled  $H_2O$  give neo-

pentane (II), m.p.  $-21^\circ$  to  $-20^\circ$ . (I) and  $H_2O$  ( $d$  1.0735) afford a mixture (A), m.p.  $-22^\circ$  to  $-21^\circ$ , of (II) and neopentyl deuteride (III); the presence of (III) is shown by the Raman spectrum (appearance of a line at approx.  $\Delta\epsilon = 2150$   $cm^{-1}$  shift from the exciting line; due to the  $C-H^2$  vibration). (A) and (II) show differences in b.p. and  $n$ .

H. B.

**Catalytic micro-hydrogenation of organic compounds.** R. KUHN and E. F. MÖLLER (Angew. Chem., 1934, 47, 145—149).—Apparatus and technique for a differential manometric method of determining double linkings by catalytic hydrogenation are described. The accuracy is  $\pm 0.5\%$  on a sample of 1—5 mg.

E. S. H.

**Oxidation with organic peracids.** J. BÖESEKEN (Chem. Weekblad, 1934, 31, 166—170).—An account of the reactions of org. compounds with  $AcO_2H$  (I) and  $BzO_2H$ . The following are recorded for the first time: the rate of reaction of (I) with ethylenic compounds depends on the no. of H atoms attached to the unsaturated C atoms, the rates for the isomeric heptenes being  $CH_2:CH:C_5H_{11} < CHMe:CHBu^a$ ,  $CH_2:CMeBu^a < CHMe:CEt_2$ . Isoprene and 1 mol. of (I) gives an unsaturated acetate of a cis-diol (isopropylidene derivative with  $COMe_2$ ), containing a tert. OH. Oxidation of  $\cdot C:C \cdot$  linkings is much less

rapid than that of  $>C:C<$  and takes place by way of the  $\alpha\beta$ -diketone and the corresponding dicarboxylic acid. Aromatic amines and dil. solutions of (I) give azo- and azoxy-compounds with very small amounts of NO-compounds, but with a large excess of conc. (I) NO<sub>2</sub>-compounds are obtained. The primary oxidation product is a labile amine oxide, R·NH<sub>2</sub>·O. Conc. solutions of (I) do not explode spontaneously below 40° in the absence of catalysts (H<sub>2</sub>SO<sub>4</sub>).

S. C.

**Laboratory preparation of pure ethylene and propylene.** P. K. SSKAMIN (Ber., 1934, 67, [B], 392—393).—96—98% C<sub>2</sub>H<sub>4</sub> is obtained by passing EtOH over unglazed porcelain contained in a Cu tube heated at 400—450°. C<sub>3</sub>H<sub>6</sub> is obtained similarly at 300°.

H. W.

**Condensation of carbonyl chloride with ethylene.** S. L. VARSCHAVSKI and E. A. DOROGANJEVSKAJA (Gazzetta, 1934, 64, 53—59).—Under the conditions described by Pace (A., 1929, 1419) the authors did not obtain CH<sub>2</sub>Cl·CH<sub>2</sub>·CO<sub>2</sub>H from COCl<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>; reaction products result from the PhMe used.

E. W. W.

**Thermal decomposition of organic compounds from the viewpoint of free radicals. VII. Ethylidene radical.** F. O. RICE and A. L. GLASEBROOK (J. Amer. Chem. Soc., 1934, 56, 741—743).—When diazoethane (I) is passed through a quartz tube at 600—650° at about 0.5 mm., the Paneth effect with Sb mirrors is not shown (even at 1000°). Slow passage of (I) at 650°/2—3 mm. results in complete decomp.; the only condensable gas formed is C<sub>2</sub>H<sub>4</sub>, indicating that CHMe rearranges easily to C<sub>2</sub>H<sub>4</sub>. Decomp. of (I) in presence of CO (method; Staedinger and Kupfer, A., 1912, i, 245) gives no CHMe·CO. Thermal decomp. of acetaldehyde gives (from about 60%) N<sub>2</sub>+C<sub>2</sub>H<sub>4</sub> (2 mols.); the remainder affords a non-volatile oil, some HCN, and (probably) CH<sub>4</sub>. The Paneth effect is shown with Sb mirrors at > 700°; this is attributed to the formation of Me.

H. B.

**Action of nitrogen trioxide on allylene and dimethylbutadiene (diisopropenyl).** N. J. DEMJANOV and A. A. IVANOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 318—323).—Interaction of allylene and N<sub>2</sub>O<sub>3</sub> in cold Et<sub>2</sub>O affords a nitrosite, C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>N<sub>2</sub>, m.p. 89° (decomp.), and an unstable oil, reduced to an unstable amine, which is converted into an aldehyde and acid. Similarly, dimethylbutadiene affords a compound, C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub>, m.p. 104—105° (reduced to an amine and hydrolysed by conc. HCl to an oil which reacts with NHPH·NH<sub>2</sub>), and an oil, reduced (Zn-HCl) to a diamine, C<sub>6</sub>H<sub>10</sub>(NH<sub>2</sub>)<sub>2</sub>, b.p. about 195° [dihydrochloride (I); platinumchloride; Bz<sub>2</sub>, derivative, m.p. 241—242°]. (I) affords a pyrrole when heated.

J. L. D.

**Action of magnesium on polyhalogenated hydrocarbons in ethereal solution. IV. Action of magnesium on ethylene dibromide.** C. L. TSENG and F. M. FAM (Sci. Quart. Nat. Univ. Peking, 1934, 4, 1—7).—(CH<sub>2</sub>Br)<sub>2</sub> and Mg in dry Et<sub>2</sub>O give C<sub>2</sub>H<sub>4</sub> and MgBr<sub>2</sub>·2Et<sub>2</sub>O with, at most, a trace of the Grignard compound.

R. S. C.

**Peroxide effect in addition of reagents to unsaturated compounds. IV. Addition of halo-gen acids to vinyl chloride.** M. S. KHARASCH and C. W. HANNUM (J. Amer. Chem. Soc., 1934, 56, 712—714).—Addition of HBr to CH<sub>2</sub>:CHCl (I) [which is more sensitive to "peroxides" than CH<sub>2</sub>:CHBr or CH<sub>2</sub>:CH·CH<sub>2</sub>Cl(Br) (cf. A., 1933, 805)] in a vac. or in presence of air, Bz<sub>2</sub>O<sub>2</sub>, or ascaridole in the dark at room temp. gives 73—87% of CH<sub>2</sub>Br·CH<sub>2</sub>Cl (II) (the "abnormal" product); the peroxide effect is destroyed by addition of anhyd. FeCl<sub>3</sub>, and CHMeClBr (III) (the "normal" product) is then obtained. (III) also results in presence of good antioxidants (IV) in the dark. The effect of (IV) is almost completely destroyed and the velocity of the "abnormal" reaction is increased enormously by sunlight or artificial light at 0°—room temp.; addition occurs more rapidly and the amount of (III) is decreased at 76° in the dark. Addition in presence of PhNO<sub>2</sub> and *s*-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub> in a vac. in the dark gives products containing 29 and 95%, respectively, of (III); the % of (III) is increased (in AcOH also) by addition of (IV), but in presence of air and no (IV), (II) is practically the sole product. Addition of HCl to (I) occurs only in presence of a catalyst such as FeCl<sub>3</sub>; CHMeCl<sub>2</sub> is the sole product (cf. Wibaut and van Dalfsen, A., 1932, 819). Addition of HI occurs rapidly in presence or absence of "peroxides" and gives CHMeCl; the "peroxide" is destroyed by the HI.

H. B.

**Preparation of chloropicrin from methane.** N. DANAILA and A. G. SOARE (Bul. Chim. Soc. Romana Stiințe, 1932, 35, 53—75).—Attempts to prepare MeNO<sub>2</sub> from CH<sub>4</sub> were unsuccessful. Max. utilisation (13%) of Cl<sub>2</sub> for production of liquid products is obtained when CH<sub>4</sub> and Cl<sub>2</sub> are passed through a SiO<sub>2</sub> tube at 400—420°; in presence of C activated with Fe<sub>2</sub>O<sub>3</sub> 40.5% of the Cl<sub>2</sub> is so utilised at 355°. Using 1 : 3 mixtures of CH<sub>4</sub> and Cl<sub>2</sub>, passed at a rate of 0.24 litre per min. over a pumice-CuCl<sub>2</sub> catalyst at 360—370°, 41% utilisation of Cl<sub>2</sub> is achieved, to yield a product containing 63% of CHCl<sub>3</sub> and 30% of CCl<sub>4</sub>. CCl<sub>4</sub> is readily reduced by the ordinary methods, to yield 70% of CHCl<sub>3</sub>, and 30% of products of further reduction. 58% yields of CCl<sub>3</sub>·NO<sub>2</sub> are obtained by heating CHCl<sub>3</sub> with HNO<sub>3</sub> (*d* 1.52) at 140—150° during 2 hr.

R. T.

**Determination of hydroxyl groups in alcohols and phenols by benzoylation in tetrahydronaphthalene at high temperatures.** T. M. MELJER (Rec. trav. chim., 1934, 53, 387—397).—The OH-compound is heated with BzCl or, better, *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COCl (I), in boiling tetrahydronaphthalene and the HCl produced swept out by dry air or H<sub>2</sub> (for readily oxidisable substances) and absorbed in H<sub>2</sub>O. In most cases, > 90% of the theoretical amount of HCl is evolved; exceptions are glycerol (48.2%) and C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub> (62%) (using BzCl), and *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> (74%) [with (I)]. With BzCl and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>, *p*-OEt·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>, *p*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>, and *p*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub>, the amounts of HCl evolved are 17.7, 22.5, 74, and 84%, respectively. The following are described: benz-*p*-anisidide, m.p. 158—162° (lit. 154.5°), *p*-phenetidide, m.p. 174.5—175.5° (lit.

173°), and *p*-chloroanilide, m.p. 193—194.5° (lit. 187—187.5°); *Ph*, m.p. 127°, *benzyl*, m.p. 83.5—84°, and *cyclohexyl*, m.p. 42—43°, *p*-nitrobenzoates; *resorcinol di-p-nitrobenzoate*, m.p. 175°; *pyrocatechol di-m-nitrobenzoate*, m.p. 144°. H. B.

**Yacarov, a secretion of the glands of alligators.** G. FESTER and F. BERTUZZI (Ber., 1934, 67, [B], 365—370).—The liquid wax, which constitutes about 35—63% of the gland, yields when hydrolysed small amounts of volatile fatty acids, chiefly unsaturated acids with one double linking, palmitic and myristic acids. P is present in small amount, but lecithin cannot be detected with CdCl<sub>2</sub>. The non-saponifiable material contains small amounts of volatile and non-volatile nitrogenous bases, glycerol, cholesterol, cetyl alcohol, and *yacarov* (I), to which the odour of musk is due. (I), b.p. 234° (corr.)/757 mm., f.p. -10°, appears to be a primary alcohol of simple structure, possibly identical with βζ-dimethyl-Δ<sup>8</sup>-hepten-α-ol. It is not directly related to muscone or zibetone. H. W.

**Butane-βγ-diol and its derivatives. I. Halogenhydrins of ψ-butylene.** M. V. LICHOSCHERSTOV and S. V. ALEXEEV (J. Gen. Chem. Russ., 1933, 3, 927—932).—Solutions of NH<sub>2</sub>·CO·NHCl containing 5% of AcOH react with gaseous or liquid ψ-butylene (I) at 15° (CuCl<sub>2</sub> catalyst) to afford a 4 : 1 mixture of β-chlorobutan-γ-ol (*Ac*, b.p. 152—156°, and *Bz* derivative, b.p. 263—265.5°) and βγ-dichlorobutane (II); the proportion of (II) increases with the acidity of the reaction mixture. 80% yields of β-bromobutan-γ-ol, b.p. 152—154° (*Ac* derivative, b.p. 165—167°), and βγ-dibromobutane (20%) are obtained from (I) and aq. NHBrAc containing 3% of AcOH. β-Iodobutan-γ-ol, an oil, decomposing at 65° to yield COMeEt, is prepared from the oxide of (I) and HI. R. T.

**Synthesis of acetopropyl alcohol.** I. L. KNU-  
NIANZ, G. B. TSHELINTSEV, and E. D. OSEIROVA  
(Compt. rend. Acad. Sci. U.R.S.S., 1934, 1,  
312—314; cf. A., 1901, i, 538).—Interaction of Et  
sodioacetoacetate with (CH<sub>3</sub>)<sub>2</sub>O in EtOH at 0° during  
24 hr. affords α-aceto-γ-butyrolactone, b.p. 142—  
143°/30 mm., hydrolysed by warm 5% HCl in 2 hr.  
to δ-keto-*n*-amyl alcohol, b.p. 115—116°/30 mm.

J. L. D.

**Reaction between primary aliphatic alcohols and sulphuric acid.** C. M. SUTER and E. OBERG (J. Amer. Chem. Soc., 1934, 56, 677—679).—The figures quoted after the following alcohols are the amounts (%) of ester (RHSO<sub>4</sub>) formed at equilibrium from approx. equimol. amounts of ROH and 96.7% H<sub>2</sub>SO<sub>4</sub> and 5.2, 22.6, and 31.98% oleum, respectively, at 25°: MeOH, 61.2, 66, 70.5, 73.2; EtOH, 52.6, 59.8, 65.1, 67.7; CH<sub>2</sub>Cl·CH<sub>2</sub>OH, 55, 59.8, 66.7, 70; Pr<sup>o</sup>OH, 56.8, 61.9, 67.3, 70.6; Bu<sup>o</sup>OH, 58.8, 63.9, 68.1, 71.5; Bu<sup>β</sup>OH, 60.8, 65.7, —, —; *n*-amyl alcohol, 59.2, 64.4, —, —; *n*-hexyl alcohol, 58.3, 63.3, —, —. Appreciable quantities of coloured by-products are formed in the last three cases with the more conc. oleums. In general the val. of the equilibrium const. (highest for MeOH and lowest for EtOH) increases with decrease in the concn. of H<sub>2</sub>O in the reaction mixture. H. B.

**Relative mobilities of the propyl and isopropyl groups and their mono- and di-chloro-derivatives.** P. CARRÉ and J. PASCHE (Compt. rend., 1934, 198, 939—940).—Substitution by Cl decreases successively the mobility of the Pr<sup>α</sup> and Pr<sup>β</sup> groups, the effect being greater with a Me than with a CH<sub>2</sub> group. Pr<sup>α</sup>, *γ*-chloro-, b.p. 111—112°/21 mm., and βγ-dichloro-propyl chlorosulphite, b.p. 110—111°/3 mm., partial decomp. at 15 mm., obtained from SOCl<sub>2</sub> and the appropriate alcohol, decompose at 34—35°, 51°, and 61°, respectively. CH<sub>2</sub>Cl·CHMe·OH or CH(CH<sub>2</sub>Cl)<sub>2</sub>·OH with SOCl<sub>2</sub> and C<sub>5</sub>H<sub>5</sub>N affords di-β-chloroisopropyl, b.p. 155—158°/37 mm., or di-ββ'-dichloroisopropyl sulphite, b.p. 215°/30 mm., which with SOCl<sub>2</sub> yield β-chloro- (I), b.p. 86—88°/20 mm., and ββ'-dichloro-isopropyl chlorosulphite (II), b.p. 120°/20 mm. SOCl·OPr<sup>β</sup>, (I), and (II) decompose at 24°, 39°, and 70°, respectively. R. S. C.

**Systematics and nomenclature of the phosphatides.** R. ROSENBUSCH (Z. Unters. Lebensm., 1934, 67, 258—268; cf. B., 1933, 330, 651).

E. C. S.

**Halides of vinyl sulphides.** S. M. KLIGER (J. Gen. Chem. Russ., 1933, 3, 904—908).—(CH<sub>2</sub>Cl·CHCl)<sub>2</sub>SO (I) is reduced to (CH<sub>2</sub>Cl·CHCl)<sub>2</sub>S (II) by HBr in AcOH, and (CHCl·CH)<sub>2</sub>S (III) is obtained by distilling (II) under reduced pressure; the corresponding Br derivatives are prepared analogously. (I), on treating with PCl<sub>5</sub>, yields the compound CHCl<sub>2</sub>·CHCl·S·CHCl·CH<sub>2</sub>Cl, which on distillation under reduced pressure affords the compound CHCl<sub>2</sub>·CHCl·S·CH·CHCl, b.p. 95—97°/5 mm.

R. T.

**Direct synthesis of acid fluorides from acids and preparation of formyl fluoride.** A. N. NESMEJANOV and E. J. KAHN (Ber., 1934, 67, [B], 370—373).—AcF is obtained in very good yield by interaction of AcCl and KF in Ac<sub>2</sub>O or AcOH. AcF is also obtained exclusively when a higher acyl chloride is substituted for AcCl owing to the change R·COCl + AcOH = R·CO<sub>2</sub>H + AcCl and the greater volatility of AcF. On this principle, numerous examples are quoted of the conversion of an acid, R·CO<sub>2</sub>H, which dissolves KF into R·COF by the action of BzCl. CPhCl<sub>3</sub> may replace BzCl. Formyl fluoride, b.p. about -26°/750 mm., is obtained from BzCl, KF, and HCO<sub>2</sub>H. H. W.

**Organic catalysts. VIII. Esterase model.** W. LANGENBECK and J. BALTES (Ber., 1934, 67, [B], 387—391; cf. A., 1933, 22).—In the case of polymeric vinyl acetate in quinoline and KOAc in Pr<sup>β</sup>OH at 160°, alkyl interchange is accelerated by CH<sub>2</sub>Ph·OH, α-C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>·OH, CH<sub>2</sub>Bz·OH (I), and, notably, by glycollanilide (II). Hydrolysis of Pr<sup>o</sup>CO<sub>2</sub>Me is hastened 4—5-fold by (II) and 6—7-fold by (I). Similar results are recorded for olive oil partly dissolved by Na deoxycholate. Addition of Pr<sup>o</sup>OH causes retardation. The possibility that esterase is an activated alcohol is expressed.

H. W.

**Catalytic hydrogenation of unsaturated compounds. II. Step-wise reduction of conjugated acids.** E. H. FARMER and L. A. HUGHES (J.C.S., 1934, 304—307).—Re-examination of the 50% hydro-

generation of sorbic acid (I) using a small amount of  $\text{PtO}_2 \cdot \text{H}_2\text{O}$  in EtOH has confirmed the results previously obtained (A., 1932, 365; 1933, 257, 935); the dihydro-derivatives formed are determined by isolation (as such or simple derivatives) and direct weighing. Dihydro-derivatives are also obtained from muconic acid (II) (as Na salt in  $\text{H}_2\text{O}$ ); *trans*- $\Delta^1$ -dihydromuconic acid has been obtained for the first time in the homogeneous condition. The failure of Ingold and Shah (A., 1933, 935) to detect the presence of dihydro-derivatives in the reduction products from (I), the Et ester of (II), and  $\beta$ -vinylacrylic acid is probably due to the use of an unsuitable analytical procedure. Much more complete reduction of (I) and (II) to dihydro-derivatives has been found using a Ni catalyst. H. B.

**Hydrogenation of ricinoleic acid by hydrazine hydrate.** J. VORIŠEK (Chem. Listy, 1934, 28, 57—58).— $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  and ricinoleic acid at room temp. yield  $\lambda$ -hydroxystearic acid (*Me*, m.p. 57—58°, *Et*, m.p. 52.5—53°, *Pr*, m.p. 50—51°, *Pr* <sup>$\beta$</sup> , m.p. 47—47.5°, *Bu* <sup>$\beta$</sup> , m.p. 40°, and *isoamyl*, m.p. 35°, ester). R. T.

**Examination of hydroxy-acids produced by oxidising paraffin with air.** P. P. SCHORIGIN and A. P. KRESCHKOV (J. Gen. Chem. Russ., 1933, 3, 825—830).—The products obtained by passing air through paraffin at 52° consists of a mixture of hydrocarbons, fatty acids and OH-acids, and their anhydrides, lactones, and lactides, amongst which the acids  $\text{C}_{13-17}\text{H}_{26-34}(\text{OH}) \cdot \text{CO}_2\text{H}$  and  $\text{C}_{35}\text{H}_{69}(\text{OH}) \cdot \text{CO}_2\text{H}$  (I) [as *lactone*, m.p. 58—59.4°, obtained by hydrolysing the *Me* ester, m.p. 46—48°, of (I)] are identified. R. T.

**Determination of acetyl values of lipins applicable to hydroxylated fatty acids.** E. S. WEST, C. L. HOAGLAND, and G. H. CURTIS (J. Biol. Chem., 1934, 104, 627—634).—The sample is acetylated with a mixture of  $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  (hot or cold), excess of  $\text{Ac}_2\text{O}$  is decomposed with hot  $\text{H}_2\text{O}$ , BuOH added to give a homogeneous solution, and the mixture titrated with alcoholic alkali with phenolphthalein as indicator. Another sample, treated with  $\text{C}_5\text{H}_5\text{N}$  only, is similarly titrated and the difference subtracted from a blank on the  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  mixture. A new definition of Ac val. is proposed: mg. of Ac taken up per g. of substance. W. O. K.

**Moderated oxidation of bixin.** V. VIEBÖCK (Ber., 1934, 67, [B], 377—383).—Methylbixin (I) rapidly absorbs 2O when treated with  $\text{Mn}(\text{OAc})_3$  in AcOH, whereas subsequent oxidation proceeds very slowly. The product is a mixture of hydroxytriacetoxyl- and dihydroxydiacetoxyl-compounds, whereas *hydroxytrihydroxytetrahydromethylbixin* (II) is obtained if  $\text{Ac}_2\text{O}$  is added to the mixture. OH is *tert.*, since further acetylation appears impossible. Bixin and norbixin behave similarly, but yield less definite compounds owing to partial production of lactone or lactide. The yellow compounds very readily lose AcOH. Thus, treatment of (II) with boiling AcOH gives a red product poorer than (II) by 1 AcOH, but retaining OH, a similar change appearing to be induced by alkaline hydrolysis, whereby a ketodihydroxy-acid is produced. Hydrogenation of the

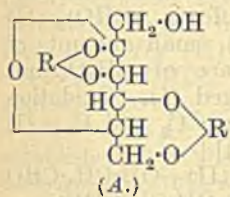
triacetate from bixin followed by alkaline hydrolysis and immediate treatment with  $\text{Me}_2\text{SO}_4$  leads to *keto-dihydroxyperhydromethylbixin* (III). Treatment of (III) with  $\text{Pb}(\text{OAc})_4$  in AcOH gives in poor yield an *ester-aldehyde* (IV),  $\text{C}_{13}\text{H}_{24}\text{O}_3$ , which readily gives a peroxide when exposed to air, and hence is converted during repeated distillation into an ester-acid (*Ag* salt), also obtained by oxidation with  $\text{CrO}_3$ ; this appears homogeneous. In the production of (IV) the original mol. is halved, but rupture appears also to occur at other points of the mol. Treatment of (I) with  $\text{Mn}(\text{OAc})_3$  in  $\text{CHCl}_3$  causes addition of 1 OH and 1 OAc. H. W.

**Enolates of carbonyl compounds. I. Dienolate of ethyl dibenzoylsuccinate.** H. LOHAUS (Annalen, 1934, 509, 130—137).—Et  $\alpha'$ -dibenzoylsuccinate (I) (mainly the  $\beta$ -ester, m.p. 128°; cf. Knorr, A., 1897, i, 63) and EtOH-KOEt give the  $K_2$  salt (II) of a dienolic form. (II) and BzCl in  $\text{Et}_2\text{O}$  afford (mainly) a *dibenzoate*, m.p. 121—122°, and a little of the *dibenzoate* (III), m.p. 203°, described by Paal and Härtel (A., 1897, i, 598). (II) and  $\text{Et}_2\text{O}-\text{I}$  yield Et dibenzoylfumarate, whilst acidification (dil.  $\text{H}_2\text{SO}_4$ ,  $\text{Et}_2\text{O}$  at 0°) gives a liquid enol (blood-red colour with  $\text{FeCl}_3$ ) which changes fairly rapidly to (I). (II) does not possess the same configuration as the  $\text{Na}_2$  salt of (I); this with  $\text{Et}_2\text{O}-\text{I}$  gives Et dibenzoylmaleate, whilst acidification yields a stable enol (bluish-violet colour with  $\text{FeCl}_3$ ), and with BzCl, (III) results. Et  $\alpha'$ -diacetylsuccinate (IV) and EtOH-KOEt give a solid  $K_2$  salt (cf. Willstätter and Clarke, A., 1914, i, 286), which with  $\text{Et}_2\text{O}-\text{I}$  yields a little Et diacetylfumarate, and with  $\text{Et}_2\text{O}-\text{BzCl}$  affords a little of the *dibenzoate* (V), m.p. 108°, described by Paal and Härtel (*loc. cit.*), and much oil. (IV) and EtOH-NaOEt in  $\text{Et}_2\text{O}$  give a  $\text{Na}_2$  salt (+EtOH), which with  $\text{Et}_2\text{O}-\text{BzCl}$  yields varying amounts of (V). H. B.

**Reductic acid, a strongly reducing degradation product from carbohydrates. II.** T. REICHSTEIN and R. OPPENAUER (Helv. Chim. Acta, 1934, 17, 390—396).—Reductic acid (I) (A., 1933, 1299) is oxidised by EtOH-I (+AgCl+ $\text{Ag}_2\text{CO}_3$ ) to 1:2:3-triketocyclopentane (as hydrate), which with  $\text{NPh} \cdot \text{NH}_2$  gives a 1:3-*diphenylhydrazone*, m.p. 248° (corr., decomp.) (*loc. cit.*), and, at 145°, a *triphenylhydrazone*, m.p. 207—208° (corr., decomp.). Oxidation of (I) with  $\text{Ag}_2\text{CO}_3$  at 10° gives  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ . With  $\text{Ac}_2\text{O}-\text{AcCl}$  (I) gives a  $\text{Ac}_2$  derivative, b.p. 112°/0.2 mm., reduced ( $\text{PtO}_2-\text{H}_2$  in AcOH) to a separable mixture of *cyclopentyl* acetate and the  $\text{Ac}_2$  derivative of *cis-cyclopentane*-1:2-diol. The structure (3-keto- $\Delta^1$ -cyclopentene-1:2-diol) assigned to (I) is thus confirmed, the 1-OH group most probably being the acidic one. J. W. B.

**Glucoreductone for standardisation of 2:6-dichlorophenol-indophenol solutions for determination of ascorbic acid.** Z. I. KERTESZ (J. Biol. Chem., 1934, 104, 483—485).—A solution of reductone, obtained by warming glucose with NaOH under standard conditions and addition of HCl, is used for the standardisation of indophenol solutions. H. D.

**Synthesis of l-ascorbic acid (vitamin-C).** T. REICHSTEIN and A. GRÜSSNER (Helv. Chim. Acta, 1934, 17, 311—328).—With the appropriate ketone and  $H_2SO_4$  or anhyd.  $CuSO_4$ , l-sorbose (I) affords its mono-, b.p.  $135^\circ/0.3$  mm., m.p.  $93^\circ$ ,  $[\alpha]_D^{20} +7.02^\circ$  in  $H_2O$ , and di-, m.p.  $77-78^\circ$ ,  $[\alpha]_D^{20} -18.1^\circ$  in  $COMe_2$ , isopropylidene, dimethylene, b.p.  $132^\circ/0.2$  mm., m.p.  $77-78^\circ$ ,  $[\alpha]_D^{20} -45.7^\circ$  in  $H_2O$ , and di-( $\alpha$ -methyl-n-propylidene), b.p.  $140^\circ/0.6$  mm., m.p.  $96-99^\circ$ ,  $[\alpha]_D^{20} -16.6^\circ$  in  $COMeEt$ , derivatives, all of type A, oxidised by  $KMnO_4-KOH$  to diisopropylidene- +  $H_2O$  (II), m.p.  $98-99^\circ$  (decomp.) (K salt  $[\alpha]_D^{18} -13.8^\circ$  in  $H_2O$ ), dimethylene-, m.p.  $129-130^\circ$ ,  $[\alpha]_D^{18} -43.25^\circ$  in  $H_2O$ , di-( $\alpha$ -methyl-n-propylidene)- +  $H_2O$



m.p.  $95-100^\circ$ , and dibenzylidene-, m.p.  $202-204^\circ$  (corr.) [from the corresponding syrupy derivative of (I)],  $\alpha$ -keto-l-gulonic acid. When hydrolysed by boiling  $H_2O$ , (II) affords  $\alpha$ -keto-l-gulonic acid (III), m.p.  $121^\circ$  (corr., decomp.),  $[\alpha]_D^{20} -48.0^\circ$  in  $H_2O$  (Et ester,  $[\alpha]_D^{20} -145^\circ$  in EtOH) [(IV) in mother-liquor]. When (III) is heated with  $CO_2$ -saturated  $H_2O$ , or better its Me ester, m.p.  $155-157^\circ$ ,  $[\alpha]_D^{18} -25.0^\circ$  in MeOH, is heated with  $NaOMe-MeOH$ , in  $CO_2$  or  $N_2$ , l-ascorbic acid (IV), chemically and physiologically identical with the natural product, is obtained, the overall yield being 25—30 g. of (IV) from 100 g. of (I). J. W. B.

**Synthesis of hexuronic acids.** V. **Synthesis of l-mannuronic acid from l-mannosaccharic acid.** C. NIEMANN, R. J. McCUBBIN, and K. P. LINK. VI. **Synthesis of l-galacturonic acid from l-galactose.** C. NIEMANN and K. P. LINK (J. Biol. Chem., 1934, 104, 737—741, 743—746; cf. this vol., 280).—V. l-Arabinose by  $HCN-Ba(OH)_2$  gives  $\gamma$ -d-mannonolactone, m.p.  $149-150^\circ$ ,  $[\alpha]_D^{20} -52^\circ$ , oxidised to l-mannosaccharic acid, m.p.  $183-185^\circ$ ,  $[\alpha]_D^{20} -202.5^\circ$ , whence, by the authors' standard methods, are obtained Ba,  $[\alpha]_D^{20} +4 \pm 1^\circ$  in  $H_2O$  (containing 30% of an unidentified, inactive, non-reducing substance) (p-bromophenylhydrazone), and brucine d-mannuronate, m.p.  $155.5-156.5^\circ$  (decomp.),  $[\alpha]_D^{20} -22 \pm 2^\circ$  in  $H_2O$ , and l-mannuronolactone (I), m.p.  $143-144^\circ$  (decomp.),  $[\alpha]_D^{20} -92 \pm 2^\circ$  in  $H_2O$  (max.). (I) and its salts give characteristic aldehyde reactions. l- and d-(I), when mixed, sinter at  $138-140^\circ$  and melt at  $155^\circ$  with decomp., probably owing to formation of a racemate.

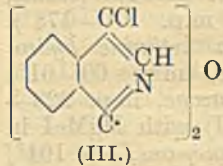
VI. The mixture of l-galactose and d-xylose obtained from flax-seed mealage was converted into the diisopropylidene compounds, b.p.  $140-150^\circ/0.018$  mm.,  $[\alpha]_D^{20} +34^\circ$ , which are oxidised by  $KMnO_4$  to diisopropylidene-l-galacturonic acid, m.p.  $152-154^\circ$ ,  $[\alpha]_D^{20} +80 \pm 3^\circ$  in  $CHCl_3$  (K salt,  $+0.5H_2O$ ), hydrolysed by hot  $H_2O$  to l-galacturonic acid,  $+H_2O$ , m.p.  $162-163^\circ$  (decomp.) after sintering at  $112-113^\circ$  [oximehydroxylamine salt of this and of the d-isomeride,  $+H_2O$ , m.p.  $151-152^\circ$  (decomp.)]. R. S. C.

**Catalytic preparation of aldehydes and ketones from monohalides of hydrocarbons.** P. SCHORIGIN and I. LOSEV (J. Gen. Chem. Russ., 1933, 3, 821—824).—The products obtained by passing various halides over a  $V_2O_5$  catalyst in presence of air and

$H_2O$  at  $360-400^\circ$  were: iso- $C_6H_{11}Br$ ,  $Bu^{\beta}CHO$  (I) 25,  $Bu^{\beta}CO_2H$  (II) 6—10, isoamylenes (III) (as dibromides) 13—20%; iso- $C_6H_{11}Cl$ , (I) 2—3, (II) 5—7, (III) 15—20%;  $Pr^{\beta}Br$  and  $Pr^{\beta}Cl$ , respectively,  $COMe_2$  4 and 10,  $AcOH$  3 and 2,  $HCO_2H$  1.5 and 0.5,  $C_3H_6$  25 and 21%;  $CH_2Ph-CH_2Cl$ ,  $PhCHO$  35,  $BzOH$  52,  $CH_2Ph-CHO$  6,  $CHPh-CH_2$  3%; cyclohexyl chloride, cyclohexanone 48%. The chief products of reaction in the absence of air and  $H_2O$  are unsaturated hydrocarbons. R. T.

**Synthesis of aldehydes.** E. B. HERSHBERG (Helv. Chim. Acta, 1934, 17, 351—358).— $MgPhBr$  and  $CH_2-CH-CH_2Br$  (I) afford  $CH_2-CH-CH_2Ph$  (80% yield), which reacts with the  $AgI(OBz)_2$  complex of Prévost (A., 1933, 711), formed *in situ*, to give the  $Bz_2$  derivative, m.p.  $74-75^\circ$  (85% yield), of  $\gamma$ -phenyl-n-propane- $\alpha\beta$ -diol, b.p.  $163-165^\circ/15$  mm., which is obtained (84% yield) by hydrolysis with  $KOH-MeOH$ , and is oxidised by  $Pb(OAc)_4-AcOH$  to  $CH_2Ph-CHO$  (72% yield) and  $CH_2O$ . Similarly  $MgBu^{\alpha}Br$  and (I) give  $\Delta^{\alpha}$ -n-heptene, b.p.  $90.5-90.8^\circ/725$  mm. (59% yield), the  $Br_2$  additive compound, b.p.  $100-101^\circ/15$  mm. (96% yield), of which is hydrolysed by  $KOAc-EtOH$  at  $130-140^\circ$  to n-heptane- $\alpha\beta$ -diol, b.p.  $127.5-128.5^\circ/15$  mm. (86% yield), oxidised to n-hexaldehyde, isolated as its dimedon compound, m.p.  $109-109.5^\circ$ . J. W. B.

**Reduction of chloral hydrate and chloral acyl chlorides [ $\alpha\beta\beta\beta$ -tetrachloroethyl acylates].** G. W. DEODHAR (J. Indian Chem. Soc., 1934, 11, 83—86).— $CCl_3-CH(OH)_2$  is reduced ( $Al-Hg, H_2O$ ) to  $CHCl_2-CHO$  (mainly as hydrate), which with  $CH_2(CO_2H)_2$  and  $C_5H_5N$  gives  $\gamma\gamma$ -dichlorocrotonic acid (I), m.p.  $100-101^\circ$ , and a Cl-containing acid, m.p.  $117-118^\circ$ .  $\alpha\beta\beta\beta$ -Tetrachloroethyl acetate (from  $CCl_3-CHO, AcCl$ , and a little conc.  $H_2SO_4$ ) and  $CCl_3-CH(OAc)_2$  are reduced (Zn dust,  $AcOH$ ) to  $\beta\beta$ -dichlorovinyl acetate (II), b.p.  $148-149^\circ$  (dibromide, b.p.  $127^\circ/40$  mm.), and not  $CH_2Cl-CHCl-OAc$  (Curie and Millet, A., 1877, i, 188). (II) and dry  $NH_3$  in  $CHCl_3$  containing anhyd.  $Na_2SO_4$  give  $\beta\beta$ -dichlorovinylamine, m.p.  $109^\circ$ , which with  $BzCl$  and aq.  $NaOH$  affords the compound (III), m.p.  $199^\circ$  (decomp.). (II) with



$CH_2(CO_2H)_2$  in  $C_5H_5N, NPh-NH_2$ , and  $NH_2-CO-NH-NH_2$  affords (I),  $(-CH_2N-NHPh)_2$ , and  $(-CH_2N-NH-CO-NH_2)_2$ , respectively.  $\alpha\beta\beta\beta$ -Tetrachloroethyl propionate, b.p.  $120^\circ/40$  mm., and n-butyrate, b.p.  $128^\circ/36$  mm., are similarly reduced to  $\beta\beta$ -dichlorovinyl propionate, b.p.  $90-92^\circ$  (dibromide, b.p.  $145-146^\circ/39$  mm.), and n-butyrate, b.p.  $100-101^\circ/36$  mm. (dibromide, b.p.  $162-164^\circ/40$  mm.), respectively.  $\beta\beta$ -Dichlorovinyl cinnamate, m.p.  $70^\circ$  (tetrabromide, m.p.  $87-88^\circ$ ), and benzoate, m.p.  $34-35^\circ$ , are described. H. B.

**$\alpha$ -Substituted ketones.** (MME.) BRUZAN (Ann. Chim., 1934, [xi], 1, 257—358).—Interaction of the Na derivative of  $COPr^{\beta}Bu^{\gamma}$  (I) with  $MeI$  affords a mixture of (I) with di-tert-butyl ketone, b.p.  $70^\circ/43$  mm., separated by its inability to form an oxime.  $\gamma\gamma\epsilon\epsilon$ -Tetraethylheptan- $\delta$ -one, similarly prepared, has m.p.  $44^\circ$ .  $COPr^{\beta}_2$  (II) (Na derivative) with excess

of allyl iodide affords  $\delta\delta\zeta\zeta$ -tetramethyl- $\Delta^{\alpha\beta}$ -nonadien- $\epsilon$ -one, b.p. 95—96°/16 mm. Improved preps. of many similar ketones are described; purification is effected by hydrolysis of the pure oxime or semicarbazone. Ph  $\alpha$ -dimethylamyl ketone (oxime, m.p. 135—136°) is converted into  $\alpha$ -dimethylhexyl alcohol, which with  $\text{CrO}_3$  affords the aldehyde (semicarbazone, m.p. 134—135°). Substitution of H adjacent to CO in (II) by alkyl displaces the absorption curve towards the visible spectrum and increases max. absorption. At the same time CO reactivity is diminished. 4-Methyl- (semicarbazone, m.p. 168—169°) and 4-methoxy-deoxybenzoin [oxime, m.p. 118—119° (lit. 111°); semicarbazone, m.p. 148—149°] amongst other deoxybenzoin are described and their absorption spectra measured. Interaction of  $\text{CHPhMe}\cdot\text{CO}\cdot\text{NH}_2$  (III) with  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  in PhMe affords 4-methyl-meso-methyldeoxybenzoin, b.p. 188—190°/19 mm. Interaction of  $\text{CPhMe}_2\cdot\text{CO}\cdot\text{NH}_2$  and  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$  in xylene followed by HBr affords the ketimine hydrobromide, m.p. 205—206°, of 4-methoxy-meso-dimethylbenzoin, hydrolysed to the ketone, m.p. 100—101° (oxime, m.p. 193—194°; semicarbazone, m.p. 210—211°). Further methylation of meso-methyldeoxybenzoin through the Na derivative (prepared with sodamide) is established.  $\text{CHPhMe}\cdot\text{COCl}$  (IV) (prep. described) with PhOMe in boiling  $\text{CS}_2$  containing  $\text{AlCl}_3$  during 3 hr. affords 4-methoxy- (V), m.p. 58—60° (*dl*-form; semicarbazone, m.p. 125—126°) and 78—80° (*d*- or *l*-form), together with 4-hydroxy-meso-methyldeoxybenzoin, m.p. 134—135°. Similarly, (IV) with PhMe affords 4-methyl-meso-methyldeoxybenzoin (VI), b.p. 190—191°/16 mm. [semicarbazone, m.p. 150—151°; oxime, m.p. 123—124°, which is hydrolysed to (VI), m.p. 46—47°]. (V) and (VI), examined spectroscopically, show traces of impurities, probably ethylenic compounds. Interaction of  $\text{CPhMe}_2\cdot\text{CN}$  (VII) with  $\text{MgPhBr}$  affords the ketimine hydrochloride, m.p. 240—241°, hydrolysed to meso-dimethyldeoxybenzoin, m.p. 46—47° (oxime, m.p. 192—193°; semicarbazone, m.p. 176—178°). 4-Methyl-meso-dimethyldeoxybenzoin ketimine hydrochloride, m.p. 246—247° (ketone, m.p. 60—61°; oxime, m.p. 205—206°; semicarbazone, m.p. 223—224°), is prepared similarly. (VII) with  $\text{MgMeI}$  in PhMe affords  $\beta$ -phenyl- $\beta$ -methylbutan- $\gamma$ -one, b.p. 104°/17 mm. (semicarbazone, m.p. 185—186°). Similarly prepared,  $\beta$ -phenylbutan- $\gamma$ -one has b.p. 93—94°/15 mm. (semicarbazone, m.p. 172—173°). PhMe (and PhOMe) with  $\text{BzCl}$  in presence of  $\text{AlCl}_3$  affords Ph *p*-tolyl (semicarbazone, m.p. 121—122°) and Ph *p*-anisyl ketone [semicarbazone, m.p. 179—180° and 151—152° (*syn*- and *anti*-forms)], respectively. Absorption (VIII) spectra measurements of these compounds show that (a) (VIII) varies with the solvent; (b) deoxybenzoin are not enolised in EtOH or hexane; (c) the extent of (VIII) varies with the degree of substitution of the meso-C atom. J. L. D.

**Oxidation of glucose by Fehling's solution at room temperature.** H. WUNSCHENDORF and P. VALIER (Bull. Soc. Chim. biol., 1934, 16, 64—67, 68—73).—The rate of oxidation of glucose by Fehling's solution (I) at room temp. is dependent on, and the amount of oxidation independent of, the concn. of

Cu salt. The products give no further ppt. with (I) on boiling, nor do they react with  $\text{NHPh}\cdot\text{NH}_2$ . Among the products of the reaction are found  $\text{MeCHO}$ , lactic, glycuronic, tartaric, and gluconic acids.

A. I.

**Oxidative degradation of carbohydrates with lead tetra-acetate.** I. P. KARRER and K. PFAEHLER (Helv. Chim. Acta, 1934, 17, 363—368).—Oxidation of  $\alpha$ -methylglucoside (I) (1 mol.) with 1 or 2 mols. of  $\text{Pb}(\text{OAc})_4$  in AcOH affords  $(\cdot\text{CHO})_2$  (II) (0.66 and 0.33 mol., respectively), small amounts of  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (III), only a trace of  $\text{CH}_2\text{O}$ , unidentified products, and unchanged (I). Oxidation probably occurs by fission between  $\text{C}_2$  and  $\text{C}_3$ : (I)  $\rightarrow \text{OH}\cdot\text{CH}(\text{OME})\cdot\text{CHO}$   $\rightarrow$  (II) +  $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}$   $\rightarrow$  (III); and (IV)  $\rightarrow \text{CH}_2\text{O} + \text{OH}\cdot\text{CH}(\text{CHO})_2$ .

J. W. B.

**Halogenoses of the  $\beta$ -series and their application to synthesis.** VIII. Crystalline  $\beta$ - $\gamma$ -ethylgalactoside (galactofuranoside). H. H. SCHLUBACH and K. MEISENHEIMER (Ber., 1934, 67, [B], 429—430).— $\gamma$ -Galactose penta-acetate in transformed by anhyd. HCl at 20° into  $\beta$ -acetochlorogalactose, converted directly by  $\text{Ag}_2\text{CO}_3$  in moist  $\text{COMe}_2$  into galactose tetra-acetate (I) in 40% yield. (I),  $\text{Ag}_2\text{O}$ , and boiling EtI afford  $\beta$ -ethylgalactofuranoside tetra-acetate, m.p. 59° (corr.),  $[\alpha]_D^{20} -50.5^\circ$  in  $\text{CHCl}_3$ , hydrolysed by aq.  $\text{Ba}(\text{OH})_2$  to  $\beta$ -ethylgalactofuranoside, m.p. 86° (corr.),  $[\alpha]_D^{20} -97.2^\circ$  in  $\text{H}_2\text{O}$ . H. W.

**Condensation of  $\alpha$ -methylmannoside with benzaldehyde.** G. J. ROBERTSON (J.C.S., 1934, 330—332).— $\alpha$ -Methylmannoside and PhCHO at 150—155°/about 330 mm. give 4 : 6-benzylidene- $\alpha$ -methylmannoside (I), m.p. 146—147°,  $[\alpha]_D +71.7^\circ$  in  $\text{CHCl}_3$  [the benzylidene derivative, m.p. 110°, of van Ekenstein and Blanksma (A., 1906, i, 511) is probably a mixture of (I) and (III) (below)], a dibenzylidene- $\alpha$ -methylmannoside (II), m.p. 181—182° (cf. *loc. cit.*), and an isomeric dibenzylidene- $\alpha$ -methylmannoside (III), m.p. 97—98°,  $[\alpha]_D -61.3^\circ$  in  $\text{CHCl}_3$ . Methylation ( $\text{MeI}$ ,  $\text{Ag}_2\text{O}$ ,  $\text{COMe}_2$ ) of (I) affords the 2 : 3- $\text{Me}_2$  derivative, b.p. 185—190°/0.47 mm.,  $[\alpha]_D +62.7^\circ$  in  $\text{CHCl}_3$ , hydrolysed ( $N\text{-HCl}$  in aq.  $\text{COMe}_2$ ) to 2 : 3-dimethyl- $\alpha$ -methylmannoside,  $[\alpha]_D +43.5^\circ$  in  $\text{CHCl}_3$  (6- $\text{CPh}_3$  derivative, m.p. 172—173°; 4 : 6-dibenzoate, m.p. 121°,  $[\alpha]_D +52.9^\circ$  in  $\text{CHCl}_3$ ), which is then hydrolysed (8% HCl) to 2 : 3-dimethylmannose,  $[\alpha]_D +10.6^\circ$  in EtOH,  $-4.3^\circ$  in  $\text{CHCl}_3$  (oxime, m.p. 112—114°). The two CHPh groups of (II) are hydrolysed ( $\text{CHCl}_3$ -EtOH containing 0.3% dry HCl) simultaneously at the same rate. H. B.

**Reactions of carbohydrates in liquid ammonia.**

I. E. MUSKAT (J. Amer. Chem. Soc., 1934, 56, 693—695).— $\alpha$ -Methylmannoside (0.02 mol.) and K (0.08 mol.) in liquid  $\text{NH}_3$  give a  $\text{K}_4$  derivative, which with  $\text{MeI}$  ( $>0.08$  mol.) and  $\text{AcCl}$  ( $>0.08$  mol.), respectively, affords tetramethyl- $\alpha$ -methylmannoside (92% yield), m.p. 40°, and  $\alpha$ -methylmannoside tetra-acetate (almost quant. yield), m.p. 65°. *iso*Propylidene- and diisopropylidene-glucose are similarly methylated to the 3 : 5 : 6- $\text{Me}_3$  (95% yield), b.p. 90—95°/0.05 mm., and 3- $\text{Me}$  (96% yield), b.p. 105°/0.3 mm., derivatives, respectively. No change in ring structure

occurs when isopropylidene- $\gamma$ -methylrhamnoside is similarly methylated. The method can be used for arylation and introduction of P (with  $\text{POCl}_3$ ) or S (with  $\text{SOCl}_2$  or  $\text{S}_2\text{Cl}_2$ ). Glucose and liquid  $\text{NH}_3$  give 1-aminoglucose, m.p.  $121^\circ$ . H. B.

**Anhydro- $\beta$ -methylhexoside from triacetyl-*p*-toluenesulphonyl- $\beta$ -methylglucoside.** A. MÜLLER (Ber., 1934, 67, [B], 421—424).—The anhydro- $\beta$ -methylhexoside (I) of Helferich and Müller (A., 1930, 1411) is converted by  $\text{Ag}_2\text{O}$  and MeI in boiling  $\text{COMe}_2$  into the  $\text{Me}_2$  (II) derivative, m.p.  $83\text{--}84^\circ$ ,  $[\alpha]_D^{25} -148.2^\circ$  in  $\text{CHCl}_3$ , or, if reaction is suitably interrupted, into the  $\text{Me}_1$  compound, m.p.  $121^\circ$ ,  $[\alpha]_D^{25} -141.6^\circ$  in  $\text{H}_2\text{O}$ . The presence of  $\cdot\text{CH}_2\cdot\text{OH}$  in (I) is established by the isolation of 6-triphenylmethyl-anhydro- $\beta$ -methylhexoside acetate, m.p.  $180.5\text{--}181.5^\circ$  after softening at  $178^\circ$ ,  $[\alpha]_D^{25} -91.8^\circ$  in  $\text{CHCl}_3$ . Treatment of (I) with  $2N\text{-HCl}$  at  $100^\circ$  and of the product (III) with  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$  at  $100^\circ$  leads to chloro- $\beta$ -hexose tetra-acetate, m.p.  $126^\circ$ ,  $[\alpha]_D^{25} -21.17^\circ$  in  $\text{CHCl}_3$ . (III) yields a sparingly sol. phenylosazone which resinifies completely during attempted purification. (II) and  $N\text{-HCl}$  at  $100^\circ$  afford chlorodimethyl- $\alpha$ -hexose, m.p. (indef.)  $135\text{--}137^\circ$ ,  $[\alpha]_D^{25} -53.7^\circ$  to  $-67.6^\circ$  in  $\text{H}_2\text{O}$ , which reduces warm Fehling's solution and retains Cl firmly. (II) is converted by the successive action of  $2N\text{-HCl}$  at  $100^\circ$  and  $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH-NH}_2$  into an osazone which could not be purified. Treatment of the acetoanhydrobromoglucose of Reichel *et al.* (A., 1932, 1237) with abs. MeOH and anhyd.  $\text{Ag}_2\text{CO}_3$  leads to a non-cryst. product, apparently not identical with anhydro- $\beta$ -methylhexoside diacetate (*loc. cit.*). H. W.

**Analysis of  $\gamma$ -methylfructoside mixtures by means of invertase.** I. II. Isolation of a new crystalline methylfructoside. C. B. PURVES and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 702—707, 708—711).—I. The hydrolysis of " $\gamma$ -methylfructoside" (I) by invertase (II) at  $20^\circ$  is followed polarimetrically and by the Cu reducing power of the hydrolysate. (I) is thus shown to contain a (II)-hydrolysable constituent (III),  $[\alpha]_D^{25} -52 \pm 2^\circ$  in  $\text{H}_2\text{O}$ , assumed to be a true methylfructoside. The optical changes suggest that (III) is a derivative of  $\gamma$ -fructose and possesses the  $\beta$ -configuration. (I) also contains a fraction (IV),  $[\alpha]_D^{25} +50^\circ$  (approx.) in  $\text{H}_2\text{O}$ , which is stable to (II). Fermentation of (I) with yeast removes (III) [and any unchanged fructose (V)] and leaves (IV). When the condensation of (V) with MeOH-HCl is stopped at the point of max. dextro-rotation, the resultant non-reducing product contains about 45% of (III) and 55% of (IV); wide variations in the conditions of condensation do not alter these proportions, but the amount of uncondensed (V) varies considerably. The non-reducing product obtained by prolonged condensation of (V) and MeOH-HCl contains only 10—20% of (III); the remainder is strongly laevorotatory (owing to the production of a fructoside of the normal ring type). Sucrose is hydrolysed 13.5 times as rapidly as (III) by (II) under comparable conditions; neither reaction is strictly unimol.

II. The material left after fermentation of a " $\gamma$ -methylfructoside" (A) containing (V) (3%), (III)

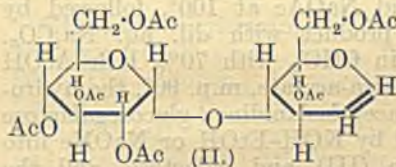
(42%), and (IV) (55%) is separated (pptn. with EtOAc from the aq. MeOH-solution; less sol. portion extracted twice with *n*-amyl alcohol) into (i) more sol. and (ii) less sol. fractions, and thence into (i) a  $\gamma$ -methylfructoside (VI) [about 10% of (A)], m.p.  $69^\circ$ ,  $[\alpha]_D^{25} +93.05^\circ$  in  $\text{H}_2\text{O}$ , and liquid  $\gamma$ -Me derivatives (21.7%),  $[\alpha]_D^{25} +51^\circ$  in  $\text{H}_2\text{O}$ , and (ii) liquid  $\gamma$ -Me derivatives (19.8%),  $[\alpha]_D^{25} +25.2^\circ$ , and a residue of normal ring type [about 7.5%; determined by hydrolysis ( $N\text{-HCl}$  at  $20^\circ$ ) and subsequent fermentation]. (A) thus contains at least three  $\gamma$ -fructose derivatives. (VI) is hydrolysed more rapidly than sucrose by dil. acid. (A) does not give Raybin's diazouracil test (A., 1933, 811), which is considered to be more sp. for the sucrose linking than the action of (II).

H. B.

**Reduction of W. C. Austin's  $\alpha$ -*d*-glucoheptulose.** (MME.) Y. KHOUVINE (Compt. rend., 1934, 198, 985—987).— $\alpha$ -*d*-Glucoheptose with saturated aq.  $\text{Ca}(\text{OH})_2$  at  $35^\circ$  gives  $\alpha$ -*d*-glucoheptulose (I), m.p.  $173^\circ$ ,  $[\alpha]_D^{25} +61^\circ$ , which with 2.5% Na-Hg and dil.  $\text{H}_2\text{SO}_4$  gives  $\alpha$ -glucoheptitol, m.p.  $129^\circ$ ,  $\alpha 0^\circ$ , and  $\alpha$ -*d*-glucoheptulitol (II), m.p.  $130^\circ$  (block),  $[\alpha]_D^{25} +2.1^\circ$  in  $\text{H}_2\text{O}$ , an isomeride of the alcohol formed by biosynthesis. (II) is oxidised by *Acetobacter xylinum* to (I).

R. S. C.

**Maltal and 4- $\alpha$ -glucosidomannose.** W. N. HAWORTH, E. L. HIRST, and R. J. W. REYNOLDS (J.C.S., 1934, 302—303).—Treatment of the product from  $\beta$ -maltose octa-acetate (I) and HBr in AcOH with Zn dust in cold aq. AcOH gives maltal hexa-acetate (II), m.p.  $131\text{--}133^\circ$ ,  $[\alpha]_D^{25} +68^\circ$  in  $\text{CHCl}_3$ , which when boiled



with 0.5% aq. AcOH passes into  $\psi$ -maltal penta-acetate (III), m.p.  $129^\circ$ ,  $[\alpha]_D^{25} +162^\circ$  in  $\text{CHCl}_3$ . (II) does not reduce Fehling's solution, but (III) does so; (III) does not decolorize Br in  $\text{CHCl}_3$ . Maltal (in  $\text{H}_2\text{O}$ ) [obtained by de-acetylation ( $\text{MeOH-NH}_3$ ) of (II)] and  $\text{BzO}_2\text{H}$  (in  $\text{Et}_2\text{O}$ ) give 4- $\alpha$ -glucosido- $\beta$ -mannose (IV), m.p.  $215\text{--}216^\circ$  (decomp.),  $[\alpha]_D^{25} +97^\circ \rightarrow +115^\circ$  (in  $\text{H}_2\text{O}$ ) [ $\alpha$ -octa-acetate (V), m.p.  $157^\circ$ ,  $[\alpha]_D^{25} +117^\circ$  in  $\text{CHCl}_3$ ]. The "epimeric difference" between the mol. rotation of  $\beta$ -maltose and (IV) is 7300; (I) and (V) show a difference of only 4000, thus affording further confirmation of the unreliability of epimeric differences as a means of assigning ring structures to carbohydrate derivatives. The maltal penta- and hexa-acetate hydrates of Bergmann and Kobel (A., 1924, i, 265) are maltose hepta- and octa-acetates, respectively. H. B.

**Flavanoneglucoside in *Glycyrrhiza glabra*, L., var. *glandulifera*, Regel et Herder.** J. SHINODA and S. UEEDA (Ber., 1934, 67, [B], 434—440).—Extraction of liquorice root with MeOH leads to the isolation of liquiritin (I),  $\text{C}_{21}\text{H}_{22}\text{O}_{11}$ , m.p.  $212^\circ$  (also  $+1\text{H}_2\text{O}$ ), hydrolysed by dil.  $\text{H}_2\text{SO}_4$  to glucose and liquiritigenin (II),  $\text{C}_{15}\text{H}_{12}\text{O}_4$ , m.p.  $207^\circ$  (also  $+1\text{H}_2\text{O}$ ). (II) gives an oxime, m.p.  $178^\circ$ , a diacetate, m.p.  $186^\circ$ , and a non-cryst. Me derivative. (II) is converted by 50% KOH at  $170\text{--}180^\circ$  into resaceto-

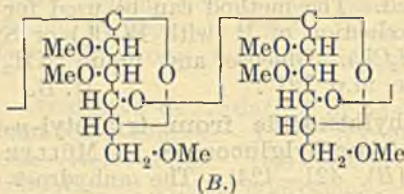
phenone (III) and *p*-OH-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H (IV). Treatment of (I) with aq. Ba(OH)<sub>2</sub> gives only (III) and unchanged (I). Treatment of (I) with anhyd. K<sub>2</sub>CO<sub>3</sub> and MeI in boiling COMe<sub>2</sub> followed by hydrolysis leads to pæonol and (IV). (II) is therefore 4':7-dihydroxyflavanone (V). Treatment of *p*-CO<sub>2</sub>Et-C<sub>6</sub>H<sub>4</sub>:CH:CH-COCl with *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> and AlCl<sub>3</sub> in PhNO<sub>2</sub> and of the product with KOH affords 2:4:4'-trihydroxychalkone and (V), m.p. 207°, identical with (II) [Tambor (A., 1916, i, 831) records m.p. 182—183°]. H. W.

**Reactions of digitoxin, digitalin, and digitonin.** L. EKKERT (Pharm. Zentr., 1934, 75, 228—229).—Colour reactions are described with phenols, naphthols, and aldehydes in the presence of acids, the colour changes depending on the condensation of pentoses or hexoses with these reagents. S. C.

**Constitution of the solanines *t* and *s*.** G. ODDO and G. CARONNA (Ber., 1934, 67, [B], 446—458; cf. Oddo *et al.*, A., 1905, i, 455; 1906, i, 527, 980; 1911, i, 671; 1929, 299; Colombano, A., 1908, i, 99; 1912, i, 798; Zemplén *et al.*, A., 1929, 51).—Treatment of *Solanine tuberosum* (I) with Ac<sub>2</sub>O and NaOAc (Zemplén) gives a product, m.p. 204—205° after incipient decomp. at 190°; contrary to Zemplén, it regenerates (I) when treated with KOH-EtOH or NaOMe, and is the acetate of *trideca-acetylsolanine-t* (II), C<sub>71</sub>H<sub>105</sub>O<sub>33</sub>. Solanine trideca-acetate is obtained from (I), Ac<sub>2</sub>O, and NaOAc at 100°, followed by treatment of the product with dil. aq. Na<sub>2</sub>CO<sub>3</sub>. Treatment of (II) in CHCl<sub>3</sub> with 70% HBr-AcOH leads to rhamnose tetra-acetate, m.p. 90°, the hydrobromide of nona-acetylsolanidine-*t*-glucosegalactose (-1H<sub>2</sub>O) converted by KOH-EtOH or NaOMe into solandine-*t*-glucoside (III) and galactose, and the hydrobromide of penta-acetylsolanidine-*t* (-H<sub>2</sub>O) hydrolysed to (III). The sequence in (I) is therefore solanidine-*t*-*d*-glucose-*d*-galactose-*d*-rhamnose. Acetylation of *S. sodomaeum* (Zemplén) yields solanine-*s*-deca-acetate, m.p. 135—138°, obtained previously. Hydrolysis with 70% HBr-AcOH leads to rhamnose diacetate (IV), m.p. 75° (slight decomp.), *hepta-acetylsolanidine-s*-glucosegalactose (-1H<sub>2</sub>O) (II), m.p. 170° after becoming yellow at 140° (hydrolysed by KOH-EtOH or NaOMe to solanidine-*s*-glucoside and galactose), and *acetobromosolanidine-s* (VI), m.p. 135° after becoming yellow at 110°. The use of 30% HBr-AcOH leads to (IV) and (V), the hydrobromide of *acetylsolanidinerhamnose*, C<sub>18</sub>H<sub>31</sub>ON, C<sub>6</sub>H<sub>12</sub>O<sub>5</sub>Ac, HBr, m.p. 132° (decomp.) [hydrolysed to (IV) and (VI)], and (VI). The sequence in the glucoside is therefore solanidine-*s*-*d*-glucose-*d*-galactose-*d*-rhamnose-solanidine-*s*. H. W.

**Ivory-nut mannans. I. Constitution of mannan-A.** F. KLAGES (Annalen, 1934, 509, 159—181).—Extraction of ivory-nut shavings with H<sub>2</sub>O and COMe<sub>2</sub>, subsequent treatment with ClO<sub>2</sub> (cf. Schmidt *et al.*, A., 1931, 1101) for 5 days, extraction of the residue with 5% NaOH, and acidification of the extract with AcOH gives mannan-A (I), [α]<sub>D</sub><sup>20</sup> -44.7° in *N*-NaOH, which is methylated (Me<sub>2</sub>SO<sub>4</sub>, aq. NaOH, C<sub>6</sub>H<sub>6</sub>) to *trimethylmannan* (II). Complete hydrolysis

(dil. HCl) of (II) gives 2:3:6-trimethylmannose (about 80%) [indicating the presence of the unit (B) in (II)] and 1.15—1.4% of 2:3:4:6-tetra-methylmannose (III) (arising from



the end grouping). Partial hydrolysis of (II) affords a mixture (C) of oligosaccharides; methylation (MeI, Ag<sub>2</sub>O) and fractionation gives non-homogeneous octa-methylmannobiose and hendecamethylmannotriose, which on further hydrolysis yield (III). Oxidation of (C) by Hönig and Ruzicka's method (A., 1930, 1166) and methylation (MeI, Ag<sub>2</sub>O) of the resulting lactones gives non-homogeneous heptamethylmannobionolactone and decamethylmannotriolactone. Hydrolysis (0.01—0.1N-HCl at 98°) of (II) is not unimol., and marked retardation occurs after about 50% hydrolysis; probable reasons are discussed and the course of the hydrolysis is considered to be similar to that of cellulose (Freudenberg *et al.*, A., 1930, 1025). The amount of (III) obtained by complete hydrolysis of (II) indicates that (II) contains 71—86 C<sub>6</sub> units; oxidation with hypiodite indicates about 68 units. In agreement with Hess *et al.* (A., 1930, 1416), the "I vals." of non-methylated sugars [*e.g.*, (I) and glucose] increase with continued action of the hypiodite. H. B.

**Enzymic amyolysis. III. Crystalline hexaose from starch.** See this vol., 449.

**Starch. VI. Iodomethyl-di-*p*-toluenesulphonylmethylglucoside from starch tri-*p*-toluenesulphonate.** K. HESS and O. LITTMANN (Ber., 1934, 67, [B], 465—466; cf. A., 1933, 1279).—Methylglucoside tri-*p*-toluenesulphonate acetate is transformed by NaI in COMe<sub>2</sub> at 125° into *iodomethylglucoside di-p-toluenesulphonate acetate*, m.p. 129—130°, [α]<sub>D</sub><sup>20</sup> +13.16° in CHCl<sub>3</sub>, -16.18° in C<sub>6</sub>H<sub>6</sub>, -8.59° in COMe<sub>2</sub>, not identical with the corresponding compound from iodostarch di-*p*-toluenesulphonate (*loc. cit.*). H. W.

**Chain length of lichenin of native composition.** E. SCHMIDT, R. SCHNEGG, and E. WÜRZNER (Naturwiss., 1934, 22, 172).—After repeated treatment with ClO<sub>2</sub> and Na<sub>2</sub>SO<sub>3</sub>, lichenin (I) is dissolved from *Cetraria islandica* by Cu(OH)<sub>2</sub>-NH<sub>3</sub>, pptd. by EtOH from the acidified solution, electro-dialysed, extracted with MeOH and Et<sub>2</sub>O, and dried. It then contains 0.1% of ash and is free from pentosans. Conductometric titration shows the presence of 0.563% CO<sub>2</sub>H (calc. as CO<sub>2</sub>), indicating a chain of 47 glucose residues and 1 residue containing CO<sub>2</sub>H. Acetylxylylan, (I), and cellulose contain therefore 2×16, 3×16, and 6×16 individual links, respectively, in the chain. H. W.

**Highly-polymerised compounds. LXXXIX. Polyoxy-methylenes as model of cellulose.** H. STAUDINGER. XC. Cellopentaose acetate and the constitution of cellulose. H. STAUDINGER and E. O. LEUPOLD (Ber., 1934, 67, [B], 475—479, 479—486).—LXXXIX. Mainly a reply to Hess *et al.* (this vol., 493).



XC. Measurements with oligosaccharide derivatives show that the sp. viscosity of a glucose residue diminished regularly from glucose penta-acetate (I) to cellobiose acetate (II), tending towards the final val. found for complex cellulose acetates. Examination of the cellobiose acetate of Zechmeister and Tóth along these lines indicates it to be a cellobiose acetate. This view is confirmed by determinations of mol. wt. in camphor in which (I), cellobiose octa-acetate, cellobiose acetate, and (II) behave normally. The  $\eta_{sp}$  val. for a glucose residue in *cellobiose hepta-acetate stearate*, m.p. 130—132°, is identical with that in the pentaose acetate and complex cellulose acetates, whereas that of the corresponding *nonoate*, m.p. 116—118°, is somewhat greater. H. W.

Assumed non-identity of cotton and wood cellulose. J. BARSHA and H. HIBBERT (J. Amer. Chem. Soc., 1934, 56, 748).—Rayon pulps from spruce, beech, and maple do not contain a "resistant portion" (to methylation) (cf. Bell, A., 1932, 934). H. B.

Reactions relating to carbohydrates and polysaccharides. XLVI. Structure of the cellulose synthesised by the action of *Acetobacter xylinus* on fructose and glycerol. J. BARSHA and H. HIBBERT (Canad. J. Res., 1934, 10, 170—179).—Fructose and glycerol are converted into bacterial celluloses [(I) and (II), respectively] (cf. A., 1931, 826) ( $C_6H_{10}O_5$ )<sub>n</sub>. (I) and (II) with  $Ac_2O$  in  $AcOH$  containing  $SOCl_2$  afford  $Ac_3$  derivatives,  $[\alpha]_D^{25} -21.0^\circ$  (III) and  $-21.8^\circ$  (IV) in  $CHCl_3$ , respectively, hydrolysed by  $2N-NaOH-MeOH$  at room temp. in 24 hr. to celluloses ( $C_6H_{10}O_5$ )<sub>n</sub>. (III) or (IV) with  $MeOH-HCl$  (0.9%) at 125° during 60 hr. affords a mixture,  $[\alpha]_D^{25} +105.9^\circ$ , of  $\alpha$ - and  $\beta$ -methylglucoside, which gives the  $\alpha$ -form, m.p. 163.5°,  $[\alpha]_D^{25} +156.6^\circ$ , when fractionally crystallised. Hydrolysis of (I) or (II) with  $ZnCl_2-HCl$  (cf. A., 1930, 1561) affords a product with  $[\alpha]$  nearly identical with that of glucose. (III) and (IV) with  $Me_2SO_4$  in warm  $NaOH$  afford trimethylcellulose, m.p. 227—230°,  $[\alpha]_D^{25} -14.2^\circ$  in  $C_6H_6$ , and m.p. 232—234°,  $[\alpha]_D^{25} -15.2^\circ$  in  $C_6H_6$ , respectively; either is hydrolysed by 1%  $MeOH-HCl$  at 100° during 50 hr. to 2 : 3 : 6-trimethylmethylglucoside, b.p. 110—113°/25 mm., hydrolysed further to 2 : 3 : 6-trimethylglucose, m.p. 104—106°. (I) or (II) with  $Ac_2O$  containing conc.  $H_2SO_4$  at 50° during 19 days affords cellobiose octacetate, m.p. 222—223°, identical with the product obtained when bacterial cellulose prepared from glucose is acetylated. The identity of these celluloses is supported by X-ray analysis. J. L. D.

Carbon double linkings and carbon-nitrogen linkings. XII. Decomposition of quaternary ammonium compounds with sodium amalgam. H. EMDE and H. KULL (Arch. Pharm., 1934, 272, 469—481).—A summary of quaternary  $NH_4$  salt degradations by the ordinary Hofmann reaction and by  $Na-Hg$  reduction classified according as to whether the two reactions do, or do not, follow similar courses. J. W. B.

Quaternary ammonium salts of possible therapeutic value. C. CUTOLO (L'Ind. Chimica,

1934, 9, 322—325).—These salts may be prepared by dissolving the Na salt of the org. acid in aq.  $EtOH$ , treating the solution with one of  $NMe_4Cl$  or  $NEt_4Cl$  in  $EtOH$  of definite concn., and adding a little  $HCl$ . Practically all the  $NaCl$  is thus pptd., whilst the  $NMe_4$  salt remains dissolved. Details are given for the prep. of  $HCO_2NMe_4$ . T. H. P.

Quaternary ammonium salts from dialkyl-bromopropylamines. IV. Formation of four-membered rings. C. F. GIBBS and C. S. MARVEL (J. Amer. Chem. Soc., 1934, 56, 725—727).—Diethyl- $\gamma$ -bromopropylamine, b.p. 52—54°/5 mm. (*platinichloride*, m.p. 150—153°) (A., 1927, 1064) [from diethyl- $\gamma$ -phenoxypropylamine, b.p. 118—120°/5 mm. (*platinichloride*, m.p. 134—135°)], passes when kept at 0—100° into *diethyltrimethyleneammonium bromide*,  $(CH_2)_3NEt_2Br$ , m.p. 175—178°, and not into a linear polymeride [as does  $NMe_2(CH_2)_3Br$  (A., 1933, 381)]. *Di-n-propyl-*, m.p. 52—59°, and *di-n-butyl-*, m.p. 120—121°, *-trimethyleneammonium bromides* are similarly obtained from *di-n-propyl-*, b.p. 77—78°/4 mm. (*platinichloride*, m.p. 194—196°), and *di-n-butyl-*, b.p. 96—98°/6 mm. (*auribromide*, m.p. 130°), *- $\gamma$ -bromopropylamine*, respectively, which are prepared (method; A., 1930, 349; 1933, 812) from *di-n-propyl-*, b.p. 137—139°/6 mm., and *di-n-butyl-*, b.p. 148—150°/5 mm., *- $\gamma$ -phenoxypropylamine*, respectively. *Diethylallylamine hydrobromide* has m.p. 189—190°. The mol. wts. (f.p. in  $H_2O$ ) of the above bromides are of the same order (50%) as those of  $NBu_4I$  and  $NEt_4Bu^+I$ . H. B.

Glucosyl-alkylamines. E. VOTOČEK and F. VALENTIN (Coll. Czech. Chem. Comm., 1934, 6, 77—96).—The following 1-derivatives are prepared by interaction of the appropriate sugar and amine in  $H_2O$  or  $MeOH$ : *arabinose-methyl-* (+2 $H_2O$ ), m.p. 101°, and *-heptyl-imine* (+3 $H_2O$ ); *fructose-methyl-*, m.p. 125° (+1 $H_2O$ ), *-n-propyl-*, m.p. 124—125° (decomp.), *-n-butyl-* (+0.5 $H_2O$ ), m.p. 88—89°, *-n-amyl-* (+1 $H_2O$ ), m.p. 95° (sinters 75°), *-n-hexyl-*, m.p. 109—110°, and *-n-heptyl-imine* (+0.5 $H_2O$ ), m.p. 84—85°; *glucose-methyl-* (+1 $H_2O$ ), m.p. 78—80°, decomp. 100—115°, *-n-butyl-* (+1 $H_2O$ ), m.p. 97—98°, *-n-amyl-* (+1 $H_2O$ ), m.p. 96—97°, *-n-hexyl-* (+1 $H_2O$ ), m.p. 79—80°, and *-n-heptyl-imine* (+1 $H_2O$ ), m.p. 97°; *rhannose-methyl-* (+1 $MeOH$ ), m.p. 126—127°, *-ethyl-* (+0.5 $H_2O$ ), m.p. 141—142°, *-n-propyl-*, m.p. 145°, *-n-butyl-* (+1 $MeOH$ ), m.p. 136—137° (decomp.), *-n-amyl-*, m.p. 139—140°, *-n-hexyl-*, m.p. 132—133°, and *-n-heptyl-imine*, m.p. 138°; *galactose-n-propyl-*, m.p. 127—128° (decomp.), *-n-butyl-* (+1 $H_2O$ ), m.p. 82—83°, *-n-amyl-* (+1 $H_2O$ ), m.p. 110° (anhyd.), and *-n-heptyl-imine* (+1 $H_2O$ ), m.p. 99—100° (sinters 80°); *xylose-n-butyl-* (+1 $H_2O$ ), m.p. 81—82°, and *-n-hexyl-imine* (+1 $H_2O$ ), m.p. 87°; and *mannose-n-butyl-* (+1 $H_2O$ ), m.p. 71—72°, *-n-amyl-* (+0.5 $H_2O$ ), m.p. 70—71°, *-n-hexyl-* (+0.5 $H_2O$ ), m.p. 75°, and *-n-heptyl-imine* (+0.5 $H_2O$ ). All show mutarotation in  $H_2O$ . H. A. P.

Oxidation of amino-acids by silver oxide. R. M. HERBST and H. T. CLARKE (J. Biol. Chem., 1934, 104, 769—788).— $\alpha-NH_2$ -acids,  $NRR'CR''R'''CO_2H$ , are oxidised by  $Ag_2O$  (excess) in boiling  $H_2O$  (not in acid or alkaline solution) quantitatively, but with varying velocity, to  $NHRR'$ ,  $COR''R'''$ , and

CO<sub>2</sub>. Aldehydes, if formed, may be further oxidised to acids. Acylation of the NH<sub>2</sub>, including peptide formation, slows down or entirely inhibits oxidation, depending on the rate of hydrolysis of the N-CO linking which must precede oxidation. Alkylation of NH<sub>2</sub> increases the rate of oxidation, but betaines are completely stable. Oxidation is thus associated with primary loss of H from the N

atom of  $\text{NHR}_2\cdot\text{CR}_2\cdot\text{CO}_2$ , and is thus not a dehydrogenation in the sense of Wieland's theory. With  $\text{NMe}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$  (I)  $\text{NHMe}_2$  is liberated more rapidly than CO<sub>2</sub>, but  $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$  is not the primary reaction product, since this compound is oxidised more slowly than (I) (although CO<sub>2</sub> is quantitatively formed).  $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$  (II) is excreted largely unchanged by dogs, and the Ag<sub>2</sub>O-oxidation thus bears no relation to the metabolic reactions of NH<sub>2</sub>-acids. Curves are given for the rate of evolution of CO<sub>2</sub> and NH<sub>3</sub>; the results are summarised as follows, the reaction products isolated being given in parentheses: (a) very rapidly oxidised: sarcosine (CO<sub>2</sub>, NH Me),  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (CO<sub>2</sub>, NHMe<sub>2</sub>),  $\text{NHMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  and  $\text{NMe}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  (CO<sub>2</sub>, NH<sub>2</sub>Me or NHMe, MeCHO, AcOH), (I) (CO<sub>2</sub>, NHMe<sub>2</sub>, COMe<sub>2</sub>); (b) rapidly oxidised: glycine [CO<sub>2</sub>, NH<sub>3</sub>, CO(NH<sub>2</sub>)<sub>2</sub> (III) (trace), N<sub>2</sub> (10%)], alanine [CO<sub>2</sub>, NH<sub>3</sub>, MeCHO, AcOH, (III)], (II) (CO<sub>2</sub>, NH<sub>3</sub>, COMe<sub>2</sub>), leucine (CO<sub>2</sub>, NH<sub>3</sub>, isovaleraldehyde and isovaleric acid),  $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  (CO<sub>2</sub>, NH<sub>3</sub>, PhCHO, BzOH),  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$  (CO<sub>2</sub>, NH<sub>3</sub>, PhCHO, BzOH,  $\text{CH}_2\text{Ph}\cdot\text{CHO}$ ,  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ ), glutamic acid [CO<sub>2</sub>, NH<sub>3</sub>, ( $-\text{CH}_2\cdot\text{CO}_2\text{H}$ )], proline,  $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  [CO<sub>2</sub>, NH<sub>2</sub>Ph, (NPh)<sub>2</sub>],  $\text{NHPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  [CO<sub>2</sub>, NH<sub>2</sub>Ph, (NPh)<sub>2</sub>, AcOH],  $\text{NHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$  [CO<sub>2</sub>, NH<sub>2</sub>Ph, (NPh)<sub>2</sub>, COMe<sub>2</sub>],  $\text{NH}_2\cdot\text{CPhEt}\cdot\text{CO}_2\text{H}$  (CO<sub>2</sub>, NH<sub>3</sub>, CPhEt),  $\text{NHAc}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (CO<sub>2</sub>), hippuric acid (CO<sub>2</sub>, NH<sub>2</sub>Bz),  $\text{NH}_2\text{Bz}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  (CO<sub>2</sub>, PhCHO),  $\text{PhSO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (CO<sub>2</sub>, NH<sub>2</sub>, SO<sub>2</sub>Ph),  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  [CO<sub>2</sub>, NH<sub>3</sub>, (III), MeCHO, AcOH],  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  (NH<sub>2</sub>Ph), 5-methyl- [CO<sub>2</sub>, NH<sub>3</sub>, (III), AcOH, NHAc·CO·NH<sub>2</sub>] and 3-phenyl-5-methyl-hydantoin (NH<sub>2</sub>Ph), creatine; (c) slowly oxidised: glycyl-, alanyl- (CO<sub>2</sub>, NH<sub>3</sub>, AcOH), *p*-toluenesulphonyl-, and benzenesulphonyl-phenyl-alanine ( $\text{CH}_2\text{Ph}\cdot\text{CHO}$ ), alanylglycine,  $\text{PhSO}_2\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ , benzenesulphonyl-leucine (isovaleric acid),  $\text{PhSO}_2\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  (PhCHO); (d) not oxidised: betaine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{NH}_2\text{Bz}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , *d*-*o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>)<sub>2</sub>·N·CHMe·CO<sub>2</sub>H,  $\text{NH}_2\text{Bz}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ ,  $\text{NH}_2\text{Bz}\cdot\text{CPhMe}\cdot\text{CO}_2\text{H}$ , 5:5-dimethyl- and 3-phenyl-5:5-dimethyl-hydantoin.

R. S. C.

**Reactions of betaine.** L. EKKERT (Pharm. Zentr., 1934, 75, 209—210).—Betaine and KOH give  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which affords CH<sub>2</sub>O on treatment with H<sub>2</sub>SO<sub>4</sub>, identified by the colour reactions with guaiacolsulphonic acid, codeine, and resorcinol.

S. C.

**Synthesis of serine.** M. S. DUNN, C. E. REDEMANN, and N. L. SMITH (J. Biol. Chem., 1934, 104, 511—517).—OEt·CH<sub>2</sub>·CH<sub>2</sub>·OH is oxidised with Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-aq. H<sub>2</sub>SO<sub>4</sub> and the fraction, b.p. 70—95°, of the distillate treated successively with 7*N*·NH<sub>2</sub>-MeOH, anhyd. HCN, and 40% HBr, neutralised

with PbCO<sub>3</sub>, filtered, boiled, treated with Pb(NO<sub>3</sub>)<sub>2</sub>, filtered, treated with H<sub>2</sub>S, and evaporated. A 64% yield of crude, and a 40% of pure, *dl*-serine (photomicrograph) is obtained.

R. S. C.

**Preparation of polypeptides containing glycine and I(+)-alanine alternately linked, and their behaviour towards enzymes.** E. ABDERHALDEN and A. NEUMANN (Fermentforsch., 1934, 14, 133—142).—The following polypeptides and precursors were prepared by Fischer's methods: glycyl-l-alanine,  $[\alpha]_D^{20} -50^\circ$  in H<sub>2</sub>O, from chloroacetyl-l-alanine,  $[\alpha]_D^{20} -45^\circ$  (NH<sub>4</sub> salt,  $[\alpha]_D^{20} -21.4^\circ$  in H<sub>2</sub>O, not  $-60^\circ$ ; cf. A., 1931, 767); l-alanylglycyl-l-alanine (I), m.p. 207°,  $[\alpha]_D^{20} -19.5^\circ$  in H<sub>2</sub>O, from l-bromopropionylglycyl-l-alanine, m.p. 103°,  $[\alpha]_D^{20} -19.2^\circ$  in H<sub>2</sub>O; glycyl-l-alanylglycyl-l-alanine,  $[\alpha]_D^{20} -24.6^\circ$  in H<sub>2</sub>O, purified through Cu salt from chloroacetyl-l-alanylglycyl-l-alanine. The following were prepared by the method of Bergmann and Zervas (A., 1932, 935): glycylglycyl-dl-leucine by catalytic hydrogenation of N-benzylcarbonatoglycylglycyl-dl-leucine, m.p. 175°; l-alanylglycyl-dl-leucine (II), m.p. 224°,  $[\alpha]_D^{20} +44.4^\circ$  in H<sub>2</sub>O, from N-benzylcarbonato-l-alanylglycyl-l-leucine, m.p. 103°,  $[\alpha]_D^{20} -5.5^\circ$  in EtOH; glycyl-l-alanine,  $[\alpha]_D^{20} -46.5^\circ$  in H<sub>2</sub>O, from N-benzylcarbonatoglycyl-l-alanine, m.p. 155—156°,  $[\alpha]_D^{20} -4.7^\circ$  in EtOH, prepared from l-alanine and N-benzylcarbonatoglycyl chloride (III). N-Benzylcarbonato-l-alanylglycyl chloride (IV), a yellow oil, crystallises in ice-salt, and is rapidly converted by atm. H<sub>2</sub>O into a substance C<sub>4</sub>H<sub>5</sub>O<sub>3</sub>N, probably  $\begin{matrix} \text{CHMe}\cdot\text{CO} \\ | \\ \text{NH}-\text{CO} \end{matrix} > \text{O}$  [(III) is also partly converted into an analogous substance, C<sub>3</sub>H<sub>3</sub>O<sub>3</sub>N]. An attempt to couple (IV) with glycyl-l-alanine (V) failed. (V), (I), and (II) are hydrolysed by erepsin.

A. E. O.

**Reactions of nitrous acid with cystine and related sulphur-containing compounds.** S. A. LOUGH and H. B. LEWIS (J. Biol. Chem., 1934, 104, 601—610).—Cystine (I) and HNO<sub>2</sub> slowly give up to 85% of the theoretical amount of H<sub>2</sub>SO<sub>4</sub>. Substitution of the SH or NH, or oxidation of the SH to SO<sub>3</sub>H, prevents formation of H<sub>2</sub>SO<sub>4</sub>. SH·CH<sub>2</sub>·CO<sub>2</sub>H (II), SH·CHMe·CO<sub>2</sub>H, and dithiodiacetic acid give H<sub>2</sub>SO<sub>4</sub>; the gas obtained from (II) is shown spectrographically to be N<sub>2</sub>. The high val. in the Van Slyke determination of (I) is thus due to oxidation of SH to H<sub>2</sub>SO<sub>4</sub> and evolution of "extra" N<sub>2</sub>.

R. S. C.

**δ-Ethoxybutylcarbamide.** E. WERTHEIM (J. Amer. Chem. Soc., 1934, 56, 735—736).—γ-Ethoxybutyronitrile, b.p. 175°/716 mm. (from the bromide and aq. EtOH-KCN), is reduced (Na, MeOH) to δ-ethoxybutylamine, b.p. 155—156°/730 mm. (lit. 153—154°/746 mm.), which with KCNO and dil. H<sub>2</sub>SO<sub>4</sub> gives δ-ethoxybutylcarbamide, m.p. 68—69°, slight bitter taste. The sweet taste of dulcin [*p*-OEt·C<sub>6</sub>H<sub>4</sub>·NH·CO·NH<sub>2</sub>] depends on the presence of the C<sub>6</sub>H<sub>6</sub> ring. *o*-OH·C<sub>6</sub>H<sub>4</sub>·NH·CO·NH<sub>2</sub> is very sweet, whilst OH·CH<sub>2</sub>·CH<sub>2</sub>·NH·CO·NH<sub>2</sub> is practically tasteless.

H. B.

**Electrolytic preparation of semicarbazide hydrochloride.** T. Y. CHANG and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 157—165).—Electrolytic reduction of NH<sub>2</sub>·CO·NH·NO<sub>2</sub> in

18% HCl with a Cu cathode and a graphite anode, c.d. 0.05 amp. per sq. cm., gives a yield of 53—55% of semicarbazide, isolated by concentrating in vac.

F. R. S.

**Electrolysis of ether solutions of the Grignard compound. Isolation, identification, and determination of anodic products.** W. V. EVANS and F. H. LEE (J. Amer. Chem. Soc., 1934, 56, 654—657).—Electrolysis (stirrer between Pt electrodes) of 1.22—3.53*M* solutions of MgEtCl(Br, I) in Et<sub>2</sub>O gives C<sub>2</sub>H<sub>6</sub> (47.7—53.3%), C<sub>2</sub>H<sub>4</sub> (45.6—51.4%), and H<sub>2</sub> (0.8—1.3%). The main reaction is considered

to be:  $2\text{Et} \xrightarrow{-2e} 2\text{Et} \longrightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$ ;  $2\text{Et} \longrightarrow 2\text{C}_2\text{H}_4 + \text{H}_2$  is probably a secondary change. MgPrBr (1.34—1.36*M*) affords C<sub>3</sub>H<sub>8</sub> (50.1—50.9%), C<sub>3</sub>H<sub>6</sub> (48—49%), and H<sub>2</sub> (0.9—1.1%), whilst an equimol. mixture of MgEtBr and MgPrBr gives C<sub>2</sub>H<sub>6</sub> (30.3%), C<sub>3</sub>H<sub>8</sub> (24.2%), C<sub>2</sub>H<sub>4</sub> (22.6%), C<sub>3</sub>H<sub>6</sub> (22%), and H<sub>2</sub> (0.7%). With low concns. (1.09—1.45*M*) of MgMeBr, the products are CH<sub>4</sub> (66.7—79.3%), C<sub>2</sub>H<sub>6</sub> (0—23.8%), C<sub>2</sub>H<sub>4</sub> (3.5—5.3%), and isobutene (8.1—17.2%); the corresponding % for 1.65—2.08 and 2.83*M* solutions are 21.2—41, 48.2—71.5, 2.1—3.9, 5.2—6.9, and 0, 100, 0, 0, respectively. The following reactions probably occur:  $4\text{Me} \longrightarrow \text{C}_2\text{H}_4 + 2\text{CH}_4$ ;  $8\text{Me} \longrightarrow \text{C}_4\text{H}_{10} + 4\text{CH}_4$ ;  $2\text{Me} \longrightarrow \text{C}_2\text{H}_6$ ; in conc. solution the change  $\text{Me} + \text{Me} \longrightarrow \text{C}_2\text{H}_6 + e$  may take place. In general, the yield of gaseous hydrocarbon is Cl > Br > I. With an equimol. mixture of MgPhBr and MgEtBr, 0.8—0.85 mol. of gaseous hydrocarbon per faraday is obtained, indicating the production of Et only. Gas evolution does not occur with an Al anode, but Al is consumed; Al<sup>+++</sup> is probably formed which then reacts with, e.g., 3Et<sup>-</sup> to give AlEt<sub>3</sub>. Electrolysis experiments favour the structure R<sub>2</sub>Mg·MgX<sub>2</sub> for the Grignard reagent. H. B.

**Sulphoacetato-salts of complex hexamine-, pentamine-, and tetrammine-cobaltic salts.** J. V. DUBSKÝ, H. J. BACKER, K. J. KEUNING, and J. TRTÍLEK (Rec. trav. chim., 1934, 53, 380—386).—Successive treatment of hexamminecobaltic chloride with AgOH and SO<sub>3</sub>H·CH<sub>2</sub>·CO<sub>2</sub>H (I) gives *hexamine-cobaltic sulphoacetate*, [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>2</sub>(SO<sub>3</sub>>CH<sub>2</sub>)<sub>3</sub>·2H<sub>2</sub>O,

orange-yellow; 1 : 6-dinitrotetramminecobaltic chloride similarly affords 1 : 6-dinitrotetramminecobaltic *H sulphoacetate*, [(NH<sub>3</sub>)<sub>4</sub>Co(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>SO<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, ochre, and some 1 : 6-nitroaquotetramminecobaltic  *sulphoacetate*, [(NH<sub>3</sub>)<sub>4</sub>Co(NO<sub>2</sub>)(H<sub>2</sub>O)]<sub>2</sub>(SO<sub>3</sub>>CH<sub>2</sub>), brownish-yellow; octammediolcobaltic chloride similarly yields *diaquotetramminecobaltic sulphoacetate*,

[(NH<sub>3</sub>)<sub>4</sub>Co(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>(SO<sub>3</sub>>CH<sub>2</sub>)<sub>3</sub> + 2H<sub>2</sub>O (violet-red) and +4H<sub>2</sub>O (red), and *sulphoacetatotetramminecobaltic NH<sub>3</sub> sulphoacetate*, pale violet-red,

[(NH<sub>3</sub>)<sub>4</sub>Co<CO<sub>3</sub>>CH<sub>2</sub>]<sub>2</sub>SO<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>NH<sub>3</sub>·2H<sub>2</sub>O; 1 : 2-dichlorodiethylenediaminecobaltic chloride similarly furnishes 1 : 6-dichlorodiethylenediaminecobaltic *H sulphoacetate*, [en<sub>2</sub>CoCl<sub>2</sub>]<sub>2</sub>SO<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, green. Successive treatment of carbonatotetramminecobaltic sulphate with BaCO<sub>3</sub> and (I) gives *sulphoacetatotetramminecobaltic H sulphoacetate*,

[(NH<sub>3</sub>)<sub>4</sub>Co<SO<sub>3</sub>>CH<sub>2</sub>]<sub>2</sub>SO<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>H·2H<sub>2</sub>O, pale

violet-red, whilst carbonatopentamminecobaltic carbonate (containing some tetrammine derivative) and (I) afford *aquopentamminecobaltic sulphoacetate*,

[(NH<sub>3</sub>)<sub>5</sub>Co(H<sub>2</sub>O)](SO<sub>3</sub>>CH<sub>2</sub>)SO<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>H + 0.5H<sub>2</sub>O, and anhyd., red, which when dried passes into sulphoacetatotetramminecobaltic sulphoacetate,

[(NH<sub>3</sub>)<sub>5</sub>CoSO<sub>3</sub>]<sub>2</sub>(SO<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>H), pale violet-red.

H. B.

**Tricyclohexylmethane series.** O. NEUNHOEFER (Annalen, 1934, 509, 115—130).—Reduction (H<sub>2</sub>, PtO<sub>2</sub>, Pr<sup>β</sup>OH) of CHPh<sub>3</sub> gives *tricyclohexylmethane* (I), b.p. 180°/12 mm., m.p. 61° (cf. A., 1927, 457); *cyclohexyldiphenylmethane*, m.p. 56°, can be isolated as an intermediate. Reduction (H<sub>2</sub>, PtO<sub>2</sub>, AcOH) of COPh<sub>2</sub> affords 25% of *dicyclohexylmethane* and 75% of *dicyclohexylcarbinol* (II), b.p. 154°/12 mm., m.p. 66° (lit. 56°) (*phenylcarbamate*, m.p. 157°; *H phthalate*, m.p. 136°). (II), also prepared from Mg *cyclohexyl chloride* (III) and HCO<sub>2</sub>Me, is oxidised (CrO<sub>3</sub>, AcOH) to *dicyclohexyl ketone* (IV), b.p. 138°/13 mm., m.p. 11° (the *oxime*, m.p. 161°, and *semicarbazone*, m.p. 208°, are formed very slowly). The Et and Pr<sup>β</sup> esters of hexahydrobenzoic acid with (III) in Et<sub>2</sub>O give (IV) (about 70%), some *dicyclohexyl*, and about 7% of *tricyclohexylcarbinol*, m.p. 93° (lit. 81.5°) [*bromide* (V), m.p. 136°, prepared in 65.5% yield using AcBr in Et<sub>2</sub>O]. MgPhBr and (IV) afford *dicyclohexylphenylcarbinol*, m.p. 83° [*bromide* (VI), m.p. 127° (decomp.) (lit. 104—105°)]. (V) and quinoline at 150° (short time) and then at room temp. (12 hr.) give *dicyclohexylcyclohexylidenemethane*, b.p. 175°/10 mm., m.p. 52°, whilst (VI) similarly affords *cyclohexylphenylcyclohexylidenemethane*, b.p. 178°/11 mm., m.p. 45°, which is reduced (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) to *dicyclohexylphenylmethane*, m.p. 36.5°, and thence to (I). When a solution of (V) in C<sub>6</sub>H<sub>6</sub> is kept for 1 month, HBr is eliminated and (probably) *dicyclohexyl-Δ<sup>1</sup>-cyclohexenylmethane*, m.p. 41°, is produced. Diphenylcyclohexylidenemethane is reduced (H<sub>2</sub>, PtO<sub>2</sub>, Pr<sup>β</sup>OH) to the *-cyclohexylmethane* and thence to (I).

H. B.

**Constitution of polymerides of cyclopentadiene.** K. ALDER and G. STEIN (Ber., 1934, 67, [B], 373—375).—The method of Pirsch (this vol., 285) is considered inadequate for elucidation of structural and configurative problems in the series of polymeric-homologous *cyclopentadienes*. H. W.

**Plant colouring matters. LIX. New oxidation products from α-carotene and physalien. α-Carotene di-iodide.** P. KARRER, U. SOLMSEN, and O. WALKER (Helv. Chim. Acta, 1934, 17, 417—419).—Oxidation of α-carotene (di-iodide C<sub>40</sub>H<sub>56</sub>I<sub>2</sub>, 20 × 10<sup>-6</sup> g. per diem causes 0.9 g. daily growth) with CrO<sub>3</sub> (= 2 O) gives *α-hydroxycarotene*, m.p. 183° (absorption max. 502, 471, and 440 mμ in CS<sub>2</sub>), and *α-carotone* C<sub>40</sub>H<sub>56</sub>O<sub>5</sub>, m.p. 148°, [α]<sub>D</sub><sup>20</sup> +341° in C<sub>6</sub>H<sub>6</sub>. Similar oxidation of physalien (zeaxanthin dipalmitate) gives a diketone *physalienone* (absorption max. 538, 503 mμ in CS<sub>2</sub>) (formula suggested) and a tetraketone, not yet isolated. J. W. B.

**Carotene. VII. Physical properties of carotenes from different plant sources.**—See this vol., 458.

[Light-]sensitivity of aromatic nitro-compounds. N. N. VOROSHCOV (Helv. Chim. Acta, 1934, 17, 286).—A reply to the priority claim of Steiger (this vol., 63). J. W. B.

**Chloro- and bromo-derivatives of diphenyl.** F. L. W. VAN ROOSMALEN (Rec. trav. chim., 1934, 53, 359—379).—Diacetylbenzidine and  $\text{Cl}_2$  (rapid stream) in boiling AcOH give the NN'- $\text{Ac}_2$  derivative (I), m.p. 350°, of 3:5:3':5'-tetrachlorobenzidine (II), m.p. 226°. (II) is de-aminated (usual method) to 3:5:3':5'-tetrachlorodiphenyl (III), m.p. 162°, also prepared from 3:5:1- $\text{C}_6\text{H}_3\text{Cl}_2\text{I}$  and Cu powder. (III) and abs.  $\text{HNO}_3$  at 0° give the 2:2'-(IV), m.p. 172°, and 4:4'-(V), m.p. > 360°,  $-(\text{NO}_2)_2$  derivatives. (V) is also prepared from (II) by way of its tetrazonium dinitrate (cf. Körner and Contardi, A., 1917, i, 85). 2:2'-Dinitrobenzidine and  $\text{Cl}_2$  in warm dil. HCl afford 3:5:3':5'-tetrachloro-2:2'-dinitrobenzidine, m.p. 251°, also obtained by hydrolysis (conc.  $\text{H}_2\text{SO}_4$ ) of its  $\text{Ac}_2$  derivative, m.p. 290° [from (I), abs.  $\text{HNO}_3$ , and conc.  $\text{H}_2\text{SO}_4$  at 0°], which is de-aminated to (IV). Short treatment of diacetylbenzidine with  $\text{Cl}_2$  (rapid stream) in boiling AcOH gives the  $\text{Ac}_2$  derivative of 3:3'-dichlorobenzidine. The latter is converted into 3:4:3':4'-tetrachlorodiphenyl, m.p. 171°, which with abs.  $\text{HNO}_3$  at 0° gives the 6:6'-( $\text{NO}_2$ ) $_2$ -derivative, m.p. 186°. This is reduced (Fe powder, AcOH) to the  $(\text{NH}_2)_2$ -derivative, m.p. 167°, which with 15% HCl at 200° affords 2:3:6:7-tetrachlorocarbazole, m.p. 267°. Reduction (Zn dust, aq. EtOH-NaOH) of 3:5- $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$  gives 3:5:3':5'-tetrachloro-azobenzene, m.p. 195°, reduced (Zn dust, AcOH) to the -hydrazobenzene, m.p. 129°; this is converted by conc.  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  (2:1 by vol.) into 2:6:2':6'-tetrachlorobenzidine (VI), m.p. 212° ( $\text{Ac}_2$  derivative, m.p. 312°), which is de-aminated to 2:6:2':6'-tetrachlorodiphenyl, m.p. 198°. 3:5:3':5'-Tetrabromobenzidine (VII) [ $\text{Ac}_2$  derivative (VIII), chars at 340°] is de-aminated to 3:5:3':5'-tetrabromodiphenyl, m.p. 186°, nitration of which affords non-homogeneous products. (VII) is converted [as (II)] into 3:5:3':5'-tetrabromo-4:4'-dinitrodiphenyl, m.p. > 360°. 2:2'-Dinitrobenzidine and  $\text{Br}-\text{H}_2\text{O}$  in dil. HCl give 3:5:3':5'-tetrabromo-2:2'-dinitrobenzidine, m.p. 272° [ $\text{Ac}_2$  derivative, m.p. 266° (slight decomp.), from (VIII), abs.  $\text{HNO}_3$ , and conc.  $\text{H}_2\text{SO}_4$  at 0°—room temp.], de-aminated to a little 3:5:3':5'-tetrabromo-2:2'-dinitrodiphenyl, m.p. 192°, and (largely) a condensation product, m.p. > 300°. 3:4:3':4'-Tetrabromodiphenyl, m.p. 169°, is prepared from 3:3'-dibromobenzidine. 3:4:5:3':4':5'-Hexachloro-, m.p. 198° [2:2'-( $\text{NO}_2$ ) $_2$ -derivative, m.p. 209°], and -hexabromo-, m.p. 248° [2:2'-( $\text{NO}_2$ ) $_2$ -derivative, m.p. 287—288°], -diphenyl are obtained (Sandmeyer) from (II) and (VII), respectively. (VI) and  $\text{Cl}_2$  in dil. HCl give octachlorobenzidine, m.p. 289°, de-aminated to 2:3:5:6:2':3':5':6'-octachlorodiphenyl, m.p. 161° and converted (Sandmeyer) into decachlorodiphenyl, m.p. 310° (Maquenne block). 2:4:6:2':4':6'-Hexachlorodiphenyl, m.p. 112°, is prepared from (VI). H. B.

Application of electronic theory to organic compounds. IV. Naphthalenemonosulphonic acids. A. M. BERKENHEIM and M. G. TSCHENTSOVA (J. Gen. Chem. Russ., 1933, 3, 933—946; cf. this vol., 176, 289).— $\beta\text{-C}_{10}\text{H}_7\cdot\text{O}\cdot\text{SOCl}$  (I), m.p. 72—75°, obtained from  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  (II) and  $\text{SOCl}_2$  in  $\text{Et}_2\text{O}$  at 0°, readily decomposes, with elimination of  $\text{SOCl}_2$  to afford a product, m.p. 200°, from which  $(\text{C}_{10}\text{H}_7)_2\text{SO}_3$  (III) is obtained on dissolving in EtOH and adding  $\text{H}_2\text{O}$ . Attempts at preparing  $\beta\text{-C}_{10}\text{H}_7\cdot\text{H}$  sulphite (IV) by hydrolysis of (I) were unsuccessful, the final product being in all cases (III). The salts of (IV) are, however, more stable; thus the Na salt, obtained by shaking an  $\text{Et}_2\text{O}$  solution of (I) with  $\text{H}_2\text{O}$ , and neutralising the aq. layer with NaOH, differs from that of 2- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$  in being readily decomposed by dil. aq. NaOH to yield  $\text{Na}_2\text{SO}_3$  and (II). An interpretation of the above results from the point of view of the electronic theory leads to the conclusion that the first product of sulphonation of  $\text{C}_{10}\text{H}_8$  is 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ , the  $\text{SO}_3\text{H}$  of which then migrates to the third C atom. During the process of fusion with NaOH the  $\text{SO}_3\text{H}$  undergoes electronic rearrangement, with conversion into the sulphite radical, which again migrates to the second C atom to afford (IV), which is converted as above into (II). R. T.

**Metallo-ammino-complexes of nitro-naphthalene- and -benzene-sulphonic acids.** N. N. VOROSHCOV and V. V. KOZLOV (J. Gen. Chem. Russ., 1933, 3, 917—926).—Salts of the type  $\text{Cu}(\text{NH}_3)_4\text{R}_2$  and  $\text{Ni}(\text{NH}_3)_6\text{R}_2$ , where R represents 1:2-, 1:5-, 1:6-, 1:7-, and 1:8- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ , and 1:4- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ , are obtained by adding salts of the appropriate metal to aq.  $\text{NH}_3$  solutions of the sulphonic acids (I). The above salts are, in contrast to those of 2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ , very sparingly sol. in  $\text{H}_2\text{O}$ . Double salts of the type  $\text{NH}_4\text{X}\cdot\text{CuR}_2$  are obtained by adding salts of  $\text{NH}_4^+$  to solutions of (I) containing  $\text{CuSO}_4$ . R. T.

**Synthesis of 1-methyl-2-ethyl- and 2-methyl-1-ethyl-naphthalene.** O. BRUNNER and F. GROF (Monatsh., 1934, 64, 76—79).— $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$  (I) condenses with  $\text{CHEt}(\text{CO}_2\text{Et})_2$  (Na in PhMe) to give Et  $\beta$ -phenylethylethylmalonate, b.p. 186—187°/11 mm., hydrolysed and decarboxylated to  $\gamma$ -phenyl- $\alpha$ -ethyl-n-butyric acid, b.p. 172—173°/11 mm., cyclised (conc.  $\text{H}_2\text{SO}_4$  at 100°) to 1-keto-2-ethyl-1:2:3:4-tetrahydro-, b.p. 140—145°/11 mm., converted by  $\text{MgMeI}$  into 1-methyl-2-ethyl-3:4-dihydro-, b.p. 135—145°/11 mm., dehydrogenated (S) to 1-methyl-2-ethyl-, b.p. 140—145°/11 mm. (picrate, m.p. 97°; styphnate, m.p. 140°), -naphthalene. Similarly with  $\text{CHMe}(\text{CO}_2\text{Et})_2$  (I) affords successively the malonic ester, b.p. 175—185°/11 mm.,  $\gamma$ -phenyl- $\alpha$ -methyl-n-butyric acid, b.p. 155—165°/11 mm., 1-keto-2-methyl-1:2:3:4-tetrahydro-, b.p. 140—150°/11 mm., and through the  $\text{H}_2$ -compound, b.p. 130—140°/11 mm., 2-methyl-1-ethyl-, b.p. 135—145°/11 mm. (picrate, m.p. 110—111°; styphnate, m.p. 141°), -naphthalene. Most b.p. are bath temp. J. W. B.

**Synthesis of 6- and 7-methyl-1-ethylnaphthalene.** O. BRUNNER and F. GROF (Monatsh., 1934, 64, 28—34).— $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COEt}$  condenses with Zn and  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$  to give the OH-ester, converted by  $\text{PBr}_3$  and  $\text{NPhMe}_2$  into the unsaturated ester, b.p.

153—155°/11 mm., reduced (Na-EtOH) to  $\gamma$ -*p*-tolyl-*n*-pentan- $\alpha$ -ol, b.p. 134—136°/11 mm. This is converted through the bromide, b.p. 133°/12 mm., and nitrile into  $\gamma$ -*p*-tolyl-*n*-hexoic acid, b.p. 189°/13 mm., the chloride, b.p. 141°/11 mm., of which is cyclised (AlCl<sub>3</sub>) to 4-keto-6-methyl-1-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 159°/11 mm. (semicarbazone, m.p. 156°), reduced (Clemmensen) to the tetrahydro-derivative, b.p. 126°/10 mm., of 6-methyl-1-ethylnaphthalene, b.p. 135—138°/12 mm. (I) (picrate, m.p. 81.5°; styphnate, m.p. 90°), which is obtained by dehydrogenation (S) at 250—280°. Similarly 1-keto-7-methyl-1:2:3:4-tetrahydronaphthalene with MgEtBr affords 7-methyl-1-ethyl-3:4-dihydro-, b.p. 135°/11 mm., dehydrogenated to 7-methyl-1-ethyl-, b.p. 128°/11 mm. (II) (picrate, m.p. 106°; styphnate, m.p. 142—143°), -naphthalene. Neither (I) nor (II) is identical with the hydrocarbon C<sub>13</sub>H<sub>14</sub> obtained by dehydrogenation of amber. J. W. B.

**Action of bromine on naphthalene-1-sulphonic acid.** J. S. SALKIND, L. VEISBRUT, and M. ALEXEEVA (J. Gen. Chem. Russ., 1933, 3, 892—895).—The products of bromination are 1:5-C<sub>10</sub>H<sub>6</sub>Br·SO<sub>3</sub>H, and 1:4- and 1:5-C<sub>10</sub>H<sub>6</sub>Br<sub>2</sub>, and not the 1:7-isomeride, as supposed by Forsling (cf. A., 1889, 718). R. T.

**$\alpha$ -Sulphonic derivatives of naphthalene.** W. M. CUMMING and G. D. MUIR (J. Roy. Tech. Coll., 1934, 3, 223—230).—Naphthionic acid (I) {NH<sub>2</sub>Ph + 3H<sub>2</sub>O,  $\beta$ - + 3H<sub>2</sub>O [converted by distillation into NH(C<sub>10</sub>H<sub>7</sub> $\beta$ )<sub>2</sub>], and  $\alpha$ - + 4H<sub>2</sub>O, -naphthylamine salts} heated with excess of NH<sub>2</sub>Ph gives only NHPh·C<sub>10</sub>H<sub>7</sub> $\alpha$ . Diazotisation of (I) (addition of aq. NaNO<sub>2</sub> to dil. HCl suspension at room temp.) followed by a Sandmeyer reaction gives 1:4-C<sub>10</sub>H<sub>6</sub>Cl·SO<sub>3</sub>H (anilide, m.p. 143°; o-toluidide, m.p. 151°, p-nitroanilide, m.p. 188°;  $\alpha$ -naphthylamide, m.p. 142°; Na + H<sub>2</sub>O and K salts), and a modified Gattermann reaction affords a 17% yield of the K salt of 1:4-C<sub>10</sub>H<sub>6</sub>I·SO<sub>3</sub>H (amide, m.p. 202°; anilide, m.p. 133°; o-toluidide, m.p. 138°), and 1-C<sub>10</sub>H<sub>7</sub>·SO<sub>3</sub>H (II) [anilide, m.p. 152° (lit. 112°); o-toluidide, m.p. 134°; p-nitroanilide, m.p. 205°] is isolated from the mother-liquor. With boiling HI diazotised 1:8-NH<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·SO<sub>3</sub>H gives only the 1:8-sultone, and with KI and Cu powder (II) is obtained, but Cu<sub>2</sub>Cl<sub>2</sub>-HCl gives 1:8-C<sub>10</sub>H<sub>6</sub>Cl·SO<sub>3</sub>H. J. W. B.

**Syntheses of phenanthrene, chrysene, and picene.** L. RUZICKA and H. HÖSLI, and (in part) A. CASSINA, K. DOLD, H. FRICKER, and F. MOSTERTS (Helv. Chim. Acta, 1934, 17, 470—474).—Mg  $\beta$ -phenylethyl bromide with 1-ketotetrahydronaphthalene (I) gives, after dehydration of the product with 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>3</sub>H, 1-( $\beta$ -phenylethyl)-3:4-dihydronaphthalene, b.p. 165—168°/12 mm., converted by AlCl<sub>3</sub> in CS<sub>2</sub> into chrysene. Similarly Mg  $\beta$ -1-naphthylethyl chloride and (I) give 1-( $\beta$ -1-naphthylethyl)-3:4-dihydronaphthalene (II), b.p. 225—227°/1 mm., converted by distillation with P<sub>2</sub>O<sub>5</sub> into (·CH<sub>2</sub>·C<sub>10</sub>H<sub>7</sub>-1)<sub>2</sub> (III). With AlCl<sub>3</sub> (II) or (III) affords picene. Dibenzyl is similarly partly converted into phenanthrene. J. W. B.

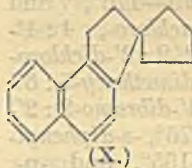
**Synthesis of compounds related to sterols, bile acids, and oestrus-producing hormones.**  
II. Formation of tetracyclic hydroaromatic hydrocarbons. J. W. COOK and C. L. HEWETT (J.C.S., 1934, 365—377).—The compound previously

described (A., 1933, 1042) as *trans*-1:2-cyclopentano-1:2:3:4-tetrahydrophenanthrene is now considered to be 7:8-dihydrophenalyl-7-spirocyclopentane (I). (I) is oxidised (dil. HNO<sub>3</sub> at 175—180°) to 4-nitrohemimellitic acid (Me ester, m.p. 143—144°), also obtained similarly from 4-nitronaphthalic acid. 1-( $\beta$ -1'-Naphthylethyl)cyclohexanol (II), b.p. 220°/7 mm., m.p. 60—70° (from cyclohexanone and 1-C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>·CH<sub>2</sub>·MgCl), is dehydrated (KHSO<sub>4</sub> at 160°) to 1-( $\beta$ -1'-naphthylethyl)- $\Delta^1$ -cyclohexene, b.p. 167—168°/3—4 mm., which is converted by AlCl<sub>3</sub> in CS<sub>2</sub> at 0° into



7:8-dihydrophenalyl-7-spirocyclohexane (III), b.p. 176—177°/5 mm., m.p. 55—56° (picrate, m.p. 141—142°), *cis*(?)-as-octahydrochrysene (IV), m.p. 78—79° (picrate, 2C<sub>18</sub>H<sub>20</sub>C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub>, m.p. 106—106.5°), and *trans*(?)-as-octahydrochrysene (V), m.p. 114—114.5° (IV and V) are dehydrogenated (Se at 300—310°) to chrysene (VI), whilst (III) and Se at 320—340° give (by ring fission and loss of 2C) some pyrene (VII). (I) is similarly converted into 1-methylpyrene (VIII) and not an indene (cf. *loc. cit.*). The absorption curves of (VII) and (VIII) are very similar. Treatment of (II) with AcOH-conc. H<sub>2</sub>SO<sub>4</sub> at 100° and subsequent dehydrogenation (Se at 310—330°) gives (VI) and unchanged (III). The dihydrophenalene of Mayer and Sieglitz (A., 1922, i, 740) could not be prepared from  $\beta$ -1-naphthylpropionyl chloride and AlCl<sub>3</sub>; the free acid and anhyd. SnCl<sub>4</sub> at 120° afford 9-phenalene, m.p. 153—154° [which has marked basic properties and is the "pyrene ketone" of Bamberger and Philip (A., 1887, 271)], and a little of a ketone, C<sub>13</sub>H<sub>10</sub>O (either 7:8-dihydro-9-phenalene or 4:5-benz-1-hydrindone), m.p. 120—121° [oxime, m.p. 226—227° (slight decomp.)]. 4-Keto-1:2:3:4-tetrahydrophenanthrene, CH<sub>2</sub>Br·CO<sub>2</sub>Et, and Zn filings (activated with I) in C<sub>6</sub>H<sub>6</sub> give [after hydrolysis (MeOH-KOH)] 1:2-dihydrophenanthryl-4-acetic acid, m.p. 173—174°, cyclised by 85% H<sub>2</sub>SO<sub>4</sub> at 100° (bath) to 5-keto-1:2:4:5-tetrahydropyrene, m.p. 130—130.5°, which when reduced (Na, amyl alcohol) and then dehydrogenated (Se at 330—340°) affords (VII). The crude carbinol from 1-keto-1:2:3:4-tetrahydronaphthalene and CH<sub>2</sub>Ph·CH<sub>2</sub>·MgCl is dehydrated (KHSO<sub>4</sub> at 160°) to 1-( $\beta$ -phenylethyl)-3:4-dihydronaphthalene, b.p. 209—212°/16 mm., which is converted by AlCl<sub>3</sub> in CS<sub>2</sub> at 0° into 1-( $\beta$ -phenylethyl)naphthalene, b.p. 175°/5 mm. (dipicrate, m.p. 116—117°) (also prepared by Clemmensen reduction of 1-C<sub>10</sub>H<sub>7</sub>·CO·CH<sub>2</sub>Ph); cyclisation to hexahydrochrysene does not occur.

The compound C<sub>17</sub>H<sub>12</sub>, described by Kon (A., 1933, 1153) as an indene, is now shown to be chrysofluorene (1:2-benzfluorene) (IX).  $\alpha$ -Hydrindone and CH<sub>2</sub>Ph·CH<sub>2</sub>·MgCl give (after dehydration) 3-( $\beta$ -phenylethyl)indene, b.p. 186°/9 mm., converted by AlCl<sub>3</sub> in CS<sub>2</sub> at 0° or AcOH-conc. H<sub>2</sub>SO<sub>4</sub> at 100° into a little tetrahydrochrysofluorene, b.p. 176°/8 mm., which is dehydrogenated (Se at 300—340°) to (IX). (IX) is probably formed by rearrangement of the spiran (X), which is considered to be present in the crude mixture of tetra-



cyclic hydrocarbons obtained from 1-( $\beta$ -1'-naphthylethyl)- $\Delta^1$ -cyclopentene. There is no evidence that dehydrogenation (Se) of a five-membered ring can occur. The 5'-methyl-1:2-cyclopentadienophenanthrene of Kon (*loc. cit.*) is (probably) 1:2-dimethylpyrene.

2- $\beta$ -Phenylethyl-trans-decahydro- $\beta$ -naphthol, b.p. 193—194°/5—6 mm., m.p. 54—59°, is dehydrated (KHSO<sub>4</sub> at 170—180°) to 2- $\beta$ -phenylethyl- $\Delta^{2:3}$ -octahydronaphthalene (XI), b.p. 155°/3—4 mm., converted by AlCl<sub>3</sub> in CS<sub>2</sub> at 0° into dodecahydro-1:2-benzanthracene (XII), m.p. 71—72°, and a mixture of stereoisomerides (A) of (XII). Dehydrogenation (Se at 320—330°) of (XII) gives 1:2-benzanthracene, also formed together with 5:6:7:8-tetrahydro-1:2-benzanthracene, m.p. 89—90° (*picrate*, m.p. 155°) [also prepared by Wolff-Kishner reduction of its 5-CO-derivative (Haworth and Mavin, A., 1933, 1043)], by similar dehydrogenation of (A). C<sub>10</sub>H<sub>8</sub>, CH<sub>2</sub>Ph·COCl, and AlCl<sub>3</sub> in CS<sub>2</sub> at 0° give (cf. Graebe and Bungener, A., 1879, 807) a mixture, m.p. 55—58°, of about 80% of 1-phenylacetyl- (XIII), m.p. 66—67° (*picrate*, m.p. 99—100°; *semicarbazone*, m.p. 162—163°), and about 20% of 2-phenylacetylnaphthalene (XIV), m.p. 99—100° [*picrate*, m.p. 143—144°; *semicarbazone* (XV), m.p. 203—205°], separable through the picrates. These results show that the conclusion (A., 1931, 1157) that (XIII) is converted into (XIV) by heat is unjustified, since a mixture was used. 2- $\beta$ -Phenylethyl-naphthalene, m.p. 99—100°, is prepared from (XV) and EtOH-NaOEt at 180—190° or by dehydrogenation (Se) of (XI). The hydrocarbon "C<sub>18</sub>H<sub>16</sub>" (A., 1928, 169) is not 1:2-cyclopentenophenanthrene. H. B.

**Thiocarbamide formation under different conditions.** L. C. RAIFORD and G. M. McNULTY (J. Amer. Chem. Soc., 1934, 56, 680—681).—*s*-Diarylthiocarbamides (I) could not be obtained from 3-nitro-, 3:5-dichloro-, and 3:4- and 3:5-dibromo-anilines, CS<sub>2</sub>, and a little S in EtOH; they can be prepared by Fry's method (A., 1913, i, 1174) (reaction is accelerated by stirring). Satisfactory yields of (I) are usually obtained from NH<sub>2</sub>Ar, CS<sub>2</sub>, and a little powdered NaOH in EtOH. Snedker's method (J.S.C.I., 1925, 44, 486T) is not generally satisfactory when solid NH<sub>2</sub>Ar is used. *o*- and *p*-NO<sub>2</sub>-derivatives do not give (I) by any method tried. The following are described: 6-acetamido-*m*-toluidine, m.p. 129—130° (lit. 143°); 2-bromo-, m.p. 129—130°, 3-bromo-, m.p. 210—211°, and 3:5-dibromo-, m.p. 244—245°, -4-acetamidoaniline; 4-chloro-2'-aminodiphenyl, m.p. 52°; 6-bromo-4-methoxy-*m*-toluidine, m.p. 96° (*Ac* derivative, m.p. 122—123°, prepared by bromination of 3-acetamido-*p*-tolyl Me ether); 3:4:3':4', m.p. 100—103°, and 3:5:3':5', m.p. 134—135°, -tetrabromo-, 2:4:2':4', m.p. 184—185°, 2:5:2':5', m.p. 175—176°, and 3:5:3':5', m.p. 156—157°, -tetrachloro-, 4:4'-dichloro-2:2'-dibromo-, m.p. 206—207°, 2:2'-dichloro-4:4'-dibromo-, m.p. 159—160°, 2:2'-dimethoxy-5:5'-dimethyl-, m.p. 143—144°, and 4:4'-dibromo-2:2'-dimethoxy-5:5'-dimethyl-, m.p. 175—176°, -*s*-diphenylthiocarbamides; *s*-di-*o*-, m.p. 154—155°, and -*p*-, m.p. 230°, -diphenylthiocarbamides; *s*-di-4'-chloro-*o*-,

m.p. 193—194°, and -*p*-, m.p. 219—220°, -diphenylthiocarbamides. H. B.

**Nitration of ethyl 2:4-dimethyloxanilate.** G. TIERIE (Rec. trav. chim., 1934, 53, 355—358).—*Et* 2:4-dimethyloxanilate (I), m.p. 56° (obtained together with a little *ox-m*-4-xylylide from approx. equimol. amounts of Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and *m*-4-xylylide), and HNO<sub>3</sub> (*d* 1.48) at 0° give the 5:6-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 172°, hydrolysed (conc. H<sub>2</sub>SO<sub>4</sub>) to 5:6-dinitro-*m*-4-xylylidine. With HNO<sub>3</sub> (*d* 1.42) at 0°, *Et* 6-nitro-2:4-dimethyloxanilate, m.p. 97°, results. (I) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in EtOH give 2:4-dimethyloxanilhydrazide, m.p. 160° (*benzylidene*, m.p. 208°, and *isopropylidene*, m.p. 140°, derivatives). H. B.

**Manufacture of *o*-aminoarylalkylsulphones, *o*-aminoarylaralkylsulphones, and azo dyes therefrom.**—See B., 1934, 267.

**Formation of cyclic compounds from diphenyl derivatives. II. Formation of 4:5:9:10-dibenzopyrene and 4:5-diphenyldiphenylene oxide from 6:6'-diphenyldiphenyl-2:2'-bisdiazonium sulphate.** S. SAKO (Bull. Chem. Soc. Japan, 1934, 9, 55—74).—2-Acetamidodiphenyl (easily obtained by use of Ac<sub>2</sub>O if AcOH formed is removed) is nitrated by HNO<sub>3</sub> in Ac<sub>2</sub>O-AcOH to 3-nitro-2-acetamidodiphenyl (I), m.p. 188—188.5°. From this 3-nitro-2-aminodiphenyl (II), m.p. 44—45°, b.p. 194—196°/6 mm., 2:3-diaminodiphenyl dihydrochloride (red diaminophenazine with FeCl<sub>3</sub>), and, using NaOAc and phenanthraquinone, 5-phenyl-2:3-(*oo'*-diphenylene)quinoxaline, m.p. 221°, are successively obtained. With (I), 5-nitro-2-acetamidodiphenyl (A., 1928, 1367) is formed, hydrolysed and reduced to 2:5-diaminodiphenyl dihydrochloride (violet ppt. with FeCl<sub>3</sub>). Diazotised (II) yields (KI) 2-iodo-3-nitrodiphenyl, m.p. 90—91°, b.p. 178°/4 mm., converted (Cu) into 2:2'-dinitro-, m.p. 201—202°, and thence into 2:2'-diamino-6:6'-diphenyldiphenyl (III), m.p. 163—164° (*hydrochloride, sulphate*); attempts to resolve (III), with a view of showing that lack of optical activity in Ph<sub>2</sub> compounds containing a 2:2':5- or 6-membered ring is not due to racemisation, were unsuccessful. Heating (III) with 2*N*-HCl at 200° leads to 4:5-diphenylcarbazole, m.p. 145—146°, and diazotisation and decomp. to products varying with temp. The main product at any temp. is 4:5:9:10-dibenzopyrene (IV), m.p. 353—355°. Decomp. at 100°, without Cu, yields in addition 4:5-diphenyldiphenylene oxide, m.p. 154—155°, with some 2:2'-dihydroxy-6:6'-diphenyldiphenyl, m.p. 145—147°. Decomp. of diazotised 6:6'-diamino-2:2'-dimethyldiphenyl yields 6:6'-dihydroxy-2:2'-dimethyldiphenyl, m.p. 161—162.5°. E. W. W.



(IV.)

**Preparation of 3:3'-diamino- and -dihydroxyazobenzene and analogous compounds.** P. RUGGLI and M. HINOVKER (Helv. Chim. Acta, 1934, 17, 396—412).—The best methods for the prep. and purification of these substances are described. 3:3'-Diaminoazobenzene (I) (Bz<sub>2</sub> derivative, m.p. 247°; lit. 272°) is obtained in 85% yield by electrolytic

reduction of  $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  (II) with a c.d. of 4.7 amp., for 23.2 amp.-hr. With conc.  $\text{H}_2\text{SO}_4$  at  $50\text{--}80^\circ$  (I) gives mainly 3 : 3'-diamino-4-hydroxyazobenzene ( $\text{Ac}_3$ , m.p.  $214^\circ$ , and  $\text{Bz}_3$ , m.p.  $289^\circ$ , derivatives) and a brown powder, m.p.  $182^\circ$ . Similar reduction of (II) for 31 amp.-hr. gives 3 : 3'-diaminoazobenzene (III) (75% yield), best purified by crystallisation from xylene with addition of  $\text{PbO}_2$  which oxidises any hydrazo-compound present. Longer reduction gives a 90% yield of 3 : 3'-diaminohydrazobenzene (IV), m.p.  $169^\circ$  (lit.  $153^\circ$ ) ( $\text{Bz}_3$ , m.p.  $198^\circ$ , and  $\text{Ac}_1$ , m.p.  $90^\circ$ , derivatives). When heated alone or in  $\text{PhNO}_2$  or  $\text{C}_6\text{H}_5\text{Cl}_3$ , (IV) gives (III) and  $\text{C}_6\text{H}_4(\text{NH}_2)_2$  which resinifies. With warm 10%  $\text{HCl}$  followed by rapid cooling (IV) gives its hydrochloride, but when heated, or with conc.  $\text{H}_2\text{SO}_4$  at  $115\text{--}120^\circ$ , rearrangement to 2 : 4 : 2' : 4'-tetra-aminodiphenyl occurs. 3 : 3'-Dihydroxyazoxybenzene ( $\text{Bz}_2$ , m.p.  $175^\circ$ , and  $\text{Ac}_2$ , m.p.  $102^\circ$ , derivatives) is obtained in 65% yield by reduction of  $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  with  $\text{Zn}$ -30%  $\text{KOH}$  at  $< 20^\circ$ , a similar reduction at the b.p. giving the corresponding azo-compound [ $\text{Bz}_2$ , m.p.  $180^\circ$  (lit.,  $129^\circ$ ), and  $\text{Ac}_2$ , m.p.  $144^\circ$  (lit.,  $137^\circ$ ), derivatives], which is obtained only in 38% yield by diazotisation of (III).  
J. W. B.

**Rearrangements of phenyl ethers.** Course of the reaction in presence of foreign aromatic compounds. R. A. SMITH (J. Amer. Chem. Soc., 1934, 56, 717—718).— $\text{PhOPr}^\beta$  is converted by  $\text{AlCl}_3$  at room temp. into a mixture (65% yield) of *o*- and *p*- $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{OH}$ ,  $\text{C}_6\text{H}_3\text{Pr}^\beta_2\cdot\text{OH}$ , and a little material of higher b.p.; in presence of an equimol. amount of  $\text{Ph}_2\text{O}$ , a 30% yield of the same products with  $\text{PhOH}$  (33%) and *o*-, b.p.  $263.4^\circ$ , and *p*-, b.p.  $288.9^\circ$ , -isopropylidiphenyl ethers are formed. *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OPr}^\beta$  and  $\text{AlCl}_3$  give 70% of 3-isopropyl-*p*-cresol (I); in presence of  $\text{C}_6\text{H}_6$  (3 vols.), *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$  (II) and cumene (about 60%) are the main products, whilst in  $\text{Ph}_2\text{O}$  (excess), (I) (8—10%), (II) (50%), and isopropylidiphenyl ether (about 40%) are formed.  $\text{PhOBu}^\beta$  and  $\text{AlCl}_3$  afford *p*- $\text{C}_6\text{H}_4\text{Bu}^\beta\cdot\text{OH}$  (III); in presence of  $\text{C}_6\text{H}_6$  (excess), 5—6% of (III) is obtained, whilst 70% is converted into mono- (mainly), di-, and tri-*tert*-butylbenzene. These rearrangements appear to be inter- and not intra-mol.  
H. B.

**Behaviour of nitrophenols with *p*-toluenesulphonyl chloride.** IV. S. S. JOSHI (J. Indian Chem. Soc., 1933, 10, 677—678; cf. A., 1925, i, 134; 1928, 1130).—Iodination of 4 : 6-dinitro-*m*-cresol in presence of  $\text{HgO}$  gives the 2-*I*-derivative, m.p.  $93^\circ$ , the *p*-toluenesulphonate of which, m.p.  $136\text{--}137^\circ$ , is converted by  $\text{NH}_3$  in  $\text{EtOH}$  into 2-iodo-4 : 6-dinitro-*m*-toluidine, m.p.  $97^\circ$ , and by  $\text{NH}_2\text{Ph}$  into 2-iodo-4 : 6-dinitro-3-methyldiphenylamine, m.p.  $143\text{--}144^\circ$ . 3 : 2 : 4- $\text{C}_6\text{H}_3\text{MeClBr}(\text{NO}_2)_2$  is similarly converted by  $\text{NH}_3$  into 2-bromo-4 : 6-dinitro-*m*-toluidine, m.p.  $80^\circ$ , and by  $\text{NH}_2\text{Ph}$  and  $\text{NaOAc}$  into 2-bromo-4 : 6-dinitro-3-methyldiphenylamine, m.p.  $128^\circ$ . 2-Bromo-4 : 6-dinitro-*m*-tolyl *p*-toluenesulphonate has m.p.  $141^\circ$ .  
H. A. P.

**Fluorescence of a new organic substance.** S. SCHLIVIC and S. LEBEDEV (Bull. Soc. Chim. Yougoslav., 1933, 4, 133—136).—Carvacrol and malic acid react with conc.  $\text{H}_2\text{SO}_4$  to yield a yellow, resinous

product, the dil. aq. alkaline solutions of which are colourless, and exhibit an intense blue fluorescence on ultra-violet irradiation.  
R. T.

**Action of sodium ethoxide on phenyl thiocyanate.** J. ROSS (J. Amer. Chem. Soc., 1934, 56, 727—729).—The main reaction between  $\text{PhSCN}$  and  $\text{EtOH}\text{-NaOEt}$  is  $\text{PhSCN} + \text{NaOEt} \rightarrow \text{PhSNa} + \text{EtOCN}$  [ $\rightarrow \text{EtNCO} \rightarrow \text{NHEt}\cdot\text{CO}_2\text{Et}$  (isolable)]; a secondary reaction (20%) gives  $\text{Ph}_2\text{S}_2$  and  $\text{PhEtS}$ , probably thus :  $\text{PhSCN} + \text{NaOEt} \rightarrow \text{NaCN} + \text{PhS}\cdot\text{OEt}$  (I);  $\text{PhS}\cdot\text{OEt} \rightarrow \text{PhEtS}\cdot\text{O} \xrightarrow{2\text{PhSH}} \text{Ph}_2\text{S}_2 + \text{PhEtS} + \text{H}_2\text{O}$ .  $\text{PhSH}$  and  $\text{PhEtS}\cdot\text{O}$  in  $\text{EtOH}$  containing a little  $\text{NaOEt}$  give  $\text{Ph}_2\text{S}_2$  and  $\text{PhEtS}$ ; similarly,  $\text{PhSH}$  and *Et benzenesulphenate* (I), b.p.  $100^\circ/4$  mm. [prepared by Lecher's method (A., 1925, i, 390)], react vigorously to give  $\text{Ph}_2\text{S}_2$ .  $\text{PhSH}$  and  $\text{KCNO}$  in boiling  $\text{EtOH}$  afford 15% of  $\text{Ph}_2\text{S}_2$ .  $\text{PhSCN}$  and  $\text{EtOH}$ -free  $\text{NaOEt}$  in  $\text{Et}_2\text{O}$  or  $\text{C}_6\text{H}_6$  give a quant. yield of  $\text{Ph}_2\text{S}_2$ .  
H. B.

**Oestrogenic activity of condensed-ring systems.**—See this vol., 457.

**5-Nitrosopyrocatechol-4-sulphonic acid and derivatives.** J. ŽIKA (Coll. Czech. Chem. Comm., 1934, 6, 60—68).—Action of  $\text{HNO}_2$  (2 equiv.) on *Na* pyrocatechol-4-sulphonate (cf. A., 1933, 947) gives 5-nitrosopyrocatechol-4-sulphonic acid [as *Na* salt (+ $3\text{H}_2\text{O}$ ); *K* salt (+ $1\text{H}_2\text{O}$ );  $\text{Me}_2$  ether [*Na* salt (I) (+ $1\text{H}_2\text{O}$ ); *K* salt; sulphonyl chloride, m.p.  $132^\circ$ ; amide, m.p.  $198\text{--}201^\circ$ ; anilide]} which is reduced by  $\text{Sn}$  and  $\text{HCl}$  to the 5- $\text{NH}_2$ -acid. Reduction of (I) similarly gives 5-aminoveratrole-4-sulphonic acid (cf. J.C.S., 1917, 111, 952). Action of  $\text{HNO}_3$  (*d* 1.41) on (I) at  $100^\circ$  gives 4 : 5-dinitroveratrole, m.p.  $128^\circ$ .  
H. A. P.

**Preparation of di- $\beta$ -naphthol by oxidising  $\beta$ -naphthol with oxides of metals.** I. S. TRAVKIN (Anilinokras. Prom., 1934, 4, 13—17).—2 : 2'-Dihydroxy-1 : 1'-dinaphthyl is obtained in 70% yield by heating  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  (I) during 7 hr. at  $260^\circ$  with  $\text{Fe}(\text{OH})_3$  (II),  $\text{CuO}$ , or  $\text{MnO}_2$ , and 92% yield by adding colloidal (II) to boiling aq. solutions of (I).  
R. T.

**Optically active *cis*- and *trans*-1-methylcyclohexan-3-ol.** M. GODCHOT and (Mlle.) G. CAUQUIL (Compt. rend., 1934, 198, 663—665).—3-Methylcyclohexanone (I) with *Na* in moist  $\text{Et}_2\text{O}$  affords only *l*-*trans*-1-methylcyclohexan-3-ol (II), b.p.  $76\text{--}77^\circ/16$  mm. (*phenylurethane*, m.p.  $117\text{--}117.5^\circ$ ; *p*-nitrobenzoate, m.p.  $45\text{--}45.5^\circ$ ; *H phthalate*, m.p.  $92\text{--}93^\circ$ ), but with  $\text{H}_2\text{-Pt}$  gives the *l*-*cis*-form (III), b.p.  $67\text{--}68^\circ/16$  mm. (cf. A., 1926, 1032) (*phenylurethane*, m.p.  $90^\circ$ ; *p*-nitrobenzoate, m.p.  $78\text{--}79^\circ$ ; *H phthalate*, an oil), and (I), separated by fractional crystallisation of their *p*-nitrobenzoates. Oxidation ( $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ ) of (II) and (III) affords optically active (I).  
J. L. D.

**Hydrogenation of optically active compounds over nickel and copper-chromium oxide.** E. BOWDEN and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 689—691).—Hydrogenation ( $\text{H}_2$  at  $150\text{--}200$  atm.;  $\text{Cu-Cr}$  oxide catalyst;  $250^\circ$  except where stated otherwise) of *Et*  $\alpha$ -phenylpropionate, + $22.9^\circ$  (all rotations are  $[\alpha]_D$ ), gives  $\text{PhPr}^\beta$  (33%) and  $\beta$ -phenyl-*n*-propyl alcohol (16%), + $2.5^\circ$ , whilst a specimen of

+65.1° affords PhPr<sup>β</sup> (80%). Similarly, Bu lactate, +4.9°, yields (at 225°) 81% of propane-αβ-diol, 0°; menthyl β-phenylbutyrate, -90.3°, furnishes γ-phenylbutyl alcohol (61—73%), -26° to -31.4°, whilst a specimen, -40.9°, gives γ-phenylbutyl alcohol (33—61%), +12.2° to +15.7°: *menthyl α-phenylbutyrate*, m.p. 58°, -82°, affords *sec.*-BuPh (26%), +0.4°, and β-phenylbutyl alcohol (17%), -3.7°; Et α-phenylbutyrate, -6° and -2.3°, yields β-phenylbutyl alcohol (50 and 61%), < -0.5° and -0.1°, respectively, and (in the former case) 24% of *sec.*-BuPh, 0°; Et α-methylbutyrate, +3.04° and -8.3°, furnishes β-methylbutyl alcohol (80 and 97%), 0° and +1.2°, respectively; Et β-methylvalerate, +1.79°, gives 90% of γ-methylamyl alcohol, +1.8°; Et α-ethylnonoate, b.p. 131°/23 mm., -0.65°, affords 50% of β-ethyl-n-nonyl alcohol, b.p. 126°/19—20 mm., -0.2°; Et δ-phenyl-α-ethylvalerate, b.p. 162—165°/23—25 mm., +0.26°, yields 47% of ε-phenyl-β-ethyl-n-amyl alcohol, b.p. 150—153°/18—20 mm., +0.26°; in the above reductions, varying amounts of ester are recovered and in some cases much racemisation has occurred. Camphor, +46.5°, gives (at 150°) a borneol, m.p. 197°, -9.2°; at 120°, α-isoborneol, m.p. 208—209°, -22.3°. The "menthol" recovered from the hydrogenation of menthyl esters has  $[\alpha]_D$  -17° and is an isomeride or mixture of isomerides. Reduction (Raney Ni catalyst at 200°) of β-, -2.4°, and γ-, +14°, -phenylbutyl alcohols affords β-, b.p. 119—121°/18 mm., -1.22°, and γ-, b.p. 130°/18—20 mm., +4.02°, -cyclohexylbutyl alcohol, respectively. dl-α-Ethylnonoic acid, b.p. 117—118°/5—6 mm., and dl-δ-phenyl-α-ethylvaleric acid, b.p. 141—143°/5—6 mm., are prepared by way of C<sub>6</sub>H<sub>13</sub>·CH<sub>2</sub>·CEt(CO<sub>2</sub>Et)<sub>2</sub> and CH<sub>2</sub>Ph·CH<sub>2</sub>·CH<sub>2</sub>·CEt(CO<sub>2</sub>Et)<sub>2</sub>, respectively. H. B.

**Marine products. III. Ostreasterol.** W. BERGMANN (J. Biol. Chem., 1934, 104, 553—557; cf. this vol., 404).—Hydrogenation (Pd-black-PtO<sub>2</sub>) of the acetate (I) of ostreasterol (II) gives ostreastanyl acetate, identical with sitostanyl acetate and giving sitostanol and sitostanone (ostreastanone). (II) is, therefore, C<sub>29</sub>H<sub>48</sub>O (lit. C<sub>27</sub>H<sub>44</sub>O), isomeric with stigmastanol. (I) gives a Br<sub>4</sub>-derivative, m.p. 150.5°, reduced to (I) by Zn and AcOH. R. S. C.

**Constitution of œstrin.** J. F. DANIELLI (J. Amer. Chem. Soc., 1934, 56, 746—747).—The work of Butenandt *et al.* (A., 1933, 540), in conjunction with the results (*ibid.*, 605) obtained with unimol. films of derivatives of œstrin, proves that the five-membered ring is in the same position as in the sterols. H. B.

**Resolution of trans-cycloheptane-1 : 2-diol.** M. GODCHOT and M. MOUSSERON (Compt. rend., 1934, 198, 837—838).—dl-cycloheptane-1 : 2-diol (I) is converted by H<sub>2</sub>SO<sub>4</sub> at -5° into its di(H sulphate) the strychnine salt of which (prep. through the Ba salt) is resolved by crystallisation from EtOH at 90° into a more sol. strychnine salt +2.5H<sub>2</sub>O,  $[\alpha]_{5460}$  -33.40°, and a less sol. strychnine salt +2.5H<sub>2</sub>O,  $[\alpha]_{5460}$  -23.50°, the latter giving 1-cycloheptane-1 : 2-diol, b.p. 138—139°/15 mm.,  $[\alpha]_{5460}$  -44.25° (phenylurethane, m.p. 275°). (I) is therefore the trans-diol. J. W. B.

**Configuration of polyalcohols deduced from their effect on the conductivity of boric acid.** J. BÖESEKEN (Bull. Soc. chim., 1933, [iv], 53, 1334—1357).—A lecture.

**Decarboxylation of 1-phenylcycloparaffin-1-carboxylic acids.** F. H. CASE (J. Amer. Chem. Soc., 1934, 56, 715—717).—1-Phenyl-cyclopropane, m.p. 86—87°, -cyclobutane-, m.p. 106—107°, -cyclopentane-, m.p. 158—159° (amide, m.p. 157—158°), and -cyclohexane-, m.p. 121° (amide, m.p. 95—96°), -1-carboxylic acids are prepared in 14.5—46% yield from CHNaPh·CN and (CH<sub>2</sub>)<sub>n</sub>Br<sub>2</sub> in Et<sub>2</sub>O and subsequent hydrolysis (EtOH-KOH). 2-Phenyl-hydrindene-2-carboxylic acid, m.p. 194—195°, is similarly obtained in 8% yield from *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub>. 1-Phenylcycloheptane-1-carboxylic acid could not be prepared by this method. Phenyl-cyclopropane (I), b.p. 79—80°/37 mm., 171°/771 mm., -cyclobutane-, b.p. 101—102°/41 mm., 190—191°/755 mm., -cyclopentane-, b.p. 116—117°/37 mm., 216°/755 mm., and -cyclohexane-, b.p. 127—128°/30 mm., 238°/759 mm., are obtained when the appropriate Ba salt (1 mol.) is heated with dry NaOMe (3 mols.) at 40 mm.; ketones are removed by fractionation. The unsaturated material accompanying (I) is removed with 1% KMnO<sub>4</sub> at 0°. H. B.

**Crystalline forms of N-substituted 3-nitrophthalimides.** P. P. T. SAH and T. S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 147—149).—Photographs of the N-substituted 3-nitrophthalimides previously described are reproduced (A., 1932, 1231). F. R. S.

**Preparation of γ-p-aminophenylbutyric and ε-p-aminophenylhexoic acids.** J. VAN DER SCHEER (J. Amer. Chem. Soc., 1934, 56, 744—745).—γ-Phenylbutyric acid and HNO<sub>3</sub> (*d* 1.42) at 20—25° give the p-NO<sub>2</sub>-derivative (I), m.p. 92—93°, reduced (Zn dust, N-HCl) to γ-p-aminophenylbutyric acid, m.p. 130—131°. ε-Phenylhexoic acid, b.p. 192—196°/20—22 mm. (lit. 180—190°/17 mm.), prepared by way of Et δ-phenylbutylmalonate, b.p. 212—215°/20—22 mm., similarly gives p-NO<sub>2</sub>- (II), m.p. 64—65°, and p-NH<sub>2</sub>-derivatives, m.p. 108—109°. (I) and (II) are oxidised (dil. HNO<sub>3</sub> at 200°) to p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H. H. B.

**ortho-Effects. II. Naphthalene series.** H. WILLSTADT and G. SCHEIBER (Ber., 1934, 67, [B], 466—474; cf. A., 1932, 55).—Condensation of CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> with α- and β-C<sub>10</sub>H<sub>7</sub>·CHO in AcOH at 100° leads to 1- (I), m.p. 214—215°, and 2-, m.p. 193° after incipient decomp. at 184°, -naphthylidene-malonic acids, respectively. (I) is converted into β-1-naphthylacrylic acid (II), m.p. 129—130°, which adds Br in CHCl<sub>3</sub> at about the same rate as does *o*-C<sub>6</sub>H<sub>4</sub>F·CH·CH·CO<sub>2</sub>H with production of αβ-dibromo-β-1-naphthylpropionic acid, m.p. 189° (decomp.). The following observations were made during attempts to prepare (II) with substituents at 2 or 8. 1 : 2-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub> (III) is diazotised and converted through the diazonium borofluoride, decomp. 181°, into 2-fluoro-1-nitronaphthalene, b.p. 120—124°/12—15 mm., m.p. 49—50°. (III) is diazotised and transformed by KI into 2 : 1-C<sub>10</sub>H<sub>6</sub>I·NO<sub>2</sub>, b.p. 172.5°/



10 mm., m.p. 81°. Nitration of 1-C<sub>10</sub>H<sub>7</sub>Me by EtNO<sub>3</sub> in presence of AlCl<sub>3</sub> affords unchanged material and 1:4-C<sub>10</sub>H<sub>6</sub>Me·NO<sub>2</sub>, b.p. 176°/12 mm., m.p. 71—72°. The product obtained by the thermal decomp. of 1-benzeneazonaphthalene-2-diazonium borofluoride, decomp. 158°, is non-cryst. and retains the red colour. 8-Chloro-1-iodonaphthalene has m.p. 80—82°. 8-Nitronaphthalene-1-diazonium borofluoride, violent decomp. 124°, is too explosive to permit regulated decomp. 2-Methylnaphthalene-1-diazonium borofluoride, decomp. 150°, and 1-fluoro-2-methylnaphthalene, b.p. 260—262°, are described. 1:2-C<sub>10</sub>H<sub>6</sub>Br·CHO gives a non-acidic condensation product with CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>. 1:2-C<sub>10</sub>H<sub>6</sub>Cl·NH<sub>2</sub> yields 1-chloro-2-naphthonitrile, b.p. 183—184°/11 mm. 1-Bromo-2-naphthonitrile, b.p. 178°/10 mm., m.p. 93°, is obtained similarly. Acetnaphthalide is transformed by ICl in AcOH into 1-iodo-2-acetnaphthalide, decomp. 167° after becoming brown at 140°, hydrolysed by EtOH-HCl to 1-iodo-β-naphthylamine, m.p. 108°. H. W.

**Preparation of 1:1':3'-triphenylrubene-3-carboxylic acid, C<sub>36</sub>H<sub>23</sub>·CO<sub>2</sub>H, and of its alkali salts.** M. BADOCHÉ (Compt. rend., 1934, 198, 662—663).—Interaction of CO<sub>2</sub> in dry C<sub>6</sub>H<sub>6</sub> with C<sub>6</sub>H<sub>5</sub>MgOPh (cf. A., 1931, 1151), followed by dil. H<sub>2</sub>SO<sub>4</sub>, affords 1:1':3'-triphenylrubene-3-carboxylic acid (I), m.p. about 405° (decomp.) [Na salt (II) (+½EtOH)]. (I) and (II) are decomposed by sunlight in presence of O<sub>2</sub>. J. L. D.

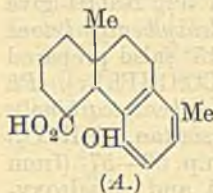
**Reaction of ethyl sodioacetate and tetramethylene dibromide.** L. J. GOLDWORTHY (J.C.S., 1934, 377—378; cf. Perkin, *ibid.*, 1888, 53, 187).—CH<sub>2</sub>Ac·CO<sub>2</sub>Et (2 mols.) and (CH<sub>2</sub>)<sub>4</sub>Br<sub>2</sub> (1 mol.) in EtOH-NaOEt (2 mols.) at 100° (sealed bottle) give Et 1-acetylcyclopentane-1-carboxylate (I), b.p. 125—127°/30 mm., and a small amount of an oil, b.p. 200—205°/30 mm. (I) is converted by a little EtOH-NaOEt into EtOAc and Et cyclopentanecarboxylate, b.p. 171—172°/760 mm., and by EtOH-KOH into cyclopentyl Me ketone, b.p. 153—155°/760 mm. (*semicarbazone*, m.p. 145°). H. B.

**Preparation of aminosalicyclic acid.** A. A. SPRISKOV (Anilinokras. Prom., 1934, 4, 22—27).—5-Aminosalicyclic acid is obtained in 95% yields by the reduction (Na-Hg) of 5-nitrosalicyclic acid. The product of diazotation is an internal anhydride, sol. in HCl with formation of the ordinary diazonium chloride. R. T.

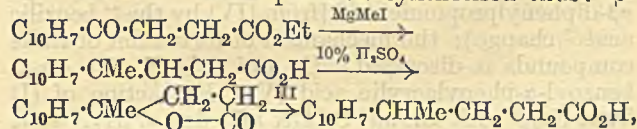
**General method of synthesis of o-aldehydo-carboxylic acids.** S. N. CHAKRAVARTI (J. Indian Chem. Soc., 1933, 10, 693—697).—A symmetrically di- or tetra-substituted [e.g., 2:6-(OMe)<sub>2</sub>] naphthalene is oxidised by alkaline KMnO<sub>4</sub> and the phthalonic acid formed decarboxylated (e.g., by evaporating with HCl and H<sub>2</sub>SO<sub>4</sub>). H. A. P.

**Podocarpic acid.** I. R. SHERWOOD and W. F. SHORT (Rept. Austral. Assoc. Adv. Sci., 1933, 21, 38—42).—Podocarpic acid, C<sub>17</sub>H<sub>29</sub>O<sub>3</sub> (I), m.p. 193.5°, [α]<sub>D</sub><sup>20</sup> +165° in 95% EtOH [Me (II), m.p. 208° (lit. 174°) (Bz derivative, m.p. 143°), Et, m.p. 161° (lit. 143—146°), and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>, m.p. 204°, esters], is best extracted from podocarp resin by 95% EtOH.

(I) with excess of NaOH and rapid addition of Me<sub>2</sub>SO<sub>4</sub>, or the Na compound of (II) with MeI in dry xylene, affords *Me methylpodocarpate*, m.p. 128°, hydrolysed by KOH-EtOH at 150° to the *Me ether*, m.p. 157—158°, of (I). With Ac<sub>2</sub>O (I) gives (?) a *mixed anhydride* (not pure), m.p. 173—176°. Contrary to the lit., p-cresol and methanthrol (III), m.p. 161° (*Me ether*, m.p. 88°; *glycollic ether*, m.p. 191°), are the only



pure substances isolated by dry distillation of the Ca salt of (I). Dehydrogenation of (I) with S gives (III), converted by distillation with Zn dust to 1-methylphenanthrene (IV). (III) is 4-hydroxy-1-methylphenanthrene, identical with a specimen synthesised thus: β-



cyclised by distillation of the acid chloride to 1-keto-4-methyltetrahydrophenanthrene, dehydrogenated (S) to (III). Dehydrogenation of (I) by Se gives (III) and (IV). Since the CO<sub>2</sub>H suffers steric hindrance (I) is most probably (A). J. W. B.

**Trihalogenomethylketonic acids of the naphthalene series.** B. A. BULL and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 736—738).—1-Trichloroacetyl- (I), m.p. 163—165° (decomp.), and 1-tribromoacetyl- (II), m.p. 171—172°, -2-naphthoxyacetic acids are prepared from 1:2-C<sub>10</sub>H<sub>6</sub>Ac·O·CH<sub>2</sub>·CO<sub>2</sub>H and cold aq. NaOH; in the hot, 1-carboxy-2-naphthoxyacetic acid (III), m.p. 189° (decomp.), results. (III) is also formed from (I) or (II) and boiling 10% NaOH; cleavage occurs much more rapidly than with 2:1-OMe·C<sub>10</sub>H<sub>6</sub>·CO·CHAl<sub>3</sub> (A., 1932, 164), presumably owing to better solubility. 2:1-C<sub>10</sub>H<sub>6</sub>Ac·O·CH<sub>2</sub>·CO<sub>2</sub>H (IV) and aq. NaOCl give 2-carboxy-1-naphthoxyacetic acid (V), m.p. 206—207°, in the cold, steric hindrance effect being absent. 4-Chloro- (VI), m.p. 184—185° (decomp.), and 4-bromo-, m.p. 195—196° (decomp.), -2-acetyl-1-naphthoxyacetic acids, prepared from (IV) and Cl<sub>2</sub> and Br in aq. Na<sub>2</sub>CO<sub>3</sub>, are converted by aq. NaOBr into 4-chloro-, m.p. 245—246° [also accompanies (VI)], and 4-bromo-, m.p. 242—243°, -2-carboxy-1-naphthoxyacetic acid, respectively [also prepared by halogenation of (V)]. H. B.

**Acetylenic hydroxy-acid: α-hydroxy-αγ-diphenylbutinenoic acid C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>.** M. LOURY (Compt. rend., 1934, 198, 834—836).—Hydrolysis of its Et ester (A., 1933, 712) in C<sub>6</sub>H<sub>6</sub> with cold aq. alkali affords α-hydroxy-αγ-diphenylbutinenoic acid (I), m.p. 129—130° (decomp.) to a resin, which gives CPhMe on alkaline hydrolysis, and from which a cryst. substance, m.p. 385°, is isolated. (I) is hydrolysed by hot KOH-EtOH to CPh·CH. Mechanisms are suggested. J. W. B.

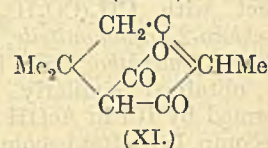
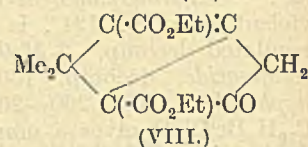
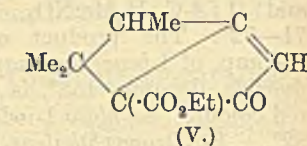
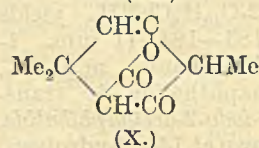
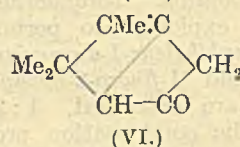
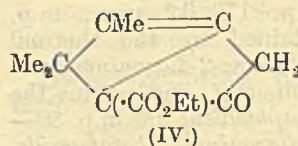
**Reactions of γ-ketonic acids. I. Ketonic β-lactones.** E. P. KOHLER and R. H. KIMBALL (J. Amer. Chem. Soc., 1934, 56, 729—731).—β-Bromo-β-benzoyl-α-phenylpropionic acid (I) (less fusible form;

A., 1927, 262) and cold 1% NaHCO<sub>3</sub> give  $\beta$ -benzoyl- $\alpha$ -phenyl- $\beta$ -propiolactone (II) (about 90%), m.p. 95°, a  $\beta$ -hydroxy- $\beta$ -benzoyl- $\alpha$ -phenylpropionic acid (III), m.p. 132° [*Me* ester, m.p. 89°, using CH<sub>2</sub>N<sub>2</sub>; also obtained from (II) and MeOH-H<sub>2</sub>SO<sub>4</sub>], and an isomeric  $\beta$ -OH-acid (*loc. cit.*). (II) is converted by 50% HBr and MeOH-40% HBr into (I) and the *Me* ester [also obtained from (III) and MeOH-HBr] of (I), respectively. (II) in Et<sub>2</sub>O and aq. 5% NaOH give CH<sub>2</sub>Ph·CO·COPh (IV), benzyl  $\alpha$ -hydroxybenzyl ketone (phenylacetylphenylcarbinol), m.p. 115° [also prepared by hydrolysis (H<sub>2</sub>O) of CH<sub>2</sub>Ph·CO·CHPhBr], Ph  $\alpha$ -hydroxy- $\beta$ -phenylethyl ketone (benzoylbenzylcarbinol), m.p. 66° [also obtained by hydrolysis (aq. NaHCO<sub>3</sub>) of Ph  $\alpha$ -bromo- $\beta$ -phenylethyl ketone, m.p. 56–57° (from CH<sub>2</sub>Ph·CH<sub>2</sub>·COPh and Br in Et<sub>2</sub>O)], and  $\alpha$ -hydroxy- $\alpha$ - $\beta$ -diphenylpropionic acid [from (IV) by the "benzilic acid" change]; the mechanism of formation of these compounds is discussed. (I) and C<sub>5</sub>H<sub>5</sub>N give *cis*- $\beta$ -benzoyl- $\alpha$ -phenylacrylic acid (V). Extraction of (I) from Et<sub>2</sub>O with dil. aq. C<sub>5</sub>H<sub>5</sub>N affords a C<sub>5</sub>H<sub>5</sub>N salt, C<sub>21</sub>H<sub>18</sub>O<sub>3</sub>NBr, m.p. 135° (decomp.). (II) is polymerised by traces of C<sub>5</sub>H<sub>5</sub>N (or KOAc) in MeOH or COMe<sub>2</sub>; the polymeride (mixture) and (II) are converted by C<sub>5</sub>H<sub>5</sub>N into (V).

H. B.

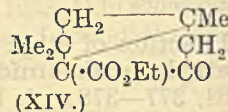
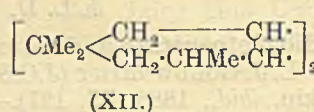
Bridge formation. III. Influence of the methyl and carbethoxy-groups in the internal dehydration of *gem*-disubstituted dihydroresorcinol esters. IV. Tautomerism of isophorone. P. S. MAYURANATHAN (J. Indian Inst. Sci., 1933, 16A, 113–122, 123–127; cf. A., 1933, 503).—III. Presence of a third *Me* group facilitates dehydration of dihydroresorcinol derivatives; this occurs most readily with the di- but also with the mono-carbethoxy-derivatives, but neither substituent is essential. Reversible wandering of a *Me* group during dehydration is considered improbable. Et 1:1-dimethylcyclohexane-3:5-dione-2-carboxylate (A) with cold 25% KOH-EtOH or 60% H<sub>2</sub>SO<sub>4</sub> gives a small amount of the ketone (I), m.p. 176° (*loc. cit.*), a trace of which is also obtained from dimethyldihydroresorcinol and P<sub>2</sub>O<sub>5</sub> in xylene at 100–120°. Et sodiomethylacetoacetate condenses with Et<sub>2</sub> isopropylidenemalonate in hot EtOH with loss of a CO<sub>2</sub>Et group to form Et 1:1:2-trimethylcyclohexane-3:5-dione-6-carboxylate (II), b.p. 187°/21 mm. [*disemicarbazone*, m.p. 225° (decomp.)], also obtained from methylmesityl oxide and CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>. (II) with hot, conc. aq. Ba(OH)<sub>2</sub> gives 1:1:2-trimethyldihydroresorcinol (III); with cold 20% KOH-EtOH (2 days) or 50% H<sub>2</sub>SO<sub>4</sub> it affords the ester (IV), or, less probably, (V), b.p. 145–147°/20 mm. [*semicarbazone*, m.p. 205° (decomp.)], which gives (III) with hot Ba(OH)<sub>2</sub>, but with cold 20% KOH-EtOH after 1 week the ketone (VI), b.p. 105°/20 mm. (*semicarbazone*, m.p. 186°), is obtained. With hot 10% KOH-EtOH (VI) gives (III). Et<sub>2</sub> 1:1-dimethylcyclohexane-3:5-dione-2:6-dicarboxylate (VII) and cold 20% KOH-EtOH (2 days) or 50% H<sub>2</sub>SO<sub>4</sub> give the ester (VIII), b.p. 195°/20 mm. [*semicarbazone*, m.p. 232° (decomp.)], hydrolysed to (I) by hot 60% H<sub>2</sub>SO<sub>4</sub>. The *N*-derivative of (A) or (VII) with MeI yields Et 1:1:4-trimethylcyclohexane-3:5-dione-2-carboxylate, m.p. 108°, b.p. 165°/5 mm. [*disemicarbazone*, m.p. 236°

(decomp.)], which with cold 20% KOH-EtOH (1 week) gives 1:1:4-trimethyldihydroresorcinol (IX)



and with hot or cold 60% H<sub>2</sub>SO<sub>4</sub> affords the lactone (X) or (XI), +0.5H<sub>2</sub>O, m.p. 79° [*semicarbazone*, m.p. 188° (decomp.)], hydrolysed to (IX) by hot 10% KOH-EtOH.

IV. Clemmensen reduction of isophorone gives a small amount of hydrocarbon, C<sub>13</sub>H<sub>22</sub>, b.p. 102°/5 mm., which does not give caronic acid on oxidation and is thus probably (XII). Mesityl oxide (XIII) and Et sodioacetoacetate in EtOH at 0° give the ester (XIV), b.p. 162°/20 mm. [*semicarbazone*, m.p. 218° (decomp.)],



or, if heated, isophorone. (XIV) with NaOEt and MeI at 100° give Et 1:1:2:5-tetramethyl- $\Delta^4$ -cyclohexen-3-one-2-carboxylate (XV), b.p. 175°/20 mm. [*semicarbazone*, m.p. 235° (decomp.)]. (XIII) and Et sodiomethylacetoacetate in EtOH give Et 5-hydroxy-1:1:2:5-tetramethylcyclohexan-3-one-2-carboxylate, b.p. 196°/20 mm., some 1:1:2:5-tetramethyl- $\Delta^4$ -cyclohexen-3-one, b.p. 143°/20 mm., and (XV).

R. S. C.

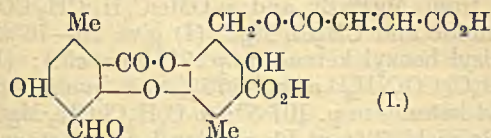
4:5-Dimethoxy-2-benzoylbenzoic acid and its derivatives. A. OLIVERIO (Gazzetta, 1934, 64, 139–148).—*m*-Hemipinic acid reacts with C<sub>6</sub>H<sub>6</sub> (AlCl<sub>3</sub>) to give 4:5-dimethoxy-2-benzoylbenzoic acid (I), m.p. 199–200° (*Me* ester, m.p. 110–111°), together with the partly demethylated 4(or 5)-hydroxy-5(or 4)-methoxy-2-benzoylbenzoic acid. (I) reacts with NHPH<sub>2</sub>, giving a compound, m.p. 212°, and is reduced by Zn-NaOH to 5:6-dimethoxy-3-phenylphthalide, m.p. 156–157°, and by Zn-AcOH to 4:5-dimethoxy-2-benzoylbenzoic acid (II), m.p. 217°. In H<sub>2</sub>SO<sub>4</sub> (II) condenses to 2:3-dimethoxy-9-anthrone (III), m.p. 135–137° (*Ac* derivative, m.p. 174°), whilst with glycerol and H<sub>2</sub>SO<sub>4</sub> (III) yields 2:3-dimethoxy-1:10-benz-9-anthrone, m.p. 276–277°; (III) is also obtained by reduction of 2:3-dimethoxyanthraquinone. *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O and veratrole combine to form 2-3':4'-dimethoxybenzoylbenzoic acid (IV) (*Me* ester, m.p. 109–110°; NHPH<sub>2</sub> derivative, new m.p. 197–197.5°). Reduction of (IV) by Zn-NaOH yields 3-3':4'-dimethoxyphenylphthalide (A., 1920, i, 437) (5'-*Br*-derivative, m.p. 122°), whilst the

product of reduction by Al-Hg in aq.  $\text{NH}_3$  or by Zn-Cu in NaOH is 2:3':4'-dimethoxybenzylbenzoic acid, m.p. 118° (Me ester, b.p. 235°/15 mm.), which is converted by  $\text{H}_2\text{SO}_4$  into (III). E. W. W.

**Structure of ethyl dibenzhydrylmalonate.** A. C. COPE (J. Amer. Chem. Soc., 1934, 56, 721—725).—Et dibenzhydrylmalonate (I), dimorphous, m.p. 136—136.5° (lit. 132°) and 176—177° (stable), is prepared by Kohler's method (A., 1905, i, 700) and from the Na enolate of  $\text{CHPh}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$  and  $\text{CHPh}_2\text{Br}$  in  $\text{C}_6\text{H}_6$ . Et *p*-methylbenzylidenemalonate (II), m.p. 50—51° (lit. 46—47°), and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  (III) in  $\text{Et}_2\text{O}$  give Et 4:4'-dimethylbenzhydrylmalonate (IV), b.p. 192—196°/1 mm., m.p. 71—71.5° [free acid, m.p. 184° (decomp.)], undergoes thermal decomp. to  $\beta\beta$ -di-*p*-tolylpropionic acid, m.p. 187—188°, the Na enolate of which with 4:4'-dimethylbenzhydryl chloride (V) in  $\text{C}_6\text{H}_6$  affords Et di-(4:4'-dimethylbenzhydryl)malonate (VI), m.p. 148—149°, also obtained by the successive action of (III) and (V) on (II). Successive treatment of  $\text{CHPh}_2\text{C}(\text{CO}_2\text{Et})_2$  (VII) with MgPhBr and (V) gives Et 4:4'-dimethyldibenzhydrylmalonate (VIII), m.p. 122—123°, also prepared from the Na enolate of  $\text{CHPh}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$  and (V) in  $\text{C}_6\text{H}_6$ . The successive action of (III) and  $\text{CHPh}_2\text{Br}$  on (II) affords (I) (7%), (VI) (12%), and (VIII) (4%). These methods of prep. of (VIII) indicate that (I) is  $\text{CR}_2(\text{CO}_2\text{Et})_2$  and not  $\text{CO}_2\text{Et}\cdot\text{CR}:\text{C}(\text{OEt})\cdot\text{OR}$  (Kohler, *loc. cit.*). Hydrolysis of (I) and  $\text{CN}\cdot\text{CR}_2\cdot\text{CO}_2\text{Et}$  ( $\text{R}=\text{CHPh}_2$ ) (Kohler and Reimer, *ibid.*, 347) causes scission of a  $\text{CHPh}_2$  group. Similar scission is found with (VI) and  $\text{CO}_2\text{Et}\cdot\text{C}(\text{CHPh}_2):\text{C}(\text{OEt})\cdot\text{OMgBr}$  [from (VII) and MgPhBr], whereby (VIII) results in 39% yield; no exchange occurs with the corresponding Na enolate. H. B.

**Some molybdo- and tungsto-quinates.** G. SARTORI (Gazzetta, 1934, 64, 17—20).—K molybdoquininate,  $(\text{KC}_7\text{H}_{11}\text{O}_6)_2\text{MoO}_3\cdot 4\text{H}_2\text{O}$  (cf. A., 1914, i, 1124), and the corresponding K, Na, Pb, and Ba tungstoquinates are prepared, and their loss of  $\text{H}_2\text{O}$  at 98° and 120° is studied. E. W. W.

**Lichen substances.** XXXVI. Fumarprotocetraric acid. Y. ASAHINA and Y. TANASE. XXXVII. Constitution of sphærophorin. Y. ASAHINA and A. HASHIMOTO (Ber., 1934, 67, [B], 411—416, 416—420; cf. A., 1933, 1161).—XXXVI. Marked analogies are traced between fumarprotocetraric acid (I) and acetylprotocetraric acid (II) as a



result of which, combined with fresh analyses, the above constitution is assigned to (I). Extraction of *Cetraria islandica* with  $\text{COMe}_2$  affords (I),  $\text{C}_{22}\text{H}_{16}\text{O}_{12}$ , decomp. 250—260° after darkening at about 230°, which yields an anil,  $\text{C}_{22}\text{H}_{16}\text{O}_{11}\cdot\text{NPh}$ , decomp. about 250°, and is hydrogenated (Pd-C in AcOH) to hypoprotocetraric acid, m.p. 240—241° (decomp.), and succinic acid. With  $\text{Ac}_2\text{O}$  containing a little conc.  $\text{H}_2\text{SO}_4$  (I) affords tetra-acetylfumarprotocetraric acid, m.p. 155° (decomp.) after softening at about

130° or (+3 $\text{H}_2\text{O}$ ) m.p. 130—131°, hydrogenated (Pd-C) to the  $\text{H}_2$ -derivative, m.p. 107—108° (also +2 $\text{H}_2\text{O}$ ), whereas (II) absorbs 3 $\text{H}_2$  with formation of hypoprotocetraric acid. Protocetraric acid (= capraric acid from *Parmelia caperata*) and its  $\text{Ac}_1$  derivative are transformed by  $\text{Ac}_2\text{O}$  containing conc.  $\text{H}_2\text{SO}_4$  into penta-acetylprotocetraric acid (+ $\text{H}_2\text{O}$ ), m.p. 112—113°, which does not absorb H (Pd-C), also obtained similarly from cetraric acid (III) and its Me ether. Treatment of (II) with boiling EtOH yields (III).

XXXVII. Extraction of the thalli of *Sphærophorus melanocarpus*, DC, with  $\text{Et}_2\text{O}$  yields (?) fragilin and sphærophorin (IV),  $\text{C}_{23}\text{H}_{28}\text{O}_7$  (instead of  $\text{C}_{23}\text{H}_{30}\text{O}_8$ ), m.p. 140°, which does not give a colour with  $\text{CaOCl}_2$  and is sol. in  $\text{NaHCO}_3$ . (IV) gives a  $\text{Ac}_2$  derivative, m.p. 133—134°, and a  $\text{Me}_3$  compound, m.p. 85—86°. (IV) is hydrolysed by KOH-EtOH to evernic acid, m.p. 170° (decomp.) (Me ester, m.p. 68°), and sphærophorol [5-*n*-heptylresorcinol] (V), m.p. 51° or (+ $\text{H}_2\text{O}$ ) m.p. 57—58°, oxidised by  $\text{KMnO}_4$  to *n*-octoic acid (anilide, m.p. 49—50°). (V) is obtained synthetically by condensation of Et *n*-decoate with Et acetonedicarboxylate in presence of Na and treatment of the product with KOH at 250°. Extraction of *S. globosus*, Wain, *f. mecophorus*, A. Zahlbr., yields (IV) in 0.025% yield and isosquamatic acid, possibly identical with Zopf's sphærophoric acid. H. W.

**Electro-organic oxidations in concentrated aqueous organic salt solutions.**—See this vol., 496.

**Highly activated carbonyl group. Mesitylglyoxal.** A. R. GRAY and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 739—741).—Acetomesitylene is oxidised ( $\text{SeO}_2$ , dioxan, little  $\text{H}_2\text{O}$ ) to mesitylglyoxal (I), b.p. 105—106°/4 mm., 118—119°/12 mm. (oxime, m.p. 138.5—139°; phenylhydrazone, m.p. 145.5—146°; semicarbazone, m.p. 207—208°), which contains a highly activated CO group since it forms a stable hydrate (II), m.p. 100—100.5°; the keto-group does not react. (II) and 5:5-dimethyldihydroresorcinol in EtOH give a methone,  $\text{C}_{27}\text{H}_{24}\text{O}_5$ , m.p. 194.5—195°. Mesitylglycollic acid, m.p. 152—153°, is obtained from (II) and aq.  $\text{Ca}(\text{OH})_2$  or KOH. (I) and MgPhBr give 2:4:6-trimethylbenzil, m.p. 136—137° (semicarbazone, m.p. 203—204°), which could not be caused to undergo the benzilic acid rearrangement. (I) and 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{MgBr}$  afford 2:4:6:2':4':6'-hexamethylbenzil, m.p. 120—121° (also prepared, together with a compound,  $\text{C}_{30}\text{H}_{33}\text{O}_3$ , m.p. 231—232°, from 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{COCl}$  and Mg in  $\text{Et}_2\text{O}$  containing a little MgMeI), and  $\alpha\beta$ -dihydroxy- $\alpha\beta$ -di-2:4:6-trimethylbenzoylthane (III), m.p. 160.5—161.5° (diacetate, m.p. 185—185.5°). (III), also prepared by reduction of (I) with Mg+MgI<sub>2</sub> in  $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$  (cf. A., 1927, 245), is reduced (red P, I, AcOH) to  $\alpha\beta$ -di-2:4:6-trimethylbenzoylthane. (III) is also formed from (I) and  $\text{MgPr}^{\text{e}}\text{Br}$ ;  $2\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CHO} + \text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CHR}\cdot\text{OMgBr} \rightarrow \text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{COR} + \text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}(\text{OMgBr})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ .

H. B.

5-Chloro-3:4-dimethoxybenzylidene-di-amides. R. M. HANN (J. Washington Acad. Sci., 1934, 24, 124—126; cf. A., 1933, 1039).—5-Chlorovanillin in warm NaOH with  $\text{Me}_2\text{SO}_4$  affords 5-chloro-3:4-dimethoxybenzaldehyde, m.p. 57°, which when heated with  $\text{NH}_2\text{Ac}$  and a little  $\text{AcOH}$  at 140° during 15 hr. affords 5-chloro-3:4-dimethoxybenzylidenediacetamide, m.p. 244—245°. The following are prepared similarly: 5-chloro-3:4-dimethoxybenzylidenedi-propionamide, m.p. 235°; -*n*-butyramide, m.p. 204—205°; -*n*-hexoamide, m.p. 172—173°; -benzamide, m.p. 217°.

J. L. D.

Isomeric oximes of ethylvanillin. R. M. HANN (J. Washington Acad. Sci., 1934, 24, 126—128).—3-Methoxy-4-ethoxybenzaldehyde with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and  $\text{NaHCO}_3$  in 95% EtOH affords the anti-oxime, m.p. 102° (*Ac* derivative, m.p. 69°), the hydrochloride of which is converted by  $\text{Na}_2\text{CO}_3$  into the syn-oxime (I), m.p. 98°. Interaction of (I) with  $\text{Ac}_2\text{O}$  at 30° affords 3-methoxy-4-ethoxybenzotrile, hydrolysed by NaOH to 3-methoxy-4-ethoxybenzoic acid.

J. L. D.

Condensation of piperonal with hippuric acid. G. LABRUTO and L. IRRERA (Gazzetta, 1934, 64, 136—138).—These substances condense ( $\text{Ac}_2\text{O}$ ) to give compounds (I), m.p. 195°, and (II), m.p. 228° (*K* salt), for which the formulæ  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C} \begin{matrix} \text{NBz} \\ \diagup \\ \text{CO} \end{matrix}$  (I) and  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}:\text{C}(\text{CO}_2\text{H})\cdot\text{NHBz}$  (II) are proposed; (I) adds 2Br to form a compound, m.p. 92°, and (II) is converted by  $\text{AcCl}$  into (I).

E. W. W.

Acetophenone derivatives.—See this vol., 445.

Synthesis of *p*-iodoacetophenone according to Friedel-Crafts and  $\omega$ -bromo-*p*-iodoacetophenone. W. KIMURA (Ber., 1934, 67, [B], 394—395; cf. Judefind *et al.*, A., 1920 i, 480).—*p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{COMe}$  (I) is obtained in 80—95% yield when  $\text{PhI}$  and  $\text{AcCl}$  are added immediately to  $\text{AlCl}_3$  in  $\text{CS}_2$  and the mixture is at once heated to gentle boiling. Addition of Br to (I) in  $\text{AcOH}$  at  $\gt 70^\circ$  gives a nearly theoretical yield of *p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ .

H. W.

Organo-magnesium derivative of pentamethylbenzene. H. CLÉMENT (Compt. rend., 1934, 198, 665—667).—Interaction of equimol. quantities of  $\text{C}_6\text{BrMe}_5$  and  $\text{EtBr}$  in boiling  $\text{Et}_2\text{O}$  with Mg (25% excess) affords Mg pentamethylphenyl bromide (I) in 1.5 hr., converted by  $\text{CO}_2$  into pentamethylbenzoic acid. (I) with  $\text{PhCHO}$  affords pentamethylbenzhydrol,  $\text{C}_6\text{Me}_5\cdot\text{CHPh}\cdot\text{OH}$ , m.p. 107.5°, and with  $\text{EtOAc}$  affords pentamethylphenyl Me ketone, m.p. 241.7° (oxime, m.p. 190.6°; semicarbazone, m.p. 241.7°).

J. L. D.

$\omega$ -Derivatives of tetrahydronaphthyl methyl ketone. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1934, 14, 160—164).—1:2:3:4-Tetrahydronaphthalene and  $\text{CH}_2\text{Cl}\cdot\text{COCl}$  in  $\text{CS}_2$  afford with  $\text{AlCl}_3$  6-tetrahydronaphthyl  $\text{CH}_2\text{Cl}$  ketone (I), m.p. 65—66°, which with  $\text{NaI}$  or  $\text{NaCNS}$  in boiling EtOH yields the  $\text{CH}_2\text{I}$  (II), m.p. 62.5°, and  $\text{CH}_2\cdot\text{CNS}$ , m.p. 79.5—80°, ketone. 6-Tetrahydronaphthyl Me ketone (III) with  $\text{Cl}_2$  yields (I), and with Br the  $\text{CH}_2\text{Br}$  ketone, m.p. 68.5—69°, which yields (II) with  $\text{NaI}$ . The  $\text{CHCl}_2$  ketone, m.p. 42—42.5°, is prepared analogously

from  $\text{CHCl}_2\cdot\text{COCl}$ , or by chlorinating (III), the  $\text{CHBr}_2$  ketone, m.p. 54.5—55°, by brominating (III), and the  $\text{CHClBr}$  ketone, m.p. 50.5°, from (I) and Br in  $\text{CS}_2$ .

R. T.

Reversible addition of aromatic compounds to phenyl styryl ketones. J. T. EATON, D. B. BLACK, and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 687—688).— $\text{C}_6\text{H}_5\text{R}\cdot\text{CH}:\text{CH}\cdot\text{COPh}$  ( $\text{R}=\text{o}$ -, *m*-, and *p*-Cl, *m*- and *p*-Br, and *p*-Me),  $\text{C}_6\text{H}_6$  (saturated with HCl), and  $\text{AlCl}_3$  give  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{COPh}$  (I). *Ph*  $\beta\beta$ -*di-p*-chlorophenylethyl ketone (II), m.p. 120—121° [oxidised ( $\text{KMnO}_4$ , NaOH, aq.  $\text{C}_5\text{H}_5\text{N}$ ) to  $\text{CO}(\text{C}_6\text{H}_4\text{Cl-}i)- $\text{p}$ ], is similarly obtained using  $\text{PhCl}$  and  $\text{R}=\text{o}$ - and *p*-Cl and *m*-Br. (II),  $\text{C}_6\text{H}_6$ , HCl, and  $\text{AlCl}_3$  give (I). The results agree with the view (cf. A., 1933, 1170) that addition of aromatic compounds to  $\alpha\beta$ -unsaturated CO- (and similarly constituted) compounds is reversible.$

H. B.

Use of  $\text{P}_2\text{O}_5$  in preparation of *p*-benzoyldiphenyl and 4-benzoylacenaphthene. A. C. DE DEGIORGI (Anal. Assoc. Quím. Argentina, 1933, 21, 135—141).—The satisfactory prep. of  $\text{C}_{10}\text{H}_7\text{Bz}$  from  $\text{BzCl}$  and  $\text{C}_{10}\text{H}_8$  with  $\text{P}_2\text{O}_5$  as catalyst (A., 1913, i, 1166) is confirmed. *o*-Benzoyldiphenyl is prepared analogously, but more of a by-product, m.p. 86—89°, is obtained than with  $\text{AlCl}_3$ . 4-Benzoylacenaphthene is obtained analogously in increased yield. *o*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$  and  $\text{SO}_2\text{Cl}_2$  at 70—90° for 2 hr. yield fluorenone; the chloride is obtained only at lower temp.

R. K. C.

Action of phosphorus pentachloride on dimethylmethone. N. J. TOIVONEN and A. KAYSER (Suomen Kem., 1934, 7, B, 79—80).—Interaction of 2:2:5:5-tetramethylcyclohexane-1:3-dione [dimethylmethone] (I) with warm  $\text{PCl}_5$  (2 mols.) during 30 hr. affords 4-chloro-2:2:5:5-tetramethylcyclohexane-1:3-dione, m.p. 129°, converted into (I) by Zn in  $\text{AcOH}$ , and into an acid,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , m.p. 87—89°, with aq. NaOH. (I) with excess of  $\text{PCl}_5$  also affords a  $\text{Cl}_2$ -derivative, m.p. 142—144°. (I) (1 mol.) with Br (2 mols.) in  $\text{AcOH}$  affords a compound,  $\text{C}_{10}\text{H}_{14}\text{O}_2\text{Br}_2$ , m.p. 145°.

J. L. D.

Grignard reaction in synthesis of ketones. IV. Preparation of unsymmetrical benzoin. S. S. JENKINS (J. Amer. Chem. Soc., 1934, 56, 682—684).—*Ph p*-methoxybenzyl ketone, m.p. 96.5° (all m.p. are corr.) (A., 1932, 516) is obtained in 30% yield from  $\text{MgPhBr}$  and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ . Anisamide and  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  (I) give 70—76% yield of anisyl benzyl ketone, m.p. 77° (*loc. cit.*); (I) and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$  afford 77% of *p*-chlorophenyl benzyl ketone, m.p. 107.5°; *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{MgCl}$  and  $\text{NH}_2\text{Bz}$  yield 70% of *Ph p*-chlorobenzyl ketone, m.p. 138°. These are brominated in  $\text{CCl}_4$  and intense light to the  $\alpha$ -Br-derivatives, m.p. 93—94°, 72.5—73.5°, 67.5—68.5°, and 62—62.5°, respectively, which are converted by  $\text{EtOH}\text{-NaOEt}$  and subsequent hydrolysis (cold dil. HCl) into benzoylanisyl-, m.p. 90°, anisoylphenyl-, m.p. 106.5°, *p*-chlorobenzoylphenyl- (II), m.p. 90—91°, and benzoyl-*p*-chlorophenyl- (III), m.p. 116—117°, -carbinol, respectively. For the prep. of these benzoin, the intermediate Br-derivatives need not be isolated. (II) is also prepared

from mandelamide and *p*-C<sub>6</sub>H<sub>4</sub>Cl·MgBr, whilst (III) is obtained from MgPhBr and *p*-chloromandelamide.

H. B.

**Action of organo-magnesium derivatives on  $\omega$ -cyanoacetophenone.** A. MAVRODIN (Bul. Soc. Chim. România, 1933, 15, 99—106).—CN·CH<sub>2</sub>·COPh (I) and an excess of MgEtI in Et<sub>2</sub>O or, better, PhMe give benzoylpropionylmethane, b.p. 276—277°, hydrolysed (aq. 25% KOH) to COMeEt, COPhMe, BzOH, and EtCO<sub>2</sub>H; the following reactions probably occur: (I) + MgEtI  $\rightarrow$  C<sub>2</sub>H<sub>5</sub> + CN·CH·CPh·OMgI  $\rightarrow$  IMg·N·CEt·CH·CPh·OMgI  $\rightarrow$  COEt·CH·CPh·OH  $\rightarrow$  COEt·CH<sub>2</sub>·COPh. Similarly, (I) and MgPhBr afford CH<sub>2</sub>Bz<sub>2</sub>.

H. B.

**Isomerisation of 2 : 2-disubstituted derivatives of indandione.** G. GHEORGHIU (Compt. rend., 1934, 198, 755—758).—Me and Et 2-methylindan-1 : 3-dione-2-acetate with Na alkoxide undergo transformation into naphthalene derivatives less readily than the 2-Ph derivative (cf. A., 1927, 243). 2-Phenyl- and less readily 2-methyl-2-acetylindan-1 : 3-dione and 2-phenyl- (I) (but not -methyl-) -2-allylindan-1 : 3-dione give C<sub>10</sub>H<sub>8</sub> derivatives. That from (I) is an oil and from the Me compounds definite products cannot be isolated. 2-Phenyl-2-benzylindan-1 : 3-dione gives *o*-carboxyphenyl  $\alpha\beta$ -diphenyl-ethyl ketone.

R. S. C.

**Tautomerism of *p*-benzoquinoneoxime-*p*-nitrosophenol systems.** L. C. ANDERSON and R. L. YANKE (J. Amer. Chem. Soc., 1934, 56, 732—735; cf. A., 1932, 1026).—Absorption spectra indicate that the equilibrium mixture of *p*-benzoquinoneoxime (I) and *p*-NO·C<sub>6</sub>H<sub>4</sub>·OH in dioxan, CHCl<sub>3</sub>, EtOH, and aq. acid consists mainly of (I). The curve for 3-chloro-*p*-benzoquinone-4-oxime (II) is very similar to that of its Me ether, but the curve for 3-chloro-4-nitrosophenol (III) differs from that of its Me ether and (II); the difference is not due to ionisation or association of (III). The spectrum of 2-chloro-4-nitrosophenol (Hodgson, A., 1932, 509) resembles those of the quinoneoxime Me ethers rather than the nitrosoanisoles. Absorption of alkaline solutions of the quinoneoximes is independent of the metal hydroxide used and is due to a highly ionised form (probably the ion of the quinonoid form). The absorption spectra are independent of [H<sup>+</sup>] at *p*<sub>H</sub> < 3 and > 7, but are very sensitive to changes between *p*<sub>H</sub> 3 and 7.

H. B.

**Optical method for the study of reversible organic oxidation-reduction systems.** II. **Halogenated benzoquinones.** III. **Preparation and use of a new optically active standard.** D. E. KVALNES (J. Amer. Chem. Soc., 1934, 56, 667—670, 670—672).—II. The relative oxidation potentials of the following halogenbenzoquinones, determined polarimetrically in C<sub>6</sub>H<sub>6</sub> using *d*-camphor-10-sulphonyl-2 : 5-dimethylquinol (cf. A., 1932, 947), are: benzoquinone, 0.711 volt (assigned arbitrarily); chloro-, 0.734; bromo-, 0.737; iodo-, 0.737; 2 : 3-, 0.750, 2 : 5-, 0.746, and 2 : 6-, 0.740, -dichloro-; 2 : 5-, 0.768, and 2 : 6-, 0.744, -dibromo-; 2 : 6-di-iodo-, 0.746; trichloro-, 0.755; tribromo-, 0.763; tetrachloro-, 0.742; tetrabromo-, 0.746. The vals. are compared

with those determined electrometrically in aq. and EtOH-solution.

3-Iodo-4-*p*-sulphobenzeneazophenol is reduced (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) to 3-iodo-4-aminophenol, m.p. 140° (charring; darkens at 135°), oxidised (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 25% H<sub>2</sub>SO<sub>4</sub>) to iodobenzoquinone, m.p. 62°. This is reduced (SnCl<sub>2</sub>) to iodoquinol, m.p. 115—116° (diacetate, m.p. 86—87°).

III. Reduction (SnCl<sub>2</sub>, HCl) of the product from  $\alpha$ -naphthaquinone and *d*-camphor-10-sulphinic acid (from Zn salt) gives *d*-camphor-10-sulphonyl- $\alpha$ -naphthaquinol (I), m.p. 159—160°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +44.7° in C<sub>6</sub>H<sub>6</sub>, oxidised (FeCl<sub>3</sub>, EtOH) to the  $\alpha$ -naphthaquinone (II), m.p. 131°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +355° in C<sub>6</sub>H<sub>6</sub> (cf. *loc. cit.*). *p*-Toluenesulphonyl- $\alpha$ -naphthaquinol, m.p. 181°, and -quinone, m.p. 172—173°, and *p*-bromobenzenesulphonyl- $\alpha$ -naphthaquinol, m.p. 221—222° (decomp.), and -quinone, m.p. 175—176°, are similarly prepared.

The relative oxidation potentials of 17 quinones are determined polarimetrically in C<sub>6</sub>H<sub>6</sub> using the system (I)-(II). Introduction of Me into benzoquinone causes a marked decrease in potential; a second Me (position of no importance) has not quite such a pronounced effect. The decrease due to one OMe is > twice that due to a second. The effect of the following groups in decreasing the potential is OH  $\gg$  OMe > Me > OPh. Increase in size of the alkyl group has little effect.

H. B.

**Action of alkali on dibromodianilinobenzoquinone.** M. M. SPRUNG (J. Amer. Chem. Soc., 1934, 56, 691—693).—3 : 6-Dibromo-2 : 5-dianilino-*p*-benzoquinone, m.p. 261° (decomp.) (from bromanil or 3 : 6-dibromo-2 : 5-diphenoxy-*p*-benzoquinone and EtOH-NH<sub>2</sub>Ph), with aq. EtOH-NaOH gives NH<sub>2</sub>Ph, 2 : 5-dianilino-3 : 6-dihydroxy-*p*-benzoquinone (I), m.p. 206—207° (decomp.), and the anil (II), m.p. 139—141° (decomp.), of (I). (II) is hydrolysed (2*N*-HCl) to (I) and is prepared from (I) and NH<sub>2</sub>Ph in aq. NaOH.

H. B.

**Application of electronic theory to organic compounds.** V. **Anthraquinonedisulphonic acids.** A. M. BERKENHEIM and L. G. TSCHENTSOVA (J. Gen. Chem. Russ., 1933, 3, 947—957; cf. this vol., 518).—In anthraquinone-2 : 6-disulphonic acid one SO<sub>3</sub>H is attached to a negative, and one to a positive, C atom; the latter group should therefore be a sulphite one, and should, on reduction, be replaceable by H. This postulate was realised experimentally by reduction with 2% Na-Hg at 0°, when 50% yields of anthraquinone-2-sulphonic acid were obtained.

R. T.

**Preparation of 1 : 4-di-*p*-toluidinoanthraquinone.** M. GALLOTTI (Annali Chim. Appl., 1934, 24, 32—34).—Quinizarin is reduced in alkaline solution with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and, without being separated, the leucoquinizarin is condensed with *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> in presence of H<sub>3</sub>BO<sub>3</sub> to give an almost theoretical yield of di- (free from mono-) -*p*-toluidinoanthraquinone, yielding Alizarin Brilliant Green G on sulphonation. The dye obtained is free from 1-hydroxy-4-*p*-toluidinoanthraquinone-*m*-sulphonic acid (Alizarin Irisol), which, even in small proportion, lowers the brilliancy.

T. H. P.

**Anthracene derivatives.**—See B., 1934, 355.

**1-Nitroanthraquinone-2-carboxyl chloride and its reaction with cholesterol.** P. P. T. SAH and T. S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 143—145).—1-Nitroanthraquinone-2-carboxyl chloride, m.p. 243—244°, with cholesterol gives cholesteryl 1-nitroanthraquinone-2-carboxylate, m.p. 227—229°.

F. R. S.

**Atractyligenin. III. Functions of oxygen atoms.** T. AJELLO (Gazzetta, 1934, 64, 59—65; cf. A., 1933, 612, 829).—Atractyligenin,  $C_{14}H_{22}O_4$ , m.p. 168°,  $[\alpha]_D^{20}$  -143°, the product of alkaline hydrolysis of K attractylate (*loc. cit.*), is a dihydroxymonocarboxylic acid, which combines with PhNCO to form the compound  $C_{14}H_{20}O_4(CO \cdot NPh)_2$ , and has no ethylenic linkings.

E. W. W.

**Asteric acid.**—See this vol., 544.

**Chlorinated derivatives of cineole. II.** A. GANDINI (Gazzetta, 1934, 64, 118—135).—When cineole is treated as before (A., 1933, 830), but with  $Cl_2$ , the products include 3-chlorocineole, b.p. 110—112°/50 mm., oxidised by  $KMnO_4$  to cineolic acid; 2-chlorocineole (*loc. cit.*), b.p. 126°/50 mm., 2:3-dichlorocineole, b.p. 109—110°/3 mm., also oxidised to cineolic acid; 2:6-dichlorocineole, b.p. 126—127°/3 mm., oxidised to terpenylic, terebic, and teracemic acids; and 2:3:6(?)-trichlorocineole, b.p. 143°/3 mm. The action of Na and of KOH on these compounds is described.

E. W. W.

**Piperitone. XII. Two varieties of piperitol.** J. READ and J. WALKER (J.C.S., 1934, 308—313).—*d*-Neopiperitol, formed from *l*-piperityltrimethylammonium iodide and  $Ag_2O$ , has  $[\alpha]_D^{20}$  +50.8° in EtOH, and on keeping for a short time eliminates  $H_2O$  giving *d*- $\alpha$ -phellandrene: it has probably the *trans*-H configuration. Reduction of *l*-piperitone with  $Pr^{\beta}OH$  and  $Al(OPr^{\beta})_3$  affords *l*-piperitol, b.p. 98.5—100.5°/13 mm.,  $[\alpha]_D^{20}$  -24.5° in EtOH (3:5-dinitrobenzoate, m.p. 84—85°,  $[\alpha]_D^{20}$  -30° in  $CHCl_3$ ), which is stable. Piperitylamine contains a stable substance,  $C_{10}H_{21}ON$ , m.p. 89—90.5°,  $[\alpha]_D^{20}$  +7.24° in  $CHCl_3$ . In an attempt to purify crude *d*-piperitylamine, the *Ac*, m.p. 101—102°,  $[\alpha]_D^{20}$  +159° in  $CHCl_3$ , *Bz*, m.p. 102—103°,  $[\alpha]_D^{20}$  +175°, and *p*-dimethylaminobenzylidene derivatives, m.p. 127—128.5°,  $[\alpha]_D^{20}$  +1°, have been prepared. *l*-Piperitylamine is methylated to the *N*-Me compound, b.p. 95—99°/16 mm.,  $[\alpha]_D^{20}$  -355°, and is hydrogenated to a mixture of *l*-iso- and *l*-menthylamine, indicating *cis*-H configuration. *l*-Piperitone and  $NH_3$  form the piperitoneimine, b.p. 99—105°/10 mm., which on reduction passes into a mixture of menthylamines, and the ketone and  $NH_2Me$  yield piperitonemethylamine, b.p. 103.5—105°/13 mm., reduced to *N*-methylmenthylamine, b.p. 96.5—98°/16.5 mm.

F. R. S.

**Menthone series. XII. Isolation and characterisation of the neoisomenthols.** J. READ and W. J. GRUBB (J.C.S., 1934, 313—317).—By reduction of *dl*-isomenthone with  $Pr^{\beta}OH$  and  $Al(OPr^{\beta})_3$  and esterification with 0.5 mol. of *p*- $NO_2 \cdot C_6H_4 \cdot COCl$ , *dl*-neoisomenthol, m.p. 14°, b.p. 81°/6 mm. (*p*-nitrobenzoate, m.p. 63—64°), purified through the 3:5-dinitrobenzoate, m.p. 73—73.5°, has been obtained. Hydrogenation of *l*-piperitone and purification by successive

treatment with phthalic anhydride and  $H_3PO_4$  gives *d*-neoisomentholphosphoric acid, decomposed to *d*-neoisomenthol, b.p. 84.2°/7.5 mm., m.p. -8°,  $[\alpha]_D^{20}$  +2.2° in EtOH (*p*-nitrobenzoate, m.p. 72.5—73°,  $[\alpha]_D^{20}$  -5.3° in  $CHCl_3$ ); 3:5-dinitrobenzoate, m.p. 100.5—101°,  $[\alpha]_D^{20}$  -9.5° in  $CHCl_3$ ; *d*-, m.p. 69—70°,  $[\alpha]_D^{20}$  +17.3° in  $CHCl_3$ , and 1-camphor-10-sulphonate, m.p. 84—86°,  $[\alpha]_D^{20}$  -41° in  $CHCl_3$ ; *d*-,  $[\alpha]_D^{20}$  +43.6°, and 1-menthoxyacetate,  $[\alpha]_D^{20}$  -71.6°.

F. R. S.

**Phosphoric acid compounds of menthols and other alcohols.** J. W. BLAGDEN and W. E. HUGGETT (J.C.S., 1934, 317—318).—With  $H_3PO_4$  menthols form cryst. derivatives  $3C_{10}H_{20}O \cdot H_3PO_4$ , used in separating and purifying the stereoisomeric menthols. The process is possible with nearly all terpene and hydroaromatic alcohols and with some aliphatic alcohols.

F. R. S.

**Rearrangement of acetylenic carbinols. *d*-isoMenthone and *l*-menthone.** H. RUPE and A. GASSMANN (Helv. Chim. Acta, 1934, 17, 283—285).—Since catalytic reduction of pulegone gives a mixture of *d*-isomenthone and *l*-menthone (Read *et al.*, A., 1926, 1147), one of these ketones, and not *d*-menthone (as in A., 1929, 314), must give rise (through the acetylenic carbinol) to *d*-3-methyl-6-isopropylcyclohexylideneacetaldehyde (I) (cryst. data shows homogeneity of oxime). The ketone, b.p. 85—87°/11 mm.,  $[\alpha]_D^{20}$  +20.25°, obtained by rearrangement of (I) gives a semicarbazone, m.p. 184° (not 181°),  $[\alpha]_D^{20}$  -37.82° in  $C_6H_6$ , and is therefore *l*-menthone.

J. W. B.

**$\beta$ -Pinene oxide in Grignard's reaction.** N. PRILESHAEV and N. PROKOPTSCHUK (J. Gen. Chem. Russ., 1933, 3, 865—868).— $\beta$ -Pinene oxide yields with  $MgMeI$  (I)  $\Delta^{1:6}$ -menthen-7-ol (II), b.p. 130—132°/30 mm., converted by  $K_2Cr_2O_7$  into an aldehyde, b.p. 122—125°/32 mm. (semicarbazone, m.p. 201°), isomeric with phellandral. Using  $MgEtBr$  in place of (I) the product is a mixture of (II) and an alcohol, which on oxidation yields an aldehyde (III), b.p. 134—136°/28 mm. (semicarbazone, m.p. 173°).

R. T.

**Action of carbon dioxide and sodium on 2:5-diketocamphane.** Y. ASAHINA and M. ISHIDATE (Ber., 1934, 67, [B], 440—446).—2:5-Diketocamphane (I) is converted by Na and  $CO_2$  in boiling xylene into 2:5-dihydroxycamphane, m.p. 233°, and a mixture of acids (II) which, on treatment with  $C_6H_6$ , yields 2:5-diketocamphane-6-carboxylic acid (III), m.p. 210—211° (loss of  $CO_2$ ),  $[\alpha]_D^{20}$  +94.4° in EtOH. (III) and its alkali salts lose  $CO_2$  slowly in cold  $H_2O$ , immediately in boiling solution, with production of (I). Similarly, (III) and  $NH_2 \cdot CO \cdot NH \cdot NH_2 \cdot AcOH$  in cold EtOH afford 2:5-diketocamphanedisemicarbazone. Treatment of (III) with Br in AcOH leads to 6-bromo-2:5-diketocamphane-6-carboxylic acid, m.p. 185—186° (decomp.), which does not give a coloration with  $FeCl_3$  and is converted by warm  $NaHCO_3$  into 6-bromo-2:5-diketocamphane (IV), m.p. 145°. Warm 10% KOH transforms (IV) into ketocampholenic acid, m.p. 124—125°, shown to be

$$\begin{array}{c} CH-CO \\ | \quad | \\ CMe \cdot CMe_2 \end{array} > CH \cdot CH_2 \cdot CO_2H$$

by its oxidation to  $\alpha$ -ketoisocamphoronic acid, m.p.

185—186° (decomp.). The residue obtained after removal of (III) from (II) is neutralised and pptd. with quinine hydrochloride. The quinine salt is extracted with boiling  $\text{COMe}_2$ . The filtered extract deposits the *quinine* salt, m.p. 165—166° (decomp.), of *acid B* (V),  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , m.p. 133—134° (decomp.) [*Me* ester, m.p. 87°]. (V) is very unstable, immediately decolorises  $\text{KMnO}_4$ , is optically inactive, and in EtOH gives a wine-red colour with  $\text{FeCl}_3$ . When its Na salt is heated in  $\text{H}_2\text{O}$  it yields a neutral, unstable *product* (VI), m.p. (indef.) 112°, which resinifies on exposure to air. (V) or (VI) is transformed by Br in EtOH into the *substance*  $\text{C}_{10}\text{H}_{16}\text{O}_2\text{Br}$ , m.p. 91—92°, by  $\text{Ac}_2\text{O}$  at 130° into the *Ac* derivative (VIII),  $\text{C}_{12}\text{H}_{18}\text{O}_3$ , m.p. 65—66°, stable to  $\text{KMnO}_4$  and giving no coloration with  $\text{FeCl}_3$ , and by  $\text{NH}_2\text{OH}$  into the *oxime*  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}$ , m.p. 165° (decomp.). The *semicarbazone*  $\text{C}_{11}\text{H}_{19}\text{O}_2\text{N}_3$ , m.p. 215° (decomp.), is derived solely from (VII). Reduction of (V) by Na—Hg leads to a neutral *product* (VIII),  $\text{C}_{10}\text{H}_{20}\text{O}_2$ , m.p. 92—93°, stable towards  $\text{KMnO}_4$ , and two *acids*,  $\text{C}_{11}\text{H}_{18}\text{O}_4$ , m.p. 125—126°, and  $\text{C}_{11}\text{H}_{20}\text{O}_4$ , m.p. 188—189°, which yields a neutral *oil*, b.p. 200°/31 mm., when heated with  $\text{Ac}_2\text{O}$ . Similar reduction of (VI) gives (VIII) and a volatile *substance* of camphoraceous odour, (?)  $\text{C}_{10}\text{H}_{18}\text{O}$ , m.p. 125°, which gives a *semicarbazone*  $\text{C}_{11}\text{H}_{21}\text{ON}_3$ , m.p. 225—226°. The quinine salt insol. in  $\text{COMe}_2$  (see above) yields *acid C*,  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , m.p. 145·5°,  $[\alpha]_D^{25} -64\cdot81^\circ$  in EtOH [*quinine* salt, m.p. 133—134° (decomp.)]; *Me* ester, m.p. 98—99°, which is unaffected by boiling 10% HCl or  $\text{AcCl}$  and does not yield an oxime or semicarbazone. H. W.

**Lipoid-soluble compound of polonium.** M. SERVIGNE (Compt. rend., 1934, 198, 731—733).—The prep. is described of *Po camphorcarboxylate*, sol. in  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , and olive oil, and partly in aq. camphorcarboxylic acid. R. S. C.

**Optical superposition.** I. H. RUPE, F. BÜRKI, and H. WERDENBERG (Helv. Chim. Acta, 1934, 17, 271—282).—By action of the Na derivative of *d*-, *l*-, or *dl*-hydroxymethylenecamphor (I) on the chloride of *d*-, *l*-, or *dl*-bornylenecarboxylic acid (II) (prep. described) in dry  $\text{C}_6\text{H}_6$  the eight stereoisomeric *hydroxymethylenecamphor bornylenecarboxylates*, respectively, *d-d* (III), m.p. 125°,  $[\alpha]_D^{20} +209\cdot07^\circ$ ; *d-l* (IV), m.p. 134°,  $[\alpha]_D^{20} +47\cdot87^\circ$ ; *d-dl* (V), m.p. 132°,  $[\alpha]_D^{20} +97\cdot36^\circ$ ; *l-l* (VI), m.p. 125°,  $[\alpha]_D^{20} -209\cdot12^\circ$ ; *l-d* (VII), m.p. 134°,  $[\alpha]_D^{20} -48\cdot09^\circ$ ; *l-dl*, m.p. 132°,  $[\alpha]_D^{20} -97\cdot28^\circ$ ; *dl-d*, m.p. 128°,  $[\alpha]_D^{20} +74\cdot99^\circ$ ; *dl-l*, m.p. 128°,  $[\alpha]_D^{20} -75\cdot01^\circ$ ; and *dl-dl*, m.p. 135°, are prepared. The  $[\mathcal{M}]_D^{20}$  vals. of these are different from those calc. by direct summation of the components, therefore in esterification of an optically active alcohol with an active acid a polar factor is superimposed on the optical. If *A* and *B*=mol. rotation of the (I) and (II) residues, respectively,  $A+B=[\mathcal{M}]_D^{20}$  of (III)=715·51°, and  $A-B=[\mathcal{M}]_D^{20}$  of (IV)=163·83°, whence  $A=439\cdot67^\circ$  and  $B=275\cdot84^\circ$ . Since  $[\mathcal{M}]_D^{20}$  of (V)=332·31°, the polar influence of (II) or (I) is 106·46°, and that of (I) or (II) is 19·20°, the same vals. being similarly obtained from (VI) and (VII). When this polar factor is taken into account, the principle of optical superposition holds throughout. *Me d*-, b.p. 106°/11 mm.,  $[\alpha]_D^{20} +122\cdot94^\circ$ , and

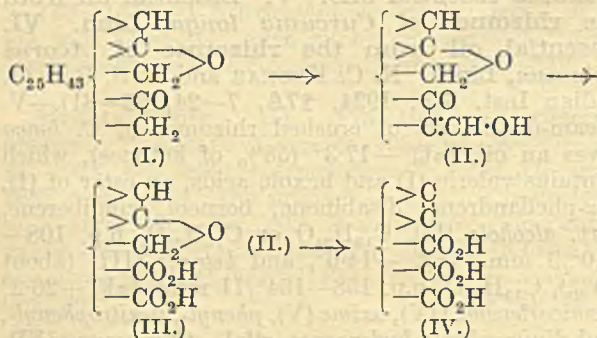
*Me l*-, b.p. 106°/11 mm.,  $[\alpha]_D^{20} -123\cdot02^\circ$ , *-bornylenecarboxylate* are described. J. W. B.

**Indian essential oils.** V. Essential oil from the rhizomes of *Curcuma longa*, Linn. VI. Essential oil from the rhizomes of *Acorus calamus*, Linn. N. C. KELKAR and B. S. RAO (J. Indian Inst. Sci., 1934, 17A, 7—24, 25—31).—V. Steam-distillation of crushed rhizomes of *C. longa* gives an oil,  $[\alpha]_D^{20} -17\cdot3^\circ$  (58% of ketones), which contains valeric (I) and hexoic acids, an ester of (I), *d*- $\alpha$ -phellandrene, *d*-sabinene, borneol, zingiberene, tert. *alcohols* (II),  $\text{C}_{15}\text{H}_{24}\text{O}$  or  $\text{C}_{15}\text{H}_{22}\text{O}$ , b.p. 108—110°/3 mm.,  $[\alpha]_D^{20} -14\cdot6^\circ$ , and *ketones* (III) (about 50%),  $\text{C}_{15}\text{H}_{22}\text{O}$ , b.p. 158—164°/11 mm.,  $[\alpha]_D^{20} +26\cdot2^\circ$  [*semicarbazone* (IV), *oxime* (V), *phenyl*-, *p*-nitrophenyl-, and *dinitrophenyl-hydrazone*s, oils]. Curcumone (VI), b.p. 112—115°/7 mm., was obtained from (II) and (III) by 30% KOH—EtOH and partly by hydrolysis of (IV) by  $\text{H}_2\text{C}_2\text{O}_4$ . (VI) and  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{MgBr}$  give  $\delta$ -hydroxy- $\zeta$ -*p*-tolyl- $\delta\zeta$ -dimethyl- $\Delta^{\alpha}$ -hexene, b.p. 140—145°/7 mm., partly decomposed by distillation at atm. pressure to (VI), giving an *acid*, m.p. 39—42°, with 4% aq.  $\text{KMnO}_4$  at 0—5°, but stable to KOH. (III) with Na—EtOH give sec. *alcohols*,  $\text{C}_{15}\text{H}_{28}\text{O}$ , b.p. 135—140°/10 mm. (V) is a mixture; the  $\text{Et}_2\text{O}$ -sol. portion with Na—EtOH gives a *base*,  $\text{NH}_2\cdot\text{C}_{15}\text{H}_{21}$ , an oil (*oxalate*, m.p. 130°); the  $\text{CHCl}_3$ -sol. portion gives a *base*, b.p. 85—95°/? mm. (III) with  $\text{HNO}_3$  (1:2) at 85—95° gives a weak *acid*, m.p. >400°, *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ , *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ , and  $\text{H}_2\text{C}_2\text{O}_4$ , but with  $\text{KMnO}_4$  (best in  $\text{COMe}_2$ ) the main product is curcumatic acid. (II) and (III) give oily mixtures with S and Se.

VI. Steam-distillation of the rhizomes of Indian *A. calamus* gives an oil (2·8%), containing palmitic (VII) and heptonic acids, esters of (VII) and  $\text{Pr}\cdot\text{CO}_2\text{H}$ ,  $\alpha$ -pinene, camphene, asaraldehyde, eugenol (0·3%) and its *Me* ether (1%), asarone (82%), calamene (4%), *calameneol*,  $\text{C}_{15}\text{H}_{23}\cdot\text{OH}$  (5%), b.p. 140—146°/8 mm.,  $[\alpha]_D^{20} +1\cdot8^\circ$ , and a ketone, *calameone*,  $\text{C}_{15}\text{H}_{26}\text{O}_2$  (1%), m.p. 167—168°. The characteristic odour is due to unidentified constituents in the fraction of b.p. 125—135°/11 mm. R. S. C.

**Polyterpenes and polyterpenoids.** LXXXVII. Dehydrogenation of betulin. Degradation of *allobetulin* and *dihydrobetulin* derivatives. Contents of birch bark. L. RUZICKA, G. F. FRAME, H. M. LEICESTER, M. LIGUORI, and H. BRÜNGGER (Helv. Chim. Acta, 1934, 17, 426—442).—*alloBetulone* (I) with *isoamyl* formate and NaOEt in  $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$  gives a *hydroxymethylene* derivative (II), m.p. 258—259°, oxidised by  $\text{CrO}_3\text{-AcOH}$  to an *anhydride-acid*  $\text{C}_{30}\text{H}_{44(46)}\text{O}_5$ , m.p. 293° (sparingly sol. in  $\text{AcOH}$ ) [*Me* ester, m.p. 290—292°, by  $\text{CH}_2\text{N}_2$ ; *Me*<sub>3</sub> ester (as IV), m.p. 253—256°, by  $\text{MeI-NaOMe}$ ], which gives no m.p. depression with oxyallobetulinic acid (A., 1932, 749; *oxime*, m.p. 215°), but does not form an oxime, and an *acid* (III), m.p. (indef.) 180—210°, giving a *Me*<sub>2</sub> ester,  $\text{C}_{32}\text{H}_{52}\text{O}_5$ , m.p. 155—156°. Oxidation of the ketone  $\text{C}_{29}\text{H}_{44}\text{O}_3$  from oxyallobetulinic acid (Dischendorfer *et al.*, A., 1929, 449, modified) with  $\text{CrO}_3\text{-AcOH}$  gives an *acid*, which is difficult to purify, but at 360—370° gives an *anhydride*,  $\text{C}_{28}\text{H}_{40}\text{O}_5$ , m.p. 385° (decomp.) [*Me*, m.p. 270° by instantaneous

heating, resolidifying and m.p. 384°, *Et*, sinters 220°, m.p. 231—232°, resolidifying and m.p. 384°, and *Me*<sub>2</sub>, m.p. 265—266°, (no oxime), esters].



Dihydrobetulonic acid (*loc. cit.*, improved prep. and purification through its semicarbazone or Na salt: *oxime*, m.p. 285—295°) with NaOH—*Me*<sub>2</sub>SO<sub>4</sub> gives its *Me* ester, m.p. 191—192° [*oxime*, m.p. 252—253° (decomp.)], which gives only an indefinite hydroxymethylene derivative from which no cryst. products could be obtained on oxidation. From the high-b.p. fraction of *Se* dehydrogenation products of betulin (V) (A., 1933, 69) a second hydrocarbon C<sub>25</sub>H<sub>20</sub>, sinters 315°, m.p. 324°, is obtained. Dehydrogenation of (V) with Pd—C at 340—360° gives similar products, 1 : 2 : 3 : 4—C<sub>6</sub>H<sub>2</sub>Me<sub>4</sub>, sapotalin, 1 : 2 : 5 : 6—C<sub>10</sub>H<sub>4</sub>Me<sub>4</sub> [compound with C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>, m.p. 178.5—179°], and fractions difficult to purify. From the EtOH-extract of birch bark are also isolated a paraffin hydrocarbon C<sub>25</sub>H<sub>52</sub>, m.p. 53—54°, and acetyloleanolic acid, identical with a specimen prepared by Winterstein *et al.* (A., 1931, 1159). J. W. B.

**Polyterpenes and polyterpenoids. LXXXVIII.** Dehydrogenation of hederagenin, oleanolic acid, and sumaresinolic acid with selenium and palladium. L. RUZICKA, H. HÖSLI, and L. EHMANN (Helv. Chim. Acta, 1934, 17, 442—455).—Reinvestigation (cf. A., 1932, 517; 1933, 69) of the *Se* and Pd—C dehydrogenation products of various triterpenes has led to the isolation of further products. The combined results are summarised thus, the numerals referring to the dehydrogenation products: 1 : 2 : 3 : 4—C<sub>6</sub>H<sub>2</sub>Me<sub>4</sub> (I), 2 : 7—C<sub>10</sub>H<sub>6</sub>Me<sub>2</sub> (II), 1 : 2 : 7—C<sub>10</sub>H<sub>5</sub>Me<sub>3</sub> (sapotalin) (III); oxysapotalin (IV), 1 : 2 : 5 : 6—C<sub>10</sub>H<sub>4</sub>Me<sub>4</sub> (V), a phenanthrene hydrocarbon C<sub>18</sub>H<sub>18</sub> (VI), m.p. 126—127° [*picrate*, m.p. 165°; *styphnate*, m.p. 174—175°; and compound with C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>, m.p. 174—175°, all decomposing into their components by recrystallisation; oxidised by CrO<sub>3</sub>—AcOH to the *quinone*, m.p. 203—104° (*quinoxaline*, m.p. 178—179°)], a picene hydrocarbon C<sub>25</sub>H<sub>20</sub> (VII), m.p. 305°, and a dinaphthyl hydrocarbon C<sub>25</sub>H<sub>21</sub> (VIII), m.p. 143°. Hederagenin+*Se* [(I)—(IV), (VI), and (VII)], +Pd [same products except (VI)]; oleanolic acid (IX)+*Se* [(I)—(V), and (VII)], +Pd [same products except (V)]; sumaresinolic acid (X)+*Se* [(I)—(V), (VII), and (VIII)], +Pd [(I)—(IV), and (VII)]. The absorption spectra of (VII) from (IV) (chief absorption max. 3421 1/λ) and from (X) (1/λ=3425) closely resemble that of tar picene (1/λ=3496), confirming the view that (VII) is a picene homologue. J. W. B.

**Orientation in furan nucleus. VIII. 3-Acylamidofurans.** R. R. BURTNER (J. Amer. Chem. Soc., 1934, 56, 666—667).—3-Furohydrazide, m.p. 124—124.5° (from the *Et* ester and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), is converted into the azide and thence (in boiling C<sub>6</sub>H<sub>6</sub>) into 3-furylcarbimide (not isolated owing to its offensive properties), which with MgPhBr gives 3-benzamidofuran, m.p. 142°. 2-Methyl-3-furohydrazide, m.p. 148°, and 3-benzamido-, m.p. 135° (cf. Blomquist and Stevenson, this vol., 300), and 3-acetamido-, m.p. 148°, -2-methylfurans are similarly prepared. H. B.

**Anomalous Friedel-Crafts reactions with furans.** H. GILMAN, M. McCORKLE, and N. O. CALLOWAY (J. Amer. Chem. Soc., 1934, 56, 745).—2-Furoic acid, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub> give α-C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H (probably through an endoxy-derivative) and not 3-phenyl-2 : 3-dihydro-2-furoic acid (King, A., 1927, 358). In the reaction between furfuraldehyde, Pr<sup>β</sup>Cl, and AlCl<sub>3</sub> in CS<sub>2</sub> (A., 1933, 1300), Pr<sup>β</sup> is introduced into the 3- or 4-position; bromination of the corresponding acid gives 5-bromo-3(or 4)-isopropyl-2-furoic acid (*Et* ester, formed from *Et* 5-bromo-2-furoate, Pr<sup>β</sup>Cl, and AlCl<sub>3</sub>), also obtained by oxidation of the product from 5-bromofurfuraldehyde, Pr<sup>β</sup>Cl, and AlCl<sub>3</sub>. H. B.

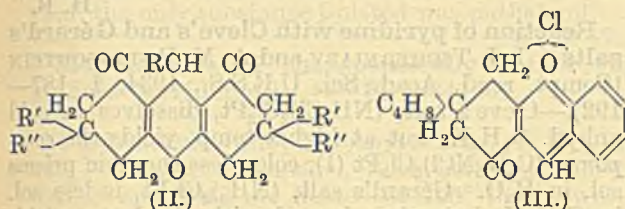
**Bases of the type of fast-violet B, with a furoyl radical in place of benzoyl.** N. KISHNER and V. KRASOVA (Anilinokras. Prom., 1933, 3, 430—433).—5-Nitro-4-methoxy-*o*-toluidine and furoyl chloride give, on keeping 24 hr. at room temp. in presence of NaOAc, quant. yields of 5-nitro-2-furamido-4-methoxytoluene, m.p. 175°, which with Zn and HCl gives the corresponding 5-amino-derivative, m.p. 134°. The analogous products from 6-nitro-4-methoxy-*m*-toluidine are 6-nitro-, m.p. 170°, and 6-amino-3-furamido-4-methoxytoluene, m.p. 169°, and from 3-chloro-4-nitro-6-methoxyaniline 3-chloro-4-nitro-1-furamido-6-methoxybenzene, m.p. 194.5°, and 3-chloro-1-furamido-4-amino-6-methoxybenzene, m.p. 181.5°. The above amines yield, on diazotising and coupling, dyes similar to those containing Bz in place of furoyl. R. T.

[Preparation of] xanthone. M. SPEKTOR (Khim. Farm. Prom., 1933, 195—196).—Acetylsalicylic acid is distilled at 120—170° until all the AcOH has passed over; the temp. is then raised in 4 hr. to 350—355°/40 mm., and xanthone crystallises. Yield (from EtOH) 70%. CH. ABS.

**Dihydroresorcinols. II. Condensation of aldehydes with cyclopentanespirocyclohexane-3 : 5-dione and dimethyldihydroresorcinol.** R. D. DESAI (J. Indian Chem. Soc., 1933, 10, 663—671; cf. Vorländer and Kalkow, A., 1900, i, 99).—The alkyl- (or arylidenebis) derivatives of dimethyldihydroresorcinol (I) and similar compounds are best formed in presence of piperidine and are dehydrated by HCl (except for *o*-OH-compounds), AcOH, or Ac<sub>2</sub>O to the corresponding octahydroxanthens (II), which are formed direct in presence of HCl, AcOH, etc. Condensation of *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO with cyclopentanespirocyclohexane-3 : 5-dione in presence of HCl, however, gives 4-keto-2-spirocyclopentanotetrahydrobenzopyrylium chloride (III), decomp. 300° (cf. A., 1932, 279); this



resists hydrolysis with KOH in EtOH, giving only the corresponding base, m.p. > 300°. The following



are described: *methylene-*, m.p. 165°, *benzylidene-*, m.p. 167°, and *salicylidenebiscyclopentanespirocyclohexane-3:5-dione*, m.p. 208—209° [*Ac* derivative, m.p. 180—184°, from *o*-AcO·C<sub>6</sub>H<sub>4</sub>·CHO (IV); converted by Ac<sub>2</sub>O or AcOH into (V) (below)]; 1:8-*diketo-3:6-bis*spirocyclopentaneoctahydroxanthen [(II): R=H, R'R''=C<sub>4</sub>H<sub>8</sub>], m.p. 180—181°, and its 9-*Ph* (R=Ph), m.p. 185—186°, and 9-*salicyl* derivative, m.p. 191° [*Ac* (V), m.p. 181—182°, and *Bz*, m.p. 137°, derivatives]; and 1:8-*diketo-9-phenyl-3:3:6:6-tetramethyloctahydroxanthen(mono)phenylhydrazone*, m.p. 266—267° (decomp.). The compound, m.p. 209—210° (*loc. cit.*) from (I) and *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO in aq. KOH appears to be the corresponding xanthen [(II): R=*o*-OH·C<sub>6</sub>H<sub>4</sub>, R'=R''=Me] (*Bz* derivative, m.p. 154—155°; *phenylhydrazone*, m.p. 235°), as it is formed by heating *salicylidenebisdimethyldihydroresorcinol*, m.p. 184° [*Ac* derivative (VI), m.p. 200—201° [from (IV)]; *Me ether* (VII), m.p. 184° (from *o*-MeO·C<sub>6</sub>H<sub>4</sub>·CHO)], with glacial AcOH, whilst its *Ac* derivative, m.p. 190—191°, and *Me ether*, m.p. 180°, are similarly formed from (VI) and (VII), respectively.

H. A. P.

**Chemical constituents of tobacco. III. Colouring matter of tobacco blossoms.** K. YAMAFUJI (*Bull. Agric. Chem. Soc. Japan*, 1933, 9, 137—139).—An anthocyanidin present as a monoglucoside and a flavone glucoside have been isolated in small yield.

R. K. C.

[Vegetable] tannins and their behaviour towards proteins. K. FREUDENBERG (*J. Soc. Leather Trades Chem.*, 1934, 18, 152—155).—The intermol. forces which cause PhOH and N compounds to combine also cause tannins to interact with proteins. Opposite electrical charges may also assist the reaction. The formation of this mol. compound, which is reversible, is followed by a partly reversible permeation process and condensation and oxidation of the tannins in the mol. compound.

D. W.

**Quebracho tannin.** K. FREUDENBERG and P. MATTLAND (*J. Soc. Leather Trades Chem.*, 1934, 18, 156—159).—Quebracho catechin (I) is synthesised from fisetinidin chloride and possesses the properties of catechin. It gave the same type of condensation without the elimination of H<sub>2</sub>O as did the natural quebracho tannin and the same degradation products. The presence of a pyran OH group is unnecessary for phlobaphen formation (*cf. A.*, 1931, 964). The evidence confirms Freudenberg's formula for (I) (*cf. B.*, 1925, 369; *A.*, 1926, 73).

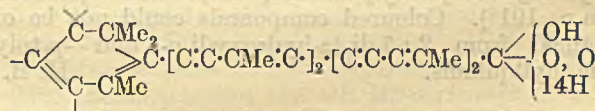
D. W.

**Action of alkalis on substituted benzodioxins.** F. D. CHATTAWAY and H. IRVING (*J.C.S.*, 1934, 325—330).—When the 6-position of a substituted 2:4-bis-trichloromethyl-1:3-benzodioxin contains an electron-

attracting group the heterocyclic ring is ruptured by KOH-EtOH, and the group also facilitates elimination of HCl from :CH·CCl<sub>3</sub> in position 4 under milder alkaline conditions. If the group is electron-donating the ring is unaffected, but the action is modified by the presence of groups in the heterocyclic ring. 6-Nitro-2-trichloromethyl-4-dichloromethylene-1:3-benzodioxin, prepared by elimination of HCl, is oxidised to 6-nitro-4-*keto-2-trichloromethyl-1:3-benzodioxin*, m.p. 172.5°, which with NaOH-EtOH gives CHCl<sub>3</sub> and 5-nitrosalicylic acid, whilst the corresponding 7-*Me* compound, m.p. 149°, prepared from 6-nitro-2-trichloromethyl-4-dichloromethylene-7-methyl-1:3-benzodioxin, m.p. 120—121°, similarly affords CHCl<sub>3</sub> and 5-nitro-2-hydroxy-4-methylbenzoic acid. 6:8-Dinitro-2-trichloromethyl-4-dichloromethylene-1:3-benzodioxin and EtOH-KOH give ω-dichloro-3:5-dinitro-2-ethoxyacetophenone. 6:8-Dinitro-1:3-benzodioxin and 1% NaOH yield CH<sub>2</sub>O and 3:5-dinitrosaligenin, m.p. 104—104.5° (*diacetate*, m.p. 81.5—82°).

F. R. S.

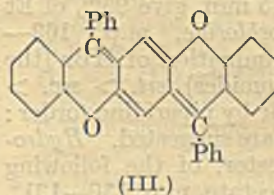
**Plant colouring matters. LVIII. New occurrence of astacin: its constitution.** P. KARRER and F. BENZ (*Helv. Chim. Acta*, 1934, 17, 412—416).—Isolation (after hydrolysis) of astacin (I) C<sub>30</sub>H<sub>36</sub>O<sub>3</sub> (from new analytical data), identical with that obtained by Kuhn (*A.*, 1933, 509), from *Ophidiaster ophidianus* is described. Oxidation of (I) with KMnO<sub>4</sub> in aq. C<sub>6</sub>H<sub>6</sub> at room temp. gives CMe<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>; (I) therefore contains the carotene ring and the partial formula



is suggested. Catalytic reduction (Pt-H<sub>2</sub>) gives perhydroastacin, C<sub>30</sub>H<sub>56</sub>O<sub>3</sub>, which is no longer sol. in alkali. The OH is therefore enolic.

J. W. B.

**Transformations of 2:5-di-(α-hydroxydiaryl-methyl)quinols.** H. LIEBERMANN and J. BARROLLIER (*Annalen*, 1934, 509, 38—50).—Et 2:5-dihydroxyterephthalate (I) and MgPhBr in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> give 2:5-di-(α-hydroxybenzhydryl)quinol (II), m.p. 220° (red at 150°), which when heated in PhNO<sub>2</sub> passes into 5:12-diphenyl-5:12-dehydrochromoxanthen (*chromanorufen*) (III), red with metallic green reflex, m.p. about 400°. (II) and HCl in COMe<sub>2</sub> afford 2:5-di-(α-chlorobenzhydryl)quinol (IV), m.p. about 250° (red at 180°), and (mainly) 2:5-di-(α-acetonylbenzhydryl)quinol, becomes red at about 250°. (IV) heated in PhNO<sub>2</sub> gives (III). 2:5-Di-(α-anilinobenzhydryl)quinol, sinters at about 255° to a dark red melt, is prepared from (IV) and NH<sub>2</sub>Ph in C<sub>6</sub>H<sub>6</sub>. (II) and boiling Ac<sub>2</sub>O give 2-hydroxy-9-phenyl-3-

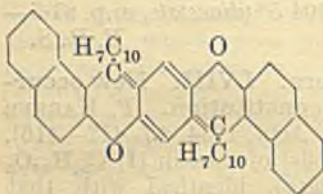


(III)

α-hydroxybenzhydrylxanthen, m.p. 165° [which when heated in O<sub>2</sub> passes into (III)], and (III) is reduced (HI-AcOH) to 5:12-diphenylchromoxanthen (*chromanorufan*), colourless, m.p. > 270° (red at 220°), and oxidised (CrO<sub>3</sub>-AcOH; Br; HNO<sub>3</sub>-

AcOH) to a peroxide,  $C_{32}H_{22}O_4$ , m.p. 270° [regenerating (III)]. Reduction (Zn dust, AcOH) of (II) gives 2:5-dibenzhydrylquinol (V) (diacetate, m.p. 235°; dibenzoate, m.p. 286°), oxidised ( $CrO_3$ , AcOH) to 2:5-dibenzhydryl-p-benzoquinone (tetraphenylphlorone), m.p. 250° (previous reddening), which when heated to about 270° passes into (III). (II) is oxidised ( $CrO_3$ , AcOH) to 2:5-di-( $\alpha$ -hydroxybenzhydryl)-p-benzoquinone, which also gives (III) when heated at 270° in  $H_2$  or  $CO_2$ . (V) is unaltered at 270° in  $CO_2$ , but in air (III) results. 1:4-Dimethoxy-2:5-di-( $\alpha$ -hydroxybenzhydryl)benzene, m.p. 240°, from MgPhBr and Me 2:5-dimethoxyterephthalate, m.p. 140°, shows no tendency to pass into a coloured compound.

(I) and  $\alpha$ - $C_{10}H_7$ ·MgBr give 2:5-di(hydroxydi- $\alpha$ -naphthylmethyl)quinol (VI), m.p. > 400° (violet at 140°), which when heated in  $PhNO_2$  passes into 5:12-di- $\alpha$ -naphthyl-5:12-dehydro-3:4-benzchroman-10:11-benzxanthen (chromanoviolen) (VII), violet with bronze reflex, m.p. > 400°, reduced (HI-AcOH) to chromanoviolan, colourless, turns violet at 240°, and oxidised ( $CrO_3$ , AcOH) to a peroxide,  $C_{48}H_{30}O_8$ , m.p. 212° (loss of  $O_2$  to a deep



(VII)

violet melt). (VI) is reduced (Zn dust, AcOH) to 2:5-di(di- $\alpha$ -naphthylmethyl)quinol. Me 3:6-dihydroxyphthalate and MgPhBr give 3:6-dihydroxy- $\alpha$ -diphenylphthalide, m.p. 296° (diacetate, m.p. 191°). Coloured compounds could not be obtained from 2:5-di-( $\alpha$ -hydroxydi-*o*- and -*p*-tolylmethyl)quinols.

H. B.

#### Reaction of organic halides with piperidine.

IV. Bromo-esters. W. V. DRAKE and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 697—700).—The rates of reaction of 1 mol. of  $CHBrR\cdot CO_2Et$  ( $R=H, Me, Et$ ),  $CBrMe_2\cdot CO_2Et$ ,  $Br[CH_2]_n\cdot CO_2Et$  ( $n=2-4$ ),  $CH_2Br\cdot CHMe\cdot CO_2Et$ , and  $CHBrMe\cdot [CH_2]_n\cdot CO_2Et$  ( $n=1-5$ ) with piperidine (I) (2 mols.) are determined at 90°, essentially as previously described (A., 1931, 494). With certain exceptions, the order of reactivity, as determined by the amount of (I) hydrobromide produced in a given time, is (as bromides) primary > sec. > tert.;  $CO_2Et$  has a general activating effect. The  $\beta$ -Br-esters are the most reactive; in these cases, piperidino-ester formation involves elimination of HBr and subsequent addition of (I).  $CH_2\cdot CH\cdot CO_2Et$  and (I) in light petroleum at 90° for 15 min. give 95% of Et  $\beta$ -piperidinopropionate (hydrochloride, m.p. 163—164°). Mechanisms for the elimination of HBr [the order of this is usually (as bromides) tert. > sec. > primary] and replacement of Br by piperidino (order: usually primary > sec. > tert.) are suggested. Hydrochlorides, m.p. quoted after ester, of the following are described: Et piperidinoacetate, m.p. 130—131°,  $\alpha$ -piperidino-propionate, m.p. 131—132°, and -butyrate, m.p. 113—114°,  $\beta$ -piperidino-butylate, m.p. 177—178°, and -isobutylate, m.p. 134—135°,  $\gamma$ -piperidino-butylate, m.p. 128—129°, and -valerate, m.p. 128—129°,  $\delta$ -piperidino-valerate, m.p. 154—155°, and

-hexoate, m.p. 135—136°,  $\epsilon$ -piperidinoheptoate, m.p. 121—122°, and  $\zeta$ -piperidino-octoate, m.p. 116—117°.

H. B.

Reaction of pyridine with Cleve's and Gérard's salts. I. I. TSCHERNIAEV and A. M. RUBINSCHTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 187—192).—Cleve's salt,  $(NH_3Cl)_2Cl_2Pt$ , dissolves in cold anhyd.  $C_5H_5N$ , but at higher temp. yields the compound  $(C_5H_5NCl)_2Cl_2Pt$  (I), colourless rhombic prisms sol. in  $H_2O$ . Gérard's salt,  $(NH_3)_2Cl_4Pt$ , is less sol. in  $C_5H_5N$ , but when heated with the latter yields the compound  $(NH_3)_2(C_5H_5NCl)_2PtCl_2\cdot 4H_2O$  (II), which is readily sol. in an excess of  $C_5H_5N$  in  $H_2O$ , whereas (I) is insol. (II) reacts with  $H_2C_2O_4$  to form the compound  $(NH_3)_2(C_5H_5NCl)_2Pt(CO_2\cdot CO_2H)_2\cdot 2H_2O$  (III), with  $Na_2PtCl_6$  to form the compound  $(NH_3)_2(C_5H_5NCl)_2Pt(PtCl_6)$ , and on reduction with  $N_2H_4\cdot 2HCl$  gives  $(NH_3)_2Cl_2Pt$ . Oxidation of  $(NH_3)_2(C_5H_5N)_2PtCl_2$  with  $Cl_2$  yields the trans-diammine-trans-dipyridine trans-dichloro-compound  $(NH_3)_2(C_5H_5N)_2Cl_2PtCl_2\cdot 4H_2O$  (IV), isomeric with (II) but less sol., yielding with  $H_2C_2O_4$  an oxalate similar to (III) but less sol. and losing  $H_2O$  only at 110°, whereas (III) also loses  $C_5H_5N$ . With  $K_2PtCl_4$  (IV) gives the chocolate-coloured compound  $(NH_3)_2(C_5H_5N)_2Cl_2Pt\cdot PtCl_4$ , with  $K_2PtCl_6$  the yellow compound  $(NH_3)_2(C_5H_5N)_2Cl_2Pt\cdot PtCl_6\cdot 3H_2O$ , and with  $N_2H_4\cdot 2HCl$ ,  $(NH_3)_2Cl_2Pt$  and  $(C_5H_5N)_2Cl_2Pt$ . After reduction,  $K_2PtCl_4$  ppts. the compound  $(NH_3)_2(C_5H_5N)_2Pt\cdot PtCl_4$ . Addition of  $C_5H_5N$  to Peirone's salt  $(NH_3Cl)_2Pt$  and oxidation of the resulting tetrammine with  $Cl_2$  yields the compound  $(NH_3C_5H_5N)_2Cl_2PtCl_2$ , isomeric with (II) and (IV), colourless, sol. in  $H_2O$ , and sparingly sol. in EtOH. It gives no ppt. with  $H_2C_2O_4$  or with  $PtCl_6''$  and with excess of  $K_2PtCl_4$  gives Magnus' salt  $(NH_3\cdot C_5H_5N)_2Pt\cdot PtCl_4$ ; reduction with  $N_2H_4\cdot 2HCl$  gives the compounds  $(NH_3\cdot C_5H_5N)_2PtCl_2$  and  $C_5H_5N\cdot NH_3Cl_2Pt$ .

J. W. S.

6-Bromo-2-methylpyridine. H. D. T. WILLINK, jun. and J. P. WIBAUT (Rec. trav. chim., 1934, 53, 417—420).—6-Hydroxy-2-methylpyridine (I) (A., 1923, i, 600) and  $POBr_3$  at 160° give 6-bromo-2-methylpyridine (II), b.p. 205.5—207°/772 mm. (picrate, m.p. 115—116°), also formed from 6-amino-2-methylpyridine (III) and  $NaNO_2$  in aq. AcOH-KBr. (III) and  $NaNO_2$  in 48% HBr afford (II) and 3(?) : 5(?) : dibromo-6-hydroxy-2-methylpyridine (IV), m.p. 250.5—251°. (I) and a large excess of  $PBr_5$  at 160° give (II) and 3(?) : 5(?) : 6-tribromo-2-methylpyridine, m.p. 75—76°, also obtained from (IV) and  $POBr_3$ , which is oxidised (alkaline  $KMnO_4$ ) to a little 3(?) : 5(?) : 6-tribromopyridine-2-carboxylic acid, m.p. 144.5—145°. Attempts to prepare a tribromopyridine from this were unsuccessful.

H. B.

Amino-derivatives of pyridine. G. B. CRIPPA and M. LONG [with E. DE MARTINI] (Gazzetta, 1934, 64, 83—91).—2-Aminopyridine yields 2-phthalimidopyridine, m.p. 224°. 2:6-Diaminopyridine, obtained from lutidine by way of dipicolinic acid and its Ag salt, Et ester (m.p. 28°), and amide, similarly yields 2:6-diphthalimidopyridine, m.p. above 340°, and with  $PhN_2Cl$  forms 2:6-diamino-3-benzeneazopyridine, m.p.

135°. When the *diphthalimido*-compound, m.p. 223°, was prepared from the last, and reduced and dehydrated, the only substance isolated was phthalanil.

E. W. W.

Manufacture of therapeutically active substances [pyridones].—See B., 1934, 301.

**4-*p*-Dialkylaminophenylpyridines.** E. KOENIGS and E. RUPPELT (Annalen, 1934, 509, 142—158).— $C_5H_5N$  and  $BzCl$  are heated at 100° (bath) with a little naturkupfer *C* until most of this dissolves; addition of  $NPhMe_2$  to the cooled mixture and subsequent heating at 100° for 5 hr. gives 67% of 4-*p*-*dimethylaminophenylpyridine* (I), m.p. 234° [hydrochloride, m.p. 220°; dihydrochloride, m.p. 205°; picrate, m.p. 246° (decomp.)]; quaternary salt (II) (+2H<sub>2</sub>O), orange-red, m.p. 265° (yellow at 145°), with 1 mol. of  $CH_2PhCl$ , also obtained in very poor yield from  $C_5H_5N$  and *p*- $NMe_2C_6H_4N_2Cl$ . The mechanism of formation of (I) is considered to be: 1-benzoylpyridinium chloride → 4-chloro-1-benzoyl-1:4-dihydropyridine → 1-benzoyl-4-*p*-dimethylaminophenyl-1:4-dihydropyridine → (I) +  $PhCHO$  (which is isolable from the reaction mixture). (I) dyes wool and tanned cotton a shade similar to auramine; (II) is a better dye than (I). (I) is oxidised ( $KMnO_4$ , dil.  $H_2SO_4$ ) to isonicotinic acid. (I), 64%  $HNO_3$ , and a little  $NaNO_2$  give (probably) the 3:3':5'-( $NO_2$ )<sub>3</sub>-derivative, m.p. 129° [crude nitrate, m.p. 195—197°; quaternary salt, m.p. 165° (decomp.)], with  $CH_2PhCl$  (and a little of a substance, m.p. 241°), which is reduced ( $SnCl_2$ , conc.  $HCl$ ) to (probably) the 3:3'-( $NH_2$ )<sub>2</sub>-derivative, m.p. 176° (trihydrochloride, decomp. 364°). (I) and hot  $HNO_3$  (*d* 1.52) afford a trinitro-4-*p*-methylaminophenylpyridine, m.p. 160° [nitrate, m.p. 211° (decomp.)], similarly reduced to a diamino-4-*p*-methylaminophenylpyridine, m.p. 174°. (I) and  $Br$  in hot  $AcOH-HBr$  give (probably) 4-3':5'-dibromo-4'-aminophenylpyridine, m.p. 136° [quaternary salts, m.p. 185° (previous sintering) and 395°, with  $CH_2PhCl$  and amyl bromide, respectively], which when diazotised and coupled with  $NPhMe_2$  affords the corresponding 4'-*p*-dimethylaminobenzeneazo-derivative, m.p. 212°. 4-*p*-Diethylaminophenylpyridine, m.p. 157° [picrate, m.p. 211°; quaternary salt, m.p. 283°, with  $CH_2PhCl$ ; ( $NO_2$ )<sub>3</sub>-derivative, m.p. 115° (nitrate, m.p. 208°), reduced to a ( $NH_2$ )<sub>2</sub>-derivative, decomp. 250°], and  $HNO_3$  (*d* 1.52) give a trinitro-4-*p*-ethylaminophenylpyridine, m.p. 143° [nitrate, m.p. 208—210° (decomp.); picrate, m.p. 223—225° (decomp.)], reduced to a diamino-4-*p*-ethylaminophenylpyridine, m.p. 139—140°. *o*- and *p*- $C_6H_4Me \cdot NMe_2$  do not react (as above), whilst *m*- $C_6H_4Me \cdot NMe_2$ ,  $C_5H_5N$ , and  $BzCl$  give a compound,  $C_{21}H_{20}ON_2$ , m.p. 94° (hydrochloride, m.p. 176°).

The following are prepared [as (I)] from the appropriate  $NPhRR'$ : 4-*p*-methyleneethyl-, m.p. 154° (picrate, m.p. 216°), 4-*p*-methyl-*n*-propyl-, m.p. 123° [picrate, m.p. 200° (decomp.)], 4-*p*-methyl-*n*-butyl-, m.p. 92° (hydrochloride, m.p. 184°), 4-*p*-methylisoamyl-, m.p. 120°, 4-*p*-benzylmethyl-, m.p. 122° [hydrochloride, m.p. 237°; picrate, m.p. 185° (previous sintering)]; quaternary salt (+ $xH_2O$ ), m.p. 103°, m.p. (anhyd.) 215° (not sharp), with  $CH_2PhCl$ , 4-*p*-ethyl-*n*-propyl-, m.p. 49°, 4-*p*-ethyl-*n*-butyl-, m.p. 41°, 4-*p*-di-*n*-propyl-, m.p. 108° [picrate, m.p. 212° (decomp.)], and 4-*p*-di-*n*-butyl-,

m.p. 156—157° (hydrochloride, m.p. 149°; picrate, m.p. 186—187°), -aminophenylpyridines. H. B.

**Nitration of  $\beta$ -phenylethylpyridines and related compounds.** II. E. A. WAGSTAFF (J.C.S., 1934, 276—278).—4'-Methyl-2-stilbazole nitrate, m.p. 147°, with  $HNO_3$  gives 3'-nitro-4'-methyl-2-stilbazole, m.p. 137° (65%), no other product being isolated, and it is concluded that  $\cdot CH:CHR$  (*R* is electron-attracting) exerts an  $-I+T$  effect. 2', 3', and 4'-Nitro-4-stilbazole, m.p. 171° (lit. 119°), have been prepared by heating the appropriate  $NO_2 \cdot C_6H_4 \cdot CHO$  with the bases obtained from mono- and di-methylpyridines with  $PhCHO$  and  $ZnCl_2$ . 2:5-Di-2', m.p. 140°, -3', m.p. 216°, and -4'-nitrostyrylpyridine, m.p. 258°, were obtained in the same reaction. 4-Stilbazole nitrate, m.p. 160°, on nitration indicates an *o/p* ratio of 1.05. 4- $\beta$ -Phenylethylpyridine is nitrated to the 4'- $NO_2$ -compound, m.p. 85°; 2- $\beta$ -4'-nitrophenylethylpyridine affords the 2':4'-( $NO_2$ )<sub>2</sub>-derivative, m.p. 78° [nitrate, m.p. 160° (decomp.); methiodide, m.p. 210°].

F. R. S.

**Mercurated substitution products of di-*p*-hydroxyphenylisatin.** S. E. HARRIS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 108—113).—Acetoxymercuri- or diacetoxymercuri-derivatives (all decomp. without melting) of 3:3'-dibromo-, m.p. 144—145°, 3:3':5:5'-tetrabromo-, 3:3'-dinitro-, m.p. 225° (decomp.), 3:3'-diphenyl-, m.p. 183—185°, 3:3'-diphenyl-5:5'-dibromo-, m.p. 115°, 3:3'-diphenyl-5:5'-dinitro-, m.p. 148°, 3:3'-dimethyl-5:5'-dibromo-, m.p. 250° (decomp.), and 3:3'-dinitro-5:5'-dimethyl-4:4'-dihydroxydiphenylisatin, m.p. 238—240°. Diresorcinolisatin [di-(2':4'-dihydroxydiphenylisatin)] and its 3:3'- $Br_2$ -compound, m.p. 250—255° (decomp.), and the  $OH \cdot Hg$ -derivative of 3:3'-dinitrodiresorcinolisatin, decomp. at 220°, are described. The highest dilutions killing *B. typhosus* in 5 min. range from 1—500 to 1—30,000. E. H. S.

**Comparison of the dimethylquinoline from aniline, isobutaldehyde, and methylal with 2:3-dimethylquinoline and the relationship of 2:3-dimethylquinoline to benzil.** G. ROHDE (Ber., 1934, 67, [B], 431—434).—Direct comparison of the dimethylquinoline from  $NH_2Ph$ ,  $CH_2(OMe)_2$ , and isobutaldehyde with 2:3-dimethylquinoline (I) and of their picrates, platinichlorides, and aurichlorides shows them to be chemically and crystallographically identical. A substance,  $C_{15}H_{21}O_2N$ , m.p. 145—146°, is the primary product of the interaction of (I) and benzil (II) at 100°, and is transformed by warm conc.  $H_2SO_4$  into the substance  $C_{25}H_{19}ON$ , needles or prisms, m.p. 180—181°, which when heated above its m.p. passes into a yellow isomeride, m.p. 246—247°. (I) and (II) at 180° afford  $CO_2$ ,  $H_2O$ , and a compound (?)  $C_9H_6NMe \cdot CH_2 \cdot CHPh_2$ , m.p. 121—122°. 2-Methylquinoline (III) and (II) similarly yield the compounds,  $C_{24}H_{19}ON_2$ , m.p. 134—135°, and  $C_{24}H_{17}ON$ , m.p. 189—189.5°. (III) and (II) at 180° afford a substance (?) ( $C_9H_6N \cdot CH:CHPh$ )<sub>2</sub>, m.p. 245—246°. H. W.

**2-Hydroxy-6-methoxy-4-methylquinoline.** O. G. BACKEBERG and W. O. KERMACK (J.C.S., 1934, 377).—The m.p. of 2-hydroxy-6-methoxy-4-methyl-

quinoline is 272° (uncorr.) and the specimens of other workers contain some impurities. F. R. S.

**Action of halogens on polycyclic indole derivatives. IV. Some reactions of 1-keto-1:2:3:4-tetrahydrocarbazole.** A. J. MEARS, S. H. OAKESHOTT, and S. G. P. PLANT (J.C.S., 1934, 272—276).—*cycloHexane-1:2-dionemono-p-bromophenylhydrazone*, m.p. 176°, obtained by Coffey's method (A., 1923, i, 803), with AcOH-HCl gives 6-bromo-1-keto-1:2:3:4-tetrahydrocarbazole (I), m.p. 222—224° (9-Ac derivative, m.p. 154—155°). The corresponding *o-bromophenylhydrazone*, m.p. 172—174°, does not undergo Fischer's reaction, whilst the *m*-compound yields a mixture of 5(or 7)-, m.p. 233—235° (9-Ac derivative, m.p. 135°), and 7(or 5)-bromo-1-ketotetrahydrocarbazole, m.p. 163° (9-Ac derivative, m.p. 186—188°). 6-Nitro-1-ketotetrahydrocarbazole (II), m.p. 259° (lit. 212°), is similarly prepared. Bromination and nitration, respectively, of 1-ketotetrahydrocarbazole gives (I) and (II), and not the additive compounds. *cycloHexane-1:2-dionemono-o-tolylhydrazone*, m.p. 95—96°, yields 1-keto-8-methyltetrahydrocarbazole, m.p. 167°, whilst the 5-bromo-, m.p. 95—97°, and 5-nitro-hydrazones, m.p. 155—157°, give the corresponding 6-bromo-, m.p. 229—230°, and 6-nitro-tetrahydrocarbazoles, m.p. 294°, also obtained by direct bromination or nitration. *cycloHexane-1:2-dionemono-3-bromo-p-tolylhydrazone*, m.p. 79—82°, gives 8-bromo-1-keto-6-methyltetrahydrocarbazole, m.p. 164°, and the corresponding 2-derivative forms a mixture of 5(or 7)-, m.p. 253—254°, and 7(or 5)-bromo-1-keto-6-methyltetrahydrocarbazole, m.p. 197°. The 3-NO<sub>2</sub>-compound yields 8-nitro-1-keto-6-methyltetrahydrocarbazole, m.p. 199—201°, and the 2-NO<sub>2</sub>-compound, m.p. 141—142°, gives a mixture of 5(or 7)-, m.p. 253—255°, and 7(or 5)-nitro-1-keto-6-methyltetrahydrocarbazole, m.p. 207—208°. Bromination or nitration of 1-keto-6-methyltetrahydrocarbazole affords the 7(or 5)-Br- or -NO<sub>2</sub>-compounds. Reduction of 1-ketotetrahydrocarbazole with P-HI gives tetrahydrocarbazole and with Sn-HCl yields *cis*-hexahydrocarbazole. F. R. S.

**Catalytic dehydrogenation of cyclic bases. II.** M. EHRENSTEIN and I. MARGGRAFF (Ber., 1934, 67, [B], 486—491).—Passage of tropine over Pd-asbestos at 280—290° occurs without evolution of H<sub>2</sub> and yields a *sec.* base isolated as the Bz derivative, C<sub>15</sub>H<sub>19</sub>ON, m.p. 94—96.5°. Hexamethyleneimine in presence of Pt- or Pd-asbestos suffers slow dehydrogenation and ring contraction, affording 2-methylpyridine and unidentified pyrrole derivatives. H. W.

**Optically active allantoin.** R. FOSSE, P. E. THOMAS, and P. DE GRÆVE (Compt. rend., 1934, 198, 689—672).—Allantoinase from soya-bean at 40° destroys *d*-allantoin (I) preferentially, giving a mixture whence was isolated the *l*-form of (I), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -92.4° in H<sub>2</sub>O. The classical formula is thus upheld. R. S. C.

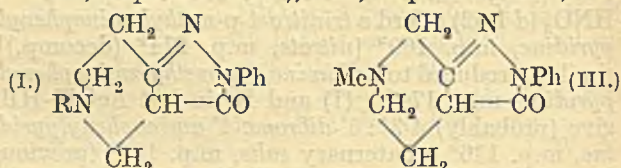
**Synthesis of ethyl 5-benzylidene-N-3-methylhydantoin-N-1-acetate and its derivatives.** A. LITZINGER (J. Amer. Chem. Soc., 1934, 56, 673—677).—The Na derivative of 5-benzylidene-3-methylhydantoin and CH<sub>2</sub>Cl·CO<sub>2</sub>Et in EtOH give *Et* 5-benzylidene-3-methylhydantoin-1-acetate (I), b.p. 215—216°/5.5 mm., m.p. 50.5—51.5°, converted by HCl in EtOH

into an *isomeride* (II), m.p. 121—122° (corresponding *Me* ester, m.p. 115.5—116°). (I) is hydrolysed (EtOH-NaOH) to 5-benzylidene-3-methylhydantoin-1-acetic acid (III), m.p. 160—161° (*Na* salt, decomp. 294—295°), whilst (II) similarly gives an isomeric acid (IV), m.p. 222—223° [*Na*, m.p. 299—300° (decomp.)], *K* (+EtOH), m.p. 235—237° (decomp.), and *Pb* (+4H<sub>2</sub>O), m.p. 241—242° (decomp.), salts]. (I)—(IV) are reduced [red P, HI (*d* 1.7)] to 5-benzyl-3-methylhydantoin-1-acetic acid, m.p. 150—151° [*Na* salt (+2EtOH), m.p. 275—276° (decomp.)], and *Et* ester, m.p. 49.5—51°, both hydrolysed [aq. Ba(OH)<sub>2</sub>] to phenylalanine-*N*-acetic acid (A., 1933, 166). (I) or (II) and Br in CCl<sub>4</sub> give (probably) *Et* 5- $\alpha$ -bromobenzylidene-3-methylhydantoin-1-acetate, m.p. 113—113.5°, decomp. 195—200°. H. B.

**Formation of histamine by irradiation of histidine.** P. HOLTZ (Arch. exp. Path. Pharm., 1934, 175, 97—103).—Ultra-violet irradiation of histidine, especially at an alkaline reaction and in N<sub>2</sub>, yields histamine. F. O. H.

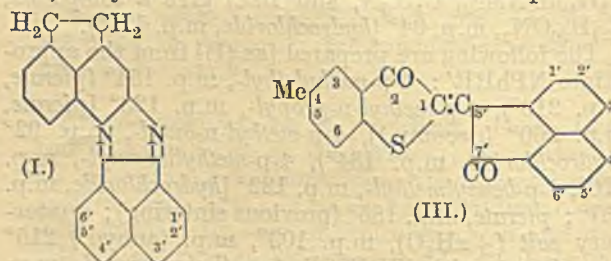
**Reactivity of deoxybenzoin.** G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1934, 64, 100—102).—2:3-Diphenyl- $\alpha$ - $\beta$ -naphthoquinoline is prepared by the interaction of deoxybenzoin and benzeneazo- $\beta$ -naphthylamine at 205—210°. E. W. W.

**Pyrazolones derived from carbethoxypiperidones.** S. M. E. ENGLERT and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 700—702).—*Pyrazolones* (I), where R is Me (II) (*hydrochloride*, m.p. 224—225°), Et (*hydrochloride*, m.p. 187—188°), Pr<sup>a</sup> (*hydrochloride*, m.p. 191—192°), Bu<sup>a</sup>, m.p. 117—118°, and



*isoamyl*, m.p. 125—126° (accompanied by a substance, m.p. 117—118°, possibly isomeric), are obtained from the requisite Et 1-alkyl-4-piperidone-3-carboxylate hydrochloride, NPh·NH<sub>2</sub>·HCl, and a little conc. HCl at 110—150°; the free bases could not be used. Et 1-methyl-3-piperidone-4-carboxylate similarly affords the pyrazolone (III) (*hydrochloride*, m.p. 191—193°). (II) could not be methylated to an antipyrine. H. B.

**Dyes derived from acenaphthenequinone. IV. Azines and indigoid vat dyes.** S. K. GUHA (J. Indian Chem. Soc., 1933, 10, 679—683; cf. A., 1933, 167).—By condensation of 2:3-diaminoacenaphthene



with acenaphthenequinone and its substitution products in AcOH 2:3:7':8'-*diacenaphthazine* (I), m.p.

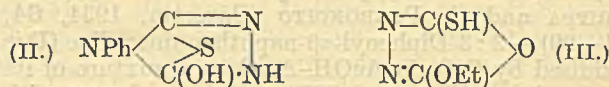
> 315°, and its 3'-chloro-, m.p. > 315°, 3'-bromo-, m.p. > 315°, 1'-methoxy-, m.p. 293°, and 3':4'-dinitro- (II), sublimes > 315°, -derivatives are formed. These dye wool in yellow to chocolate (II) shades from an acid bath. 1-Methoxyacenaphthaphenazine has m.p. 187—188° (lit. 182—183°). Similarly, with 3-hydroxy-4-methylthionaphthen 4-methyl-2:8'-thionaphthenacenaphthenylindigo (III), m.p. 265—266°, its 3'-chloro-, m.p. 284—285° (sinters 281°), 3'-bromo-, m.p. 282°, and 1'-methoxy-, m.p. 279—280°, -derivatives, are formed. These dye cotton scarlet from a Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> vat, and dye wool from an acid bath (? suspension). H. A. P.

Acetyl derivatives of diphenylthiosemicarbazide. M. BUSCH and W. RENNERT (Ber., 1934, 67, [B], 384—387).—The compound obtained by the action of AcCl on 1:4-diphenylthiosemicarbazide (I) cannot have the structure NPh·NH·C(NPh)·S·Cl·Ac ascribed to it by McKee (J.C.S., 1915, 107, 1133), since analysis shows it to contain 1 H<sub>2</sub>O < is thereby required. Since hydrolysis by hot H<sub>2</sub>O is accompanied by intermediate production of the carbinol base  $\text{N}=\text{C}(\text{NPh})\text{C}(\text{OH})\text{NH}$ , m.p. 173°, it is regarded as  $\text{N}:\text{C}(\text{NPh})\text{C}(\text{OH})\text{NH} > \text{S}$ , the possible triazole formula being excluded, as desulphurisation is not effected by HgO. McKee's "anhydride" is identified as 1:4-diphenyl-5-methyl-3:5-endothiotriazole (II), also obtained by the action of Ac<sub>2</sub>O on (I), whereby a thermally unstable form, m.p. about 233°, is immediately produced. Treatment of 2:4-diphenylthiosemicarbazide with Ac<sub>2</sub>O gives, in addition to 1-acetyl-2:4-diphenylthiosemicarbazide, m.p. 133° (McKee, *loc. cit.*), (I) and thence (II). McKee's "4-acetyl-1:4-diphenylthiosemicarbazide," m.p. 161° (decomp.), is probably  $\text{N}=\text{C}(\text{NPh})\text{C}(\text{Me})\text{NH} > \text{S}$ . H. W.

N-Aminotriazoles of higher fatty acids. J. VORIŠEK (Coll. Czech. Chem. Comm., 1934, 6, 69—76).—Prolonged heating of the higher aliphatic acids with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O gives, in addition to the hydrazides, aminotriazole derivatives. The following are described: 1-amino-3:5-bis-λ-hydroxyheptadecyltriazole, m.p. 139.5—140.5°. [Ac<sub>3</sub> (an oil) and Ac<sub>2</sub> derivatives; hydrochloride, m.p. 105—106° (decomp.); sulphate, m.p. 106.5—107.5°]; 1-amino-3:5-bisheptadecyltriazole, m.p. 135.5—136° (hydrochloride; 1-Ac derivative, m.p. 87—88°). H. A. P.

Formation of heterocyclic compounds from derivatives of ethyl carbazinate. D. N. MAJUMDAR and P. C. GUHA (J. Indian Chem. Soc., 1933, 10, 685—692).—Et carbazinate (I) (prep. improved) adds PhNCS to form Et 4-phenylthiosemicarbazide-1-carboxylate, m.p. 141—142° (cf. A., 1923, i, 858); this with boiling 2N-aq. KOH loses 1EtOH and gives a compound, m.p. 283—284° (decomp.), which is not desulphurised by HgO and is therefore regarded as 3-hydroxy-4-anilo-3:5-endothio-2:3-dihydro-1:3:4-triazole (II), and with conc. HCl loses NH<sub>2</sub>Ph to form 2-ethoxy-5-thiol-1:3:4-oxdiazole (III), m.p. 274—275° (decomp.) With PhNCO (I) gives Et 4-phenylsemicarbazide-1-carboxylate, m.p. 154—155°, and with

CS<sub>2</sub> and KOH it gives a K salt converted by MeI into Me carbethoxydithiocarbazinate, CO<sub>2</sub>Et·NH·NH·CS<sub>2</sub>Me, m.p. 90—91°, which is also formed from ClCO<sub>2</sub>Me and Me dithiocarbazinate. (I) forms normal hydrazones with mono- and dialdehydes, and normal acyl derivatives with dicarboxylic chlorides. The o-nitrobenzylidene, m.p. 130—131°, salicylidene, m.p. 129—130°, p-toluylidene, m.p. 116—118°, cinnamylidene, m.p. 196—197°,



piperonylidene, m.p. 123—124.5°, furfurylidene, m.p. 132.5—133.5°, vanillylidene, m.p. 152.5—153.5°, glyoxyldenebis-, m.p. 305—306° (decomp.), carbonylbis-, m.p. 119—120°, oxalyldis-, m.p. 182—183° (decomp.), and o-phthalylbis-, m.p. 166—167°, -derivatives, camphorquinone-, m.p. 199.5—200°, and phenanthrenequinone-monocarbethoxyhydrazone, m.p. > 320° (sinters 275°), acetophenonecarbethoxyhydrazone, m.p. 119.6—120.6°, and Et<sub>2</sub> hydrazinedicarboxylate, m.p. 131.5—132.5° (ClCO<sub>2</sub>Et), are described. H. A. P.

Chlorophyll-A. H. FISCHER (J.C.S., 1934, 245—256).—A lecture. 1:3:5:8-Tetramethyl-2:4-diethyl-6-carboxyporphin-7-propionic acid has been synthesised and found to be identical with natural rhodoporphyrin, which on loss of the 6-CO<sub>2</sub> group yields pyrroporphyrin (I), also obtained by direct synthesis. Ethylation of (I) leads to phylloporphyrin (II), showing that the unsubstituted group is at position 6. (I), (CH<sub>2</sub>Cl)<sub>2</sub>O, and HBr give bromomethylpyrroporphyrin (haemin). γ-Methylpyrroporphyrin (1:3:5:8-tetramethyl-2:4-diethyl-γ-methylporphin-7-propionic acid) is identical with natural (II). Reduction (HI-AcOH) of phæophorbide yields phæoporphyrins and of chlorin-e, chloroporphyrins; the constitution of these is discussed. Reduction with HI in the cold of chlorophyll, the phorbides, purpurins, and chlorins gives ketoporphyrins ("oxo-reaction"), but porphyrins and their leuco-compounds do not undergo the reaction. The "oxo-reaction" is due to the presence of a ·CH<sub>2</sub> group which gives rise to ·CHO. The relationship between chlorophyll and haemin is discussed (cf. this vol., 420).

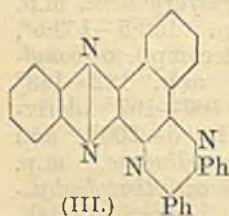
F. R. S.

Chlorophyll. VII. Oximes of phæophorbide-b. A. STOLL and E. WIEDEMANN (Helv. Chim. Acta, 1934, 17, 456—470; cf. A., 1932, 1265; this vol., 308).—Methylphæophorbide-b with cold C<sub>2</sub>H<sub>5</sub>N and NH<sub>2</sub>OH·HCl gives its monoxime I, m.p. 280° (corr.), which is phase-positive, hydrolysed by HCl-Et<sub>2</sub>O successively to phæophorbide-b monoxime I (II) and phæophorbide-b (III), which with NH<sub>2</sub>OH gives (II); hydrolysis of (II) with MeOH-KOH-C<sub>5</sub>H<sub>5</sub>N gives rhodin-g oxime (IV), hydrolysed (HCl) to rhodin-g, which with NH<sub>2</sub>OH gives (IV). Longer treatment at 100° converts (I) into a dioxime (V), not melting at 280° (corr.), which is phase-negative and is hydrolysed (HCl-Et<sub>2</sub>O) to phæophorbide-b dioxime [absorption spectrum identical with that of (V)], and then to phæophorbide-b monoxime II (phase-negative), which gives 60% of (III) with 24% aq. HCl-Et<sub>2</sub>O at 50°, but some decarboxylation (C<sub>11</sub>)

also occurs giving, probably, pyrophæophorbide-*b*. The monoxime *I* in which the (rhodin) CO-*I* group is oximated, and the dioxime, give *a*-type absorption spectra, whereas monoxime *II* gives the *b*-type, and Fischer's hypothesis of a second CO group (CO-*II*) in chlorophyll-*b* is accepted, but it is not considered that CO-*I* can be in the propionyl side-chain.

J. W. B.

**Oxidation of naphthoquinoxalines.** G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1934, 64, 91—99).—2 : 3-Diphenyl- $\alpha$ - $\beta$ -naphthoquinoxaline (I) is oxidised by CrO<sub>3</sub> in AcOH-Ac<sub>2</sub>O to a mixture of its 5 : 6-quinone (II), m.p. 267°, which condenses with *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> giving the phenazine (III), m.p. above 300°, with 2 : 3-diphenyl-6-*o*-carboxyphenylpyrazine-5-carboxylic acid (IV), m.p. 148° (decomp.), also formed by action of KMnO<sub>4</sub> on (I). Heating (IV) with CaO furnishes 2 : 3 : 5-triphenylpyrazine (?), m.p. 143°. The action of H<sub>2</sub>O<sub>2</sub>-AcOH



on (I) and (IV) gives the respective 1(or 4)-oxides, m.p. 252° and 224°, which are reduced by SnCl<sub>2</sub> to (I) and to (IV). 3-Phenyl-naphthoquinoxaline (A., 1931, 1169) similarly yields a 1(or 4)-oxide, m.p. 236°, further oxidised to the quinone. E. W. W.

**Violacein, the violet pigment of *Bacillus violaceus*.** I. F. WREDE and A. ROTHHAAS (Z. physiol. Chem., 1934, 223, 113—118).—The cryst. pigment violacein (I), C<sub>42</sub>H<sub>35</sub>O<sub>6</sub>N<sub>5</sub> or C<sub>50</sub>H<sub>42</sub>O<sub>8</sub>N<sub>6</sub>, decomp. > 350° (hydrochloride, sulphate, decomp. > 300°), is a monacid base, which on hydrogenation takes up 14 or 16 H. With Ac<sub>2</sub>O-NaOAc, (I) yields a Ac<sub>5</sub> (or Ac<sub>6</sub>) derivative, decomp. > 300°.

J. H. B.

**Synthesis with  $\beta\beta'$ -dichlorodiethyl ether. Morpholine derivatives.** W. N. AXE and C. FREEMAN (J. Amer. Chem. Soc., 1934, 56, 478—479).—(CH<sub>2</sub>Cl-CH<sub>2</sub>)<sub>2</sub>O (1 mol.), NPh-NH<sub>2</sub> (1 mol.), and 40% KOH (2 mols.) give *N*-anilinomorpholine, m.p. 107.5°, in 20—30% yield. *p*-Phenylene- (I), m.p. 196°, and diphenyl-4 : 4', m.p. 228.5°, -NN'-dimorpholines are similarly prepared from *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and benzidine, respectively. (I) forms coloured additive compounds with various acids and heavy metal salts.

H. B.

**1 : 3 : 4-Oxdiazines.** W. J. HOPPENBROUWERS (Rec. trav. chim., 1934, 53, 325—354; cf. van Alphen, A., 1928, 780, 1386; 1929, 334, 707).— $\beta$ -Aroyl(acyl)- $\alpha$ -chloroacetyl- $\alpha$ -phenylhydrazines are converted by anhyd. K<sub>2</sub>CO<sub>3</sub> (NaOEt, NH<sub>2</sub>Me, NHMe<sub>2</sub>, or conc. aq. NH<sub>3</sub>) in COMe<sub>2</sub> into  $\Delta^2$ -5-keto-4-phenyl-2-aryl(alkyl)-1 : 3 : 4-oxdiazines. The following compounds are new :  $\beta$ -benzoyl- $\alpha$ -*p*-bromophenylhydrazine, m.p. 156° ( $\alpha$ -chloroacetyl derivative, m.p. 180°);  $\beta$ -*o*-, m.p. 171—172°, -*m*-, m.p. 156°, and -*p*-, m.p. 200°, -bromobenzoyl- $\alpha$ -phenylhydrazines ( $\alpha$ -chloroacetyl derivatives, m.p. 163—164°, 162°, and 142°, respectively);  $\beta$ -*p*-bromobenzoyl- $\alpha$ -*p*-bromophenylhydrazine, m.p. 201° ( $\alpha$ -chloroacetyl derivative, m.p. 191°);  $\beta$ -*p*-nitrobenzoyl- $\alpha$ -*p*-nitrophenylhydrazine, m.p. 265—268°;  $\beta$ -phenylacetyl- $\alpha$ -chloroacetyl- $\alpha$ -phenylhydrazine, m.p. 85°;  $\beta$ -acetyl- $\alpha$ -chloroacetyl- $\alpha$ -*p*-bromophenylhydrazine, m.p.

130°;  $\beta$ -benzoyl-, m.p. 150—151°, and  $\beta$ -acetyl-, m.p. 207°, - $\alpha$ -chloroacetyl- $\alpha$ -*p*-nitrophenylhydrazines;  $\beta$ -*o*-, m.p. 204°, -*m*-, m.p. 164°, and -*p*-, m.p. 188°, -nitrobenzoyl- $\alpha$ -chloroacetyl- $\alpha$ -phenylhydrazines; substituted 5-keto-1 : 3 : 4-oxdiazines : 4-phenyl-2-benzyl-, b.p. 180—188°/0.5—1 mm., 4-*p*-bromophenyl-2-methyl-, m.p. 58—59°, 2-phenyl-4-*p*-bromophenyl-, m.p. 136°, 4-phenyl-2-*o*-, m.p. 112—113°, -*m*-, m.p. 119°, and -*p*-, m.p. 137°, -bromophenyl-, 2 : 4-di-*p*-bromophenyl-, m.p. 164°, 4-*p*-nitrophenyl-2-methyl-, m.p. 97—98°, 2-phenyl-4-*p*-nitrophenyl- (I), m.p. 175°, 4-phenyl-2-*o*-, m.p. 148°, -*m*-, m.p. 156°, and -*p*-, m.p. 146° (II), -nitrophenyl-. The oxdiazines containing Ph (or substituted Ph) in the 2- and 4-positions are not hydrolysed [except with (I)] by 10% H<sub>2</sub>SO<sub>4</sub>; partial hydrolysis occurs with 15% H<sub>2</sub>SO<sub>4</sub> in some cases. (II) is reduced (EtOH-NH<sub>4</sub>HS) to  $\Delta^2$ -5-keto-4-phenyl-2-*p*-aminophenyl-1 : 3 : 4-oxdiazine, m.p. 143° (*Ac* derivative, m.p. 213—215°). Attempts to benzoylate or methylate the enolic form of  $\Delta^2$ -5-keto-2 : 4-diphenyl-1 : 3 : 4-oxdiazine were unsuccessful.

$\Delta^2$ -5 : 6-Diketo-4-phenyl-2-aryl(alkyl)-1 : 3 : 4-oxdiazines are obtained from  $\beta$ -aroyl(acyl)- $\alpha$ -phenylhydrazines and (COCl)<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>. Thus,  $\beta$ -phenylacetyl- $\alpha$ -phenylhydrazine (III) and 2 equivs. of (COCl)<sub>2</sub> give  $\Delta^2$ -5 : 6-diketo-4-phenyl-2-benzyl-1 : 3 : 4-oxdiazine (IV), m.p. 102—103° [use of 1 equiv. of (COCl)<sub>2</sub> affords a compound, m.p. 214—215°, which may be  $\beta\beta'$ -di(phenylacetyl)- $\alpha\alpha'$ -diphenyloxalhydrazide, (·CO·NPh·NH·CO·CH<sub>2</sub>Ph)<sub>2</sub>, and which is not hydrolysed by H<sub>2</sub>O, dil. acid, or dil. alkali]. (IV) is hydrolysed by H<sub>2</sub>O to (III), by H<sub>2</sub>O-Et<sub>2</sub>O to a substance, m.p. 138°, and by EtOH to  $\beta$ -phenylacetyl- $\alpha$ -ethoxyoxalyl- $\alpha$ -phenylhydrazine, CO<sub>2</sub>Et·CO·NPh·NH·CO·CH<sub>2</sub>Ph, m.p. 104—105° [also prepared from (III) and CO<sub>2</sub>Et·COCl in C<sub>6</sub>H<sub>6</sub>]. (IV) and conc. aq. NH<sub>3</sub> in EtOH give oxamide; with NH<sub>2</sub>Ph and NPh-NH<sub>2</sub>, ox-anilide and -phenylhydrazide, respectively, are formed. The following substituted 5 : 6-diketo-1 : 3 : 4-oxdiazines are described : 4-*p*-bromophenyl-2-methyl-, m.p. 178°, 2-phenyl-4-*p*-bromophenyl-, m.p. 206°, 4-phenyl-2-*o*-, m.p. 138—140°, -*m*-, m.p. 245°, and -*p*-, m.p. 183—185°, -bromophenyl-, 2 : 4-di-*p*-bromophenyl-, m.p. 314°, 2-phenyl-4-*p*-nitrophenyl-, m.p. 212°, and 4-phenyl-2-*o*-, m.p. 183.5°, -*m*-, m.p. 179°, and -*p*-, m.p. 212—213°, -nitrophenyl- [the last three are also accompanied by  $\beta\beta'$ -*di*-, m.p. 254°, -*m*-, m.p. 254°, and -*p*-, m.p. 275°, -nitrobenzoyl- $\alpha\alpha'$ -diphenyloxalhydrazide (·CO·NPh·NH·CO·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>)<sub>2</sub>]. These are hydrolysed (EtOH) to  $\beta$ -acetyl- $\alpha$ -*p*-bromophenyl-, m.p. 96°,  $\beta$ -benzoyl- $\alpha$ -*p*-bromophenyl-, m.p. 178°,  $\beta$ -*o*-, m.p. 118°. -*m*-, m.p. 110°, and -*p*-, m.p. 138.5°, -bromobenzoyl- $\alpha$ -phenyl-,  $\beta$ -*p*-bromobenzoyl- $\alpha$ -*p*-bromophenyl-, m.p. 138°,  $\beta$ -benzoyl- $\alpha$ -*p*-nitrophenyl-, m.p. 130°, and  $\beta$ -*o*-, m.p. 161°, -*m*-, m.p. 151.5°, and -*p*-, m.p. 159°, -nitrobenzoyl- $\alpha$ -phenyl- $\alpha$ -ethoxyoxalylhydrazine, respectively.  $\beta$ -Acetyl- $\alpha$ -*p*-nitrophenylhydrazine and (COCl)<sub>2</sub> give a substance, m.p. about 70°.

$\beta$ -Phenylacetyl- $\alpha$ -chloroacetyl- $\alpha$ -phenylhydrazine and the requisite NH<sub>2</sub>Ar at 100° give  $\beta$ -phenylacetyl- $\alpha$ -anilinoacetyl- (V), m.p. 154°, - $\alpha$ -*p*-bromoanilinoacetyl-, m.p. 186°, and - $\alpha$ -*o*-, m.p. 165°, -*m*-, m.p. 129—130°, and -*p*-, m.p. 163°, -toluidinoacetyl- $\alpha$ -phenylhydrazines.  $\beta$ -Acetyl-, m.p. 201°, and  $\beta$ -benz-

oyl, m.p. 167°,  $\alpha$ -*p*-bromophenyl-,  $\beta$ -acetyl- $\alpha$ -*p*-nitrophenyl-, m.p. 202°,  $\beta$ -*o*-, m.p. 174—175°, and -*p*-, m.p. 179—180°, -bromo- and  $\beta$ -*o*-, m.p. 222°, and -*m*-, m.p. 193·5°, -nitro-benzoyl- $\alpha$ -phenyl-, and  $\beta$ -*p*-bromobenzoyl- $\alpha$ -*p*-bromophenyl-, m.p. 183°,  $\alpha$ -anilinoacetylhydrazines are also prepared. (V) is hydrolysed (20% H<sub>2</sub>SO<sub>4</sub>, EtOH) to  $\alpha$ -anilinoacetyl- $\alpha$ -phenylhydrazine, m.p. 157° (*anisylidene*, m.p. 175—176°, and *piperonylidene*, m.p. 190°, derivatives).  $\beta$ -Acetyl- $\alpha$ -*p*-bromoanilinoacetyl- $\alpha$ -phenylhydrazine, m.p. 189—190°, is similarly hydrolysed to  $\alpha$ -*p*-bromoanilinoacetyl- $\alpha$ -phenylhydrazine, m.p. 194° (*benzylidene*, m.p. 224°, *anisylidene*, m.p. 205°, and *piperonylidene*, m.p. 218°, derivatives). H. B.

**Toxoflavin, the yellow poison from Bongkrek.** A. G. VAN VEEN and W. K. MERTENS (Rec. trav. chim., 1934, 53, 398—404).—The yellow pigment previously described (A., 1933, 1207; this vol., 454) is now termed *toxoflavin* (I), probably C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>N<sub>4</sub>, m.p. 172°, containing a >NMe group. (I) dialyses rapidly through parchment and is stable towards H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, and Br-H<sub>2</sub>O; reduction (SO<sub>2</sub>) in slightly acidic or alkaline solution gives a colourless compound, which is re-oxidisable (air; H<sub>2</sub>O<sub>2</sub>; Br-H<sub>2</sub>O) to (I). (I) gives an additive compound with NaHSO<sub>3</sub>, does not afford CO(NH<sub>2</sub>)<sub>2</sub> on hydrolysis [Ba(OH)<sub>2</sub>], has no acidic properties, and is decolourised by aq. NH<sub>3</sub> and very dil. alkali (the colour is restored only by immediate neutralisation). Careful treatment of (I) with *N*-HCl gives a colourless compound, C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>N<sub>4</sub>, m.p. 250° (decomp.), sublimes at 230°, which is unaffected by conc. HCl at 100° and dissolves in alkali to an intense yellow solution. Oxidation (KClO<sub>3</sub>, HCl) of (I) affords NH<sub>3</sub>, NH<sub>2</sub>Me, and alloxan (or methylalloxan). Reduction (H<sub>2</sub>, PtO<sub>2</sub>, AcOH) results in the uptake of 3 mols. of H<sub>2</sub> per mol. of (I) (about 1 mol. is absorbed using Pt-black and EtOAc); aeration of the resultant solutions restores the original colour. Evidence is given to show that (I) is probably formed in combination with some complex. H. B.

**Derivatives of benzoyl- and furoyl-thiocarbimides and their use in synthesising heterocyclic compounds.** I. B. DOUGLAS and F. B. DAINS (J. Amer. Chem. Soc., 1934, 56, 719—721).—BzNCS (I) (from NH<sub>4</sub>SCN and BzCl in COMe<sub>2</sub>) and NHPH·CH<sub>2</sub>·CH<sub>2</sub>·OH give *N*-benzoyl-*N'*-phenyl-*N'*- $\beta$ -hydroxyethylthiocarbimide (II), m.p. 154°, converted (cold 80% H<sub>2</sub>SO<sub>4</sub> or 48% HBr) into 2-benzoylimino-3-phenylthiazolidine, m.p. 122°, which is hydrolysed to 2-keto-3-phenylthiazolidine, and converted by EtOH-NaOH into a compound (III), m.p. 173—174°. (II) and yellow HgO in C<sub>6</sub>H<sub>6</sub> afford 2-benzoylimino-3-phenyloxazolidine, m.p. 117°. *N*-Benzoyl-*N'*- $\beta$ -hydroxyethyl-, m.p. 128°, and -*N'*-*o*-, m.p. 141°, and -*p*-, m.p. 136°, -tolyl-*N'*- $\beta$ -hydroxyethyl-thiocarbimides are similarly prepared and converted into 2-benzoylimino-, m.p. 168°, and 2-benzoylimino-3-*o*-, m.p. 137—138°, and -*p*-, m.p. 154°, -tolyl-thiazolidine, respectively. 2-Benzoylimino-3-*o*- and -*p*-tolylloxazolidines have m.p. 103° and 134°, respectively. NHPH·CH<sub>2</sub>·OH [*?* NHPH·(CH<sub>2</sub>)<sub>3</sub>·OH] and (I) give *N*-benzoyl-*N*-phenyl-*N'*- $\gamma$ -hydroxypropylthiocarbimide, m.p. 94°, convertible (H<sub>2</sub>SO<sub>4</sub>) into 2-benzoylimino-3-phenylthiazan, m.p. 137°. *N*-Benzoyl-*N'*-phenyl-*N'*-carbethoxymethyl-, m.p.

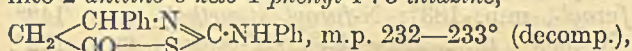
165° [from (I) and NHPH·CH<sub>2</sub>·CO<sub>2</sub>Et], or the -carboxymethyl-, m.p. 166—167°, -thiocarbimide similarly gives 3-benzoyl-1-phenyl-2-thio-4-glyoxalone, m.p. 163°. *o*-Benzoylthiocarbamidobenzoic acid (IV), m.p. 159—160° (decomp.), re-solidifying with m.p. 190—200° [from (I) and *o*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H], and H<sub>2</sub>SO<sub>4</sub> afford 4-keto-2-thio-3-benzoyl-1 : 2 : 3 : 4-tetrahydroquinazoline, m.p. 157—158°; this and (IV) are hydrolysed (NaOH) to 4-keto-2-thio-1 : 2 : 3 : 4-tetrahydroquinazoline (V), m.p. 305—310°. (IV) heated at 160—175° gives H<sub>2</sub>S and a *S*-free compound, m.p. 207—208°. (V) is methylated [Me<sub>2</sub>SO<sub>4</sub>; aq. NaOH (min. amount)] to 4-keto-2-methylthiol-3 : 4-dihydroquinazoline, m.p. 219°; excess of the reagents gives 2 : 4-diketo-3-methyl-1 : 2 : 3 : 4-tetrahydroquinazoline, m.p. 236°. *S*-Methylphenylthiocarbimide and (I) afford a methylthiol-1 : ?-diphenyl-?thiodihydrotriazine, m.p. 211°. The following substituted thiocarbimides are prepared from furoylthiocarbimide and the appropriate amine: *N*-furoyl-, m.p. 183°; *N*-furoyl-*N'*-methyl-, m.p. 142°, -*N'*-ethyl-, m.p. 101—102°, -*N'*-benzyl-, m.p. 122°, -*N'*-phenyl-, m.p. 116°, -*N'*-*o*-, m.p. 115—116°, -*m*-, m.p. 99°, and -*p*-, m.p. 130°, -tolyl-, -*N'*- $\alpha$ -, m.p. 186°, and - $\beta$ -, m.p. 139—140°, -naphthyl-, -*N'*-phenyl-*N'*-methyl-, m.p. 98—99°, -*N'*-phenyl-*N'*-benzyl-, m.p. 124°, -*N'*-*N'*-diphenyl-, m.p. 139—140°, and -*N'*-phenyl-*N'*- $\beta$ -hydroxyethyl- (VI), m.p. 111°. 2-Furoylimino-3-phenylthiazolidine, m.p. 123° [from (VI) and 80% H<sub>2</sub>SO<sub>4</sub>], is hydrolysed (alkali) to (III). H. B.

**Reactions of aldehydes and ketones. Synthesis of thiodiazolines from aldehydes.** H. WUYTS and (MLLE.) A. LACOURT (Bull. Acad. roy. Belg., 1934, [v], 20, 156—167).—The appropriate aldehyde and thioacetylhydrazine in EtOH with a little HCl give the following substituted 2 : 3-dihydro-1 : 3 : 4-thiodiazoles (thiodiazolines) (I) (cf. A., 1933, 839): 3 : 5-diphenyl-2-*o*-, m.p. 120°, -*m*-, m.p. 139°, and -*p*-nitrophenyl, m.p. 129°; 3 : 5-diphenyl-*p*-dimethylaminophenyl, m.p. 144°; 3-phenyl-2-*p*-anisyl-5- $\alpha$ -naphthyl, m.p. 101°; 3-phenyl-2-piperonyl-5- $\alpha$ -naphthyl-, m.p. 131°; 5-phenyl-3-*p*-bromophenyl-, m.p. 128°, and 3- $\alpha$ -naphthyl-2-(1-furyl), m.p. 118°; 3-phenyl-2-tolyl-5- $\alpha$ -naphthyl, m.p. 150°; 3-phenyl-2 : 5-di- $\alpha$ -naphthyl, m.p. 196°; 3-phenyl-5- $\alpha$ -naphthyl-2- $\beta$ -naphthyl (II), m.p. 197·5° (*picrate*, m.p. 202°). The m.p. quoted are the temp. at which the substance melts within 20 sec. when suddenly immersed. The m.p., similarly determined, of other derivatives of (I) are 1—3° > previously quoted (*loc. cit.*), and those of thiobenzoyl-, thiobenzoylbromo-, and  $\alpha$ -naphthoyl-phenylhydrazine are 92°, 132°, and 164°, respectively. 3-Phenyl-5-methyl- and -5-benzyl- and 3 : 5-diphenyl-thiodiazoline give *picrates*, m.p. 147·5°, 145°, and 176°, respectively. (II) forms a compound with 1 mol. of AgNO<sub>3</sub> and the other derivatives slowly reduce AgNO<sub>3</sub>. R. S. C.

**Optical analysis and rotatory power of glycothiodiazolines.** H. WUYTS and R. VERSTRAETEN (Bull. Acad. roy. Belg., 1934, [v], 20, 168—177).—The glycothiodiazolines from glucose, mannose, and galactose (A., 1933, 810) are mixtures of dextro- and lævo-rotatory isomerides, the max.  $[\alpha]_{D}^{20}$  observed being -406·6° and +697°; -233·6° and +1203°; -568·2° and +1974°, respectively. R. S. C.

**Isolation of hepaflavin.** P. KARRER, H. SALOMON, and K. SCHÖPP (Helv. Chim. Acta, 1934, 17, 419—425).—A detailed scheme for the isolation of cryst., hepaflavin (I)  $C_{17}H_{20}O_6N_4$ , m.p. about 280°, from liver extract is given. The composition, m.p., cryst. form, and absorption spectra of (I) are identical with those of lactoflavin. J. W. B.

**Influence of attached rings on formation and stability of heterocyclic compounds. II.** T. N. GHOSH (J. Indian Chem. Soc., 1934, 11, 23—32; cf. this vol., 307).— $NH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$  (I) with *o*- and *p*- $C_6H_4Me \cdot NCS$  in aq. EtOH gives  $\beta$ -*o*-, m.p. 144—145° (decomp.), and  $\beta$ -*p*-, m.p. 151—152° (decomp.), *-tolylthiocarbamidopropionic acid*, respectively, which could not be hydrolysed (conc. HCl).  $NH_2 \cdot CHPh \cdot CH_2 \cdot CO_2H$  and PhNCS in EtOH afford  $\beta$ -*phenylthiocarbamido*- $\beta$ -*phenylpropionic acid* (II), m.p. 145—146° (decomp.), converted by  $Ac_2O$  into 2-*anilino*-6-*keto*-4-*phenyl*-1:3-*thiazine*,



which is not desulphurised by HgO and is readily hydrolysed (cold *N*-KOH) to (II).  $\beta$ -*o*-*Tolylthiocarbamido*- $\beta$ -*phenylpropionic acid*, m.p. 154—155° (decomp.), similarly gives 2-*o*-*toluidino*-6-*keto*-4-*phenyl*-1:3-*thiazine*, m.p. 169°. 2:4-Diketo-1:2:3:4-tetrahydroquinazoline [1:3-Et<sub>2</sub> derivative, m.p. 108° (lit. 105—106°)] is not hydrolysed by EtOH-KOH,

whereas  $CH_2 \left\langle \begin{array}{l} CH_2 \cdot NH \\ CO \quad NH \end{array} \right\rangle CO$  similarly gives (I).

*o*-NHPh-CO-NH-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H and Ac<sub>2</sub>O give the *oxazine*, *o*-C<sub>6</sub>H<sub>4</sub>  $\left\langle \begin{array}{l} N \\ CO \quad O \end{array} \right\rangle C \cdot NHPh$ , m.p. 124—125°, whilst

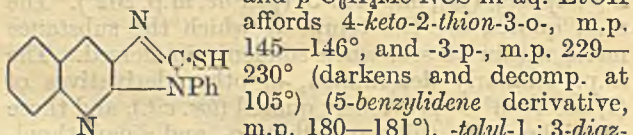
$\beta$ -*phenylcarbamido*- $\beta$ -*phenylpropionic acid*, m.p. 168—169° (decomp.), similarly affords 2-*anilino*-6-*keto*-4-

*phenyl*-1:3-*oxazine*,  $CH_2 \left\langle \begin{array}{l} CHPh \cdot N \\ CO \quad O \end{array} \right\rangle C \cdot NHPh$ , m.p.

221—222°; these oxazines are hydrolysed very rapidly by hot 0.1*N*-alkali. *Salicylideneanthranilic acid*, m.p. 188—190°, and Ac<sub>2</sub>O give the *lactone*,

*o*-C<sub>6</sub>H<sub>4</sub>  $\left\langle \begin{array}{l} CH \cdot N \\ CO \quad O \end{array} \right\rangle C_6H_4 \cdot o$ , m.p. 156—157°, which is

relatively stable (owing to the presence of the two C<sub>6</sub> rings) to cold alkali.  $NH_2 \cdot CH_2 \cdot CO_2H$  with *o*- and *p*- $C_6H_4Me \cdot NCS$  in aq. EtOH affords 4-*keto*-2-*thion*-3-*o*-, m.p. 145—146°, and 3-*p*-, m.p. 229—230° (darkens and decomp. at 105°) (5-*benzylidene* derivative, m.p. 180—181°), *-tolyl*-1:3-*diazole*,



(III.)

ole,  $\left\langle \begin{array}{l} NH \cdot CS \\ CH_2 \cdot CO \end{array} \right\rangle N \cdot C_6H_4Me$ , respec-

tively, hydrolysed (EtOH-KOH) to *o*-, m.p. 141—142° (decomp.), and *p*-, m.p. 147—148° (decomp.) [*K* salt, m.p. 240° (decomp.)], *-tolylthiocarbamidoacetic acid*, respectively. The 5-*o*-*nitrobenzylidene* derivative, m.p. 216—218°, of 4-*keto*-2-*thion*-3-*phenyl*-1:3-*diazole* (5-*benzylidene* derivative, m.p. 196—197°), is reduced (Sn, conc. HCl) to the *quinoline* (III), m.p. 186°. H. B.

**Ergot alkaloids. II. Degradation of ergotinine with alkali.** Lysergic acid. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1934, 104, 547—551; cf. A., 1932, 1147).—When ergotinine is dis-

solved in *N*-KOH-MeOH, the MeOH removed, and the resinous residue treated with 8% aq. KOH, there are formed *lysergic acid*,  $C_{14}H_{12}N(N \cdot NMe) \cdot CO_2H$ , m.p. 238° (decomp.),  $[\alpha]_D^{25} +40^\circ$  in  $C_6H_5N$  (*Me* ester, m.p. 168°),  $Pr^\beta \cdot CO \cdot CO_2H$  [ $NH_4$  salt, m.p. 175° (sublimation); phenylhydrazone, m.p. 152°], and  $NH_3$ . Similar treatment of ergine gives a different acid. R. S. C.

**Amidation with sodium and potassium amides in the alkaloid series. I.  $\alpha$ -Aminoanabasine.** M. M. KATZNELSON and M. J. KABATSCHEK (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 406—411).—With  $NaNH_2$  in various solvents (best in  $NMe_2Ph$  at 120—150°) anabasine (Orékhov *et al.*, A., 1931, 498) gives an  $\alpha$ -*NH*<sub>2</sub>-derivative (2- or 6-), m.p. 105—106° [*picrate*, m.p. 233—233.5° (decomp.)]; *platinichloride*, m.p. 225°. J. W. B.

**Action of hydriodic acid on lupanine.** G. R. CLEMO and R. RAPER (Ber., 1934, 67, [B], 463—464; cf. Winterfeld *et al.*, A., 1931, 371, 1433; Clemo, *ibid.*, 1931, 970).—Treatment of lupanine (I) with very conc. HI and red P at 150—260° does not appear to afford  $\beta$ -lupinane unless lupinine (II) is present in the initial material, which is probably the case in the absence of special purification. Winterfeld's results would require the presence of  $\leq 10\%$  of (II) in (I) which would cause a very profound depression of the m.p. H. W.

**Stereochemistry of 2:2'-disubstituted diphenyls. IV. Diphenates of the cinchona alkaloids.** (Miss) M. S. LESSLIE and E. E. TURNER (J.C.S., 1934, 347—350).—*Quinine diphenate alcoholate* (I) (1EtOH), m.p. 217—218°, and *acetone* (1COMe<sub>2</sub>), m.p. 217—218°, *quinidine* (+2EtOH), *cinchonine* (1EtOH), *cinchonidine* (1EtOH), and *dihydroquinine diphenate* (+3EtOH) are strongly dextrorotatory and show slight mutarotation. A possibility is that in solution the alkaloid diphenate undergoes a very rapid process of asymmetric induction, only the last stages being detectable. The optical rotation of (I) in a series of EtOH-H<sub>2</sub>O mixtures shows that the extent of the induction process varies inversely as the dissociation; induction is greater in conc. than in dil. EtOH solution. *Quinine phthalate alcoholate* is levorotatory and does not show mutarotation. F. R. S.

**Microchemistry of quinine carbonate (Aristochine).** M. WAGENAAR (Pharm. Weekblad, 1934, 71, 316—319).—Quinine carbonate (I) dissolved in dil. mineral acids fails to give all the reactions of quinine, particularly the formation of the sparingly sol. iodosulphate. (I) reacts with KI-I solution and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> giving the *iodo-oxalate* (characteristic dichroic needles), which differentiates it from euquinine. (I) forms a sparingly sol. nitrate, but this compound is unsuitable for microchemical identification. Directions are given for carrying out microchemically the colour reaction produced by Cl<sub>2</sub> and NH<sub>3</sub> on quinine alkaloids. S. C.

**Alkaloids of *Alstonia* barks. I. *A. constricta*.** F. Muell. T. M. SHARP (J.C.S., 1934, 287—291).—The bark of *A. constricta* contains at least 4 alkaloids, one of which is cryst. and appears to be *alstonine*,



$C_{21}H_{20}O_3N_2 \cdot 4H_2O$ , sinters  $77^\circ$ , transparent  $130^\circ$  (from EtOH, containing  $1.25H_2O$ ) (Hesse, Ber., 1878, 11, 1546). It forms a *sulphate*, m.p.  $209^\circ$ ,  $[\alpha]_D +118.6^\circ$  in  $H_2O$ ; *acid sulphate*, m.p.  $246-248^\circ$  (decomp.),  $[\alpha]_D +113.1^\circ$  in  $H_2O$ ; *hydrochloride*, m.p.  $286^\circ$  (decomp.),  $[\alpha]_D +131.9^\circ$  in  $H_2O$ ; *acid oxalate*, m.p.  $239^\circ$  (decomp.); *nitrate*, m.p.  $262-263^\circ$  (decomp.); *picrate*, m.p.  $194-195^\circ$ ; *hydriodide*, m.p.  $291^\circ$  (decomp.); and *monomethiodide*, m.p.  $246^\circ$ . Preliminary experiments on the constitution are described. F. R. S.

**Strychnos alkaloids. LXXIX. Nature of the acidic products of the oxidation of benzylidene- and 11-hydroxy-dihydrostrychnine.** H. LEUCHS and H. BEYER (Ber., 1934, 67, [B], 459-463).—Contrary to Kotake *et al.* (A., 1933, 1061), the acid (I) obtained by oxidising benzylidenedihydrostrychnine with  $KMnO_4$  in  $COMe_2$  is  $C_{21}H_{22}O_5N_2$ ; it is frequently mixed with a *hydrate*, whereas the *perchlorate* gives consistent analytical results. Hydrolysis of (I) with  $Ba(OH)_2 \cdot H_2O$  at  $95^\circ$  gives  $BaC_2O_4$  and a *substance* isolated as the *perchlorate*  $C_{19}H_{24}O_3N_2 \cdot 2HClO_4$ ,  $[\alpha]_D^{20} -84.4^\circ/d$ . Bromination of (I) affords the *compound*  $C_{21}H_{21}O_5N_2Br$ , m.p.  $237-239^\circ$  (decomp.),  $[\alpha]_D^{20} -63.8^\circ/d$  in NaOH, hydrolysed by  $Ba(OH)_2$  at  $100^\circ$  to  $BaC_2O_4$  and the *substance*  $C_{19}H_{23}O_3N_2Br$  (*diperchlorate*,  $[\alpha]_D^{20} -103.5^\circ/d$ ).

H. W.

**Narcotine.**—See this vol., 476.

**Recent syntheses of alkaloids.** E. SPATH (Bull. Soc. chim., 1933, [iv], 53, 1358-1387).—A lecture.

**Diarsyls. VII. 4 : 4''-Dihydroxy- and 3 : 3' : 3'' : 3'''-tetrahydroxy-tetraphenyldiarsyl.** Reaction between *p*-hydroxy- and *p*-aminophenylarsine and tetraphenyldiarsyl oxide. F. F. BLICKE and J. F. ONETO (J. Amer. Chem. Soc., 1934, 56, 685-687).—*p*-Nitrodiphenylarsinic acid, m.p.  $177-179^\circ$  [prepared by Sakellarios' method (A., 1924, i, 1247)], is reduced ( $FeSO_4$ , aq. NaOH) to the *NH*<sub>2</sub>-acid, m.p.  $215-216^\circ$ , convertible into *p*-hydroxydiphenylarsinic acid, m.p.  $202-203^\circ$ . This is reduced ( $H_3PO_2$ , little HI, AcOH) to 4 : 4''-dihydroxy-tetraphenyldiarsyl, m.p.  $161-163^\circ$  (sealed tube in  $N_2$ ). 3 : 3'-Dihydroxydiphenylarsinic acid (I), darkens about  $202^\circ$  ( $Me_2$  ether, m.p.  $151-153^\circ$ ), prepared from the  $(NH_2)_2$ -acid, is similarly reduced (in EtOH) to 3 : 3' : 3'' : 3'''-tetrahydroxytetraphenyldiarsyl, m.p.  $207-208^\circ$  (sealed tube in  $N_2$ ), also obtained [with  $(\cdot AsPh_2)_2$  (II)] from  $AsHPh_2$  and  $[3 : 3'-(OH)_2C_6H_4 \cdot As]_2O$ . 3 : 3'-Dihydroxydiphenylbromo-, m.p.  $131-133^\circ$ , and -iodo-, m.p.  $130-131^\circ$ , -arsines are prepared from (I) by the usual methods. The above diarsyls absorb  $O_2$  readily.  $(AsPh_2)_2O$  and *p*-OH-C<sub>6</sub>H<sub>4</sub>·AsH<sub>2</sub> in  $C_6H_6$  give (II) and (*p*-OH-C<sub>6</sub>H<sub>4</sub>·As)<sub>2</sub>; *p*-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>·AsH<sub>2</sub> similarly affords (II) and (*p*-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>·As)<sub>2</sub>. H. B.

**Hexa-alkyltriaminotriphenyl-phosphines and -phosphine oxides.** E. KOENIGS and H. FRIEDRICH (Annalen, 1934, 509, 138-141).— $NPhMe_2$ ,  $C_3H_5N$ , and  $POCl_3$  at  $140^\circ$  give *pp'p''*-hexamethyltriaminotriphenylphosphine oxide, m.p.  $290^\circ$  (lit.  $149-152^\circ$  and  $319-320^\circ$ );  $NPhEt_2$  similarly affords *pp'p''*-hexaethyltriaminotriphenylphosphine oxide, m.p.  $239^\circ$ .

*pp'p''*-Hexamethyl-, m.p.  $308^\circ$  (lit.  $262^\circ$  and  $273^\circ$ ), and *pp'p''*-hexaethyl-, m.p.  $274^\circ$ , -triaminotriphenylphosphines are similarly prepared using  $PCl_3$ .

H. B.

**Organic selenium compounds. III. Decomposition of selenium phenyl halides.** D. G. FOSTER (Rec. trav. chim., 1934, 53, 405-416).— $SePhCl_3$  (A., 1933, 407) heated at  $110-115^\circ$  (bath) gives *Se p*-chlorophenyl chloride (I), b.p.  $103-104^\circ/4$  mm.;  $SePhCl_3 \rightarrow SePhCl + Cl_2 \rightarrow HCl + p-C_6H_4Cl \cdot SeCl$ .  $SePhBr_3$  (*loc. cit.*) similarly affords *Se p*-bromophenyl bromide (II), b.p.  $127-129^\circ/4$  mm. When (I) and (II) are kept, crystals of *pp'*-dichloro- (III), b.p.  $192^\circ/1$  mm., m.p.  $89^\circ$ , and *pp'*-dibromo- (IV), m.p.  $114-115^\circ$ , -diphenyl diselenide, respectively, are deposited. *p*-Chloroselenophenol, m.p.  $57^\circ$  (from *p*-C<sub>6</sub>H<sub>4</sub>Cl·MgBr and Se followed by decomp. with dil. HCl), EtBr, and aq. EtOH-NaOH give *p*-chlorophenyl Et selenide, b.p.  $85^\circ/1$  mm.,  $90^\circ/3$  mm.; the dichloro, m.p.  $84-85^\circ$  (decomp.), of this decomposes when heated to EtCl and (I) [and (III)]. *p*-Bromoselenophenol, m.p.  $84^\circ$ , similarly affords *p*-bromophenyl Et selenide, b.p.  $146^\circ/18$  mm.; the dibromide, m.p.  $123-124^\circ$  (decomp.), of this decomposes to EtBr and (II) [and (IV)]. *Se p*-chlorophenyl trichloride (V), m.p.  $184^\circ$  (decomp.) [from (III) or *Se Ph chloride* (VI), b.p.  $92^\circ/5$  mm., m.p.  $64-65^\circ$  (prep.; *loc. cit.*), and  $Cl_2$  in  $Et_2O$ ], decomposes at  $>160^\circ$ :  $3p-C_6H_4Cl \cdot SeCl_3 \rightarrow 3p-C_6H_4Cl_2 + SeCl_4 + Se_2Cl_2$ . *Se p*-bromophenyl tribromide (VII), m.p.  $132^\circ$  (decomp.) [from (IV) and Br in light petroleum], decomposes at  $135^\circ$  to (II) and Br. (I) is hydrolysed ( $H_2O$ ) to (III) and *p*-chlorophenylseleninic acid (VIII), m.p.  $183-184^\circ$ ; (II) similarly gives (IV) and *p*-bromophenylseleninic acid (IX), m.p.  $187^\circ$  (decomp.), whilst (VI) and  $SePhBr$  afford  $(\cdot SePh)_2$  and  $PhSeO_2H$ . It is considered that Se aryl monohalides are normally equilibrium mixtures:  $3SeArX \rightleftharpoons SeArX_3 + (\cdot SeAr)_2$ . (VIII) and (IX) are also prepared by hydrolysis ( $H_2O$ ) of (V) and (VII), respectively, and by oxidation ( $HNO_3$ ; Pyman, J.C.S., 1919, 115, 166) of (III) and (IV), respectively. H. B.

**Action of thioglycollanilide and of thiophenol on arylstibinic acids.** G. SCHUSTER (J. Pharm. Chim., 1934, [viii], 19, 264-265).—Thioglycollanilide (I) with  $SbPhCl_2$  (II) and with  $SbPh_2Cl$  (III) gives only dithioglycollanilide. (I) reacts neither with *p*-SbO·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub> (IV) nor with *p*-SbO·C<sub>6</sub>H<sub>4</sub>·OEt (V).  $PhSH$  (VI) gives with (II) an unstable *substance*, m.p.  $65^\circ$  approx., which could not be purified, and with (III) in  $C_6H_6$  a white, cryst., unstable *substance*, m.p.  $83^\circ$ , *M* 377 ( $SbPh_2 \cdot SPh = 383$ ), which readily hydrolyses with regeneration of (VI). (IV) and (V) gave products with (VI) which could not be purified.

W. S.

**Spectroscopic identification of phenylalanine in protein material** W. F. ROSS (J. Biol. Chem., 1934, 104, 531-534).—Phenylalanine (I) shows at 2680, 2640, 2585, 2525, and 2480 Å. absorption bands suitable for identifying (I) in proteins, e.g., gelatin and lucerne proteins, or their hydrolysates after removal of tryptophan and tyrosine. C. G. A.

**Sericin fractions of silk.** H. MOSHER (Canad. Text. J., 1934, 51, 31-32).—Silk sericin is separable

by fermentation and microscopic methods into three fractions (*A* and *B* form an outer layer of the fibre, and *C* an inner layer). *A*, sol. in hot  $H_2O$ , is readily attacked by enzymes, and acid and alkali gives peptones and proteoses. Its aq. solution disperses acid alizarin dyes, but is not generally a good peptising agent. *B*, sparingly  $H_2O$ -sol., resists proteolysis by enzymes; it is dispersed by  $H_2O$  at  $105^\circ$  under pressure and is then an efficient dispersing agent for fats, oils, and waxes. The high dispersing power of boiled-off liquor is due to its content of *B*. *B* is converted into *A* by atm. influences or by acid or alkali treatment so that the  $H_2O$ -sol. content of silk increases during storage. *C* is insol. in all common solvents and resists enzyme attack; it resembles fibroin. The decomp. products (acid; alkali) differ from those obtained from *A* and *B*. Most of the yellow silk pigment lies between the inner (*C*) and outer (*A* and *B*) sericin layers. A. J. H.

**Use of sulphuric, hydrochloric, phosphoric, and nitric acids, and of alkalis for catalytic fission of ovalbumin.** V. S. SADIKOV, V. A. VADOVA, and R. G. KRISTALLINSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 411—415).—Hydrolysis of ovalbumin with 2—4% solutions of  $H_2SO_4$ ,  $HCl$ ,  $H_3PO_4$  (I), and  $HNO_3$  (II) at  $180^\circ$  for 3—6 hr. brings 81.5—88.4% of the total N (*A*) into solution, mainly as *cyclopeptides*, since only 25.4—29% of (*A*) is  $NH_2-N$  (*B*). (I) causes rather more deep-seated fission, and (II) forms basic products. With 2%  $Na_2CO_3$  under similar conditions 86.4% of (*A*) goes into solution, only 13% being (*B*). With 0.1%  $NaOH$  (*B*) is 30.35%. J. W. B.

**Preparation of dipeptidephosphoric acid from caseinogen.** G. SCHMIDT (Z. physiol. Chem., 1934, 223, 86—88).—A dipeptidephosphoric acid consisting of serine, glutamic acid, and  $H_3PO_4$  is obtained from caseinogen (cf. Levene and Hill, A., 1933, 1062) by tryptic digestion, pptn. by  $Pb$  acetate, regeneration by  $H_2S$ , and pptn. of the *Ba* salt ( $C_8H_{10}O_9N_2P_2$ ) $_2Ba$ , by  $EtOH$ . J. H. B.

**Gelatin-tannin reaction.** F. C. THOMPSON (J. Soc. Leather Trades Chem., 1934, 18, 175—178).—Vegetable tannin (*T*) combines with gelatin (*G*) in the same way as does  $HCl$ . Evidence is adduced to show that *T* displaces the  $HCl$  from a *G*- $HCl$  compound in accordance with the theory of addition of strong acids to weak ones. D. W.

**Quantitative organic semi-micro-methods of combustion.** B. L. MANJUNATH and S. SIDDAPPA (J. Mysore Univ., 1932, 6, 123—139).—Methods and apparatus based on existing micro-technique have been developed for the determination of C, H, and N, using 20—30 mg. of substance and an ordinary balance. Unlike micro-technique proper, the new methods are claimed to be practicable for general adoption. W. S.

**Recent improvements introduced by ter Meulen into his methods of analysis.** (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1934, 43, 73—92).—The ter Meulen methods for the determination of C, H, O, N, S, Cl, Br, I, As, Hg, Cd, and Zn are described in detail and experimental results for

numerous substances are quoted. The following modifications in procedure have been introduced. In the determination of O, asbestos is dispensed with, owing to the difficulty of drying it thoroughly, and reduced Ni containing about 10%  $ThO_2$  is used as catalyst. If halogens are present, pure Ni must be used. In the determination of N as  $NH_3$ , asbestos impregnated with the same catalyst is used. This method is of more general application than the ordinary oxidation method in which the N is measured as  $N_2$ . A red-hot Pt spiral is used to ensure completion of the combustion in the determination of C and H and of the reduction in the determination of S as  $H_2S$ . Where the reduction of S compounds presents exceptional difficulty, asbestos may be used. If N is present in addition to S,  $(CN)_2$  is formed during the reduction and aq.  $KOH$  therefore cannot be used for the absorption of the  $H_2S$ . A mixture of equal vols. of 10% aq.  $ZnSO_4$  and 10% aq.  $NaOAc$  acidified with one drop of  $AcOH$  should be employed. Certain improvements in the apparatus used are also described. D. R. D.

**Volumetric determination of formaldehyde in presence of sulphites.** J. EURY (J. Pharm. Chim., 1934, [viii], 19, 261—264).—The  $CH_2O$  (I) is made to reduce standard  $HgCl_2$  (II) in presence of  $Na_2SO_3$ , the resulting Hg is removed, and the amount of (I) is calc. from the excess of (II) determined in a convenient manner in the filtrate. The accuracy of the method is checked by an assay of  $CH_2O-KHSO_3$ . W. S.

**Styphnic acid. III. Use as a reagent for the identification of aromatic compounds containing benzene nuclei.** T. S. MA, C. T. HSIA, P. P. T. SAH. IV. Use as a reagent for the identification of heterocyclic nitrogen compounds. V. Hoo, T. S. MA, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 151—156, 191—199).—III. Additive compounds of styphnic acid with the following compounds have been prepared and the acid determined with  $NaOH$ :  $C_{10}H_8$ , m.p. 168—169° (lit. 165.6°), 1- $C_{10}H_7Cl$ , m.p. 126—128° (lit. 109.8°), 1- $C_{10}H_7Br$ , m.p. 116—118° (lit. 101.2° and 107.8°),  $\alpha$ -, m.p. 183—184°, and  $\beta$ - $C_{10}H_7OH$ , m.p. 169—170°,  $\alpha$ -, m.p. 181—182°, and  $\beta$ - $C_{10}H_7NH_2$ , m.p. 194—195°, anthracene, m.p. 180—181° (lit. 176.3°), and phenanthrene, m.p. 138—139° (lit. 132.7° and 125.6°).

IV. The following *styphnates* have been prepared as above:  $C_5H_5N$ , m.p. 184.5—185.5°,  $\alpha$ -, m.p. 179.5—180.5°, and  $\beta$ -picoline, m.p. 153—154°, piperidine, m.p. 231—232°, quinoline, m.p. 207—208°, 8-hydroxyquinoline, m.p. 193—194°, *p*-nitro-, m.p. 189.5—190.5°, *p*-amino-, m.p. 239—240°, *o*-, m.p. 218—219°, and *p*-tolu-quinoline, m.p. 201—202°, quinaldine, m.p. 213—214°, *p*-toluquinaldine, m.p. 199—200°, carbazole, m.p. 178.5—179.5°, and phenyl-acridine, m.p. 209—210°. F. R. S.

**Determination of saturated and unsaturated sterols, dihydrocholesterol, coprosterol, and cholesterol.** H. DAM (Biochem. Z., 1934, 268, 297—303).—A crit. review of existing methods. P. W. C.

**Determination of furfural[dehyde] at  $0^\circ$  with bromine.** E. E. HUGHES and S. F. ACREE (Ind.

Eng. Chem. [Anal.], 1934, 6, 123—124).—Furfuraldehyde is converted quantitatively into the dibromide when treated for 5 min. at 0° with excess of 0.1N-KBrO<sub>3</sub>-KBr solution in 3% HCl; the free Br is determined with KI and 0.1N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solutions. The temp. is very important, since the secondary reaction (formation of tetrabromide) has a high temp. coeff.

S. C.

Application of the ter Meulen methods for the determination of sulphur and nitrogen to the analysis of the thiodiazolines. (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1934, 43, 93—99).—Analytical results are given for 27 substituted thiodiazolines with practical details of the methods used.

D. R. D.

Action of mercurous chloride on alkaloid salts and its significance for toxicological investigation. J. J. L. ZWIKKER (Pharm. Weekblad, 1934, 71, 22—29).—Reduction of Hg<sub>2</sub>Cl<sub>2</sub> (I) to Hg is not sp. for cocaine, novocaine, and pilocarpine hydrochloride, being also obtained with cotarnine, narcotine, quinine, narceine, and thebaine hydrochloride in solvents (EtOH, EtOH-CHCl<sub>3</sub>) in which the solubility is > 1:4. Alkaloid hydrochlorides (II) react with (I) in highly conc. solutions forming complexes (III) of the type [HgCl<sub>4</sub>]<sup>2-</sup>B<sub>2</sub> and Hg. (III) are stable only in conc. solutions and revert on dilution to sparingly sol. mercurichlorides of the type HgCl<sub>2</sub>.2B. Colloidal Hg, obtained by the action of NH<sub>3</sub> or (II) on (I), will not amalgamate with Au.

S. C.

## Biochemistry.

Excitation metabolism of red blood-cells. I. Increase in respiration during faradic stimulation. II. Mechanism of the increase in respiration during faradic stimulation. I. VON HATINGBERG (Z. Biol., 1934, 95, 44—54, 55—63).—I. Faradisation (I) produces an increase in the respiration (II) (the O<sub>2</sub> consumption increasing up to 170%) of erythrocytes (III) (pigeon, goose, rabbit, man, frog) which is proportional to the applied current and is not due to the rise in temp.

II. The above phenomenon is not related to the salts present in the suspension medium (Ringer-NaHCO<sub>3</sub>, aq. PO<sub>4</sub>-NaCl, and serum) nor to any change in [H<sup>+</sup>]. (I), which increases anaërobic acid-formation by (III), increases the (II) of hæmolysed (III), but not the oxidation of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in presence of C. F. O. H.

Red cell diameter and red cell volume measurements [in blood]. J. M. VAUGHAN and H. M. GODDARD (Lancet, 1934, 226, 513—517).—Mean corpuscular vol., diameter, corpuscular hæmoglobin and its concn. have been determined in various samples of human blood.

L. S. T.

Regulation of the hæmoglobin level in poultry. S. F. COOK and I. W. HARMON (Amer. J. Physiol., 1933, 105, 407—417).—The hæmoglobin val. (I) of normal hens' blood shows great individual variations (5—19 mg. per 100 c.c.), varying inversely with the rate of egg production (II). During broodiness (I) rises, falling again with resumption of laying. (I) in normal hens and chicks on a standard normal diet increases when additional Fe (FeSO<sub>4</sub>) is fed. The spleen (III) of the chick contains practically no stored Fe. During growth (III) size increases greatly and the Fe concn. rises to double the initial val., after which it remains const. In the adult, (III) size and Fe content cannot be correlated with (I) or (II). The hen has not a store of reserve Fe for hæmatopoiesis and depends on the current intake of dietary Fe. Since this probably varies widely, it may account for the great fluctuations in (I) in normal hens.

NUTR. ABS. (m)

Proportion of cystine yielded by hæmoglobins of the horse, dog, and sheep. H. B. VICKERY and A. WHITE (Proc. Soc. Exp. Biol. Med., 1933, 31,

6—7).—By the Cu<sup>I</sup> mercaptide method, hydrolysed hæmoglobin of the horse, sheep, and dog yielded, respectively, 0.41, 0.6, and 1.16% of cystine.

CH. ABS.

Equilibria between native and denatured hæmoglobin in salicylate solutions and the theoretical consequences of the equilibrium between native and denatured protein. M. L. ANSON and A. E. MIRSKEY (J. Gen. Physiol., 1934, 17, 399—408).—Denaturation of hæmoglobin (I) by salicylate (II) in neutral solution is completely reversed by removal of (II) by dialysis or on dilution with H<sub>2</sub>O. Amounts of (II) not conc. enough to denature (I) completely produce an equilibrium mixture of native and denatured (I) as shown by a study of the absorption of monochromatic green light. The higher the (II) concn., the higher is the % denaturation.

A. L.

Light absorption of hæmatoprosthetic, its reduced form, carbonyl compound, and its ammonia hæmochromogen. A. HERZOG (Biochem. Z., 1934, 268, 260—264).—The absorption curves for hæmatoprosthetic (I) show a max. at 608 and a min. at 566 m $\mu$ , and for its NH<sub>3</sub>-hæmochromogen max. at 553 and 524 m $\mu$  and min. at 536 m $\mu$ , the curve thus corresponding with those for the analogous modifications of hæmin. The curve for reduced (I) shows two flat max. at 573 and 562 m $\mu$  with a min. at 566 m $\mu$  and for CO-(I) max. at 560 and 530 m $\mu$  and a min. at 543 m $\mu$ .

P. W. C.

Protein content of blood and cœlomic liquid of invertebrates. M. FLORKIN and H. F. BLUM (Bull. Acad. roy. Belg., 1934, [v], 20, 239—252).—The blood-protein is as follows: Bivalves 0.1%, *Cirripedia* 0.2%, *Decapoda* 4%, *Polychæta* 2%. The cœlomic liquid is practically protein-free.

H. G. R.

Colloid-osmotic (oncotic) pressure. XXX. Albumin and globulin fractions. A. GRÖNWALL (Arch. exp. Path. Pharm., 1934, 174, 544—554; cf. this vol., 201).—Solutions of pure albumin (I) and globulin (II) can be prepared from human serum by cataphoresis (III). The colloidal particles of aq. (I) thus prepared do not exhibit a uniform rate of

cataphoretic migration (IV) and can be further divided by (III) into fractions varying both in (IV) and in the colloid-osmotic pressure/% albumin ratio (V). The aq. (II), however, does not yield fractions of different (V).

F. O. H.

**Physical properties of blood-serum.** M. DOLADILHE (Compt. rend., 1934, 198, 1189—1191).—Each of the individual proteins of serum exerts a flocculating or protective action on a colloidal hydro-sol, the flocculating zone of the euglobulin being wider than that of the other proteins. The protective and dispersive power of whole serum results from the dispersive action of the albumins counterbalanced by the flocculating effect of the euglobulins. Sharp differences exist in the protective zones of normal and syphilitic sera.

P. G. M.

**Blood volume regulation and blood composition in experimental hydræmia.** I. **Regulation of blood volume.** D. B. CALVIN, A. H. SMITH, and L. B. MENDEL (Amer. J. Physiol., 1933, 105, 135—145).—Tests on female dogs receiving intravenous injections of 0.95% NaCl at the rate of 250 c.c. per min. until amounts equal to the calc. blood vol. are injected, show that there is a 16% increase in blood vol. after 45 min. and 5% after 235 min.

NUTR. ABS. (m)

**Maintenance of salt content of the fresh-water crab (*Potamobius*).** E. HUF (Pflüger's Arch., 1933, 232, 559—573).—The blood-Cl (I) of *P. astacus* kept for 2 weeks under almost natural conditions varies by  $\pm 10\%$ , averaging 6.5 mg. per g. of blood. The variations are less on longer keeping in fresh H<sub>2</sub>O, indicating adaptation. After 4—5 weeks there is an average fall of 6—7%. A diet of pond mussels does not suffice to maintain (I) at a level  $>$  in starving crabs, in which, however, the dry wt. of the blood is less. (I) of crabs kept in distilled H<sub>2</sub>O falls by 30—35% in 8 days and death ensues. Return to natural fresh H<sub>2</sub>O or dil. artificial sea-H<sub>2</sub>O (II) causes rapid recovery, although (I) remains low. (II) without either Ca or K, but of the usual osmotic pressure, suffices to maintain the mineral content of the blood at normal level.

NUTR. ABS. (m)

**Regulation of the salt content of the hæmolymph of some Crustacea and their adaptation to changes in salinity.** A. DRILHON-COURTOIS (Compt. rend., 1934, 198, 1079—1081).—The Na, K, and Ca content of the hæmolymph of *Carcinus manas* and *Potamobius astacus* increases, whilst that of the sol. phosphates and proteins decreases, with increasing salinity of the H<sub>2</sub>O in which the animals are placed.

R. S. C.

**Alkali reserve in the pigeon.** H. SCHARNKE (Compt. rend. Soc. Biol., 1933, 113, 1169—1170).—For normal adults on normal diet determinations average 53.2 c.c. of total CO<sub>2</sub> per 100 c.c. of plasma; for normal fasting adults they vary from 36.7 to 43.4. Similar figures are obtained for cock, duck, and goose. In birds made to inspire air rich in CO<sub>2</sub> for 60—70 min., the alkali reserve (I) rises from 43.3—50.2 to 49.2—74.8. These results are analogous to those obtained under like conditions in mammals; hence a similar mechanism for adjustment of (I) probably exists.

NUTR. ABS. (m)

**Acid-base balance of blood.** I. **Micro-technique for determination of the acid-base balance of blood.** N. W. SHOCK and A. B. HASTINGS. II. **Nomogram for calculation of acid-base data of blood.** A. B. HASTINGS and N. W. SHOCK. III. **Variation in acid-base balance of blood in normal individuals.** N. W. SHOCK and A. B. HASTINGS (J. Biol. Chem., 1934, 104, 565—573, 575—584, 585—600).—I. Apparatus and technique are described for the determination of percentage cells (I),  $p_{\text{H}}$  of the serum (II), and total CO<sub>2</sub> (III) on the same 0.1-c.c. sample of blood, the accuracy being  $\pm 1.0\%$  for (I),  $\pm 0.02 p_{\text{H}}$  for (II), and  $\pm 1.0\%$  for (III).

II. The construction and use of a nomogram for the solution of the various forms of the Henderson-Hasselbalch equation are described.

III. The normal variations in acid-base balance between males may be from  $p_{\text{H}}$  7.35 to 7.45; serum-HCO<sub>3</sub>' 23.0 to 30.0 millimol. per litre; CO<sub>2</sub>-tension of blood 40.0 to 50.0 mm. of Hg, and for females 7.37—7.47, 22.0—23.0, and 36.5—46.0, respectively. Normal individuals differ from one another and some show large daily variations. During the day there is no characteristic change in the acid-base balance of an individual.

C. G. A.

**Micro-determination of sodium in serum and plasma.** A. D. MARENZI and R. GERSCHMAN (Compt. rend. Soc. Biol., 1933, 114, 1212—1214).—The Na of the CCl<sub>3</sub>·CO<sub>2</sub>H filtrate of serum or plasma is pptd. as U Zn Na acetate. The washed ppt. is dissolved in AcOH, treated with K<sub>4</sub>Fe(CN)<sub>6</sub>, and compared colorimetrically with a standard solution of UO<sub>2</sub>(OAc)<sub>2</sub> (of known equivalence to Na) similarly treated.

NUTR. ABS. (b)

**Determination of chloride, potassium, and calcium in blood.** F. RAPPAPORT (Klin. Woch., 1933, 12, 1774—1775).—Modifications of Rusznyák's and the Kramer and Tisdall methods are described.

NUTR. ABS. (m)

**Micro-determination of calcium in blood-serum.** P. WENGER, C. CIMERMAN, and P. BORGEAUD (Mikrochem., 1934, 14, 141—158).—2 c.c. of serum are evaporated and ashed in a Pt capsule over a free flame, dissolved in HCl, and brought to  $p_{\text{H}}$  5 (Mc-red), CaC<sub>2</sub>O<sub>4</sub> is pptd. at 100°, dissolved in H<sub>2</sub>SO<sub>4</sub>, and titrated at 70° with 0.01N-KMnO<sub>4</sub>. J. S. A.

**Microcrystallographic determination of phosphates in blood-serum.** E. A. PRIBRAM (Arch. Path., 1933, 16, 520—521).—Equal quantities of serum are diluted with increasing amounts of 2.5% NaCl and Dowd's (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-MgSO<sub>4</sub> reagent is added. The last tube in which crystals are formed after 45 min. contains 3 mg. of P per 100 c.c. The method is sensitive to 0.5 mg. of P.

NUTR. ABS. (m)

**Inorganic phosphate contents of serum, fluoride-plasma, and native plasma.** H. L. WHITE and B. MONAGHAN (Proc. Soc. Exp. Biol. Med., 1933, 31, 1—5).—Colour production in the Benedict-This method for inorg. PO<sub>4</sub>''' is not affected by the use, as an anticoagulant, of NaF in a concn. of 0.3%, but is inhibited at 1%. The inorg. P content of serum is the same as that of native plasma.

NUTR. ABS. (m)

**Blood-bromine.** F. HOLTZ and C. ROGGENBAU (Klin. Woch., 1933, 12, 1410—1411; Chem. Zentr., 1933, ii, 2567).—Zondek's method for the micro-determination of blood-Br (A., 1933, 739) is untrustworthy.

H. J. E.

[Blood-bromine.] H. ZONDEK (Klin. Woch., 1933, 12, 1411—1412; Chem. Zentr., 1933, ii, 2567; cf. preceding abstract).—A reply, reaffirming the correctness of the method.

H. J. E.

[Blood-bromine.] L. PINCUSSEN (Klin. Woch., 1933, 12, 1412; Chem. Zentr., 1933, ii, 2567; cf. preceding abstracts).—Some unknown factor is responsible for the occasional failure of Zondek's method.

H. J. E.

**Determination of blood-bilirubin.** G. FERRARI (Diagnostica Tecn., 1933, 4, 696—716).—A crit. review of methods of determination in serum and other org. liquids of both total bilirubin (I), and of  $\text{CHCl}_3$ -sol. and  $\text{H}_2\text{O}$ -sol. (I) separately.

R. N. C.

**Creatine and creatinine metabolism. I. Creatinine determination in urine and blood.** H. LIEB and M. K. ZACHERL (Z. physiol. Chem., 1934, 223, 169—179).—Creatinine is determined following Folin's method, but using the Pulfrich photometer in place of the colorimeter.

J. H. B.

**Micro-determination of urea in blood.** P. WENGER, C. CIMMERMAN, and A. MAULBETSCH (Mikrochem., 1934, 14, 132—140).—Minor modifications of the methods of Nicloux and Welter (gravimetric) (A., 1922, ii, 170) and of Allen and Luck (volumetric) (A., 1929, 962) are described.

J. S. A.

**Blood-chemistry of pigs. I. Blood changes following ingestion of glucose.** D. F. EVELETH (J. Biol. Chem., 1934, 104, 559—563).—Ingestion of glucose by pigs evokes an increase in  $\text{NH}_2$ -acid-N, urea-N, and serum-Ca and a fall in inorg. P, the peaks of the curves occurring approx. 30 min. after the peak of the blood-sugar curve which occurs 30—60 min. after administration.

C. G. A.

**Influence of the carotid sinus on the blood-sugar.** F. BRAUCH (Arch. exp. Path. Pharm., 1934, 175, 104—112).—"Pernocton" narcosis in rabbits is not accompanied by a rise in blood-sugar (I) nor by a change in the hyperglycaemic response to adrenaline or urethane. During and after elimination of the influence of the carotid sinus (by clamping the common carotids), (I) is unchanged, a result not influenced by section of the adrenal nerves. Section of the two depressor nerves produces an immediate rise in (I) lasting for several hr. No correlation appears to exist between the pressor-receptor centres and carbohydrate metabolism.

F. O. H.

**Determination of blood-sugar by the picric acid reaction.** E. KAUFMANN (Z. ges. exp. Med., 1933, 92, 480—489).—Improvements are suggested so that the method can be easily used to give approx. results where there are no adequate laboratory facilities.

NUTR. ABS. (m)

**Effect of anticoagulants and antiglycolitics on determination of blood-sugar.** R. C. FORMIGUERA and E. BIETO (Compt. rend. Soc. Biol., 1933, 114, 116—118).—The addition of 0.2% of NaF lowers

the apparent blood-sugar level by 6.8 mg. per 100 c.c., whilst the addition of 0.2% of  $\text{Na}_2\text{C}_2\text{O}_4$  causes an apparent decrease of 7.9 mg.

NUTR. ABS. (m)

**Determination of fibrinogen in blood.** G. BOEHM (Diagnostica Tecn., 1933, 4, 683—687).—A syringe rinsed with 20% aq. K oxalate was used to draw blood. The greatest dilution of the plasma which when treated with a drop of 10%  $\text{CaCl}_2$  solution coagulated in  $\frac{1}{2}$ —1 hr. was considered to be the fibrinogen unit. Normal human blood contained 40—60 units per c.c.

R. N. C.

**Determination of phosphatides in blood.** B. NORBERG (Biochem. Z., 1934, 269, 1—3; cf. A., 1933, 1183).—Phosphatide (I)-P is colorimetrically determined in 0.2—0.5 c.c. of blood after dilution with 3 c.c. of  $\text{H}_2\text{O}$ , pptn. of (I) with 3.5 c.c. of 10% aq.  $\text{CCl}_3\text{-CO}_2\text{H}$  (II), extraction of the ppt. with  $\text{EtOH-CHCl}_3$  (3 : 1) after washing with 1—2% aq. (II), evaporation to dryness of the extract, and treatment of the residue with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  at 250°.

W. McC.

**Chemistry of the lipin involved in the coagulation of blood.** A. FISCHER and E. HECHT (Biochem. Z., 1934, 269, 115—132).—The coagulating power (I) of kephalin (II) decreases as its purity increases. The active substance (III) which accompanies (II) is optically inactive, non-sp., thermostable, sol. in  $\text{EtOH}$ , and probably complex. Increase in the activity of (III) is accompanied by parallel increase in power to absorb ultra-violet light. Lipins (lecithin, cerebroside), cholesterol, and simple degradation products of these (glycerophosphoric acid, triolein, stearic and oleic acids, etc.) have no (I).

W. McC.

**Hæmolysis and the solar spectrum.** W. W. LEPESCHKIN and G. E. DAVIS (Protoplasma, 1933, 20, 189—194).—Decreased resistance and hæmolysis of corpuscles produced by light is due to a chemical change in the hæmoglobin.

A. G. P.

**Nature and physical properties of an antibody; electrophoresis of hæmolytic sera.** P. GIRARD and M. LOURAU (Compt. rend., 1934, 198, 1081—1083).—Hæmolysin undergoes cataphoresis; the velocity of movement is much slower than that of proteins or  $\text{Cl}^-$ . It behaves as an ion with isoelectric point at  $p_{\text{H}}$  6.2.

R. S. C.

**Reducing substances of living tissue.** R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1934, 223, 136—143).—Jensen sarcoma of the rat contains vitamin-C (I) (cf. Boyland, A., 1933, 851). In the separation of glutathione (II) from other reducing substances with Ag lactate, a yellow pigment, probably vitamin- $B_2$  (III), is pptd. Liver-tissue probably contains, besides (I), (II), and (III), a fourth reducing substance, mainly in the oxidised condition. (II) is present in living tissue almost entirely in the reduced form. Activation of enzymes depends not so much on the presence of reduced (II) as on that of a heavy metal complex.

J. H. B.

**Reducing substance in brain tissue.** F. G. YOUNG and M. MITOLO (Nature, 1934, 133, 572).—Brains of the mouse, rat, guinea-pig, and ox contain a substance (I) which reduces  $\text{AgNO}_3$  in neutral or  $\text{AcOH}$  solution, but not in cold aq.  $\text{NH}_3$  solution.

Extracts from brain tissue containing (I) reduce phenol-2 : 6-dichloroindophenol under the conditions laid down for determining ascorbic acid (II) in tissues. The chemical and physiological properties of (I) are different from those of (II), and thus the determination of (II) by the indophenol titration method is untrustworthy. The activity of solutions of (I) is destroyed in acid and alkaline solutions. A cryst. semicarbazone, m.p. 251—252° (uncorr.), has been isolated from active extracts, but this may or may not be a derivative of (I). L. S. T.

**Asteric acid, a carotenoid acid from starfish.** H. VON EULER and H. HELLSTRÖM (Z. physiol. Chem., 1934, 223, 89—97).—The pigments from various species of starfish were examined spectroscopically. The H<sub>2</sub>O-sol. blue pigment of *Asterias rubens* (C 55·2, H 7·75, N 11·1, S 2·3%) contains a carotenoid *asteric acid*, C<sub>28</sub>H<sub>40</sub>O<sub>4</sub>, m.p. 185°. J. H. B.

**Occurrence of flavins in animal tissues.** H. VON EULER and E. ADLER (Z. physiol. Chem., 1934, 223, 105—112).—Examination of a large no. of animal organs and tissues shows that those richest in vitamin-B<sub>2</sub>, viz., liver and kidney, are also richest in flavin (I). The retina of fish contains about the same amount of (I) in dialysable form. Corpus luteum contains, in addition to (I), a blue fluorescent substance, which may be a derivative of (I). J. H. B.

**Lyochromes: a new group of animal pigments.** P. ELLINGER and W. KOSCHARA (Nature, 1934, 133, 553—556).—A summary. L. S. T.

**Lyochrome in the pigmented epithelium of the eye.** H. VON EULER and E. ADLER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 21, 4 pp.).—Extraction with COMe<sub>2</sub> of the pigmented epithelium (I), but not of the retina (II), of eyes (III) of oxen yields a green-fluorescing solution which on evaporation and treatment with H<sub>2</sub>O and Et<sub>2</sub>O yields an aq. layer containing lyochrome (IV) and an Et<sub>2</sub>O layer containing carotene. Aq. alum used for fixation of (III) also contains (IV), which can be separated by acidification with HCl, adsorption on fuller's earth, and elution with H<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N-MeOH. Fish-(III) contain varying amounts of (IV), the purified (IV) of shellfish (III) having an absorption max. at 447 mμ corresponding with lactoflavin (this vol., 227). The irises of pike's (III) yield an unstable COMe<sub>2</sub>-sol. colouring matter which, in light petroleum, has absorption max. at 470 and 441 mμ; after keeping in the dark for 3 weeks the max. are at 493 and 457 mμ. F. O. H.

**Visual purple.** H. VON EULER and E. ADLER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 20, 6 pp.).—Extraction of ox-retina (I) (hardened with MgSO<sub>4</sub>, alum, or CH<sub>2</sub>O) with 2—3% aq. digitonin yields a clear violet solution from which digitonin is removed by dialysis. Heating yields a dark yellow solution from which 95% EtOH (1 vol.) ppt. the colouring matter. Extraction of the dry residue with MeOH gives a yellow solution containing a lyochrome and having absorption max. at 490 and 460 mμ. The aq. Na cholate or AcOH extract of visual purple from fish-eyes gives a ppt. with cholic acid. COMe<sub>2</sub>-followed by Et<sub>2</sub>O-extraction of unhardened (I)

yields carotene (II), 20 (I) yielding 95×10<sup>-6</sup> g. and twenty pigmented epithelial layers 240×10<sup>-6</sup> g. Vitamin-A also appears to be present. (II) occurs in the retina of a few fishes. F. O. H.

**Free and bound cholesterol content of different parts of the brain of normal and polyneuritic animals.** H. G. K. WESTENBRINK (Arch. Néerland. Physiol., 1934, 19, 122—131).—The bound is much < the free cholesterol (I) in all parts of the brain. The (I) contents decrease in the order medulla oblongata, mid-brain, cerebellum, and cerebrum in both rats and pigeons. There is no difference in the (I) contents of the brains of normal and polyneuritic animals. C. G. A.

**Details of muscle structure revealed by salt extraction.** H. N. BAKER, H. C. MCPHEE, and P. E. HOWE (J. Agric. Res., 1933, 47, 1009—1014).—Ox muscle tissue is extracted for 1·5 hr. at 15° with either 1·25M-NaCl or a 0·225M-mixture of KH<sub>2</sub>PO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub> (p<sub>H</sub> 7·0—7·4). This removes sol. proteins without materially damaging the remaining structures. The fibrils are completely removed by NaCl-extraction, the fibres appearing as short tubes. Characteristic swelling of the fibre membrane occurs. P. G. M.

**Are oxalylmethylguanidine (creatone), methylguanidine, and oxalic acid normal constituents of muscular tissue?** T. MANN (Biochem. Z., 1934, 268, 339—344).—The oxalylmethylguanidine (I) isolated from muscle by Gulewitsch (A., 1933, 735) is an artefact arising from creatinine during manipulation, and since (I) readily gives methylguanidine and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> on hydrolysis, it appears probable that these also are artefacts. P. W. C.

**Linking of purine bases in the unfertilised sea-urchin's egg.** G. SCHMIDT (Z. physiol. Chem., 1934, 223, 81—88).—The unfertilised ripe egg has high total purine (I), but only traces of acid-sol. (I). All (I) compounds are extracted by 0·03N-NH<sub>3</sub>. About 70% of the total (I) is contained in the proteins pptd. by AcOH. The nucleic acid components contain the thymonucleic acid group. J. H. B.

**Osmotic pressures in the hen's egg.** E. J. BALDES (Proc. Roy. Soc., 1934, B, 114, 436—440).—There is a difference of osmotic pressure (I) between the yolk (II) and the white in the hen's egg and a gradient of (I) in (II). There is very little difference in (I) across the vitelline membrane. H. G. R.

**Vapour-pressure isotherm of muscle.** J. BROOKS (Proc. Roy. Soc., 1934, B, 114, 258—272).—The vals. obtained for bound H<sub>2</sub>O in muscle are of similar magnitude to those for protein and H<sub>2</sub>O only. In rigor, probably only a small fraction of H<sub>2</sub>O is bound. Drying over P<sub>2</sub>O<sub>5</sub> does not produce any change in the H<sub>2</sub>O-binding capacity. H. G. R.

**Coagulation of muscle-plasma. II. Solubility of myosin.** E. C. SMITH (Proc. Roy. Soc., 1934, B, 114, 494—505).—Not more than 10% of the myosin (I) in rabbit muscle is in the form of a sol. Coagulation of muscle-plasma is due to the pptn. of (I) from a sol formed by previous addition of salt.

Data for the effect of salt concn.,  $p_H$ , and total protein concn. on the solubility of (I) in KCl are given.

C. G. A.

**Distribution of calcium and magnesium in the organs of the dog.** BARTHÉLEMY and R. WOLFF (Compt. rend., 1934, 198, 1370—1372).—The Ca and Mg content varies, but they are present in definite proportions which are characteristic for each organ. The total mol. concn. of Ca and Mg (1.08—1.72) is approx. const. in kidney, lungs, pancreas, spleen, and muscle.

H. G. R.

**Distribution of inorganic salts in the tissues of birds. III.** A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1934, 268, 369—371).—Two tables give the  $H_2O$ , P, Ca, Mg, and Cl contents of certain tissues of the hen and of *Perdix coturnix*.

P. W. C.

**Factors affecting determination of the ash content of the tibiae of chicks.** R. M. BETHKE and P. R. RECORD (Poultry Sci., 1934, 13, 29—33).—Differences in the technique for determining ash contents are examined. The preliminary extraction of the bones with 95% EtOH is as effective as with EtOH followed by  $Et_2O$ . Removal of proximal cartilage causes a significant increase in the ash val. recorded. Extracted bones absorb sufficient  $H_2O$  to cause a significant change in results. Ash vals. are preferably calc. on a fat-free,  $H_2O$ -free basis.

A. G. P.

**Nature of "preformed water."** J. P. PETERS and P. H. LAVIETIES (J. Clin. Invest., 1933, 12, 695—712).—There is little evidence that  $H_2O$  is chemically or physically held by protein, fat, or carbohydrate in the body, but the proportion of  $H_2O$  to solutes tends to remain const. within wide limits. There is little support for the hypothesis that the proportion of protein or protein+glycogen to  $H_2O$  in the cells remains const. There appears to be a physiological distinction between intracellular (I) and extracellular (II)  $H_2O$ , and separate movements of the two seem to occur. Since "preformed  $H_2O$ " must be regarded as (I), which cannot be distinguished from (II) by purely metabolic methods, there is no valid reason for retaining it in Newburgh and Johnston's calculations.

NUTR. ABS. (m)

**Storage in the kidney cortex.** R. KELLER (Biochem. Z., 1934, 268, 336—338).—The cortex stores pigmented colloids, sugar, urea, K, and Mg salts, and  $PO_4'''$ .

P. W. C.

**State of potassium in the central nervous system and its dependence on the degree of stimulation.** E. PICHLER (Arch. exp. Path. Pharm., 1934, 175, 85—91).—Extraction of the brain and spinal cord of normal (or strychninised) frogs by 96% EtOH and 0.01N-HCl in 96% EtOH yields, respectively, 52.3 and 87.4% of the total K, whilst with frogs narcotised by urethane, respectively, 67.9 and 98.5% are extracted. With normal frogs, abs. EtOH or  $Et_2O$  extracts from the dried tissue an average of 17.2%. The nature of the K fractions sol. and insol. in lipin-solvents and their variations with narcotisation are discussed.

F. O. H.

**Iodine content of the thyroids and other organs of Argentine cattle.** G. DUFF (Folia biol., 1933, 1,

131—132).—The thyroids contained 357—410 mg. I per 100 g. (dry); vals. are independent of age or sex, but are lower in summer than in winter. Other vals are: spleen 10.3, adrenals 5.5, testicles 3.8, ovaries 1.2, pancreas 1.0, placenta 0.7, mammary glands 0.2, liver 0.2, anterior pituitary lobe (I) 0.4—0.6, posterior (I) 0.16—0.34.

CH. ABS.

**Diffuse vital staining of certain flagellates and the chemical affinity of the cytoplasm and its constituents.** P. GAVAUDAN (Compt. rend., 1934, 198, 848—850).—Vital staining by cresol-blue of the cytoplasm of a no. of flagellates is described and the chemical mechanism of the process discussed.

A. G. P.

**Relationship between chloride content and blood-cerebrospinal fluid-bromide ratio.** W. MALAMUND, B. M. MULLINS, and J. R. BROWN (Proc. Soc. Exp. Biol. Med., 1933, 30, 1084—1087).—Br added to  $H_2O$ , blood-serum, or cerebrospinal fluid from which Cl had been removed was recovered quantitatively. Recovery of 100 mg. of Br' in presence of 0.2, 0.3, and 0.6% NaCl was, respectively, 86.5, 78.0, and 73.7 mg. per 100 c.c.

CH. ABS.

**Effect of gastric secretion on circulation rate, oxygen utilisation, and sugar and chloride content of arterial and venous blood.** D. F. OKUNEV and M. S. SOLNZEVA-RJASANOVA (Arch. Verdauungs-Krankh., 1933, 54, 78—96).—During gastric secretion (I) in man the circulation rate, as measured by the arterial-venous difference (II) in  $O_2$  concn., is increased, and is partly related to the acidity of the gastric juice. The Boas-Ewald meal produced a general fall in the circulating sugar, EtOH a rise, changes which appeared to be connected with tissue metabolism and insular activity. The resting Cl' (II) in the normal was on the average 5.5% in favour of arterial blood (III); in anacidity 3.4, and in hyperacidity, 7.1%. (I) caused the Cl' in the (III) to be increased, in venous blood diminished, so that these differences at the height of secretion were 14.2, 7.2, and 19%, respectively.

NUTR. ABS. (b)

**Occurrence of glycogen and fat in liquor folliculi and uterine secretion in *Loris lydekkerianus*,** Cabr. C. R. N. RAO (J. Mysore Univ., 1932, 6, 140—170).

**Constants of normal human milk.** M. TALENTI (Ann. Ig., 1933, 43, 876—882).—Six samples of normal human milk contained: total solids, 10.8—15.8, ash 0.24—0.38, fat 3.0—4.7, lactose 4.6—7.8, protein 2.2—3.0%. The ratios fat:lactose, fat:protein, and fat:ash were approx. const. In milk from pathological cases, the vals. varied considerably.

NUTR. ABS. (m)

**Caseinogen.** M. RONSE (Compt. rend. Soc. Biol., 1933, 114, 1380—1381).—By the reverse of Demanez's technique the author has confirmed his findings as to the specificity of the caseinogen (I) of human milk. Benzoylated (I) behaves in the same way as (I) itself. (I) of milks is distinguished from the proteins of serum by its stability towards physical and chemical agents.

NUTR. ABS. (m)

**Phosphopeptone obtained in the early stages of digestion of caseinogen by activated tryptase.**

P. GRABAR (Compt. rend. Soc. Biol., 1933, 114, 13—15).—The substance gives a ppt. with  $\text{CCl}_3\text{CO}_2\text{H}$ , picric acid, and Cu acetate, but not with phosphotungstic acid. It contains traces of tyrosine, but no tryptophan. Only 1 in 14 of its N atoms is free  $\text{NH}_2\text{-N}$ .  
NUTR. ABS. (m)

$\text{H}_2\text{O}$  content of the water of milk. H. ERLMAYER and H. GARTNER (Helv. Chim. Acta, 1934, 17, 334).—By improving the method previously employed (this vol., 262) 8 litres of pure  $\text{H}_2\text{O}$  gave 20 c.c. of  $d$  1.00087.  $\text{H}_2\text{O}$  from cows' milk under similar treatment gave  $\text{H}_2\text{O}$  of  $d$  1.00083, thus showing, within the limits of experimental error, that no change in the  $\text{H}_2\text{O}$  content of milk had taken place in the animal organism.  
M. S. B.

Effect of different planes of protein intake on milk productions. II. Further comparisons of 16, 20, and 24% mixtures. E. S. HARRISON, E. S. SAVAGE, and S. H. WORK (Cornell Univ. Agric. Exp. Sta. Bull., 1933, No. 578, 12 pp.).—No significant improvement in milk yield was produced by raising the protein level of the ration to > 16%.  
A. G. P.

Effect of feeding on the fat content of cow's milk. E. J. SHEEHY (J. Dept. Agric. Irish Free State, 1933, 32, 18—29).—Short-period feeding experiments show that, apart from cod-liver oil, vegetable, animal, or fish oils or oilcakes have no sp. quant. effects on the % of fat in milk. The amount of fat necessary in a cow's ration is small. Introduction of sugar-beet pulp, mangolds, beet, treacle, wet grains, rice meal, or fresh grass in the ration does not affect the % of fat, if the milk yield is unaltered; but if it alters there may be a temporary lag in the total fat. Alteration in the plane of nutrition of the cow does not alter the % of fat. Feeding of separated or whole milk (I) powder does not influence the % of fat. The possible effect of (I) or cream in raising the fat is to be attributed to some substance or substances rather than to the fat *per se*.  
NUTR. ABS. (m)

Yacarov, a secretion of glands of alligators.—See this vol., 509.

Secretion of phosphorus and sulphur in the sweat. G. A. TALBERT, F. STINCHFIELD, and H. STAFF (Amer. J. Physiol., 1933, 105, Proc. 94).—Sweat contains appreciable, although variable, amounts of inorg. and org. P and S, S being generally in excess of P. The amount of P secreted depends on the P content of the diet.  
NUTR. ABS. (m)

Blood and urine of colts. W. W. DEMOCK and D. J. HEALY (J. Amer. Vet. Med. Assoc., 1933, 36, 806—809).—Blood-serum of normal and over-fed fillies contained (mg. per 100 c.c.), respectively: Ca 12.0, 12.5; K 15.4, 18.5; P 4.9, 5.0; non-protein-N 28.1, 19.9;  $\text{SO}_4\text{-S}$  13.4, 10.0; sugar 106, 123. Urine from the same animals had  $d$  1034, 1038,  $p_{\text{H}}$  7.4, 6.6, and contained albumin 0, 0;  $\text{NH}_2$  50.0, 100.0; Ca 128.5, 184.9;  $\text{SO}_4\text{-S}$  81.9, 63.1.  
CH. ABS.

Determination of albumin in urine. D. GANASINI (Arch. Ist. Biochim. Ital., 1934, 6, 3—12).—Albumin (I) in urine (II) is determined rapidly by observing at the same temp. the sp. gr. of (II) both

before and after coagulation of the (I) by heat, the sp. gr. of coagulated (I) being taken as 1.315 (const., experimental val.).  
R. N. C.

Micro-determination of uric acid in urine. P. WENGER, C. CEMERMAN, and A. MAULBETSCH (Mikrochem., 1934, 14, 129—131).—Uric acid in 2 c.c. of urine is pptd. as  $\text{NH}_4$  urate (I) by addition of aq.  $\text{NH}_3 + \text{NH}_4\text{Cl}$ . (I) is redissolved in AcOH, the solution made alkaline with borax, and titrated with 0.01N-I.  
J. S. A.

Influence of parenteral administration of amino-acids, sodium chloride, and glucose on the urinary quotients. A. ROEHDER (Biochem. Z., 1934, 268, 265—271).—A single subcutaneous injection into male white rats of the  $\text{NH}_2$ -acid mixture obtained by hydrolysis of proteins (particularly vegetable) or of pure glutamic acid causes on the day of injection a considerable increase of urinary C:N, vacate-O:N, and vacate-O:C, the extent of the increase diminishing on repeating the injection daily. A single injection of 15% NaCl also does, but of 7—16% glucose does not, affect the quotient.  
P. W. C.

Application of Benedict's solution to the micro-detection of sugar in urine and other liquids. H. TAUBER (Mikrochem., 1934, 14, 169—170).—0.1% of glucose may be detected in a drop of urine by Benedict's solution (I) (A., 1909, ii, 442). Urates, if present, also give a turbidity. Bioses also reduce (I).  
J. S. A.

Acetone and acetoacetic acid in urine. P. FISCHER (Pharm. Zentr., 1934, 75, 189—191).—Lange's nitroprusside test (I) is a sensitive one for  $\text{CH}_2\text{AcCO}_2\text{H}$ . If (I) is negative,  $\text{COME}_2$  may be recognised by the  $\text{CHI}_3$  reaction.  
R. K. C.

Excretion of inorganic phosphate by the aglomerular kidney. E. K. MARSHALL, jun., and A. L. GRAFFLIN (Proc. Soc. Exp. Biol. Med., 1933, 31, 44—46).—Urine of the angler fish (*Lophius piscatorius*) contained 0.0007—0.045 mol. of inorg.  $\text{PO}_4$  per litre; the plasma contained 0.0042—0.0077 mol. per litre. Intramuscularly injected inorg.  $\text{PO}_4$  was not excreted in the urine.  
CH. ABS.

Dependence of acidity ratio of urine on diet. E. HELMS (Z. ges. exp. Med., 1933, 89, 631—640).—The acidity ratio (I) of the urine represents the % ratio of acid  $\text{PO}_4$  to total  $\text{PO}_4$ . After a meal (I) falls, reaching the min. in about 4 hr. The fall is greatest after the chief meal of the day, and if this is taken < 4 hr. after the preceding meal, the fall continues. When the diet is vegetarian the acidity curve is shifted towards the alkaline side, but is otherwise similar to that found on mixed diet.  
NUTR. ABS. (m)

Nitrogenous compounds of the excrement from the caecum of the fowl. K. SUZUKI and A. KAWABATA (J. Agric. Chem. Soc. Japan, 1933, 9, 1095—1103).—The excrement contained  $\text{H}_2\text{O}$  78.80, crude protein 9.86, pure protein 6.25, crude fat 1.36, crude fibre 0.79, ash 3.83, sol. N-free matter 5.36, and  $\text{NH}_2\text{-N}$  0.099%. The protein is > in ordinary faeces. The distribution of N in the dry material was: total N 6.584, protein-N 5.225,  $\text{H}_2\text{O}$ -sol. N 2.153, N pptd. by  $\text{Pb(OAc)}_2$  0.648, N pptd. by



phosphotungstic acid 0.840%. Tyrosine and valine, but not  $(\text{NH}_2)_2$ -acids, were isolated. CH. ABS.

**Mechanism of sodium depletion in Addison's disease.** R. F. LOEB, D. W. ATCHLEY, E. B. GUTMAN, and R. JILLSON (Proc. Soc. Exp. Biol. Med., 1933, 31, 130—133).—The loss of Na is not dependent on the excretion of unusual quantities of acid as determined by the excretion of  $\text{NH}_3$  and titratable acid. The Na regulatory mechanism is disturbed. The clinical condition parallels the blood-Na and depends on the amount of Na ingested. CH. ABS.

**Non-protein-iron of the blood.** J. F. McINTOSH (J. Clin. Invest., 1933, 12, 967).—The non-protein-Fe (I) of whole blood, determined on the  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  filtrate, averages 1.02 mg. per 100 c.c. in health. In various anæmias it varies directly with the severity of the anæmia. The greater part of (I) is in the red cells. NUTR. ABS. (m)

**Tissue metabolism in secondary anæmia.** H. H. RIECKER (J. Clin. Invest., 1933, 12, 986—987).—Tissues from anæmic rabbits use only half as much  $\text{O}_2$  [determined by mixing with defibrinated rabbits' blood of known  $\text{O}_2$  content (I) and measuring (I) after 1 hr.] as do those from normal rabbits. Anæmia affects all the tissues, probably because of Fe starvation. NUTR. ABS. (m)

**Value of cod-liver oil in the treatment of anæmia.** A. D. HOLMES, M. G. PIGOTT, and L. P. BOWSER (New Engl. J. Med., 1933, 209, 839—842).—Cod-liver oil (I) alone does not regenerate blood in anæmic rats. Rats given 0.5 mg. Fe and 0.05 mg. Cu daily with (I) show more rapid blood-regeneration than rats receiving Fe and Cu but not (I). However, when the Fe administered is 1.5, 2.5, or 3 mg. the rate of hæmoglobin increase is normal. Similar results were obtained with peanut oil free from vitamin-A. CH. ABS.

**Anti-anæmic principle in stomach tissue.** J. F. WILKINSON (Proc. Roy. Soc. Med., 1933, 26, 1341—1350).—Carnivore stomach (silver fox) is active, but ruminant stomach (ox and sheep) is inactive. The active principle (I) is destroyed by temp.  $> 45^\circ$ , by autolysis, and by digestion with pepsin (II) or trypsin. Press juice of pig's stomach (III) is active in doses of 150 c.c. daily. EtOH treatment yields a ppt. which contains all the (I) and (II). The ppt. is efficient in daily doses of 5 g., equiv. to 50 g. of fresh (III). Further fractionation by isoelectric pptn. separates (II) from (I). The active fraction has a high P content, and is practically free from Cu, Mn, and Fe. NUTR. ABS. (m)

**Muscular dystrophy and atrophy. Clinical and biochemical results following oral administration of amino-acids.** C. J. TRIPOLI and H. H. BEARD (Arch. Int. Med., 1934, 53, 435—452).—The administration of glycine or glutamic acid in cases of muscular dystrophy or atrophy results in an increase in the excretion of creatine and, to a smaller extent, of creatinine in the urine. W. O. K.

**Mineral metabolism in bursitis calcarea.** T. AOKI (Tôhoku J. Exp. Med., 1933, 21, 556—591).—Ca, Mg, and P metabolism, urinary uric acid excre-

tion, serum-proteins and blood viscosity, and the renal function were normal. NUTR. ABS.

**Hormonal control of tumour growth and metabolism.** M. REISS, H. DRUCKREY, and A. HOCHWALD (Z. ges. exp. Med., 1933, 90, 408—420, and Klin. Woch., 1933, 12, 1049—1050).—Removal of the pituitary gland from rats in which Jensen sarcoma is growing rapidly causes an immediate cessation of growth (I) and rapid appearance of degeneration of the tumour accompanied by reduction of  $\text{O}_2$  consumption (II). Administration of the pituitary growth hormone leads to reappearance of (I) with increase in (II). The sexual hormone of the pituitary favours (I) independently of the presence of the sex glands which seem to hinder (I) independently of the pituitary growth factor. Regressive changes in the tumour, however produced, are always accompanied by reduction in (II). The old view of the autonomous growth of tumour tissue seems to be erroneous. NUTR. ABS. (m)

**Effect of the ingestion of aluminium on cancer.** G. BERTRAND and P. SERBESCU (Compt. rend., 1934, 198, 1100—1103).—Ingestion of 20 mg. of Al per kg. body-wt. per day in the rabbit for 6 months has no harmful effect on the alimentary canal. It does not increase the incidence of cancer due to the application of a carcinogenic tar. P. G. M.

**Effect of a dinitrophenol on tumour metabolism.** E. C. DODDS and G. D. GREVILLE (Lancet, 1934, 226, 398—399).—Respiration of Jensen rat sarcoma is increased by  $10^{-5}M$ -4:6-dinitro-*o*-cresol in the presence of glucose, lactate, and pyruvate, but not in the absence of added substrate. Simultaneously, the aerobic glycolysis is increased. L. S. T.

**Balance of phosphatase in the carcinomatous organism.** F. KÖHLER (Z. physiol. Chem., 1934, 223, 98—104).—Considerable differences are shown in the activation of phosphatase (I) by  $\text{MgCl}_2$  in the organs of normal (II) and carcinomatous rats (III). The auto-activated (I) of tumour, muscle (IV), and kidney (V) decreases as the tumour ages, although (V) shows increased (I)-action in (III). (V)-(I) of immune Wistar rats is much  $>$  the normal val. The (I) of (IV) and (V) of (II) are fully active, but in (V) of (III) only 30% active, although the tumour-(I) is highly active. In the blood, which shows increased (I) in (III), the auto-activity is doubled. J. H. B.

**Gelatinisation of serum by organic acids.** W. KORACZEWSKI (Compt. rend., 1934, 198, 1271—1273).—With lactic acid, or, more slowly, AcOH or  $\text{HCO}_2\text{H}$ , serum sets to a transparent gel, which only slowly aggregates. In cancer and, possibly, syphilis, the gelatinisation is accelerated. R. S. C.

**Prevention of tar cancer by barium salts.** J. MAISIN and J. DETROUX (Compt. rend. Soc. Biol., 1933, 113, 926—928).—Very small repeated doses of Ba saccharate in saccharic acid reduce the incidence of tar tumours in mice. NUTR. ABS. (m)

**Importance of the anion and of dosage in the prevention of tar cancer by barium salts.** J. DETROUX (Compt. rend. Soc. Biol., 1933, 113, 928—930).—The effect of Ba salts on the growth (I) of tar

tumours in mice depends partly on the anion. Small doses of  $\text{BaCl}_2$  retard, larger doses accelerate (I), and large doses of Ba gluconate inhibit (I).

NUTR. ABS. (m)

**Chemical composition of saliva and blood-serum of children in relation to dental caries.** R. B. HUBBELL (Amer. J. Physiol., 1933, 105, 436—442).—Children (I) with active caries show a moderate or high *B. acidophilus* count, whilst those (II) free from caries are negative or nearly so. The chemistry of the blood and of the saliva shows no great variation in either group except as regards  $\text{CO}_2$  capacity (III) and titratable alkalinity (IV) of the saliva. In (I) (III) is 44% and (IV) 24% < in (II).

NUTR. ABS. (m)

**Etiology and pathogenesis of darmous (spontaneous fluorosis of phosphate zones).** H. VELU (Bull. Soc. Path. exot., 1933, 26, 616—621).—The favourable effect of  $\text{Ca}_3(\text{PO}_4)_2$  on sheep receiving rations containing  $\text{CaF}_2$  indicates that a lack of mineral balance may be a contributory cause of darmous, and that the severity of the F intoxication may depend on the  $\text{PO}_4$  content of the ration. F is regarded as interfering with fixation of Ca to a degree depending on the form in which it is present. Although both plants and bone powder contain as much F as certain waters and natural phosphates, they are not toxic. Apparently F loses its toxicity when fixed by the vegetable or animal organism.

NUTR. ABS.

**Diabetes mellitus and pregnancy.** E. SKIPPER (Quart. J. Med., 1933, 2, 353—380).—Insulin exerts a beneficial effect on the fertility of diabetics (I), lowering the maternal mortality (II) during pregnancy (III) and the puerperium (IV), but leading to no reduction in foetal (II). (I) usually lose tolerance during the later months of (III), and regain it after childbirth, so that hypoglycæmia is common during (IV). With adequate treatment (III) is not harmful to (I). There is a marked tendency to ketosis in pregnant (I).

NUTR. ABS. (m)

**Relationship of excretion of water, anions, and cations to glycosuria in diabetes mellitus.** H. KEILHACK (Z. ges. exp. Med., 1933, 89, 159—172).—In diabetes the vol. and sp. gr. of single specimens of urine are related to the amount and concn. of the glucose, and in about half the specimens examined the output of Cl,  $\text{SO}_4$ , and  $\text{P}_2\text{O}_5$  is in inverse proportion to the glycosuria (I), no such relationship being found with Na, K, and Ca. No difference is noted relative to the severity of the diabetes. In renal (I) no similar correlation is observed.

NUTR. ABS. (m)

**Insulin ketonuria in children.** N. SICK and M. WEICHSEL (Monatsschr. Kinderheilk., 1933, 58, 383—387).—Healthy, normally fed children, given 15 units of insulin in the morning, fasting, show no  $\text{COMe}_2$  in the urine 5 hr. after the injection. Diabetic children given twice that dose with their usual food, or the same dose fasting, if the urine is sugar-free, show no  $\text{COMe}_2$  in 5 hr.

NUTR. ABS. (m)

**Mineral threshold in young epileptics.** R. ENGEL, I. MCQUARRIE, and M. ZIEGLER (Arch. exp. Path. Pharm., 1934, 174, 555—574; cf. A., 1933,

1337).—The balance of  $\text{H}_2\text{O}$ , Cl, Na, K, Ca, Mg, N, S, and P was determined in young epileptics under normal conditions and following treatment with luminal,  $\text{NH}_4\text{Br}$ , pituitary preps., etc., and the results were correlated with the incidence of epileptic convulsions.

F. O. H.

**Alimentary lipæmia of man in fever.** W. RAAB (Z. ges. exp. Med., 1933, 89, 616—621).—The blood-fat (petrol extract) curve after 100 c.c. of olive oil is flatter in patients with fever. This is attributed to increased storage of circulating fat in the liver, an effect similar to that of lipoitrin which apparently takes part in the chemical regulation of temp.

NUTR. ABS. (m)

**Urinary excretion of iodine.** G. M. CURTIS and F. J. PHILLIPS (J. Clin. Invest., 1933, 12, 963).—The urinary excretion (I) of I by patients with non-toxic goitre is not > that of those without thyroid disease. Administration of I to subjects with diffuse hyperplastic goitre is followed by slow (I), which rises parallel with clinical improvement. During the early stage of menstruation blood-I and (I) of I increase.

NUTR. ABS. (m)

**Pathology of toxicosis in infants. Acid-base balance in parenteral infections.** J. CSAPO and E. KERPEL-FRONIUS (Monatsschr. Kinderheilk., 1933, 59, 18—23).—Acidosis in all cases is due to increase in org. acids. Increases in P and Cl are not observed.  $\text{HCO}_3'$  of blood is much reduced.

NUTR. ABS. (m)

**Blood-brain barrier in infectious diseases; its permeability to toxins in relation to their electrical charges.** U. FRIEDEMANN and A. ELKELES (Lancet, 1934, 226, 719—724).—Lambdysentery toxin and cobra venom pass, but toxins of tetanus, diphtheria, and botulinus do not pass, the selective mechanism which regulates the exchange of substances between blood and brain.

L. S. T.

**Composition of pus.** R. VARA-LOPEZ and K. THORBECK (Zentr. inn. Med., 1933, 54, 913—917; Chem. Zentr., 1933, ii, 3151).—The  $p_n$  and sugar, K, Ca, Mg, albumin, and globulin content of pus from different sources have been examined.

H. J. E.

**Phosphatase. IV. Serum-phosphatase of non-osseous origin. Significance of variations of serum-phosphatase in jaundice.** A. BODANSKY and H. L. JAFFE (Proc. Soc. Exp. Biol. Med., 1933, 31, 107—109).—Serum-phosphatase was decreased by prolonged fasting and increased by administration of dextrin or in jaundice of hepatic origin, but not in that associated with anæmia.

CH. ABS.

**Phosphatase. VII. Phosphatase of blood, spleen, liver, and kidney in acute lymphatic leucæmia.** R. IWATSURU and Y. MINAMI (Biochem. Z., 1934, 268, 394—398).—The phosphatase content of the blood in chronic myelitic leucæmia (I) increases considerably, but in acute lymphatic leucæmia (II) shows scarcely any change. The phosphatase content of liver, spleen, and kidney in (II) gives vals. < in (I).

P. W. C.

**Blood-proteins during experimental liver-impairment by Eck fistulæ.** R. JÜRGENS and F.

GEBHARDT (Arch. exp. Path. Pharm., 1934, 174, 532—543).—In dogs with Eck fistulae, ingestion of large amounts of horse-flesh produces a marked increase in the blood-fibrinogen and -globulin. The extent of the increase indicates an extra-hepatic source of blood-proteins, probably the reticulo-endothelial system.

F. O. H.

**Proteinuria in chronic nephritis.** P. M. T. KERRIDGE (Lancet, 1934, 226, 675—678).—Proteins have been separated from the urine of cases of chronic nephritis by dialysis against NaCl solution. When injected intravenously into anaesthetised cats they were not excreted.

L. S. T.

**Effect of renal insufficiency on plasma-magnesium and magnesium excretion after ingestion of magnesium sulphate.** A. D. HIRSCHFELDER (J. Biol. Chem., 1934, 104, 647—653).—In normal animals and man about 42% of  $MgSO_4$  administered orally is excreted by the kidneys in 24 hr. Little rise of plasma-Mg takes place, but in animals with excised or injured kidneys a marked rise in plasma-Mg is found which frequently exceeds 16.0—17.0 mg. per 100 c.c. and results in coma. The rate of excretion of Mg by injured kidneys is similar to that of phenolsulphonephthalein rather than that of xylose, so that it is probably excreted by the tubules.

W. O. K.

**Rôle of the kidney in experimental acidosis in healthy subjects.** W. MARKERT (Compt. rend. Soc. Biol., 1933, 113, 957—959).—In man administration of 10—13 g. of  $NH_4Cl$  daily for 5—8 days causes the alkali reserve of the plasma to fall to 20 vol.-%. The urinary output increases by 27—171% on the second day, then decreases to nearly normal.  $NH_3$  excretion increases up to sixfold and urea and  $Cl^-$  excretion rise. The  $p_H$  of the urine falls to 4.7.

NUTR. ABS. (m)

**Rôle of the kidney in experimental acidosis. Site of production of ammonia.** W. MARKERT (Compt. rend. Soc. Biol., 1933, 113, 962—964).—The  $NH_3$  content of the blood in the healthy subject under  $NH_4Cl$  acidosis and with free  $NH_3$  excretion is 12—18 mg. per 100 c.c. In uræmic acidosis, when  $NH_3$  excretion is low, the val. is 23 mg. The glomerular system of the kidney is the site of  $NH_3$  production.

NUTR. ABS. (m)

**Rôle of the kidney in experimental acidosis in Bright's disease.** W. MARKERT (Compt. rend. Soc. Biol., 1933, 113, 959—961).—In chronic nephritis daily administration for 5—8 days of 10—13 g. of  $NH_4Cl$  causes a rapid fall in the alkali reserve of the blood and an increase in blood-urea. Urinary excretion of  $NH_3$  increases slightly.

NUTR. ABS. (m)

**Relation of plasma-cholesterol to obesity and to some of the complicating degenerative diseases (diabetes mellitus, essential hypertension, osteo-arthritis, and arterio-sclerosis).** B. BRUGER and C. A. POINDEXTER (Arch. Int. Med., 1934, 53, 423—434).—Simple obesity in man is not associated with hypercholesterolaemia (I), but obese subjects suffering from degenerative diseases frequently develop (I).

W. O. K.

**Blood in normal pregnancy. III. Haemoglobin and cell volume coefficients; erythrocyte volume, haemoglobin content and concentration; colour, volume, and saturation indexes. IV. Percentages and grams per kilogram of serum-protein and fibrin and variations in total amount of each.** W. J. DIECKMANN and C. R. WEGNER (Arch. Int. Med., 1934, 53, 345—352, 353—366).—III. In normal human pregnancy (I) from the 26th to the 35th week, the erythrocytes are slightly larger and contain more haemoglobin than normally, becoming normal at term. The individual variation of the various indexes is large.

IV. During (I) a slight fall occurs in the concn. of serum-protein (II), which is at a min. a few days *post partum*. The amount of (II) per kg. of body-wt. remains approx. const. The concn. of fibrin in the plasma and the amount per kg. of body-wt. increase during (I).

W. O. K.

**Acid-base balance of the minerals retained during human pregnancy.** C. M. COONS, R. R. COONS, and A. T. SCHIEFELBUSCH (J. Biol. Chem., 1934, 104, 757—768).—A preponderance of the base-forming elements was retained, usually in amounts exceeding the foetal requirements. The mean daily retentions in g. were: Ca 0.28, Mg 0.06, Na 1.26, K 0.51, Cl 0.89, S 0.0, P 0.30.

H. G. R.

**Effect of a calcium-deficient diet on pregnant ewes.** A. H. H. FRASER, W. GODDEN, and W. THOMSON (Vet. J., 1933, 89, 408—411).—Serum-Ca was lower on a Ca-deficient diet.

NUTR. ABS.

**Cholesterol balance in pregnancy and the puerperium. Pregnancy hypercholesterolaemia.** C. KAUFMANN and O. MÜHLBOCK (Z. ges. exp. Med., 1933, 89, 200—210).—During pregnancy (two primiparæ) the output of cholesterol (I) was > the intake, although serum-(I) was high and (I) was being stored in the foetus. In one case, over 36 days, the negative balance was 8 g., which is about the same as that for non-pregnant women. In one patient, from the tenth to the forty-first day of the puerperium, the output [milk (5.8 g.) and excreta] was > the intake by 15.3 g., so that during lactation the organism must synthesise large amounts of (I).

NUTR. ABS. (b)

**Phosphorus and rickets. III. Inhibition of bone calcification of rachitic rats by metallic carbonates and phosphates.** R. LECOQ and H. VILLETTE (J. Pharm. Chim., 1934, [viii], 19, 201—206).— $MgCO_3$  and  $SrCO_3$  inhibit the calcifying effect of  $Na_2HPO_4$  on rats rendered rachitic by the Randoim-Lecoq diet (A., 1928, 556). Mg and Sr phosphates exert a calcifying effect. Fe and Mn carbonates and phosphates all inhibit calcification. Bi and Ca carbonates cause only slight inhibition, whilst the phosphates are strongly inhibitory. Thus the anti-rachitic activity of phosphates is affected both by the metal itself and by the basicity of the salt.

C. G. A.

**Treatment of tetany.** I. SNAPPER (Lancet, 1934, 226, 728—731).—Oral administration of small amounts of the oil-sol. fraction of irradiated ergosterol in tetany restores blood-Ca to the normal level.

L. S. T.

**Diet of tuberculous and non-tuberculous children. Effect of increased supply of vitamin-B concentrate and minerals.** P. D. CRIMM, I. J. RAPHAEL, and L. F. SCHNUTE (Amer. J. Dis. Children, 1933, 46, 751—756).—Children receiving a cereal mixture supplying Ca, P, Fe, Cu, and vitamins-B<sub>1</sub>, -B<sub>2</sub>, and -E showed greater increases in wt. and in blood-haemoglobin than those receiving regular diets or diets containing added vitamin-B or minerals. Serum-Ca and -P also increased. CH. ABS.

**Lipins and lipin diseases. III. Lipin content of tissues in Schüller-Christian's disease (xanthomatosis) and lipin content of human tissues.** D. M. COWIE and M. C. MAGEE (Arch. Int. Med., 1934, 53, 391—399).—In a case of Schüller-Christian's disease, no significant change in the tissue lipins (I) was found except that the xanthomatous masses had a high content of (I), about 50% of which was cholesterol. W. O. K.

**Blood-calcium and -potassium in totally gastrectomised dogs.** L. BOUISSET and G. DUCLOS (Compt. rend. Soc. Biol., 1933, 113, 1360—1362).—The alkali reserve, total blood-Ca, plasma-Ca, total blood- and plasma-K are all lowered in the dog after gastrectomy. All return to normal levels in time, the Ca levels last. The absence of the stomach does not affect the assimilation of the Ca and K in the diet. NUTR. ABS. (m)

**Water and sodium chloride balance in patients before and after surgical operations.** J. D. STEWART, J. H. TALBOTT, and E. D. CHURCHILL (J. Clin. Invest., 1933, 12, 978).—After herniotomy there is a slight, and after thoracoplasty a marked, decrease of serum-Cl (I), but no significant change in NaCl retention. After partial gastrectomy there is a slight fall in (I) and a marked negative balance of NaCl. NUTR. ABS. (m)

**Glutathione and irradiated yeast.** C. T. BAUMANN and J. VON DESCHWANDEN (Mitt. Lebensm. Hyg., 1933, 54, 281—302; Chem. Zentr., 1933, ii, 3445).—Statistics are given correlating the glutathione (I) content of the blood with frequency of illness. The average content of (I) was 25.32 mg. per 100 c.c., the val. undergoing seasonal fluctuations. H. J. E.

**Co-ordination of the reproductive processes.** A. S. PARKES (Lancet, 1934, 226, 557—563).—A lecture. L. S. T.

**Respiration of *Arbacia* eggs.** R. W. GERARD and B. B. RUBINSTEIN (J. Gen. Physiol., 1934, 17, 375—381).—Discrepancies in the results obtained by Tang and Gerard (A., 1933, 87) and Whitaker (A., 1933, 304) with preps. of *Arbacia* eggs for respiration studies are due to errors of measurement of egg vols. by centrifuging. The respiration rate of unfertilised eggs of *A. punctulata* at 21° is 0.9 cu. mm. O<sub>2</sub> per hr. per 10 cu. mm. of eggs. A. L.

**Biochemistry and biophysics of the developing hen's egg. I. Influence of composition of air.** A. L. ROMANOFF and A. J. ROMANOFF (Cornell Univ. Agric. Exp. Sta. Mem., 1933, No. 150, 36 pp.).—During the first few days of incubation a moderate proportion (<1%) of CO<sub>2</sub> in the atm. tended to

stimulate and higher proportions (>1%) to retard the growth of the embryo. Very low and very high CO<sub>2</sub> contents increased mortality during early incubation. The [H<sup>+</sup>] of ovalbumin was directly related to the [CO<sub>2</sub>], of the incubator atm. during the first week of incubation, and affords a measure of the trustworthiness of the incubator and the efficiency of hatching. A. G. P.

**Germ layer origin and mitotic potentiality of regenerating tissues in *Clymenella torquata*.** F. S. HAMMETT (Protoplasma, 1933, 20, 161—168).—Mitotic activity in all three chief germ-layer derivatives of regenerating *C. torquata* was favoured by SH and retarded by its suboxidised products. The extent of the effects differed in the three types of growing tissue. A. G. P.

**Metabolism and anaërobiosis of tissue cultures.** H. LASER (Biochem. Z., 1934, 268, 451—456).—Cultures of heart tissue live anaërobically for a long time, retaining pulsation for > 3 days. Connective tissue cultures can also live and grow for a long time both in N<sub>2</sub> and after respiration is inhibited by HCN. The respiration insensitive to HCN possessed a relatively greater action on fermentation than on total respiration. Addition of lactoflavin to these cultures increases the activity of respiration on fermentation. P. W. C.

**Oxidation-reduction properties of "evolved carbohydrates" in absence of oxygen.** N. MAYER-REICH (J. Chim. phys., 1934, 31, 9—42).—By "evolved carbohydrates" is understood the active substance described by Wurmser and Geloso (A., 1929, 719). The lack of agreement between potentiometric titration curves for oxidation and subsequent reduction is due to instability of the oxidised form, leading to formation of CO<sub>2</sub>. Apart from this phase of the reaction, evidence is adduced in favour of the reversibility of the oxidation-reduction. When an inert electrode is placed in the solution in absence of an oxidising agent, a definite p.d. is set up, which is a function of the temp. and the activity of H<sup>+</sup>. E. S. H.

**Oxidation-reduction processes in muscular work. I. Potential of Ringer's solution after perfusion through an isolated frog's heart. II. Potential of blood and urine in muscular work.** A. J. CHARIT and I. I. FEDEROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 68—73, 130—135).—I. The  $E_H$  of Ringer's solution (I) perfused through a beating frog's heart falls sharply to a min. after 30 min., and then gradually rises. On adding KCN (0.0002M) to (I) the  $E_H$  rises during perfusion, whilst if (I) is saturated with CO the  $E_H$  rises during the first 30 min., and then falls.

II. The  $E_H$  of femoral arterial and venous blood-filtrates falls to a min. 15 min. after prolonged clonic contraction of a dog's gastrocnemius; that of the urine is at a min. after 1 hr. R. T.

**Chemical changes accompanying muscular activity and hyperthermia. I. Analytical methods.** T. CAHN, J. HOUGET, and R. JACQUOT (Ann. Physiol. Physico-chim. biol., 1933, 9, 205—245).—Methods are described for the determination

in muscle, blood, and liver of  $H_2O$ , total reducing carbohydrates, lactic acid, total P and P fractions, total fat, fatty acids, unsaponifiable matter, urea,  $NH_3$ , creatine, creatinine, Na, K, and Ca. Results are accurate to within 3%.  
NUTR. ABS. (m)

**Post-mortem breakdown of glycogen and accumulation of lactic acid in fish muscle. I.** J. G. SHARP (Proc. Roy. Soc., 1934, B, 114, 506—512).—The rates of breakdown of glycogen (I) and accumulation of lactic acid (II) decrease with fall of temp. from  $15^\circ$  to  $0^\circ$ . At  $-2^\circ$  the rates are as great as at  $15^\circ$ , but fall to approx. zero at  $-10^\circ$ . If excess of (I) is present, no further change of concn. of (I) or (II) occurs when the concn. of (II) reaches 0.40 g.-%,  $\frac{1}{2}$  to  $\frac{2}{3}$  of (I) being recovered as (II). With insufficient (I), all of it disappears, giving (II) quantitatively.  
C. G. A.

**Electric potentials determined in the striped muscle of the frog.** J. W. LANGELAAN (Arch. Néerland. Physiol., 1934, 19, 58—77).—Two potential levels, +0.360 volt and -0.340 volt at  $p_H$  7.4, are determined by the O and H electrodes, respectively. They correspond with the reactions  $AcCO_2H$  (I)  $\rightarrow$  lactic acid and glycogen  $\rightarrow$  (I).  
C. G. A.

**Influence of sympathetic nerves on the metabolism of striped muscle of the frog.** J. W. LANGELAAN (Arch. Néerland. Physiol., 1934, 19, 78—87).—Section of the sympathetic nerves raises the lower (H electrode) potential corresponding with a 7% decrease of free energy in the reaction glycogen  $\rightarrow$  lactic acid, but has no effect on the higher (O electrode) potential.  
C. G. A.

**The amphibian organiser.** J. NEEDHAM, C. H. WADDINGTON, and D. M. NEEDHAM (Proc. Roy. Soc., 1934, B, 114, 393—422).—Induction of a secondary embryonic axis in gastrulae can be accomplished by (a) cell-free and (b)  $Et_2O$  and petrol- $Et_2O$  extracts of the neurula and by adult amphibian tissues and  $Et_2O$  extracts of adult viscera.  
H. G. R.

**Glutathione concentration and hereditary body size. II. Glutathione concentration in non-nursed young of six populations of rabbits differing in genetic constitution for adult size.** P. W. GREGORY and H. GOSS (J. Exp. Zool., 1933, 66, 155—173).—In races of rabbits differing in genetic constitution for adult size, the concn. of glutathione (possibly with other SH-compounds) in the unnursed young at birth increases in proportion to potential adult size from the smallest to the largest.  
NUTR. ABS. (m)

**Biochemistry of Magaki (*Ostrea gigas*, Thunberg). II. Seasonal variation in chemical composition.** B. MASUMOTO, M. MASUMOTO, and M. HIBINO (J. Sci. Hiroshima Univ., 1934, A, 4, 47—56).—During the period of fattening of the oyster (autumn and winter) and the early part of the period of gonad ripening (early spring) the ratio (I) of dry meat to shell rapidly increases, glycogen (II) and fat (III) accumulate [(III) being probably derived from (II)], and the  $H_2O$  content (IV) falls to a min. In late spring and summer (period of discharge of sexual products), (I), (II), and (III) diminish rapidly,

and (IV) rises to a max. Total N and ash contents (V) change in harmony with the total amount of meat, reaching a max. in June. There is an intimate correlation between growth of shell and (V).  
A. E. O.

**Relation between toxicity, resistance, and time of survival and related phenomena. L. REINER (J. Gen. Physiol., 1934, 17, 409—444).**—The equation (I)  $t = -a \log_e(h-r) + k$ , where  $a$  and  $k$  are const.,  $t$  is time of survival,  $r$  the resistance, and  $h$  toxicity, is derived. If vals. proportional to  $r$  are calc. with (I) and the % mortality is plotted against them, symmetrical curves are obtained, even although the corresponding mortality-time curves are asymmetrical. Assuming that  $r$  varies according to probability rules, theoretical mortality-time curves can be constructed from (I) which are similar to the experimental curves. Variation of temp. affects mainly the const.  $a$ . (I) is tested in four different combinations of the variables, concn.,  $r$ ,  $t$ , and temp., and the agreement with experimental vals. is satisfactory. Any noxious agent acting on a unicellular organism may be characterised by three consts.:  $r$ , which is the threshold val. at which the agent is still fatally toxic for the organism;  $a$ , the time corresponding with a difference of 1 between  $h$  and  $r$ ; and the const.  $\gamma$  of the function representing the relation between  $h$  and the concn.  
A. L.

**Possible cause of old age. I. W. D. HACKH and E. H. WESTLING (Science, 1934, 79, 231).**—The increase in the proportion of  $H_2O$  in the body-fluids may account for the increasing inhibitory action of the protoplasm during senility.  
L. S. T.

**Physico-chemical factors in the ecology of mosquito larvæ in Tong-king. II.** H. G. S. MORIN and H. BADER (Ann. Inst. Pasteur, 1934, 52, 332—351).—The constituents of the earth (e.g.,  $SiO_2$ , clay) participate in the liberation of  $CO_2$  from  $CaCO_3$ , whilst NaCl and KCl modify the solubilities of  $CaCO_3$  and  $MgCO_3$  in  $H_2O$  containing  $CO_2$ . The bearing of these factors, together with that of the permeability, adsorption, etc. of the various strata of the soil, on the development of mosquito larvæ is discussed.  
F. O. H.

**Chemistry of embryonic growth. IV. Copper requirement of the pig embryo. V. A. WILKERSON (J. Biol. Chem., 1934, 104, 541—546).**—There is a const. increase in Cu throughout the embryonic period. In embryos 10—20 mm. long the liver (I) constitutes 14% of the wt. and contains approx. 100% of the total Cu. The (I) of embryos 160 mm. long constitutes 4% of the wt. and contains about 65% of the Cu. The blue colour of the ash in the early stages is due to its higher Cu content.  
C. G. A.

**Sodium chloride requirement and its relation to mineral metabolism. H. GLATZEL (Z. ges. exp. Med., 1933, 90, 59—77).**—In an adult male on potato diet there was an increase of  $p_H$ , org. acids, and vol. of urine with reduction of  $NH_3$ , Ca, P, and Cl (alkalotic); on rice there was increase of  $NH_3$ , Ca, P, and org. acids, decrease of vol., and no change or decrease of  $p_H$  (acidotic). The increased intake of K delayed the reduction in Na output.

There was little change in the composition of the serum, but the  $\text{CO}_2$  dissociation curve was shifted to the alkaline side, especially with roasted potatoes. It is incorrect that vegetarian diets (I), with the exception of rice, require addition of  $\text{NaCl}$  because of the large intake of  $\text{K}$ ; the  $\text{NaCl}$  prevents the alkalotic action of (I) and is unnecessary with rice which has an acidotic tendency. NUTR. ABS. (m)

**Mineral balance with (a) calcium chloride acidosis, (b) sodium hydrogen carbonate alkalosis.** G. JOOS and W. MECKE (Arch. exp. Path. Pharm., 1934, 174, 676—686, 687—694).—(a) Ingestion (I) of  $\text{CaCl}_2$  by man produces an increase in serum- $\text{Cl}$  and a fall in  $-\text{HCO}_3^-$  and -org. acids (II); subsequently  $[\text{HCO}_3^-]$  further diminishes, whilst (II) increase. The urine- $p_{\text{H}}$  decreases from 5.9 to 4.9, the excretion of  $\text{NH}_3$ ,  $\text{Ca}$ , and  $\text{Cl}$  markedly increasing. The balances (III) (i.e., differences between ingested and excreted amounts) of  $\text{Na}$ ,  $\text{Mg}$ , and  $\text{P}$  before (I) are positive, whilst those of  $\text{K}$ ,  $\text{Ca}$ , and  $\text{Cl}$  are approx. zero. During (I), (III) of  $\text{Na}$ ,  $\text{Ca}$ ,  $\text{Cl}$ , and  $\text{P}$  increase, whilst after (I) (when a compensatory alkalosis occurs) those of  $\text{Na}$  and  $\text{Cl}$  attain high negative and that of  $\text{K}$  high positive vals. The presence in the urine of significant amounts of unknown bases is not confirmed (cf. A., 1929, 343).

(b) (I) of  $\text{NaHCO}_3$  produces a marked rise in serum- $\text{Na}$  and a respectively gradual and sudden fall in the  $\text{Mg}$  and  $\text{Ca}$  levels, whilst the  $\text{Cl}$  and inorg.  $\text{P}$  decrease slightly. The (III) of  $\text{Na}$ ,  $\text{K}$ , and  $\text{Cl}$  decrease to zero or negative vals., those of  $\text{Mg}$  and  $\text{P}$  decrease slightly, but remain positive, whilst that of  $\text{Ca}$  markedly increases. Other changes in the cations and anions of the blood and urine are described and compared with those due to  $\text{CaCl}_2$  acidosis. F. O. H.

**Relations between serum-calcium and basal metabolism.** L. LENGYEL (Biochem. Z., 1934, 269, 133—149).—Single injections of  $\text{Ca}$  gluconate temporarily increase the  $\text{Ca}$  content (I) of the blood-serum in healthy rats (II), but continued daily injections of large doses, although they raise and maintain (I) in rats (III) suffering from chronic rickets, do not affect (I) in (II). Low (I) is always accompanied by increase in  $\text{O}_2$  consumption (IV), and when (I) is increased by giving  $\text{Ca}$ , or in (III) also by giving vitamin- $\text{D}$ , (IV) decreases in parallel, although it afterwards increases, whilst (I) remains normal. Prolonged giving of  $\text{Ca}$  to (II) increases (IV).

W. McC.

**Relative utilisation of calcium from calcium carbonate and calcium gluconate by chickens.** J. E. HUNTER, R. A. DUTCHER, and H. C. KNANDEL (Proc. Soc. Exp. Biol. Med., 1933, 31, 70—75).—Equiv. amounts of  $\text{Ca}$  as carbonate and gluconate were fed to laying hens receiving sub-optimal amounts of vitamin- $\text{D}$ . The average shell-wt., % of shell-ash, and  $\text{Ca}$  content of the eggs were greater in the group receiving gluconate. NUTR. ABS. (b)

**Absorption and storage of ingested calcium by rabbits.** O. RIESSER and K. SALOMON [with L. KARBE] (Arch. exp. Path. Pharm., 1934, 175, 38—61).—Ingestion of 0.22—0.5 g. of  $\text{Ca}$  malonate (I), gluconate, or phosphate increases the serum- $\text{Ca}$  (II)

by approx. 20% and the ultrafilterable (II) by approx. 40%. A small but definite increase also occurs in the  $\text{Ca}$  content of the skeletal muscle (III), heart (IV), liver, and brain (V); the lung- $\text{Ca}$  is unchanged. Continuous intravenous injection of isotonic aq.  $\text{CaCl}_2$  increases the  $\text{Ca}$  level of (III) and (IV), but not that of (V). Similar results are obtained with rats by feeding (I). F. O. H.

**Soya-bean flour in infant feeding. Relation of the comparative intakes of nitrogen, calcium, and phosphorus to the excretion and retention of these elements by infants.** G. STEARNS, M. J. OELKE, J. B. MCKINLEY, and E. A. GOFF (Amer. J. Dis. Children, 1933, 46, 7—16).—In children receiving diets containing adequate vitamin supplies high intakes of  $\text{N}$  and  $\text{Ca}$  relative to  $\text{P}$  cause high urinary  $\text{Ca}$  and low  $\text{P}$ , and a shift in the mode of excretion of other bases from urine to faeces. Addition of  $\text{Ca}_2(\text{HPO}_4)_2$  to the soya-bean food instead of  $\text{CaCO}_3$  improves retention of  $\text{N}$ ,  $\text{Ca}$ , and  $\text{P}$ . The relative amounts of these elements in the diet of infants are of greater importance than their abs. amounts; the proportions in cow's milk may be used as a guide. NUTR. ABS. (m)

**Diffusion of inorganic phosphate into and out of the skeletal muscles and bones of the frog.** M. G. EGGLETON (J. Physiol., 1933, 79, 31—48).—Only interspace  $\text{H}_2\text{O}$  is involved in phosphate (I) interchange in living muscle, the cell membranes being impermeable to (I). The results are correlated with the slight increase in inorg. (I) in the blood after exercise to exhaustion. NUTR. ABS. (m)

**Bromine metabolism in hibernation.** P. SUOMALAINEN (Suomen Kem., 1934, 7, B, 82).—The posterior brain of hibernating (I) and non-hibernating (II) hedgehogs contains, respectively, 0.386 and 0.193 mg.  $\text{Br}$  per g. of fresh wt. The remainder of the brain of (I) and (II) contains 0.023 and 0.022 mg. per g. of fresh wt., the blood 0.65 and 1.67 mg.  $\text{Br}$  per 100 c.c., respectively. J. L. D.

**Biological significance of sterols.** H. DAM (Nyt nordisk Forlag, København, Thesis, 1933, pp. 162).—In part a review. Chicks, from hatching to 2 months of age, synthesise sterol. Administration of cholesterol (I) for 3 days to a lactating goat gave no increase in milk-(I).

Chicks on a diet of casein, sol. starch, salt mixture, marmite, and filter-paper showed hæmorrhages resembling those of scurvy. These were not prevented by addition of lemon juice in presumably adequate quantities, by substituting yeast or wheat germ (II) for marmite (III), by altering the composition of the mineral mixture, or by feeding moderate amounts of gallstone-(I), cod-liver oil or fractions of it, or linseed oil, or by irradiation. Substitution of (II) for (III) caused "pellagrous" symptoms. NUTR. ABS. (b)

**Origin, metabolism, and elimination of cholesterol in the animal organism.** S. MINOVIĆ, M. VANGHELOVIĆ, and G. MĂRZA (Bul. Soc. Chim. România, 1933, 15, 137—152).—Dogs, mice, and cockroaches synthesise cholesterol from oleic acid, but not from stearic or margaric acid. The liver and spleen are active. C. G. A.

**Distribution in the organism of fats absorbed from the intestine.** G. PERETTI (Riv. Patol. sperim., 1933, 11, 47—56).—After administration of iodised fat to rabbits, by stomach tube, the blood-fat rose until the twentieth hr., fell to a min. at the forty-fourth hr., and again rose to a val. much > the initial. A similar sequence was observed in the lungs, spleen, pancreas, bone marrow, and muscles. In the liver, however, the fat val. was much > in the blood and rose steadily until the seventy-second hr. The liver plays the chief part in the fixation of fat, for which, as the rôle of the spleen is unimportant, the reticulo-endothelial system is probably not responsible.

NUTR. ABS. (b)

**Distribution in the organism of fats introduced directly into the circulation.** G. PERETTI, L. REALE, and L. CIOGLIA (Riv. Patol. sperim., 1933, 11, 73—98).—After the intravenous injection of iodised fat emulsions into dogs, there was at first a rapid disappearance of the fat from the blood, with an increased concn. in the liver, the spleen, and, to a smaller extent, the bone marrow. Later the blood val. rose, whilst the others fell. Variable amounts were found in the lungs.

NUTR. ABS. (b)

**Fat-splitting in the lungs.** L. JANKOVICH (Beitr. path. Anat., 1933, 92, 110—118).—Fat embolism can be detected morphologically in human lung up to about 14 days. Absorption of fat does not occur in lung by cellular activity. The decrease of fat droplets accompanying various lung processes previously observed in lower animals, and now in man, may be due to either lung- or blood-lipase.

NUTR. ABS. (b)

**Fat metabolism in the lung.** G. HOPPE (Z. ges. exp. Med., 1933, 89, 97—104).—The total Et<sub>2</sub>O-sol. fraction of blood from the right auricle and femoral artery in dogs and rabbits showed little difference in seventeen cases, an increase of 18% in femoral artery blood in five cases, and a decrease of 9.5% in eight cases. There was no apparent correlation between these changes and the val. of the blood-fat. The lungs are probably not of special significance in the metabolism of fat.

NUTR. ABS. (b)

**High-carbohydrate and high-fat diets. Variations in blood with dieting.** E. M. GREISHEIMER, E. GOLDSWORTHY, and G. THOMAS (Proc. Soc. Exp. Biol. Med., 1933, 30, 1426—1428).—After a high-fat diet, the sugar-tolerance curve for a normal individual was of the mild diabetic type—blood-sugar 0.201% at 120 min. Urea-N was increased slightly, relative to the protein intake. Total non-protein-N was 29.5—47.7 mg. per 100 c.c.

NUTR. ABS. (b)

**Alimentary metabolic reactions. V. Metabolic reactions after fat, glucose, and meat feeding.** S. LEITES, V. JUSSIN, and M. VODINSKI. **VI. Metabolic reactions after glucose and fat feeding in splenectomised animals.** S. LEITES, V. JUSSIN, M. VODINSKI, and A. KOSLOVA (Z. ges. exp. Med., 1933, 90, 378—395, 396—407).—V. Administration of linseed oil (I) or butter (II) to dogs produces, within 7 hr., no increase of blood-fat (III), and ingestion of hempseed oil (IV) causes only a slight rise; in man a corresponding amount of (II) causes hyperlipæmia. These fats cause an

increase in blood-ketones (V) and cholesterol (VI) and frequently a fall in non-protein-N (VII) and sugar. Prolonged ingestion (one month) of (I) or (IV) causes a reduction of (III) and (V) and a smaller increase of (VI). Ingestion of glucose leads to reduction of (III) and (V) parallel with the hyperglycæmia (VIII). Ingestion of meat causes increase in (VII) and (VI) (slight) and decrease in (V). A meal of fat and peptones (or meat) lessens the increase in lipæmia, (V), and (VII), whilst glucose with fat reduces the hyperketonæmia. Glucose tolerance is decreased by previous ingestion of oil or meat. Adrenaline (VIII) is increased and insulin hypoglycæmia (IX) decreased when fat is administered. After long-continued administration of oil the action of insulin is increased in normal and decreased in splenectomised dogs (X).

VI. In (X) the blood-sugar curve after glucose is more prolonged and > in normal for the first month after operation: thereafter it is reduced. (IX) is more pronounced. (I) or (II) ingestion produces little increase of (III) and (V) and occasionally a reduction. After long-continued administration, oil causes a greater increase of (V). After prolonged feeding with unsaturated fats the fat content of the liver and omentum is greatly increased with rise of the I val. which is greater in (X); in the normal dog there is a very large increase in the fat of the spleen with a fall in the I val.

NUTR. ABS. (m)

**Sexual variation in carbohydrate metabolism.**

**III. Comparative glycogen and fat content of liver and muscles of rats and guinea-pigs.** H. J. DEUEL, jun., M. GULICK, C. F. GRUNEWALD, and C. H. CUTLER (J. Biol. Chem., 1934, 104, 519—530; cf. A., 1933, 631).—The liver-glycogen (I) of fasting male rats was > that in females after administration of glucose; after 96—120 hr. a sharp rise in (I) occurred in the females, producing a (I) > that of the males. The liver-fat of the females was > that of the males. After a high-carbohydrate diet with no fasting (I) was the same in males and females. The (I) of female guinea-pigs after 48 hr. fasting was > that of males.

H. D.

**Magnesium and carbohydrate metabolism.**

H. FRANKE (Arch. exp. Path. Pharm., 1934, 174, 727—741).—The liver-glycogen (I) of rabbits is increased by 300—400% by continuous (1 hr.) intravenous injection (II) or by ingestion of aq. MgCl<sub>2</sub> (but not MgSO<sub>4</sub>) and, to a greater extent, of MgCl<sub>2</sub>+Mg gluconate; the muscle-glycogen (III) remains const. or is slightly increased. Both (I) and (III) are markedly diminished by (II) of adrenaline, the action of which on (III), but not on (I), is inhibited by simultaneous (II) of Mg salts. Ingestion of Ca salts has no influence on (I) or (III).

F. O. H.

**Nutritive value of alfalfa leaves and stems.** J. SOTOLA (J. Agric. Res., 1933, 47, 919—945).—The protein (I) content of stems (II) of lucerne hay is approx. 8%, and of leaves (III) 19%, on the basis of 10% H<sub>2</sub>O content. The ash, crude fat, N, and P in (III) are all > those in (II). The Ca : P ratio is approx. 16 : 1 in (III) of the first and third cuttings, but only 8 : 1 (owing to increase of P) in (III) of the

second cutting. The urinary vol. of lambs fed on (III) was 3.3 times that of lambs fed on (II) alone, and the urine was richer in N, whilst the faeces contained less H<sub>2</sub>O. (III) are 3.5 times as efficient as (II) in providing digestible (I), and the biological val. of (I) of (III) is higher. In spite of the high Ca : P ratio in (III), these are an important source of Ca and P, since the ratio of Ca retained to P retained is approx. 3.3 : 1.

P. G. M.

**Effect of ripening of cheese on the nutritive value of milk-curd protein.** J. R. BEADLES, J. H. QUISENBERRY, F. I. NAKAMURA, and H. H. MITCHELL (J. Agric. Res., 1933, 47, 947—965).—American Cheddar, Swiss (I), and Roquefort, but not Limburger (II), cheese are superior to rennet milk curd (III) as a source of protein for rats. (III) has a somewhat higher coeff. of digestibility (89.65) than any of the cheeses [(II), 87.22]. The biological val. of (III) (73.1) is essentially the same as that of (I) (73.3), whilst that of (II) is approx. 6% lower, since the ripening process in (II) involves destruction of cystine.

P. G. M.

**Long-period metabolism investigations on healthy infants.** Breast-milk, cow's milk with alkali salts of plant acids. G. KRAUSE (Arch. Kinderheilk., 1933, 99, 228—243).—The N retention (I) was determined in four healthy infants kept for periods of 6 weeks on breast-milk (II) and cow's milk (III) and 12 days on (III) with "Basika" (a mixture of alkaline salts derived from vegetables). On (II) the (I) was 58—114 mg. per kg. per day; the absorption was 69.5—78% of the intake. On (III) (I) was increased only for the first few days; thereafter it was practically the same as on (II). Although the intake was nearly three times greater, the absorption was 86—88%. There is thus no evidence of excessive (I) in the bottle-fed infant. When "Basika" was added to (III) the urine became alkaline, the NH<sub>3</sub> output was decreased, and the (I) was raised (101—123 mg. per kg. per day). This supports Berg's view that, for an optimum utilisation of protein, an excess of alkali is necessary.

NUTR. ABS. (b)

**Proteins causing alimentary unbalance.** R. LECOQ (Compt. rend., 1934, 198, 1269—1271).—The peptone of ovalbumin, or, less so, of muscle, causes alimentary unbalance in pigeons.

R. S. C.

**Nutritive value of the silkworm pupa produced in Manchuria.** I. Protein from the pupa of *Bombyx mori* and *Antherea pernyi*. II. Vitamin-A, -B, and -D in the pupa of *B. mori* and *A. pernyi*. S. IZUME, Y. YOSHIMARU, and K. YOSHIMARU (J. Agric. Chem. Soc. Japan, 1933, 9, 922—931, 932—939).—I. The proteins are similar to muscle-protein in respect of the (NH<sub>2</sub>)<sub>2</sub>-acid, cystine, tryptophan, and tyrosine contents. The nutritive val. of *B. mori* protein is equal to, and of *A. pernyi* protein <, that of beef protein.

II. The pupa oil is rich in vitamin-A, but poor in -D. Vitamin-B<sub>1</sub> and -B<sub>2</sub> contents of the pupa are high if the pupa is separated from fresh cocoons.

CH. ABS.

**Cystine deficiency of soya-bean protein at various levels in a purified ration and as a sup-**

**plement to maize.** C. L. SHREWSBURY and J. W. BRATZLER (J. Agric. Res., 1933, 47, 889—895).—Additions of cystine to rations containing 10% of soya-bean meal (I) improved the live-wt. increases in rats except when the ration included yellow maize. With 15% of (I) in the ration the benefit of cystine was less marked.

A. G. P.

**Specific dynamic action of intravenous injection of amino-acids: its relation to basal metabolism.** A. SZAKÁLL (Biochem. Z., 1934, 269, 196—204).—In resting dogs the basal metabolism (I) fluctuates during 8—14-hr. periods. The extent of sp. dynamic action (II) produced by giving NH<sub>2</sub>-acids (III) [glycine, alanine (IV), glutamic acid (V)] is independent of the nature and amount of (III), but is influenced by the capability of the organism to react to their stimulating effects. (IV) always increases (I), (V), which causes decrease in body temp., sometimes produces no (II).

W. McC.

**Tryptophan metabolism.** V. Growth on tryptophan-deficient diets supplemented with  $\beta$ -3-indolylacrylic,  $\alpha$ -oximino- $\beta$ -3-indolylpropionic, and *l*- and *dl*- $\beta$ -3-indolyl-lactic acids. VI. Production of kynurenic acid from indole derivatives. L. C. BAUGUESS and C. P. BERG (J. Biol. Chem., 1934, 104, 675—689, 691—699).—V.  $\beta$ -3-Indolylacrylic acid (I), m.p. 195—196°, was synthesised from indole-3-aldehyde by condensation with malonic acid and elimination of CO<sub>2</sub>,  $\alpha$ -oximino- $\beta$ -3-indolylpropionic acid (II), m.p. > 175°, from  $\beta$ -3-indolylpyruvic acid (III) and NH<sub>2</sub>OH. Of the three acids tested, only *dl*- $\beta$ -3-indolyl-lactic acid (IV) could replace tryptophan in the diet. There were indications that the *d*-acid was particularly effective.

VI. (III) and (IV) were the only indole derivatives converted into kynurenic acid by the rabbit. (II), (I), and (IV) were partly recovered from the urine after administration. Following the administration of (IV) *dl*- and *l*-(IV) were obtained. No appreciable amount of (III) was recoverable.

H. G. R.

**Renal excretion of creatinine.** I. Functional relation between rate of output and concentration in plasma. R. DOMINGUEZ and E. POMERENE (J. Biol. Chem., 1934, 104, 449—471).—The urinary excretion (I) and plasma concn. (II) of creatinine are exponential functions of *t*, after an initial disturbance due to its ingestion, approaching asymptotically the endogenous levels. The average rates of decrease of these functions are equal. The plot of (I) against (II) is a straight line not passing through the origin, so that the ratio of (I) to (II) is not a const. and variations found by Rehberg (A., 1926, 858) are accounted for on this basis together with errors of observation which may produce variations up to 28%.

H. D.

**Origin of urinary ammonia.** H. FASOLD (Z. ges. exp. Med., 1933, 90, 502—507).—Kids fed on goat's milk excreted large amounts of NH<sub>4</sub><sup>+</sup> when they were given HCl. Adult goats and rabbits excrete only minimal amounts of NH<sub>4</sub><sup>+</sup>. Slices of kidney from kids, goats, and rabbits produce very little NH<sub>4</sub><sup>+</sup> from *dl*-alanine in contradistinction to the kidney of rats and other carnivora. All NH<sub>2</sub>-acids cannot, therefore, be precursors of NH<sub>4</sub><sup>+</sup>.

NUTR. ABS. (b)



**Uricolysis.** W. SCHULER (Klin. Woch., 1933, 12, 1253—1254).—Oxidation of uric acid to allantoin takes place in three stages, viz., oxidation, hydrolysis, and decarboxylation. NUTR. ABS.

**Chemistry of mitogenetic radiation. IV. Specificity of mitogenetic spectra of oxidation reactions and the atomic basis of mitogenetic radiation.** A. E. BRAUNSTEIN and A. POTOZKY (Biochem. Z., 1934, 268, 422—443).—The phenomenon of mitogenetic radiation is regarded as an ultra-violet oligoluminescence (I). Using various inorg. and org. systems, it is shown that the spectra of cathodic (I) are sp. for the reduction processes occurring at the cathode and independent of the current strength and tension. The oxidation-reduction spectra with inorg. cation oxidation in  $H_2O$  depend only on the electron acceptor, and not on the electron donor. The spectra of the chemical and electrochemical reductions of the same electron acceptor are identical. P. W. C.

**Effect of mitogenetic rays on eggs of *Drosophila melanogaster*.** L. K. WOLFF and G. RAS (Nature, 1934, 133, 499).—Irradiation by Gurwitsch rays from a culture of *Staphylococcus pyogenes aureus* increases the no. of eggs hatched by 16—47%. L. S. T.

**Effect of temperature of an odorous gas on the olfactory sensation.** H. WOERDEMAN (Arch. Néerland. Physiol., 1934, 19, 88—93).—*iso*Amyl acetate at  $50^\circ$  has a more powerful olfactory effect than at  $20^\circ$ . C. G. A.

**Chemotropic response of a chironomid fly to petroleum oils.** T. AHMAD (Nature, 1934, 133, 462—463).—*Forcipomyia* sp. is attracted in large nos. to petroleum oils, oils containing hydrocarbons with low b.p. being the least attractive. L. S. T.

**Variations in the amount of yellow pigment (xanthophyll) in certain fishes, and of the possible effects upon this of coloured backgrounds.** F. B. SUMNER and D. L. FOX (J. Exp. Zool., 1933, 66, 263—301).—When *Fundulus parvipinnis* (I), *Gillichthys mirabilis*, and *Girella nigricans* (II) were kept in aquaria with red, yellow, or white backgrounds, their colour varied with expansion or contraction of the xanthophores, but there was no evidence that the xanthophyll (III) increased or decreased in response to environmental change except with (II) which showed a slow decrease, particularly on a white background. In (I) the (III) content was maintained, although the food contained chiefly carotene. NUTR. ABS. (b)

**Adsorption of optical isomerides by nerve tissue.** G. H. RICHTER and R. C. DOSSER (Biochem. Z., 1934, 268, 399—405).—Optical isomerides are usually adsorbed to differing extents on optically active substrates and nervous tissue, but to the same extent on optically inactive substrates, e.g., animal charcoal. P. W. C.

**Influence of  $[H^+]$  on nerve chronaxie.** L. DELIUS (Z. Biol., 1934, 95, 27—43).—With frog nerve-muscle preps., increase of  $[H^+]$  produces a rise in the rheobase (I) and a disproportionate fall in the chronaxie (II). In weakly and strongly alkaline buffers (when steady vals. are not attained) (I), respectively, de-

creases and increases, (II) slightly increasing in each case. These effects are reversible even after long exposure to acid or alkaline media. F. O. H.

**Tissue reactions in immunity. XIV. Specific reacting capacities of different tissues of an immunised animal.** R. L. KAHN (Science, 1934, 79, 172—175).—The degree of immunity of different tissues in a protein-immunised rabbit is determined by establishing quantitatively the capacities of the tissues to react with sp. antigen. The skin has a sp. reacting capacity for antigen > ten times those of muscle, brain, and *in-vivo* plasma. L. S. T.

**Biochemistry of anaesthesia.** F. F. NORD (Science, 1934, 79, 159).—Critical (cf. A., 1932, 550). L. S. T.

**Pharmacological action of the whole secretion and of extracts of male accessory sex glands.** U. S. VON EULER (Arch. exp. Path. Pharm., 1934, 175, 78—84).—The secretions of prostate gland (man, dog, rabbit) and seminal vesicles (sheep, pig, ox) contain a substance (I) which has a depressor action (not affected by atropine) and stimulates the isolated intestine (rabbit). (I), which is pptd. by phosphotungstic acid and  $HgCl_2$  and migrates to the cathode on electro-dialysis, resembles or is identical with the substance isolated by Euler and Gaddum (J. Physiol., 1931, 72, 74). F. O. H.

**Chemistry and pharmacology of the kola nut.** W. GEHLEN (Arch. exp. Path. Pharm., 1934, 174, 695—714).—Digestion of the fresh nuts with  $EtOH-HCO_2H$  and subsequent treatment with org. solvents yields colocatechin (I) (0.4%), m.p.  $170-175^\circ$ , caffeine (II), and cola-red (III). Admixture of (I) (1 mol.) in  $EtOH$  and (II) (2 mols.) in  $CHCl_3$  affords caffeine-catechin (IV), m.p.  $137-139^\circ$  (cf. A., 1930, 1223; 1931, 96). (I) and (IV) do not agglutinate red blood-corpuscles, whilst (III) behaves as a tannin, producing tonic contraction of the frog's heart. (I), which has a slight toxic action, has no influence on the diuresis or isolated intestine (rabbit), but inhibits the action of (II) on the latter. Conens. of (I) of 1:500 stop the frog's heart in diastole. The action of (IV) mainly resembles that of (II). F. O. H.

**Effect of phenylethanolamine and ephedrine on nasal membranes.** T. B. GRAVE and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 35—36).— $OH-CHPh-CH_2-NH_2$  as the hydrochloride in  $H_2O$  or as oleate in mineral oil has the same effect on nasal membranes as corresponding ephedrine solutions. C. G. A.

**Percutaneous absorption of salicylic acid and its derivatives.** C. A. ROJAHN and E. WIRTH (Arch. exp. Path. Pharm., 1934, 175, 26—37).—Free salicylic acid (I), its alkali salts, and, to a smaller extent, its esters are absorbed by the rabbit's skin from ointments and fluid media. The presence of (I) or of skin irritants markedly increases the absorption. F. O. H.

**Pharmacological actions of acetylsalicylic acid and strontium acetylsalicylate.** I. SIMON (Arch. Farm. sperim., 1934, 57, 53—67).—Acetylsalicylic acid (I) and its Sr salt (II) are similar in their pharmacological actions, but (II) is less toxic than (I), and shows

less hæmolytic power, but more coagulative activity on the blood-proteins; unlike (I), it does not cause hæmoglobinuria *in vivo*. The beat of the isolated heart of the frog, inhibited by (I), can be restored temporarily by (II). The actions of (I) and (II) on the isolated blood-vessels, their behaviour in the animal organism when administered *per os*, and their augmentative effects on uric acid excretion are similar.

R. N. C.

**Diuresis and metabolism.** J. AMAR (Compt. rend., 1934, 198, 1179—1181).—The diuretic action of H<sub>2</sub>O, beer, asparagus, cherries, and strawberries is a nutritive as opposed to a nervous effect. Urinary secretion is modified in proportion to metabolism.

P. G. M.

**Excretion of aloes.** G. F. HALL and W. M. KEIGHTLEY (Analyst, 1934, 59, 152—155; cf. A., 1933, 1198).—A small amount of aloes, hydrolysed (I) and unhydrolysed (II), is excreted in the urine, (I)+(II) up to 10 hr., (II) up to 60 hr., after ingestion of (II). The modified Schoutelen reaction for (II) is more delicate and distinctive than the Bornträger reaction for (I).

E. C. S.

**Influence of ammonium carbonate and atophan on blood-uric acid and urate excretion with various diets.** W. VON MORACZEWSKI, S. GRZYCKI, H. JANOWSKI, and R. SŁAWINSKI (Arch. exp. Path. Pharm., 1934, 174, 575—588).—The influence of substances which form uric acid (I) or increase its excretion is modified by the diet. Thus with a fat or sugar diet, nucleins and atophan significantly increase the blood- and urine-(I), respectively, but with a protein diet the effects are less marked. When a change of diet produces retention of H<sub>2</sub>O by the body, there also occurs a retention of (I) and other urinary constituents which produces excretion of org. acids, a diminution in the alkali reserve of the blood, and liver impairment. Other metabolic disturbances accompanying diuresis are discussed.

F. O. H.

**Phloridzin. II. Relation between phloridzin diabetes and glycosuria in normal rabbits and in rabbits with disturbance of liver function. III. Glutathione content of the tissues of phloridzinised rabbits.** T. ONODERA (Sei-i-kwai Med. J., 1932, 51, No. 8, 17—29, 30—37).—II. In liver injury the disappearance of glycosuria (I) is slower than normal.

III. Average reduced glutathione contents of tissues of normal rabbits are: liver 0.2424, kidney 0.0823, adrenals 0.0193, muscle 0.0424, spleen 0.1249, testicles 0.0696, lungs 0.058, heart 0.0329%. The effect of max. phloridzin (I) is given by, respectively: -11, -1.0, +495.4, -2.4, +21, +60.8, +22.0, -4.0%.

CH. ABS.

**Organoleptic bioassays.** J. C. MUNCH, G. E. BYERS, and H. J. PRATT (J. Amer. Pharm. Assoc., 1934, 23, 24—25).—The bioassay of capsicum and ginger is possible by comparison with the threshold concns. (20 mg. and 400 mg. per litre, respectively) required to detect pungency in the throat.

C. G. A.

**Bioassay of picrotoxin and *Cocculus indicus* preparations.** J. C. MUNCH and A. M. PONCE (J. Amer. Pharm. Assoc., 1934, 23, 98—104).—Although

individual animals show large variations in their reactions to picrotoxin (I) and its preps. an assay based on the simultaneous injection of a standard amount of (I) (5 mg.) and the drug into similar groups of mice has been evolved.

E. H. S.

**Detection and determination of novocaine.** H. WILLSTAEDT (Biochem. Z., 1934, 269, 182—186).—The most sensitive reagent for detection of novocaine (I) (< 0.005 mg. per c.c.) is Reinecke's salt, although the test is not sp. For determination [if necessary after extraction (II) from biological material with Et<sub>2</sub>O] of (I) it is diazotised and coupled with Na 8-amino- $\alpha$ -naphthol-3 : 6-disulphonate. The red colour produced is then compared with that of a standard. (II) is inapplicable if the amounts of (I) are small.

W. McC.

**Combined [pharmacological] action of Solanaceæ alkaloids.** H. YAMADA (Folia Pharmacol. Japon., 1933, 16, No. 3, 351—360).—The combined action of *l*-hyoscyamine, *l*-scopolamine, and *l*-homatropine on the parasympathetic fibres of the rabbit intestine and isolated frog heart is > that of any one in removing the effect of acetylcholine.

CH. ABS.

**Pharmacology and chemistry of curine.** F. HAUSCHILD (Arch. exp. Path. Pharm., 1934, 174, 742—754).—Curine (I) has a marked action on the heart, but has not the effect on the circulation characteristic of curare preps. (I) resembles caffeine in the paralyzing action of high concns. on striped muscle. The pharmacological properties of (I) confirm its identity with *l*-bebeerine (A., 1928, 1265) [or *l*- $\alpha$ -chondodendrine (A., 1922, i, 569)]. A quant. distinction between amorphous and cryst. (I) could not be detected.

F. O. H.

**Preparation of highly-active calabash-curarine.** F. HAUSCHILD (Arch. exp. Path. Pharm., 1934, 175, 14—16).—The min. lethal dose (I) of curarine for rats is 15—20% > that for rabbits (II). The purification and crystallisation of tube-curarine claimed by Zanelli (Arch. Ital. Sci. Farm., 1932, 1, No. 3) could only partly be confirmed; the prep. of Boehm (A., 1898, i, 283) appears therefore to be of max. purity. Calabash-curarine (III) is purified 200—300% by repeated pptn. with HgCl<sub>2</sub>, but not by ultrafiltration, a (I) of 0.1 mg. per kg. for (II) being attained. Hence the purity of the (III) of Boehm (*loc. cit.*) is doubtful.

F. O. H.

**Application of the mouse-tail phenomenon to the assay of morphine and scopolamine preparations.** W. KEIL and A. KLUGE (Arch. exp. Path. Pharm., 1934, 174, 493—501).—The determination of morphine (I) (up to 0.013 mg. with an accuracy of  $\pm 5\%$ ) and (I) derivatives by means of the mouse-tail reaction (II) (A., 1912, ii, 611) is described. The analgesic action of (I) and its derivatives is generally  $\propto$  the strength of (II). Scopolamine and genoscolamine diminish and, in sufficiently large doses, inhibit the (II) of (I); on this inhibition is based a method for their determination (up to 0.0005 mg. with an accuracy of approx.  $\pm 15\%$ ). Atropine has no influence on the (II) due to (I).

F. O. H.

**Distribution of nicotine in cigarette smoke.** A. WENUSCH (Chem.-Ztg., 1934, 58, 206—207).—40—50% of the nicotine content (I) of the tobacco is

retained in the "secondary stream" smoke (II) of a freely glowing cigarette, 14% of the (I) in the (II) of a normally smoked cigarette, 25% being in the "main stream" smoke (III). In the smoke of a rapidly continuously drawn cigarette 3% of the (I) is in the (II) and 80% in the (III). The remaining (I) is decomposed.

C. G. A.

**Tobacco smoke. IV.** E. WASER and M. STÄHLI (Z. Unters. Lebensm., 1934, 67, 280—284).—The HCN content (I) of cigarette (II) smoke (0.020—0.034% of the wt. of dry tobacco) is too small to be dangerous. Under const. conditions of smoking, (I) is const. for any one type of (II). It is independent of the nicotine content, but increases with increasing rate of smoking. Injection of H<sub>2</sub>O or Bonicot into (II) has no effect on (I).

E. C. S.

**Effects of cigarette smoking on the blood-sugar.** H. W. HAGGARD and L. A. GREENBERG (Science, 1934, 79, 165—166).—Smoking produces a temporary increase in blood-sugar (I) and a corresponding increase in the rate of sugar combustion in the body. These effects are due to nicotine, and arise from its action on the adrenal glands. Smoking has no appreciable effect until the R.Q. and (I) have fallen below the respective vals. of 0.85 and 0.13%. By inducing a hyperglycemia smoking may temporarily delay the development of hunger.

L. S. T.

**Biochemistry of sleep and stimulation and the significance of cations.** M. CLOETTA, H. FISCHER, and M. R. VAN DER LOEFF (Arch. exp. Path. Pharm., 1934, 174, 589—675).—Methods for the determination of Ca, K, and Mg in plasma (2—4 c.c.) or tissue (0.1—0.2 g.) are given. With men, dogs (I), and rabbits (II) sleep [normal or induced by narcotics (III)] is accompanied by a decrease in the plasma-Ca and -K (averaging 9.9, 16.6; 7.9, 15.3; 5.9, 12.9%, respectively) whilst the Mg level is not significantly changed. With cats (IV), in which (III) produce a stupor, the plasma-cations are approx. unchanged. With (I), (II), and (IV), psychomotor stimulation by administration of  $\beta$ -tetrahydronaphthalene produces corresponding increases in the Ca and K levels. Intracerebral injection of Ca into (I), (II), and (IV) induces a condition of sleep which, like that produced by (III), is accompanied by a fall of plasma-Ca and -K. The brains of (I) awake and asleep have Ca, K, and Mg contents of, respectively, 5.51, 350, 14.42, and 5.73, 358, 14.39 mg. per 100 g. Greater differences (which appear to be quantitatively related to the degree of sleep), although < those of the plasma, occur in the Ca content of the infundibular region (V) (cf. A., 1931, 386). Corresponding decreases occur in the brain on stimulation. Infundibular injection of KCl acts like that of stimulants, increasing the plasma-Ca and -K and lowering the Ca level of (V), whilst that of Ca-saponin does not induce sleep, indicating that the effect is not ionic, but due to a "dispersive" action of Ca. That injection of KCN into (V) induces sleep indicates that an increased [Ca] in (V) acts by inhibiting local oxidation processes. With (I), (II), and (IV), faradic stimulation lowers the Ca and K levels of striped muscle, indicating that the increase in plasma-Ca and -K due to stimulants is of peripheral origin; this is confirmed by the diminished action of

narcotics in lowering the Ca and K levels after curarisation.

F. O. H.

**Biology of heavy water.** G. N. LEWIS (Science, 1934, 79, 151—153).—H<sub>2</sub>O is not highly toxic to tobacco seeds, yeast, flatworms, and mice and is tolerated in high concns. by lower organisms. The rate of the vital processes appears to be approx.  $\propto$  the fraction of H<sup>1</sup> in the total H, and when all H<sup>1</sup> is replaced by H<sup>2</sup> growth is extremely slow, if not completely inhibited.

L. S. T.

**Diplogen and fish.** G. VON HEVESY and E. HOFER (Nature, 1934, 133, 495—496).—Goldfish behave normally in H<sub>2</sub>O containing 0.5 mol.-% H<sub>2</sub>O. Using H<sub>2</sub>O as indicator of the movement of the total H<sub>2</sub>O in fish, nearly all the H<sub>2</sub>O mols. leave the body of the fish within a few hr. and are replaced by H<sub>2</sub>O mols. from the surrounding H<sub>2</sub>O.

L. S. T.

**Effect of fluorine in the nutrition of the chick.** C. H. KICK, R. M. BETHKE, and P. R. RECORD (Poultry Sci., 1933, 12, 382—387).—CaF<sub>2</sub> is tolerated better than rock phosphate or NaF, with which > 0.036% F in the food proportionally decreased growth and food consumption. Blood-clotting time decreased with increase in ration-F. F ingestion did not affect Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in the tibiae at 8 weeks.

CH. ABS.

**Effects of inhalation of hydrogen fluoride. I.** Response following exposure to high concentrations. W. MACHLE, F. THAMANN, K. KITZMILLER, and J. CHOLAK (J. Ind. Hygiene, 1934, 16, 129—145).—The toxicity of HF to rabbits and guinea-pigs appears to be of the same order as that of HCl and SO<sub>2</sub>.

H. G. R.

**Halogen storage in eggs and their therapeutic value.** L. BERKESSY and K. GÖNCZI (Magyar Orvosi Arch., 1933, 34, 402—409).—Hens were injected intravenously with 0.13—0.18 g. of NaI during 3 weeks. The eggs then contained 700—800  $\times 10^{-6}$  g. I per 100 g. After discontinuing the NaI the I content of the eggs fell to normal within a week. Feeding eggs with a high I content proved to be beneficial in Graves' disease.

NUTR. ABS. (b)

**Absorption of iodine in relation to the organism as a whole.** A. STURM and H. SCHULTZE (Z. ges. exp. Med., 1933, 90, 173—207).—After one cutaneous application of I-containing substances (0.08—0.4 g. of I) 1—11.6% appeared in the urine, most of it 4—6 hr. after inunction. Only insignificant amounts appeared in the faeces and sweat. The I concn. of the blood ran parallel with that of the urine. A considerable amount appeared in the saliva and gastric juice. The I content of the body was at times enriched by 50%. Alteration of cutaneous blood-flow by heat, ultra-violet light, or local stimuli, or changing the NaCl content of the diet, had no effect on the urinary excretion of I, which was diminished during great perspiration. The amount retained appears to depend on the state of the thyroid gland; during periods of hyperthyroidism greater amounts appeared in the urine. In a patient with advanced pulmonary tuberculosis large amounts were retained.

NUTR. ABS. (b)

**Fate of iodide injected into frogs.** O. EICHLER (Arch. exp. Path. Pharm., 1934, 175, 67—77).—In-

jection of aq. NaI into frogs is followed by its rapid passage by means of the lymph-stream from the site of injection (abdominal lymph and peritoneal cavities) into the blood and other tissues, finally returning to the main lymph circulation, where a high concn. of NaI is attained. The skin (through which a slight excretion of NaI occurs) functions as a reservoir for NaI.

F. O. H.

**Mercury-laden air; toxic concentration, proportion absorbed, and urinary excretion.** A. M. FRASER, K. I. MELVILLE, and R. H. STEHLE (J. Ind. Hygiene, 1934, 16, 77—91).—To produce chronic toxic effects in dogs the min. concn. of vapour inhaled for 8 hr. daily for 40 days is 3.05 mg. per cu.m. Under these circumstances, the average daily excretion is 0.5 mg. With a concn. of 2.91—26.18 mg. Hg per cu.m., 24.16% is absorbed on inhalation.

H. G. R.

**Formation of cadmio-lipin complexes in the organism.** A. CIRIMINNA (Arch. Farm. sperim., 1934, 57, 68—77).—Intravenous injection of CdCl<sub>2</sub> in the dog results in formation of cadmio-lipin complexes (I) in the liver. The Cd in (I) is linked to the fatty acids, the linking being stable to saponification with cold KOH. The formation of (I) takes place very slowly, larger quantities being found in more prolonged cases of Cd poisoning.

R. N. C.

**Substance in *Tribulus* plants which produces methæmoglobinæmia.** C. RIMINGTON and J. J. QUIN (Biochem. Z., 1934, 269, 4—13).—*Tribulus* plants (S. Africa) contain inorg. NO<sub>3</sub>, chiefly as KNO<sub>3</sub> (up to 7% of dry wt.). It is this, reduced to NO<sub>2</sub> by an oxidoreduction system, which rapidly poisons animals (sheep), converting hæmo- into methæmo-globin intracellularly.

W. McC.

**Substances of higher plants and yeast which protect against uranium poisoning.** M. JACOBY and G. EISNER (Biochem. Z., 1934, 268, 322—325).—The active substances of plants and yeast are possibly identical, are sol. in 90%, but not in abs. EtOH, and cannot be fractionated with Et<sub>2</sub>O, light petroleum, and COMe<sub>2</sub>. Vitamin-B<sub>2</sub> probably also belongs to this group of substances.

P. W. C.

**Localisation of uranium in the organs of rabbits during uranium intoxication determined by the magneto-optic method.** H. D. JONES, R. GOSLIN, K. D. CRANE, and G. B. JOHNSTON (Amer. J. Physiol., 1933, 105, 693—696).—The sensitivity of the method is 0.663 × 10<sup>-12</sup> g. U per c.c. After injection of 0.5 mg. per kg. body-wt. of U nitrate U is found in the blood, urine, and urinary system, kidney, spleen, and liver, but not in the bile or gall-bladder. On an average 20% of the total U is found in the liver and 23% in the kidney (I). The U is excreted through (I) during the first 24 hr. and not through the bile.

NUTR. ABS. (m)

**Determination of enzyme dissociation constants.** H. LINEWEAVER and D. BURK (J. Amer. Chem. Soc., 1934, 56, 658—666).—Graphical methods involving const. slopes and straight-line extrapolations are developed for testing and interpreting kinetic data and for determining dissociation (and related) consts. of enzyme-substrate and enzyme-inhibitor

compounds [when the data (lit.) are found to be consistent with an assigned mechanism]. Representative analyses are given for invertase (I), raffinase (II), amylase (III), citric acid dehydrogenase (IV), catalase (V), oxygenase, esterase (VI), and lipase, involving substrate activation and inhibition, general competitive and non-competitive inhibition, steady states, and reactions of various orders. In the simplest cases [(I)—(III)], plotting of 1/v (v=observed velocity) against 1/S (S=substrate concn.) gives a straight line, the slope of which is K<sub>s</sub>/V<sub>max</sub>. (K<sub>s</sub>=Michaelis dissociation const.; V<sub>max</sub>=theoretical max. velocity) and the ordinate intercept is 1/V<sub>max</sub>. In presence of competitive inhibitors, the slope is increased but the intercept is unchanged; with non-competitive inhibitors, the intercept is raised also. When the active intermediate contains *n* mols. of substrate, a straight line is obtained by plotting 1/v against 1/S<sup>*n*</sup> [as with (IV)]. Occurrence of a steady state before the formation of the active intermediate results in a curve with two limiting slopes. When the curve of *v* against *S* passes through a max. and then approaches a zero val., the existence of an additional inactive intermediate [as with (V)] is indicated; approach to a const. val. indicates two or more active intermediates [(—)Et mandelate-(VI)]. The methods described are applicable to general chemical catalysis (homogeneous or heterogeneous).

H. B.

**Detection of enzymes by spot tests.** B. N. SASTRI and M. SREENIVASAYA (Mikrochem., 1934, 14, 159—160).—Enzymes may either alter the colour or the *p*<sub>H</sub> of the substrate, or liberate reducing sugars. Spot tests for the more common enzymes, based on these principles, are described.

J. S. A.

**Mechanism of oxidation processes. XXXIX. Dehydrogenation by yeast in presence of methylene-blue and benzoquinone.** H. WIELAND and O. B. CLAREN [with P. COUCEIRO] (Annalen, 1934, 509, 182—200).—The course of reaction between methylene-blue (I) and "impoverished" yeast (II) (A., 1932, 303) with EtOH is determined by the velocity of diffusion of (I). (I) also exerts an irreversible retarding action with (II). The aerobic dehydrogenation of AcOH is retarded, probably owing to partial inactivation of the active enzyme surface by (I). Aerobic dehydrogenation of EtOH is greatly retarded by HCN (0.001—0.004*M*); a gradual diminution in retardation occurs, probably owing to the formation of OH·CHMe·CN. HCN also causes a retardation when dehydrogenation is carried out using (I) in absence or presence of O<sub>2</sub>. Dehydrogenation [O<sub>2</sub> or (I)] of EtOH is also retarded by CO; CH<sub>2</sub>I·CO<sub>2</sub>H (*M*/600) has no effect. Lactic acid with (I)+(II) gives MeCHO, EtOH, and AcOH (part formed by direct dehydrogenation of MeCHO); (I) or its leuco-compound suppresses (partly) the Cannizzaro reaction with MeCHO. Decolorisation of (I) with AcCO<sub>2</sub>H occurs very slowly. Dehydrogenation of EtOH (to AcOH) with (II)+benzoquinone (III) (0.01*M*) occurs rapidly at first and then ceases owing to destruction of the enzyme. There is little difference in the rate of disappearance of (III) (0.05*M*) in absence or presence of EtOH; (III) is

reduced by (II). Aërobic dehydrogenation of AcOH in presence of (II) is retarded by (III) to about the same extent as with HCN. (III) also retards the aerobic dehydrogenation of EtOH, but quinol has no effect. HCN has a slight retarding action on the dehydrogenation of EtOH by (III). The ability of (II) to ferment *d*-glucose is completely destroyed by 0.005*M*-(III). H. B.

**Oxidation-reduction by yeast dehydrogenase.** H. VON EULER and C. MARTIUS (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 22, 6 pp.).—Yeast apozymase preps., free from cozymase, in  $\text{PO}_4'''$  buffer at  $p_{\text{H}}$  7 dehydrogenate lactic acid (I) (as indicated by the decolorisation of methylene-blue or 2:6-dichlorophenol-indophenol) to  $\text{AcCO}_2\text{H}$ , the action being totally inhibited by  $\text{CuSO}_4$  and partly by  $\text{NH}_3$  or  $\text{AcCO}_2\text{Na}$ . The dehydrogenation (II) of lactylglycine (probably to  $\text{Ac}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ) or of EtOH is almost as rapid as that of (I); that of Et lactate, alanine, or glycine is much slower. The correlation between (II) of (I) and the resynthesis of glycogen in muscle is discussed. F. O. H.

**Enzymes.** H. VON EULER and E. KLUSSMANN (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 23, 6 pp.).—Apozymase preps. from bottom yeast, in presence of cozymase,  $\text{PO}_4'''$  buffer at  $p_{\text{H}}$  6.8–8.0, and hexose monophosphate (Robison), decolorise methylene-blue (I); the reaction, which is not appreciably inhibited by NaF or lyochrome (ovoflavin), is much slower when the ester is replaced by glucose or xylose. Certain aq. dehydrogenase preps. have absorption max. at 265  $\mu$ , indicating the presence of cytoflavin or Warburg's yellow enzyme (A., 1932, 1285). Extract of rat's muscle decolorises (I), the action being accelerated by cozymase or pyruvate, but not by lactate or ovoflavin. Corpus luteum, ovarian tissue, and anterior pituitary gland resemble muscle, whilst posterior pituitary gland and liquor folliculi have a less marked action. F. O. H.

**Potential of the yellow oxido-reduction pigment.** R. BIERICH and A. LANG (Z. physiol. Chem., 1934, 223, 180–184).—The normal potential (I) of the oxidation pigment at  $p_{\text{H}}$  7 is –208 mv. at 20° with reference to the normal electrode. The (I) of the pigment not denatured by NaOH at  $p_{\text{H}}$  1.17–6.45 is about 15 mv. more positive than the  $\text{CHCl}_3$ -sol. pigment. J. H. B.

**Hæmatin content of horse-radish peroxidase.** K. A. C. ELLIOT and D. KEILIN (Proc. Roy. Soc., 1934, B, 114, 210–222).—Hæmatin (I) is determined microspectrographically after transformation into a  $\text{C}_5\text{H}_5\text{N}$ -hæmochromogen. The parallelism between (I) content and enzyme (II) activity was not observed in highly active preps., and the whole (I) was present as acid (I). Complete combination of free (I) with nitrogenous substances is obtained only above  $p_{\text{H}}$  10.5 when (II) is nearly inactive. Willstätter's method of purification of peroxidase is inapplicable to uncultivated English horse-radish. H. G. R.

**Specificity of fumarase.** K. P. JACOBSON (Fermentforsch., 1934, 14, 175–181).—Neither  $\text{Et}_2$  (I) nor Et H fumarate (II) is hydrated by liver

fumarase. (I) was partly hydrolysed to (II), which was recovered unchanged. A. E. O.

**Enzymes of *Bombyx mori*, L. III. Tyrosinase and catalase of the blood of the silkworm.** K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1933, 9, 172–177, and J. Agric. Chem. Soc. Japan, 1933, 9, 940–948).—The blood-tyrosinase (I) of the silkworm has optimum  $p_{\text{H}}$  6.6 and optimum temp. 37°; it has greater activity in males than in females, but is independent of growth. The activity is high in the larval stage, falls during spinning and in the pupal stage, and rises to a max. in the moth. The blood-catalase (II) has optimum  $p_{\text{H}}$  6.6, optimum temp. 23°, greater activity in males and in well-grown than in females and poorly grown specimens. Activity increases at spinning, and is a max. in the early pupal stage, then falls, to rise again in the moth. Chinese and Japanese strains have greater (I) and (II) activity than European strains. C. G. A.

**Purification and properties of malt amylase.** H. C. SHERMAN, M. L. CALDWELL, and S. E. DOEBBELING (J. Biol. Chem., 1934, 104, 501–509; cf., A., 1930, 1316).—Amylase preps. with activities of 3800–4500 are obtained by fractional pptn. of extracts of barley malt by  $(\text{NH}_4)_2\text{SO}_4$ , dissolution of the most active fraction, dialysis in a min. of  $\text{H}_2\text{O}$  to remove  $\text{SO}_4''$ , repeating until no increase in activity results, fractional pptn. with EtOH, and finally pptn. with EtOH and  $\text{Et}_2\text{O}$ . The preps. contain approx. 16% N, are denatured on prolonged contact with EtOH, thereby losing their activity, and behave generally like typical protein. H. D.

**Action of certain alkaloids on invertase.** G. MEZZADROLI and A. AMATI (Atti R. Accad. Lincei, 1933, [vi], 18, 226–231).—0.05% of strychnine nitrate, caffeine, or quinine sulphate reduces the activity (velocity coeff.) of invertase to 29.9, 97.3, and 96.1%, respectively; for 0.1% the corresponding figures are 20.8, 95.2, and 87.7; for 0.2%, 14.9, 95.2, and 79.9 and for 0.3%, 13.0, 95.2, and 79.9. T. H. P.

**Oxynitrilese of emulsin. II. Kinetics of the synthesis of *d*-mandelonitrile accelerated by emulsin.** H. ALBERS and K. HAMANN. III. Effect on this synthesis of hydrogen-ion concentration. H. ALBERS, K. HAMANN, and H. ALBRECHT. IV. Absorption of ultra-violet light by the system emulsin-benzaldehyde. H. ALBERS, I. MEYER, and K. MEYER. V. Intermediate products in the synthesis. H. ALBERS and H. ALBRECHT (Biochem. Z., 1934, 269, 14–25, 26–34, 35–42, 43–62; cf. A., 1933, 93).—II. The asymmetric enzymic synthesis is a reaction of the second order; it is inhibited by PhOH. The initial reaction velocity, which is  $\propto$  the amount of enzyme (I), gives a measure of the amount of active (I), this amount being independent of the degree of purity of (I).

III. The kinetics of the reaction and the effect of  $[\text{H}^+]$  are not affected by accompanying impurities. The dissociation of the enzyme-substrate compounds is independent of  $[\text{H}^+]$  and of the concn. of the substrates (II). The curve showing relation between  $p_{\text{H}}$  and activity of (I) exhibits max. at  $p_{\text{H}}$  5.4, 5.85, and 6.5. Only one (I), however (oxynitrilese), is involved;

it reacts with (II) under different conditions. (I) is purified by dialysis.

IV. The  $[H^+]$  ( $p_H$  5.3, 6.0, 6.5) at which the ultra-violet light absorption curves (III) of PhCHO in 50% aq. EtOH indicate the presence of max. amounts of unchanged carbonyl form (IV) are identical with those at which (I) exhibits max. activity, the amounts of (IV) varying with varying  $p_H$ . The (III) of emulsin and these results indicate that PhCHO forms an intermediate compound (V) with (I). (V) is decomposed into its constituents only with difficulty.

V. (Cf. A., 1933, 862.) (V) consists of PhCHO + one mol. of (I) but other compounds containing, in addition, 2PhCHO, loosely bound, also exist and, further, a corresponding compound of (I) with HCN as well as [(I) + 2HCN] + 2HCN, loosely bound, [(I) + 2PhCHO] + 2HCN, loosely bound, and [(I) + 2HCN] + 2PhCHO, loosely bound. (I) has a greater affinity for PhCHO than for HCN. Possibly (I) contains  $2NH_2$ .

W. McC.

Activation of glycolysis by copper. F. LIPMANN (Biochem. Z., 1934, 268, 314—316).—Cu ( $10^{-5}$ — $10^{-4}$  mol. per litre) increases by 100% and  $10^{-4}$ — $10^{-3}$  mol. per litre decreases glycolysis in Meyerhof's muscle extract.  $Fe^{++}$  also inhibits. The action of Cu is independent of the presence of  $O_2$ .

P. W. C.

Function of phosphoric acid in the glycolytic fission of carbohydrates. R. NILSSON (Svensk Kem. Tidskr., 1934, 46, 24—39).—The glycolytic fission of carbohydrates and the correlated phenomena of yeast fermentation and lactic acid production in muscle are discussed. The formation of a labile 6-hexosemonophosphoric acid (which can yield a stable mixture of glucose- and fructose-monophosphoric acids) as intermediary in both processes is emphasised. This compound, on oxido-reduction, affords glyceraldehyde- $\gamma$ -phosphoric acid [giving hexosediphosphoric acid by condensation of 2 mols. and, as a secondary product, phosphoglyceric acid (A., 1930, 641)] and a non-phosphorylated compound,  $C_3H_6O_3$  (probably hydrated AcCHO) which yields EtOH and  $CO_2$  with yeast and lactic acid with muscle.

F. O. H.

Detection of triosephosphoric acid as intermediate product in the enzymic fission of carbohydrates. O. MEYERHOF and K. LOHMANN (Naturwiss., 1934, 22, 134—135).—When hexose diphosphate (I) is added in low concn. to co-enzyme-free muscle juice, or to yeast maceration juice, up to 60% is changed in a few min. into triosephosphoric acid (II), as shown by its ready hydrolysis by 0.5N-NaOH to  $H_2PO_4$  and lactic acid and by acid hydrolysis to  $H_2PO_4$  and AcCHO. From the action of dil. dialysed rabbit-muscle extracts on (I) at room temp., (II) was isolated as Ba salt and agreed in most of its properties with the synthetic glyceraldehyde- $\gamma$ -phosphoric acid of Fischer (A., 1932, 364, 834) but differed in its low uptake of Br or I. It is probably largely dihydroxyacetonephosphoric acid, the small optical activity ( $[\alpha]_D + 0.8^\circ$ ) being due to impurity.

W. O. K.

Influence of  $\alpha$ - and  $\beta$ -glucosides on the phosphorylation of glucose. E. ABDERHALDEN and G. EFFKEMANN (Biochem. Z., 1934, 268, 461—468).—

Parenterally administered amygdalin (I) is only partly recovered in the urine. (I), arbutin (II), salicin (III), phenol- $\alpha$ - and - $\beta$ -glucosides and -galactosides inhibit phosphorylation in muscle extracts containing NaF,  $\beta$ -glucosides being more active than  $\alpha$ -glucosides. (I) and (II) inhibit the reabsorption of glucose in the kidney tubules, and (I), (II), and (III) inhibit its absorption from the intestine.

P. W. C.

Phosphatase hydrolysis of diphospho-*l*-glyceric acid. O. BODANSKY and H. BAKWIN (J. Biol. Chem., 1934, 104, 747—755).—Diphospho-*l*-glyceric acid resides entirely in the org. acid-sol. fraction of blood-P, not hydrolysable by bone-phosphatase at  $p_H$  9.0 and 4%  $CCl_3 \cdot CO_2H$  concn.

H. G. R.

Phosphatase. VI. Non-osseous origins of serum-phosphatase. Its increase after ingestion of carbohydrates. A. BODANSKY (J. Biol. Chem., 1934, 104, 473—482).—The serum-phosphatase of fasting dogs made hyperglycaemic by the administration of dextrin or glucose increases, whilst the serum-inorg. P decreases; meat ingestion under the same conditions produces the reverse effects.

H. D.

Serum-phosphatase in the domestic fowl. R. H. COMMON (Nature, 1934, 133, 572; cf. A., 1933, 1326).—Serum-phosphatase determinations on birds at different stages of the reproductive cycle give vals. for cockerels and sexually-immature pullets which are comparable, those for laying and moulting birds being higher.

L. S. T.

Phosphatase. VII. Inorganic phosphorus and serum-phosphatase in new-born puppies. A. BODANSKY (J. Biol. Chem., 1934, 104, 717—726).—Serum-phosphatase (I) averaged about 40 units per 100 c.c. at birth, rapidly increased, and then decreased to 20 units. Highest (I) was found in well-nourished animals, and was associated with a fall of inorg. serum-P and evidence of lipæmia.

H. G. R.

Glucosulphatase. IX. Specificity of the enzyme. T. SODA (Bull. Chem. Soc. Japan, 1934, 9, 83—88; cf. A., 1933, 749).—The enzyme is most active on glucose sulphate. It also hydrolyses, with decreasing activity, mannose sulphate (Ba salt; brucine salt,  $[\alpha]_{5461} - 14.26^\circ$ ) and disulphate (brucine salt);  $\alpha$ -methylglucoside sulphate; invert sucrose sulphate; galactose tetrasulphate and disulphate (brucine salt); and maltose sulphate (Ba salt,  $[\alpha]_{5461} + 97.0^\circ$ ). Sucrose and diisopropylidene-glucose sulphates are still less readily attacked, whilst the enzyme has little or no action on mannitol tetrasulphate, starch disulphate, fructose trisulphate ( $K_3$  salt,  $[\alpha]_{5461} - 5.4^\circ$ ), chondroitinsulphuric acid, or  $Et_2SO_4$ .

E. W. W.

Cerace of the larva of *Galleria mellonella*. H. KRAUT, H. BURGER, and W. VON PANTSCHENKO-JUREWICZ (Biochem. Z., 1934, 269, 205—210; cf. Sieber and Metalnikov, Pflüger's Arch., 1904, 102, 269).—Although glycerol extracts of freshly killed larvæ are rich in lipase, there is no evidence that they contain a cerase capable of hydrolysing myricyl palmitate. Pertzoff (A., 1928, 1054) failed to take account of acid not derived from the wax, hence his results are untrustworthy.

W. McC.

**Determination of pancreatic lipase.** H. STEUDEL (Biochem. Z., 1934, 269, 175—176; cf. A., 1933, 981).—Waldschmidt-Leitz (this vol., 450) overlooks the author's finding that Willstätter's method is applicable only when the degree of hydrolysis is 10—24%, but confirms the inapplicability for certain purposes. W. McC.

[Determination of] ester formation and hydrolysis by the dilatometric method. R. AMMON and K. BARTSCHT (Biochem. Z., 1934, 268, 331—335).—A new dilatometer is tested using the system  $\text{PrCO}_2\text{Bu}^a$  and powdered pig's pancreas. The synthesis of 1 mol. of ester corresponds with a vol. increase of 4.12 c.c. Hydrolysis is accompanied by a decrease in vol., but the results are not quant. P. W. C.

**Limits of specific formation of defence enzymes and their origin.** E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 215—240).—Parenteral injection of the various plasma-proteins into rabbits (I) gives rise to proteinases (II) with sp. action only on the single protein injected, but alterations in the nature of the diet of (I) could not be sharply differentiated by this method. Removal of the spleen (III) or blockage of the reticulo-endothelial system has no effect on the production or specificity of (II). (III)-protein injected into splenectomised (I) gives rise to sp. (II) in the urine. A. E. O.

**Activation of 'papain' by vitamin-C-iron and its inhibition by vitamin-C (ascorbic acid).** E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1934, 223, 127—135).—The hydrolysis of gelatin by papain, which is inhibited by vitamin-C (I) alone, is accelerated by (I) + Fe. Fe cannot be replaced by Mn or Cu; indeed, traces of Cu neutralise the activation. The hydrolysis in presence of (I) + Fe is at first slower than with no addition, acceleration occurring only after some hr. J. H. B.

**Action of rennin on the complex calcium caseinogenate-phosphate.** C. C. CHRISTEN and E. VIRASORO (Anal. Inst. invest. cient. tecn., 1931, 2, 59—69).—The complex is prepared by treating milk-caseinogen with  $\text{Ca}(\text{OH})_2$  suspension and neutralising ( $p_{\text{H}}$  6.5, temp. 10—20°) with  $\text{H}_3\text{PO}_4$ . For the process of coagulation by rennin (I) the product of time and (I) conen. increases slowly as the latter is decreased, whereas for the coagulation of milk the product decreases. H. F. G.

**Crystalline pepsin. VI. Inactivation by  $\beta$ - and  $\gamma$ -rays from radium and by ultra-violet light.** J. H. NORTHROP (J. Gen. Physiol., 1934, 17, 359—363).—The loss in activity towards haemoglobin of cryst. pepsin when exposed to  $\beta$ - and  $\gamma$ -rays from Ra or to ultra-violet light (I) is accompanied by a corresponding decrease in pepsin-protein. The rate of inactivation by (I) depends on the  $p_{\text{H}}$  and is a max. about  $p_{\text{H}}$  2.0. A. L.

**Trypsin of cold- and warm-blooded animals; its optimum temperature and heat-resistance.** C. S. KOSCHTOJANZ and P. A. KORJUIEV (Fermentforsch., 1934, 14, 202—214).—The chief difference between trypsin (I) of cold- and warm-blooded animals lies not in the temp. optimum, but in the heat-resist-

ance (II), which is greater for the latter. The (II) of (I) of arctic fish is < that of fresh-water fish.

A. E. O.

**Equilibrium between active native trypsin and inactive denatured trypsin.** M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1934, 17, 393—398).—The mobile equilibrium between native and denatured trypsin depends on the conen. of acid, alkali, and EtOH and on the temp. The heat of denaturation in 0.01N-HCl calc. from the effect of temp. on the equilibrium const. is —67,600 g.-cal. per mol. A. L.

**Tryptic digestion of collagen.** M. BERGMANN and G. POJARLIEFF (Biochem. Z., 1934, 269, 77—79; cf. A., 1932, 1064; B., 1927, 342, 636).—Until it reaches > 20%, degradation of collagen by pancreatin proceeds proportionally to time. W. McC.

**Tyndallometric method for determination of trypsin.** E. HERZFELD (Mikrochem., 1934, 14, 245—250; cf. A., 1933, 1064).—By progressive dilution with 1%  $\text{NaHCO}_3$ , the min. amount of material to halve the Tyndall effect of a serum-albumin solution after 2 hr. incubation is determined. The limit corresponds with  $3\text{—}4 \times 10^{-9}$  g. of trypsin. J. S. A.

**Effect of parenteral injection of polypeptides on the content of certain polypeptidases in blood-plasma or -serum.** H. HANSON (Fermentforsch., 1934, 14, 189—201).—Repeated parenteral injection of glycyl-*dl*-leucylglycine and *dl*-leucylglycine produces a definite and persistent increase in the hydrolytic power of plasma (I) towards these peptides. The acylase action of (I) is also increased. Injection of triglycylglycine or liver-protein has no marked action on (I)-polypeptidase. An acylase active against chloroacetyl-*L*-tyrosine could not be developed. A. E. O.

**Determination of peptidase action of urine of man and animals.** S. BUADZE (Fermentforsch., 1934, 14, 143—174).—The poly- (I) and di-peptidase (II) activities of urines can be accurately measured at  $p_{\text{H}}$  7.8 (optimum), the respective substrates being peptone and *dl*-leucylglycine. No preliminary conen. of the enzymes is usually necessary. (I) is usually more active than (II).  $\text{H}_2\text{S}$  inhibits (I). A. E. O.

**Enzymic histochemistry. VII. K. LINDERSTRÖM-LANG and H. HOLTER. a. Peptidase in the eggs of *Psammechinus miliaris*.** T. PHILIPSON. b. Division of the mitochondria of the egg on centrifuging (Z. physiol. Chem., 1934, 223, 119—125, 125—126; cf. this vol., 338).—a. When the unfertilised eggs of *P. miliaris* are centrifuged they divide into two fragments, the lighter of which is about five times the size of the heavier (I), but both have the same abs. peptidase action.

b. When the eggs are first treated with Janus green, the stained constituents, at first evenly distributed, collect after centrifuging mainly in (I). J. H. B.

**Digestion in insectivorous plants.** J. DE ZEEUW (Biochem. Z., 1934, 269, 187—195; cf. Stern and Stern, A., 1932, 1064).—Opened (I) and unopened traps from the plants (varieties of *Nepenthes*) contain a catheptic (but not a tryptic) enzyme which acts in acid media only. The tryptic action of the contents of (I) is due to bacteria (*B. fluorescens liquefaciens*, *B. prodi-*

*giosum*, and two others). As a result of chemical (not mechanical) stimulation the glands secrete acid.

W. McC.

**Specific effects of buffers on urease activity.** S. F. HOWELL and J. B. SUMNER (J. Biol. Chem., 1934, 104, 619—626).—At 20° the optimum  $p_H$  for recryst. Jack bean urease (I) acting on 2.5% urea (II) depends on the buffer, being 6.4 for OAc', 6.5 for citrate, and 6.9 for  $PO_4'''$ , whilst with 0.1% (II) the corresponding figures are 6.7, 6.7, and 7.6, respectively. In  $PO_4'''$  buffer, (I) is active from  $p_H$  5 to 9, in citrate buffer from 4.0 to 8.5 and in OAc' buffer from < 3.0 to 7.5. At a given  $p_H$  with any buffer a max. rate is reached as the concn. of (II) is increased, higher concns. being inhibitory. The concn. corresponding with max. rate decreases with increase of  $p_H$ . The concn. of buffer also influences the rate of the reaction. The max. activity occurs in presence of 1.0% (II) and 0.125M-citrate buffer at  $p_H$  6.5.

W. O. K.

**Pigments of a red yeast.** H. FINK and E. ZENGER (Woch. Brau., 1934, 51, 89—93).—Two pigments have been isolated from a red yeast obtained from the air and cultivated on unhopped wort. Pigment I was neutral; it appeared to be a hydrocarbon having some properties in common with carotene and lycopene, but was distinguished from these by crystallographic and spectroscopic examination, and by colour tests with conc.  $H_2SO_4$ , with  $AsCl_3$ , and with  $SbCl_3$ . Pigment II exceeded I in amount; it was acidic and appeared to be an ester of a polycarboxylic acid. It was distinguished from bixin and  $\alpha$ - and  $\beta$ -crocetin crystallographically and spectroscopically, and by colour tests.

I. A. P.

**Yeast autolysis.** H. HAEHN and H. LEOPOLD (Woch. Brau., 1934, 51, 97—100).—Autolysis in alkaline solution reduces the yield of  $NH_2$ -acids although the total acid production is increased.

C. G. A.

**Conversion of the alcoholic fermentation of sugar by yeast into a lactic acid fermentation.** II. E. AUHAGEN and T. AUHAGEN (Biochem. Z., 1934, 268, 247—252).—Under the author's conditions (A., 1933, 1204), AcCHO is present as such, and is not formed in some secondary reaction on adding 2:4-dinitrophenylhydrazine.

P. W. C.

**Formation of malic acid from asparagine by fermentation at different  $p_H$ .** E. GLIMM and M. NITZSCHE (Biochem. Z., 1934, 268, 444—450).—A study of the fermentation at various  $p_H$  shows that more acid reaction tends to the conversion by way of the half amide of oxalacetic acid into malic acid, and more alkaline to the conversion by way of aspartic acid probably into oxalacetic acid and MeCHO.

P. W. C.

**Action of oxygenated yeast on the system amino-acid-aldehyde.** F. LIEBEN and V. GETREUER (Biochem. Z., 1934, 269, 69—76; cf. A., 1923, i, 424; 1932, 1114).—The interaction of glycine (I) and MeCHO in presence of yeast and  $O_2$  leads to increased  $CO_2$  production (II) [as compared with the action when only (I) is absent] and increased growth (III) of dry material of yeast [as compared with the action when only MeCHO is absent]. (II)

is derived from the MeCHO. Similar results are obtained with *d*-alanine, *dl*-phenylalanine, and sarcosine, but not with *dl*-alanine and proline. (II) and (III) are probably interrelated.

W. McC.

**Bios. IX. So-called bios I and II.** Y. HAMAMURA and M. CHIKAMATSU. **X. Distribution of bios in animals.** Y. HAMAMURA and K. OBATA (J. Agric. Chem. Soc. Japan, 1933, 9, 1018—1021, 1090—1094).—IX. Bios II has only a growth-promoting action on yeast; addition of bios I or inositol does not increase its action. There are probably two kinds of bios, one stable and the other unstable to  $Ba(OH)_2$ .

X. Bios is present in abundance in the leaves of plants and in the organs of the fowl, especially the pancreas and liver.

CH. ABS.

**Oxygen as an accelerator in the growth of *Empusa* on flies.** W. A. HIESTAND (Science, 1934, 79, 160).— $O_2$  accelerates the growth of *Empusa* on house-flies.

L. S. T.

**Biochemistry of moulds. III. Metabolic product of *Aspergillus melleus*, Yukawa.** 2. E. NISHIKAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 1059—1063).—Mellein (I) contains no OMe; monoacetylmellein, m.p. 126°, does not give the  $FeCl_3$  reaction. Dinitromellein, m.p. 160°, has  $[\alpha]_D^{25} -508.68$ . When fused with KOH at 200° (I) affords (monobasic) melleic acid (II),  $C_{10}H_{10}O_3$ , m.p. 170° (Ac derivative, m.p. 110°;  $H_2$ -derivative, m.p. 116°; Me ester, m.p. 59°). (I) with KOH at 300° affords 3-hydroxy-*o*-toluic acid. (II) is 2:6-OH·( $C_3H_5$ ) $C_6H_3$ · $CO_2H$  and (I) is the lactone of 6- $\alpha$ - (or  $\beta$ )-hydroxypropylsalicylic acid.

CH. ABS.

**Deuterium oxide and *Aspergillus*.** S. L. MEYER (Science, 1934, 79, 210—211).—Small concns. of  $H^2$  stimulate the vegetative growth and development of *Aspergillus* sp.

L. S. T.

**Nutritional interrelationships between bacteria and moulds.** H. BUCHERER (Zentr. Bakt. Par., 1933, II, 89, 273—283).—In N-free media, *Penicillium glaucum* and *Aspergillus niger* can utilise N fixed by *Azotobacter* (I) and liberated on the death of the bacterial cell. Carbohydrates which are not attacked by (I) in pure culture may be utilised in the presence of the above moulds.

A. G. P.

**Influence of the temperature and water content of soil on the life processes of soil bacteria.** D. FEHÉR (Arch. Mikrobiol., 1933, 4, 447—486).—Organisms concerned in the N cycle and in the decomp. of cellulose in soil are examined. In general, the relationship between bacterial growth and the product of soil temp. (°C.) and  $H_2O$  content (wt.-%) may be expressed as a parabolic function.

A. G. P.

**Influence of the tension of oxygen on the respiration of *Rhizobia*.** C. E. GEORGI and P. W. WILSON (Arch. Mikrobiol., 1933, 4, 543—564).—With *R. trifolii*, *R. leguminosarum*, and *R. meliloti* the glucose (I) consumed, the  $CO_2$  produced from (I), and the rate of respiration increased with increasing partial pressure of  $O_2$  (II). Approx. 60—80% of the (I) used reappeared as  $CO_2$ , the balance being largely utilised in gum formation. The R.Q. of these



cultures was approx. 1, and was independent of (II). With *R. japonicum*, O<sub>2</sub> consumption and CO<sub>2</sub> production were < the above and the (I) consumed increased with decreasing (II). The conversion of (I) into CO<sub>2</sub> was maintained at a high level with small (5%) vals. of (II) if the abs. quantity of O<sub>2</sub> available was sufficient for requirements. A. G. P.

**Stimulative action of yeast extract in the respiration of *Rhizobium*.** R. H. WALKER (Science, 1934, 79, 160—161; cf. A., 1933, 1080).—Yeast extract (I) stimulates O<sub>2</sub> consumption and hence respiration (II) to an extent > any of the N compounds used. The extent of (II) is approx.  $\propto$  the amount of (I) present in the medium. L. S. T.

**Influence of iodine on physiological activities of micro-organisms.** A. ITANO and A. MATSUURA (Ber. Ohara Inst. landw. Forsch., 1933, 6, 73—81).—In small amounts I stimulated certain micro-organisms. Larger proportions were harmful. The optimum I content of media for *Azotobacter chroococcum* (I), *B. subtilis* (II), and *Sacc. cerevisiae* (III) was 0.007%. Lethal doses were 2% for (I) and (II) and 0.5% for (III). A. G. P.

**Growth of *Bacillus megatherium* in relation to the oxidation-reduction potential and the oxygen content of the medium.** G. KNAYSI and S. R. DUTKY (J. Bact., 1934, 27, 109—119).—The factor limiting growth under reduced pressure (> 10 mm.) is the O<sub>2</sub> content, and not the oxidation-reduction potential of the medium. A. G. P.

**Negative oxidation-reduction system of *B. coli*.** L. H. STICKLAND and D. E. GREEN (Nature, 1934, 133, 573).—The catalytic reduction of methylene-blue by H<sub>2</sub> due to an enzyme in *B. coli* (I) (A., 1931, 525) closely resembles the H electrode (II). Examination of the reversibility of this reaction of (I) using 4:4'-dimethyldipyridyl gives observed potentials in agreement with those calc. for (II) under identical conditions. This reversible hydrogenase system of (I) is the most negative oxidation-reduction system known in living cells. L. S. T.

**Bacterial cell metabolism under anaërobic conditions.** H. H. WALKER, C. E. A. WINSLOW, and M. G. MOONEY (J. Gen. Physiol., 1934, 17, 349—357).—A peptone-H<sub>2</sub>O medium saturated continuously with N<sub>2</sub> to produce an aerobic conditions greatly inhibits growth and metabolic activity of *Escherichia coli*. Addition of glucose to the medium under these conditions has no effect during the first hr., but after the second hr. growth is rapid, and at the end of the fifth hr. the no. of organisms increases from 11 × 10<sup>6</sup> to 142 × 10<sup>6</sup>. This growth is accompanied by increased CO<sub>2</sub> production (211 × 10<sup>-11</sup> mg. per cell per hr.) amounting to nearly double the max. vals. obtained under aerobic conditions. A. L.

**Acetic acid bacteria produced in Formosa.** III. S. TANAKA (J. Agric. Chem. Soc. Japan, 1933, 9, 1104—1116).—Five varieties of *B. xylinum*, Brown, were isolated. The membrane produced gave the cellulose reaction. Acid production was 4.4—5.4%. The bacteria assimilated the AcOH produced. CH. ABS.

**Development and structure of acetic acid bacteria.** A. A. BATSHINSKAJA (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1189—1204).—Variations in the shape, dimensions, and internal structure of *B. acetii*, Hansen, with relation to the temp.,  $p_H$ , and composition of the culture medium are recorded. R. T.

**Unknown factor stimulating the formation of butyl alcohol by certain butyric acid bacteria.** E. L. TATUM, W. H. PETERSON, and E. B. FRED (J. Bact., 1934, 27, 207—217).—A substance stimulating the decomp. by bacteria of starch and the production of BuOH (but not of other solvents formed simultaneously) occurs in a no. of plant materials, notably lettuce, cabbage, and orange. The prep. of active extracts is described. The latter are free from protein, glucose, or carbohydrates hydrolysable to glucose. A. G. P.

**Hitherto unknown activators for the growth of lactic acid bacteria.** S. ORLA-JENSEN (J.S.C.I., 1933, 52, 374—379T).—In the course of sterilisation by heat of carbohydrate substrates substances are formed which activate the growth of lactic acid bacteria. The activation is stronger if the source of N (I) (e.g., yeast extract) is sterilised together with sugars, or with AcCHO (II). *Thermobacterium acidophilum* will scarcely ferment sucrose (III) even when (III) and (I) have been sterilised together, but when (I) has been sterilised with (II), (III) is strongly fermented. Furfuraldehyde (IV) is nearly as effective as (II). (IV) is formed from pentoses (V) during sterilisation, but since 0.05% of xylose is as effective as 0.04% of (I) and only a very small part of (V) is converted into (IV) during sterilisation, (V), *per se*, must be able to form activating substances. The latter are probably similar in nature to cozymase. E. C. S.

***Lactobacillus acidophilus*. III. Composition of phosphatide fraction.** J. A. CROWDER and R. J. ANDERSON (J. Biol. Chem., 1934, 104, 487—495; cf. this vol., 453).—Acid hydrolysis of the phosphatide gave glycerophosphoric acid, choline, a cryst. non-reducing *polysaccharide*, m.p. 160—170°,  $[\alpha]_D +72^\circ$ , hydrolysing to *d*-galactose, glucose, and fructose, and a mixture of fatty acids containing palmitic (I) and stearic (II) acids and unsaturated acids which on hydrogenation yielded (I) and (II). H. D.

**Biological occurrence of hydrogen persulphide.** M. BERGMANN (Naturwiss., 1934, 22, 135—136).—The persulphide observed in S bacteria is probably produced from cystine (or glutathione) by elimination of H<sub>2</sub>S<sub>2</sub>. W. O. K.

**Violacein, the violet pigment of *Bacillus violaceus*.**—See this vol., 536.

**Bacterial proteins, with special consideration of gonococcus and meningococcus.** A. K. BOOR and C. P. MILLER (J. Exp. Med., 1933, 59, 63—74).—The toxic action of gonococcus and meningococcus is probably due, chiefly or entirely, to some constituent of the nucleoprotein fraction. Extraction with COMe<sub>2</sub> and Et<sub>2</sub>O in the cold did not appreciably reduce the toxicity of these organisms and their nucleoproteins, and did not alter their immunological behaviour. Cross-precipitin reactions are discussed. CH. ABS.

**Carbohydrates of gonococcus and meningococcus. I. Alcohol-precipitable fraction.** C. P. MILLER and A. K. BOOR (J. Exp. Med., 1933, 59, 75—82).—The EtOH-insol. polysaccharides of gonococcus and meningococcus contain, respectively, 4.2 and 3.7% N; they give no protein reaction and reduce Fehling-Benedict solution only after hydrolysis. They are non-toxic to rabbits and mice, and fail to produce antibodies in rabbits. Both carbohydrates react in high dilution with antipneumococcus serum type III.

CH. ABS.

**Dissociation of certain paratyphoid bacilli. Rôle of variants in the precipitation of calcium sulphite.** M. E. CALDWELL (J. Bact., 1934, 27, 121—161).—Variant cells appear to have the property of pptg. CaSO<sub>4</sub>.

A. G. P.

**Effect of meat-curing solutions on anaërobic bacteria. II. Sodium nitrate.** F. W. TANNER and F. L. EVANS (Zentr. Bakt. Par., 1933, II, 89, 48—54).—In concns. up to 2.21% NaNO<sub>3</sub> did not inhibit *Clostridium botulinum* (types A and B), *C. putrificum*, or *C. sporogenes* on pork infusion or egg-meat media. Higher amounts (to 4.43%) produced irregular inhibitory effects.

A. G. P.

**Effect of chlorides of bases on bacterial growth.** J. P. TODD and I. M. SILLAR (Pharm. J., 1934, 132, 333—334).—Quinine and strychnine hydrochlorides inhibit the growth of non-sporing organisms and of anaërobics and slightly retard that of spore-bearing anaërobics. The effect is not due to the Cl<sup>-</sup>.

C. G. A.

**Soluble specific substance in spirochaetes. E.** HINDLE and P. B. WHITE (Proc. Roy. Soc., 1934, B, 114, 523—529).—A highly sp. sol. haptén (I) is obtained from cultures of *Spirochaeta biflexa* by pptn. from acid solution with COMe<sub>2</sub>. (I) ppts. homologous antisera only at a dilution of 1 in 10<sup>5</sup>, gives a positive Molisch test and a negative biuret reaction. (I) inhibits antibody formation in rabbits subsequently injected with large doses of *S. biflexa*.

C. G. A.

**Influence of the mol. wt. of the antigen on the proportion of antibody to antigen in precipitates.** W. C. BOYD and S. B. HOOKER (J. Gen. Physiol., 1934, 17, 341—348).—The antibody-antigen ratios of pneumococcus S III haptén, ovalbumin, hæmoglobin, pseudoglobulin, and L-hæmocyanin, calc. on the assumption that at the equivalence point in sp. precipitin reactions the antigen mol. is completely covered with a single layer of antibody-globulin mols., agree fairly well with the observed vals.

A. L.

**Utilisation of carbohydrates and salts of organic acids by *C. diphtheriae* in the production of toxin of high Lf value.** G. F. LEONARD and A. HOLM (Amer. J. Pharm., 1934, 106, 97—101).—The addition of maltose (0.45%) and NaOAc (0.75%) to a medium containing lactate, glucose, and peptone ensures the regular production of a uniform toxin with min. lethal dose 0.001 c.c., L+ 0.04 c.c., and Lf val. of 32—34 units per c.c. Na succinate, replacing NaOAc, gives inferior results.

A. E. O.

**Recovered diphtheria anatoxin.** N. N. SPASSKY and H. J. ODRINA (Ann. Inst. Pasteur, 1934, 52, 308—315).—The anatoxin is treated with diphtheria serum

to max. pptn., centrifuged, and the ppt. washed with 0.35% aq. NaCl and finally dissolved in aq. HCl at p<sub>H</sub> 6.2. Heating at 82° for 20 min. to destroy any antitoxin present yields solutions which, unlike toxin + antitoxin preps., do not inhibit the growth or carbohydrate metabolism of embryonic chick's heart, and are effective in the immunisation of children.

F. O. H.

**Antigenic power of a lecithin-diphtheria anatoxin complex.** C. E. PICO and F. MODERN (Folia biol., 1933, 1, 132—143).—Lecithin (I) decreases the toxicity of diphtheria toxin. A precipitin for (I) is present in the blood of rabbits given injections of (I).

CH. ABS.

**Lecithin in fractionation of antitoxic sera and transformation of pseudo- into eu-globulin. I.** PIROSKY and F. MODERN (Anal. Assoc. Quim. Argentina, 1933, 21, 142—148).—Addition of varying amounts of lecithin to antidiphtheria sera does not alter the proportion of activity pptd. by certain amounts of Na<sub>2</sub>SO<sub>4</sub>. Anaphylaxis experiments with guinea-pigs show no difference in the antigenic properties of pseudo-globulin mixed with lecithin and no indication of conversion into euglobulin.

R. K. C.

**Protein fractions of the human strain (H-37) of tubercle bacillus.** M. HEIDELBERGER and A. E. O. MENZEL (J. Biol. Chem., 1934, 104, 655—665).—From the proteins of the defatted strain a no. of fractions, nucleoprotein in nature, have been obtained, the immunological reactions of which indicate the presence of < two distinct protein antigens.

W. O. K.

**Tubercle bacilli. I. Extraction and fractionation of the lipins of heat-killed bacilli.** M. MACHEBŒUF, G. LÉVY, and N. FETHKÉ [with J. DIERYCK and A. BONNEFOI] (Ann. Inst. Pasteur, 1934, 52, 277—307).—A mixture of heat-killed human and bovine bacilli was washed with H<sub>2</sub>O and 1 kg. was successively extracted with COMe<sub>2</sub> (fraction A), warm 96% EtOH [yielding on cooling insol. (C) and sol. (B)], Et<sub>2</sub>O (D), and CHCl<sub>3</sub> (E). A (11.0 g.) contained 67.3% of fatty acids and yellow pigments, but no reducing substances, cholesterol, and haptens (I). B (7.1 g.) yielded on further fractionation a wax-like mixture (P, 2.1%), m.p. 105—107°, a (I)-rich mixture, m.p. 145° (P 4.9, N 1.9%, fatty acids 67%, reducing sugars 6.25%; a non-sp. antibody), a mixture of esters of glycerol and other alcohols the purified glycerides (m.p. 30—32°) of which were free from P. C (5.4 g.) contained two non-acid-resisting fractions, m.p. 220—225° and 41—42°, 1.9 and 1.37% P, respectively, and two acid-resisting fractions (II), m.p. 50—55° and 45—52°, 0.27 and 0.45% P, respectively. Treatment of (II) with C<sub>6</sub>H<sub>6</sub> followed by EtOH-HCl, etc., afforded a waxy substance, m.p. 57—58° (85.6% fatty acids; 10.8% unsaponifiable). D (5.2 g.) on dissolution in C<sub>6</sub>H<sub>6</sub> and pptn. by EtOH yielded a fraction, m.p. 243—244°, mol. wt. 4—5 × 10<sup>3</sup> (12% fatty acids; 40% unsaponifiable), and a mixture, m.p. 45° (12% fatty acids; 73% unsaponifiable). E (1.8 g.) treated with EtOH, Et<sub>2</sub>O, and CHCl<sub>3</sub> gave a fraction, m.p. 204°, P 0.77%, which on alkaline hydrolysis in C<sub>6</sub>H<sub>6</sub>-EtOH yielded a pentose (xylose?), but no glycerol.

F. O. H.

**Peptone water as diluent in bacteriological investigation.** E. L. K. DAGNEAUX (Chem. Weekblad, 1934, 31, 155—156).—Peptone solution can be used as diluent in the determination of the bacterial count (I) of milk. The tubes are incubated at 37° and (I) is determined by Erlich's indole-titre method. In 98% of the cases examined (I) is a measure of *B. coli*. S. C.

**Bacteriophage.** F. HODER (Arch. Mikrobiol., 1933, 4, 589—635).—A review with extensive bibliography. A. G. P.

**[Are the viruses] enzymes or organisms?** H. BECHHOLD (Kolloid-Z., 1934, 66, 329—340; 67, 66—79).—Determination of the size of subvisible viruses by ultra-violet photomicrography, ultrafiltration, and centrifuging indicates that they are organisms.

E. S. H.

**Differentiation of hormones by the Reid Hunt reaction, the Aschheim-Zondek reaction, and the œstrus reaction, especially in ovarian cyst liquids.** H. O. KLEINE and H. PAAL (Arch. Gynäkol., 1933, 154, 147—160; Chem. Zentr., 1933, ii, 2546—2547).—Pituitrin (I), adrenaline (II), and œstrin (III) give a positive Reid Hunt reaction (IV), but they do not activate the thyroid. (II) lacks the protective action of (I), (III), and thyroxine. After several hrs.' heating in an O<sub>2</sub> stream, (I) no longer gives (IV), but (II) and (III) do so. H. J. E.

**Production by the stomach of a hormone stimulating the alimentary canal of birds.** P. NOLF (Bull. Acad. roy. Belg., 1934, [v], 20, 204—206).—On stimulation of the vagus nerve, the stomach secretes a hormone which increases the muscular tonus of the intestine. H. G. R.

**Mode of action of thymocrescin.** H. BACHMANN (Biochem. Z., 1934, 268, 272—284).—Thymocrescin (I) after repeated pptn. with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> still possesses a powerful growth-promoting action, the effect being greater on the sexual than on the total organs. (I) is not identical with vitamin-B<sub>2</sub>, but does increase the growth-promoting action of the pituitary hormone. P. W. C.

**Metabolic effects of intravenous injection of callicrein.** R. W. NEFFLEN and A. SZAKÁLL (Biochem. Z., 1934, 269, 80—91).—In dogs, the injection (I) causes decrease to zero, followed by increased urinary excretion of P, increase followed by decrease in diuresis, and a parallel variation in urinary N excretion. These changes do not affect the daily P and N balances. The min. dose of callicrein (II) required to produce general metabolic changes (III) is 7 units. After repeated (I) of large doses acquired tolerance is exhibited. Pancreatectomy is without effect on (III) caused by (II). There are great individual differences as regards magnitude of dose required to produce (III). The kind of food consumed is immaterial. W. McC.

**Morphological changes produced by intravenous injection of callicrein as cause of metabolic changes.** A. SZAKÁLL (Biochem. Z., 1934, 269, 92—114).—Administration (I) of large doses of callicrein (II) to dogs causes rigor accompanied by decrease in the leucocyte content of peripheral blood, rise in body temp., followed by a fall and long-continued

leucocytosis. Small doses also cause typical changes in the blood, but no rigor. The inorg. P content of the blood first falls and then rises. These and other changes result from the increased permeability of the capillary vessels (III) which is the primary consequence of (I). (II) is probably a normal constituent of the organism, in which it acts as a regulator of the state of (III). W. McC.

**Action of parathormone on basal metabolism.** G. VON LUDÁNY and L. LENGYEL (Biochem. Z., 1934, 269, 150—157).—In normal (I) rats and in those (II) suffering from chronic rickets injection of parathormone leads to a 10—15% decrease in the O<sub>2</sub> consumption (III) and an increase (IV) in the Ca content (V) of the blood-serum, both lasting 8 hr. During the succeeding 10 hr. (III) rises by as much as 20%. In (II) (V) is much < in (I). The % (IV) in (I) = that in (II), but the abs. (IV) in (I) is > that in (II). The effects on the gaseous metabolism are a consequence of the increase in (V). W. McC.

**Histological changes in the bone responsible for the action of parathyroid hormone on the calcium metabolism of the rat.** L. I. PUGSLEY and H. SELYE (J. Physiol., 1933, 79, 113—117).—In rats 110—115 days old administration of 20 units of parathormone daily causes an immediate increase in serum- and urinary-Ca. Both vals. return to normal after 4—6 days. During the period of high Ca excretion an increased no. of osteoblasts and osteoclasts (I) appear in the bones, and the return to the normal excretory level coincides with the disappearance of (I). NUTR. ABS. (m)

**Effect of parathyroid hormone and of irradiated ergosterol on the calcium content of the parotid saliva of the dog.** L. ANDREYEV and L. I. PUGSLEY (J. Physiol., 1933, 80, 96—100).—The Ca content of parotid saliva (I), secreted after stimulation with meat powder, NaCl, or HCl, was three times that of the serum (II). Stimulation with pilocarpine hydrochloride produced (I) with a Ca content only a little > twice that of the (II). The rise in (II)-Ca following parathormone injection or irradiated ergosterol ingestion was in actual amount < the accompanying rise in the Ca content of the (I). NUTR. ABS. (b)

**Precipitation of insulin in aqueous solution by hydrochloric acid.** N. LARA (Folia biol., 1933, 1, 141—142).—The sample lost 18% of its total activity, but the purified material contained 20 units per mg. (dry) instead of 13. CH. ABS.

**Carbohydrate metabolism of the rabbit. I. True blood-sugar value in convulsions due to insulin administration.** L. B. DOTTI (J. Biol. Chem., 1934, 104, 535—539).—The true (fermentable) sugar val. of the blood of a rabbit in convulsions is approx. zero, although the amount of non-fermentable reducing substance (I) is the same in normal blood as in blood during convulsions. (I) in rabbit blood is independent of the total reducing power, and is not affected by doses of insulin large enough to produce convulsions. C. G. A.

**Hypoglycæmic action of insulin after vagotomy or atropinisation.** K. WACHHOLDER (Arch. exp. Path. Pharm., 1934, 175, 62—66).—Bilateral

vagotomy in rabbits is followed by a short period during which the hypoglycaemic response (I) to insulin is somewhat diminished [probably due to the narcotic used for the operation (II)], and then by a period when (I) is normal; some days after (II), (I) is much > the normal. Large doses of atropine cause an increased (I), probably due to inhibition of convulsions.

F. O. H.

**Influence of insulin and adrenaline on the blood-creatinine, -creatinine, and -phosphate.** L. RIGÓ and K. FREY (Arch. exp. Path. Pharm., 1934, 175, 8—13).—Injection of insulin (0.25—0.75 unit per kg.) or adrenaline (0.05—0.5 mg. per kg.) into dogs produces a fall in the total creatinine (I), creatinine, and inorg. P levels of the blood, no diminution occurring in the preformed (I) or total acid-sol. P. F. O. H.

**Adrenaline excitation in insulin hypoglycaemia and in Pal's vascular crises.** B. KUGELMANN (Klin. Woch., 1933, 12, 1488—1489; Chem. Zentr., 1933, ii, 3445).—The hypoglycaemia following insulin (I) is accompanied by a series of vasomotor disturbances, which are a secondary effect due to increased entry of adrenaline into the blood-stream. Pal's vascular crises have the same cause. The disturbances may often be stopped by administering Gynergen simultaneously with (I). H. J. E.

**Action of adrenaline on oxidations in isolated cells.** A. HODEL (Biochem. Z., 1934, 268, 285—296).—The respiration of a slice of tissue in Ringer's solution is unaffected by addition of adrenaline, but is greatly increased by addition also of a little serum. The activator present in serum passes into the dialysate, and is inactivated by boiling for 5 min. The dialysate also increases the effect of Na lactate on the O<sub>2</sub> utilisation. P. W. C.

**Cortical hormone requirement of the adrenalectomised dog, and method of assay.** J. J. PFIFFNER, W. W. SWINGLE, and H. M. VARS (J. Biol. Chem., 1934, 104, 701—716).—The individual cortical requirement (I) of adrenalectomised dogs varies by approx. 100% and by about 25% for the same animal on check assays. (I) remains steady over 16 months, is not influenced by sex, but is increased by fasting. Oral administration is < 8% as efficient as subcutaneous; in the latter case the hormone is not excreted in the urine, nor is there any demonstrable storage. H. G. R.

**Effects of administration of iodide and diiodotyrosine on iodine and thyroxine content of thyroid.** G. L. FOSTER (J. Biol. Chem., 1934, 104, 497—500).—Thyroxine (I) was determined in the thyroids of rats treated with anterior pituitary extracts and subsequently injected with KI or diiodotyrosine (II), by a micro-adaptation of the Leland-Foster method (A., 1932, 432). There is no difference in the rates of return of total I or (I) with administration of either KI or (II). H. D.

**Action of thyroxine on tissue respiration.** J. A. DYE (Amer. J. Physiol., 1933, 105, 518—524).—Thyroidectomy in young pups leads to a 25% decrease in the O<sub>2</sub> consumption (I) of surviving muscle strips. Thyroxine (II) administration, on the other hand, leads to an increased (I) by similar tissues. In producing

this increased oxidative capacity (II) acts not directly but indirectly to increase the amount, potency, or effectiveness of the cell respiratory catalysts.

NUTR. ABS. (m)

**Effect of thyroxine on the metabolism of isolated normal and malignant tissue.** O. O. MEYER, C. McTIERNAN, and J. C. AUB (J. Clin. Invest., 1933, 12, 723—736).—Administration of thyroxine (I) to mice produces an increase of about 20% in the O<sub>2</sub> consumption (II) of liver tissue, and a definite increase in anaerobic glycolysis, but no significant change in R.Q. The (II) of transplanted sarcoma No. 180 (III) is depressed by 25% in about 80% of cases; CO<sub>2</sub> production and aerobic glycolysis are not significantly affected. The results with carcinoma No. 63 are similar. Denervation of kidneys makes no difference to the (I) effect on (II), so that the effect of (I) on tumour metabolism cannot be due to lack of nerve supply, but to some factor within the tumour tissue. (I) seems to inhibit slightly the growth of (III). NUTR. ABS. (m)

**Relation between the thyreotropic substance of the anterior pituitary lobe and the adrenal capsule.** A. LOESER (Klin. Woch., 1933, 12, 1614; Chem. Zentr., 1933, ii, 3444).—In guinea-pigs, the thyroid (I) of which has been removed, injection of the thyreotropic hormone (II) causes no hypertrophy of the adrenal capsule (III). (II) therefore acts on (III) through (I). The hormone from (I) alone causes enlargement of (III). H. J. E.

**Metabolism hormone of the anterior pituitary lobe.** H. MAGISTRIS (Wien. klin. Woch., 1933, 46, 908—911; Chem. Zentr., 1933, ii, 3443).—The properties and action of the hormone (I) ("orophysin") which regulates fat metabolism are described. A rabbit unit for standardising (I) is defined. H. J. E.

**Hormones of the anterior lobe of the pituitary gland.** ANON. (Nature, 1934, 133, 401—403).—A summary of the work of the University of California school. L. S. T.

**Blood-fat-lowering pituitary substance "lipopittrin."** W. RAAB and E. KERSCHBAUM (Z. ges. exp. Med., 1933, 90, 729—749; Chem. Zentr., 1933, ii, 3444).—The lipopittrin (I) content of a series of pituitary (II) preps. has been examined. (I) is especially abundant in "pituisan," in thyreotropic anterior (II) hormone, and in anterior (II) extract. (I) is more abundant in the anterior (II) than in the posterior (II). (I) is not identical with any known hormone from (II). H. J. E.

**Melanophore hormone.** III. F. G. DIETEL (Klin. Woch., 1933, 12, 1358—1364; Chem. Zentr., 1933, ii, 2547—2548; cf. A., 1933, 869).—The melanophore hormone is not identical with any other active substance from the posterior pituitary lobe. It is less sol. in BuOH and more sol. in EtOH than the other materials, and differs from them in resistance to alkalis and in its diffusion through collodion filters. In cold-blooded animals the action is limited to the expansion of the melanophores. H. J. E.

**Melanophore hormone and the eye.** A. JORES (Klin. Woch., 1933, 12, 1599—1600; Chem. Zentr.,

1933, ii, 3442—3443).—An eye treated with a solution of the melanophore hormone (I) exhibits a more rapid adaptation to the dark. The increased rate of adaptation is not related to the quantity of (I). Rabbits kept in the dark show a much larger content of (I) in the blood and the eye than when kept in the light. The pituitary of a cat contains sixty times as much (I) as that of the hen, showing the amount of (I) to be related to the ability of an animal to see in the dark.

H. J. E.

**Oxytocic hormone of the pituitary gland.** I. B. C. GUHA and P. N. CHAKRAVORTY (Indian J. Med. Res., 1933, 21, 429—436).—The oxytocic principle is most stable (1 hr. autoclaving at 1 atm.) at  $p_{H}$  3—5. It is not adsorbed by fuller's earth ( $p_{H}$  1.5 or 4.5) or kieselguhr ( $p_{H}$  4.5). The effects of various reagents have been investigated.

CH. ABS.

**Content of oxytocic hormone in the human pituitary gland.** A. JORES and E. ZSCHIMMER (Arch. exp. Path. Pharm., 1934, 174, 715—722).—The oxytocic hormone (I) of human pituitary glands (II) does not rapidly disappear after death. The content of (I) in whole (II) or in the posterior lobe (III) alone varies with age (being greatest during puberty and persisting during old age), but not with sex. The anterior lobe has a content of (I) < that of (III), the highest content being in the most anterior region. The pars intermedia probably plays no part in the formation of (I).

F. O. H.

**Does an increase in oxytocic hormone occur during pregnancy?** A. JORES and V. VON WITTERN (Arch. exp. Path. Pharm., 1934, 174, 723—726).—During pregnancy in rabbits the content of oxytocic hormone in the pituitary gland increases approx. tenfold. The phenomenon occurs to a smaller extent in multipara.

F. O. H.

**Effect of pitressin and pitocin on oxygen consumption of excised tissue.** M. H. PINCUS (Proc. Soc. Exp. Biol. Med., 1933, 30, 1171—1174).—Pitressin in low concn. increased, and in high concn. lowered, the  $O_2$  consumption. Various tissues have different activity thresholds. Pitocin gave inconclusive results.

CH. ABS.

**Action of posterior pituitary preparations on liver-glycogen.** P. GÖMÖRI and E. CSOMAY (Arch. exp. Path. Pharm., 1934, 175, 17—22).—The injection into rats of "onasthin" (a prep. of the oxytocic hormone) and "tonephin" (a prep. of the pressor substance) produces diminutions of 64 and 74%, respectively, in the liver-glycogen.

F. O. H.

**Separation of the gonadotropic hormone of the anterior pituitary lobe in functional disturbances of the female sex glands.** C. KAUFMANN and O. MÜHLBOCK (Klin. Woch., 1933, 12, 1480—1483; Chem. Zentr., 1933, ii, 3443).—In severe functional disturbances with prolonged amenorrhœa, the separation of the gonadotropic hormone is not increased, but corresponds with the normal relations.

H. J. E.

**Excretion of ovary-stimulating hormone in the urine during pregnancy.** D. P. MURPHY (Surg. Gynecol. Obstet., 1933, 56, 914—917).—The amount of hormone secreted in 24 hr. in the urine of

pregnant women ranged from < 100 to 12,000 rabbit units, the amount being usually < 2000 units. The individual daily excretion is relatively const.

CH. ABS.

**Female sexual hormone. XI. Determination of the constitution of the follicular hormone.** II. Degree of saturation and aromatic character. A. BUTENANDT and U. WESTPHAL (Z. physiol. Chem., 1934, 223, 147—168; cf. A., 1933, 870).—Follicular hormone (I), solubility in  $H_2O$ , 0.00021%, forms with quinoline a cryst. mol. (1:1) compound, decomp. < 200°, clears 230°, readily decomposed by dil. HCl, which facilitates purification. Hydrogenation (PtO<sub>2</sub>) of the deoxyhormone (II) gives *hexahydrodeoxyhormone*,  $C_{18}H_{20}OH$ , m.p. 110°, + $H_2O$ , m.p. 82—85°, clears 96°,  $[\alpha]_D -2.8^\circ$  in EtOH. The hydrate of (I) yields, in addition to the hexahydrotriol (A., 1932, 781), *hexahydrodeoxyhormone hydrate* (III),  $C_{18}H_{30}O_2 (+0.5H_2O)$ , m.p. 153°,  $[\alpha]_D -12.2^\circ$  in EtOH (*diacetate*, m.p. 84°), and *isohexahydrodeoxyhormone hydrate* (IV), m.p. 162° (*diacetate*, m.p. 131°). By distillation with  $KHSO_4$  in vac., (III) and (IV) gave *hexahydrodeoxyhormone*,  $C_{18}H_{28}O$ , and *isohexahydrodeoxyhormone (semicarbazides)*, m.p. 262.5° and 278.5°, respectively. (II), m.p. 134°,  $[\alpha]_D +89^\circ$  in EtOH (*Me ether*, m.p. 76.5°,  $[\alpha]_D +85^\circ$  in EtOH), obtained (Wolff-Kishner) from (I), was identical with that obtained by Clemmensen reduction (cf. lit.). Determinations of sp. exaltations of mol. refraction indicate that (I) has only three double linkings. Therefore (I) has a benzene ring (with OH) and three reduced rings, the saturated hydrocarbon on which it is based being a 4-ring system  $C_{18}H_{30}$ . The dissociation consts. for (I) and its hydrate are  $0.44$  and  $0.77 \times 10^{-9}$ , respectively.

J. H. B.

**Estrogenic hormone in the urine of the stallion.** B. ZONDEK (Nature, 1934, 133, 494; cf. this vol., 332).—The biological reactions characteristic of the follicular hormone are exhibited by the estrogenic hormone of the urine of the stallion. The view that the metabolism of the sex hormones is, in the main, the same in both sexes, and that the male sex hormone is first synthesised and then converted into the female hormone, is advanced.

L. S. T.

**Female sexual hormone (folliculin).** B. ZONDEK (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 24, 5 pp.; cf. A., 1931, 878).—Stallion's urine (I) (which contains 6—8 units per litre of male sexual hormone) contains an average of 42,000 and that of non-pregnant mares < 500 mouse units of folliculin (II) per litre; the blood contains only small amounts. That the testes (III) are concerned with the formation of (II) is indicated by the low content (< 400 units per litre) of (II) in gelding's (I). Implantation of 0.05—0.10 g. of horse's (III) into spayed mice produces œstrus. Extraction with  $COMe_2-C_6H_6$  of (III) yields 54,000 units of (II) per kg. Man and male animals other than the horse excrete < 200 units per litre, whilst ox (III) contain < 50 units per kg. (II) is extractable with  $Et_2O$  or  $C_6H_6$  from stallion's (I) only after a short heating with acid.

F. O. H.

**Follicular hormone content of human urine.** H. BORCHARDT, E. DINGEMANSE, and E. LAQUEUR (Naturwiss., 1934, 22, 190).—The follicular hormone

content of human urine was determined in various cases by extraction with  $C_6H_6$  of (a) neutral urine, (b) urine after acidifying to  $p_H$  3, and (c) urine after addition of 150 c.c. of 25% HCl per litre. The hormone appears to exist in different urines in different forms.  
A. J. M.

**Separation of the male and female sexual hormones.** O. O. FELLNER (Klin. Woch., 1933, 12, 1374; Chem. Zentr., 1933, ii, 2547).—The male hormone is dissolved from a mixture of the two by conc. acids, in which the female hormone is insol. or sparingly sol. More of the male hormone is extracted from organs by acidified EtOH than by neutral EtOH,  $C_6H_6$ , or  $COMe_2$ .  
H. J. E.

**Effect of alkali on the testicular hormone.** T. F. GALLAGHER and F. C. KOCH (J. Biol. Chem., 1934, 104, 611—617).—Treatment of the male hormone (I) from bull testis with boiling 3.3% KOH in EtOH results in loss of activity, but similar treatment of male (I) from human male urine produces no loss. This loss occurs with (I) from testis even in presence of urine hormone, indicating that the difference is not due to the presence in urine of a protective substance but that the two hormones are different compounds.  
W. O. K.

**Tests on male sexual hormone with fish.** E. GLASER and O. HAEMPEL (Klin. Woch., 1933, 12, 1491—1494; Chem. Zentr., 1933, ii, 3443).—Polemical against Zondek and Krohn (A., 1933, 319).  
H. J. E.

**Antagonism between thyroxine and vitamin-A.** H. FASOLD and H. PETERS (Z. ges. exp. Med., 1933, 92, 57—62).—Hypervitaminosis-A in the rat could be prevented or cured by thyroxine (I). Conversely a solution of vitamin-A (II) in arachis oil (III), or (III) by itself, prevented the toxic action of (I) and permitted the storage in the liver of carotene and (II), but not of normal amounts of fat and glycogen.  
NUTR. ABS. (b)

**Biological activators and inhibitors.** H. VON EULER (Arkiv Kemi, Min., Geol., 1934, 11, A, No. 12, 7 pp.).—The compensation of the loss in body-wt. due to thyroxine administration to rats on a carotene-free diet by feeding of  $\beta$ -carotene is confirmed (cf. A., 1932, 782). The functions of catalytic and oxidation-reduction activators and inhibitors (e.g., Cu, KCN,  $H_2S$ , ascorbic acid, glutathione) in enzyme and other systems are discussed.  
F. O. H.

**Biological action of vitamins.** H. VON EULER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 19, 6 pp.). Carotene increases the resistance of rats to an infection of *B. haemosepticum* without any concomitant increase in antibody formation in the serum. Vitamin-C produces in rats a protective action against pneumococcal infection. Other anti-infective properties of vitamins are discussed. Rats on a normal diet experience a max. growth during March and April and a min. from October to February (cf. A., 1932, 886, 1294).  
F. O. H.

**Vitamin-A in Indian fish-liver oils.** A. R. GHOSH, P. N. CHAKRAVORTY, and B. C. GUHA (Indian J. Med. Res., 1933, 21, 441—446).—The vitamin-A potencies by the Carr-Price colorimetric technique

were for the oils of chital, shilong, kalibaas, dhain, and ar (fresh- $H_2O$  fishes of Bengal) > for cod-liver oil.

NUTR. ABS. (b)

**Canned strained vegetables as sources of vitamin-A.** F. HANNING (J. Amer. Dietetic Assoc., 1933, 9, 295—305).—Vegetables canned after being cooked anaerobically for just long enough to make straining possible were tested biologically; 20 mg. of spinach, 40 mg. of carrot, and 50 mg. of tomato thus treated contained > one Sherman unit of vitamin-A; 250 mg. of green beans contained one, and 150 mg. of green peas, so cooked, < one, unit.

NUTR. ABS. (b)

**Vitamin-A content of different milks and milk products.** R. DEBRÉ and A. BUSSON (Compt. rend. Soc. Biol., 1933, 114, 1297—1299).—The vitamin-A (I) contents of various milks were compared. The (I) was extracted by the alkali digestion method. Doses corresponding with 3.5 c.c. of fresh or boiled cow's milk sufficed for slow growth in rats. Human milk was ineffective at doses corresponding with 3 c.c., but effective at 6 c.c. Doses corresponding with 6 c.c. of sweetened condensed milk, 4.5 c.c. of reconstituted dried milk, or 6 c.c. of buttermilk were ineffective.

NUTR. ABS. (b)

**Yellow pigmentation of the milk of thyroid-ectomised goats.** H. FASOLD and E. R. HEIDEMANN (Z. ges. exp. Med., 1933, 92, 53—56).—Goat's milk normally contains vitamin-A (I) but no carotene (II), although the diet is rich in (II). After thyroidectomy there was (II) but no (I). This was attributed to inability to transform (II) into (I) in the absence of the thyroid secretion.

NUTR. ABS. (b)

**Crystalline carotene in the cow's ovary.** V. DEMOLE (Arb. Ungar. biol. Forsch.-Inst. Tihany, 1933, 6, 230—231).—Cross-sections of cow's ovary fixed in formalin, lightly stained with hæmatoxylin, and mounted in glycerol, showed small red crystals in the corpora rubra and in the interstitial tissue. The crystals *in situ*, or extracted with fat solvents, gave the Carr-Price reaction. The carotene probably crystallises from the cell-fat in the process of degeneration of the corpora lutea.

NUTR. ABS. (b)

**Vitamin-A required by pullets for maintenance and egg production.** B. M. SHERWOOD and G. S. FRAPS (Vet. J., 1933, 89, 474—477).—The amount of vitamin-A (I) which was needed to support egg laying in hens was much > that needed for maintenance of wt. Yellow corn, ordinary lucerne meal or lucerne leaf meal, or other sun-cured green feeds did not supply sufficient (I), but green grass or green growing plants did.

NUTR. ABS. (b)

**Effect of quantity and composition of diet on the course of vitamin-B<sub>1</sub> deficiency.** H. G. K. WESTENBRINK (Arch. Néerland. Physiol., 1934, 19, 94—115).—Polyneuritis in pigeons is manifest sooner on a fat-poor, carbohydrate-rich, vitamin-B<sub>1</sub>-free (I) diet than on a fat-rich, carbohydrate-free, (I) diet.

C. G. A.

**Disappearance of vitamin-B<sub>1</sub> from the organs of pigeons on vitamin-B<sub>1</sub>-free diets.** Comparison of vitamin-B<sub>1</sub> contents of organs of rats and pigeons. H. G. K. WESTENBRINK (Arch. Néerland.

Physiol., 1934, 19, 116—121).—Vitamin- $B_1$  (I) disappears from all the organs of pigeons (II) in 13 days whether on carbohydrate-rich or fat-rich diets. The heart and brain of normal (II) contain less (I) than the muscle (III). In rats (III) contains < other organs.

C. G. A.

**Vitamin- $B_2$  and the pellagra-like dermatitis in rats.** P. GYÖRGY (Nature, 1934, 133, 498—499).—The “pellagra-like” dermatitis (I) of rats is not produced by a lack of vitamin- $B_2$  as isolated in flavin pigment. (I) can be produced more readily, and unaccompanied by non-sp. and non-characteristic secondary symptoms, in presence of  $B_1$  (possibly contaminated with  $B_4$ ) and  $B_6$ . It can be cured by administration of the  $B_1+B_2$  eluate from the C adsorbate from yeast extract. This antidermatitis factor is not identical with  $B_4$  and as a “rat-pellagra-preventive factor” it is temporarily named vitamin- $B_6$ . Administration of  $B_1+B_4(+B_6)$  produces skin changes, but they are non-sp., mostly trivial, and never pellagra-like. They can be cured by  $B_2$ . Vitamin- $B_2$ , the antidermatitis factor, has thus been separated into two components, the real vitamin- $B_2$  (flavin) and vitamin- $B_6$ .

L. S. T.

**Vitamin-A and -C.** H. VON EULER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 18, 6 pp.).—The anterior and posterior lobes of ox-pituitary glands contain 1.0—1.5 mg. of ascorbic acid (I) (determined by 2:6-dichlorophenol-indophenol reagent) per g. of wet tissue. (I) sometimes occurs in the lens of the eye, whilst urine of pregnancy contains the same amount as normal urine. Serum (horse and pig, but not ox) contains 2 mg. per litre. Pig's bile has a reducing val. equiv. to 0.7 mg. of (I) per c.c. The corpora lutea of pig's and cow's ovaries contain 1.8 and 1.4 mg. per g., respectively. The berries of mountain ash and hawthorn have a high content of (I) (0.5 mg. per g. with the former). The presence of carotenoids in the above sources of (I) is discussed.

F. O. H.

**Glucoreductone for standardisation of 2:6-dichlorophenol-indophenol solutions for determination of ascorbic acid.**—See this vol., 510.

**Chemistry of the antirachitic vitamins.** O. RYEN (Tidsskr. Kjemii, 1934, 14, 26—31).—A lecture.

H. F. H.

**Vitamin-D.** V. Determination of the antirachitic power of sunlight. A. JENDRASSIK and S. PAPP (Biochem. Z., 1934, 268, 364—368).—An apparatus which permits the irradiation of a solution of ergosterol under standardised conditions is described and tables show the biological activity in international units for varying times and with varying distance from the light source. The apparatus was used for the determination of the antirachitic power of sunlight from 1932 to 1933 in Budapest, and the results are given in the form of a graph which shows a very sharp max. in June.

P. W. C.

**Effect of increased vitamin-D administration on the glutathione content of the blood. (Behaviour of glutathione in the fasting condition.)** H. HESSE (Biochem. Z., 1934, 268, 304—313).—Neither administration to rabbits of increased amounts of vitamin-D nor 48 hr. starvation has any effect on,

whilst toxic doses of the vitamin decrease, the blood-glutathione content.

P. W. C.

**Action of irradiated ergosterol on blood-calcium in chronic hypoparathyroidism.** F. MATHIEU (Compt. rend. Soc. Biol., 1933, 114, 1375—1377).

NUTR. ABS. (b)

**Carbon assimilation by *Chlorella* in Windermere.** L. LOOSE, W. H. PEARSALL, and F. M. WILLIS (Proc. Leeds Phil. Soc., 1934, 2, 519—524).—The increase of dry wt. of cultures of *C. vulgaris* in synthetic medium containing  $\text{NaHCO}_3$  as C source suspended at varying depths in the lake was directly proportional to the intensity of light at the given depth. Photosynthesis balances respiration at approx. 10 m. deep. The rate of cell division is highest at the greatest depth. The rates of mortality and cell-growth are highest at the surface.

C. G. A.

**Age of plants and the photoperiodic reaction.** M. C. TSCHAJLACHJAN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 306—314).—The sensitivity of millet plants to variations in the duration (I) of diurnal illumination is greatest for sprouts and month-old plants. Increasing (I) to 24 hr. has only an insignificant effect, whilst diminishing (I) from 18 to 10 hr. daily leads to marked differences in the dimensions and habitus of plants of the above ages.

R. T.

**Chemical affinities and hybrids of *Iris*.** H. COLIN and J. CARLES (Compt. rend., 1934, 198, 1257—1258).—Varieties of *Iris* differ widely in starch, fructosan, glucose, tannin, and lipin contents.

R. S. C.

**Growth of *Lupinus albus* seedlings in solutions of some amino-acids.** D. I. MACHT (Amer. J. Bot., 1934, 21, 72—76).—The *l*-forms of leucine, cystine, alanine, valine, and aspartic acid have a greater physiological activity (inhibitory or stimulatory, according to concn.) than the *d*-forms; *r*-forms are intermediate in effect. Combinations of stereoisomeric valines produce a simple additive effect; those of leucines, cystines, and aspartic acids, a potentiation; and those of alanines an antidynamic action.

A. G. P.

**Germination of seeds. III. Transformation of carbohydrates during germination of soya-bean seeds.** S. SASAKI (Bull. Agric. Chem. Soc. Japan, 1933, 9, 181—182).—The course of germination of the seeds is marked by an initial increase (5 days) and a subsequent decline in reducing sugar content, a steady decrease in sucrose, stachyose, and galactan, and an increase in starch, dextrin, pentosan, and crude fibre. The total carbohydrate content of the seeds did not change appreciably during the first 10 days of germination.

A. G. P.

**Dormancy in *Tilia* seeds.** L. V. BARTON (Contr. Boyce Thompson Inst., 1934, 6, 69—89).—Germination of the seeds was accelerated by softening the seed coat by placing in moist peat or by treatment with conc.  $\text{H}_2\text{SO}_4$ . The capacity of seeds to absorb  $\text{H}_2\text{O}$  was increased by the acid treatment. Excised embryos from  $\text{H}_2\text{SO}_4$ -treated seed which had been exposed to low temp. (after-ripening) grew more rapidly than those softened in peat. The catalase

activity of seed increased as the after-ripening progressed. A. G. P.

**Physiological and chemical changes preceding and during the after-ripening of *Symphoricarpos racemosus* seeds.** F. FLEMING (Contr. Boyce Thompson Inst., 1934, 6, 91—102).—Disintegration of the seed coat by soaking in moist peat or treatment with conc.  $H_2SO_4$  for 72 min., followed by after-ripening (A) at 25° for several weeks, induces germination. During A at 5° the catalase and peroxidase activity of seeds was markedly increased. At 25° the activity of the enzymes decreased slightly.

A. G. P.

**Morphology of the seed of *Symphoricarpos racemosus* and the relation of fungal invasion of the coat to germinating capacity.** N. E. PFEIFFER (Contr. Boyce Thompson Inst., 1934, 6, 103—122).—Fibre walls and the epidermis of the integument contain cellulose, pentosans, and lignins deposited in the order named. Coats of seed stored in moist peat are subject to decomp. by fungi, and become disintegrated, thus favouring germination. Reduction in fibre tissue of seed coats by treatment with  $H_2SO_4$  is proportional to the period of treatment. If the latter is prolonged inferior germination may result from excessive growth of fungi. A. G. P.

**Concentrations of inorganic ions as related to growth of excised root-tips of wheat seedlings.** P. R. WHITE (Plant Physiol., 1933, 8, 489—508).—The effects of varying concns. of K, Ca, Mg, Fe,  $NO_3^-$ ,  $NH_4^+$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $CO_3^{2-}$ , and Cl on the growth of root-tips in modified Uspenski media supplemented with glucose and yeast are recorded. A. G. P.

**Physiological rôle of boron.** M. SCHKOLNIK (Compt. rend. Acad. Sci. U.R.S.S., 1934, 141—146).—Assimilation by flax and *Vicia faba* roots of  $PO_4^{3-}$ ,  $NO_3^-$ , and  $Ca^{2+}$ , but not of  $K^+$ , is greatly diminished by the presence of B compounds (I) in the nutritive mixture, whilst the growth of the seedlings is considerably enhanced. The permeability of the cell membranes is probably specifically affected by (I), in the absence of which intoxication of the cell contents by high contents of the above anions takes place. R. T.

**Chemical stages in the growth of wood layers.** H. HEMPEL (Cellulosechem., 1934, 15, 41—43).—The youngest layers of spruce wood contain about 10% lignin, 46% C and 2.8% OMe, the top of the stem containing more lignin than the bottom; rings one year old contain an average of 30% lignin and 50.2% C, which represent the average composition of spruce wood. Hence the cellulose skeleton built from the sap of the cambium is only very gradually lignified. Two morphologically different lignins isolated from the same wood showed practically the same C, H, and OMe contents, indicating that the lignin found in the central lamellæ and the cell wall of the fibre is chemically identical. D. A. C.

**Nutrient elements used by leaves and growth of apple trees.** E. BURKE and H. E. MORRIS (Plant Physiol., 1933, 8, 537—544).—Of the mineral constituents of the current year's growth and leaves of apples, at the stage when full leaf size is reached, 67% of the N, 98% of the P, 100% of the K, 82% of

the Ca, and 61% of the Mg have been obtained from roots and soil. During active growth reserve N from all parts of the tree was utilised. The supply of K to all parts of trees is largely controlled by the flow of sap. Comparison is made of mineral distribution in an actually growing and a dormant tree. A. G. P.

**Isotopic fractionation of water by physiological processes.** E. W. WASHBURN and E. R. SMITH (Science, 1934, 79, 188—189).—During the synthesis of org. compounds by a growing willow tree an isotopic fractionation of H occurs.  $H^2$  is preferentially selected and the sap and combined H of the woody parts of this tree both yield  $H_2O$ . No isotopic fractionation occurs during the passage of the  $H_2O$  into the tree through the root membranes. L. S. T.

**Relationship between physiological phenomena and the occurrence of pigments in plants.** VI. Synopsis of results obtained and their practical application. H. KOSAKA (J. Dept. Agric. Kyushu, 1934, 4, 127—160).—Not only the factors light, temp., etc., but also the functions of assimilation, growth, etc., may influence the occurrence of anthocyanins in certain plants. P. G. M.

**Synthesis of proteins in plants. I. Conversion of nitrates into protein in *Helianthus annuus*.** Linn. K. S. VARADACHAR (J. Indian Inst. Sci., 1933, 16, A, 129—138).—When  $KNO_3$  is continuously injected into the N-starved plant the amount of free  $KNO_3$  in the plant remains approx. const., the total N increasing, suggesting continuous conversion into proteins, probably through an amide stage. C. G. A.

**Evolution of phospholipins of leaves during autumnal yellowing.** R. ECHEVIN (Compt. rend., 1934, 198, 1254—1256).—The phospholipin content of the green leaves of five trees is the same per unit of leaf-area; it becomes 0 after autumnal yellowing. R. S. C.

**Accumulation of rubber in the roots of *Tau-sagiz* as a result of its disappearance from the leaves.** V. A. NOVIKOV, A. I. GRETSCHUSCHNIKOV, and J. N. BARMENKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 205—209; cf. this vol., 228).—Latex cells of *Tau-sagiz* roots play no part in formation of rubber, but are merely the channels through which it is conveyed and in which it is deposited. By checking the latex flow in some roots by ringing and comparing with unringed roots, it is shown that the disappearance of rubber from leaves on shading is due to its migration to the roots. J. W. S.

**Fungi. III. *Parmelia physodes*, L.** J. ZELLNER (Monatsh., 1934, 64, 6—11).—Extraction of the residue from the  $COMe_2$  extract (14.2%) of air-dried *P. physodes* (7.77%  $H_2O$ ; ash 2.81%) with ligroin gives 1.3% of fat (hydrolysis of which gives fatty acids, m.p. 72—74°, and an unsaponifiable portion containing ergosterol and a paraffin hydrocarbon), whereas  $C_6H_6$  extracts atranonin (0.5%) and amorphous acids (3.0%) leaving an insol. residue of capraric (6%,  $Et_2O$ -insol.) and physodic (3.4%, sol.) acids. The  $EtOH$  extract of the  $COMe_2$ -insol. residue contains the  $H_2O$ -insol. aliphatic alcohols (1.3%) *hypogymol*-I, m.p. 190° (decomp.), and -II,  $C_{30}H_{62}O_9$ , m.p. 218°, the  $H_2O$ -sol.



fraction containing amorphous polysaccharides (1.9%) and erythritol (< 0.1%). The H<sub>2</sub>O-sol. portion (COMe<sub>2</sub>- and EtOH-insol.) (20.5%) contains only lichenin and accompanying material. J. W. B.

**Chemistry of the red and brown algæ.** B. RUSSELL-WELLS (Nature, 1934, 133, 651).—*Corallina officinalis*, *Bostrychia scorpioides*, *Chondrus crispus*, *Rhodymenia palmata*, *Laminaria saccharina*, *L. digitata*, *Fucus serratus*, *F. vesiculosus*, *Ascophyllum nodosum*, and *Pelvetia canaliculata* contain cellulose. L. S. T.

**Chemical examination of bark of *Holarrenha antidysenterica*.** S. SIDDIQUI and P. P. PILLAY (J. Indian Chem. Soc., 1933, 10, 673—675).—The best method of extracting the alkaloids from the powdered bark is with Et<sub>2</sub>O—EtOH (10%)—aq. NH<sub>3</sub> (2%). The Et<sub>2</sub>O-sol. neutral products give on hydrolysis lupleol, m.p. 213—214° (benzoate, m.p. 266°), amorphous sterols, and oleic, linoleic, and linolenic acids. H. A. P.

**Plant chemistry. XXV. Chemistry of barks.** IX. J. BISCO and J. ZELLNER (Monatsh., 1934, 64, 12—16).—The lignoin extract of the bark of *Zizyphus vulgaris*, Lam., contains ceryl alcohol (I) and, after hydrolysis, fatty acids, m.p. 61—65°. The Et<sub>2</sub>O extract (resin) is hydrolysed to give (I), a sterol, amorphous resin acids, and an EtOH-insol. K salt of a cryst. acid, m.p. 283° (amorphous Ac derivative). The EtOH extract contains only phlobaphens, and the H<sub>2</sub>O extract, tannins and invert sugar (II). The lignoin extract of the ash (*Fraxinus excelsior*, L.) contains (I), and an EtOH-sol. portion containing stigmasterol, sitosterol, and a carotenoid (SbCl<sub>3</sub> reaction), and giving, after hydrolysis, fatty acids, m.p. 66—70°, and dihydroxystearic acid, glycerol, but no choline or H<sub>3</sub>PO<sub>4</sub>. The products of the EtOH extract, separated by the Pb salt method, agree with those in the lit., mannitol and (II) also being isolated. J. W. B.

**Chemistry of bark substances. II. Hazel bark.** O. BRUNNER and R. WÖHRL (Monatsh., 1934, 64, 21—27; cf. Zellner *et al.*, A., 1924, i, 814).—From the unsaponifiable portion of the EtOH extract of *Corylus avellana*, L., are isolated a hydrocarbon, b.p. 170—190°/10 mm. f.p. 16°, lignoceryl alcohol (p-methoxy-, m.p. 99° and 2:3-dimethoxy-, m.p. 93°, -phenylurethane) (Sandquist *et al.*, A., 1931, 1272), sitosterol, and betulin. The sterol, m.p. 200°, and corylol, isolated by Zellner (*loc. cit.*), could not be detected. J. W. B.

**Constituents of *Cascara sagrada* extract. I. Isolation of a rhamnoglucoside of emodin.** H. L. SIPPLE, C. G. KING, and G. D. BEAL (J. Amer. Pharm. Assoc., 1934, 23, 205—208).—The isolation, in 0.5% yield, of a rhamnoid of emodin from an EtOH extract of the bark is described. The glucoside is relatively inactive as a cathartic. A. E. O.

**Ceryl alcohol from the grass, *Agrostis*.** C. E. BILLS and G. E. STEEL (Proc. Soc. Exp. Biol. Med., 1933, 31, 134—135).—The ceryl alcohol of cocksfoot and rye grass is chiefly *n*-hexacosanol (I); that of bent grass, essentially (I), had a slightly higher mean C content. CH. ABS.

**Odorous substances of green tea. II.** S. TAKEI, Y. SAKATO, and M. ŌNO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 11—12).—The yields of oil obtained by distillation in steam from green tea- (0.015%), mulberry- (0.0025%), acacia- (0.01%), and black radish-leaves (0.002%) vary with the age of the leaves. All these oils contain 5—6% of Δ<sup>α</sup>-hexenaldehyde, b.p. 138—140° (2:4-dinitro-, m.p. 144°, and p-nitro-phenylhydrazone, m.p. 137°; semicarbazone, m.p. 173°), 30—50% of Δ<sup>β</sup>-hexenol, and a little *n*- and iso-butaldehyde and isovaleraldehyde. The characteristic odours are due to less volatile constituents. R. S. C.

**Tannin from fresh tea leaves.** Y. OSHIMA and T. GOMA (J. Agric. Chem. Soc. Japan, 1933, 8, 948—952).—The fresh leaves afforded 0.2% of tannin; quercetin was also obtained. Oxidation of the tannin afforded the compound C<sub>12</sub>H<sub>12</sub>O<sub>8</sub>, [α]<sub>D</sub><sup>20</sup>—70.22°. CH. ABS.

**Corms of *Arisaema triphyllum* (L.), Schott.** L. MARION (Canad. J. Res., 1934, 10, 164—169).—Light petroleum removes 5% and MeOH 0.9% (I) of the dried corms. Steam-distillation of (I) affords an oil; the non-volatile part gives an acid, m.p. 183—184°, glucosazone (with NHPH-NH<sub>2</sub>), *i*-inositol, a substance, C<sub>6</sub>H<sub>10</sub>O<sub>6</sub>, m.p. 120° after softening at 105° (which may be a lactone), myricyl alcohol, *arisaesterol*, C<sub>36</sub>H<sub>64</sub>O<sub>2</sub>, m.p. 135°, linoleic, oleic, and palmitic acids, and a phytosterolin, m.p. 297°. J. L. D.

**Essential oil in desert plants. IV. Oil of *Tetrademia glabrata*.** M. ADAMS and G. R. ADAMS (J. Amer. Chem. Soc., 1934, 56, 991—992).—The oil (B., 1928, 106) contains α-pinene (15%), dipentene (25%), caryophyllene (8%), nonacosane (7%), aldehydes (10%), an unidentified ketone (1%) (2:4-dinitrophenylhydrazone, m.p. 132—133°), and colophonium and unidentified terpenes (34%). H. B.

**Indian essential oils. V. Essential oil from the rhizomes of *Curcuma longa*, Linn. VI. Essential oil from the rhizomes of *Acorus calamus*, Linn.**—See this vol., 529.

**Phosphatides of wheaten meal.** F. E. NOTT-BOHM and F. MAYER (Z. Unters. Lebensm., 1934, 67, 369—379).—The choline (I) content of the gluten, aq. extract, and starch fractions of wheaten meal (II) increases in the order named. (I) is present as (I)-lecithin. A method of prep. of the wheat phosphatide (III) is described. The P.-L. no. (cf. B., 1934, 425) of (III) is 1.56, the carbohydrate content (as glucose) 26%. Trigonelline is absent from (II) and from the bran (IV). (II) contains less (III) than do groats. (II) contains thrice as much (III) as has hitherto been recognised, and (IV) contains even more. E. C. S.

**Plant-phosphatides.** E. BUREŠ and J. SCHIDLÖF (Časop. českoslov. Lék., 1933, 13, 229—235; Chem. Zentr., 1933, ii, 3144—3145).—Analysis of phosphogamin (I) shows that it resembles inositolhexaphosphoric acid (28.19% P) very closely. Hydrolysis yields H<sub>3</sub>PO<sub>4</sub> and optically-inactive unresolvable mesoinositol. The sample of (I) analysed contained 2.8% of phosphates, and small amounts of non-ionised combined Ca, Mg, Na, K, and Fe. H. J. E.

**Distribution of methionine in food-proteins.** T. TOMIYAMA and M. HANADA (J. Biochem. Japan, 1934, 19, 345—351).—Methionine was isolated from the proteins of sardine (0.52%) and whale-muscle (0.37%), silk-worm pupa (0.43%), soya bean (0.08%), and from caseinogen (0.41%). F. O. H.

**Determination of amino-acids in the globulin of sunflower seeds.** A. V. BLAGOVESHCHENSKI and T. A. SCHUBERT (Biochem. Z., 1934, 269, 375—378).—The globulin contains arginine 9.10, histidine 14.29, lysine 1.80, and proline 5.26% of the dry wt.

P. W. C.

**Sterols from stramonium seed.** O. GISVOLD (J. Amer. Pharm. Assoc., 1934, 23, 106—108).—The sterol fraction (13.21%) of the seed-oil unsaponifiable matter contains sitosterol; stigmasterol is absent.

E. H. S.

**Determination of the acids of plant tissue. II. Total organic acids of tobacco leaf.** G. W. PUCHER, H. B. VICKERY, and A. J. WAKEMAN (Ind. Eng. Chem. [Anal.], 1934, 6, 140—143).—Plant tissue is acidified with  $H_2SO_4$  to  $p_H$  1, extracted with  $Et_2O$ , and the org. acids in the extract determined by titration in presence of  $HNO_3$ , between the limits  $p_H$  7.8 and 2.6, using a quinhydrone electrode according to the method of Van Slyke and Palmer (A., 1920, i, 459). Under these conditions,  $H_2C_2O_4$  (I) reacts as a mono-basic acid and is determined independently as  $CaC_2O_4$ . Citric, malic, succinic, and tartaric acids titrate to approx. 90%, and therefore, after correcting for (I), a further correction of 10% is introduced in the determination of the org. acids. S. C.

**Acid secretion of the chick-pea (*Cicer arietinum*).** G. R. MILNE (J. Roy. Tech. Coll., 1934, 3, 330—331).—The acid secretion from the hairs of the chick-pea consists mainly of citric, malic, and oxalic acids (0.75% of cryst. acids isolated, separated as Ca salts), and a small quantity of volatile acids of which AcOH is the chief. J. W. B.

**Iodine content of Pennsylvania potatoes.** D. E. H. FREAR (J. Agric. Res., 1934, 48, 171—182).—The I content of 135 samples of potatoes (I) varied from 0.01 to 0.216 (mean, 0.0778) pts. per  $10^6$  pts. of dry tissue. The I content of (I) grown on marine soil was significantly high. No significant correlation was found with size or variety nor with the incidence of goitre in the various districts. W. O. K.

**Character of hemicellulose in certain fruit trees.** W. E. TOTTINGHAM (Plant Physiol., 1933, 8, 559—561).—Differences in the galactose, glucose, xylose, and uronic acid fractions of the hemicellulose extract from wood of various fruit trees are recorded and discussed. A. G. P.

**Examination of starch and hemicellulose extracts from apple wood.** H. OTTERSON and W. E. TOTTINGHAM (Plant Physiol., 1933, 8, 561—564).—A method for calculating starch content and hemicellulose fraction from customary analytical determinations is given. A. G. P.

**Carbohydrates in the bulbs of *Narcissus tazetta*.** III. Comparison with *Lycoris radiata*. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1933, 9, 1005—1007).—*L. radiata* bulbs afforded total sol. carbo-

hydrates 75.57 (air dried), sugar sol. in hot  $EtOH$  3.74, reducing sugar 0.27, carbohydrates sol. in cold  $H_2O$  18.28, in hot  $H_2O$  21.95, in superheated  $H_2O$  18.65%. The content of lower sugars is < in *N. tazetta*. The cold- $H_2O$  extract contained fructan with 6% of glucan. The carbohydrates consist chiefly of starch. CH. ABS.

**Mannitol in olives.** R. NUCCORINI (Annali Chim. Appl., 1934, 24, 20—25).—Green olives with a faint pink tinge contained, on dry matter, about 2.5% of mannitol or about 3.75% on the pericarp-free fruit. The proportion varies from year to year and diminishes as the fruit develops. T. H. P.

**Detection and determination of formaldehyde within the cell of a green plant by the Allison apparatus.** A. L. SOMMER, E. R. BISHOP, and I. G. OTTO (Plant Physiol., 1933, 8, 564—567).—Allison's photometric apparatus (cf. A., 1932, 240) is adapted to the determination of  $CH_2O$  in algal cells. A. G. P.

**Pectic acid and methyl alcohol in tobacco leaves produced in Japan.** III. S. MACHIDA (J. Agric. Chem. Soc. Japan, 1933, 9, 1140—1142).—Vals. were, respectively, 10—15 and 0.3—0.64%. Pectic acid was probably present as the Me or  $Me_2$  ester. CH. ABS.

**Chemical constituents of tobacco. III. Pigments of tobacco blossoms.** K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1933, 9, 137—139).—Extraction of 1260 g. of dried tobacco-flower meal with  $MeOH-HCl$  yielded 0.6 g. of an anthocyanin (sugar and anthocyanidin not identified). Extraction of the residue from the above with 95%  $EtOH$  yielded 1.5 g. of a flavone glucoside which gave a yellow cryst. flavone on hydrolysis with 5%  $H_2SO_4$ . C. G. A.

**Reduction of silver nitrate by chloroplasts.** R. GAUTHERET (Compt. rend., 1934, 198, 1252—1254).—The reduction of  $AgNO_3$  by the chloroplasts of yellow leaves is catalysed by very short exposure to light, particularly red light. The reaction takes place in the dark after previous exposure, is not affected by keeping in the dark or by anaesthesia by  $KCN$  or  $NHPhCO_2Et$ , but ceases with death of the leaf. The reducing substances of fresh spinach and green salad are probably tannins or hydroxyflavones. R. S. C.

**[Plant] amides.** K. TAUBÖCK and A. WINTERSTEIN (Handb. Pflanzenanalyse, 1933, 4, 190—221; Chem. Zentr., 1933, ii, 3321).—A review of the plant-physiological significance, properties, and determination of various  $NH_2$ -compounds is given. A. A. E.

**Nitrogen balance. Determination of nitrogen fractions in plants.** E. KEYSSNER and K. TAUBÖCK (Handb. Pflanzenanalyse, 1933, 4, 1345—1402; Chem. Zentr., 1933, ii, 3321).—A review and crit. discussion. A. A. E.

**Presence of norleucine in seeds of *Ricinus communis*, L.** R. NUCCORINI (Annali Chim. Appl., 1934, 24, 25—32).—The ricinin in castor seeds increases in amount as the seeds germinate. The products of hydrolysis of the seeds contain norleucine, which has not previously been found in vegetable products. T. H. P.

**Volatile base of valerian root.** A. E. TSCHITSCHIBABIN and M. P. OPARINA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 119—122).—A saturated liquid pyridine base,  $C_{10}H_{15}N$  (picrate, m.p. 147—148°; *platinichloride*), has been isolated. R. T.

**Yohimbine Rubiaceae, *Corynanthe paniculata*, Welwitsch.** RAYMOND-HAMET (J. Pharm. Chim., 1934, [viii], 19, 209—214).—Extraction of the bark by Schomer's method yields 1.60 g. of yohimbine hydrochloride per kg. By Chemnitz's method the yield is 8.4 g. of yohimbine base per kg. of bark. C. G. A.

***Thermopsis lanceolata*, K. Br.** M. VARLAKOV (Khim. Farm. Prom., 1933, 226—228).—Alkaloids (0.37%) sol. in  $H_2O$ ,  $CHCl_3$ , and EtOH, but insol. in Et<sub>2</sub>O and  $C_6H_6$ , are present. Their physiological action is described. CH. ABS.

**Bismarck-brown [as stain for] pollen-grain walls.** L. A. MARGOLENA (Stain Tech., 1934, 9, 71).—Sections of buds fixed in Bouin's fluid and embedded in paraffin are stained for 6—10 min. in 0.5% aq. Bismarck-brown and dehydrated in EtOH. They are then counterstained with 0.3% fast-green FCF in clove oil. The sections, cleared with xylene, display a green extine and a brown entire layer of the pollen-grain wall. H. W. D.

**Method for determining the purity of pollen for the preparation of pollen extracts** F. BERGER (Pharm. Zentr., 1934, 75, 239—243).—The pollen is examined in the presence of a "Fluorochrome" with a fluorescence microscope. Results on about 80 species of pollen are tabulated. S. C.

**Distribution of phosphorus in wheat and flour.** A. FEYTE (Ann. Agron., 1933, 3, 787—798).—The total, phytin-, and mineral P contents of a no. of samples are recorded and discussed. The proportion of the total P existing as phytin is lower in hard than in soft wheats. No direct relationship was apparent between the distribution of P in the grain and the baking val. of the flour as determined by extensimeter measurements. A. G. P.

**Zinc content of green and etiolated leaves.** G. BERTRAND and ANDREITCHEVA (Ann. Inst. Pasteur, 1934, 52, 249—251).—Normal green leaves (chicory, endive, sorrel, spinach, dandelion, cress, lettuce, cabbage) have a Zn content of 0.36—8.99 mg. per kg. of dried material; that of etiolated (*e.g.*, interior) leaves is much < that of the green leaves of the same plant. F. O. H.

**Cryoscopic determination of "bound water."** R. A. GORTNER and W. A. GORTNER (J. Gen. Physiol., 1934, 17, 327—339).—The criticisms by Grollman (A., 1931, 975) of the cryoscopic method for the determination of bound  $H_2O$  (I) are considered. The coriol formula does not change the conclusion that winter-hardiness in plants is accompanied by (I). Using a new method of calculating the true f.p. of a solution, gum acacia (II) in aq. sucrose shows 0.6—0.7 g. (I) per g. of (II), and in aq. KCl or KBr, negative amounts of (I) indicating preferential absorption of solute. A. L.

**Spike-disease of sandal (*Santalum album*, Linn.). XV. Rôle of plant-acids in health and**

**disease.** A. V. V. IYENGAR (J. Indian Inst. Sci., 1933, 16, A, 139—152).—With the onset of spike-disease the  $p_H$  of the tissue fluids rises, then falls; the malic acid and  $H_2C_2O_4$  content of the healthy sandal falls and succinic acid appears. The  $PO_4^{''}$  content of diseased tissues is higher than that of the healthy plant. A micro-sublimation apparatus is described. C. G. A.

**Physiology of the virus diseases of the potato.** II. Comparison of the carbohydrate metabolism of normal with that of crinkle potatoes and observations on carbohydrate metabolism in a "carrier" variety. III. Comparison of the nitrogen metabolism of normal with that of leaf-roll potatoes. E. BARTON-WRIGHT and A. McBAIN (Ann. Appl. Biol., 1933, 20, 525—548, 549—589; cf. A., 1933, 546).—II. In the early stages of disease the process of carbohydrate formation was not significantly different in healthy and diseased leaves, although, in the latter, transport was somewhat delayed. The % of starch (I), sucrose (II), and hexoses (III) was higher in the diseased leaves, and the max. and min. points in the fluctuations were approx. 2 hr. in advance of those of healthy leaves. In both cases (II) was the sugar of transport. Later in the season (I) accumulated in diseased and (III) in healthy laminae. In the former case (II) was derived from (I) hydrolysis and in the latter by synthesis from (III) which was in turn produced by hydrolysis of (I). Transport of sugar [still as (II)] was less readily effected in diseased petioles.

III. Diurnal variations in the total N and constituent fractions indicated no marked differences in the N metabolism resulting from virus infection. A process of protein synthesis from  $NO_3^-$ , not involving  $NH_2$ -acids as an intermediate stage, is suggested. The residual N fraction is probably an important factor in N-translocation. A. G. P.

**Potato wart disease.** W. SZYMANSKI (Trans. Phytopath. Sect. State Inst. Agric. Bydgoszczy, 1933, 13, 141—162).—Dry wt. is <, but ash >, normal; Fe, Mn, Cu, and N are especially high in warty tissue. CH. ABS.

**Colorimetric determination of sodium in vegetation.** J. G. LOUW (Onderstepoort J. Vet. Sci., 1933, 1, 425—435).—A modification of Malan and Van der Lingen's method is described. The proportion of P to Na which does not interfere with the determination is given, and it is shown that the interference of K is dependent on the abs. concn. and temp. NUTR. ABS. (b)

**Standardisation of biological stains. IV. Triphenylmethane derivatives.** A. R. PETERSON, H. J. CONN, and C. G. MELIN (Stain Tech., 1934, 9, 41—48).—Methods for the qual. and quant. analysis, and for biological testing, of 11  $CHPh_3$  dyes are given. Quant. analysis depends on reduction with  $TiCl_3$  in the presence of a suitable buffer. H. W. D.

**Differential titration of mixed strong and weak acids. Method for "free HCl" in gastric contents etc.** G. M. RICHARDSON (Proc. Roy. Soc., 1934, B, 115, 170—180).—For determination of "free HCl" in acid mixtures, titration in 90%  $CO_2$  to successive end-points at  $p_H$  3.4 and 4.0, using

naphthylamine-orange, is suggested. Of other methods, the Gunzberg method or a  $p_H$  2 titration is most satisfactory. H. G. R.

**Colorimetric determination of ammonia in small amounts of material.**—See this vol., 500.

**Determination of mercury in air and urine.**—See this vol., 502.

**Colorimetric determination of magnesium in bones, by a modification of the Denis method.** M. C. FRANKLIN (Univ. Cambridge, Inst. Animal Path., Rep., 1932—1933, 130—134).—2.5 g. of bone are ashed and dissolved in HCl. In one tenth of the solution the Ca is pptd. as oxalate. The Mg in the filtrate is pptd. as  $MgNH_4PO_4$ . The ppt. is dissolved in HCl and then in an aliquot the Mg is determined as in blood. NUTR. ABS. (b)

**Adaptation of Kolthoff's colorimetric method for the determination of magnesium in biological fluids.** A. D. HIRSCHFELDER and E. R. SERLES (J. Biol. Chem., 1934, 104, 635—645).—After removal of Ca from the plasma as  $CaC_2O_4$ , 5.0 c.c. of the fluid (=0.5 c.c. plasma) are treated with 3.0 c.c. of dextrin or starch solution, 1.0 c.c. of solution of Titan- or Clayton-yellow (0.01%), and 1.0 c.c. of 0.4N-Ba(OH)<sub>2</sub>. The colour is compared with that of a standard Mg solution, using a colour screen. A micro-method for the determination of both Ca and Mg in 0.5 c.c. blood or 0.1 c.c. of plasma is also given. For determination of Mg in urine, the Ca is first pptd. as  $CaC_2O_4$  and  $PO_4'''$  by  $UO_2(OAc)_2$ . W. O. K.

**Micro-incineration process and determination of calcium in organs.** J. ERDÖS (Magyar gyógys. Társas. Értes., 1933, 9, 391—396; Chem. Zentr., 1933, ii, 3166).—200—300 mg. of material are evaporated three or four times in a micro-Kjeldahl flask with fuming  $HNO_3$ , saturated aq.  $NH_4NO_3$ , and 30%  $H_2O_2$ . Ca is determined by extracting the residue with dil. HCl, pptn. as  $CaC_2O_4$ , and titration with  $KMnO_4$ . H. J. E.

**Determination of iron in biological material by modified permanganate titration.** F. H. L. TAYLOR and J. F. BROCK (Biochem. J., 1934, 28, 442—446).—Fe is determined in biological material by ashing with conc.  $H_2SO_4$  and  $HClO_4$ , reduction with Zn, and titration with  $KMnO_4$ . H. D.

**Micro-determination of phosphorus (inorganic, acid-soluble, lipin, total) in blood and excreta.** F. FERRANTI and O. GIANNETTI (Diagnostica Tecn., 1933, 4, 664—682).—The inorg., org., acid-sol., lipin, and total P in blood, urine, and faeces have been determined colorimetrically by a modification of the method of Bell and Doisy, consisting in adding NaOAc to remove strong acids left from the destruction of org. matter, and to bring the  $p_H$  near neutrality. The org. P vals. by this method from wts. of the same substance in the proportion 1 : 2 : 4 were in the same proportion with a max. error of 4%, whilst the inorg. P agreed with other methods. R. N. C.

**Determination of total, organic, and inorganic phosphorus by the Pulfrich step-photometer.** C. URBACH (Biochem. Z., 1934, 268, 457—460).—A

modification of the author's previously described (A., 1931, 1323) method is given which avoids the disadvantageous changes of colour intensity on keeping. P. W. C.

**Determination of phosphoric acid by the phosphomolybdate method and its use for plant ashes.**—See this vol., 500.

**Determination of small amounts of bromine in body-fluids and organs.** A. STOLL and B. BRENKEN (Biochem. Z., 1934, 268, 229—246).—A method is described which determines Br down to  $4 \times 10^{-6}$  g. in KBr and KBr-KCl mixtures with a fair degree of accuracy and is applied to its determination in rabbit blood and urine. Curves show the variation of these vals. on oral administration of Br. P. W. C.

**Destruction of organic substances with chlorine.** J. ERDÖS and B. GROÁK (Magyar gyógys. Társas. Értes., 1933, 9, 397—399; Chem. Zentr., 1933, ii, 3166).—The material is heated under reflux with conc. HCl and conc. saturated aq.  $KClO_3$ . The method is used for the determination of Pb in faeces. H. J. E.

**Micro-determination of carbon in biological fluids. II. Gasometric method.** I. CLAUDATUS and D. PETREA (Bul. Soc. Chim. România, 1933, 15, 107—110).—The C is oxidised by  $KMnO_4$  in NaOH-Ba(OH)<sub>2</sub> solution and the  $CO_2$  formed determined in a Van Slyke apparatus. C. G. A.

**Biological determination of amino-nitrogen.** G. M. RICHARDSON (Proc. Roy. Soc., 1934, B, 115, 142—169).—The Van Slyke method is recommended for coloured extracts (I), but the  $CH_2O$  (phenolphthalein) titration may be used for colourless (I).  $Pb(OAc)_2$  at  $p_H$  6.0 is recommended as a decolorant for leaf (I) in preference to norit. All EtOH and  $COMe_2$  methods are discarded, since Mg and various weak acids are titrated as  $NH_2-N$ . H. G. R.

**Determination of glutathione.** L. BINET and G. WELLER (Compt. rend., 1934, 198, 1185—1187).—1—2 g. of tissue are minced and treated with 5 c.c. of 10%  $CCl_3 \cdot CO_2H$ . The extract is filtered and the extraction repeated thrice. The combined extracts are neutralised to bromothymol-blue (first appearance of blue) with NaOH and treated with 2 c.c. of 1% Cd lactate and 1 or 2 drops of 2% NaOH. The ppt. flocculates in 1—2 hr. and is collected, dissolved in 10 c.c. of 10%  $CCl_3 \cdot CO_2H$ , and titrated with 0.004N-I (starch indicator). A correction is required for the  $CCl_3 \cdot CO_2H$  present. The method is sp. The following vals. have been found: liver, 130; suprarenals, 114; spleen, 102; pancreas, 97; cardiac muscle, 62; skeletal muscle, 27 (mg. per 100 g. of fresh tissue). P. G. M.

**Determination of carnosine in biological fluids.** R. KAPPELLER-ADLER and F. HAAS (Biochem. Z., 1934, 269, 263—270).—Methods are given for the determination of carnosine (I) alone [hydrolysed to histidine (II) and determined colorimetrically] and in mixtures with (II) and with anserine (III). Muscle of ox, horse, and pig contains 0.238, 0.324, and 0.304% of (I), of hen 0.12% of (I) with 0.421% of (III), and of carp 0.088% of (II) with 0.059% of (I). P. W. C.