

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1936.

General, Physical, and Inorganic Chemistry.

Effects of pressure and current on the intensities of the Balmer lines of hydrogen. W. W. JACKSON (Phil. Mag., 1936, [vii], 22, 633—654).—A detailed investigation indicates that thermodynamic equilibrium is not established in a discharge tube; the excitation function governs the variation of the intensities of the lower members of the Balmer series. The ratio of the no. of dispersion electrons associated with H_α and H_β is 5.07 at 0.18 mm. and 675 ma. N. M. B.

Spectrum of doubly excited helium. A. T. KIANG, S. T. MA, and T. Y. WU (Physical Rev., 1936, [ii], 50, 673).—None of the calc. strongest lines was found when electrons from a hot cathode were accelerated through low-pressure He with 1100—1800 volts corresponding with an electron energy on impact of 500—700 volts, for which the calc. excitation cross-section is a max. Probable explanations of the failure are discussed. N. M. B.

Zeeman effect in the first negative oxygen bands. L. BOZÓKY and R. SCHMID (Physical Rev., 1935, [ii], 48, 466).—The Zeeman effect in the 5631 Å. band has been photographed. L. S. T.

Additional first negative oxygen bands. L. BOZÓKY and R. SCHMID (Physical Rev., 1935, [ii], 48, 465).—Nine additional bands have been recognised. L. S. T.

Dependence of intensities of rotation lines of a band on the conditions of excitation. H. BRINKMAN (Physikal. Z., 1936, 37, 726—728).—The anomaly in the intensity distribution of rotation lines of N_2 bands with different conditions of excitation, noticed by Herrmann (this vol., 261), is due to experimental error. The individual rotation lines of a band have the same abs. efficiency. A. J. M.

Dependence of intensities of rotation lines of a band on the conditions of excitation. O. HERRMANN (Physikal. Z., 1936, 37, 729).—A reply to Brinkman (preceding abstract). A. J. M.

Effect of temperature on absorption of resonance radiation by sodium atoms. J. L. TUCK and E. WARHURST (Trans. Faraday Soc., 1936, 32, 1501—1503).—The variation with temp. of absorption of resonance radiation by Na atoms has been determined for const. atom density between 140° and 320°. The absorption decreases linearly with temp. over this range. A. J. E. W.

Absorption of sulphur vapour between 3600 and 5000 Å. B. ROSEN and L. NEVEN (Compt.

rend., 1936, 203, 663—665; cf. A., 1928, 687).—The C bands are attributed to the principal system of S_2 , and are present even at 1100°, when the band intensity depends only on the no. of S_2 mols. and not on the concn. Recorded contradictory observations may be reconciled by the existence of a continuous region of absorption due to polyat. S situated in the same spectral region as the predissociated bands of the principal system. R. S. B.

Glow spectra of halogen molecules. Y. UCHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 71—82).—The vapours of I_2 at >1200°, Br_2 at >450°, and Cl_2 at >1200° emit a glow consisting of emission bands superimposed on an independent continuum. The emission bands are due in each case to the transition $O_u^+ \rightarrow {}^1\Sigma_u^+$, the O_u^+ mols. arising from thermally dissociated ${}^2P_{3/2}$ atoms by the successive ternary collision processes $3X({}^2P_{3/2}) \rightarrow X_2({}^1\Sigma_u^+) + X({}^2P_{1/2}) + \text{kinetic energy}$; $X({}^2P_{1/2}) + X({}^2P_{3/2}) + \text{wall} \rightarrow X_2(O_u^+) + \text{wall} + \text{kinetic energy}$. J. S. A.

Absorption spectrum of chlorine. C. F. GOODEVE and B. A. STEPHENS (Trans. Faraday Soc., 1936, 32, 1517—1518).—The absorption of thick layers of Cl_2 between 600 and 1150 $m\mu$ has been investigated. The band system at 579—614 $m\mu$ (A., 1923, ii, 48) was not confirmed. Additional bands conforming to Birge and Weizel's analysis are given. A. J. E. W.

New terms in the arc spectrum of tellurium. S. G. KRISHNAMURTY (Indian J. Physics, 1936, 10, 365—373).—Full data for the range 1600—5000 Å. arc tabulated, and 8 new odd levels in addition to those due to 5d and 6s configurations are reported. N. M. B.

Near ultra-violet band spectra of iodine. O. STUHLMAN, jun. (Physical Rev., 1935, [ii], 48, 381).—The results of an examination of the emission spectrum of I vapour under high-frequency electrodeless discharge conditions are given. L. S. T.

Arc spectrum of tungsten. D. D. LAUN (Physical Rev., 1935, [ii], 48, 572).—The structure obtained from the Bureau of Standards measurements is summarised. L. S. T.

Characteristics of mercury-rare gas discharge tubes. H. W. MELVILLE (Trans. Faraday Soc., 1936, 32, 1525—1531).—The characteristics have been determined to find optimum conditions for a tube taking an input of 400 watts and emitting the resonance line at 2537 Å. For an input of 70 watts it is possible to obtain an output of 10^{19} quanta per



sec. The mechanism of the collision processes occurring is discussed. E. S. H.

Characteristics of mercury arc between solid electrodes. W. ENDE (Z. tech. Physik, 1934, 15, 601—604; Chem. Zentr., 1936, i, 511).—The characteristics of an arc between oxide electrodes were studied. H. J. E.

Forbidden lines in the spectrum of neutral lead with high-frequency excitation. H. NIEWODNICZANSKI (Acta phys. polon., 1934, 2, 375—382; Chem. Zentr., 1936, i, 505; cf. A., 1935, 138). H. J. E.

Photographic and spectroscopic investigation of arcs with high current density. B. KIRSCHSTEIN and F. KOPPELMANN (Z. tech. Physik, 1934, 15, 604—606; Chem. Zentr., 1936, i, 511). H. J. E.

Change of striking potential on illumination. I. W. FUCKS and W. SEITZ (Z. Physik, 1936, 103, 1—17).—The striking voltage in A, He, N₂, and air for the electrode materials Ag, Cu, Ni, and Zn has been determined. Under most conditions the voltage was increased by illumination with Hg lamp ultra-violet light, that of short λ alone being effective. A. E. M.

Disappearance of spectral lines in strong electric fields. V. FABRIKANT (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 215—217; cf. A., 1930, 828; 1931, 1203).—Theoretical. Lanczos' wave-mechanical treatment is based on incorrect assumptions; Smurov's classical expression $0.086e/\rho^2$ (e =electronic charge, ρ =orbital radius) for the potential required to ionise an H atom yields vals. agreeing with those required to cause the disappearance of the corresponding spectral lines. R. C. M.

Light wave-length measurements with a divergent beam and plane grating. D. L. DAS (Z. Physik, 1936, 101, 447—455). A. B. D. C.

Luminescence of solid substances produced by direct excitation in a Geissler tube. M. SERVIGNE (Compt. rend., 1936, 203, 581—583).—Ultra-violet Hg light is produced in the tube containing the solid by passing a discharge through the contained Ne or A saturated with Hg vapour. The specimen emits cathode luminescence when the pressure is 0.01 mm. The spectral bands emitted by a substance under the influence of these different radiations are generally the same, but the distribution of intensity is changed. J. G. A. G.

Townsend coefficients and spark discharge. D. Q. POSIN (Physical Rev., 1936, [ii], 50, 650—658).—A quant. study has been made of the pre-spark current between plane parallel electrodes in purified N₂. Data for X/p , α/p , and β/p , where X is the field strength, and α and β the Townsend coeffs., are tabulated and plotted, and are discussed in relation to the Townsend equation. N. M. B.

Yield of the characteristic X-rays of aluminium (Al K lines) excited by protons. O. PETER (Ann. Physik, 1936, [v], 27, 299—311).—The yield of emitted quanta per proton falling on Al has been found to be $(6.22 \pm 0.31) \times 10^{-6}$ for excitation of the Al K lines by protons of 132 e.kv. energy. This is in

agreement with the theory of Henneberg (A., 1934, 127). O. D. S.

Röntgen emission spectra and chemical combination. IV. $K\alpha_1\alpha_2$ lines of phosphorus compounds. O. LUNDQUIST (Z. Physik, 1936, 102, 768—771).—In compounds of P the $K\alpha_1\alpha_2$ doublet is shifted towards shorter λ . Compared with red P the mean shifts are, 1.58 X for hypophosphite, 2.19 X for phosphite, and 2.49 X for phosphate. H. C. G.

Fine structure in the K X-ray edge of gallium. W. W. MUTCH (Physical Rev., 1935, [ii], 48, 569—570).—A preliminary report of absorption spectra near the Ga K edge investigated at -150° and -67° . L. S. T.

Probability of K-shell ionisation of silver by cathode rays. H. S. W. MASSEY and E. H. S. BURHOP (Physical Rev., 1935, [ii], 48, 468; cf. this vol., 656). L. S. T.

L-Series for uranium. H. CLÆSSON (Z. Physik, 1936, 499—508). A. B. D. C.

X-Ray satellites, relative intensities, and line widths. L. G. PARRATT (Physical Rev., 1936, [ii], 50, 598—602; cf. this vol., 1041).—Preliminary data on the $L\alpha_{1,2,3,4,5,6,7}$ lines for Ag (47), and on the $M\alpha, \beta$ lines for Au (79), recorded with a two-crystal spectrometer, are reported and discussed. N. M. B.

Feeble emissions in the L spectrum of radium (88). H. HULUBEI (Compt. rend., 1936, 203, 665—667; cf. this vol., 1169, 1311).—Satellites of α_1, β_2 , and γ_2 rays have been observed with Ra. R. S. B.

$M_{IV, V}$ Absorption edges of protoactinium (atomic number 91). V. DOLEJŠEK and V. KUNZL (Nature, 1936, 138, 590). L. S. T.

Atomic dispersion and absorption of X-rays according to the relativistic wave mechanics of Dirac. I. K. SEILER (Ann. Physik, 1936, [v], 27, 329—372).—Mathematical. The component of at. absorption and dispersion of X-rays due to the K level is calc. Agreement with experimental vals. of the scattering coeff. in the neighbourhood of K lines is good for light and medium atoms. For heavy atoms relativity and spin effects must be taken into account. O. D. S.

Absorption of X-rays in the anticathode of the ion tube at low voltage. V. KUNZL (Acta phys. polon., 1934, 2, 447—457; Chem. Zentr., 1936, i, 718).—The M_{II} lines of Ta, Tm, and Pt and the $L_I, L_{II},$ and L_{III} lines of Sn were not observed in absorption. Only the L_I line of Mo was observed. H. J. E.

Production of polarised X-rays. W. H. GEORGE (Proc. Roy. Soc., 1936, A, 156, 96—107).—An account is given of the method used to get a 10^3 -fold increase in the intensity of the polarised beam obtainable from a given initial X-ray intensity, so that the beam is strong enough to use for the study of vectorial phenomena in the interactions of X-rays and matter. L. L. B.

Intensity of the central spot produced by X-rays penetrating piezoelectrically oscillating

quartz crystals. G. E. M. JAUNCEY and A. T. JAKES (Physical Rev., 1936, [ii], 50, 672).—Causes of variation of intensity and area of the central spot were investigated. The increases found by FOX (cf. A., 1935, 1059) were probably due to an accidental combination of photographic reversal and halation.

N. M. B.

Double Compton scattering. F. BOPP (Naturwiss., 1936, 24, 680—681).—The scattered radiation from Pb at an angle of 114° is considered. The intensity of double scattered radiation for thin films increases more rapidly than with the square of the distance.

A. J. M.

Photo-electric properties of barium and calcium. N. C. JAMISON and R. J. CASHMAN (Physical Rev., 1936, [ii], 50, 624—631).—With repeated fractional distillation of Ba in a photo-electric cell, the work function at room temp. was 2.520 and 2.510 e.v., the difference being attributed to differences in crystal structure or in purity. Measurements at room temp. to 100° gave a temp. coeff. of $(2.2 \pm 0.7) \times 10^{-5}$ e.v. per 1° . The abs. photo-electric yield of the surface was determined. The optical reflexion coeff. varied 43—63% over 4000—7000 Å. The work function of a Ca surface prepared by single distillation was 2.706 e.v. After repeated surface heating to 100° , the data did not fit Fowler's theoretical curve, the discrepancy indicating surface inhomogeneity. Analysis of data indicates two emitting surfaces having work functions differing by approx. 0.2 e.v.

N. M. B.

Dependence of the field electron stream on the work of emission. E. W. MÜLLER (Z. Physik, 1936, 102, 734—761).—Measurements were made of electron emission from Ba, Mg, and Cs on W. The results are somewhat at variance with wave-mechanical theory.

A. E. M.

Irregularities in thermionic emission from tungsten. F. L. YERZLEY (Physical Rev., 1936, [ii], 50, 610—616; cf. Johnson, this vol., 553).—A tube with a moving electrode is used to investigate variations in emission density over a length of W filament. Above a crit. temp. range positive ion emission is limited to narrow regions near the wire connections. Electron emission, even after careful filament ageing, is not uniform from point to point, but occurs in a stable pattern, with irregularities, the causes of which are discussed.

N. M. B.

Where can negative protons be found? F. ZWICKY (Physical Rev., 1935, [ii], 48, 169).—Negative protons should be sought in cloud chambers at high altitudes.

L. S. T.

Free atoms and molecular dissociation in high frequency discharges. A. A. BALANDIN and J. EIDUS (Acta Physicochim. U.R.S.S., 1936, 4, 527—546).—The instantaneous pressure increase on starting a high-frequency discharge was studied for discharges through a no. of pure and mixed bimol. gases and Ne. The effect, observed with all bimol. gases, is dependent on the nature of the electrodes, the initial pressure of the gas, and the current and voltage in the secondary. No effect is observed with Ne. The presence of H atoms in the discharge

through H_2 is indicated by the reduction of MoO_3 in the discharge tube.

O. D. S.

Possibility of a unified interpretation of electrons and protons. V. ROJANSKY (Physical Rev., 1935, [ii], 48, 108—109).—Theoretical.

L. S. T.

Polarisation of electrons by double scattering. O. HALPERN and J. SCHWINGER (Physical Rev., 1935, [ii], 48, 109—110).

L. S. T.

Absorbability of energy-rich electrons. M. WALDMEIER (Helv. phys. Acta, 1935, 8, 517—518; Chem. Zentr., 1936, i, 9).—The mass absorption coeff. of high-speed electrons in Pb is much $>$ in Al, in qual. agreement with the theory of Bethe and Heitler.

J. S. A.

Behaviour of oxygen on electron bombardment. N. NEKRASSOV and I. STERN (Acta Physicochim. U.R.S.S., 1936, 4, 283—300).— O_2 in a three-electrode discharge tube at pressures 0.01—0.03 mm. is adsorbed on metal surfaces at 150—200°. On electron bombardment activated O_2 mols. are formed and the pressure sinks rapidly. The velocity of decrease is greatly reduced by decreasing the surface of the Pt anode. The nature of the excited O_2 mols. and the behaviour of secondary electrons are discussed.

R. S. B.

Space charge for electrons with initial velocities. G. PLATO, W. KLEEN, and H. ROTHE (Z. Physik, 1936, 101, 509—520).

A. B. D. C.

Scattering of high-speed electrons of varying energy. H. J. YEARIAN and J. D. HOWE (Physical Rev., 1935, [ii], 48, 381—382).—The atom factor of Au and Ag at different voltages has been investigated.

L. S. T.

Electron diffraction by gas molecules. I. Structure of phosphorus. II. Valency angle of oxygen. L. R. MAXWELL, V. M. MOSLEY, and S. B. HENDRICKS (Physical Rev., 1935, [ii], 48, 476; cf. this vol., 17).

L. S. T.

Electron velocity distribution in gases. K. G. EMELÉUS and R. J. BALLANTINE (Physical Rev., 1936, [ii], 50, 672—673).—Druyvesteyn's method of analysis, applied to probe data for arcs and glows with electron concns. of 10^7 — 10^9 per c.c., shows the frequent existence of a wide depression in the distribution function for electron velocities rather $>$ the mean, as predicted by Morso (cf. A., 1935, 1294), and the common occurrence of a fairly distinct group of electrons of mean energy order 5—10 e.v., in accordance with the quantum theory of ionisation.

N. M. B.

Use of complex Riemannian geometry in the theory of the electron. U. KAKINUMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 83—98).

J. S. A.

Carbon reactions and the corrected mass scale. M. A. TUVE and L. R. HAFSTAD (Physical Rev., 1935, [ii], 48, 106—107).—The reactions of C under deuteron bombardment are discussed in relation to the new mass vals. (cf. this vol., 1171).

L. S. T.

At. wt. of molybdenum. Analysis of molybdenum pentachloride. O. HÖNIGSCHMID and G.

WITTMANN (Z. anorg. Chem., 1936, 229, 65—75).—The mean of 19 nephelometric titrations of MoCl_5 with AgNO_3 gives Mo 95.95 ± 0.004 (Ag 107.880, Cl 35.457).
F. L. U.

At. wt. of erbium. O. HÖNIGSCHMID (Naturwiss., 1936, 24, 619).—By titration of impure ErCl_3 with AgNO_3 , and correcting for Y and Tm content, the val. 167.24 was obtained for the at. wt. of Er. This is in agreement with the mass-spectrograph val. The previous low val. (165.2) is ascribed to impurity in the Er prep.
A. J. M.

At. wt. of tungsten. Analysis of tungsten hexachloride. O. HÖNIGSCHMID and W. MENN (Z. anorg. Chem., 1936, 229, 49—64).—The purification of W by fractional sublimation of WCl_6 is described. Nephelometric titration of purified WCl_6 by AgNO_3 gives, as the mean of 22 experiments, W 183.92 ± 0.014 (Ag 107.880, Cl 35.457).
F. L. U.

Double-focussing mass spectrograph and the masses of ^{15}N and ^{18}O . J. MATTAUCH (Physical Rev., 1936, [ii], 50, 617—623).—The theory and description of an instrument working as an "achromatic lens" for all masses are given. The differences of packing fraction of doublets containing ^{15}N and ^{18}O were determined. Isotopic wts. referred to $^{16}\text{O} = 16$ are $^{15}\text{N} = 15.0040 \pm 0.0008$, and $^{18}\text{O} = 18.0037 \pm 0.0007$.
N. M. B.

Evidence for the existence of an isotope of potassium of mass 40. A. O. NIER (Physical Rev., 1935, [ii], 48, 283—284).—The data obtained with a mass spectrograph of increased resolving power are considered to establish the existence of ^{40}K . The abundance ratio $^{39}\text{K} : ^{40}\text{K}$ is 8600 approx.
L. S. T.

Further evidence for the existence of ^{40}K . A. K. BREWER (Physical Rev., 1935, [ii], 48, 640).—Mass spectra of positive thermions emitted from various K sources confirm the existence of ^{40}K (cf. preceding abstract). The $^{39}\text{K} : ^{40}\text{K}$ abundance ratio calc. is 8300 ± 100 .
L. S. T.

Separation of mercury isotopes. K. ZUBER (Helv. phys. Acta, 1935, 8, 488—490; Chem. Zentr., 1936, i, 494).—The III and IV components of the 2537 Å. Hg line excite respectively the 200 and the 202 Hg isotopes. Irradiation of a Hg- O_2 mixture with either of these lines causes selective oxidation of one isotope. The method gave positive results.
H. J. E.

Evidence against ^5He . R. D'E. ATKINSON (Physical Rev., 1935, [ii], 48, 382).—Evidence against the view that ^5He should be stable is discussed.
L. S. T.

Self-excitation of Geiger-Müller counters. G. MEDICUS (Z. Physik, 1936, 103, 76—112).—Of two H_2 -filled counter tubes with Cu cathodes, one exhibited self-excitation, probably due to H_2O adsorbed on the glass walls. The influence of light, temp., and the presence of Hg vapour on the no. and distribution of impulses recorded over a given time was investigated.
H. C. G.

Range of α -particles and chemical linking. M. FÖRSTER (Ann. Physik, 1936, [v], 27, 373—388).—

The stopping power of H_2O vapour for α -particles has been found to be about 3% < that of the H_2-O_2 mixture from which it was formed.
O. D. S.

Separation of β - and γ -radiation of radioactive preparations. H. STAUB (Helv. phys. Acta, 1935, 8, 512—513; Chem. Zentr., 1936, i, 14).—The material is placed at one end of a solenoid, by means of which β -rays of uniform velocity are focussed at a point outside the solenoid, and shielded by a Pb cylinder from direct γ -radiation.
J. S. A.

Cloud chamber experiments with γ - and β -rays in xenon and krypton. H. KLARMANN and W. BOTHE (Z. Physik, 1936, 101, 489—498)
A. B. D. C.

Liberation of electrons from solids by hard γ -rays. T. G. KUJUMZELIS (Z. Physik, 1936, 102, 762—767).—Measurements were made of the nos. of electrons liberated from C, Al, Cu, Sn, and Pb in forward and backward directions by γ -rays with energies between 2.6×10^6 and 7.7×10^6 e.v. Results plotted against at. no. give characteristic curves which indicate a possible method for determining the energy of unknown γ -radiation.
H. C. G.

Effect of a magnetic field on the visible light produced in liquids by γ -rays. P. A. TSCHERENKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 413—416; cf. A., 1934, 938).—Vavilov's theory that " γ -luminescence" is due to Compton electrons liberated by the primary photons is supported by the asymmetric distribution of intensity of this light in a 9500 gauss magnetic field.
R. C. M.

Excitation of secondary γ -rays by β -rays. E. STAHEL and P. KIPFER (Helv. phys. Acta, 1935, 8, 508—511; Chem. Zentr., 1936, i, 10).—The intensity of the secondary γ -radiation excited in Pb by the primary β -radiation from U-X has the same intensity as the primary γ -radiation of U-X, and is shown by absorption measurements to consist of two (possibly three) components.
J. S. A.

Energy differences on addition of neutrons. R. FLEISCHMANN (Z. Physik, 1936, 103, 113—124).—Quantum energies of γ -rays resulting from the bombardment of H, Al, Fe, Cu, Se, Ag, Cd, Sm, Gd, Hg, and Pb by slow neutrons have been measured by a coincidence method using two Geiger-Müller counters. Results plotted against at. no. show max. for Fe and flat min. for rare earths, and then a further rise. The min. corresponds with a max. in the effective cross-section for the addition of slow neutrons. Cd was shown to emit γ -rays.
H. C. G.

Neutrons from different sources. R. LADENBURG, R. ROBERTS, and M. B. SAMPSON (Physical Rev., 1935, [ii], 48, 467).—A preliminary report of the yields of neutrons obtained from targets of D compounds, Be metal, and LiF bombarded by accelerated deuterons under various conditions.
L. S. T.

Slow neutrons. W. M. BRUBAKER and T. W. BONNER (Physical Rev., 1935, [ii], 48, 470).—Measurements of the tracks of the short-range recoil protons which are projected by neutrons in the energy interval 0.03—0.6 m.e.v. indicate no anomalous absorption within this range.
L. S. T.

Scattering of neutrons in matter. L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 810—812).—The statistics of the scattering of neutrons by protons and nuclei are discussed.

D. C. J.

Absorption of slow neutrons in silver. L. N. RIDENOUR and D. M. YOST (Physical Rev., 1935, [ii], 48, 383—384).—Data for the absorption by Ag of slow neutrons from B+Rn and Be+Rn sources as measured by detectors of Ag, Cu, V as NH_4VO_3 , Br as NH_4Br , and I as CHI_3 are recorded and discussed.

L. S. T.

Absorption of neutrons in silver, cadmium, and boron. II. N. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 291—293; cf. this vol., 1314).—The absorption of neutrons (from Ra and Rn on Be) by B has been studied as a function of the thickness (l) of paraffin used to slow down the neutrons; results are similar to those with Cd. Filtration through Cd reduces the coeff. of absorption of neutrons in Ag. The relations between the activities of the two Ag isotopes have been studied, using different filters and vals. of l ; half periods of 24 sec. and 2.33 min. have been obtained. The ratio of the activities depended very little on l .

R. S. B.

Slowing down of neutrons by the nuclei of heavy elements. P. I. LUKIRSKI and T. CAREVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 411—412; cf. A., 1935, 141; this vol., 132, 402).—Neutrons from a Rn+Be source are slowed down to thermal velocities when passing through an enclosing Pb sphere of 7.4 cm. diameter.

R. C. M.

Coincidence experiments with neutrons and γ -rays of beryllium. H. MAIER-LEIBNITZ (Z. Physik, 1936, 101, 478—485).—Disintegration of Be with α -rays gives coupled neutrons and γ -rays, and γ -ray quanta in pairs.

A. B. D. C.

γ -Rays from nitrogen bombarded with deuterons. H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], 48, 100).—The energy spectrum of recoil electrons from N, as NH_4Cl , bombarded with deuterons at 900 kv. indicates that the principal γ -ray lines are 1.9, 3.1, 4.0, 5.3, and 7.0 m.e.v.

L. S. T.

α -Radioactivity of argon formed by radiochlorine. W. F. LIBBY, M. D. PETERSON, and W. M. LATIMER (Physical Rev., 1935, [ii], 48, 571—572).—Radio-Cl from Ag radiochloride gives active A which yields a radiation, probably an α -particle, of approx. 3.1 ± 0.2 mm. range in air. Probable reactions are $^{38}\text{Cl} = ^{38}\text{Ar} + e^-$ and $^{38}\text{Ar} = ^{34}\text{S} + \alpha$, ^{38}Cl being formed by $^{37}\text{Cl} + \frac{1}{2}n = ^{38}\text{Cl}$.

L. S. T.

β -Ray spectra of radioactive manganese, arsenic, and indium. M. V. BROWN and A. C. G. MITCHELL (Physical Rev., 1936, [ii], 50, 593—598; cf. Gaertner, this vol., 918).—The β -ray spectra were obtained by measuring tracks produced in a cloud-chamber in a magnetic field. Mn and As spectra were resolved into two components, the end-points being: Mn, 1.2 and 2.9; As, 1.09 and 3.4 m.e.v. The end-point for In is 1.45 m.e.v.

N. M. B.

γ -Rays from boron bombarded with protons. H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and

C. C. LAURITSEN (Physical Rev., 1935, [ii], 48, 102—103).—Bombardment of B by protons gives a γ -radiation of intensity \ll than obtained with deuterons as projectiles. The energy spectrum of recoil electrons indicates γ -ray lines at 2.5, 4.2, 5.7, 7.5, 9.8, and 13 (?) m.e.v. The upper limit of the γ -ray spectrum is at 14.5 m.e.v. approx. The probable reaction is $^{11}\text{B} + ^1\text{H} \rightarrow ^{12}\text{C}$.

L. S. T.

Heavy particle component of the cosmic radiation. R. B. BRODE, H. G. MACPHERSON, and M. A. STARR (Physical Rev., 1936, [ii], 50, 581—588).—Investigation with a large Wilson cloud-chamber showed, in 8500 pictures, about 80 heavy tracks, of which 21 were made by particles of about the ionisation of slow protons. About 1% of the sea-level cosmic ionisation is due directly to heavy particles.

N. M. B.

Artificial transmutation of light elements bombarded by ions of hydrogen and heavy hydrogen. I. B. ARAKATSU, K. KIMURA, and Y. UEMURA (Mem. Fac. Sci. Agric. Taihoku, 1936, 18, 75—94).—With apparatus of the type used by Oliphant and Rutherford, the relative probability of two alternative types of disintegration of ^6Li and of ^{10}B was measured.

A. E. M.

Temporary excess of 10% in the cosmic radiation. J. CLAY, E. M. BRUINS, and J. T. WIERSMA (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 813—815).—A sudden temporary increase in cosmic-ray intensity is reported.

D. C. S.

Cosmic-ray showers produced by electrons. E. C. STEVENSON and J. C. STREET (Physical Rev., 1935, [ii], 48, 464—465).—Photographs of showers produced by an electron and by a non-ionising ray are reproduced.

L. S. T.

Heavy particles from lead. J. C. STREET, E. G. SCHNEIDER, and E. C. STEVENSON (Physical Rev., 1935, [ii], 48, 463).—Heavy particles from a Pb plate have been observed in cloud-chamber photographs of cosmic-ray showers.

L. S. T.

Cosmic-ray measurements with a Wilson chamber on Jungfraujoch. G. HERZOG and P. SCHERRER (Helv. phys. Acta, 1935, 8, 514—515; Chem. Zentr., 1936, i, 279).

J. S. A.

Apparatus for prolonged registration of intensity course of cosmic radiation. P. SCHERRER, H. STAUB, and H. WAFFLER (Helv. phys. Acta, 1935, 8, 516—517; Chem. Zentr., 1936, i, 279).

J. S. A.

Energy distribution of cosmic rays. A. LONGACRE (Physical Rev., 1936, [ii], 50, 674).—Statistical variations in Anderson and Neddermeyer's data are discussed. Analysis indicates that a sample of 100 vertical cosmic rays will contain 37 negative and 63 positive rays, the latter containing 18 in a low, and 45 in a higher, energy distribution.

N. M. B.

Residual current in ionisation-pressure chamber, and variation with pressure of ionisation due to cosmic rays. W. MESSERSCHMIDT (Z. Physik, 1936, 103, 18—26).—Ionisation due to α -particles was eliminated by working at 10—25 atm. γ -Rays and cosmic rays show differences of ionisation between 0 and 25 atm.

A. E. M.

Effect of paraffin and lead on the rate of production of very large cosmic-ray bursts. D. HEYWORTH and R. D. BENNETT (Physical Rev., 1936, [ii], 50, 589—593; cf. Doan, this vol., 265).—Using an intensity meter, data are given for the effects, at sea level for bursts $> 15 \times 10^6$ ion pairs, on the rate of production of bursts of different magnitudes of degree of shielding of the ionisation chamber, heavy building structure above the instrument, and Pb and paraffin placed immediately above the ionisation chamber. The effect of paraffin is much $<$ that of Pb. N. M. B.

Cosmic-ray bursts. W. MESSERSCHMIDT (Z. Physik, 1936, 103, 27—56).—Collision distribution curves as regards size and frequency are given for Al, Fe, Pb, and C. A. E. M.

Dependence of nuclear forces on velocity. J. A. WHEELER (Physical Rev., 1936, [ii], 50, 643—649).—Mathematical. The Majorana force may be considered as a special case of a neutron-proton interaction dependent on velocity and angular momentum. The most general dependence of two-particle forces on spin, separation, and velocity, consistent with the conservation laws, is determined. N. M. B.

Structure of atomic nuclei. N. S. JAPOLSKY (Phil. Mag., 1936, [vii], 22, 537—581; cf. A., 1935, 1442).—Mathematical. The theory previously reported is developed and extended. N. M. B.

Modification of the Moseley law. V. DOLEJSEK (Acta phys. polon., 1934, 2, 439—446; Chem. Zentr., 1936, i, 503).—A general equation, valid for all the elements and all electron shells, is given. H. J. E.

Must neutron-neutron forces exist in the ^3H nucleus? R. D. PRESENT (Physical Rev., 1936, [ii], 50, 635—642; cf. White, this vol., 400; Tuve, *ibid.*, 539).—Mathematical. Evidence points to the existence of direct like-particle forces in the nucleus. N. M. B.

The neutron and structure of the atomic nucleus. C. LOREY (J. pr. Chem., 1936, [ii], 147, 78—82).—Since, with the exception of ^1H , all known isotopes have an at. wt. $<$ double the nuclear charge (z), it is suggested that each proton is associated with one neutron (neutron of the first kind). Since, however, most isotopes have an at. wt. $> 2z$, these must contain neutrons of the second kind, or “ballast neutrons.” The nos. of protons and of neutrons of the two kinds are tabulated for a no. of isotopes. The no. of neutrons in the outermost quantum group of the at. nucleus has a bearing on the at. stability. J. W. S.

Higher-order derivatives in the interaction “Ansatz” of the Fermi theory. E. J. KONOPINSKI and G. E. UHLENBECK (Physical Rev., 1935, [ii], 48, 107—108; cf. A., 1935, 1048).—Mathematical. L. S. T.

Recombination of neutrons and protons. E. FERMI (Physical Rev., 1935, [ii], 48, 570).—Theoretical. L. S. T.

Self-interaction of neutrons and protons. D. IVANENKO and A. SOKOLOV (Nature, 1936, 138, 684).—The interaction between two heavy nuclear particles is computed on Fermi's theory, assuming

the interaction transfer by one pair and also by an arbitrary no. of pairs of electrons and neutrinos. L. S. T.

Relativity corrections in the theory of the deuteron. E. FEENBERG (Physical Rev., 1936, [ii], 50, 674; cf. Margenau, this vol., 1175).—Mathematical. N. M. B.

Comparison of Majorana-Heisenberg and velocity-dependent forces. K. WAY and J. A. WHEELER (Physical Rev., 1936, [ii], 50, 675). N. M. B.

Magnetic nuclear moment of platinum, ^{195}Pt . T. SCHMIDT (Z. Physik, 1936, 101, 486—488).—This moment is $+0.6$ nuclear magneton. A. B. D. C.

Quadrupole moment and magnetic moment of $^{76}_{33}\text{A}$. H. SCHULER and M. MARKETU (Z. Physik, 1936, 102, 703—708).—From fine structure measurements, the quadrupole moment q is $+0.3 \times 10^{-24}$ and the mean val. for the magnetic moment μ is $+1.5$ nuclear magnetons. L. G. G.

Dissociative equilibrium and pair generation. J. KISHEN (Indian J. Physics, 1936, 10, 389—397).—Mathematical. A general formula for the dissociative equilibrium in an external radiation field is developed and applied to thermal ionisation and to the formation and annihilation of pairs of electrons and positrons existing in statistical equilibrium with radiation. N. M. B.

Self-consistent field, with exchange, for Cl^- . D. R. HARTREE and W. HARTREE (Proc. Roy. Soc., 1936, A, 156, 45—62).—Fock's equations for the self-consistent field, with exchange, for the Cl^- ion have been solved, and the results are compared with those of the self-consistent field without exchange. The inclusion of exchange terms causes a contraction of the ($3p$) radial wave function. The effects of the inclusion on the X-ray scattering factor, the diamagnetic susceptibility, and the electrical polarisability are discussed. L. L. B.

Fundamental frequencies and energy constants. H. S. ALLEN (Proc. Roy. Soc., 1936, A, 156, 85—96).—The sp. heat of solids, energy, and optical data are considered. L. L. B.

Fundamental physical constants. W. N. BOND (Phil. Mag., 1936, [vii], 22, 624—632).—Estimates of numerical vals. of the consts. are deduced from Eddington's theories concerning M/m , $hc/2\pi e^2$, and the universal gravitational const. Confirmatory experimental evidence is given, and the remaining discrepancies are pointed out. Full data and deductions are tabulated. N. M. B.

Lorentz contraction of a liquid. L. COURVOISIER (Z. Physik, 1936, 101, 422—436).—Observation of the Lorentz contraction through 1934 and 1935 showed a contraction of the correct frequency but of small amplitude. A. B. D. C.

Lorentz contraction determined with levelled apparatus free to rotate. L. COURVOISIER (Z. Physik, 1936, 101, 437—446).—Contractions observed agree with theory. A. B. D. C.

Isotope relations in the spectra of LiH and LiD. F. H. CRAWFORD and T. JORGENSEN, jun.

(Physical Rev., 1935, [ii], 48, 475; cf. A., 1935, 1051).
L. S. T.

Spin coupling in $^3\Sigma$ states of PH and PD. M. ISHAQUE and R. W. B. PEARSE (Proc. Roy. Soc., 1936, A, 156, 221—232).—The spectrum of PD, like that of PH, consists of one intense band near λ 3400 containing five max., which are more sharply defined in PD. The spin fine structure of the $^3\Sigma$ states of PH and PD are compared with Kramers' formulæ and the const. ϵ and γ evaluated. ϵ remains almost unchanged by the substitution of D for H, whilst γ is reduced to almost half.
L. L. B.

Molecular spectra of magnesium deuteride. Y. FUJIOKA and Y. TANAKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 121—137).—Seven $^2\Pi \rightarrow ^2\Sigma$ bands of MgD between 4900 and 5500 A. have been analysed, and the mol. const. evaluated.
J. S. A.

Spectrum of indium oxide. W. W. WATSON and A. SHAMBON (Physical Rev., 1936, [ii], 50, 607—609; cf. Guernsey, A., 1934, 1055).—Wave no. data and assignments and intensities of the complex spectrum of InO lying between the two In resonance lines at 4102 and 4511 A. are tabulated. An expression for the band heads is given.
N. M. B.

New ultra-violet bands of SO_2 in emission. G. KORNFIELD (Trans. Faraday Soc., 1936, 32, 1487—1492).—59 bands between 2443 and 2123 A., degraded to the red, are recorded in the spectrum of a blue electrodeless discharge in SO_2 , 49 being known SO_2 bands. None can be added to the known band system of SO . All the bands are attributed to SO_2 in emission; a proposed classification is given.
A. J. E. W.

Absorption spectrum of chlorine heptoxide. C. F. GOODEVE and B. A. M. WINDSOR (Trans. Faraday Soc., 1936, 32, 1518—1519).—The spectrum consists of a single continuous band, setting in at about 3000 A., and increasing in intensity to 2000 A., the limit of observation. An extinction coeff. curve is given. Parallelism between the absorption spectra of Cl and N oxides is noted.
A. J. E. W.

Ultra-violet absorption spectrum of hydrogen fluoride. K. SIGA and H. J. PLUMLEY (Physical Rev., 1935, [ii], 48, 105).—With HF at 2 to 76 cm. pressure, band systems from 3200 to 2400 A., with a max. at approx. 2800 A., and from 2300 A. to shorter $\lambda\lambda$ have been found. The structure of both systems indicates that the absorbing mol. is a polymeride of HF.
L. S. T.

Spectra of tellurium halides. M. WEHRLI (Helv. phys. Acta, 1935, 8, 487—488; Chem. Zentr., 1936, i, 506).—The absorption bands of TeCl_2 at $\lambda\lambda$ 6400—4700 A. are diffuse. At 170° continuous absorption occurs at 2450 A. TeBr_2 has a similar band system at $\lambda\lambda$ 6500—5270 A.
H. J. E.

Band spectra of MgCl , MgBr , and MgI in absorption. F. MORGAN (Physical Rev., 1936, [ii], 50, 603—607).—Data, and analyses consistent with the respective isotope shifts, are recorded for single systems of four-headed bands in the range 3600—3950 for MgCl and 3800—4000 A. for MgBr . All the bands degrade towards the violet. The analysis

of the MgCl system disagrees with that of Parker (cf. A., 1935, 562). A band system in the region 4040—4200 A., degrading towards the violet, was observed for MgI .
N. M. B.

Ultra-violet absorption spectra of Pr^{+++} and Nd^{+++} ions in solution. P. C. MUKHERJI (Indian J. Physics, 1936, 10, 319—323).— $\text{Pr}_2(\text{SO}_4)_3$ solution gave a broad diffuse band in the region 2750—2530 A., resolving at increased dilution into components at 2730, 2605, and 2560 A. $\text{Nd}_2(\text{SO}_4)_3$ gave four new lines, 2775, 2730, 2600, and 2505 A. The band 2280—2100 A., reported by Freed (cf. A., 1932, 211), was not observed with $\text{Nd}_2(\text{SO}_4)_3$ or NdCl_3 . In PrCl_3 and NdCl_3 the bands are partly masked by continuous ultra-violet absorption.
N. M. B.

Absorption spectrum of cobalt chloride in presence of magnesium chloride in aqueous solution. O. R. HOWELL and A. JACKSON (J.C.S., 1936, 1268—1273).—Graphs show the absorption spectra of a series of solutions containing a fixed amount of CoCl_2 with increasing concns. of MgCl_2 . The extinction coeffs. at the max. of the chief bands, plotted against the concns. of MgCl_2 , show that no blue constituent is formed until a crit. concn. of MgCl_2 is reached; the amount of blue constituent then increases rapidly. The mechanism is similar to that caused by the addition of HCl to aq. CoCl_2 .
W. R. A.

Absorption spectra. I. (Mlle.) C. L. HARBERTS, P. M. HEERTJES, L. J. N. VAN DER HULST, and H. I. WATERMAN (Bull. Soc. chim., 1936, [v], 3, 1916—1917; cf. this vol., 661).—A new method of calculating the mean absorption coeff. is developed and applied to the results reported previously.
J. W. S.

Spectrum of the cold flame of ether. V. KONDRATEEV (Acta Physicochim. U.R.S.S., 1936, 4, 556—558).—The measurements by Emelëus of the bands in the spectrum of the cold flame of Et_2O (A., 1929, 1215) are similar to those by Herzberg and Franz of the fluorescence spectrum of CH_2O (A., 1932, 896). It is concluded that the emitters in the cold flame of Et_2O are CH_2O mols.
O. D. S.

Absorption spectra of polyatomic molecules containing methyl and ethyl radicals. III. H. W. THOMPSON and J. W. LINNETT (Proc. Roy. Soc., 1936, A, 150, 108—129; cf. A., 1934, 828; 1935, 1188).—All the mols. examined had all the linkings of a given element combined with an alkyl radical. Most of such compounds show continuous absorption in the region studied (2000—7000 A.), but band systems, which have been analysed, are found for the Et derivative of Zn, Cd, and Hg, and for the thioethers. The photochemical significance of the continua is discussed.
L. L. B.

Ultra-violet absorption spectrum of pyridine vapour. Relation to Raman spectrum. V. HENRI and P. ANGENOT (J. Chim. phys., 1936, 33, 641—665).—The ultra-violet absorption spectrum of 0.01—910 mm. of $\text{C}_5\text{H}_5\text{N}$ at 0—308° has been photographed. Fine bands extend from 3105 to 2750 A. At shorter λ , the bands are broader and

absorption is continuous at $< 2510 \text{ \AA}$. Light of $\lambda < 2750 \text{ \AA}$. causes decomp. The bands of longer λ appear only as the temp. is raised, and correspond with higher vibration states of the normal mol. Analysis of the spectrum shows that the unexcited mol. has five fundamental frequencies: 600, 857, 993, 1031, and 1159 cm^{-1} , corresponding closely with the Raman spectrum vals., and, for each of the five series of bands, the normal frequency is 600 and that of the excited state, 542 cm^{-1} . The frequencies are assigned to appropriate vibrations of the mol. J. G. A. G.

Optical absorption of porphyrins. VIII. A. STERN and H. MOLVIG. **IX. Ultra-violet absorption.** I. F. PRUCKNER and A. STERN (Z. physikal. Chem., 1936, 177, 365—386, 387—397; cf. this vol., 1318).—VIII. Introduction of one or two NO_2 into the α tioporphen mol. shifts the absorption max. towards the red, but the curve is still of the α ti type. Therefore the NO_2 are not attached to a C of the methine bridge of the porphin system (I). If a Br is introduced into each of two adjacent nuclei in (I) the type of the absorption curve is unaltered, but if the substitution is in nuclei I and III the curve changes to the rhodo type, which supports the view that these nuclei have a pyrrolenine structure. $\cdot\text{SO}_3\text{Me}$ influences the light absorption of (I) in the same way as a group containing CO, the absorption curves of these derivatives being of the rhodo type. The free porphinsulphonic acids apparently are inner salts, the $\cdot\text{SO}_3\text{H}$ reacting with one of the N of nucleus III. Comparison of the absorption spectra of the Cu salts shows that the Cu in the phorbin (i.e., dihydroporphin) system (II) is bound in the same way as in (I), but by the action of secondary valencies between the C:N in (II) and the metal atom the chromophoric power of this group is intensified. The absorption curve of *Spirographis*-hæmin (cf. *ibid.*, 1273) is of the rhodo type.

IX. In the ultra-violet down to $240 \text{ m}\mu$ various normal porphyrins have only one absorption band, the mol. extinction coeff., ϵ , of which is high. The band is shifted appreciably only by the introduction into (I) of large chains or of groups containing CO. In the ultra-violet the absorption curve of porphin has a single band, and substitution even of alkyl groups only shifts the band max. and min. towards the red and depresses ϵ . Monoimido- and $\beta\delta$ -di-imido-porphyrins have only one band, the max. of which is at a much shorter λ than that of the corresponding porphyrin. The absorption spectra of the octasubstituted porphins and phorbins have the same no. of bands, the red band of the porphin being much intensified and shifted towards longer $\lambda\lambda$ in the phorbins. R. C.

Ultra-violet absorption of phthiocol.—See this vol., 1423.

Infra-red absorption spectrum of heavy phosphine (PD_3). G. B. B. M. SUTHERLAND and G. K. T. CONN (Nature, 1936, 138, 641—642).—This spectrum agrees with the Raman spectrum but not with the frequencies predicted from the spectrum of PH_3 , indicating that a simple valency force field

is not satisfactory for correlating the vibration frequencies of a mol. of this type. L. S. T.

Rotation-vibration spectrum of acetylene (C_2H_2). R. MECKE and R. ZIEGLER (Z. Physik, 1936, 101, 405—417).—Eight new bands have been examined between 11,000 and 5700 \AA ., and an analysis is given that accounts for 35 of the observed bands. A. B. D. C.

Absorption spectra in the near infra-red of [saturated and] ethylenic hydrocarbons. M. L. SHERRILL and P. MOLLET (J. Chim. phys., 1936, 33, 701—718).—The absorption spectra have been investigated at $1.3\text{--}3.6 \mu$, and absorption coeffs. are recorded. The substances conform to four types: (i) $n\text{-C}_5\text{H}_{12}$, $n\text{-C}_7\text{H}_{16}$, (ii) $\text{CH}_2\text{:CHPr}^a$, $\text{CH}_2\text{:CH}\cdot\text{C}_5\text{H}_{11}$, $\text{CH}_2\text{:CHPr}^b$, $\text{CH}_2\text{:CMeEt}$, (iii) CHMe:CHEt , $(\text{CHEt})_2$, CHEt:CHPr^a , and (iv) CHMe:CMe_2 , CHMe:CET_2 , $(\text{CMe}_2)_2$, and all have strong absorption bands at $7143\text{--}7246$, $5715\text{--}5847$, $4210\text{--}4264$, $2906\text{--}2949$, and $2853\text{--}2877 \text{ cm}^{-1}$. The $2906\text{--}2949 \text{ cm}^{-1}$ bands of 'CRR' compounds are double, and compounds of type (ii) also have a strong band at $3072\text{--}3091 \text{ cm}^{-1}$ which is attributed to C-H vibrations in the (CH_2) group. The interpretation of the results is discussed. J. G. A. G.

"Wing" accompanying the Rayleigh line in liquid mixtures. II. S. C. SIRKAR and B. K. MOOKERJEE (Indian J. Physics, 1936, 10, 375—387; cf. this vol., 777, 923).—The distribution of intensity in the wing accompanying the Rayleigh line due to CS_2 , CHCl_3 , PhCl , COMe_2 , and xylene has been compared microphotometrically with that due to the solution of each in MeOH. The relative intensity of the wing with respect to that of any particular vibrational Raman line increases for solutions in MeOH, except in the case of PhCl where there is no appreciable change. In no case is there any marked diminution in intensity of any portion of the wing due to dissolution. Theoretical explanations are discussed. N. M. B.

Polarisation of Raman lines in some inorganic acids. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1936, 4, A, 174—185).— HNO_3 , HIO_3 , H_2SO_4 , H_2SeO_4 , and H_2SeO_3 were investigated. The lines of conc. HNO_3 showed depolarisations $< 6/7$. Polarisation of the lines due to NO_3' support the plane equilateral structure. Six lines of the undissociated HNO_3 mol. were identified with those of an unsymmetrical pyramidal model. H_2SO_4 , HSO_4' , SO_4'' , and H_2SeO_4 are tetrahedral and structural formulæ are discussed. Bands of HIO_3 and H_2SeO_3 are assigned to different mol. species. W. R. A.

Raman effect of non-aqueous solutions of electrolytes. I. Solutions of arsenic halides. V. FINKELSTEIN and P. KURNOSOVA (Acta Physicochim. U.R.S.S., 1936, 4, 123—134).—The Raman spectra of AsCl_3 and AsBr_3 in Et_2O and C_6H_6 consist of the spectra of the pure solute and pure solvent only, indicating that the solvate is not a chemical compound. It is suggested that solvation occurs by dipole association. R. S.

Raman spectra of trimethylamine and some compounds of hydroxylamine and hydrazine.

R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1936, 4, A, 204—212).—The observed frequencies are discussed with the aid of polarisation data. A comparison with the spectrum of *isobutane* assists in the assignment of frequencies. The hydrochlorides of NH_2OH and N_2H_4 in the cryst. state show a single line which remains strong in aq. solution. Possible structures are discussed.

W. R. A.

Raman effect of a complex tungstotartrate in water. (MLLE.) M. THÉODORESCO (Compt. rend., 1936, 203, 668—669).—The Raman spectra of aq. solutions of NaH tartrate (I), Na_2WO_4 (II), and $\text{Na}_2\text{T}_2\text{WO}_3$ (III) (T=tartrate) have been studied. Strong lines appear at 321, 832, and 934 (II), 837 and 943 cm^{-1} (III). The lines 362, 837, 1088, and 1273 of (I) are not displaced in (III); the C:O line 1730 in (I) appears as 1606 and 1646 in (III); other lines of tartaric acid are displaced. The results favour the existence of (III) in solution.

R. S. B.

Raman spectrography and its importance in chemical investigations. M. NORIEGA DEL AGUILA (Bol. Soc. Quim. Peru, 1936, 2, 86—125).—A review.

Second-order lines in Raman spectra. G. S. LANDSBERG and V. J. MALISHEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 365—368).—Six new lines were found in the Raman spectrum of CCl_4 (529, 625, 919, 989, 1091, 1225 cm^{-1}) and nine new lines in that of SnBr_4 (132, 144, 176, 193, 305, 370, 386, 438, 497 cm^{-1}). The frequencies, except 144, 386 of SnBr_4 , are in agreement with calc. combination frequencies. The intensity of the second-order lines is approx. 3×10^{-3} that of the first order.

O. D. S.

Depolarisation of Raman lines of tetrachloroethylene. T. Y. WU (J. Chinese Chem. Soc., 1936, 4, 402—405).—A discussion of the fundamental vibrations of the mol., based on the depolarisation measurements and the infra-red data (cf. A., 1934, 1288).

D. C. J.

Raman spectra. I. Benzoyl chloride and its substitution products. D. D. THOMPSON and J. F. NORRIS (J. Amer. Chem. Soc., 1936, 58, 1953—1957).—Data are recorded for BzCl and for *o*-, *m*-, and *p*-methyl-, -methoxy-, -chloro-, and -nitrobenzoyl chloride.

E. S. H.

Structure by means of the Raman effect (2 phenylacetic acid-1 sodium phenylacetate) (2 acetic acid-1 sodium acetate). E. VITALE (Gazzetta, 1936, 66, 566—570).—The Raman spectra of the compounds $2\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ and $2\text{AcOH}\cdot\text{NaOAc}$ have been measured. In both spectra the line characteristic of the C:O group is missing. Structural formulæ are suggested.

O. J. W.

Raman spectra of *cis*- and *trans*-isoeugenol. B. SUSZ and E. PERROTTET (Helv. Chim. Acta, 1936, 19, 1158—1163; cf. this vol., 923).—Data for the Raman spectra of purified commercial *isoeugenol* and for the *cis*- (I) and *trans*- (II) -isomerides separated by fractional distillation are recorded and discussed. The frequency for the ethylenic linking is lowered by 25 cm^{-1} in passing from (II) to (I), in conformity with observations on similar isomerides.

F. L. U.

Raman effect of organic substances. VI. Raman effect of sesquichamene and other terpenes. K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1936, 11, 576—586).—Raman spectra of sesquichamene (I), *d*-sabinene, *d*- α -pinene, *d*-verbenol, *dl*- Δ^1 -terpinen-4-ol, menthyl and *isobornyl* acetates have been studied. From a comparison of their spectra, it is thought that if cedrene has a 1-methyl- Δ^1 -cyclopentene ring, (I) has a 1-methyl- Δ^1 -cyclohexene ring.

C. R. H.

Raman spectrum and constitution of ozonides. Raman spectrum of ozonides of ethyl maleate and fumarate. E. BRINER, E. PERROTTET, and B. SUSZ (Helv. Chim. Acta, 1936, 19, 1163—1168; cf. this vol., 839).—Data for the Raman spectra of Et_2 maleate and fumarate and their ozonides are recorded and discussed. The mol. refractions observed are $>$ those calc. by 4—5 units.

F. L. U.

Light-scattering of crystalline-liquid *p*-azoxyanisole. W. DE BRAAF and L. S. ORNSTEIN (Kolloid-Beih., 1936, 44, 427—475).—The variation of scattering with the strength of a superimposed magnetic field has been determined. The results are in accordance with the swarm theory.

E. S. H.

Sensitisation of phosphors. II. S. ROTH-SCHILD (Physikal. Z., 1936, 37, 757—764; cf. A., 1934, 1056).—The sensitising effect of small amounts of Bi, Pb, Ag, Cu on Sm and Pr phosphors with CaS and SrS, and of Pr and Sm+Nd+Y on CaS-Ag and SrS-Ag phosphors has been investigated. Bi is effective in sensitising Sm but not Pr phosphors, Pb sensitises both, whilst Cu is ineffective in both cases. In most cases the sensitising effect is observable only during excitation. The theory is discussed.

A. J. M.

Fluorescence of rare earths in glasses. O. DEUTSCHBEIN (Z. Physik, 1936, 102, 772—780).—The fluorescence spectra of glasses activated with rare earths are generally similar to those of the corresponding rare-earth compounds.

L. G. G.

Influence of molecular rotations on measurements of the duration of fluorescence. W. KESSEL (Z. Physik, 1936, 103, 125—132).—Jabłoński's theory of influence of mol. rotations has been tested by measurements with fluorescein in glycerol and H_2O .

A. E. M.

Quenching of fluorescence of dye solutions by foreign substances. I. B. SVESHNIKOV (Acta Physicochim. U.R.S.S., 1936, 4, 453—470).—The quenching of fluorescent dye solutions by inorg. and org. quenchers has been followed by observing the increase of polarisation. It is independent of the λ of the exciting light, confirming the view that in the excited state the mols. have the same energy level. Some quenchers exercise a selective action on some dyes. The results indicate that quenching action is produced by factors depending on time, and in many cases is due to deactivation through collisions of the second kind.

C. R. H.

Quenching of fluorescence due to solution medium. S. I. VAVILOV and A. N. SEVTSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 277—284).—The intensity (ρ) and degree of polarisation (p) of fluor-

escence from rhodamine-*B* (I) have been studied in glycerol, *iso*-C₅H₁₁·OH, and Bu^oOH at 289—363° abs. $1/\rho$ is a linear function of $T\rho/\eta\rho_1$, where T is the abs. temp. η the viscosity, and ρ_1 is the val. of ρ at room temp. τ_1 and ρ have been determined for (I) in H₂O and org. solvents at room temp. Two types of quenching of fluorescence are discussed. R. S. B.

Fluorescence intensity and duration. S. I. VAVILOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 271—276).—The intensity (ρ) and mean life of fluorescence phenomena are discussed. The relation $\rho = s\tau/\tau_0$ is deduced, where s is the fraction of the absorbed energy which is quenched by collisions of the second kind, τ the mean life of the excited state, and $\tau = \tau_0$ for $s = 1$. R. S. B.

Photodissociation of gallium halides. A. PETROVA (Acta Physicochim. U.R.S.S., 1936, 4, 559—566).—The first doublet, 4033 and 4172 Å., of the principal series of Ga is observed in the fluorescence excited in GaI vapour above 200° by $\lambda\lambda < 2200$ Å. This fluorescence is ascribed to $\text{GaI} + h\nu = \text{Ga}^+ + \text{I}$. The fluorescence excited in GaBr vapour by $\lambda\lambda > 1850$ Å. does not contain the resonance lines of Ga. O. D. S.

Photo-electric phenomena at the surface of electronic semi-conductors. G. LIANDRAT (Ann. Physique, 1936, [xi], 6, 391—454; cf. A., 1935, 1303).—On the basis of a crit. study of available experimental and theoretical data a simple description of the mechanism of the action of photo-elements is developed. The three essentials determining the direction and order of magnitude of the photo-electric effect are: in the cryst. lattice of a semi-conductor or insulator the photo-electrons traverse the surface with a kinetic energy, the max. val. of which satisfies the Einstein relation, they originate in the semi-conductor, and the high yield can be related to a sp. property of the lattice; in a metallic lattice they rapidly lose energy and become ordinary conductivity electrons; between the semi-conductor and the metal a thin cryst. layer of high resistivity controls the appearance of a p.d. Secondary modifications of the conductivity of the surface layer can be attributed to the ultimate behaviour of the electrons originating in the semi-conductor but stopped in the surface layer by the opposing electric field. N. M. B.

Electrical investigation of oxidic semi-conductors. W. HARTMANN (Z. Physik, 1936, 102, 709—733).—The variation of the electrical conductivity with temp. of Al₂O₃, Ta₂O₅, UO₂, and CuO is expressed by a simple exponential relation. Al₂O₃ and Ta₂O₅ showed changes of resistance after heating in vac., in O₂, or in H₂. The variation of the Hall const. with temp. of UO₂ and CuO was also investigated. A. E. M.

Electrical conductivity of thin metals, particularly of molybdenum layers. J. H. DE BOER and H. H. KRAAK (Rec. trav. chim., 1936, 55, 941—953).—The conductivity of thin Mo layers deposited on glass increases with temp. in a reversible manner up to the temp. of deposition, above which there is an irreversible change to the properties of a layer deposited at the highest temp. attained. Unimol.

layers of Mo have appreciable conductivity, whereas a thickness of 16 mols. is required before that of Ag can be determined, owing to the difference in mol. mobility. The distribution of electron levels in a thin metallic layer, which is regarded as a state intermediate between vapour and massive solid, has been studied. R. S.

Conductivity of copper oxide. G. KAPP and M. TREU (Sitzungsber. physik.-med. Soz. Erlangen, 1935, 65—66, 215—228; Chem. Zentr., 1936, i, 285).—The electrical conductivity of thin CuO layers between 20° and -100° is recorded. J. S. A.

Electrical energy set free on melting electrets. H. FREI and G. GROETZINGER (Physikal. Z., 1936, 37, 720—724).—When an electret, with no electric field associated with it, is melted between two electrodes, a current flows, the total quantity of which is independent of the time which has elapsed between the polarisation and melting (depolarisation) of the electret. The current in the case of an electret which was formed by the action of an electric field on the substance in the solid state is much smaller. If a non-polar substance, such as paraffin, is submitted to the action of an electric field when it is solidifying, or when it is solid, the amount of electricity obtained on melting is the same in both cases. The results agree with the theory that a permanent electric polarisation independent of time has occurred in electrets. A. J. M.

Variation of the dielectric constant of mercury with density at different temperatures. P. WÜSTHOFF (Ann. Physik, 1936, [v], 27, 312—328).—The dielectric const. of Hg vapour has been measured at several temp. between 401° and 470° and pressures up to 3 atm. No deviation from the Clausius-Mosotti relationship was observed. The dielectric const. of Hg at atm. pressure and 0° is calc. to be 1.00170. O. D. S.

Dielectric coefficients of gases. III. Allene, allylene, butanes, butylenes, cyanogen, and hydrogen cyanide. H. E. WATSON and K. L. RAMASWAMY. **IV. Flourides of boron, nitrogen, and carbon.** H. E. WATSON, G. P. KANE, and K. L. RAMASWAMY (Proc. Roy. Soc., 1936, A, 156, 130—143; cf. A., 1934, 347).—The measurements were made by means of the "parallel condenser" method used previously. *n*- and *iso*-C₄H₈, allene, allylene, and NF₃ have small moments, and HCN a large one, whilst the remaining gases are electrically neutral. L. L. B.

Electric moments of aliphatic diamines. P. TRUNEL (Compt. rend., 1936, 203, 563—565).—Measurements were made in C₆H₆ at 25°, 45° and 75°. The dipole moments at 25° are: (CH₂·NH₂)₂ 1.90, NH₂·[CH₂]₃·NH₂ 1.94, NH₂·[CH₂]₄·NH₂ 1.93, NH₂·[CH₂]₅·NH₂ 1.91, and NH₂·[CH₂]₆·NH₂ 1.98 *D*, and the vals. are not affected significantly by the changes of temp. There is negligible interaction between the ·NH₂ groups and their rotation is not restricted. J. G. A. G.

Structure of coumarin. M. A. G. RAU (Current Sci., 1936, 5, 132).—The dipole moment of coumarin

at 20° (4.51×10^{-18} e.s.u.) indicates a state of resonance between the normal and an excited state.

F. N. W.

Evidence of wave-mechanical resonance in the carboxylic ester and lactone group, from electric dipole moments. R. J. B. MARSDEN and L. E. SUTTON (J.C.S., 1936, 1383—1390).—The calc. moments for the two extreme possible configurations of the CO_2R group are given. From these vals. and the moment of γ -butyrolactone it is shown that the esters have the *trans* configuration. This cannot be due to electrostatic forces alone but to stiffening produced by resonance with another structure. The resonance interaction of phenolic and benzoic esters with the benzene ring supports the Robinson-Ingold theories. The configuration of nitrous esters is discussed.

W. R. A.

Carbon valency angle and dipole induction in benzyl compounds. F. C. FRANK (J.C.S., 1936, 1324—1327).—Solvent effects do not invalidate stereochemical calculations from dipole moment data. In considering benzyl compounds, it is assumed that, in compounds of the type $\text{CH}_2\text{Ph}\cdot\text{Y}$, the induced moment in the Ph due to the C-Y moment lies parallel to the Ph-C linking, and that, in compounds of the type $\text{C}_6\text{H}_4\text{X}\cdot\text{CH}_2\text{Y}$, vector addition is permissible only if X and Y are each outside the sphere of induction of the other. Equations are given from which, by a graphical method, the induced moment along Ph-C and the C valency angle are obtained. The valency angle of aliphatic C is 110° .

W. R. A.

Theory of polarisation of dipole moments. J. FRENKEL (Acta Physicochim. U.R.S.S., 1936, 4, 341—356).—Expressions for the elastic (static) and frictional (kinetic) effects in the orientation of dipole mols. are derived mathematically and considered in relation to Debye's recent theories.

C. R. H.

Dipole moments and the fixation of aromatic double linkings. Bromohydrindenes and bromotetralins.—See this vol., 1497.

Volume of an anisotropic liquid in a magnetic field. D. BENESZEVICZ (Acta Physicochim. U.R.S.S., 1936, 4, 607—612).—No change in vol. is observed in the anisotropic phase of dibenzylidenebenzidine and *p*-azoxyanisole under the influence of magnetic fields from 3000 to 17,000 gauss.

O. D. S.

Refractive index of deuterium. W. J. C. ORR (Trans. Faraday Soc., 1936, 32, 1556—1559).—The difference in n of H_2 and D_2 has been measured. Assuming $n=1.00013966$ for H_2 at λ 5462, n for D_2 is 1.0001378(7).

E. S. H.

Refractive index, dispersion, and polarisation of gases. H. E. WATSON and R. L. RAMASWAMY (Proc. Roy. Soc., 1936, A, 156, 144—157).—The refractions and dispersions of CH_4 , C_2H_6 , C_3H_8 , *n*- and *iso*- C_4H_{10} , C_2H_4 , C_3H_6 , *n*-, *iso*-, and *sec*- C_4H_8 , $\text{C}(\text{CH}_3)_2$, C_2H_2 , $\text{CMe}:\text{CH}$, SiH_4 , Si_2H_6 , HCN , $(\text{CN})_2$, BF_3 , NF_3 , CF_4 , SiF_4 , SF_6 , and CO_2 have been measured and the electronic polarisations calc. The vals. are compared with the polarisations deduced from dielectric measurements of the same samples of gas. The at. polarisations are obtained by deduction,

and vary from 0 for the rare gases and most bimol. gases to 70% of the electronic polarisation for $(\text{CN})_2$. For the aliphatic hydrocarbons, they follow the sequence acetylenes > olefines > paraffins, and increase with the size of the mol.

L. L. B.

Streaming double refraction of high-molecular substances. IV. **Polystyrenes with different degrees of branching.** R. SIGNER (Helv. Chim. Acta, 1936, 19, 897—899; cf. A., 1933, 902).—The fluxional birefringence of polystyrenes is the lower, the higher is the temp. at which polymerisation occurred. A similar relation holds with regard to the extinction angle. These observations support the conclusion of Staudinger and Schulz (this vol., 146) that the degree of branching increases with rise of the temp. of polymerisation.

F. L. U.

[Optical] dispersion of natural and mercerised cellulose. A. FREY-WYSSLING (Helv. Chim. Acta, 1936, 19, 900—914; cf. this vol., 140).—The n of fibres of ramie cellulose varies with the liquid in which they are immersed in consequence of adsorption, especially with glycerol and with $\text{CH}_2\text{Ph}\cdot\text{OH}$. The dispersion, $n_D - n_C$, is 0.0070—0.0077 both for natural (I) and mercerised (II) fibres. The n_D vals. for (I) are >1.596 and 1.528 for the extraordinary and ordinary ray, respectively, the corresponding vals. for (II) being <1.574 and 1.525. The decrease in refraction on mercerisation is consistent with the resulting broadening of the cryst. lattice.

F. L. U.

Optical rotatory dispersion in the glucal series.—See this vol., 1363.

Optical rotatory dispersion of bridged derivatives of alkyltartrates. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1936, 11, 586—592).—The rotatory dispersion between 6708 and 4358 Å. of Et_2 and Me_2 isopropylidenedioxysuccinate, Et_2 and Me_2 ethylidenedioxysuccinate, and Et_2 methylenedioxysuccinate (cf. A., 1935, 1106; this vol., 967) in the pure state has been measured. The vals. can be expressed by a one-term Drude equation, and this, together with the dispersion ratio and the characteristic λ , appears to indicate that the rotatory dispersion is simple.

C. R. H.

Optical rotatory power of solutions in an electric field. J. KUNZ and S. H. BABCOCK (Phil. Mag., 1936, [vii], 22, 616—624; cf. this vol., 13).—When various optically active menthyl compounds were subjected to an electric field no Kerr effect was observed, but the rotation of the plane of polarisation depended on the angle between that plane and the field, and was a function of the field strength quite different from the Kerr effect.

N. M. B.

Magneto- and electro-optical properties of *p*-azoxyanisole. (MRS.) J. Z. K. EISENMANN (Ann. Physique, 1936, [xi], 6, 455—501).—A detailed description and discussion of an investigation previously reported (cf. A., 1935, 568).

N. M. B.

Magnetic birefringence in solutions of organic substances. L. D. MAHAJAN (Phil. Mag., 1936, [vii], 22, 717—725).—Results are tabulated for the following substances, the solvent being shown in parentheses; *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ (Et_2O); phloro-

glucinol, durene, and C_6Me_6 ($COMe_2$); C_6Et_6 (CCl_4); $C_6(HCl)_6$ (Et_2O); C_6Cl_6 (CS_2); *o*-toluidine ($COMe_2$); *m*-nitroaniline (Et_2O); *p*-benzoquinone, chloranil, and bromanil ($COMe_2$); dimesityl (CCl_4); diphenylene oxide (CCl_4 and $COMe_2$); α - $C_{10}H_7 \cdot NH_2$, and phenanthraquinone ($COMe_2$); α -naphthaquinone and anthraquinone (CCl_4); C_6H_6 . Results are discussed in relation to mol. structure and the influence of the structure on magnetic and optical anisotropy of the mols.
N. M. B.

Natural classification of chemical compounds. F. M. SCHEMJAKIN (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 49—54).—Previous theories (A., 1935, 569) are developed.
R. T.

Valency problem of the quinquevalent phosphorus atom.—See this vol., 1377.

Constitution of phosphorous, hypophosphorous, and sulphurous acids. G. SCHWARZENBACH (Helv. Chim. Acta, 1936, 19, 1043—1052; cf. this vol., 680).—From consideration of the several dissociation consts. of H_3PO_3 , H_3PO_2 , and H_2SO_3 it is concluded that H_3PO_3 contains one, and H_3PO_2 two H atoms linked directly to P, and that H_2SO_3 has a symmetrical structure. These conclusions do not apply to their metal or alkyl derivatives. F. L. U.

Maximum valency of elements and atomic structure. VI. Quantum characteristics of valency electrons and the m.p. of simple substances. VII. Quantum characteristics of valency electrons and the structure and lattice strength of simple substances. B. ORMONT (Acta Physicochim. U.R.S.S., 1936, 4, 409—426, 427—440).—A discussion on the deviations from the Grimm-Sommerfeld law and on the quantum characteristics of valency electrons as revealed by a study of the m.p. and lattice structure of the elements (cf. A., 1935, 1058; this vol., 141).
C. R. H.

Interaction of atoms and molecules with solid surfaces. III, IV. Condensation and evaporation of atoms and molecules. J. E. LENNARD-JONES and A. F. DEVONSHIRE. V. Diffraction and reflexion of molecular rays. A. F. DEVONSHIRE (Proc. Roy. Soc., 1936, A, 156, 16—28, 29—36, 37—44; cf. A., 1935, 1070).—III. Theoretical. Formulae have been found for the probability that an impinging particle will condense on to a solid surface, and for the length of time it will remain there. The theory thus provides explicit formulae for the consts. C and T of Langmuir's adsorption isotherm. Evaporation may, even at low temp., take place in two stages, an atom first being excited to a higher vibrational level and then receiving another quantum of thermal energy from the solid sufficient to cause evaporation. To illustrate the effect of mass, the probabilities of evaporation and condensation of the isotopic mols. H_2 , HD , and D_2 have been calc. The coeff. of condensation is in some cases quite small (of the order of 0.1).

IV. A model is considered in which an adsorbed atom can vibrate both radially and laterally about its point of attachment, but cannot migrate. Evaporation is controlled by the rate at which thermal energy is communicated from the solid to the adsorbed atom.

V. The theory of the reflexion and diffraction of mol. rays from crystal surfaces is worked out. The minima found by Frisch and Stern in the reflexion and diffraction curves of He and Li (A., 1933, 994) are explained. The experimental curves may be used to give information about the potential field in the neighbourhood of the solid.
L. L. B.

Relation between the tension τ of Baeyer and the characteristic Raman frequency for cyclic hydrocarbons. M. AUBERT (Compt. rend., 1936, 203, 661—663).—Baeyer's tension τ for a cyclic hydrocarbon with n C atoms, defined by $\tau = 1/2[109 \cdot 28'' - 180^\circ(n-2)/n]$, or $\tau = (10800 - 2116n)/n$ in min., is related to the characteristic Raman frequency ν according to $\nu = 0.2266\tau + 868 \text{ cm.}^{-1}$ for $n = 2-8$, when there is no side-chain. The combination of the formulae for ν and τ gives $n\nu^2 = (2447.3 + 388.5n)^2/n$ which gives a min. for $n\nu^2$ at $n = 6.29$. $n\nu^2$ is const. for vals. of n near to 6, as found by Godchot *et al.* (A., 1932, 213).
R. S. B.

Atomic and ionic radii. II. E. HERLINGER (Z. Krist., 1936, 93, 399—408).—The radii of action of atoms and ions are compared, and the constancy of radius of ions not built on the pattern of the noble gases is derived.
B. W. R.

Relation between internuclear distances and the force constants of diatomic molecules. R. M. BADGER (Physical Rev., 1935, [ii], 48, 284—285; cf. A., 1936, 14).
L. S. T.

Energy levels in crystals of samarium salts. C. B. ELLIS (Physical Rev., 1936, [ii], 50, 675; cf. Spedding, A., 1934, 1154).—The more than fourfold increase in the no. of lines in a close group in Sm over the no. in similar groups of Gd is attributed to the coupling of a set of vibrational levels to the crystal field levels, and the presence of higher coupling frequencies different for each compound in addition to crystal field splitting.
N. M. B.

Theory of movable voids and inter-lattice atoms in crystals. J. FRENKEL (Acta Physicochim. U.R.S.S., 1936, 4, 567—574).—The mechanism of void formation in crystals is discussed. The dependence of the no. of voids and of the no. of dissociated atoms in monat. crystals on temp. is calc. statistically. The result of a similar calculation for binary ionic crystals is in agreement with that of Schottky (A., 1935, 1302).
O. D. S.

Approximation method in the problem of many electrons. II. H. HELLMANN (Acta Physicochim. U.R.S.S., 1936, 4, 225—244; cf. A., 1935, 278).—Mathematical. A wave-mechanical discussion is given.
R. S. B.

Solving variational problems in quantum chemistry. A. SCHUCHOVITZKI (Acta Physicochim. U.R.S.S., 1936, 4, 803—818).—Theoretical.
H. J. E.

Quantisation of a theory arising from a variational principle for multiple integrals with application to Born's electrodynamics. P. WEISS (Proc. Roy. Soc., 1936, A, 156, 192—220).—Mathematical.
L. L. B.

Spectroscopic investigation of molecular association. M. V. VOLKENSTEIN (*Acta Physicochim. U.R.S.S.*, 1936, 4, 357—364).—The influence of mol. association on mol. symmetry as deduced from infra-red and Raman spectra is discussed. If the association forces are weak, corresponding with energies > 10 kg.-cal. per mol., the mols. can be regarded as unassociated but having their symmetry distorted. If association energy approaches that of homo- or hetero-polar linking, the product is intermediate between a chemical compound and a van der Waals complex. The existence of a frequency band at 622 cm.^{-1} in the Raman spectrum of AcOH and its weakening with dilution is attributed to the association of two AcOH mols. C. R. H.

Parachors of some metal carbonyl compounds. J. S. ANDERSON (*J.C.S.*, 1936, 1283—1286).—Surface tensions and parachors of $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_3(\text{NO})$, $\text{Fe}(\text{NO})_2(\text{CO})_2$, and $\text{Fe}(\text{CO})_5$ have been measured. As with other co-ordination compounds the apparent parachor of the central atom shows an anomaly for which no adequate explanation has so far been advanced. W. R. A.

Combination of fatty acids with nitrogen bases. I. Piperidine and lower fatty acids: surface tensions, molecular volumes, and parachors. E. B. R. PRIDEAUX and R. N. COLEMAN (*J.C.S.*, 1936, 1346—1353).—The salts formed by mixing piperidine with the lower fatty acids (acetic to octoic) have been prepared and examined. The effect of chemical combination on the densities of pairs of liquids having a similar polar constitution has been measured. Variations of surface tension with temp. have been determined. Salt formation is accompanied by considerable diminution of the parachors, although association also produces diminutions but of a much smaller order. W. R. A.

Cleavage and X-ray planes of calcite crystals. J. A. BEARDEN and H. H. ROSEBERRY (*Physical Rev.*, 1935, [ii], 48, 110).—In many cleaved calcite crystals which have good optical surfaces, the cleaved surface does not coincide with the at. or X-ray plane. The angle between the cleavage and X-ray planes is not the same for all crystals. L. S. T.

Elimination of errors in Debye-Scherrer pictures—experiment or calculation? A. LEVIŠ and M. STRAUMANIS (*Z. Krist.*, 1936, 94, 40—52).—An improved procedure for obtaining lattice const. from powder photographs with max. accuracy is described, and illustrated from measurements on TiCl_3 , As_2O_3 , and $\text{Pb}(\text{NO}_3)_2$. The Cohen formula is criticised. B. W. R.

Calculation of the Laue patterns from plastically bent crystals of NaCl. A. KOMAR (*Z. Krist.*, 1936, 94, 22—32).—A method of calculation of the Laue pattern for a bent rock-salt crystal is developed, with certain assumptions as to the behaviour of the slip planes. The calculation agrees quantitatively with experiment. B. W. R.

Calculation of structure factors and summation of Fourier series in crystal analysis: non-centrosymmetrical projections. J. M.

ROBERTSON (*Nature*, 1936, 138, 683—684).—A rapid numerical method is described. L. S. T.

Interpretation of the powder radiograms of crystals by the method used for argillaceous mica slates. J. DE LAPPARENT (*Compt. rend.*, 1936, 203, 596—599).—A discussion. H. J. E.

Historical and systematic survey of the use of the "reciprocal lattice" in the study of crystal structure. P. P. EWALD (*Z. Krist.*, 1936, 93, 396—398). B. W. R.

Alteration in the axial ratio and in the position of the rhombic section with temperature of anorthite from Vesuvius. H. SCHNAASE (*Z. Krist.*, 1936, 93, 444—463).—An anorthite crystal is measured goniometrically over the range room temp.— 973° , and regular alterations in the fundamental symmetry angles are found. B. W. R.

Physical properties of crystals. A. GANGULI (*Current Sci.*, 1936, 5, 128—130).—A review.

Theoretical basis for selection of optimum temperatures for monophasic metals. I. Recrystallisation diagrams. A. A. BOTSCHVAR and G. G. PUTZIKIN (*Ann. Sect. d'Anal. Physico-Chim.*, 1936, 9, 153—158).—The process of recrystallisation of deformed metals is best represented by three-dimensional diagrams (crystal size-% deformation-temp.). R. T.

Ring phenomenon in sputtered metallic films. U. K. BOSE (*Nature*, 1936, 138, 684—685).—When cathodically sputtered on a clean glass plate Ag or Cu forms coloured rings surrounding a drop of oleic acid or a bead of plasticine placed on the plate. An explanation of the effect is discussed. L. S. T.

Differences in lattice constants. G. WASSERMANN (*Metallwirts.*, 1935, 14, 813—815; *Chem. Zentr.*, 1936, i, 22).—Differences between lattice const. for single crystals and polycryst. materials (A., 1932, 330) may be attributed to impurities or to chilling stresses. J. S. A.

X-Ray analysis in chemistry. J. A. A. KETELAAR (*Chem. Weekblad*, 1936, 33, 648—654).—A review.

Ideal and real crystals (*Z. Krist.*, 1936, 93, 161—228).—A discussion of the papers on this subject (A., 1935, 16, 151). B. W. R.

Etch-forms in glasses. B. MARKIN, R. MÜLLER, and C. VEINSTEIN (*Acta Physicochim. U.R.S.S.*, 1936, 4, 119—122).—The etch-forms occur only when the glass surface has been in contact with a solid. The microscopic depressions so produced spread as the glass is uniformly dissolved, giving the characteristic honeycomb forms. R. S.

Action of the electric field on the smectic meso-phase. V. FREDERICKSZ and A. REPIEVA (*Acta Physicochim. U.R.S.S.*, 1936, 4, 91—98).—The production of focal-conical forms in the smectic meso-phase of Et *p*-azoxy-benzoate and -cinnamate has been studied. The elongated droplets produced near the temp. of transition to the amorphous liquid state orient themselves perpendicularly to weak electric fields, but turn through 90° when the field

strength is increased. With steadily increasing temp. and field strength the groups arrange themselves in regularly oriented series, and finally melt or explode to form the amorphous liquid. It is suggested that the orientation in weak electric fields is due to the orientation of dipoles, whilst in strong fields the effect of the induced polarisation is dominant. R. S.

Elastic vibration of an anisotropic liquid. V. ZOLINA (Acta Physicochim. U.R.S.S., 1936, 4, 85—90; cf. A., 1933, 1108).—Interference phenomena in anisotropic melts of Et *p-p'*-ethoxybenzylideneamino- α -methylcinnamate, acetoxybenzylideneazine, and dibenzylbenzidine, subject to tuning-fork vibrations, have been studied with the polarising microscope. R. S.

Structure of crystalline bismuth and selenium layers produced by condensation in vacuum. A. GOETZ and L. E. DODD (Physical Rev., 1935, [ii], 48, 165).—Similarities in the cryst. condensation of Bi and Se evaporated in a vac. are described. The cross-section in the direction of crystallisation of the condensed layers shows two distinct structures. The layer first deposited is microcryst. and 10^{-2} cm. thick and then changes abruptly to a macrocryst. layer with fibrous texture. L. S. T.

Relation between morphology and structure of potassium sulphate. K. CHUDOBA and H. BEHMENBURG (Zentr. Min., 1935, A, 327—336; Chem. Zentr., 1936, i, 721). H. J. E.

Arrangement of lattice blocks in the mosaic crystal, investigated with fused sodium nitrate crystals. J. LEONHARDT and R. TREMEYER (Z. Physik, 1936, 102, 781—790).—The disposition of lattice blocks in a mosaic crystal is discussed from a consideration of X-ray interference patterns. A. E. M.

Crystallography of magnesium, cobalt, and nickel sulphites. H. A. KLASSENS, W. G. PERDOK, and P. TERPSTRA (Z. Krist., 1936, 94, 1—6).—Goniometric measurements, *d*, cell consts., and space-groups are given for MgSO₃·6H₂O and the corresponding Co and Ni salts. Assuming that the six H₂O are symmetrically arranged around the metal ion, and the SO₃ has a distinct entity, a possible structure is suggested which agrees with Zachariasen's theory of the pyramidal shape of the SO₃. B. W. R.

Crystal lattices of heteropolyacids and their salts. II. Constitution of the silicotungstates of trivalent metals. O. KRAUS (Z. Krist., 1936, 93, 379—395).—The higher hydrates of these salts have the general formula M^{III}H(SiW₁₂O₄₀)_{*n*}·*n*H₂O. Several new hydrates (M=Fe or Cr) are described and their rotation photographs obtained. B. W. R.

Lattice constants and space-group of lievrite. P. KOKKOROS (Naturwiss., 1936, 24, 619).—Lievrite, [CaFe₂(FeOH)(SiO₄)₂], has *a* 8.76, *b* 13.04, *c* 5.82 Å., with 4 mols. in the unit cell. A. J. M.

Alterations of the ionic distances in hydroxyl layer lattices. W. LOTMAR and W. FEITKNECHT (Z. Krist., 1936, 93, 368—378).—From cell size measurements on mixed crystals of Zn(OH)₂ with Ni and Co hydroxides, an extrapolated val. for the non-

existent Zn(OH)₂ lattice of C6 type is deduced. Variations of the layer distance and alterations in the *a* axis and in the metal-OH distance, in the basic salts derived from this C6 lattice, are discussed. B. W. R.

Lattice shrinkage and structure of montmorillonite. G. NAGELSCHMIDT (Z. Krist., 1936, 93, 481—487).—This aluminosilicate shows a one-dimensional lattice shrinkage on drying. Measurements of the *d*(100) spacing are given over a range of 2—40 mols. of H₂O per unit cell; probably the first 4 mols. enter between the structure layers and thus alter *d*, while subsequent H₂O mols. remain at the crystal surface. B. W. R.

Polyphosphonitrilic chloride, an inorganic "rubber." K. H. MEYER, W. LOTMAR, and G. W. PANKOW (Helv. Chim. Acta, 1936, 19, 930—948; cf. this vol. 276).—X-Ray diagrams of unstretched polyphosphonitrilic chloride (I) are amorphous, but become cryst. on stretching. The unit cell contains 8 PNCl₂ groups and has *a* 11.07, *b* 4.92, *c* 12.72 Å. The space-group is probably C_{2v}². The P atoms (with attached Cl) are arranged in a zigzag chain with the N occupying intermediate positions. The dimensions of the crystallites are > 500 Å. in every direction, corresponding with a mol. wt. < 20,000. Thermo-elastic measurements indicate that stretching is accompanied by progressive orientation of P-N linkings, the subsequent contraction being due to the tendency to disorientation. In details of behaviour (I) is closely analogous to rubber. F. L. U.

Optical crystallographic data for some salts of the cinchona alkaloids. M. L. SHANER and M. L. WILLARD (J. Amer. Chem. Soc., 1936, 58, 1977—1978).—Crystallographic data are recorded and the fluorescent properties in ultra-violet light described for quinine, quinidine, cinchonine, and cinchonidine. E. S. H.

Crystallographic investigation of isomerides arising from the combination of *d*- and *l*-acids with *d*- and *l*-bases. B. GOSSNER and H. NEFF (Z. Krist., 1936, 93, 488—493).—The four isomeric H tartrates of *d*- and *l*-*p*-ephedrine have been investigated by X-rays. B. W. R.

Fine structure and transformations of alkali salts of long-chain fatty acids. P. A. THIESSEN and J. STAUFF (Z. physikal. Chem., 1936, 177, 398).—Corrections to a previous paper (this vol., 1186). R. C.

X-Ray investigation of the crystals of *p*-nitrodiphenyl. M. PRASAD, M. P. LAKHANI, and J. SHANKER (J. Indian Chem. Soc., 1936, 13, 519—522).—The crystals belong to space-group *Q*₁¹⁹ with F0 Bravais lattice and the unit cell is asymmetric and contains 8 mols.; *a* 23.25, *b* 11.38, *c* 7.55 Å. The ratio *b*:*c* agrees with Groth and the ratio *a*:*b* is double. C. R. H.

X-Ray measurements on diflavylene, rubrene, and related compounds. W. H. TAYLOR (Z. Krist., 1936, 93, 151—155).—Diflavylene, monoclinic, has *a*₁ 6.7, *b*₁ 7.3, *c*₁ 16.7 Å., β ₁ 102°, 4 mols. in unit; space-group C_{2h}²—P2₁/*n*. An alternative unit cell with *a*₂ 13.0, *b*₂ 7.3, *c*₂ 10.5 Å., β ₂ 90° contains

2 mols.; same space-group. The results indicate a *trans*-configuration for the mol. Rubrene *A* has a 14.3, c 7.0 Å., β 107°; rubrene *B* (distinguishable from *A* only by X-rays), monoclinic, has a 17.9, b , 10.1, c 8.8 Å., β 120°; 2 mols. in cell; space-group $C_{2h}^2-P2_1/n$. Didiphenylene-ethylene, orthorhombic, has a 36.7, b 34.3, c 8.15 Å., 24 mols. in cell; space-group D_{2h}^2-Pmcb or C_{2v}^2-Pcb ; its 2:2'-F₂-derivative, d 1.357, is similar in structure. Some optical data are also given. B. W. R.

Crystal structure of condensed ring compounds. III. Three carcinogenic compounds: 1:2-benzpyrene, methylcholanthrene, and 5:6-cyclopenteno-1:2-benzanthracene. J. IBALL (Z. Krist., 1936, 94, 7-21).—1:2-Benzpyrene occurs in two modifications, (a) monoclinic, space-group C_{2h}^2 , a_0 4.52, b_0 20.32, c_0 13.47 Å., β 97° 4', (b) orthorhombic, space-group C_{2h}^2 , a_0 7.59, b_0 7.69, c_0 22.38 Å. The other two compounds are both monoclinic, space-group C_{2h}^2 , a_0 4.86, b_0 11.31, c_0 27.7 Å., β 116° 5', and a_0 12.02, b_0 8.61, c_0 13.78 Å., β 103° 0', respectively. Based on intensity measurements, probable mol. positions are given. A comparison is made with the structure of monoclinic 1:2:5:6-dibenzanthracene. B. W. R.

X-Ray crystallographic data on the sex hormones, estrone, androsterone, testosterone, progesterone, and related substances. J. D. BERNAL and D. CROWFOOT (Z. Krist., 1936, 93, 464-480).—A summary of the data (chemical formula, cell size and structure, crystal habit, and general physical properties) now available for this group of substances. B. W. R.

X-Ray diffraction studies of chitin, chitosan, and derivatives. G. L. CLARK and A. F. SMITH (J. Physical Chem., 1936, 40, 863-879).—Natural chitin (I) shows preferred orientation of crystallites, with the b axis parallel to the surface in that produced in sheets, and to the axis of the fibre in tendons. After treatment with EtOH, fibres of (I) can be separated into uniform fibrils of diameter about 1 μ . On treatment with HCl at room temp. the ether linkings, and less rapidly the NH₂-groups, of (I) are hydrolysed. At 200° (I) forms a definite additive compound with LiCNS, whilst at lower temp. intramolecular swelling occurs. Chitin nitrate is probably orthorhombic with a 9.2, b 10.3, and c 23 Å., but fractions separated with different solvents show different average lengths of the C chain. The unit cell of chitosan is orthorhombic with a 8.9, b 10.25, and c 17.0 Å. When formed from (I) in sheet form its (002) planes are parallel to the surface. Analyses show only about half the N required by Löwy's structure for chitosan, so it is suggested that there may be hydrolysis of the NH₂-group. It is suggested that steric hindrance from another mol. causes only half the Ac groups to be hydrolysed in converting (I) into chitosan. J. W. S.

Fine structure of crystallised caoutchouc. W. LOTMAR and K. H. MEYER (Monatsh., 1936, 69, 115-124).—Redetermination of the consts. of the unit cell of cryst. (stretched) caoutchouc (cf. A., 1928, 1186) shows it to be monoclinic with a 8.57 \pm 0.05, b 8.20 \pm 0.05 (fibre axis), c 12.65 \pm 0.05 Å., β 83° 20'.

The most probable space-group is C_{2h}^2 . The crystallite is a mol. racemate of right- and left-handed spiral threads. F. L. U.

Origin of the "extra rings" in electron diffraction patterns. K. LARK-HOROVITZ, H. J. YEARIAN, and J. D. HOWE (Physical Rev., 1935, [ii], 48, 101).—The extra rings, similar to those reported for Au (A., 1931, 1206), obtained in the electron diffraction patterns of thin films of various metals deposited in a vac. on C₁₀H₈, are due to adsorbed layers of org. substances forming thin, cryst. layers and random oriented cross gratings. When NH₄Cl replaces C₁₀H₈ in the prep. of the films no extra rings appear in the diffraction patterns. L. S. T.

Surface of copper formed by solidification in a vacuum. S. DOBINSKI and C. F. ELAM (Nature, 1936, 138, 685).—X-Ray examination of Cu surfaces cryst. in a vac. showed that the orientation of the crystals differed from specimen to specimen, whilst electron diffraction showed spots from Cu crystals oriented with either {111} or {100} planes parallel to the surface, the {111} orientation being more frequent. L. S. T.

Molecular structures of the methyl derivatives of silicon, germanium, tin, lead, nitrogen, sulphur, and mercury, and the covalent radii of the non-metallic elements. L. O. BROCKWAY and H. O. JENKINS (J. Amer. Chem. Soc., 1936, 58, 2036-2044).—Electron diffraction investigations of gaseous SiMe₄, GeMe₄, SnMe₄, PbMe₄, NMe₃, SMe₂, and HgMe₂ yield the following vals. (in Å.) for interat. distances: Si-C 1.93 \pm 0.03, Ge-C 1.98 \pm 0.03, Sn-C 2.18 \pm 0.03, Pb-C 2.29 \pm 0.05, N-C 1.47 \pm 0.02, S-C 1.82 \pm 0.03, Hg-C 2.20 \pm 0.10. These vals. agree with published data for the sums of covalent radii. E. S. H.

Electron diffraction experiments on crystals of galena. L. H. GERMER (Physical Rev., 1936, [ii], 50, 659-671).—Electron diffraction patterns for cleaved, filed, and ground surfaces of galena crystals are photographed and described. The relation of results to the study of strain-hardening in metals is discussed. N. M. B.

Diffraction of electrons by molybdenite. G. I. FINCH and H. WILMAN (Trans. Faraday Soc., 1936, 32, 1539-1556).—Anomalous diffractions are explained in terms of the lattice limitation theory. Single crystals, only a few lattice layers thick, yield on rotation the two-dimensional cross-grating effect of continuous diffraction lines, which decrease in intensity with increasing crystal thickness. The axial ratio of molybdenite is 3.904; c appears to be independent of crystal thickness. The general theory of the loci of diffractions from rotating, undistorted and from stationary, curved molybdenite crystals is developed. E. S. H.

Electron diffraction by films built from many unimolecular layers. K. H. STORKS and L. H. GERMER (Physical Rev., 1936, [ii], 50, 676; cf. Holley, this vol., 539).—Patterns produced by films of multiple compressed layers of stearic acid and of mixed Ba and Cu stearates show symmetrical spot arrangements, proving that the mols. are regularly

arranged and that the crystal orientation is not random. The patterns differ entirely from those of a single stearic acid crystal obtained by evaporation from C_6H_6 solution. N. M. B.

Continuous magnetic spectrum at audio-frequencies of transformer lamina. V. ARKADIEV (Z. Physik, 1936, 101, 527—532).

A. B. D. C.

Gyromagnetic effect in pyrrhotine. F. COETIERER (Helv. phys. Acta, 1935, 8, 522—564; Chem. Zentr., 1936, i, 288).—The theory of the gyromagnetic effect is discussed. Measurements on pyrrhotine, Fe_nS_{n+1} , along the direction of easiest magnetisation, give $g = 0.63$ as compared with $g = 2$ for all other ferromagnetic substances, indicating that orbital momentum, and not only spin momentum, of the electrons is involved, in agreement with the strong magnetic anisotropy. J. S. A.

Ferromagnetic phenomena. J. L. SNOEK (Nederl. Tijds. Natuurkunde, 1935, 2, 180—189; Chem. Zentr., 1936, i, 26—27).—In pure, unstrained material the crystal axes in Fe represent the directions of least, and in Ni the direction of greatest, energy. Fe-Ni alloys constitute a transition series, an alloy with 70% Ni being isotropic. Stress can produce an anisotropy. J. S. A.

Physico-technical problems of ferromagnetism in weak fields. R. GOLDSCHMIDT (Helv. phys. Acta, 1935, 8, 497—498; Chem. Zentr., 1936, i, 287).—The loss angle is resolved into two components: one linearly \propto field strength and frequency, and one independent of field strength and frequency. The latter is investigated in a high-Si transformer sheet, and related to after-working effects. J. S. A.

Magnetism and cold working in metals. II. Single crystals of bismuth, zinc, and tin. S. R. RAO (Proc. Indian Acad. Sci., 1936, 4, A, 186—203).—Single crystals of Bi, Zn, and Sn have been investigated for the influence of cold-work on the principal susceptibility. Bi showed a decrease, Zn showed a very small decrease in diamagnetic, and Sn in paramagnetic, susceptibility. The theory of Honda and Shimizu explains these changes. W. R. A.

Effect of an external magnetic field on transition temperatures. E. JUSTI (Physikal. Z., 1936, 37, 766—768).—If the phases of a system of one component have different susceptibilities, the transition temp. of the phases are displaced by the application of a magnetic field. The displacement, which is very small, can be calc. from the change of susceptibility and entropy on transition. A. J. M.

Heat effect of metallic transitions. IV. Nickel. H. VON STEINWEHR and A. SCHULZE (Physikal. Z., 1936, 37, 753—757).—The heat evolved in the magnetic transition of Ni (99.1%) is 0.65 ± 0.06 g.-cal per g. The transition takes place over the range 333—362°. There was a small heat evolution at a temp. approx. 100° below the Curie point. A. J. M.

Electrical anisotropy of single tungsten crystals at low temperatures in strong transverse magnetic fields. E. JUSTI and H. SCHEF-

FERS (Physikal. Z., 1936, 37, 700—708).—The resistance of W crystals at temp. $< 20.38^\circ$ abs. is about 0.001 of that at 0° . On application of a transverse magnetic field (20,000 gauss) the resistance increases to its normal val. At low temp. the resistance is anisotropic, and the val. depends on the direction of the magnetic field. When the latter is perpendicular to a principal crystal plane, there is a smaller increase of resistance on applying the field, the increase being smallest for the [100] direction. Space-centred crystals of W show only half the no. of max. and min. in resistance shown by a face-centred crystal such as Au. At temp. $<$ b.p. of H_2 the resistance increases on application of the field approx. with the square of the field strength. The curve between field strength and increase of resistance varies by a const. factor as the crystal is rotated. A. J. M.

Anode-sputtering and the deposition of metallic film on the cathode of a Hadding X-ray tube. S. SHARAN (Indian J. Physics, 1936, 10, 325—340).—The structure of the deposits and application to anode sputtering are discussed.

N. M. B.

Cathodic sputtering. H. DAMIANOVICH (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 23—31; Chem. Zentr., 1936, i, 497; cf. A., 1935, 1060).—The d of the product obtained in He corresponds with that calc. for Pt_5He . H. J. E.

Rate of polymorphic transformations. IV. Influence of mechanical deformation on rate of transformation of polymorphic metals. II. Influence of admixed metals. E. COHEN and A. K. W. A. VAN LIESHOUT (Z. physikal. Chem., 1936, 177, 331—336; cf. A., 1935, 918).—The rate of transformation of white into grey Sn is much accelerated by small amounts of Zn (max. effect with 0.05%) and Al and retarded by Pb, Sb, Bi, Cd, and Ag. R. C.

Molecular magnitude of metaphosphates. P. NYLÉN (Z. anorg. Chem., 1936, 229, 30—35).—Cryoscopic measurements, by Richards' method, with a $(NaPO_3)_x$ prep. described in the literature as monomeric, give $x=2-3$. Similar measurements with salts reported as tri- and tetra-meric, respectively, have confirmed the reports. F. L. U.

Molecular size distribution in linear condensation polymerides. P. J. FLORY (J. Amer. Chem. Soc., 1936, 58, 1877—1885; cf. this vol., 295).—Size distributions of linear condensation polymerides are calc. on a wt. fraction and a mol. fraction basis, and on the assumption that the reactivity of functional groups is independent of the size of the mols. to which they are attached. The form of the distribution curves is not greatly changed when one of the reactants is in excess. Relations between "no.-average" (M_n), "wt.-average" (M_w), and "Z-average" mol. wts. are deduced in terms of p , the fraction of the total no. of functional groups which have reacted. Staudinger's viscosity term is not KM_n , but $0.5KM_w$, where $M_w=(1+p)M_n$. The original equation is valid only for polymerides of high mol. wt., i.e., for high vals. of p . F. L. U.

Magnetic susceptibility of molecular hydrogen.

E. E. WITMER (Physical Rev., 1935, [iii], 48, 380).—A summary of calc. results not yet completed.

L. S. T.

Magnetic susceptibility of mixed oxides of the rare earths. II. Samarium-gadolinium mixtures. L. MAZZA and E. BOTTI (Gazzetta, 1936, 66, 552—562; cf. this vol., 19).—For Sm_2O_3 $\chi=6.00 \times 10^{-6}$, for Gd_2O_3 $\chi=139.2 \times 10^{-6}$. Mixtures of the two oxides do not obey Urbain's additive law. The results do not indicate the existence of any lower oxides, and give a single magnetic moment for Gd^{+++} of 39 Weiss magnetons. This agrees with the val. obtained from the susceptibility of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, for which fresh measurements are recorded.

O. J. W.

Magnetochemical investigation of metal ketyls of 4-pyrones.—See this vol., 1396.

Diamagnetism and particle size. H. LESSHEIM (Current Sci., 1936, 5, 119—127).—A review.

Cavitation caused by ultrasonic waves. K. SÖLLNER (Trans. Faraday Soc., 1936, 32, 1537—1539).—Cavitation can be made visible by irradiating with high energy long columns of de-gassed liquids.

E. S. H.

Velocity of ultrasonic waves in heavy water. R. BÄR (Helv. phys. Acta, 1935, 8, 500—502; Chem. Zentr., 1936, i, 708).—The velocity in 99.2% D_2O at 20° was 1.381×10^5 cm. per sec. The adiabatic compressibility of D_2O was 4.733×10^{-11} sq. cm. per dyne. The val. for H_2O is 4.5477×10^{-11} sq. cm. per dyne.

H. J. E.

Visibility of ultrasonic waves in liquids. S. PARTHASARATHY (Current Sci., 1936, 5, 136).—Parallel monochromatic light falls on one face of a cell containing a liquid through which ultrasonic waves are passing. Through the opposite face a microscope is focussed on the optical grating formed by the sound waves.

C. W. G.

Ultrasonic velocities in organic liquids. VI. Related compounds. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1936, 4, A, 213—215; cf. this vol., 1189).—Diffraction of light by high-frequency sound waves is used to determine the acoustic velocity in four esters, three nitro-compounds, two aldehydes, in thyme oil, and in oil of turpentine. Adiabatic compressibilities are recorded.

W. R. A.

Absorption of ultrasonic waves in acetic acid [and benzene and toluene]. P. BASHULIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 285—288).—The absorption coeff. (α) of ultrasonic waves has been determined in AcOH at 17.5—28° for frequencies (ν) $(3.73-31.3) \times 10^6$. α is an approx. linear function of ν . α has been determined in 0—100% mixtures of PhMe and C_6H_6 at 18° and $\nu=11.47 \times 10^6$. The difference in α for PhMe and C_6H_6 is \gg that in d , η , and velocity of propagation of sound. α departs considerably from the additive law.

R. S. B.

Dispersion of sound in liquids. E. HIEDE-MANN, N. SEIFEN, and E. SCHREUER (Naturwiss., 1936, 24, 681).—The dispersion of ultrasonic waves in PhMe , xylene, NH_2Ph , and PhNO_2 , but not in

H_2O , has been demonstrated, and its extent determined.

A. J. M.

Entropy of deuterium oxide and the third law of thermodynamics. Heat capacity of deuterium oxide from 15° to 298° abs. M.p. and heat of fusion. E. A. LONG and J. D. KEMP (J. Amer. Chem. Soc., 1936, 58, 1829—1834).—Heat capacity data are recorded and the entropy deduced. D_2O has m.p. 276.92 ± 0.05 abs., and heat of fusion 1501 g.-cal. per mol.

E. S. H.

Exact measurement of the specific heats of metals at high temperatures. XXV. Specific heats and the allotropy of nickel between 0° and 1000°. M. EWERT (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 833—838).—A rapid increase of c_p with temp. occurs up to 345° for α -Ni (cubic, ferromagnetic). The field of stable existence of the α' form (hexagonal) is between 345° and 351°. From 351° upwards a much less rapid increase of c_p with temp. occurs for the β form. The heat effects of transition are approx.: $\alpha \rightleftharpoons \alpha'$, at 345°, 0.08 g.-cal.; $\alpha' \rightleftharpoons \beta$, at 351°, 0.31 g.-cal.

D. C. J.

Determination of the true specific heats of silver, nickel, β -brass, quartz crystal, and quartz glass between 50° and 700° by an improved method. H. MOSER (Physikal. Z., 1936, 37, 737—753).—The apparatus employed consisted of a Ag calorimeter in an atm. of A at low pressure. c_p of Ag was found to vary little with temp. The anomalies in c_p of Ni, β -brass, and quartz crystal extend over a wide temp. range, and begin about 300° < the accepted transition temp. at which c_p is a max. The return to the normal val. takes place over a very narrow temp. range in the case of quartz crystal. For the α - β transition of quartz, associated with a lattice change from the trigonal to the hexagonal, the abnormal increase in c_p before the transition can be explained as due to an expansion of the lattice, since c_p (cryst.)— c_p (glass) = Δc_p is approx. equal to the val. calc. from the coeffs. of cubic expansion and compressibility.

A. J. M.

Heats of crystallisation of methyl and ethyl esters of monobasic fatty acids. (Miss) A. M. KING and W. E. GARNER (J.C.S., 1936, 1372—1376).—The sp. heats and heats of crystallisation of several Me and Et esters of long-chain (straight) fatty acids (C_{16} — C_{22}) have been determined. Two equations are derived connecting the m.p. with the no. of C in the chain, one for the Me esters of the even series, the other for the Et esters of the odd series.

W. R. A.

Rare earth halides. X. M.p., particularly of the bromides. G. JANTSCH and K. WEIN (Monatsh., 1936, 69, 161—166; cf. A., 1932, 1194; 1934, 157).—Previous work has been amplified by the determination of the m.p. of LaBr_3 , CeBr_3 , PrBr_3 , NdBr_3 , and SmBr_3 , which are respectively $783 \pm 3^\circ$, $732 \pm 2^\circ$, $693 \pm 2^\circ$, $684 \pm 2^\circ$, and $664 \pm 2^\circ$. The relationship between the m.p. of various halides is discussed.

F. L. U.

M.p. of long-chain carbon compounds. (Miss) A. M. KING and W. E. GARNER (J.C.S., 1936, 1368—1372).—The heat increments and entropy

increments per CH_2 are const. for homologous series with >10 C in the chain. Differences in the physical properties of polymorphic modifications of long-chain compounds with vertical and tilted chains are given; for compounds with very long chains vertical chains are more stable than tilted chains at the m.p.

W. R. A.

Position of λ -points of helium. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 822—823).—A correction of the val. quoted in former paper (this vol. 787).

D. C. J.

Optical experiments on liquid helium II. L. V. SCHUBNIKOV and A. K. KIKOIN (Nature, 1936, 138, 641).—No evidence of the formation of liquid crystals could be obtained in liquid He between 4.22° and 1.72° abs. Hence, the anomaly in the sp. heat of liquid He at 2.19° abs. cannot be ascribed to a transition to the liquid crystal state.

L. S. T.

Vapour pressure and heat of sublimation of carbon. P. GOLDFINGER and W. JEUNEHOMME (Trans. Faraday Soc., 1936, 32, 1591—1598).—V.-p. curves have been deduced from published data for the heat of vaporisation of C. The most probable val. for the heat of vaporisation is 123.6 ± 0.5 kg.-cal.

E. S. H.

Density of saturated vapours. M. F. SOONAWALA (Indian J. Physics, 1936, 10, 353—363).—Mathematical. The surface of a liquid is treated as a potential barrier, and the probability of transition across it of a mol. is obtained by wave mechanics. Application to experimental data shows that a mol. in a liquid has potential as well as kinetic energy. The val. of this potential energy is calc. for 13 liquids.

N. M. B.

Single linking energies. IV. V.p. of hexaphenylethane. G. R. CUTHBERTSON and H. E. BENT (J. Amer. Chem. Soc., 1936, 58, 2000—2003; cf. this vol., 291).—For C_6H_5 (26.5—90.5°) $\log p = -5260/T + 12.72$, $\Delta H = 24.1 \pm 1.0$ kg.-cal.; for C_2Ph_6 (75.4—120.8°) $\log p = -5987/T + 12.85$, $\Delta H = 27.4 \pm 1.5$ kg.-cal.; for CPh_3 peroxide (119.8—161.0°) $\log p = -8259/T + 16.98$, $\Delta H = 37.8 \pm 1.5$ kg.-cal. The heat of vaporisation shows that the C-C linking in C_2Ph_6 vapour is weaker than the normal C-C linking.

E. S. H.

Vapour density of hexaphenylethane. H. E. BENT and E. S. EBERS (J. Amer. Chem. Soc., 1936, 58, 2073—2074).—Rapid decomp. prevents determination.

E. S. H.

U-Effect of Amagat and Weiss. Equation of state on the basis of selection theorems and the Joule-Thomson effect. II. V. JACYNA (Z. Physik, 1936, 103, 67—75).—Mathematical. The theoretical basis for the behaviour of gases at high pressures is reviewed.

H. C. G.

Compensation state ("basis line") for helium and carbon dioxide. I. V. JACYNA (Z. Physik, 1936, 103, 61—66).—Mathematical. A new equation of state having the parabolic form of the van der Waals-Berthelot equation is obtained and discussed in relation to available data for He and CO_2 . The significance of the basis line is pointed out.

H. C. G.

X-Ray determination of the thermal expansion coefficients of beryllium and tin. G. F. KOSSELAPOV and A. K. TRAPESNIKOV (Z. Krist., 1936, 94, 53—59).—The coeffs. are measured parallel and perpendicular to the a axis, using a back-reflexion camera, over the range 18 — 454° for Be and 23 — 150° for Sn, and are compared with previous results by the macroscopic method.

B. W. R.

Viscosity of air and electronic charge. V. D. MAJUMDAR and M. B. VAJIFDAR (Current Sci., 1936, 5, 133).—The method involves flow of air through a capillary tube. $\eta = 1816.2 \times 10^{-7}$ c.g.s. unit at 20° ; $e = 4.8022 \times 10^{-10}$ e.s.u.

C. W. G.

Influence of magnetic field on the coefficient of viscosity of liquids. II. S. D. CHATTERJEE (Indian J. Physics, 1936, 10, 399—401; cf. A., 1935, 1198).—Results are given for three non-polar liquids (C_6H_6 , p -xylene, and hexane) and for 9 monohydric alcohols. The former group shows a change of η in a magnetic field; in the latter the change seems to depend on the shape of the mol., the presence of a straight or a side chain, or general symmetry. The abs. change $d\eta$ is given for 8 liquids for which η is altered by the magnetic field.

N. M. B.

Viscosity nomographs for alkaline solutions. D. S. DAVIS (Ind. Eng. Chem., 1936, 28, 953—956).—Nomographs for obtaining the η of aq. solutions of NaOH, Na_2CO_3 , KOH, K_2CO_3 , $\text{NaOH} + \text{Na}_2\text{CO}_3$, and $\text{NaOH} + \text{K}_2\text{CO}_3$ at 20 — 40° are given.

D. K. M.

Temperature of vapour from boiling solutions.] K. SCHREBER (Z. ges. Kälte-Ind., 1935, 42, 131—135; Chem. Zentr., 1936, i, 604).—A discussion.

H. J. E.

Refractometry of binary liquid systems. III. V. J. ANOSOV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 255—270).—A classification of the refractometric isotherms is proposed.

R. T.

Periodic variations of labile [alcohol-water] molecular complexes and their equilibrium position. L. SPLAIT (Acta phys. polon., 1934, 2, 459—464; Chem. Zentr., 1936, i, 507).—Recorded observations of periodic variations in the longitudinal light scattering effect of EtOH— H_2O mixtures are confirmed (cf. A., 1931, 900).

H. J. E.

Complex formation between polynitro-compounds and aromatic hydrocarbons. III. Systems containing tetranitromethane. D. L. HAMMICK and R. P. YOUNG (J.C.S., 1936, 1463—1467; cf. this vol., 722).—The formation of coloured complexes has been studied by determination of the colour density, D , at λ 4300 Å. There is a linear relationship between D and the hydrocarbon (or substituted hydrocarbon) concn. b for C_6H_6 , PhMe, o -, m -, and p -xylene, PhOEt, C_{10}H_8 , $2\text{-C}_{10}\text{H}_7\text{Me}$, $2:4\text{-C}_{10}\text{H}_6\text{Me}_2$, $\beta\text{-C}_{10}\text{H}_7\text{OH}$, $1\text{-C}_{10}\text{H}_7\text{NO}_2$, and anthracene, whilst in the case of mesitylene, D/b decreases as b increases. Relative vals. of the equilibrium const. and heats of interaction have been calc.

R. S.

Thermal examination of chemical compounds in the system zinc-magnesium. M. I. ZACHAROVA and A. B. MŁODZIEJEWSKI (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 193—202).—1:1 Mg—Zn alloys consist of a mixture of MgZn_2 , eutectic, and

MgZn; after heating at 340–354° for 80 days the alloy consists predominately of MgZn, as shown by crystallographic examination. Thermal data afford additional evidence for the formation of MgZn.

R. T.

System iron-antimony. P. FOURNIER (Rev. Chim. ind., 1935, 44, 195–198; Chem. Zentr., 1936, i, 422).—The system has been studied from 0.5–70% of Sb. With $\leq 60\%$ of Sb, the position of the magnetic transformation is unaltered; the alloy with 70% of Sb is non-magnetic. The solubility of Sb in α -Fe increases with rise of temp. up to 35% at the eutectic temp., 1060°. FeSb undergoes a transition at 620°. The addition of Sb to steels produces brittleness.

J. S. A.

Magnetic stability of ferromagnetic iron alloys. I. V. S. MESSKIN and J. M. MARGOLIN (Z. Physik, 1936, 101, 456–477).—The magnetic stability of Fe alloys increases with increasing concn. of the solid solution and homogenisation of the structure. High-resistance alloys of technical interest are described.

A. B. D. C.

Phase transformations in the solid state in iron-chromium alloys. N. N. KURNAKOV and N. I. KORENOV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 85–98).—Thermal, conductivity, and hardness data confirm the formation of the compound FeCr in Fe-Cr alloys subjected to prolonged heating at 950°. The solid solutions formed by FeCr with Fe have a lower conducting power than those formed by FeCr in Cr.

R. T.

Formation of liquid eutectic alloys. N. V. GEVELING (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 63–83).—When molten Cd and Bi or Sn are mixed a fall in temp. results, which is at a max. when the components are present in the same proportions as in the eutectic alloy. No temp. effect is obtained by adding one of the components to a mixture containing the same component in excess of that present in the eutectic alloy. Liquid eutectic alloys are regarded as solutions of one or the other component in the pure eutectic. A sharp break occurs in the d - and η -concn. curves of the system H₂O-NaCl at the eutectic composition (23.5% NaCl), suggesting that the mixtures are solutions of H₂O or NaCl in the eutectic.

R. T.

Hall effect in antimony-tellurium and anti-mony-silver alloys. E. VAN AUBEL (Compt. rend., 1936, 203, 614–615).—The Hall effect and the thermoelectric power of Sb are reduced to 64% and 70% of their respective normal vals. by 4.26% of Te. Formation of the compound Ag₃Sb is indicated by the variation of Hall effect for a series of Sb-Ag alloys.

H. J. E.

Electrical conductivity and diagram of state for binary alloys. XXI. System palladium-chromium. G. GRUBE and R. KNABE. XXII. System palladium-manganese. G. GRUBE, K. BAYER, and H. BUMM (Z. Elektrochem., 1936, 42, 793–804, 805–815).—XXI. Evidence has been obtained for the existence of Pd₂Cr₃, which forms solid solutions with Pd, but not with Cr. Cr₂O₃ dissolves in molten Cr.

XXII. The equilibrium diagram has been deter-

mined by thermal, electrical conductivity, microscopical, and X-ray methods. The compounds Pd₃Mn₂ and PdMn are formed.

E. S. H.

Magnetic susceptibility and diagram of state for binary alloys. II. System palladium-manganese. G. GRUBE and O. WINKLER (Z. Elektrochem., 1936, 42, 815–830; cf. A., 1935, 291).—The results support those obtained by thermal and other methods (cf. preceding abstract).

E. S. H.

Magnetic susceptibility of binary alloys of thallium. (Miss) A. W. DAVID and J. F. SPENCER (Trans. Faraday Soc., 1936, 32, 1512–1516).—Magnetic susceptibilities (χ) of complete series of Tl-Bi and Tl-Cd alloys have been measured. The existence of compounds Bi₅Tl₃ and Bi₂Tl₃ is indicated. χ for Tl-Cd alloys conforms to the simple mixture rule.

A. J. E. W.

Theory of equilibrium in alloys. I. W. HUME-ROTHERY (Phil. Mag., 1936, [vii], 22, 1013–1047).—The effect of lattice distortion on the α -solid solubilities of certain *B* sub-group metals in Cu and Ag has been investigated, and is discussed in relation to the electron concns. existing in the alloys at the solubility limits, and to the causes of lattice distortion. Possible types of ternary solid solubility isothermals, and the systems in which they occur, are reviewed. One of these types is characteristic of systems containing two components which unite to form a compound; a theoretical treatment of such ternary systems is given.

A. J. E. W.

Structural change and distortion of the ordered distribution of atoms in metallic mixed phases by plastic deformation. H. J. SEEMANN (Naturwiss., 1936, 24, 618–619).—The disordering effect of plastic deformation on metallic mixed phases observed with Cu₃Au and Ni₃Mn has also been found to occur with a Cu-Pd alloy (47 at.-% Pd). The sp. resistance increases steadily as the arrangement of atoms becomes more disordered, the val. for the completely disordered state being unaffected by cold-working. This example is noteworthy since in addition to a change in the ordered distribution of atoms there is also a lattice change.

A. J. M.

Velocity of dissolution of gold, silver, and copper alloys in aqueous cyanides in connexion with the phase diagrams of the systems: gold-copper, silver-copper, and gold-silver. I. N. PLAKSIN and S. V. SCHIBAIEV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 159–182).—The velocity of dissolution (V)-composition diagrams for Au-Cu alloys in 0.15–0.6% KCN at 19° have two max., corresponding with the compounds AuCu and AuCu₃. The V of Cu from Ag-Cu alloys is least, and that of Ag greatest, at the eutectic point; no Ag is dissolved from alloys containing <37 at.-% Ag. The V of Au from Au-Ag alloys falls with increasing [Au] to a min. at 40 at.-%, and then rises to a max. at 60 at.-%. The [KCN] giving max. V of Au from Au, Au-Ag and Au-Cu are, respectively, 0.25, 0.30, and 0.35%.

R. T.

System iron-cobalt-copper. W. JELLINGHAUS (Arch. Eisenhüttenw., 1936–1937, 10, 115–118).—Cu, Co, and Fe are completely miscible in the liquid state, but separation into two solid phases occurs in

all alloys with 8–96% Cu on solidification. Alloys within a small range in the Fe corner of the ternary diagram solidify as δ Fe solid solution and all other alloys with $\geq 8\%$ Cu as γ Fe-Co solid solution. The γ - α transformation occurs in all alloys on the Fe side of a straight line joining the Cu corner with the 21% Fe point on the Fe-Co side. Addition of Co to Fe-Cu alloys raises the $\gamma \rightleftharpoons \alpha + \text{Cu}$ eutectoid point to a max. on the line joining the Cu corner with the 50:50 Fe-Co point and then rapidly decreases it to room temp. The existence of FeCo has been confirmed by X-ray analysis and d measurements.

A. R. P.

Solubility of methyl chloride and ethyl chloride in certain solvents at -10° to 20° , at pressures less than atmospheric. S. I. KAPLAN and M. A. ROMANTSCHUK (J. Gen. Chem. Russ., 1936, 6, 950–954).—Data are recorded for $(\text{CH}_2\text{Cl})_2$ and CCl_4 at 100–760 mm.; the former is always the better solvent.

J. J. B.

Mutual solubilities of hydrocarbons. I. F-p. curves of dotriacontane (dicetyl) in propane and butane. W. F. SEYER and R. FORDYCE (J. Amer. Chem. Soc., 1936, 58, 2029–2031).—The data indicate the occurrence of two forms of dotriacontane. The variation of n with temp. shows a transition point at 55° .

E. S. H.

Thermal variation of electrical birefringence of a liquid mixture presenting a critical point of miscibility. A. GOLDET (Compt. rend., 1936, 203, 716–718).—Variation of the Kerr effect with temp. for a mixture of PhNO_2 and C_7H_{16} has been investigated in the neighbourhood of the crit. solution temp. T_c . The effect increases sharply as T_c is approached from higher temp., probably owing to changes in the electric field in the liquid.

A. J. E. W.

Influence of addition of salts on the water-phenol system. A. BANCHETTI (Atti Soc. Toscana Sci. Nat., 1935, 44, No. 3, 5 pp.; Chem. Zentr., 1936, i, 314).—Addition of c g.-mols. of KCl per 1000 g. to a mixture of 34.8% of PhOH and 65.2% of H_2O raises the crit. solution temp. by $t^\circ = 64.87c^{0.87}$.

H. N. R.

System nitrobenzene-sulphuric acid-water. K. C. BAILEY and J. HILTON (J.C.S., 1936, 1571).— PhNO_2 and H_2SO_4 are miscible in all proportions at 17° . Miscibility data are given for mixtures of PhNO_2 , H_2O , and H_2SO_4 at 17° .

R. S.

Solubility of nitrogen in water at pressures up to 4500 kg. per sq. cm. J. BASSET and M. DODÉ (Compt. rend., 1936, 203, 775–777).—Measurements at 18° are recorded. The solubility increases with the pressure up to approx. 3000 kg. per sq. cm. and then decreases up to 4500 kg. per sq. cm. Several days are needed for saturation at the higher pressures.

H. J. E.

Partial vapour pressures of methylamine solutions. W. A. FELSING and B. A. PHILLIPS (J. Amer. Chem. Soc., 1936, 58, 1973–1975).—Partial v.p. of aq. NH_2Me , NHMe_2 , and NMe_3 , respectively, have been determined over the concn. range 0.2–2.5M. The v.p. of liquid NMe_3 (-20° to 45°) is given by $\log_{10} p(\text{mm.}) = -1410.5/T + 8.574 - 0.0021158T$; d ,

determined over the same temp. range, is given by $0.87406 - 4.433 \times 10^{-4}T - 1.29236 \times 10^{-4}T^2$. The calc. b.p. is 2.90° , and calc. heat of vaporisation 5706 g.-cal. per mol. The calc. free energy of solution (in g.-cal. per mol.) is 3474 for NHMe_2 , 2991 for NH_2Me , and 2090 for NMe_3 .

E. S. H.

Solubility and activity of the halogenates of some bivalent metals. III. Solubility and activity of radium iodate in water and in solutions of electrolytes. A. POLESICKI and P. TOLMATSCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 319–320).—The solubility has been determined in H_2O at 0 – 100° , and in solutions of KNO_3 , $\text{Ca}(\text{NO}_3)_2$, and KIO_3 at 25° . The activity coeffs. at different ionic strengths have been calc.

D. C. J.

Solubility of solids in liquefied gases. Solubility of KNO_3 and NaCl in liquid ammonia. A. I. SCHATTENSTEIN and M. M. VIKTOROV (Acta Physicochim. U.R.S.S., 1936, 5, 45–62; cf. A., 1934, 1304).—A method for the accurate measurement of solubilities of solids in liquefied gases is described. Sources of error are discussed and published data critically examined.

F. L. U.

Effect of one salt on the solubility of another. VII. Solubilities of cobaltammines in aqueous sodium, potassium, and barium thiocyanates. J. R. PARTINGTON and H. J. STONEHILL (Phil. Mag., 1936, [vii], 22, 857–882).—Data for $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{NO}_3)_2$ and $[\text{Co}(\text{NH}_3)_5\text{NCS}]_2$ are recorded. The results are not in accord with the Debye-Hückel theory, assuming either point ions or finite ionic diameters. The La Mer equation applies when the ionic strength is ≥ 0.52 , provided that a val. for the mean ionic radius characteristic of each solution is assumed; this val. is not simply related to the crystallographic ionic diameters for the ions present.

A. J. E. W.

Solubility of cobaltous iodate in presence of sodium chloride, sodium iodate, and cobaltous sulphate. H. M. TRIMBLE (J. Amer. Chem. Soc., 1936, 58, 1868–1869).—Data at 30° are recorded.

E. S. H.

Solubility of cupric oxide in alkali and the second dissociation constant of cupric acid. Analysis of very small amounts of copper. L. A. McDOWELL and H. L. JOHNSTON (J. Amer. Chem. Soc., 1936, 58, 2009–2014).—The solubility of CuO in 0.04–8.4N-KOH and in 2.2–4.2N-NaOH at 25° has been determined. The calc. dissociation const. for $\text{HCuO}_2' = \text{H}^+ + \text{CuO}_2''$ is 7.9×10^{14} . The relative proportions of HCuO_2' and CuO_2'' in the solutions have been evaluated. The solubility of CuO in H_2O is 3×10^{-5} g.-mol. per litre. A potentiometric method for the determination of Cu in low concns. is described.

E. S. H.

Derivation of a general expression for the velocity of dissolution of a solid body. R. L. MÜLLER (Acta Physicochim. U.R.S.S., 1936, 4, 481–493).—The dissolution of a solid over which a liquid is flowing is considered mathematically.

C. R. H.

Coefficient of fractionation of radium and its isotopes in the crystallisation of barium chlorate. B. GOLDSCHMIDT (Compt. rend., 1936, 203, 617–

618).—Data are recorded for the ratio of the concns. of Ra, Ac-X, and Th-X in crystals and mother-liquor, on slowly crystallising aq. $\text{Ba}(\text{ClO}_3)_2$ solutions at 30° . The distribution coeff. is the same for the three isotopes.

H. J. E.

Theory of adsorption of radioactive elements on polar crystals. A. P. RATNER (*Acta Physicochim. U.R.S.S.*, 1936, 4, 889—898).—Equations are deduced for the exchange adsorption of ions which do not give solid solutions with the adsorbing crystal and also for the influence of foreign ions.

H. J. E.

Inner adsorption in salt crystals. IV. D. BALAREV (*Z. anal. Chem.*, 1936, 106, 349—353).—Polemical, in reply to Kolthoff (this vol., 677).

J. S. A.

Mechanism of the phenomenon of base exchange. M. G. AUSTERWEIL (*Bull. Soc. chim.*, 1936, [v], 3, 1782—1790; cf. A., 1932, 1007).—It is confirmed that base exchange is governed by the laws of distribution, the solid base exchanger playing the rôle of a solvent non-miscible with the solution containing the cations. The extraction formula is related to the empirical adsorption formula by which the phenomenon has been previously represented.

J. W. S.

Adsorption of radium ions on glass, and Guy's theory. V. VDOVENKO and A. SAMOILOVICH (*Acta Physicochim. U.R.S.S.*, 1936, 4, 613—616).—Theoretical. The adsorption isotherms for Ra ions at concns. from 10^{-7} to 10^{-11} mol. per litre and p_H 2—7 can be explained in terms of Guy's theory.

O. D. S.

Polymolecular adsorbed films. I. Adsorption of argon on salt crystals at low temperatures, and the determination of surface fields. R. S. BRADLEY (*J.C.S.*, 1936, 1467—1474; cf. A., 1931, 421).—The equation $T \log_{10} (p_0/p_a) = K_1 K_2^a$, where p_0 and p_a are the saturation pressures of the bulk liquid and the adsorbed film, respectively, has been deduced for the formation of thick films by polarisation. Data relative to the adsorption of A on powdered CuSO_4 , $\text{Al}_2(\text{SO}_4)_3$, and KCl at 84.5 — 88° abs. are in good agreement with the equation. Thick films are formed on the two former, but not on KCl, polarisation being small in this case due to anion and cation having approx. the same size. The induced dipole moments and the surface fields are calc.

R. S.

Adsorption of vapours on glass spheres. I. Adsorption of nitrogen. J. L. SHERESHEFSKY and C. E. WEIR (*J. Amer. Chem. Soc.*, 1936, 58, 2022—2029).—Adsorption data for liquid-air temp. are recorded and discussed in relation to adsorption theories. At low pressures the adsorption isotherm shows recession of the equilibrium pressure. Measurements of the thermal flow effects of H_2 and He show agreement at pressures corresponding with equal mean free paths.

E. S. H.

Adsorption of hydrogen and nitrogen on iron-molybdenum ammonia catalysts. V. ROITER, S. GAUCHMANN, and M. LEPERSON (*Acta Physicochim. U.R.S.S.*, 1936, 4, 145—158).—The adsorption of H_2 on Fe-Mo (I) and Fe-Mo- Al_3 (II) catalysts is rapid and reversible at low temp., but slow and irreversible

between 0° and 450° . Adsorption is slowest with old (I) and fastest with (II). The presence of Al_2O_3 increases the no. of active centres and prevents the reduction of catalyst surface by recrystallisation, but has little effect on the adsorptive capacity. In the case of N_2 , the rapid, reversible adsorption could alone be observed up to 450° , and the heats of adsorption for (I) and (II) are 5500 and 12,000 g.-cal., respectively.

R. S.

Adsorption properties of promoted iron oxide in relation to the distribution of the promoter in the oxide form of the ammonia catalyst. A. DUBROVSKAJA and N. I. KOBOSEV (*Acta Physicochim. U.R.S.S.*, 1936, 4, 841—858).—Adsorption isotherms of O_2 on Fe_2O_3 and on Fe_2O_3 promoted with 10% of Al_2O_3 have been measured at -190° and 400° . When heated in vac. at 600° , Fe_2O_3 crystallises completely. The adsorption decreases with the degree of crystallisation, as determined by X-rays. The rate of desorption at 150 — 400° has been measured. The activation energy for desorption is the same in the promoted and unpromoted oxide. 10% of Al_2O_3 reduces the sp. adsorption of Fe_2O_3 by 4—5 times. In Fe_2O_3 with relatively large crystals, 1% of Al_2O_3 suffices to cover approx. 50% of the crystal surface.

H. J. E.

Recombination of atomic hydrogen in adsorbed layers. O. I. LEPUNSKI (*Acta Physicochim. U.R.S.S.*, 1936, 5, 271—298).—The adsorption and recombination of H atoms on Ni, Fe, Cu, and Al between -180° and 0° has been studied. An equation for the recombination velocity has been deduced assuming an activated surface diffusion of H, which is in good agreement with the results. Deviations are attributed to inhomogeneity of the surface. Metals which are most efficient as hydrogenation catalysts give the greatest recombination velocities. The energy of activation of the surface diffusion calc. from the temp. coeff. is $<$ that calc. from the abs. velocity of recombination owing to the operation of a steric factor, the nature of which is discussed.

R. S.

Influence of p_H on adsorption from solutions. N. A. YAJNIK, D. N. GOYLE, I. DAS, and J. R. JAIN (*Kolloid-Z.*, 1936, 77, 99—103).—Measurements of the adsorption of different dyes by SiO_2 gel, $\text{Al}(\text{OH})_3$, and animal charcoal show that the acid dyes are adsorbed most strongly by the acid adsorbents and the basic dyes by $\text{Al}(\text{OH})_3$. Addition of acid reduces the adsorption of methylene-blue and Bismarck-brown, but increases the adsorption of water-blue and picric acid. The rôle of p_H is discussed.

E. S. H.

Adsorption of bromine ions by argillaceous sludges. V. I. NIKOLAIEV, A. M. SOLOVOV, and M. A. FRISCHMUT (*Ann. Sect. d'Anal. Physico-Chim.*, 1936, 9, 317—326).—Adsorption of Br^- by clay or argillaceous sludge from salt lake H_2O is at a max. when the latter has d 1.32. Adsorption of KBr or NaBr does not take place in absence of chlorides.

R. T.

Action of potassium on the mechanism of activation of charcoal. B. BRUNS and E. ZOLOTAREVSKAJA (*Acta Physicochim. U.R.S.S.*, 1936, 5, 63—78; cf. A., 1933, 1112).—The adsorptive capacity for C_5H_{12} of activated sugar C decreases linearly with

increasing K content between 0.02 and 7.8%. It is immaterial whether K_2CO_3 is added initially to the sugar, or the C is heated in K vapour before activation. The effect is due to the greater rapidity with which the surface layer burns in the presence of K.

F. L. U.

Discontinuities in the sorption process. A. G. FOSTER (Trans. Faraday Soc., 1936, 32, 1559—1569).—Using a static vac. method, no well-defined discontinuities are observed in the adsorption isotherms of CCl_4 on SiO_2 gel at 25°. After prolonged heating at 120° with CCl_4 , residual H_2O is removed from the gel and the shape of the isotherm alters, resulting in greatly increased adsorption at low pressures. Adsorption measurements of H_2O , EtOH, and CCl_4 on SiO_2 gel by the dynamic retentivity method show, when compared with results of the static technique, that the retentivity method is untrustworthy when applied to isotherms of abnormal type.

E. S. H.

Range of action of surface forces. J. M. MACAULAY (Nature, 1936, 138, 587).—Observations on the creeping of H_2O between glass plates are described.

L. S. T.

Unimolecular adsorption layers and surface films. I. Measurement of surface pressure of adsorption layers. A. S. ACHMATOV (Kolloid-Z., 1936, 77, 20—26).—Apparatus is described.

E. S. H.

Surface properties of non-aqueous solutions. R. ASCHAFFENBURG (Nature, 1936, 138, 644—645).—For solutions of *n*-alcohols in NH_3Ph the lowering ($\Delta\gamma$) of the surface tension is < for aq. solutions. For equimol. solutions, $\Delta\gamma$ is the greater the higher is the mol. wt. The γ -concn. curves are of the same type as those for aq. solutions, and for dil. solutions ($c < 0.1$ g.-mol. per litre) $\Delta\gamma/c$ is const. In homologous series the influence of an additional CH_2 on the surface energy becomes less as the C chain becomes longer.

L. S. T.

Discussion on surface phenomena. Films. (Proc. Roy. Soc., 1936, A, 155, 684—711).—E. K. RIDEAL discussed the evidence on which the concept of the oriented mono-layer is based. Two experimental methods, an optical and an electrical, are available for the determination of film uniformity. Other properties of surface films were reviewed.

N. K. ADAM discussed the principal forces stabilising unimol. surface films at an air- H_2O surface: (a) the perpendicular attraction of the H_2O -sol. groups at or near the end of the mol., and (b) the lateral adhesion between the mols.

G. GEE described the results of an investigation of the autoxidation and polymerisation of unsaturated glycerides (drying oils) spread as mono-layers on the surface of 0.01N- H_2SO_4 or -HCl.

F. A. ASKEW described a method for the study of unimol. films at liquid-liquid interfaces.

J. S. MITCHELL discussed the photochemical properties of certain complex org. compounds spread in mono-layers at the surface of aq. substrates.

J. H. SCHULMAN. The methods of measuring phase boundary potentials and surface pressures at air-liquid phase boundaries may be used to examine the

interaction between large mols. A new phenomenon is described which consists in the penetration of a film of oriented mols., each possessing a large hydrophobic portion and a dipole situated near the end of the mol., by similar mols. which possess different dipoles and are readily sol.

O. GATTY. Differences in potential between the inside and outside of the isolated skins of the common frog have been measured, and time-potential curves obtained as functions of the composition of the solutions in contact with the skin.

K. GORTER described certain results of work on the spreading of complex proteins.

J. F. DANIELLI discussed the tension at the surface of living cells.

A. HUGHES described experiments on unimol. films of chlorophyll, hæmin, and certain recently isolated metallic phthalocyanine derivatives.

L. L. B.

Alteration of the free surface energy of solids. I. Vertical-rod method for the measurement of contact angles and effect of heat-treatment on magnitude of contact angles. F. E. BARTELL, J. L. CULBERTSON, and M. A. MILLER. II. Effect of heat-treatment of metals in air. III. Effect of heat-treatment of metals in a vacuum and in several gases. F. E. BARTELL and M. A. MILLER (J. Physical Chem., 1936, 40, 881—888, 889—894, 895—904).—I. A method has been developed for measuring contact and interfacial contact angles against either transparent or opaque solids which can be formed into rods, and has been applied to changes in the adhesion tension of H_2O on Pyrex glass, SiO_2 , Au, and Pt. The method of cleaning and previous heat-treatment of solids changes the magnitude of the contact angle. Careful annealing of glass decreases the H_2O -air contact angle on its surface to zero. Ageing of glass and metal surfaces increases the contact angle on them.

II. A method of pretreatment of Au and Pt rods to furnish standard reference surfaces has been developed. Similar standard surfaces could not be obtained on steel treated in air. Treatment of standard Au and Pt surfaces at 100—600° in air for 1 hr. decreases the H_2O -air contact angle, this decrease being the greater the higher is the temp. of the treatment, but on keeping in air the contact angle gradually increases again. Measurements of the contact angles at H_2O - C_6H_6 , H_2O -1- $C_{10}H_7Br$, and H_2O - $C_2H_2Br_4$ interfaces indicate that the metals treated at low temp. were fairly strongly organophilic, but at higher temp. became less strongly so or even hydrophilic. The changes are attributed to oxidation and recrystallisation.

III. Standard reference surfaces were prepared on rods of Au, Pt, Cu, 18:8 stainless steel, Ag, Al, W, and brass by polishing in N_2 and heating in a vac. at 100°. Heat-treatment in a vac. rendered the surfaces more hydrophilic with rise of temp. of treatment. Heating in gases made them less hydrophilic than when heated in a vac. in the order vac. $> H_2 >$ air $> N_2$. All the metals except Pt and W react readily with $C_2H_2Br_4$ after heating in N_2 , whilst Au, Cu, and brass similarly treated react with 1- $C_{10}H_7Br$. Al and W react with $C_2H_2Br_4$ after heating in H_2 .

The contact angles at liquid-air interfaces vary considerably with the metal and its pretreatment.

J. W. S.

Properties of metallic solutions. III. Surface tension of amalgams. V. K. SEMENTSCHENKO, B. P. BERING, and N. L. POKROVSKI [with E. E. SHVAREVA] (Acta Physicochim. U.R.S.S., 1936, 5, 181—192).—The surface tensions of Hg amalgams of Cs, Rb, K, Na, Li, Ba, Sr, Pb, Sn, Ag, Cu, Zn, Bi, Co, Mg, and Cd have been determined at 18—20°. The data are in agreement with Sziszkovski's equation up to a crit. concn. c_k of active metal, c_k being a linear function of the ultimate activity. K, Rb, and Cs form surface layers of 3.76, 5.8, and 7.8 mols. thick, respectively, whilst Ba, Li, Na, etc. form unimol. layers. The application of the Gibbs equation to amalgams is discussed.

R. S.

Properties of metallic solutions. II. Surface tension of amalgams. B. P. BERING and N. L. POKROVSKI (Acta Physicochim. U.R.S.S., 1936, 4, 861—872; cf. this vol., 1192, 1331).—The surface tension of amalgams of Hg with 0—0.2 at-% of Cs, Rb, K, Na, Li, Ba, Sr, Mg, Pb, Sn, Cu, Ag, Cd, Bi, Co, and Zn has been measured at 20° by the method of max. bubble pressure in an atm. of H₂. H. J. E.

Electrocapillarity curve of gallium. II. A. MURTAZAJEV and A. GORODETZKAJA (Acta Physicochim. U.R.S.S., 1936, 4, 75—84; cf. A., 1928, 1193).—More exact results have been obtained. PhOH, *iso*-C₅H₁₁·OH, pyrogallol, CS(NH₂)₂, and KI displace the max. of the electrocapillarity curve of Ga in the same direction as in the case of Hg, but the degree of adsorption is different.

R. S.

Mechanical properties of foams. I. A. SIEHR (Kolloid-Z., 1936, 77, 27—32).—In a column of foam (up to 50 cm.) the sideways pressure exerted on the tube walls increases linearly with the height of the foam. Foam pressure and wetness (c.c. of liquid/c.c. of foam) decrease with time, although not proportionally. Dil. saponin solutions give drier and lighter foams than conc. saponin solutions.

E. S. H.

Wetting power of powders of different degrees of dispersion. Z. V. VOLKOVA (Acta Physicochim. U.R.S.S., 1936, 4, 635—644; cf. A., 1935, 1071).—The velocity of wetting by H₂O and PhMe of powdered quartz (I), calcite (II), fluorite (III), and corundum (IV) of different degrees of dispersion has been measured. The ratio r/r_0 of the penetration radii for H₂O and PhMe, respectively, remains const. for (I) and (II) at medium dispersion, but falls at high dispersions. This decrease is ascribed to the formation of H₂O layers between the particles. r/r_0 for (III) and (IV) decreases with decrease in particle size. For particles covered with an adsorbed layer of oleic acid r/r_0 decreases to 0 when the surface is only partly covered with acid.

O. D. S.

Anomalies of thin liquid layers. III. Ultramicrometric study of solvent envelopes and of the fundamental swelling process. B. DERJAGUIN [with E. OBUCHOV] (Acta Physicochim. U.R.S.S., 1936, 5, 1—22; cf. A., 1934, 1068).—A method is described for determining, by means of an optical lever, the pressure exerted by a thin film of liquid in

contact with lyophilic surfaces. When H₂O penetrates between plane parallel plates of mica, the resulting linear separation of the plates varies inversely with the pressure opposing separation, e.g., 2.1 μ at 4.4, and 0.55 μ at 14.0 g. per sq. cm. CCl₄ produces no effect with mica, but when saturated with H₂O gives the same val. as does pure H₂O. At a steel surface H₂O is inactive, whilst paraffin oil gives an effect which is increased by addition of oleic acid. The observed effect is invoked to explain the swelling of ppts. and colloids. The subject is discussed theoretically.

F. L. U.

Film formation from emulsions. H. WAGNER and G. FISCHER (Kolloid-Z., 1936, 77, 12—20).—Films formed by the drying of emulsions of the H₂O-in-oil and oil-in-H₂O types are classified in a scheme in which the extreme members are (a) reversible, hydrophilic, and porous (e.g., glue), and (b), irreversible, hydrophobic, and non-porous (e.g., lacquer), respectively. The structure of dried films from several emulsions has been examined microscopically and is discussed in relation to the system of classification.

E. S. H.

Formation of phosphatide films on cholesterol. H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 299—302).—The film consists of mols. of both phosphatide (I) and cholesterol, the latter acting as an activator for (I), contrary to the effect of TiO₂.

H. G. R.

Osmotic pressure and viscosity of polystyrenes. (MME.) A. DOBRY and (MME.) A. SCHWOB (Bull. Soc. chim., 1936, [v], 3, 1790—1794).—In sufficiently dil. solution the mol. wt. of polystyrenes calc. from the osmotic pressure is independent of the solvent, but decreases rapidly with increasing concn. and for 0.5% solutions is half the true mol. wt. This change is attributed to colloidal effects. Fractional pptn. of a polystyrene yields fractions with the same mol. wt., but differing viscosities.

J. W. S.

Complex formation involving weak acids. XV. Optical rotation of *l*-malic and *l*-lactic acids during neutralisation with sodium hydroxide. H. T. S. BRITTON and A. A. MOSS (J.C.S., 1936, 1487—1489).—The rotations of undissociated malic (I) and lactic (II) acids and the malate, hydro-malate, and lactate ions have been determined. The variation of rotation during titration of (I) and (II) with NaOH is given by the sum of the mol. and ionic rotations.

R. S.

Raman effect in non-aqueous electrolytic solutions. II. Solutions of antimony trichloride. M. ASCHKINASI, P. KURNOSOVA, and V. FINKELSTEIN (Acta Physicochim. U.R.S.S., 1936, 4, 317—324; cf. this vol., 1203).—The Raman spectra of 5.8—25% solutions of SbCl₃ in Et₂O have been determined. Undissociated mols. exist in solution and there is no evidence of compound formation, since no new lines appear. The Raman spectra of 15—22% solutions of SbCl₃ in C₆H₆ show two new lines, of frequencies 477 and 1236 cm.⁻¹, corresponding with the compound 2SbCl₃·C₆H₆.

R. S. B.

High-frequency measurement of the dielectric constant of dilute solutions of salts in different solvents. M. BEAUVILAIN (*Ann. Physique*, 1936, [xi], 6, 502—560).—The dielectric const. of 45 salts in H₂O and of KCl in glycerol and H₂O-glycerol mixtures decreases linearly as the salt concn. increases. In general, the decrease is the more marked the higher is the valency of the ions and the greater the proportion of H₂O in the mixtures. The dielectric const. of solutions of KCl in EtOH, MeOH, BuOH, COMe₂, glycol, and glycerol, and in mixtures of these with H₂O, decreases at a certain concn. of solute, which depends on the H₂O content of the mixtures. The lowering depends on the non-aq. constituent of the solvent.

N. M. B.

Magnetic study of colour changes in cobalt chloride. II. S. S. BHATNAGAR, A. N. KAPUR, and P. L. KAPUR (*J. Indian Chem. Soc.*, 1936, 13, 489—493).—The mol. magneto-optic rotation of CoCl₂·6H₂O in H₂O, C₅H₁₁OH, and HCl varies with concn., although the effect is only just detectable in H₂O. This disagrees with the theory that colour change is due to formation of anhyd. CoCl₂, but supports the theory that complexes of the type CoCl₃' and CoCl₂'' are present (cf. A., 1932, 1083).

C. R. H.

Analysis of magnetogalvanic effect. V. SIHVONEN and P. VEIJOLA (*Z. Elektrochem.*, 1936, 42, 833—837).—Changes in the effect with time for Cu in aq. Cu(NH₃)₄Cl₂ and Fe in aq. FeCl₃ are traced to the reactions $Cu^{++} + Cu = 2Cu^+$ and $2Fe^{+++} + Fe \rightleftharpoons 3Fe^{++}$.

E. S. H.

Colloid synthesis by means of gaseous explosions and colloidochemical investigations on disperse systems so prepared. N. SATA (*Bull. Chem. Soc. Japan*, 1936, 11, 598—627).—By the method previously described (cf. this vol., 1198, 1337), sols of Hg, Se, and S have been prepared and examined. It was necessary to use Na₂S or NaI as a stabiliser for the Hg sols. The vals. of η for the sols are almost the same as for H₂O and the vals. of γ only slightly > for H₂O. Electrophoretic properties and coagulation by means of halides have also been studied.

C. R. H.

Mechanism of the formation of fogs by ultrasonic waves. K. SÖLLNER (*Trans. Faraday Soc.*, 1936, 32, 1532—1536).—The production of the fogs is traced to the collapse of cavities which is brought about by external gas pressure or by the v.p. of the irradiated liquid.

E. S. H.

Action of ultrasonic waves on suspensions. F. J. BURGER and K. SÖLLNER (*Trans. Faraday Soc.*, 1936, 32, 1598—1603).—In suspensions of particles of microscopic dimensions and in colloidal solutions containing rod- or plate-like particles orientation is produced under the influence of ultrasonic waves. Conc. rheopectic suspensions of gypsum, kaolin, etc. are solidified by ultrasonics of low and medium energy; at higher energies the pastes are liquefied as a result of cavitation. Mixtures of sea-sand or quartz powder with H₂O, which are normally dilatant, lose this property when exposed to ultrasonic waves.

E. S. H.

Behaviour of aerosols in the acoustic field. III. Theory of acoustic coagulation. O. BRANDT,

H. FREUND, and E. HIEDEMANN (*Kolloid-Z.*, 1936, 77, 103—115; cf. this vol., 794).—Theoretical.

E. S. H.

Aërogels. I. Structure of metallic oxides. V. CAGLIOTTI and O. D'AGOSTINO (*Gazzetta*, 1936, 66, 543—548).—The structures of Fe₂O₃ and of Al₂O₃, prepared as aërogels by oxidising Fe and Al vapours in electric arcs with a strong current of air, have been investigated by X-rays. Both oxides have the γ -phase structure.

O. J. W.

Measurement of light scattered by disperse systems by means of tubular scattering cells. B. KLAGES and H. KLUMB (*Physikal. Z.*, 1936, 37, 725—726).—Tubular photo-electric cells can be used for the investigation of scattering of light by stationary or moving disperse systems. Aerosols containing 10 mg. per cu.m., and hydrosols containing 1 mg. per litre, could be detected. The apparatus is also useful for the detection of light scattered by biological preps. and for the study of fluorescence.

A. J. M.

Gold colloids in sylvine crystals. J. C. REPSCHÉ (*Acta Physicochim. U.R.S.S.*, 1936, 5, 173—180).—The absorption curves of colloidal Au in KCl agree closely with Mie's theory, but the particle size bears little relation to the [Au].

R. S.

Colloid-chemical phenomena in metals. III. Micellar structure of liquid and solid metals and alloys. J. A. KLJATSCHKÓ (*Kolloid-Beih.*, 1936, 44, 387—426; cf. this vol., 25).—Published evidence is reviewed.

E. S. H.

Colloid-chemical processes at high temperatures. II. Reduction of the disperse phase with hydrogen under pressure. S. I. DJATSCHKOVSKI (*Kolloid-Z.*, 1936, 77, 74—78; this vol., 287).—At 200° and 200 atm. colloidal Fe(OH)₃ is reduced by H₂ to Fe, WO₃ and V₂O₅ to W₃O₈ and V₂O₄, respectively. Cr(OH)₃ is not reduced under these conditions.

E. S. H.

Classification of emulsions. A. RABINERSON and L. KREMNEV (*Acta Physicochim. U.R.S.S.*, 1936, 5, 105—110).

F. L. U.

Appearance of some emulsions. W. S. URBAŃSKI (*Acta phys. polon.*, 1934, 3, 39—41; *Chem. Zentr.*, 1936, i, 29).—A reply to Piekara (A., 1934, 1306). Ag emulsions show evidence of an ordered structure.

J. S. A.

Molecular and colloid solubility of acid and salt dyes, especially benzopurpurin. II. Dissolution of acid dyes in sodium hydroxide + neutral salt and in sodium hydroxide + ethyl alcohol. W. OSTWALD and R. WALTER (*Kolloid-Z.*, 1936, 77, 54—64; cf. this vol., 1338).—Small amounts of neutral salts increase the solubility of benzopurpurin in NaOH, but large amounts cause flocculation. EtOH behaves similarly to neutral salts at low concns., but at higher concns. there is a sp. solubility of the dye in EtOH. The relative rôles of chemical reaction, peptisation, and dissolution in these processes are discussed.

E. S. H.

Spontaneous structure formation of ferric hydroxide sols. G. FUCHS and A. RABINERSON (*Acta Physicochim. U.R.S.S.*, 1936, 4, 441—452).—Fe^{III} salts in the intermicellar liquid of freshly pre-

pared $\text{Fe}(\text{OH})_3$ sols gradually hydrolyse, hydrolysis terminating after 3—6 days according to whether the colloid content is low or high. The hydrolysis is accompanied by a decrease in $[\text{Fe}^{+++}]$ followed by desorption and gradual coagulation. Even when hydrolysis has ceased and there is no further decrease in charge, coagulation continues at a velocity depending on the val. of the adjusted ζ -potential.

C. R. H.

Influence of adsorbed cations on structure formation in aluminosilicate suspensions. A. RABINERSON and V. KNIASEV (*Acta Physicochim. U.R.S.S.*, 1936, 5, 93—104).—Viscosities and times of setting to a thixotropic gel have been determined for 8% suspensions of three varieties of kaolin containing adsorbed H^+ and Na^+ in varying proportions. Setting takes place only when the kaolin is partly saturated with Na^+ . More conc. (10—20%) suspensions can develop structure when fully saturated either with H^+ or with Na^+ . The existence of an optimum Na content is explained by the tendency of this ion to cause both increased hydration and peptisation, the first of which promotes whilst the second hinders the formation of structure.

F. L. U.

Activity of ions in colloidal solutions. I. Suspension effect in the ultrafiltration of positive colloids. P. VASSILIEV, T. GATOVSKAJA, and A. RABINOVITSCH. **II. Suspension effect in the ultrafiltration and centrifuging of negative colloids.** T. GATOVSKAJA and P. VASSILIEV (*Acta Physicochim. U.R.S.S.*, 1936, 4, 1—36, 37—50).— Fe_2O_3 sols of different concns. have been subjected to ultrafiltration and the activities of Cl^- and H^+ in the ultrafiltrate and the residue determined potentiometrically. The vals. of α_{Cl^-} and α_{H^+} in the ultrafiltrate remain approx. const. with increasing sol concn., whilst α_{Cl^-} increases and α_{H^+} decreases in the direction ultrafiltrate \rightarrow sol \rightarrow residue, according to linear functions of the Fe_2O_3 concn. The ratio $\alpha_{\text{Cl}^-} : \alpha_{\text{H}^+}$ is const. on both sides of the ultrafilter in agreement with the Donnan equilibrium condition. A theory based on the Donnan equilibrium is put forward.

II. WO_3 , TiO_2 , and V_2O_5 sols have been investigated. The α_{H^+} in the ultrafiltrate is const. with increasing sol concn., but in the series ultrafiltrate \rightarrow sol \rightarrow residue, α_{H^+} increases approx. linearly with sol concn. Similar results are obtained when the system is centrifuged.

R. S.

High-frequency conductivity of colloidal electrolytes. I. Congo-red and Congo-blue sols. G. SCHMID and A. V. ERKKILA (*Z. Elektrochem.*, 1936, 42, 737—741).—The high-frequency conductivity is about 30% > that at low frequencies. The significance of this result in elucidating the electrical structure of colloid micelles is discussed.

E. S. H.

Physicochemical investigations of photographic emulsions. C. S. LIALIKOV and V. N. PISKUNOVA (*Acta Physicochim. U.R.S.S.*, 1936, 4, 325—340).—The solubility (S) of AgBr has been determined at 25—45° in presence of gelatin, 0.00625—1.6M-KBr, 1M- NH_3 , and 0.5M- KNO_3 . S in NH_3 decreases on addition of small quantities of Br^- , remains const. on further additions, and then in-

creases. The expression $6.3 \times 10^{-13} [\text{NH}_4\text{OH}]^2 / [\text{Br}^-][\text{Ag}(\text{NH}_3)_2^+] f_{\text{Br}^-} f_{\text{Ag}(\text{NH}_3)_2^+}$ remains approx. const. for $[\text{Br}^-] = 0.00606—0.0995N$. The val. of S in NH_3 in presence of KBr is increased by KNO_3 , the influence of the KNO_3 increasing with decreasing $[\text{KBr}]$, and the presence of 1% gelatin causes only a slight decrease in S .

R. S. B.

Rôle of dielectric constant, polarisation, and dipole moment in colloid systems. XVII. Swelling and solubility of cellulose derivatives and their relations to dielectric values. W. L. H. MOLL (*Kolloid-Z.*, 1936, 77, 85—93).—Published data show a relation between the optimum conditions for swelling and the dielectric const., surface tension, and chemical character of the solvent.

E. S. H.

Electro-kinetic investigation of the organosols of highly polymerised natural substances. M. TANIGUCHI and I. SAKURADA (*J. Soc. Chem. Ind. Japan*, 1936, 39, 316B).—Cellulose nitrate and acetate are negatively charged in COMe_2 solution.

A. G.

Electrolyte coagulation of weakly solvated sols and electrolyte activity. V. Determination of exact coagulation values by turbidity measurements. H. A. WANNOW (*Kolloid-Z.*, 1936, 77, 46—53; cf. this vol., 1200).—When As_2S_3 sols are coagulated by electrolytes, the turbidity decreases and the sedimentation vol. increases with increasing valency of the pptg. ion (K^+ , Mg^{++} , Al^{+++} , Th^{++++}). Turbidity measurements are not suitable for the exact determination of coagulation vals.

E. S. H.

Flocculation of lyophilic colloids by non-electrolytes and salts. B. JIRGENSONS (*Kolloid-Beih.*, 1936, 44, 285—386).—Published work on the behaviour of sols of ovalbumin, casein and its degradation products, hæmoglobin, starch, and lecithin is reviewed and certain regularities are indicated. In flocculation of the pure sols by alcohols and similar non-electrolytes, max. and min. with increasing concn. appear, their positions depending on the dielectric const. of the non-electrolyte and on the p_{H} of the solution. With combinations of capillary-active non-electrolytes and salts in low or medium concns. coagulation is more rapid than with non-electrolytes or salts alone, but at higher concns. the non-electrolyte stabilises the sol.

E. S. H.

Peptisation of colloids by electrolytes. I. Reversion of coagulation with formation of insoluble salts. P. VASSILIEV and N. DESCHALIT (*Acta Physicochim. U.R.S.S.*, 1936, 4, 51—74).—When $\text{Fe}(\text{OH})_3$ sol is coagulated by Na_2SO_4 , Cl^- is displaced from the surface of the particle to the intermicellar liquid by SO_4^{--} . The gel can be peptised by addition of an equiv. amount of BaCl_2 , with formation of BaSO_4 , and it has been shown that Cl^- is reabsorbed during the peptisation. Repeated coagulations and peptisations are possible. Part of the BaSO_4 is pptd., whilst part remains in the sol, and this has been shown by X-rays to have the ordinary crystal structure. Reversion of $\text{Al}(\text{OH})_3$ and $\text{Ti}(\text{OH})_2$ gels is possible, but gels of negative colloids could not be peptised. The formation of CaSO_4 or SrSO_4 does not produce reversion, but PbCrO_4 is efficacious because of its low solubility product.

R. S.

Elastoidin fibres. I. Imbibition of water. E. FAURÉ-FRÉMIET and R. WOELFFLIN. **II. Elastic properties.** E. FAURÉ-FRÉMIET. **III. Titration curve.** E. FAURÉ-FRÉMIET and R. WOELFFLIN (J. Chim. phys., 1936, 33, 666—680, 681—694, 695—700).—I. The prep. of elastoidin fibres (I) from the fins of the blue shark is described. The imbibition of H_2O by dried (I) bears a sigmoid relation to the pressure of the added H_2O vapour, and the free energy of imbibition falls rapidly as H_2O is absorbed. In the absence of salts, the imbibition by submerged (I) is const. at p_H 4—11, but rises sharply at p_H 12 and has a sharp max. at p_H 2.4. Neutral salts augment imbibition, the effect corresponding with the Hofmeister series, but inhibit the large absorption at low p_H vals. The breadth of a fibre in acid increases linearly with imbibition and the length increases linearly to a flat max. equal to the val. at p_H 4—11. The effects of temp. are recorded.

II. (I) exist in two interconvertible forms. Modification *A* follows Hooke's law at 7—58°, but has small extensibility. Modification *B*, formed at approx. 62° under zero tension, follows Hooke's law at 63—66° and is highly elastic. Below 62°, *B* undergoes changes, largely permanent, corresponding with the existence of false equilibria.

III. (I) absorb acid and alkali strongly at p_H vals. < 2.5 and > 10, respectively. *A* and *B* at p_H 6.2—7.6 and p_H 5—7, respectively, do not absorb acid or alkali.

J. G. A. G.

Isoionic point of proteins. A. PASSINSKI and Z. ZOLOTAREVA (Acta Physicochim. U.R.S.S., 1936, 4, 505—526).—The effect of neutral salts on the iso-electric and isoionic points of ampholytes is discussed theoretically. Measurements of the isoionic points of solutions of gelatin (I) and of ovalbumin (II) in the presence of $BaCl_2$, KCl , and KI show that for both proteins $BaCl_2$ causes a shift of isoionic point towards the acid side, whilst KI causes a shift to the alkaline side. The isoionic point of (I) is unaltered by KCl , but that of (II) is shifted to the alkaline side.

O. D. S.

Solubility and flocculation of proteins and other lyophilic colloids. I. F. HAUROWITZ and F. MARX (Kolloid-Z., 1936, 77, 65—74).—In the heat-coagulation of ovalbumin and serum solutions there is a small vol. increase, and in blood-pigment solutions a small vol. decrease. The vol. change is about 3—6% of the contraction on adding albumin to H_2O ; thus, denatured albumin has almost the same degree of hydration as natural albumin. Proteins containing negative exionic groups are pptd. by clupein. Addition of $NaCl$ inhibits the pptn.; the ppt. has an approx. const. composition. The colloidal structure of proteins and the nature of the solvate sheath are discussed.

E. S. H.

Adsorption of benzene derivatives by serum colloids and organ pulps. C. SCAGLIONI (Kolloid-Z., 1936, 77, 78—85).— OH - or NH_2 -derivatives are strongly adsorbed by serum or muscle, but when present together the degree of adsorption is < when present singly. The presence of CO_2H practically inhibits the adsorption due to OH or NH_2 in the same mol. All the compounds except NH_2Ph are

more strongly adsorbed by serum and muscle than by liver, spleen, lung, or kidney. The bearing of the observations on metabolism is discussed.

E. S. H.

Undulating cracks and periodical crystallisation in gelatin gel in the formation of mercuric carbonate. F. M. SCHEMJAKIN and A. I. LAZAREVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 371—374).—The periodic crystallisation observed in the formation of $HgCO_3$ from Na_2CO_3 and $HgCl_2$ in gelatin gel has been studied. The colour and form of the crystals are changed by reversing the inner and outer components.

O. D. S.

Sensitisation of phosphatide sols by cholesterol in aqueous media. H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 303—305).—Phosphatide sols with H_2O can be sensitised by cholesterol if the suspension is very fine and the temp. raised.

H. G. R.

Film formation in a mixture of two hydrophilic sols: phosphatides and sodium nucleinate. H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 511—516).—The nature of the film formed depends on the ionic concn. of the medium.

H. G. R.

Moving-boundary method of measuring cataphoresis. J. J. BIKERMAN (Trans. Faraday Soc., 1936, 32, 1648—1652).—The movement of the boundary between two almost identical sols of different colour is observed. Data are recorded for the boundary between an As_2S_3 sol and a similar sol containing HgS .

E. S. H.

Chemical constant and thermodynamic potential of nitric oxide gas and the gaseous equilibrium $2NO + O_2 = 2NO_2$, calculated from spectroscopic data. H. ZEISE (Z. Elektrochem., 1936, 42, 785—789).—Theoretical.

E. S. H.

Thermodynamics of endothermic processes of nitrogen fixation. N. I. KOBOSEV, S. S. VASSILIEV, and J. S. KASARNOVSKI (Acta Physicochim. U.R.S.S., 1936, 4, 245—262).—Equilibrium and energy relations have been calc. thermodynamically at 2000°, 3000°, and 3500° for the reactions $0.5N_2 + 0.5O_2 = NO$ (a), $0.5N_2 + CO_2 = NO + CO$ (b), $0.5N_2 + 0.5H_2 + C = HCN$ (c), $0.5N_2 + 0.5C_2H_2 = HCN$ (d), and $0.5N_2 + CH_4 = HCN + 1.5H_2$ (e). The neglect of concomitant changes such as dissociation gives rise to serious errors, and the results obtained by Krase and Mackey (A., 1928, 1324) for (b) are considered to be incorrect. The reactions (c) and (d) give considerable yields of HCN and require little energy. The considerable yields of NO obtained in the glow discharge are connected with the low temp.

R. S. B.

Displacement of equilibrium by substances which simultaneously act as catalytic accelerators. III. N. SCHLESINGER (Acta Physicochim. U.R.S.S., 1936, 5, 79—92; cf. A., 1927, 837).—The equilibrium const. (*K*) in the reaction $EtOH + AcOH = EtOAc + H_2O$ has been determined at 100° in presence of various salts and inorg. acids. In all (15) cases *K* decreases linearly with increase of salt concn. when the latter is expressed in millimol.

per mol. of H_2O . The displacement of equilibrium cannot be accounted for by ion hydration.

F. L. U.

Dissociation equilibrium of sulphur trioxide. A. F. KAPUSTINSKI and L. M. SHAMOVSKI (Acta Physicochim. U.R.S.S., 1936, 4, 791—802).—The equilibrium $SO_3 \rightleftharpoons SO_2 + 0.5O_2$ has been studied at 850—1000° abs. in a static system containing a heated Pt wire. The data are expressed by $\log (p_{SO_2})(p_{O_2})^{1/2}/p_{SO_3} = 5005/T + 4.743$. $\Delta S = 21.68$ g.-cal. per 1° and $\Delta H = 22.88$ kg.-cal. per mol.

H. J. E.

Evidence for the complete dissociation of salts at all concentrations in aqueous solutions. W. H. BARNES (J. Chem. Educ., 1936, 13, 428—431).—A lecture.

L. S. T.

Dissociation constants of different oxides in deuterium oxide. G. SCHWARZENBACH, A. EPRECHT, and H. ERLNMEYER (Naturwiss., 1936, 24, 714).—The dissociation consts. of some weak acids and bases in D_2O (99.6%) have been determined potentiometrically. The normal potential of the D_2 electrode is -0.0022 volt, and the ionic product in D_2O (99.6%) is $10^{-14.804}$ at 20°. The influence of η and the dielectric capacity on the dissociation const. is discussed.

A. J. M.

Ionisation constant of acetic acid in dioxan-water mixtures. H. S. HARNED and G. L. KAZANJIAN (J. Amer. Chem. Soc., 1936, 58, 1912—1915).—E.m.f. of the cells H_2 (1 atm.)|AcOH(m_1), NaOAc(m_2), NaCl(m_3), dioxan- H_2O |AgCl-Ag have been determined at 5° intervals from 0° to 50° in solutions containing 20, 45, and 70 wt.-% of dioxan. The ionisation const. of AcOH, calc. for the above temp. range, is in agreement with the empirical equation of Harned and Embree (A., 1935, 1321).

E. S. H.

Anomalies in the dissociation constant of some halogenated organic acids. M. BETTI and E. LUCCHI (Atti R. Accad. Lincei, 1936, [vi], 23, 465—469; cf. A., 1935, 564).—*o*-Chloro-, m.p. 162°, $[\alpha]_D + 450.9^\circ$ in C_6H_6 , $[M]_D + 1792^\circ$, and *o*-bromo-, m.p. 123°, $[\alpha]_D + 410.5^\circ$ in C_6H_6 , $[M]_D + 1815^\circ$, *cinnamylidenephényl*- β -hydroxynaphthylmethylamine have been prepared from the corresponding *cinnamaldehydes*, m.p. 56—57°, b.p. 138°/10 mm., and m.p. 67°, b.p. 160°/14 mm., respectively. The results indicate that the *o*- $C_6H_4Cl \cdot CH:CH$ radical is more negative than the corresponding Br-radical. The dissociation consts. of the two halogenocinnamic acids are 0.39×10^{-4} and that of cinnamic acid 0.365×10^{-4} .

O. J. W.

Solutions of aluminium fluoride. V. CAGLIOTTI (Gazzetta, 1936, 66, 549—551).—When CaF_2 is dissolved in $AlCl_3$ a complex F ion is formed. F.p. and electrolytic data for AlF_3 solutions indicate that these probably contain the complex $[AlF_6]'''$ ion.

O. J. W.

Equilibrium between the trioxalatomanganate and dioxalatoaquomanganate ions. G. H. CARTLEDGE and W. P. ERICKS (J. Amer. Chem. Soc., 1936, 58, 2065—2069).—Extinction coeffs. of $K_4[Mn(C_2O_4)_3]$ (I) and $K[Mn(C_2O_4)_2(H_2O)_2]$ (II) in aq. solutions at various concns. have been determined in the visible region. (I) has max. absorption at about 520

$m\mu$ and (II) at about 450 $m\mu$. Equilibrium between (I) and (II) is established almost instantaneously according to $[Mn(C_2O_4)_3]''' + 2H_2O \rightleftharpoons [Mn(C_2O_4)_2(H_2O)_2]' + C_2O_4''$; the equilibrium const., determined spectrophotometrically, is 3.8×10^{-3} at 0°. Green and yellow forms of (II) give solutions with the same absorption curve; the solution probably contains an equilibrium mixture of *cis* and *trans* isomerides. The complex manganates may be derived from a covalent dsp^2 structure, the fifth and sixth valency linkings being ionic or ion-dipole in character.

E. S. H.

Effect of sugar alcohols and their anhydrides on the dissociation of boric acid. J. C. KRANTZ, jun., C. J. CABE, and F. F. BECK (J. Physical Chem., 1936, 40, 927—931; cf. this vol., 289).—In general the anhydrides of sugar alcohols increase the dissociation of H_3BO_3 < the sugar alcohols themselves, but the effect of erythritan is > that of erythritol or mannitol. Propylene glycol has no effect. The effect of $CO(CH_2 \cdot OH)_2$ and glyceraldehyde is > that of glycerol.

J. W. S.

Dynamics of the formaldehyde-hydrogen sulphite reaction. A. SKRABAL and R. SKRABAL (Monatsh., 1936, 69, 11—41; cf. A., 1936, 684).—Redetermination of the equilibrium const. for the reaction $OH \cdot CH_2 \cdot SO_3' \rightleftharpoons CH_2O + SO_3H'$ has confirmed the accepted val. The reaction velocities have been measured and the results are discussed theoretically. They do not afford support for the "principle of microscopic reversibility."

F. L. U.

Theory of binary solutions. E. HÜCKEL (Z. Elektrochem., 1936, 42, 753—778).—A re-statement of thermodynamical principles on which Hückel's theory rests, with particular reference to solutions of long-chain mols.

E. S. H.

Determination of activity coefficients from the potentials of concentration cells with transference. II. Hydrochloric acid at 25°. T. SHEDLOVSKY and D. A. MACINNIS (J. Amer. Chem. Soc., 1936, 58, 1970—1972).—E.m.f. of the cells $Ag, AgCl|HCl(c_1), HCl(c_2)|AgCl, Ag$, where $c_1 = 0.1N$ and $c_2 = 0.003—0.08N$, have been determined. The activity coeffs. follow the Debye-Hückel theory with a distance of closest approach of 5.62 Å. up to about 0.04N. At 0.003—0.1N accurate agreement with the Hückel equation is observed.

E. S. H.

Thermodynamics of hydrochloric acid in dioxan-water mixtures from electromotive force measurements. I. Standard potentials. H. S. HARNED and J. O. MORRISON (J. Amer. Chem. Soc., 1936, 58, 1908—1911).—E.m.f. of the cells H_2 (1 atm.)|HCl(m), dioxan- H_2O |AgCl-Ag have been determined at 5° intervals from 0° to 50° in solutions containing 20, 45, and 70% of dioxan and 0.003—0.2M-HCl. The standard electrode potentials have been evaluated.

E. S. H.

Activity and osmotic coefficients of aqueous solutions of lanthanum chloride at 25°. C. M. MASON and G. L. ERNST (J. Amer. Chem. Soc., 1936, 58, 2032—2033).—The activity and osmotic coeffs. have been calc. from v.-p. data, determined by the isopiestic method.

E. S. H.

Thermodynamic properties of fused salt solutions. IX. Lithium chloride in silver chloride. E. J. SALSTROM, T. J. KEW, and T. M. POWELL (J. Amer. Chem. Soc., 1936, 58, 1848—1850).—E.m.f. of the cells $\text{Ag}(s), \text{AgCl}$ in $\text{LiCl}(l), \text{Cl}_2(g)$ have been determined at mol. fractions of AgCl from 1.000 to 0.136 and 500—635°. The activity, activity coeff., free energy of formation and of dilution, entropy, and heat of formation of AgCl at 500° and 600° have been calc. The activity, activity coeff., and partial mol. free energy of LiCl have been calc. from the Duhem relations. Positive deviations of the activities from ideality are discussed. E. S. H.

Comminution and chemical affinity. R. SCHENCK (Z. Elektrochem., 1936, 42, 747—752).—Published work on the influence of particle size on chemical equilibria is discussed. E. S. H.

Significance of solubility product of very sparingly soluble salts. E. LANGE and K. NAGEL (Z. physikal. Chem., 1936, 177, 321—330).—Theoretical. The relation between the solubility product, s , and the standard free energy of formation, K , and the e.m.f., E , of a standard galvanic cell in which the salt is formed is given by $K = -EF = ET \log_e s$. If the concns. of the ions of the salt are large enough to be thermodynamically significant ($\ll 10^{-10}N$), the usual calculations made by means of the solubility product principle are thermodynamically free from objection. When small concns. are involved, however, such calculations, whilst yielding vals. for electrode potentials in accord with experiment, have no theoretical significance, and in such cases the only theoretical basis for the calculation of electrode potentials is the above equation. R. C.

Solubility relationships in mixtures of brassidic acid with erucic acid, methyl brassidate, and ethyl brassidate. L. J. P. KEFFLER and A. M. MAIDEN (J. Physical Chem., 1936, 40, 905—917).—Determination of m.p. is to be preferred to the study of cooling curves in the determination of the phase-rule diagrams for mixtures of long-chain compounds. The binary systems of brassidic acid (I) with erucic acid (II), Me and Et brassidate are all simple eutectic systems. The solubility curves of (I) in the two esters are identical. The ideal solution law holds for (I) and (II), but not for systems containing the esters, which yield an S-shaped curve when $\log N$ is plotted against $1/T$. The solubility of (I) in the esters is always less than the ideal solubility. All these compounds appear to exist in the simplest possible mols. in the liquid state, and no evidence could be obtained for the existence of a second cryst. form of any of them. J. W. S.

Crystal chemistry. I. Graphic classification of binary systems. C. W. STILLWELL (J. Chem. Educ., 1936, 13, 415—419).—In the classification adopted, crystal structure and other data are used to illustrate the influence of the properties of ions and atoms on the structure and properties of the crystals formed by their compounds. The binary systems are divisible into groups which include respectively the alloys, the ionic and at. compounds, and the mol. compounds. L. S. T.

Thermodynamic calculation of the composition of binary compounds. H. W. HERREILERS (Rec. trav. chim., 1936, 55, 921—924).—The p - T diagram near a quadruple point is considered and the equilibrium has been calc. R. S.

Water of crystallisation of certain complex salts and of nickel sulphate. I. N. PLAKSIN (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 271—278).—Tensimetric measurements confirm the existence of $\text{NiSO}_4 \cdot 1, 6$, and $7\text{H}_2\text{O}$, but not of 3 and $4\text{H}_2\text{O}$, and establish the existence of $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$. Tensimetric data for the system $\text{Cr en}_3\text{Cl}_3 \cdot \text{H}_2\text{O}$ at 25° suggest the formation of a dihydrate, and of a series of solid solutions of H_2O in the latter, whilst in the system $(\text{NH}_4)_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$ a series of solid solutions of H_2O in the anhyd. salt and its pentahydrate are indicated. R. T.

Dissociation pressure of crystal hydrates of variable composition. B. A. MUROMTSEV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 279—289).—Tensimetric data at 25° and 35° indicate that the systems $[\text{Co en}_3\text{Cl}_3]_2, \text{CoCl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ consist of unbroken series of solid solutions. R. T.

Static method for the determination of the equilibria of metals with carbon dioxide. A. F. KAPUSTINSKI and A. SILBERMAN (Acta Physicochim. U.R.S.S., 1936, 4, 495—504).—A method is described by which equilibria of the type $\text{M} + \text{CO}_2 = \text{MO} + \text{CO}$ can be investigated at const. pressure of CO_2 . It is applied to the equilibrium between Sn and CO_2 with results in agreement with those obtained by dynamic methods. The data correspond with $0.5 \log K_p = 606.4/T - 1.1576$ from 600° to 1100°, $\Delta F = 5546 - 10.587T$, and $\Delta H_0 = 5546$ g.-cal. O. D. S.

Basic acetates of lead. R. DUBRISAY and A. SAINT-MAXEN (Compt. rend., 1936, 203, 584—586).—The systems obtained on the addition of aq. NH_3 or NaOH to $\text{Pb}(\text{OAc})_2$ have been examined and evidence obtained for the existence of solid phases corresponding with $(\text{OAc})_2[\text{Pb}_3\text{O}(\text{OH})_2]$ and $\text{O}[\text{Pb}_3\text{O}(\text{OH})_2]$. J. G. A. G.

System magnesium sulphate-carbamide-water at 30°. C. W. WHITTAKER, F. O. LUNDSTROM, and J. H. SHIMP (J. Amer. Chem. Soc., 1936, 58, 1975—1977).—Data for 30° show the solid phases $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$, and $\text{CO}(\text{NH}_2)_2$. E. S. H.

Equilibria in the system water-lithium chloride-ammonium chloride. N. K. VOSKRESENSKAJA and O. K. JANATJEVA (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 291—293).—Equilibrium data are recorded. R. T.

System bismuth iodide-rubidium iodide-water. (MLLE.) M. L. DELWAULLE (Bull. Soc. chim., 1936, [v], 3, 1820—1822).—Data for 12° indicate the existence of the compounds, $\text{BiI}_3 \cdot 3\text{RbI}$ and $2\text{BiI}_3 \cdot 3\text{RbI}$. J. W. S.

System $\text{K}_2\text{O}-\text{PbO}-\text{SiO}_2$. R. F. GELLER and E. N. BUNTING (J. Res. Nat. Bur. Stand., 1936, 17, 277—289).—The system has been examined by methods involving quenching, petrographic study, and, in certain cases, heating curves. The existence

of four ternary compounds with mol. ratios 1:2:2, 1:4:8, 1:1:4, and 2:1:3 has been established, and optical properties indicate the existence of a fifth. The fields of stability of the various unary, binary, and ternary compounds have been determined, and 14 quintuple invariant points located. D. C. J.

System alkali oxide-CaO-Al₂O₃-SiO₂-CO₂. VI. Equilibria in the system CaO-SiO₂-CO₂. C. KRÖGER and K. W. ILLNER (Z. anorg. Chem., 1936, 229, 197-224; cf. A., 1936, 31).—Dissociation pressures of CaCO₃ are unaffected by the presence of Ca₂SiO₄, but considerably increased by Ca₃Si₂O₇. Equilibria in the reaction $2Ca_2SiO_4 + CO_2 \rightleftharpoons Ca_3Si_2O_7 + CaCO_3$ have been determined. Direct reaction occurs between SiO₂ and CaCO₃, independent of the dissociation of the latter. Heats of reaction are calc. F. L. U.

Hydrolytic equilibria of calcium aluminate hydrates. E. P. VON POLHEIM (Mitt. zementtech. Inst. Tech. Hochsch. Berlin, 1935, 51, 45 pp.; Zement., 1935, 24, 643-648; Chem. Zentr., 1936, i, 142).—The limiting concns. of dissolved CaO and Al₂O₃ permitting the stable existence of 2CaO, Al₂O₃, 7H₂O (I), and 3CaO, Al₂O₃, 6H₂O (II) in solution, are considered. According to the [CaO], any consecutive pair of the substances Al(OH)₃, (I), (II), and 4CaO, Al₂O₃, nH₂O may coexist as solid phase. The reactions of the anhyd. Ca aluminates with H₂O are discussed. J. S. A.

Complex formation involving weak acids. XVI. (a) Isotherms at 18° of the systems: sodium oxalate-copper (or zinc or magnesium) oxalate-water. (b) Solubility of copper, zinc, and magnesium oxalates in solutions of oxalic acid and sulphuric acid. (c) Potentiometric investigation of the complex anion, Cu(C₂O₄)₂". H. T. S. BRITTON and A. A. MOSS. XVII. System sodium oxalate-thorium oxalate-water at 25°. H. T. S. BRITTON and M. E. D. JARRATT (J.C.S., 1936, 1489-1493, 1494-1495).—XVI. M¹¹³C₂O₄-Na₂C₂O₄-H₂O mixtures have been studied at 18°. The solid components Na₂Zn(C₂O₄)₂·2H₂O, Na₂Mg(C₂O₄)₂·2H₂O could not be isolated. CuC₂O₄ and ZnC₂O₄ are insol. in H₂C₂O₄ but MgC₂O₄ dissolves to form Mg(HC₂O₄)₂. The solubility product of MgC₂O₄ has been calc. Evidence of the existence of Cu(C₂O₄)" has been obtained from potentiometric and analytical determinations.

XVII. Phase-rule studies show that Na₄Th(C₂O₄)₄·6H₂O is stable only in presence of excess of C₂O₄". R. S.

Addition compounds of phosphorous acid with certain organic compounds. H. L. REDFIELD and G. B. KING (J. Physical Chem., 1936, 40, 919-925).—The f.-p. diagrams for the binary systems of H₃PO₃ with AcOH, CCl₃·CO₂H, AcCO₂H, PhOH, COPhMe, piperonal, and coumarin have been determined, but no compound formation is indicated. The solubilities at 25° of PhOH, H₂C₂O₄, succinic and citric acid in aq. H₃PO₃ of various concns. have been determined and compared with similar data for H₃PO₄ (A., 1931, 922). Kendall's acidity rule holds for solutions, but not for f.-p. equilibria. The m.p. (corr.) of H₃PO₃ is 74.4°. J. W. S.

Double decomposition in the absence of a solvent. XXIX. Stable complex of mutual systems. XXX. Representation of quinary complex mutual systems. V. P. RADISCHTSHEV (Ann. Sect. d'Anal., Physico-Chim., 1936, 9, 203-218, 219-253).—Theoretical. R. T.

(A) Representation of multicomponent systems. Spiral co-ordinates. (B) Representation of properties in ternary systems. Method of central and peripheral vectors. V. J. ANOSOV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 5-25, 27-32).—Theoretical. R. T.

Equilibria in the saturated solutions of salts occurring in sea-water. II. Quaternary system MgCl₂-CaCl₂-KCl-H₂O at 0°. I. IGELSRUD [with T. G. THOMPSON] (J. Amer. Chem. Soc., 1936, 58, 2003-2009; cf. this vol., 429).—The solid phases occurring are KCl, MgCl₂·6H₂O, CaCl₂·6H₂O, and MgCl₂·KCl·6H₂O. The isotherm at 0° is characterised by the slight solubility of KCl or MgCl₂·KCl·6H₂O in solutions saturated with MgCl₂·6H₂O. E. S. H.

Heat of formation of the nitrogen molecule from atoms set free in the thermal decomposition of Pt-N. H. DAMIANOVICH and G. BERRAZ (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 61-71).—The product formed by cathodic sputtering in a N atm. glows when heated quickly in air or vac., due to the formation of N₂. The heat of formation is approx. 150,000 g.-cal. H. J. E.

Specific heat, entropy, and heat of formation of iron carbide, Fe₃C. C. SCHWARZ and H. ULICH (Arch. Eisenhüttenw., 1936-1937, 10, 11-12, 91).—Calculations from published data give the heat content of Fe₃C at 25.2° as 4072 g.-cal. per mol., entropy 23.9 g.-cal. deg.⁻¹ per mol., and the free energy of formation from α-Fe and β-graphite +2600 g.-cal. per mol. The heat contents for temp. between 104.3° and 763.3° are shown to agree closely with the experimental vals. A. R. P.

Hydrogen cyanide. IX. Conductivity of electrolytes in anhydrous hydrogen cyanide: some ammonium and tetra-alkylammonium salts at 18°. J. E. COATES and E. G. TAYLOR (J.C.S., 1936, 1495-1500; cf. this vol., 1341).—The conductivities of NH₄, NMe₄, and NEt₄ chloride, bromide, iodide, nitrate, and perchlorate, and of NH₄CNS and NMe₄ picrate in HCN have been determined. The NMe₄ and NEt₄ compounds show large negative deviations from the Debye-Hückel-Onsager equation, but for NH₄ compounds the agreement is good. R. S.

Electrolytic dissociation of αγγ-tetracyano-propene and αγγ-tetracyano-β-methylpropene. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1936, 11, 569-575).—According to conductivity and e.m.f. data the degrees of dissociation of αγγ-tetracyano-propene (I) and -β-methylpropene (II) are shown to be comparable with the val. for HCl. (I) and (II) are strongly acidic and dissolve Zn, Mg, and Sn at room temp. The metallic salts resemble the corresponding chlorides in their solubility in H₂O. The solubilities of the Ag salts of (I) and (II) are respectively 0.1 and 0.388 g. per litre. In aq. solution

the dissociation is supposed to be directly attributable to the enimine form as represented by
 $(\text{CN})_2\text{C}:\text{CH}\cdot\text{C}(\text{CN})\cdot\text{C}:\text{NH} \rightleftharpoons (\text{CN})_2\text{C}:\text{CH}\cdot\text{C}(\text{CN})\cdot\text{C}:\text{N}^+ + \text{H}^-$
 C. R. H.

Electrical conductivity of glass-forming barium borate. B. MARKIN and R. MÜLLER (*Acta Physicochim. U.R.S.S.*, 1936, 4, 471—480).— κ data for fused mixtures (glasses) of $\text{BaO} + \text{B}_2\text{O}_3$, $\text{Na}_2\text{O} + \text{BaO} + \text{B}_2\text{O}_3$, and $\text{ZnO} + \text{B}_2\text{O}_3$ indicate bivalent cation movement where the amount of corresponding metallic oxide is large. In the expression $\log_e \kappa = -A/T + B$, where A and B are consts., the val. of A is increased by introducing Ba glasses into Na glasses. The energy of dissociation of the ions, $E = 2AR$, for Ba and Zn glasses is considered to be double that for the Na glasses.
 C. R. H.

High-frequency conductivity of colloidal electrolytes. II. Alkali and alkaline-earth caseinates. G. SCHMID and A. V. ERKKILÄ (*Z. Elektrochem.*, 1936, 42, 781—785; cf. this vol., 1461).—The high-frequency effect is about twice as great for the alkaline-earth as for the alkali caseinates, but there is little difference between the individual members of each series. The charge of the cation appears to be the dominating factor. Published work on transport nos. in these solutions is discussed.
 E. S. H.

Use of the "skin" effect in the investigation of thin metallic layers. J. GOLDFELD and N. I. KOBOSEV (*Acta Physicochim. U.R.S.S.*, 1936, 5, 243—270).—The variation of the high-frequency resistance R_H of thin layers of metals on a metal of different magnetic permeability μ has been calc. In the case of Fe deposited on Pt or Ag, R_H reaches a max. after about 6 min. The influence of layer thickness and c.d. has been investigated. For a given thickness R_H depends on μ , whilst μ varies with the structure of the layer. The increase of μ with time is attributed to the crystallisation of the layer. If the wire is heated in H_2 , diffusion of Fe into the interior occurs and the rate of diffusion has been calc., but in air, all the Fe is oxidised. The diffusion of Zn in Fe has also been studied.
 R. S.

Absorption and dispersion of short electric waves in solutions of electrolytes in glycerol. W. SCHMACKS (*Ann. Physik*, 1936, [v], 27, 285—298).—The dielectric const. and high-frequency conductivity of glycerol and glycerol solutions of MgSO_4 of concn. from 10^{-1} to 10^{-3} g. per litre have been measured at $\lambda\lambda$ from 10 to 20 m. A max. conductivity of MgSO_4 has been observed at about 14 m.
 O. D. S.

Transfer resistance. G. CHEN (*Sci. Rep. Nat. Univ. Peking*, 1936, 1, No. 3, 13—18).—A review.

Gold and copper in salt crystals and synthetic sylvine. M. J. BOGOMOLOVA (*Acta Physicochim. U.R.S.S.*, 1936, 5, 161—172).—The diffusion velocities of Au and Cu in NaCl and KCl have been studied and the ionic mobilities μ determined, making use of the colouring action of electrons from a Na cathode. μ is greater in KCl, and Cu^{++} is more mobile than Au^{+++} in each case, contrary to the order expected from the ionic diameters, whilst the plot of $\log \mu$ against $1/T$

is a straight line. When the crystal has been subjected to previous electron-colouring μ is diminished owing to colloid formation.
 R. S.

Contact potential between fluid amalgam and mercury in a vacuum. I. Contact potential between sodium amalgam and mercury. O. CHALTIKIAN and M. PROSKURNIN (*Acta Physicochim. U.R.S.S.*, 1936, 4, 263—274).—The contact potential between Hg and Na amalgam has been found to rise to an approx. const. val. of 1.1 ± 0.1 volt at 0.025—0.09% of Na.
 R. S. B.

Platinum electrode. II. Adsorption properties of the platinum electrode. A. SCHLIGIN, A. FRUMKIN, and V. MEDVEDOVSKI (*Acta Physicochim. U.R.S.S.*, 1936, 4, 911—928; cf. this vol., 1207).—The adsorption of H_2SO_4 , HCl, HBr, $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$, NaCl+HCl, NaBr+HBr, NaCl+NaOH, NaBr+NaOH, and KOH at various potentials of the Pt electrode has been determined by p_H measurements. The results are compared with capacity measurements with the same electrode. Changes in the amount adsorbed on treating a H_2 -saturated electrode with O_2 and also on reducing an oxidised electrode by H_2 are recorded.
 H. J. E.

Germanium. XVII. Electrochemical behaviour of germanium. R. SCHWARZ, F. HEINRICH, and E. HOLLSTEIN (*Z. anorg. Chem.*, 1936, 229, 146—160; cf. this vol., 618).—The e.m.f. of Ge-calomel electrode combinations, using various aq. electrolytes, is neither const. nor reproducible unless O_2 is excluded, and even in the latter event it is not exactly reproducible owing to variations in the surface condition. The normal potential $\text{Ge}/\text{Ge}^{+++}$ cannot be determined by e.m.f. measurements in aq. solution. Ge can be determined electrolytically by deposition with Sn from alkaline oxalate solution.
 F. L. U.

Potential of platinum in solutions of silver salts. A. OBRUTSCHEVA and A. FRUMKIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, 4, 11—13).—Bright Pt and Au in AgNO_3 solution exhibit the potential of Ag in a few min. (cf. A., 1934, 257). Small platinised electrodes behave similarly although a much longer time is required. In this case the potential is at first (in the acidified solution) more positive than the Ag potential and changes in a direction opposed to that expected by an adsorption of Ag^+ . Ag crystals are formed when the electrodes reach the val. of the reversible Ag potential, especially in the case of the platinised electrodes. Large platinised electrodes give a change of potential in the same direction, but do not reach the val. for the reversible Ag^+ potential. When the large electrodes are agitated in the solution until a const. val. is reached the latter is no longer able to alter the potential of a new small electrode. A bright Pt electrode in this solution attained the Ag potential only after some hr. This solution recovered its original properties after warming with Ag powder at 50° or after strong illumination for many hr. These effects are not due to Ag^+ adsorption, but to a small amount of a reducing substance in the Ag solution. This substance reduces the acids chemically bound to the Pt surface and then the separation of Ag results. A Ag ion of lower

valency (Ag_2^+) is suggested as the electrochemically active material.

D. C. J.

Periodic potential oscillations of iron in chromic-sulphuric acid solutions. III. M. KARSCHULIN (Z. Elektrochem., 1936, 42, 722—729; cf. A., 1934, 601, 1072).—Fe dissolves primarily as Fe^{2+} , which is subsequently oxidised to Fe^{3+} by CrO_2 . The oscillations in the negative direction (with respect to a saturated Hg_2Cl_2 electrode) occur when formation of Fe^{2+} and oxidation to Fe^{3+} are separated by a time interval in consequence of the diffusion layer at the Fe surface. The potential limits are then conditioned by the $[\text{Fe}^{2+}]$ and the ratio $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ at the Fe surface. Oscillations in the positive direction occur when $[\text{H}^+]$ in the neighbourhood of the Fe surface decreases so that $\text{Fe}(\text{FeO}_2)_2$ is formed. The positive potential then reached is several hundred mv. < that of passive Fe in aq. CrO_3 .

E. S. H.

Meaning of diffusion potential. E. A. GUGGENHEIM (Phil. Mag., 1936, [vii], 22, 983—987).—The significance of diffusion potential in cells with liquid-liquid junctions is discussed.

A. J. E. W.

Electromotive force of the cell Zn-Hg (2-phase) ZnSO_4 (m) PbSO_4 (s) Pb-Hg (2-phase) and its temperature coefficient at 25° and concentrations from 0.05 to 1.5M. J. KIELLAND (J. Amer. Chem. Soc., 1936, 58, 1855—1857).—E.m.f. data and activity coeffs. of ZnSO_4 are recorded.

E. S. H.

Voltaic pile readily made from electrolytes. A. THIEL (Z. Elektrochem., 1936, 42, 742—744). Electrical effects produced by the contact of series of electrolytic solutions are described.

E. S. H.

Passive metals in bimetallic electrode pairs. L. WOLF (J. pr. Chem., 1936, [ii], 147, 133—144; cf. this vol., 305, 582).—The use of one passive metal as reference electrode in the bimetallic electrode pairs employed in potentiometric titrations is described. This electrode is rendered passive by addition of a passivator, generally NaNO_3 or HNO_3 , to the solution to be titrated. The following electrode pairs have been tested; Cr/Ag, Cr/Hg, Cr/Pt, V2A alloy/Ag, V2A/Hg, V2A/Pt.

J. W. S.

Energy of electrolytic reduction of some substances with the atomic groups C:O and C:C. G. SEMERANO and A. CHISINI (Gazzetta, 1936, 66, 510—518).—The molar reduction potentials at a dropping Hg cathode of $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHO}$, $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$, and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ dissolved in 0.1N- NH_4Cl in 50% EtOH are -1.383, -0.784, and -1.456 volts, respectively. The two aldehydes are converted into the corresponding hydrobenzoin, and the acid is reduced to $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The relation between chemical constitution and molar reduction potential is discussed.

O. J. W.

Colouring matters of Drosera Whittakeri. IV. Reduction potentials of some naphthaquinones. J. W. H. LUGG, A. K. MACBETH, and F. L. WINZOR (J.C.S., 1936, 1457—1462; cf. A., 1935, 623).—The normal reduction potentials, E_0 , of 1:4-naphthaquinone, methylnaphthaquinone, lawsone, juglone, phthiocol, isonaphthazarin, methylnaphthazarin (I), naphthazarin, hydroxyjuglone, naphtha-

purpurin (II), hydroxydroserone (III) (natural and synthetic), and lomatiol have been determined by Fieser's method (A., 1935, 585). Fieser's conclusions relative to the additivity of E_0 are confirmed. The results indicate that in (I), (II), and (III), the substituent is in the quinonoid ring.

R. S.

Determination of decomposition potentials of fused salts. R. C. KIRK and W. E. BRADT (Trans. Electrochem. Soc., 1936, 70, Preprint 26, 317—326; cf. this vol., 430).—Decomp. potentials for fused alkali and alkaline-earth halides and certain other salts have been measured by the direct method. The depolarisation found by this method is cathodic rather than anodic and may be eliminated by the substitution of Pt for graphite cathodes. Vals. obtained by extrapolation to zero current with Pt cathodes are in good agreement with those given by the commutator method (cf. A., 1928, 135) and also with the calc. equilibrium reaction potentials.

O. J. W.

Determination of decomposition potentials of fused salt mixtures containing tantalum oxide. R. C. KIRK and W. E. BRADT (Trans. Electrochem. Soc., 1936, 70, Preprint 27, 327—333).—The decomp. potential of K_2TaF_7 in fused KCl (with and without the addition of Ta_2O_5) is < that of fused KCl, and Ta is deposited. Measurements with 14 fused salts containing Ta_2O_5 gave no decomp. potential corresponding with the Ta compound, and no Ta was deposited from these mixtures. It is suggested that current-potential diagrams obtained by the direct method may provide information relative to the behaviour of fused salt mixtures in electrodeposition.

O. J. W.

Polarisation capacity of the mercury electrode. T. BORISOVA and M. PROSKURNIN (Acta Physicochim. U.R.S.S., 1936, 4, 819—828).—The capacity of the double layer on Hg in N-HCl, -KCl, and -CsCl first decreases with increasing negative polarisation, then increases to a max. at 0.4—0.5 volt, and finally passes through a min. at approx. 1.1 volt. The max. persists after careful purification and is attributed to a deformation or dehydration of the anion. The rise in the curve at high cathode polarisations is due to deformation of the cation.

H. J. E.

Hydrogen overvoltage at high current densities. B. KABANOV (Acta Physicochim. U.R.S.S., 1936, 5, 193—200).—An apparatus for the determination of H overvoltages with c.d. up to 100 amp. per sq. cm. is described. The relation between overvoltage and log c.d. for Ag amalgam, Ag, and Pt is linear, in agreement with Volmer's theory.

R. S.

Hydrogen overvoltage in non-aqueous solutions. I. S. LEVINA and M. SILBERFARB (Acta Physicochim. U.R.S.S., 1936, 4, 275—282).—H overvoltage (V) on a Hg cathode has been determined for c.d. 10^{-6} — 10^{-2} amp. per sq. cm. at 25° in 0.01—0.54N-HCl in EtOH. For c.d. (i)= 10^{-6} — 10^{-3} amp. per sq. cm., $V=a+b \log i$, where a and b are const., and $b=0.11$ — 0.12 , in agreement with the theory of Erdey-Gruz and Volmer (A., 1930, 1376). V is independent of the duration of the experiment and of $[\text{HCl}]$, and is < for aq. solutions.

R. S. B.

Overvoltage. G. CHEN (Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 3, 1—11).—A review and discussion.

Effect of pressure on the passivity of iron powder in alkali medium. T. C. HUANG (J. Chinese Chem. Soc., 1936, 4, 406—412).—When the Fe powder in an Edison cell is packed under increasing pressure, the discharge potential shows a corresponding decrease in the passivity of the Fe. D. C. J.

Passivity phenomena. XXX. Passivity phenomena at magnesium anodes in acid solutions. W. J. MÜLLER and E. NACHTIGALL (Monatsh., 1936, 69, 1—10; cf. A., 1928, 713).—When Mg in the form of a protected electrode is anodically polarised at 3—12 volts in $N\text{-H}_2\text{SO}_4$, the current gradually falls to about $\frac{1}{3}$ of its initial val. In the early stages the bright metal becomes covered with a black film, which breaks down and gives place to a matt grey surface. The latter is formed before the min. current is established, and persists during the period of passivity. By decreasing $[\text{H}^+]$ at const. $[\text{SO}_4^{2-}]$ the time required to attain passivity is slightly shortened. Mg also exhibits passivity in aq. HNO_3 , but not in HCl. F. L. U.

Polarographic studies with the dropping mercury electrode. IV. Influence of circuit resistance on maxima of current-voltage curves. R. BRDIČKA (Coll. Czech. Chem. Comm., 1936, 9, 419—433; cf. this vol., 430).—The current max. obtained with 0.01N- $\text{Hg}_2(\text{NO}_3)_2$ in 0.005N- HNO_3 decreases as the resistance, R_e , external to the electrolyte is increased. Oscillographically recorded current-time curves for the formation of single drops show that the cathode is unpolarisable at $<$ a sp. e.m.f. and yields large currents \propto the e.m.f. With e.m.f. $>$ the sp. val., the Hg drop is polarised at all stages of growth. The polarisation increases linearly with e.m.f., so that the current always reaches the same val., corresponding with the "diffusion current." The discontinuous fall of current at a polarographic max. occurs at the same e.m.f. whatever the val. of R_e and is attributed to the polarisation of drops at the moment of formation. If R_e is increased, however, the drop becomes depolarised during growth unless the e.m.f. is sufficiently raised, in which case the diffusion current is always attained. J. G. A. G.

Polarographic analysis in the study of keto-enol tautomerism.—See this vol., 1488.

Electrolysis of aqueous solutions of sodium and zirconyl sulphates. I. W. E. BRADT and H. B. LINFORD (Trans. Electrochem. Soc., 1936, 70, Preprint 30, 363—371).—From these solutions Zr is deposited under certain conditions as a silver-white, compact, and adherent metal similar to Ni electroplate. This changes slowly to a non-adherent black powder, which may be Zr or some oxidation product. O. J. W.

Conception of electrokinetics as an integral part of electrochemistry of solutions. J. W. McBAIN (Acta Physicochim. U.R.S.S., 1936, 4, 169—172).—The analogies between electrokinetic and electrolytic phenomena are discussed. The electrokinetic potential is regarded as having no real existence. R. S. B.

Maximum yield of the intermediate product C in two successive bimolecular reactions, (I) $A+B \rightarrow C$ and (II) $A+C \rightarrow D$ when the constants k_1 and k_2 are known. J. STUURMAN (Rec. trav. chim., 1936, 55, 934—936).—The calculation has been applied to the oxidation of thianthren by AcO_2H (cf. this vol., 1518). R. S.

Chemical kinetics of dielectric relaxation. F. C. FRANK (Trans. Faraday Soc., 1936, 32, 1634—1647).—Theoretical. The theory of unimol. chemical reaction velocities is applied to the process of change of orientation of a polar mol. in a substance showing dielectric loss and dispersion. Published data for different types of physical systems are discussed. E. S. H.

Explosive limits of gaseous mixtures. I. Explosion limits of mixtures of hydrogen and air. M. RIVIN and A. SOKOLIK (Acta Physicochim. U.R.S.S., 1936, 4, 301—316).—The conditions for initiating detonation waves have been investigated for H_2 -air mixtures. The curve for explosion limit as a function of pressure and % H_2 shows two min. which depend on energy of the igniting spark. With H_2 - O_2 mixtures the curve for explosion limits has a min. at 100 mm. and 55% H_2 . At 1 atm. explosion is possible between 23 and 85% H_2 . The velocity of the explosion wave does not agree with theory, owing probably to dissociation in the front of the wave. The propagation and extinction of the flame and change in pressure have been studied in a long tube below the explosion limit for H_2 and O_2 . R. S. B.

Effect of a chemically inert gas on the velocity of the chain reaction in mixtures of n -pentane and oxygen. M. PRETTE (Compt. rend., 1936, 203, 561—563).—At 250—270°, near the lower inflammation limit of mixtures of 119—210 mm. of O_2 and 119—209 mm. of C_5H_{12} , N_2 accelerates the reaction, but at 300—350°, near the upper limit of inflammation, N_2 retards the reaction between 20—57 mm. of C_5H_{12} and 82—100 mm. of O_2 . J. G. A. G.

Inhibition by hydrogen of the chain reaction of mixtures of n -pentane and oxygen. M. PRETTE (Compt. rend., 1936, 203, 619—620).—Addition of H_2 (approx. 150—300 mm.) to a mixture of C_5H_{12} (50—308 mm.) and O_2 (84—306 mm.) at 240—280° retards the slow oxidation and may prevent ignition. The H_2 is most effective at 260—280°. H. J. E.

Cold flames in mixtures of pentane and oxygen. B. AIVAZOV and M. NEUMANN (Acta Physicochim. U.R.S.S., 1936, 4, 575—606; cf. this vol., 1344).—The conditions under which cold flames are propagated in mixtures of C_5H_{12} and O_2 have been investigated. The pressure changes and change in composition of the gas during the induction period, the flame reaction, and the slow reaction which follows have been observed. Aldehydes and peroxides are formed in large amount during the flame reaction. The amounts of CO and CO_2 formed are small. A slow autocatalytic reaction is observed outside the limits of the cold flame. O. D. S.

Flame of carbon monoxide and oxygen. I. Influence of pressure on the intensity of visible

radiation from the flame. H. KONDRATEEVA and V. KONDRATEEV (Acta Physicochim. U.R.S.S., 1936, 4, 547—555).—The ratio of the intensity of blue light emitted to the no. of CO_2 mols. formed per sec. in the combustion of CO in O_2 has been measured between 11 mm. and 140 mm. It rises to a max. about 40 mm. and then decreases at higher pressures in a manner corresponding with the quenching of excited mols. with an efficiency of the order of 1. It is deduced that the preliminary increase corresponds with a change from a heterogeneous reaction at low pressures to a homogeneous reaction in which CO_2^* mols. are produced.

O. D. S.

Influence of a longitudinal electric field on the combustion processes in flames. A. E. MALINOVSKI and K. E. JEGOROV (Acta Physicochim. U.R.S.S., 1936, 4, 929—936; cf. A., 1930, 424).—The retardation of the movement of flame in a C_2H_2 -air mixture by means of an electric field is not a mechanical effect due to transport of neutral gas mols. by the charged particles. Negative ions play an important part in propagating flame. The effect of the field on the inner cone of a 25% C_2H_2 -air flame is almost independent of the rate of supply of gas. The inner cone in flames of CH_4 or heavy hydrocarbons in air is affected only by voltages approaching the breakdown voltage.

H. J. E.

Propagation of combustion along the surface of inflammable liquid. V. Effect of wind on velocity of propagation. I. T. KINBARA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 871—885).—Experimental results for EtOH-air flames are discussed.

J. S. A.

Propagation of combustion along [the] surface of inflammable liquids. VI. Effect of wind on the velocity of propagation. T. KINBARA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 1090—1104; see preceding abstract).—The effect of favourable as well as unfavourable winds in decreasing the velocity of flame propagation could not be explained by the change in appearance of a moving flame, nor by the lowering of surface temp. on EtOH caused by such winds.

R. C. M.

Kinetics of simultaneous polymerisation and ring formation. G. SALOMON (Trans. Faraday Soc., 1936, 32, 1627—1628).—A reply to Stoll (this vol., 1073).

E. S. H.

Kinetics of thermal decomposition of methylamine. H. J. EMELÉUS and L. J. JOLLEY (J.C.S., 1936, 1524—1529; cf. A., 1935, 172, 1081).—The kinetics of the slow thermal decomp. of NH_2Me at 330—390°, and of the explosive oxidation at 400—600°, have been studied by a pressure change method. The rate of the slow reaction is given by an expression of the form $v = Ae^{\phi t}$, where $\phi = B'p^{0.83}e^{-15,000/T}$. The crit. explosion pressure p_c is given by $\log_e p_c/T = A'/T + B$ (A, A', B, B' are const.). Results for the slow and explosive oxidations are correlated on the basis of the Semenov theory of degenerate chain reactions.

A. J. E. W.

Rate of oxidation of *o*-iodobenzoic acid by peracetic acid. J. BÖESEKEN and E. WICHERLINK (Rec. trav. chim., 1936, 55, 936—940).—

o- $\text{C}_6\text{H}_4\text{I}\cdot\text{CO}_2\text{H}$ is oxidised by AcO_2H , the unchanged AcO_2H destroyed by NaOH and a trace of CuO , and the $\text{IO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ formed determined by $\text{KI}\text{--}\text{Na}_2\text{S}_2\text{O}_3$. E and B in the equation, $\log K = B - E/2.303RT$, for this reaction are 15,920 and 7.9, respectively, k being about 10^{-4} at 20°.

R. S. C.

Prototropy in relation to exchange of hydrogen isotopes. II. Comparison of the velocities of dissociation of a proton and a deuteron from a ν -acid. C. L. WILSON (J.C.S., 1936, 1550—1553; cf. this vol., 1344).—The rate of ionisation of 2-*o*-carboxybenzylindan-1-one (I) and its 2-deutero analogue (II) have been studied indirectly by observing the rate of bromination in aq. AcOH containing NaOAc . The first-order velocity coeff. for (I) is several times that for (II), the observed difference corresponding with a difference in the activation energies of 0.9 kg.-cal., in accord with the estimated difference of crit. energy of approx. 1 kg.-cal.

A. J. E. W.

Kinetics of certain bimolecular reactions in solution. E. A. MOELWYN-HUGHES (Acta Physicochim. U.R.S.S., 1936, 4, 173—224).—A crit. review.

R. S. B.

Kinetics of oxidation of ferrous ion by nitrous acid. E. ABEL, H. SCHMID, and F. POLLAK (Monatsh., 1936, 69, 125—143; cf. A., 1930, 1128).—Oxidation of Fe^{2+} by HNO_2 takes place by means of concurrent reactions between Fe^{2+} and HNO_2 , Fe^{2+} , HNO_2 , and H^+ , and Fe^{2+} and NO_2 , the last-named being related to the HNO_2 and NO present. Velocity coeffs. of the above reactions have been determined at 25° using a wide range of concns. The mechanism of the opposing reaction between Fe^{3+} and NO is discussed.

F. L. U.

Kinetics of sulphonium compounds. I. N. HELSTRÖM (Z. physikal. Chem., 1936, 177, 337—354; cf. A., 1932, 26).—The rate of formation in aq. solution at 25° of sulphonium salts by reaction of alkyl- and aryl-substituted thioglycolic acids and sulphide di-acids with $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$, $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{NH}_2$, and α - and β -iodopropionic acid has been measured. The velocity, v , is small in acid solution, but increases with the degree of neutralisation; in neutral solution the reaction is bimol. and exhibits a salt effect, v falling with $[\text{Na}^+]$. OH^- ions have little or no effect on v . CO_2H and Ph in the reacting mols. retard the reaction. In some cases the sulphonium salt decomposes into alcohol and sulphide compound.

R. C.

Mechanism of elaidinisation reaction.—See this vol., 1488.

Mechanism of aromatic side-chain reactions.—See this vol., 1497.

Reaction kinetics and the Walden inversion.—See this vol., 1487.

Kinetics of adsorption of hydrogen and of deuterium by platinum. E. B. MAXTED and C. H. MOON (J.C.S., 1936, 1542—1546).—The initial adsorption of H_2 and D_2 on Pt follows the equation $\log a/(a-x) = kt^n$ (a = saturation capacity, x = vol. adsorbed after time t). nk , expressing the rate of adsorption, is approx. 1.5 times as great for H_2 as for D_2 in the temp. range -79° to 50° . The approxim-

ation of this ratio to the square root of the ratio of the masses of D_2 and H_2 , and the low activation energy (approx. 2500 g.-cal.), suggest control of the process by diffusion to the internal surface. A. J. E. W.

Evaporation of nickel in a vacuum. G. BRYCE (J.C.S., 1936, 1517—1518).—The rate of evaporation of Ni in a vac. has been determined for the temp. range 1250—1450° abs. by colorimetric determination of the Ni evaporated from a hot filament. The v.p. of Ni is given by $\log_{10}(cp) = 9.148 - 2.00 \times 10^4/T$ (c = condensation coeff.). A. J. E. W.

Wicke's reaction. W. BÖTTGER and E. THOMÄ (J. pr. Chem., 1936, [ii], 147, 11—21).—The time required for the production of blackening on $Ni(OH)_2$ over which a mixture of moist SO_2 and O_2 (or air) is passed has been studied for $Ni(OH)_2$ prepared and treated in different ways, for different $[SO_2]$, and for different temp. The effect is attributed to the formation of $Ni(OH)_3$ through the action of a relatively stable intermediate product with a peroxide-like O-linking in the $SO_2-O_2-H_2O$ mixture. J. W. S.

Rate of absorption of oxygen by sodium sulphite solution. W. S. E. HICKSON (Nature, 1936, 138, 645).—Stirring the interior of a solution of $N-Na_2SO_3$ without disturbing the surface decreases the rate at which O_2 is absorbed by 48% compared with the unstirred solution. L. S. T.

Absorption velocity of sulphur dioxide by sodium iodide. I. HIGUTI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 1105—1116).—Measurements of v.p. and composition of solid phase confirmed the existence of $3NaI \cdot 8SO_2$ and $NaI \cdot 4SO_2$ described by Foote and Fleischer (A., 1931, 799). The rate of absorption at 0° and -21° agreed with the expression $\log s/(s-x) = Kt^n$ previously found applicable in other cases (cf. this vol., 561). R. C. M.

Kinetics of the sulphite process. A. J. COREY and O. MAASS (Canad. J. Res., 1936, 14, B, 336—345).—The delignification of wood chips and meal in H sulphite solutions at 100—140° follows an approx. unimol. law, deviations being probably due to the colloidal nature of lignin and the submicroscopic structure of the wood. The energy of activation is 21,000 g.-cal. per g.-mol. The influence of pressure has been studied at 5—10 atm., using an atm. of N_2 . Increase of pressure above 7 atm., the v.p. of the H sulphite solution, has no influence on the rate of delignification or quality of the product. R. S. B.

Thermal decomposition of calcium carbonate. A. OLIVERIO (Rend. Sem. Fac. Sci. R. Univ. Cagliari, 1934, 4, 119—121; Chem. Zentr., 1936, i, 521).—The decomp. in an air stream of 2 litres per hr. in a tube 15 mm. wide was 1.67% in 56 hr. at 420° and was almost complete in 200 hr. at 620°. H. J. E.

Influence of form of intermediate phases on the velocity of the reduction of iron oxide by hydrogen. G. TSCHUFAROV and B. AVERBUCH (Acta Physicochim. U.R.S.S., 1936, 4, 617—635).—The velocity of reaction of natural cryst. magnetite and hæmatite with H_2 has been measured at intervals of 20° from 300° to 700°. The change in porosity during reduction was followed and the structure at

different stages of the reaction investigated by X-ray analysis. The reaction appears to be autocatalytic. Fe_3O_4 is present at all stages of incomplete reduction. FeO is not observed. From 300° to 500° the porosity is independent of T and determined by the degree of reduction. Above 500° the porosity decreases rapidly with T , whilst the size of the crystals of $\alpha-Fe$ increases. The temp. coeff. of the reaction is normal up to 550° and low above this temp. The activation energy is calc. to be 16,500 g.-cal. for magnetite and 19,500 g.-cal. for hæmatite below 550°.

O. D. S.

Kinetics of dissolution of alkali borate glasses. R. L. MÜLLER (Acta Physicochim. U.R.S.S., 1936, 4, 99—118; cf. this vol., 1074).—Previous work is reviewed. The rate-determining process in the case of alkali borate glasses in which the mol. fraction of $M_2B_2O_7$ is < 0.5 occurs at the surface. H_2O is first adsorbed by the surface ions, which then become fully hydrated and go into solution. The energy of activation is 10—15 kg.-cal. The results are discussed in relation to current theories of dissolution and evaporation. R. S.

Elementary processes in the formation of metal oxide from metal and oxygen, and in related reactions. C. WAGNER (Angew. Chem., 1936, 49, 735—740).—The diffusion processes responsible for the propagation of heterogeneous reactions of the type indicated through the compact boundary layer of compound are reviewed with reference to the author's published work. Diffusing species may be: (a) Ions, wandering by migration to empty lattice positions or between-lattice positions. In compounds with non-stoichiometric composition (e.g., FeO , Cu_2O), the former mechanism operates, as shown by the rise in ionic conductivity at high temp. with the excess of O. (b) Electrons, in compounds of semi-metallic character. Where ions of variable valency occur (e.g., Cu_2O), these may propagate points of electron-deficit. Velocity of reaction is conditioned by the slower of the two diffusion processes, (a) or (b). The theory is applicable also to the solid reactions of silicate and spinel formation, in which the small cations are the diffusive species. J. S. A.

Catalytic action of hydrogen on carbon monoxide flame. H. J. WALLS (Trans. Faraday Soc., 1936, 32, 1495—1501).—When the infra-red radiation on explosion of $CO-O_2$ mixtures containing H_2 is plotted against the initial pressure of the reactants, a step occurs in the curve at pressure p_s (cf. A., 1929, 973). p_s rises with temp., and is thus not a lower ignition limit. p_s is probably the pressure at which two combustion mechanisms are equally rapid, these involving probably an O atom or thermal chain, and a H atom chain, respectively. Effects on the step produced by heating the reaction vessel are ascribed to removal of H atoms by the walls. A. J. E. W.

Catalytic influence of chromic sulphate on the speed of decomposition of chromic acid by heat, when dissolved in sulphuric acid of varying concentration. H. C. S. SNETHLAGE (Rec. trav. chim., 1936, 55, 874—880; cf. this vol., 1073).—The decomp. of CrO_3 in aq. H_2SO_4 is catalysed by $Cr_2(SO_4)_3$, the effect decreasing as $[H_2SO_4]$ is increased and

becoming negative when $[H_2SO_4]$ is $>95\%$. The results are in agreement with the theory that decomp. involves a bimol. and a unimol. reaction, the velocity coeffs. of which have been calc. R. S.

Decomposition of alkaline-earth carbonates in aqueous solution on boiling. B. L. VANZETTI and A. OLIVERIO (Rend. Sem. Fac. Sci. R. Univ. Cagliari, 1934, 4, 112—118; Chem. Zentr., 1936, i, 521).—The decomp. is influenced by the presence of Cu and Ni salts. H. J. E.

New catalytic behaviour of mercuric salts. I. G. TRAVAGLI (Gazzetta, 1936, 66, 525—528).— Hg^{II} salts dissolved in H_2SO_4 or H_3PO_4 are able to catalyse the conversion of nitriles into amides. The catalytic behaviour has been investigated in detail for the conversion of $(CN)_2$ into $(CO-NH_2)_2$. O. J. W.

Reducing action of mercury. III. Hydrogen peroxide formation and the copper-catalysed autoxidation of quinquevalent molybdenum and other strong reductants in acid solution. W. M. MURRAY, jun., and N. H. FURMAN (J. Amer. Chem. Soc., 1936, 58, 1843—1847; cf. this vol., 1353).—Reduction by Hg may be used for the determination of Fe, V, or Mo, as these ions decompose catalytically any H_2O_2 formed. For micro-determinations O_2 must be excluded. Mo^V is autoxidised rapidly in presence of small amounts of Cu. A mechanism for this and similar reactions is discussed. E. S. H.

Acid catalysis in non-aqueous solvents. III. Rearrangement of N-iodoformanilide in anisole solution. R. P. BELL and J. F. BROWN (J.C.S., 1936, 1520—1524).—The rearrangement of $HCO-NIPh$ into $HCO-NH-C_6H_4I-p$ in PhOMe solution is a unimol. reaction catalysed by H^+ . The reaction has been studied in presence of 8 org. acids, for which the catalytic consts. (α) are given approx. by $\alpha=3.63K_d^{2/21}$ (K_d = dissociation const. in H_2O). A side reaction occurs with production of I. A. J. E. W.

Influence of some colloids on the velocity of inversion of sucrose. S. BERLINGOZZI and M. TESTONI (Annali Chim. Appl., 1936, 26, 366—369; cf. B., 1931, 134; this vol., 35).—The velocity of inversion of sucrose in aq. citric acid is lowered by lyophilic and by metallic colloids. L. A. O'N.

[Organic catalysts.] W. LANGENBECK and F. BAEHREN (Ber., 1936, 69, [B], 2406; cf. this vol., 589).—A reply to Eistert (this vol., 844). H. W.

Hydrocatalase. R. RETOVSKY (Bull. Soc. Chim. biol., 1936, 18, 1106—1114).—The kinetics of the decomp. of H_2O_2 by certain mineral waters shows that two processes, a catalase action and auto-decomp., are involved. The decomp. is dependent on p_H , and the activity decreases with time. A. L.

Oxidation of glucose.—See this vol., 1491.

Relative catalytic activity of several metals for the isotopic interchange reaction, $H_2O+HD\rightarrow HDO+H_2$. K. HIROTA and J. HORIUTI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 151—168; cf. this vol., 162, 163, 430, 684).—The interchange series (order of catalytic activity) is Pt (sp. catalytic activity $k=5\times 10^{-1}$ at 0°) $>$ Ni (7×10^{-2} at

100°) $>$ Fe (3×10^{-4} at 100°) $>$ Cu (2×10^{-3} at 180°) $>$ Au (3×10^{-4} at 180°) $>$ Ag (1×10^{-4} at 180°). No activity for Hg could be established. The parallelism between this series and that for H atom recombination, overvoltage, and hydrogenation catalysis is pointed out. The results for Pt suggest that in all cases the rate of reaction is determined by the genuine interchange. R. C. M.

Autoxidation of chromite solutions. F. HEIN and O. STUMM (J. pr. Chem., 1936, [ii], 147, 53—59).—The oxidation of suspensions of $Cr(OH)_3$ in aq. KOH, when shaken with O_2 or air, has been studied for various $[KOH]$ and in presence of various catalysts. The best activators for conversion into $CrO_4^{''}$ are $Mn(OH)_2$, $Cu(OH)_2$, $Mn(OH)_2+Cu(OH)_2$, and amalgamated Cu+liquid Hg. Possible mechanisms of the action are discussed. J. W. S.

Oxidation of ferrous sulphate solutions. J. R. POUND (J.S.C.I., 1936, 55, 327—330r).—The catalytic action of Pt-black, NO, and activated C in the oxidation of aq. $FeSO_4$ was confirmed. Numerous other substances examined gave negative results. The reaction in presence of NO is bimol. with respect to $FeSO_4$ and unimol. with respect to NO. The dependence of the rate of oxidation on concn., time, surface of solution, and dissolved O_2 was studied. Aq. $FeSO_4$ is oxidised rapidly by $HNO_3 > 0.5N$. H. J. E.

Method of investigating catalyst surfaces. B. JEROFEEV and K. MOCHALOV (Acta Physicochim. U.R.S.S., 1936, 4, 859—860).—On admitting air to a tube containing Fe filings reduced *in situ* at 450° the resistance increased greatly and the tube functioned as a coherer for Hertz waves. Fe containing 1% of Al_2O_3 as a promoter did not lose its capacity for acting as a coherer after 46 hr. reduction at 450° . The Fe surface is coated with an Al_2O_3 film which is not reduced under these conditions. H. J. E.

Catalytic decomposition of ammonia. I. CHRISMAN (Acta Physicochim. U.R.S.S., 1936, 4, 899—910).—The kinetics of the decomp. of NH_3 on a $Fe-Al_2O_3-K_2O$ catalyst at $300-450^\circ$ were studied by a flow method. The activation energies for the temp. ranges $300-350^\circ$ and $350-450^\circ$ were 12.4 and 39.7 kg.-cal. per g.-mol., and were attributed to the formation and decomp. of nitride. H. J. E.

Mechanism of the arresting action of the promoter on the reduction of the iron ammonia catalyst. N. I. KOBOSEV (Acta Physicochim. U.R.S.S., 1936, 4, 829—840).—Data for the effect of Al_2O_3 , K_2O , KF , BeO , and MgO on the rate of reduction of Fe_3O_4 and FeO by H_2 are discussed (cf. B., 1936, 629). The promoter forms a surface film which protects the Fe oxide from reduction, and also favours the formation of small crystals of Fe. H. J. E.

Oxidation of carbon. II. J. D. LAMBERT (Trans. Faraday Soc., 1936, 32, 1584—1591; cf. this vol., 434).—The secondary conversion of CO into CO_2 in the combination of C occurs more rapidly at a pure C surface than at a surface of C containing Fe. C treated with Mn behaves similarly to C treated with Fe on oxidation at 400° , but without secondary oxidation of CO to CO_2 . The mechanism is discussed.

Possibly the primary reaction product is a gaseous complex similar to C_3O_2 . E. S. H.

Selective combustion of hydrogen, carbon monoxide, and methane by palladium catalysts. M. S. PLATONOV and O. V. NEKRASSOVA (Z. anal. Chem., 1936, 106, 416—418).—A Pd catalyst on a ceramic carrier, prepared by reduction of $PdCl_2$ with H_2 at 120—140°, burns H_2 catalytically at room temp., CO at 140—150°, and CH_4 at 400—450°. The selective combustion of H_2 in presence of CO is not possible; such mixtures are burned at 150°, and the composition is calc. from the vol. contraction. J. S. A.

Interaction of carbon disulphide and sulphur dioxide. B. CRAWLEY and R. H. GRIFFITH (Trans. Faraday Soc., 1936, 32, 1623—1626).—A survey of a wide range of catalysts for the reaction has been made. Interaction appears to occur by collision of a free CS_2 mol. with an adsorbed SO_2 mol. Activated adsorption of only one reactant is necessary. E. S. H.

Hydrogenation with hydrogen dissolved in palladium. D. DOBITSCHIN and A. FROST (Acta Physicochim. U.R.S.S., 1936, 5, 111—130; cf. A., 1935, 940).—The hydrogenation of C_2H_4 , $CH_2:CHEt$, and C_2H_2 by H absorbed in sputtered films of Pd has been followed by measuring the electrical resistance of the films, which varies with the H content. With C_2H_4 and $CH_2:CHEt$ the reaction is more rapid than the desorption of H at -78° . The rate of hydrogenation of C_2H_4 by H_2 dissolved in Pd is $>$ when it is in the gas phase. Ageing of the Pd film leads to parallel decrease of catalytic activity and of the rate of absorption of H_2 . F. L. U.

[Catalytic] synthesis of benzene.—See B., 1936, 1028.

Catalyst poisoning from the point of view of the specificity of active centres. III. Relative durations of sojourn of *n*-propyl alcohol and propaldehyde molecules, and true energy of activation of *n*-propyl alcohol dehydrogenation on copper. A. BORK and A. A. BALANDIN. IV. Orientation of molecules of reactants and resultants on catalyst surface in catalysed dehydrogenations and analogous catalytic reactions. A. BORK (Z. physikal. Chem., 1936, B, 33, 435—442, 443—453).—III. The rate of dehydrogenation of PrOH to EtCHO on Cu at 252° and the influence on the velocity of EtCHO may be represented by $dm/dt = k(M-m)/N$, where k contains no adsorption coeffs. (cf. this vol., 1076). The durations of sojourn on the catalyst and the heats of adsorption of PrOH and EtCHO are equal over a temp. range of 40°. The true energies of activation of the dehydrogenation of EtOH and PrOH are both 12,200 g.-cal. The logarithmic relation between the consts. of Arrhenius' equation (cf. *ibid.*, 435) holds.

IV. Existing experimental data and theoretical reasoning indicate that the rate of catalytic dehydrogenation and similar catalyses is given by $dm/dt = k(M-m)/M$, where M is the no. of mols. of reactant entering the reaction tube and m the no. of mols. reacting in unit time, and k contains no adsorption coeffs. Homologous reactants have the same energy of activation. If two homologous reactants undergo

dehydrogenation at the same rate, and if for one the adsorption coeffs. of reactant and resultant are equal, this is true of the other also, and for each reaction the duration of sojourn on the catalyst of reactant and resultant is the same. A method of determining relative adsorption coeffs. is described. R. C.

Catalytic conversion of natural gas into carbon monoxide and hydrogen.—See B., 1936, 1075.

High-pressure hydrogenation of low-temperature tar. V. Molybdenum catalysts.—See B., 1936, 1075.

Twitchell's reagent as promoter of esterification.—See this vol., 1487.

Kinetics of the process at the iron anode of a galvanic element. V. ROITER and V. JUSA (Acta Physicochim. U.R.S.S., 1936, 4, 135—144).—The results of polarisation determinations can be expressed by $\Delta\epsilon = abI/(1+bI)$, where ϵ is the potential and I the c.d. By analogy with the Langmuir equation it is suggested that the potential decrease is due to the adsorption of a substance of which the concn. in the electrolyte \propto c.d. R. S.

Electrolytic oxidation. VIII. Apparent reducing properties of an anode. A. HICKLING (J.C.S., 1936, 1453—1456).—The ratio of the vols. of O_2 and H_2 evolved during electrolysis of acid solutions of $KMnO_4$ and $K_2Cr_2O_7$ has been determined under varying conditions of c.d. and concn., and with different acids present. This ratio is abnormally large, the discrepancy being attributed to formation of H_2O_2 from OH^- discharged at the anode, and subsequent reaction of this with the $KMnO_4$ or $K_2Cr_2O_7$. A. J. E. W.

Production of electrolytic zinc.—See B., 1936, 1100.

Electrolytic refining of aluminium.—See B., 1936, 1100.

Theory of electrolytic chromium plating. I.—See B., 1936, 1044.

Electrochemical protection of metallic surfaces.—See B., 1936, 1044.

Formation of carbon dendrites. H. TRIELE (Nature, 1936, 138, 688).—Further experiments illustrating the reduction of graphitic acid at a cathode and the formation of dendrites are described (cf. this vol., 1089). L. S. T.

Mechanism of catalytic interchange of hydrogen with water and alcohol. J. HORIUTI and G. OKAMOTO (Trans. Faraday Soc., 1936, 32, 1492—1494; cf. this vol., 430).—The rate-determining step for the electrode process at a polarised Ni-H electrode is the atomisation of the H_2 mol. on the metal. A homopolar Ni-H linking is assumed. The application of this result to the Pt-H electrode process is discussed. A. J. E. W.

Chemical activity of the rare gases. VII. Action of helium on bismuth under the influence of electrical discharges at low pressure. H. DAMIANOVICH (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 20—22; Chem. Zentr., 1936, i, 497).—He was combined with Bi in a discharge at 1—2 mm.

pressure. The product contained 4.5 c.c. of He per g. of Bi. H. J. E.

Cathodic platinum obtained in a hydrogen atmosphere. H. DAMIANOVICH and C. CHRISTEN (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 72—75; Chem. Zentr., 1936, i, 498).—No evidence of compound formation was found. H. J. E.

Thermal decomposition of reversible and irreversible systems forming a gas phase. I. Cathodic platinum oxide and chemically produced platinum oxyhydrate. II. Platinum-helium and platinum-nitrogen compounds and the systems reduced platinum, electrolytic platinum, and carbon. J. PIAZZA and H. DAMIANOVICH (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 32—45, 46—56; Chem. Zentr., 1936, i, 497—498).—I. The Pt oxide obtained by cathodic sputtering in an O₂ atm. is identical in its thermal decomp. and X-ray pattern with that obtained from H₂Pt(OH)₆, and resembles the Pt-N and Pt-He compounds in its decomp. curve and autocatalytic phenomena.

II. The Pt-He and Pt-N compounds produced in a discharge undergo irreversible thermal decomp. The decomp. is compared with that in Pt-O and C-air systems. H. J. E.

Reaction kinetics in electric discharges. S. S. VASSILIEV, N. I. KOBOSEV, and E. N. ERJEMIN (Acta Physicochim. U.R.S.S., 1936, 5, 201—242).—The following discharge reactions have been subjected to kinetic analysis: the oxidation of N₂, the formation of O₃ and H₂, and the cracking of CH₄. The relation between the actual yield and the limiting energy yield and the influence of the power of the discharge are discussed. R. S.

Effect of temperature on photochemical formation of ozone. A. EUCKEN and F. PATAT (Z. physikal. Chem., 1936, B, 33, 459—474; cf. A., 1924, ii, 159).—The formation of O₃ from O₂ at 20—50 mm. by ultra-violet light of λ chiefly 1720 Å. (Al spark) has been examined. Assuming that the mechanism is O₂ + h ν = 2O, O + O₂ + M = O₃ + M, O₃ + O = 2O₂ it may be shown that at equilibrium [O₃] = k[O₂]² and that the position of equilibrium is independent of the intensity of radiation. Both deductions are confirmed by experiment. The variation of k with temp. gives 6160 ± 100 g.-cal. per mol. for the energy of activation of O + O₂ = 2O₂. From the results [O₃] at various heights in the atm. has been calc., the results showing that the effective O₃ layer is at a height of <<40 km. R. C.

Effect of light on the ignition of monosilane-oxygen mixtures. H. J. EMELÉUS and K. STEWART (Trans. Faraday Soc., 1936, 32, 1577—1584).—SiH₄, Si₂H₆, and Si₃H₈ absorb light of λ <1850, <1980—2020, and <2140—2190 Å., respectively. SiH₄ mixed with Hg vapour is decomposed by the 2537 Å. Hg resonance line, giving H₂ and solid polymerised SiH_x (x <0.9). Light from an Al spark or Hg resonance arc causes explosion of SiH₄-O₂ mixtures at temp. < the normal range for thermal ignition. SiH₄-O₂ mixtures at pressures > the crit. explosion pressure undergo slow oxidation on exposure to the Hg resonance arc. The reaction has

an induction period and in the initial stages follows the law $\Delta p = ke^{kt}$, which characterises hydrocarbon combustion. E. S. H.

[Photochemical] reduction of ferric salts by organic acids. P. LAL and P. B. GANGULY (Z. anorg. Chem., 1936, 229, 16—18).—Reduction of aq. solutions of pure normal Fe^{III} citrate and tartrate by light from a quartz Hg lamp follows a zero-mol. course. The quantum yield (λ 546 m μ) is 0.5 for the citrate and 0.62 for the tartrate. The reaction is strongly catalysed by traces of Th, U, Cu, and Zr salts in the decreasing order given. F. L. U.

Action of various elements and compounds on photographic plates. III. S. AOYAMA, T. FUKUROI, and K. SUZUKI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 923—936; cf. A., 1935, 47, 1087).—Physical factors are considered. J. S. A.

Latent images below the threshold. LÜRPO-CRAMER (Phot. Korr., 1935, 71, 137—138; Chem. Zentr., 1936, i, 942).—A strong Becquerel effect occurs in AgI-gelatin plates if an I acceptor is present and physical development is used. The absence of the effect in AgBr dry plates is ascribed to the fact that unilluminated AgI is relatively much more sensitive to blue light than is AgBr. H. J. E.

Destruction of latent images and desensitisation by dyes.—See B., 1936, 1131.

Photochemical reactions of iron gluconates. R. NEIGER and P. NEUSCHUL (Z. physikal. Chem., 1936, 177, 355—364).—Fe^{II} gluconate (I) in aq. solution is oxidised in the dark under the influence of atm. O₂ to a Fe^{III} salt (II) of unknown constitution, which is stable in the dark. Fe^{III} gluconate (III) is stable in the dark in air. In an O₂-free atm. (I) and (III) are stable in the dark. In daylight (II) and (III) are reduced to a Fe^{II} salt, which from the solution of (II) separates as a solid (IV). Invert sugar delays the appearance of (IV). (III) is reduced more readily if O₂ is excluded. These reductions are apparently genuine photochemical reactions. Fe^{II} mannonate behaves similarly to (I). R. C.

Photochemical peroxide formation. IV, V.—See this vol., 1489, 1492.

Initiation of gas reactions by ions. II. Hydrogen-chlorine mixtures. P. GÜNTHER and K. HOLM (Z. physikal. Chem., 1936, B, 33, 407—434).—Investigation of the induction of reaction in a H₂-Cl₂ mixture, by allowing N ions to diffuse into it, has confirmed results previously reported (A., 1934, 975). Each ion initiates ~2.5 reaction chains, which shows that the chemical action of the ions is approx. the same whether they are introduced into the reaction mixture by diffusion or produced *in situ* by α -particles or X-rays. The mobility of Cl ions in moist Cl₂ is greatly reduced by the addition of a small amount of H₂, suggesting that in presence of H₂ HCl is formed in the immediate vicinity of the ions and, dissolving in H₂O, associates itself with the ion and so slows it down. Hence the formation of HCl under the influence of ions occurs during the life of the ions, not at their neutralisation. The no. of reaction chains initiated by an ion appears to be

independent of the life of the ion. Following Lind's cluster theory it may be supposed that the electrostatic fields of the N ions cause Cl_2 mols. to become associated with them, and some of these are so distorted as to give Cl atoms, which start the reaction. The present experiments indicate that α -particles initiate reactions by their electrostatic action on the ions to be excited. R. C.

Enrichment of the light argon isotopes by diffusion. H. BARWICH and W. SCHÜTZE (*Naturwiss.*, 1936, 24, 667).—An enrichment of ^{36}A and ^{38}A by diffusion into a current of Hg vapour has been observed. A. J. M.

Action of atomic hydrogen on inorganic compounds. H. KROEPELIN and E. VOGEL (*Z. anorg. Chem.*, 1936, 229, 1—15; cf. A., 1935, 730).—Observations on the action of H_2 containing about 14% of H on 86 solid inorg. elements and compounds are recorded. The experiments were conducted at room temp., but in some cases considerable local rise of temp. was observed. With a few substances luminescence was produced. Generally, compounds of heavy metals are reduced readily. The action is, however, sometimes only superficial, owing either to catalysis of H by the reaction products, or to impermeability of the latter to H. Alkali metal salts are reduced to metal when the anion is destroyed by H (e.g., NO_3' , NO_2' , CN' , ClO_3'). Films of gelatin and of Cellophane are impermeable to H. Aq. solutions of AgNO_3 , HgCl_2 , and $\text{Cu}(\text{OAc})_2$ are reduced to metal, CrO_4'' and MnO_4' in acid solution to Cr^{+++} and Mn^{++} , I_2 to I' , H_2O_2 to H_2O , and methylene-blue and indigotin in H_2SO_4 to leuco-compounds. Working details are given. F. L. U.

Influence of combustion conditions on the density of water formed from commercial hydrogen and oxygen. W. H. HALL and H. L. JOHNSTON (*J. Amer. Chem. Soc.*, 1936, 58, 1920—1922).—The vol. ratio $\text{H}_2:\text{O}_2$ has no significant influence on the d of the H_2O produced when reaction occurs in a flame, but the d may be affected by several p.p.m. if combination takes place over a Pt catalyst. When O_2 is in excess d may be low, probably by reason of the lower reaction velocities of the higher isotopes of O. With excess of H_2 , d may be high, owing to incomplete exchange between steam and excess of H_2 . E. S. H.

Isotopic interchange reaction between chloroform and water. J. HORIUTI and Y. SAKAMOTO (*Bull. Chem. Soc. Japan*, 1936, 11, 627—628).—The isotopic interchange between CHCl_3 and D_2O in alkaline solution proceeds more quickly than the decomp. In neutral or acid solution the interchange is much slower. C. R. H.

Sodium fluorenone as a dehydrating agent. H. E. BENT and H. M. IRWIN, jun. (*J. Amer. Chem. Soc.*, 1936, 58, 2072—2073).—Na fluorenone has a higher efficiency than $\text{Mg}(\text{ClO}_4)_2$ or activated Al_2O_3 . E. S. H.

Thermal dissociation and absorption spectra of vapours of KNO_2 , KNO_3 , NaNO_3 , and AgNO_3 . K. BUTKOV and V. TSCHASSOVENNI (*Acta Physicochim. U.R.S.S.*, 1936, 5, 137—159).—The products

obtained by heating NaNO_3 , KNO_3 , KNO_2 , and AgNO_3 in an evacuated quartz tube have been studied spectrographically in the range 7000—1880 Å. Vapours of the complete mol. are present in all except NaNO_3 . KNO_3 gives NO at temp. $> 550^\circ$, and NO_2 on cooling. KNO_2 behaves similarly, except that on cooling NO persists and no NO_2 is formed. AgNO_3 gives NO_2 only at 270° . The mols. are not ionised in the vapour state. Bond linking energies are calc., that corresponding with the semipolar $\text{N}\rightarrow\text{O}$ linking being 92 kg.-cal. per mol. F. L. U.

Active oxides. CIII. Course of reactions in which solid substances take part. G. F. HÜTTIG (*Monatsh.*, 1936, 69, 42—74; cf. this vol., 1216 and previous abstracts).—A summary of the author's work on reactions involving metal oxides is given. The reactions are classified under 11 main types, and the characteristics of each are described. F. L. U.

Theory of corrosion phenomena. V. Application of the pore theory of corrosion to the phenomenon of the difference effect of Thiel and Eckell. W. J. MÜLLER and E. LÖW. VI. **Determination of the metal potential of a working anode and of the potential and resistance requisite for local cells.** W. J. MÜLLER (*Z. Elektrochem.*, 1936, 42, 789—792, 830—833; cf. this vol., 940).—V. Published work is reviewed in the light of Müller's theory.

VI. The determination of potential at two different c.d. through the pores is described. Published results are discussed. E. S. H.

Corrosion of metals by water and carbon dioxide under pressure.—See B., 1936, 1098.

Influence of sodium chloride and hydrogen peroxide in rapid corrosion experiments.—See B., 1936, 1098.

Etching of copper by oxygen. C. F. ELAM ([Mrs.] C. F. TIPPER) (*Trans. Faraday Soc.*, 1936, 32, 1604—1614).—The etching effect obtained by heating Cu in vac. is due to the presence of Cu_2O ; it can be reproduced by oxidising the surface and appears to be due to attack by O_2 along crystal planes, especially [100] and [110]. The relation between the orientation of the Cu crystal and the Cu_2O formed has been investigated. E. S. H.

Copper peroxide and nascent copper oxide. E. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1936, [v], 3, 1913—1915).—Addition of H_2O_2 to slightly alkaline aq. CuSO_4 yields a brownish-yellow colour apparently due to CuO_2 . $\text{Cu}(\text{OH})_2$ in presence of aq. CuSO_4 has a slight oxidising effect on tincture of guaiacum, with reduction to $\text{Cu}_2(\text{OH})_2$. J. W. S.

Compounds of copper salts with tertiary amines.—See this vol., 1395.

Combination of magnesium chloride and magnesium methoxide. (MLLE.) M. L. QUINET (*Bull. Soc. chim.*, 1936, [v], 3, 1823—1829).—Action of Mg on a conc. solution of MgCl_2 in MeOH, of $\text{Mg}(\text{OMe})_2, 2\text{MeOH}$ on MgCl_2 in MeOH, or of $\text{MgCl}_2, 6\text{MeOH}$ on a conc. solution of $\text{Mg}(\text{OMe})_2$ in MeOH, gives the cryst. compound $\text{MgCl}_2, 3\text{Mg}(\text{OMe})_2, 11\text{MeOH}$. E. W. W.

Formation of magnesium oxysulphate. (MLLE.) M. L. DELYON (Bull. Soc. chim., 1936, [v], 1811—1817).—MgO dissolves in conc. aq. MgSO_4 (>500 g. per litre) at 80° , and then gradually gives a ppt. which after 24 hr. has the const. composition $\text{MgSO}_4 \cdot 3\text{MgO} \cdot 11\text{H}_2\text{O}$. (I) The ppt. from solutions containing <300 g. of MgSO_4 per litre is $\text{Mg}(\text{OH})_2$, whilst solutions of intermediate concn. yield a mixture of $\text{Mg}(\text{OH})_2$ and (I). Attempts to prepare (I) from $\text{Mg}(\text{OH})_2$ were unsuccessful but it was pptd. by addition of NaOH to aq. MgSO_4 at 80° . J. W. S.

Generating media of montmorillonite and sepiolite. J. DE LAPPARENT (Compt. rend., 1936, 203, 553—555).—Montmorillonite is probably formed by devitrification of a glass in a medium containing Mg. Sepiolite (this vol., 957) results from direct action of Mg salt solutions on siliceous gels.

J. G. A. G.

Existence of zinc metaborate. R. TOURNAY (Compt. rend., 1936, 203, 558—560).—Heat is evolved at 580 — 630° and at 775 — 820° when the temp. of an equimol. mixture of B_2O_3 and ZnO is slowly raised. $2\text{B}_2\text{O}_3 \cdot 3\text{ZnO}$ is formed at $>700^\circ$, but the existence of $\text{B}_2\text{O}_3 \cdot \text{ZnO}$ is denied.

J. G. A. G.

Cadmium suboxides and subhalides. R. E. HEDGER and H. TERREY (Trans. Faraday Soc., 1936, 32, 1614—1616).—X-Ray examination shows that the so-called subhalide prepared by dissolving Cd in molten CdCl_2 is a mixture of CdCl_2 and Cd; the so-called suboxide formed by treating the above with H_2O is a mixture of CdO and Cd. The solubility of Cd in CdCl_2 at 570 — 810° has been determined.

E. S. H.

Oxidation of metals. IV. Oxide film on aluminium. G. D. PRESTON and L. L. BIRCUMSHAW (Phil. Mag., 1936, [vii], 22, 654—665; cf. A., 1935, 1469; this vol., 569).—The oxide film found on Al at room temp. was isolated by removing the metal by treatment in HCl gas at 250° . Electron diffraction photographs show that the film is amorphous. Crystallisation begins slowly on heating at 680° , but not at temp. up to 650° . The film becomes a random mass of small crystals of cubic $\gamma\text{-Al}_2\text{O}_3$ as found on the surface of molten Al.

N. M. B.

Reaction aluminium oxide-carbon-chlorine. N. M. STOVER and C. CONSTANTINESCU (Canad. J. Res., 1936, 14, B, 328—335).—The reaction between Al_2O_3 , C and Cl_2 has been studied at 644 — 880° , using varying proportions of Al_2O_3 and C, and static and streaming Cl_2 . O_2 was present in the reaction product, suggesting that the main reaction is $2\text{Al}_2\text{O}_3 + 6\text{Cl}_2 = 4\text{AlCl}_3 + 3\text{O}_2$, the rôle of the C being primarily catalytic. For a given ratio $\text{Al}_2\text{O}_3 : \text{C}$ the ratio $\text{CO}_2 : \text{O}_2$ in the gaseous product increased with the wt. of solid mixture. CO was obtained in the static experiments, but not with streaming Cl_2 . The temp. at which AlCl_3 first sublimed decreased with decreasing ratio $\text{Al}_2\text{O}_3 : \text{C}$. Less C was consumed, in many experiments, than that required to form CO_2 with the O of the Al_2O_3 . Using WO_3 instead of Al_2O_3 , O_2 and good yields of CO_2 were formed with streaming Cl_2 (cf. Sears and Lohse, A., 1935, 834).

R. S. B.

Preparation and properties of indium dichloride. J. K. AIKEN, J. B. HALEY, and H. TERREY (Trans. Faraday Soc., 1936, 32, 1617—1622).—The prep. of InCl_2 and its analogies with SnCl_2 in physical properties and lattice structure are described. InCl_2 and SnCl_2 appear to be associated in the solid state.

E. S. H.

Disappearance of carbon monoxide in presence of electrically heated nickel filaments. G. BRYCE (J.C.S., 1936, 1513—1517).—When a Ni filament is heated to above 1200° abs. in CO at low pressure in a bulb at -190° , the CO disappears rapidly and completely, but can be recovered by heating the bulb. The action is slow at room temp., and negligible at 100° . The CO is removed by evaporated Ni as it condenses on the bulb, 2 mols. of CO being removed per atom of Ni, probably with formation of a subcarbonyl. This absorbs more CO on gentle warming. CO was also adsorbed by Ni freshly condensed in a bulb in a vac. Hot Ni does not affect CO_2 or N_2 under similar conditions. Mo at temp. $>1900^\circ$ abs. removes CO in a similar manner.

A. J. E. W.

Physical and chemical properties of liquid hydrogen phosphide (diphosphine, P_2H_4). P. ROYEN and K. HILL (Z. anorg. Chem., 1936, 229, 97—111; cf. this vol., 440).—The limiting d of the vapour of liquid H phosphide, purified by fractionation at a low temp., corresponds with the formula P_2H_4 . No indication of the existence of higher homologues in the product of the action of aq. KOH on P has been observed. The v.-p. curve of P_2H_4 has been determined between -70° and 10.8° and is expressed by a two-const. formula. B.p. by extrapolation = 51.7° ; mean mol. heat of vaporisation between -25° and -8° = 7890 g.-cal.; m.p. -99° . P_2H_4 is decomposed by HCl even at temp. $<$ m.p., and there is no evidence for the existence of a hydrochloride. The decomp. is expressed by $3\text{P}_2\text{H}_4 = 2\text{P} + 4\text{PH}_3$, the solid product consisting of a yellow modification of P with adsorbed PH_3 . The proportion of the latter varies with the state of division of the solid.

F. L. U.

Partly halogenated phosphines. Formation of so-called solid hydrogen phosphide, particularly of its phenyl derivatives. P. ROYEN and K. HILL (Z. anorg. Chem., 1936, 229, 112—128; cf. preceding abstract).—Attempts to isolate PH_2X ($\text{X} = \text{Cl}, \text{Br}$) by the action of Br, PBr_5 , PCl_5 , or $\text{HCl} + \text{AlCl}_3$ on PH_3 have been unsuccessful. Compounds of the type PHRX cannot be isolated owing to their rapid conversion into PX_3 and PH_3RX . By condensation of PPh_2Cl with PH_3 a yellow product containing 42% of adsorbed Ph phosphines is obtained, resulting from the decomp. of $\text{P}_2\text{H}_2\text{Ph}_2$. Me and Ph derivatives of " P_{12}H_6 " described in the lit. are not compounds, but adsorbates of Me and Ph phosphines on yellow amorphous P.

F. L. U.

New oxide of phosphorus. P. W. SCHENK and H. PLATZ (Naturwiss., 1936, 24, 651).—If a mixture of P_2O_5 vapour and O_2 is passed through a hot discharge tube (pressure about 1 mm.) a bluish-violet product separates in the cool part of the tube immediately behind the discharge zone. This substance

liberates I from KI, and may be preserved for a day at room temp. in the absence of H_2O . It is considered to contain 2% of a new peroxide, PO_3 (or P_2O_6).

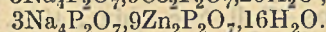
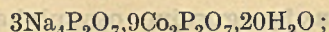
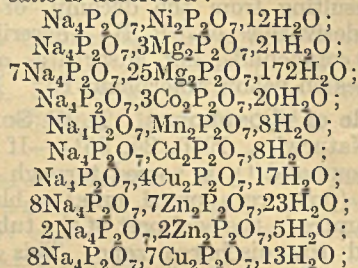
A. J. M.

Preparation and properties of some lower acids of phosphorus. I, II. V. N. OSIPOV (J. Gen. Chem. Russ., 1936, 6, 933—940, 941—946).—I. The acid mixture formed when colourless P is oxidised by air in H_2O (3—6 days, 10—15°) has been investigated. The mixture and Mg salts give no crystals. Metallic Mg yields $Mg_2H_2P_2O_7 \cdot 11H_2O$, which differs from the known $Mg_2P_2O_6 \cdot 12H_2O$ since it loses H_2O at 105° more slowly, dissolves in 25% H_2SO_4 more slowly and with evolution of gas, becomes brown when treated with $AgNO_3$, etc. $AgOAc$ in dil. $AcOH$ converts the new salt into $Ag_1H_2P_2O_7$, different from $Ag_1P_2O_6$ since it evolves H_2 when heated in CO_2 . The reaction between Mg and $Na_2H_2P_2O_6 \cdot 6H_2O$ in dil. $AcOH$ produces $Mg_2P_2O_6 \cdot Mg_2H_2P_2O_7 \cdot 13H_2O$, which is converted by $AgNO_3$ into brown $Ag_4P_2O_6 \cdot Ag_4H_2P_2O_7$.

II. When P undergoes oxidation by air in H_2O for a longer time than in the above experiments, the $H_4P_2O_6$, which presumably is the first reaction product, reacts with H_2O : $H_4P_2O_6 \rightarrow H_6P_2O_7 \rightarrow H_8P_2O_8$; the usual equation $H_4P_2O_6 + H_2O = H_3PO_3 + H_3PO_4$ may be incorrect. After 2—3 weeks the acid mixture and Mg give $MgHPO_4 \cdot MgH_2PO_4 \cdot 5 \cdot 5H_2O$ (I), after 4 weeks $3MgHPO_4 \cdot MgH_2PO_4 \cdot 10H_2O$ (II) is produced. Both (I) and (II) evolve H_2 when heated in CO_2 . $AgNO_3$ changes the colour of (I) to yellow \rightarrow brown \rightarrow black, the colour of (II) to greenish-yellow \rightarrow black. (I) is insol. in H_2O and is not pptd. by $Th(NO_3)_4$ in dil. HNO_3 . It is converted by $AgNO_3$ in neutral solution into $Ag_{11}H_2P_4O_{16}$ (brown), in dil. $AcOH$ into $Ag_{10}H_3P_4O_{16}$ (yellow), and in dil. H_2SO_4 into $Ag_5H_5P_4O_{16}$ (brown). (II) and $AgNO_3$ afford in neutral solution $Ag_{11}H_3P_4O_{16}$, a brown ppt.

J. J. B.

Phosphates. IV. Pyrophosphates of some bivalent metals and their double salts, and solid solutions with sodium pyrophosphate. H. BASSETT, W. L. BEDWELL, and J. B. HUTCHINSON (J.C.S., 1936, 1412—1429).—The pyrophosphates $M_2P_2O_7 \cdot xH_2O$ ($M=Mg, Mn, Co, Ni, Cu, Zn, \text{ and } Cd$) have been studied. x may have the vals. 8, 7, 6.5, 6.25, 6, 5, 4.2, 4, 3.3, 3.6, 3.25, 3, 2.3, or 2.1, the whole series of hydrates not being found with any one metal. Such "parent" hydrates give solid solutions or definite double salts with $Na_4P_2O_7$, these probably being formed by replacement of $[M(H_2O)_4]^{2+}$ by $[Na_2(H_2O)_2]^{2+}$, or $[M(H_2O)_2]^{2+}$ by Na^+ , or in some cases $[M(H_2O)_2]^{2+}$ by $[H_2(H_2O)_2]^{2+}$. The prep. of the following double salts is described:



All these crystallise with difficulty from the mother-liquors owing to the low concn. of some constituent ions existing in solution. They are very sparingly sol. in H_2O . Probable structures are given, in which the metal is assumed to be entirely in the cationic condition, and 2- or 4-co-ordinate. One true complex salt $Na_6[Cu(P_2O_7)_2] \cdot 16H_2O$ was obtained. $Na_4P_2O_7 \cdot 10H_2O$ is probably $[Na(H_2O)_4]_2^+ [Na_2(H_2O)_2]^{2+} [P_2O_7]^{4-}$.

A. J. E. W.

Spontaneous transformation of hypophosphoric acid. P. NYLÉN (Z. anorg. Chem., 1936, 229, 36—44).—Crystals of $H_4P_2O_6$ preserved in a sealed tube change in 1—2 months at room temp. to a viscous liquid. The anhyd. acid undergoes a similar change in 5 days. The product is a mixture of H_3PO_3 , H_3PO_4 , and $H_4P_2O_7$. An explanation based on the constitution of the acids is offered.

F. L. U.

Phosphorus nitrides P_3N_5 and PN. H. MOUREU and P. ROCQUET (Bull. Soc. chim., 1936, [v], 3, 1801—1811).—Continued heating of PN_2H at 450° in a vac. yields P_3N_5 . When heated to 730° in a vac. P_3N_5 yields PN which sublimes in a vac. PN exists in two forms. The more stable red form reduces warm conc. H_2SO_4 , but this reaction is very slow in the cold. The yellow form, which can be isolated only at low temp., is readily sol. in H_2SO_4 and reduces the latter even at room temp. On warming in air it ignites. Neither form shows cryst. structure when examined by X-rays. PN does not react with N_2 at any temp., but a current of dry NH_3 at 850° converts it back into P_3N_5 .

J. W. S.

Pyroantimonates of bivalent metals: $Ca_2Sb_2O_7$, $Cd_2Sb_2O_7$, $Pb_2Sb_2O_7$. M. BACCAREDDA (Gazzetta, 1936, 66, 539—543; cf. A., 1933, 692).—Pure $Ca_2Sb_2O_7$ and $Cd_2Sb_2O_7$ are prepared by heating to redness Sb_2O_5 mixed with excess of $Ca(NO_3)_2 \cdot 4H_2O$ or $Cd(NO_3)_2 \cdot 4H_2O$, respectively, and washing the products with H_2O and dil. $AcOH$. $Pb_2Sb_2O_7$ is obtained by heating a mixture of Sb_2O_5 and $Pb(OAc)_2 \cdot 3H_2O$ in the theoretical amounts. The three substances are cubic, space-group O_h^2 , 8 mols. per unit cell, and a 10.30, 10.16, 10.68 Å., $d_{calc.}$ 5.32, 7.34, 8.40, $d_{obs.}$ 4.30, 5.62, 6.72, for the Ca, Cd, and Pb compounds, respectively.

O. J. W.

Formation of dithionate by the action of pyrosulphate on sulphite. P. BAUMGARTEN (J.C.S., 1936, 1569—1570; cf. A., 1932, 1219).—Contrary to the observation of Bassett and Henry (A., 1935, 1090), K_2SO_3 prepared from KOH and SO_2 reacts with $K_2S_2O_7$ in aq. solution in presence of $KHCO_3$ with formation of $K_2S_2O_6$.

A. J. E. W.

Higher polythionates. II. A. KURTENACKER and K. MATEJKA (Z. anorg. Chem., 1936, 229, 19—29; cf. A., 1928, 1201).—By increasing the $[HCl]$ used in Raschig's method for preparing $K_2S_5O_6$, $K_2S_6O_6$ can be prepared and separated from the former by crystallisation. Working details are given. Still further increase in the $[HCl]$ results in the production of higher polythionates which, however, cannot be crystallised or otherwise obtained as individuals. $K_2S_6O_6$ is obtained as a white cryst. powder, stable

when dry. Neutral aq. solutions slowly deposit S and form $K_2S_5O_6$, whilst alkalis provoke immediate decomp. X-Ray powder diagrams of $K_2S_nO_6$ ($n=3, 4, 5, 6, >6$) are given. The absence from the last-named of lines proper to any of the others indicates the existence of one or more definite higher polythionates.
F. L. U.

Molybdenum and nitrogen. A. SIEVERTS and G. ZAPF (Z. anorg. Chem., 1936, 229, 161—174; cf. B., 1934, 676).—Mo foil and Mo wire which have been heated at 1400° in a mixture of H_2 and N_2 absorb only very small quantities of N_2 at 900 — 1200° . The foil becomes brittle and recrystallises, whilst the wire is unaffected. Absorption of N_2 by wire which has not been preheated is much greater, and on cooling in N_2 a nitride phase, characterised both microscopically and by X-rays, separates. The initially flexible wire becomes brittle and shows a smooth instead of a fibrous fracture. A nitride with 23.5 at.-% of N still absorbs N_2 freely at 820° .
F. L. U.

Amphoteric hydrated oxides, solutions of their hydrolysing salts, and their compounds of high mol. wt. XXX. Phosphotungstates and their inter-relations. G. JANDER and H. BANTHIEN (Z. anorg. Chem., 1936, 229, 129—145; cf. this vol., 29).—The conditions under which various phosphotungstates separate from aq. solutions of their components are described. $6Na_2O, 1.5P_2O_5, 12WO_3, 17H_2O$ is new. All compounds of this type are derived from the units $H_3PO_4, H_6W_6O_{21}$, and $P_2O_5, 12WO_3, xH_2O$.
F. L. U.

Fluorine and its compounds. O. RUFF (Ber., 1936, 59, [A], 181—194).—A lecture.

Oxidation of inorganic reagents by ozone. II. Potassium iodide. Influence of the characteristics of the solution. (MME.) G. GUÉRON, M. PRETTRE, and J. GUÉRON (Bull. Soc. chim., 1936, [v], 3, 1841—1847; cf. this vol., 440, 441).—The action of O_3 on solutions of KI in MeOH, EtOH, BuⁿOH, CO_2Me_2 , or cyclohexanol produces KIO_3 to a greater extent than in aq. solution. Dry KI is only slightly attacked by O_3 dried with H_2SO_4 . After dissolution of the product, 92% of the oxidising power is found to be due to KIO_3 . Addition of KCl or K_2SO_4 to aq. KI has no effect on the oxidation by O_3 , which yields both I and KIO_3 . Buffering with conc. $KH_2PO_4 + K_2HPO_4$, however, decreases the amount of IO_3^- produced. The formation of KIO_3 appears to occur only in regions of local alkalinity. Attempts to demonstrate this were unsuccessful, owing to irregularities, apparently of an electro-kinetic nature. The limitations of the KI method of determining O_3 are discussed.
J. W. S.

Oxalato complex compounds of tervalent manganese. G. H. CARTLEDGE and W. P. ERICKS (J. Amer. Chem. Soc., 1936, 58, 2061—2065).—The prep. and properties of $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$, $K[Mn(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$, $K[Mn(C_2O_4)(H_2O)_2]$, $[Co(NH_3)_6][Mn(C_2O_4)_3] \cdot xH_2O$, and $K[Mn(C_3H_5O_4)_2(H_2O)_2] \cdot 2H_2O$ are described.
E. S. H.

Ferrites. R. S. HILPERT (Rec. trav. chim., 1936, 55, 963—966).—A reply to van Arkel *et al.* (this vol., 810).
R. S.

Compact disperse ferric hydroxide. H. W. KOHLSCHÜTTER and H. NITSCHMANN (Z. anorg. Chem., 1936, 229, 45—48; cf. this vol., 167).—Comments on a paper by Krause and Krzyżanski (*ibid.*, 947).

F. L. U.

Calcium ferrite hydrates. H. HOFFMANN (Zement, 1936, 25, 675—680, 693—698, 711—716, and Mitt. zementtech. Inst. Tech. Hochschule Berlin, 1935, 52, 63 pp.).—Interaction of a mixture of $FeCl_3$ and $CaCl_2$ in H_2O with a large excess of CO_2 -free NaOH solution afforded material containing $CaO : Fe_2O_3 : H_2O = 4 : 1 : 14$ and $4 : 1 : 7$. A mixture of EtOH and glycerol extracted no CaO, and the X-ray powder patterns were distinct from one another and from those of $Fe_2O_3 \cdot H_2O$ (α - and β -forms), $Ca(OH)_2$, and $CaCO_3$. Anhyd. $2CaO, Fe_2O_3$ shaken with H_2O or aq. $Ca(OH)_2$ gave a solution containing about 1060 mg. of CaO per litre and no Fe_2O_3 . In two experiments analysis of the solid phase gave $CaO : Fe_2O_3 = 3.4$ and 2.9, respectively, and an X-ray powder pattern similar to the $4 : 1 : 7$ prep. CaO, Fe_2O_3 does not react with H_2O or aq. $Ca(OH)_2$ whilst $4CaO, Fe_2O_3, Al_2O_3$ gives an equilibrium solution containing 640 mg. of CaO per litre, and a solid phase containing $Fe(OH)_3, 3CaO, Al_2O_3$ hydrate, and an unknown hydrated Ca ferrite which probably also exists in equilibrium with solutions containing between 1060 and 640 mg. of CaO per litre.
G. H. C.

Ferric ammonium chlorides. Anomalous mixed crystals. E. GRUNER and L. SIEG (Z. anorg. Chem., 1936, 229, 175—187).— NH_4Cl forms anomalous mixed crystals only with those chlorides of heavy metals which show a moderate tendency to double salt formation, and then only when such double salts are readily sol. The phenomenon is observed with $MnCl_2, CoCl_2, NiCl_2, FeCl_2$, and especially $FeCl_3$. Crystals in which the $FeCl_3$ content is $> 14\%$ show only NH_4Cl in the X-ray diagram, with the lattice const. very little changed. When the proportion of $FeCl_3$ is $> 45\%$ the lattice of the double salt $(NH_4)_2[FeCl_5 \cdot H_2O]$ (characterised by its H_2O -v.p.) is observed. The structure of the mixed crystals is discussed.
F. L. U.

Constitution of compounds formed in A. Martini's micro-reactions. J. V. DUBSKÝ and A. LANGER (Chem. Listy, 1936, 30, 227—230).—The compounds described by Martini (A., 1929, 287) are of the type $M(CNS)_2, B_2$ ($M=Co, Ni, \text{ or } Cd; B=C_5H_5N \text{ or } NH_2Ph$); the formulæ proposed by Martini are erroneous.
R. T.

Quantitative spectral analysis. H. TRICHÉ (Bull. Soc., chim., 1936, [v], 3, 1817—1820).—The methods of controlled comparison spectra and of internal scale are equally accurate and both yield trustworthy results.
J. W. S.

Crystallographic identification of substances. V. V. DOLIVO-DOBROVOLSKI (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 33—48).—A discussion.
R. T.

Accuracy of acid-base titrations calculated from the titration curves. S. KILPI (Suomen Kem., 1936, 9, A, 93—94; B, 19—20; cf. A., 1935, 594, 1091, 1214; this vol., 692).—Expressions based

on Van Slyke's equation for the buffer capacity (cf. A., 1922, i, 893) are derived for the inaccuracy in a weak acid or base-strong base or acid titration due to an error in the end-point η_{π} .
R. C. M.

Roqui-purple, a new indicator. F. L. RODUTA and G. A. QUIBILAN (Searchlight, 1936, 1, No. 1, Reprint).—Roqui-purple, prepared from dinitrophenylhydrazine and naphthaquinonesulphonate in MeOH, is claimed to be a good indicator, comparing very favourably with phenolphthalein.
F. R. S.

Interferometric analysis of heavy water. N. S. FILIPPOVA and M. M. SLUCKAJA (Acta Physicochim. U.R.S.S., 1936, 5, 131—136).—A modification of the method hitherto used (A., 1934, 618) for the interferometric analysis of H₂O-D₂O mixtures is described. The temp. coeff. of Δn has been determined at 18—25° for a series of mixtures.
F. L. U.

Titration errors due to formation of mixed crystals in potentiometric analysis. H. FLOOD (Z. anorg. Chem., 1936, 229, 76—84).—Expressions for the displacement of the end-point obtained from the potentiometric titration curves in pptn. reactions are deduced for the cases where (1) complete equilibrium between ppt. and solution is rapidly established, (2) equilibrium is not established after each addition of titration liquid.
F. L. U.

Titration errors in the potentiometric determination of bromide and chloride in mixtures. H. FLOOD and B. BRUUN (Z. anorg. Chem., 1936, 229, 85—96; cf. preceding abstract).—The % displacement of the end-point in potentiometric titrations of Br⁻-Cl⁻ mixtures by AgNO₃ after addition of Ba(NO₃)₂ is given by $100(b/a)\{1 - (b/La)^{1/L} - (1/L)\}$, in which $b/a = \text{Cl}^-/\text{Br}^-$, $L = 400 = \text{ratio of solubility product of AgCl to that of AgBr}$. The function of Ba(NO₃)₂ is to coagulate colloidal Ag halide. Errors in the absence of coagulating electrolyte are not entirely explicable by mixed crystal formation, but are due partly to adsorption.
F. L. U.

Colorimetric determination of small quantities of bromine in presence of a large excess of chlorine. P. BALATRE (J. Pharm. Chim., 1936, [viii], 24, 409—413).—Small amounts of Br⁻ are best determined (error <5%) by a modification of the method of Stenger *et al.* (A., 1935, 835) in which Br is liberated by 0.005*N*-NH₂Cl, suitably buffered, followed by Na₂S₂O₃. The technique is described.
J. W. B.

Determination of dissolved oxygen in boiler feed-water.—See B., 1936, 1023.

Determination of small concentrations of sulphur dioxide and hydrogen sulphide in air. II. V. G. GUREVITSCH and V. P. VENDT (J. Gen. Chem. Russ., 1936, 6, 962—971; cf. A., 1930, 879).—SO₂ and H₂S are converted into H₂SO₄, which is determined. SO₂ is oxidised by air in 0.2% aq. NH₃ during 30 min.; only 3% of H₂S present in SO₂ is oxidised under the same conditions. The (NH₄)₂S thus formed gives (NH₄)₂SO₄ when treated with H₂O₂. The determination of SO₄^{''} before and after the treatment with H₂O₂ affords the vals. of SO₂ and H₂S. Klinke's method of determining H₂SO₄ (A., 1925, ii, 239)

is not sensitive enough. The nephelometric method of determining PbSO₄ in dil. EtOH is convenient; the error is $> 2.5 \times 10^{-7}$ g. of SO₂ or H₂S. J. J. B.

Determination of sulphur in plain and alloy steels.—See B., 1936, 1098.

Direct titration of sulphate with barium chloride using sodium rhodizonate as external indicator. A. MUTSCHIN and R. POLLAK (Z. anal. Chem., 1936, 106, 385—399).—The use of Na rhodizonate (I) as external indicator, and titration in cold neutral solution, is recommended in order to avoid the decomp. of (I) by acids. In presence of much NH₄Cl, 10—20% of COMe₂ is added to overcome the resulting interference with the pptn. of BaSO₄. In presence of Na and small amounts of K, COMe₂+AcOH is added. Mg interferes slightly owing to the pink coloration developed with (I). Titration is not possible in presence of Ca or heavy metals.
J. S. A.

Determination of small quantities of nitric acid by means of phenoldisulphonic acid. E. REMY and H. ENZENAUER (Arch. Pharm., 1936, 274, 435—439).—The NO₃['] content of H₂O in presence of NO₂['] is determined colorimetrically using a solution of the product of PhOH and fuming H₂SO₄, neutralised with 50% KOH. Alkaline K Na tartrate solution is used to prevent pptn. of Ca^{''} and Mg^{''}.
F. R. G.

Detection of nitrites. J. C. GIBLIN and G. CHAPMAN (Analyst, 1936, 61, 686).—The test, sensitive to 1 p.p.m., is based on the formation of Me-orange from NPhEt₂ and sulphanilic acid.
E. C. S.

Colorimetric determination of phosphorus. H. L. BROSE and E. B. JONES (Nature, 1936, 138, 644).—The method described enables a reaction to be followed by means of a photo-electric colorimeter until equilibrium is reached. In a modification of the Fiske-Subarow microchemical method, 10⁻⁹ g. of P per c.c. can be detected and changes of <10⁻⁷ g. can be accurately measured. With very small amounts of P the approx. steady state is reached in 20 min., but with $\sim 0.5 \times 10^{-6}$ g. per c.c. the colour should not be read for 2 hr.
L. S. T.

Oceanographical chemical investigations with the Zeiss Pulfrich photometer. I. Apparatus. II. Procedure. III. Determination of phosphate. IV. Influence of other substances on the phosphate determination. V. Determination of total phosphate, plankton phosphate (living matter) and of turbidity. H. KALLE (Ann. Hydrogr. marit. Meteorol., 1931, 59, 313—317; 1933, 61, 124—128; 1934, 62, 65—74, 95—102; 1935, 63, 58—65, 195—204; Chem. Zentr., 1936, i, 830—831).—III. The optimum conditions for the use of Osloer's molybdate reagent were determined.

IV. Traces of Cu reduce the colour intensity in the determination of PO₄^{'''} in sea-H₂O. SiO₂ has no effect. AsO₄^{'''} and oxalic acid interfere. As₂O₃ intensifies the colour.

V. 25 c.c. of the sea-water are evaporated with 1 c.c. of conc. H₂SO₄ and 0.2 c.c. of 0.001*M* aq. CuSO₄. The residue is dissolved in 5 c.c. of H₂O, and 1 c.c. of 4% CS(NH₂)₂ solution is added to reduce As^v

to As^{III}. 5 drops of 0.05% aq. 2:5 dinitrophenol are added and the solution is neutralised with aq. NH₃. Total PO₄^{'''} is then determined. The plankton PO₄^{'''} is determined by difference after filtering through a fine paper to remove plankton. The determination of turbidity with the Pulfrich photometer is described.

H. J. E.

Determination of phosphoric acid.—See B., 1936, 1036, 1059.

Boric acids and borates. Borax as titration substance. G. KILDE (Dansk Tidsskr. Farm., 1936, 10, 273—296).—Analytical borax should be recryst. below 50° and kept over saturated aq. NaCl+sucrose to avoid formation of the pentahydrate. M. H. M. A.

Micrometric estimation of quartz in rocks.—See B., 1936, 1093.

Detection of carbon monoxide. A. LABÒ (Boll. chim.-farm., 1936, 75, 521—531).—Methods for the detection and determination of CO are discussed.

O. J. W.

Determination of krypton content of air. F. KÖRÖSY (Magyar chem. Fol., 1935, 41, 21—25; Chem. Zentr., 1936, i, 385).—The Kr:A ratio is determined spectrographically in an unfractionated inert gas mixture.

J. S. A.

Causes of contamination of precipitates. III. Precipitation processes in which various electrolytes take part. Classification. Z. KARAOGLANOV (Z. anal. Chem., 1936, 106, 399—407).—From the author's previous work, pptn. processes are classified into four types. (a) Pptns. unaccompanied by any secondary reactions, e.g., pptn. of AgCl or CaC₂O₄. The formation of pure pptns. in these cases is contrary to adsorption theories of contamination. (b) Pptns. accompanied by a simultaneous secondary reaction, e.g., pptn. of SO₄^{''} or CrO₄^{''} with BaCl₂, Ba(NO₃)₂, PbCl₂, or PbBr₂ (cf. this vol., 1352). (c) Pptns. followed by a secondary reaction; e.g., pptn. of Cu(OH)₂ in presence of excess of CuSO₄, followed by formation of basic salt. (d) Pptns. accompanied by a secondary physical process, such as adsorption or mixed crystal formation.

J. S. A.

Qualitative analysis of cations without use of H₂S or (NH₄)₂S. M. B. SCHTSCHIGOL and N. M. DOUBINSKI (Ann. Chim. Analyt., 1936, [iii], 18, 257—261).—Ag, Hg, and Pb are pptd. with HCl, and the solution is evaporated down with HNO₃, removing Sn and Sb as oxides. The solution is treated with Na₂CO₃+NH₄Cl+aq. NH₃, thereby pptg. Bi, Fe, Mn, Al, Cr, Ca, Sr, Ba, and Mg (in presence of PO₄^{'''}). Al and Cr are dissolved by treating the ppt. with Na₂O₂, and Ba, Ca, Sr, and Mg are dissolved away from Bi, Fe, and Mn by warming with Na₂HPO₄+AcOH.

J. S. A.

Potentiometric determination of calcium in solutions. D. M. GREENBERG and C. E. LARSON (J. Biol. Chem., 1936, 115, 769—770).—Ultrafiltration experiments show that gelatin adsorbs little or no Ca at its isoelectric point (p_H 4.8) or at p_H 4.3, in disagreement with Tendeloo's results (this vol., 443) obtained by an e.m.f. method.

F. A. A.

Detection of zinc with potassium ferricyanide and *p*-phenetidine. L. SZEPELLÉDY and S. TANAY (Z. anal. Chem., 1936, 106, 342—348).—0.00005 mg. of Zn may be detected by the blue coloration given by *p*-OMe·C₆H₄·NH₂+K₃Fe(CN)₆ in presence of Zn. In presence of Ag, Pb, Bi, and Sn the sensitivity is lowered by the simultaneous formation of white ferrocyanide ppts. A large excess of Mg, K, Na, Ca, Sr, or Ba has no influence.

J. S. A.

Internal electrolysis. I. Determination of small quantities of cadmium and nickel in zinc. J. G. FIFE (Analyst., 1936, 61, 681—684; cf. A., 1930, 884).—To determine Cd an anolyte containing ZnCl₂ and NH₄Cl and a catholyte containing the mixture to be analysed, NH₄Cl, NaOAc, AcOH, and N₂H₄.HCl are recommended. Electrolysis for 30 min. is required for >10 mg. of Cd, and 45 min. for >10 mg., at 70°. For the determination of Ni, the anolyte contains, in addition, aq. NH₃, and the catholyte contains the mixture to be analysed, NH₄Cl, and Na₂SO₃. The electrolysis is carried out for 30—60 min. at 65°.

E. C. S.

[Spectrographic] determination of cadmium and lead in zinc.—See B., 1936, 1099.

Determination of lead in potable waters.—See B., 1936, 1134.

Electrolytic determination of copper. H. MOHLER and J. HARTNAGEL (Mitt. Lebensm. Hyg., 1936, 27, 131—133).—The apparatus described provides for voltage and current control over a wide range and enables 5—10 mg. of Cu to be deposited at 60—70° in 40 min. on a Pt gauze cathode, using a Pt spiral anode. Canned vegetables are ashed and extracted in presence of H₂SO₄, removal of SiO₂ being unnecessary; 66—102 mg. of Cu per kg. were found.

J. G.

Determination of cuprous oxide as applied to sugar analysis.—See B., 1936, 1063.

Sensitive test for copper.—See this vol., 1398.

8-Hydroxyquinoline method for determination of aluminium, iron, and titanium. L. STUCKERT and F. W. MEIER (Sprechsaal Keram., 1935, 68, 527—529; Chem. Zentr., 1936, i, 386).—The gravimetric method is trustworthy if SiO₂ is first removed. Titration with KBrO₃+KBr gives low results in presence of Fe.

J. S. A.

Analysis of felspar. Volumetric determination of alumina.—See B., 1936, 1036.

Catalytic detection of manganese. L. SZEPELLÉDY and M. BARTFAY (Z. anal. Chem., 1936, 106, 408—416).—10⁻⁹ g. of Mn in 5 c.c. of solution may be detected by the catalysed oxidation of *p*-phenetidine (I) [0.1 c.c. of 0.1% (I) hydrochloride] by KIO₄ (0.5 c.c. of saturated solution) in neutral solution. 1000 parts of Cr, Fe (in presence of NaF), Co, or Sn do not interfere; in presence of Zn, Sn, Hg, and Al, NaOAc is added.

J. S. A.

Determination of manganese in tungsten and ferrotungsten.—See B., 1936, 1099.

Macro-detection of cobalt. II. F. P. DWYER (J. Proc. Austral. Chem. Inst., 1936, 3, 277—280).—

Methylene-blue (I) + KCN, or (I) + dimethylglyoxime (II) + NH_3 are added to the solution. The strong reducing action of $\text{K}_4\text{Co}(\text{CN})_6$ or the Co-(II) complex reduces (I) in presence of $5\text{--}10 \times 10^{-6}$ g. of Co. Fe, Ni, Cr, Cu, Sn, and Ti, which interfere, are removed by successive treatment with KMnO_4 , aq. SO_2 , and KCNS before adding an excess of the reagent. J. S. A.

Gravimetric separation of quadri- and hexavalent uranium. I. F. HECHT and H. KRAFFT-EBING (*Z. anal. Chem.*, 1936, **106**, 321—330).— U^{IV} may be quantitatively separated from U^{VI} by pptn. with $\text{H}_4\text{P}_2\text{O}_6$ in acid solution. Subsequent oxidation of the ppt. and determination of U as $(\text{UO}_2)_\text{P}_2\text{O}_7$ gives high results. Mo and U^{VI} may be separated by pptg. U from 0.5% H_2SO_4 solution by means of 8-hydroxyquinoline (I). U may then be pptd. by (I) on addition of NH_4OAc . The method is proposed, following the removal of P with $(\text{NH}_4)_2\text{MoO}_4$, for the determination of U after pptn. with $\text{H}_4\text{P}_2\text{O}_6$. J. S. A.

Systematic analytical procedure without use of hydrogen sulphide. V. J. PETRASCHENJ (*Z. anal. Chem.*, 1936, **106**, 330—342).—The method is based on the solubilities of the phosphates. Sn and Sb are first removed by evaporation with HNO_3 ; Pb and Ag are pptd. as chlorides. The solution is then treated with $(\text{NH}_4)_2\text{HPO}_4$ and a large excess of NH_3 . The ppt. is further subdivided into groups based on the differing solubility of the phosphates in 2*N*-AcOH and in 0.5*N*- HNO_3 . J. S. A.

Analysis of gold-palladium-silver alloys.—See B., 1936, 1099.

Determination of gold in dental gold alloys.—See B., 1936, 1099.

Gas-tight furnace for thermocouple standardisation. C. D. NIVEN (*Canad. J. Res.*, 1936, **14**, A, 177—180).—A gas-tight furnace with H_2O -cooled lid for calibrating thermocouples in molten metals in an atm. of N_2 or coal gas is described. R. S. B.

Preparation of a sensitive vacuum thermoelement. E. PICKER and G. RUDINGER (*Z. tech. Physik*, 1935, **16**, 265—267; *Chem. Zentr.*, 1936, **i**, 814).—The element consists of two thin overlapping layers of Fe and constantan, prepared by evaporation in vac. onto a thin strip of mica, which is finally mounted in vac. H. J. E.

Simple apparatus for measuring light absorption. J. AUSCHKAP (*Latvij. Univ. Raksti*, 1936, **3**, 11—14).—An absorption cell for the comparison of two liquids is described. H. J. E.

Complementary filters for photographing the Raman spectra of crystal powders. R. ANANTHAKRISHNAN (*Current Sci.*, 1936, **5**, 131—132).—Monochromatic light is used for excitation, and all scattered light of this λ is absorbed before entering the spectrograph. C. W. G.

Filter opaque to ultra-violet light. G. HEYNE and M. SCHÖN (*Angew. Chem.*, 1936, **49**, 784).—Durophen lacquer 218V in thin layers is opaque to light of $\lambda < 4000$ Å., but practically non-absorbing in the visible region. J. S. A.

Quantitative analysis of the photochemical bleaching of visual purple solutions in monochromatic light. H. J. A. DARTNALL, C. P. GOOD-EVE, and R. J. LYTCHGOE (*Proc. Roy. Soc.*, 1936, **A**, **150**, 158—170).—An apparatus has been devised for determining the rate of bleaching and an equation is derived for the change of absorption with time, under ideal photochemical conditions. L. L. B.

Photo-electric sedimentation measurement. C. ENDERS and A. SPIEGL (*Kolloid-Z.*, 1936, **77**, 37—38).—The measurement of sedimentation by determination of the change in absorption of light compares favourably with the kinetic method. E. S. H.

Standardisation of photo-electric cells for the measurement of energy. H. H. POOLE and W. R. G. ATKINS (*Sci. Proc. Roy. Dublin Soc.*, 1936, **21**, 363—379).—Using a W-filament lamp having a rated colour temp. of 2360° abs. the consts. for a Weston Se rectifier cell have been determined for different regions of the spectrum isolated by means of Jena, and Corning sextant green, glass filters. Owing to uncertainties in the colour temp. of the source, these consts. may contain an error up to 20%; further, the spectral distribution of energy for the standard lamp is very different from that for daylight, which may account for differences between the results of daylight measurements (using the consts.) and those of Abbot (A., 1931, 592). R. C. M.

Large quartz spectrograph for examination of biological material. J. S. FOSTER (*Canad. J. Res.*, 1936, **14**, A, 173—176).—A comparatively inexpensive apparatus with a Cornu prism is described. R. S. B.

Spectro-pleochroism-meter and investigation of mineral dichroism. N. VEDENEVA and S. GRUM-GRSHIMAILO (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **3**, 383—385; cf. A., 1935, 58).—Apparatus for the measurement of the spectral distribution of dichroism at varying temp. is described. With increasing temp. the max. dichroism of coloured tourmaline is decreased and shifted to longer λ . For pink and blue tourmalines the change is irreversible above 425° and 275° , respectively. O. D. S.

Measurements of the intensity of X-ray radiation with a proportional amplifier. V. VEKSLER and B. ISAEV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **3**, 369—370).—The amplifier was tested by means of the continuous spectrum of W. O. D. S.

X-Ray fluorescent screens. H. STEPS (*Fortschr. Röntgenstr.*, 1935, **52**, 293—299; *Chem. Zentr.*, 1936, **i**, 826).—A photometric method of measuring the intensity of fluorescence is described. H. J. E.

Thermal control in minimum-deviation refractometry and temperature coefficients for a medium flint glass. L. W. TILTON (*J. Res. Nat. Bur. Stand.*, 1936, **17**, 389—400).—Details are given of an arrangement in which the spectroscopy prism is mounted and adjusted in a thermostated bath of stirred air contained in a water-jacketed cylinder provided with plane-parallel windows capable of adjustment to cover a wide range of prism angles.

and refractive media. Data showing the variation of n with temp. for a medium flint glass are recorded.

J. W. S.

Step compensator for the Jamin interference refractometer when illuminated with white light. H. BILLING (*Z. Physik*, 1936, 103, 57—60).—For direct readings the eyepiece scale has a limited measurement range. A five-fold extension is obtained by inserting a glass plate cut into four steps, each 10 μ thick, in the beam passing through the comparison tube. The field of view is thereby divided into five strips in one of which the interference fringe appears.

H. C. G.

High-temperature vacuum Debye-Scherrer X-ray camera. J. E. DORN and G. GLOCKLER (*Rev. Sci. Instr.*, 1936, [ii], 7, 389—390).—Temp. up to 500° can be used, and are measured by means of a thermocouple.

C. W. G.

Use of high-frequency discharge tubes as electrical counters. S. C. CURRAN (*Phil. Mag.*, 1936, [vii], 22, 599—616).—An investigation of the working conditions and sensitivity of various kinds of tubes is reported.

N. M. B.

Amplifier for the coincidences of proportional wire counters. G. BERNADINI, D. BOCCIARELLI, and F. OPPENHEIMER (*Rev. Sci. Instr.*, 1936, [ii], 7, 382—383).—The coincidences between two proportional wire counters are used to detect the recoil protons ejected by neutrons from a thin layer of paraffin.

C. W. G.

Stereo-comparator for work with Wilson's chamber. L. GROSCHEV, N. DOBROTIN, and J. FRANK (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, 3, 289—290).—An instrument for calculating the spatial distribution of tracks of particles in the Wilson chamber from stereoscopic photographs is described.

R. S. B.

Photography of minima in the magneto-optic apparatus. G. HUGHES (*J. Amer. Chem. Soc.*, 1936, 58, 1924—1932).—Technique demonstrating the reality of the min. is described.

E. S. H.

Resonance method of determining dielectric constants. F. HUMMEL (*Z. tech. Physik*, 1935, 16, 264—265; *Chem. Zentr.*, 1936, i, 116).—Apparatus is described.

J. S. A.

Application of radio waves to measurement of dielectric constants of non-conducting liquids. D. DOBORZYŃSKI (*Hochfrequenztech.*, 1935, 46, 92—94; *Chem. Zentr.*, 1936, i, 116—117).—The use of radio-frequencies in measurements by the resonance method is described.

J. S. A.

Applications of dielectric constant measurement. J. HENRION (*Rev. Univ. Mines*, 1935, [viii], 11, 412—415; *Chem. Zentr.*, 1936, i, 117).—A review.

J. S. A.

Normal element of small potential. W. GREMMER (*Physikal. Z.*, 1936, 37, 697—699).—The use of Cd amalgams of different concn. in CdSO₄ solution as a normal element of small potential has been investigated.

A. J. M.

Applications of the glass electrode in conjunction with the valve potentiometer. F. MÜLLER

and W. DÜRICHEN (*Z. Elektrochem.*, 1936, 42, 730—732).—Apparatus and technique for automatic p_H control are described.

E. S. H.

Agar and potassium chloride bridge for use with calomel half-cells. I. M. ROBERTSON (*Analyst*, 1936, 61, 687—688).

E. C. S.

Electrometric p_H equipment and hysteresis of calomel electrodes. B. WINGFIELD and S. F. ACREE (*J. Amer. Leather Chem. Assoc.*, 1936, 31, 403—406).—The temp. error of a saturated calomel electrode is 0.04 p_H for a change of 8.4°. Measurements should be conducted in a const.-temp. bath or under conditions which have varied $\pm 1^\circ$ for 7—10 hr. A glass electrode assembly in which the calomel electrode is enclosed in a protecting Dewar flask is described.

D. W.

Electrolysis stand. W. BORKENSTEIN (*Z. anal. Chem.*, 1936, 106, 427—429).

J. S. A.

Phosphorus pipette for determination of oxygen. Z. B. SÓLYOM (*Magyar chem. Fol.*, 1935, 41, 94—95; *Chem. Zentr.*, 1936, i, 385).

J. S. A.

Automatic pipette for sedimentation analysis. E. HOFFMANN (*Kolloid-Z.*, 1936, 77, 44—45).

E. S. H.

Pore viscosimetry of molecular aggregation in solution. H. WISLICENUS (*J. pr. Chem.*, 1936, [ii], 147, 124—132; cf. *A.*, 1933, 801).—An improved form of the pore viscosimeter is described and its use is illustrated by results obtained for sucrose and sol. starch solutions.

J. W. S.

Forceps for handling radioactive substances. L. F. CURTISS (*Rev. Sci. Instr.*, 1936, [ii], 7, 393—394).—Protection for the operator's hand is secured by a length of about 20 cm. The forceps are self-closing.

C. W. G.

Pyrex glass seals. V. H. FRAENCKEL (*Rev. Sci. Instr.*, 1936, [ii], 7, 395).—Corning glasses suitable for sealing to Pyrex glasses are listed.

C. W. G.

Metal oil diffusion pump: multiple nozzle type. I. AMDUR (*Rev. Sci. Instr.*, 1936, [ii], 7, 395—396).—A simple all-metal pump with a speed of 250 litres per sec. is described.

C. W. G.

Arrangement for mixing liquids in bottles. H. WOLLENBERG (*Pharm. Zentr.*, 1936, 77, 660).—A rotary shaking device is described.

J. S. A.

Adjustable support and stand for Bunsen burners. I. A. BALINKIN (*J. Chem. Educ.*, 1936, 13, 414).

L. S. T.

Calculation of surface tension from experiment. IV. A. W. PORTER (*Phil. Mag.*, 1936, [vii], 22, 726—729; cf. this vol., 552).—Corrections previously considered for the rise in tubes of circular section and various widths for zero angle of contact are extended to various angles in the range 0—90°.

N. M. B.

Thermal decomposition of systems of solid and gaseous components. J. PIAZZA (*An. Inst. Invest. cient. tec.*, 1934, No. 3—4, 57—60; *Chem. Zentr.*, 1936, i, 384).—A dilatometric technique is described.

J. S. A.

Preparation of tin and tin alloys for microscopical examination. H. J. TAFFS (*J. Roy. Micro-*

scop. Soc., 1936, [iii], 56, 300—306).—Modified procedure for polishing, etching, and mounting is described. E. S. H.

Ebulliometry. W. SWIENTOSLAWSKI (Mem. Acad. Polonaise, 1936, A, No. 3, 1—196).—A monograph giving detailed descriptions of the construction and applications of modern ebulliometers. J. W. S.

Efficient expansible mechanical stirrer and its use in organic syntheses. J. G. HILDEBRAND, jun., and M. T. BOGERT (Coll. Czech. Chem. Comm., 1936, 9, 391—394).—The lower ends of pieces of heavy steel spring are attached to the bottom of a vertical brass rod and the other ends are attached to a brass tube sliding over the rod. When the stirrer has been inserted into the flask the stirrer blades are bowed out by forcing down the brass tube with nuts. The device includes a Hg seal and is especially useful for stirring very viscous material. The prep. of Et cyclopentanone-2-carboxylate from Et adipate and Na in PhMe is described, and the yield was increased from 66% to 80% by using the stirrer. J. G. A. G.

Tables for converting d_{20}^{20} into d_4^{20} (vac.). W. FRIEDEL (Arch. Pharm., 1936, 274, 392—397).—Vals. of $d_{20}^{20} - d_4^{20}$ (vac.) to four decimal places are given for vals. of d_{20}^{20} between 0.5892 and 1.5319. F. R. G.

Test for vacuum-tightness of glass grindings. W. A. BOUGHTON (J. Chem. Educ., 1936, 13, 436). L. S. T.

Grinding [ends of] glass tubing and apparatus flat. H. DRAUTZ (Chem.-Ztg., 1936, 60, 886). J. S. A.

Valve for fine regulation of gas pressures and its application in ion [X-ray] tubes. V. KUNZL and J. B. SLAVÍK (Z. tech. Physik, 1935, 16, 272—276; Chem. Zentr., 1936, i, 814—815). H. J. E.

Measurement of small pressure differences at high absolute pressures. E. SCHMIDT (Z. Ver. deut. Ing., 1936, 80, 635—636).—The ring balance frequently employed for this purpose, and a more sensitive apparatus of the horizontal beam balance type, are described. The latter instrument has been satisfactorily employed for determining η of H₂O and steam at pressures \geq 250 atm. and temp. of 350°. R. B. C.

Lecture experiments on inorganic and general chemistry. A. KUTZELNIGG (Angew. Chem., 1936, 49, 813).—The experiments illustrate the rapid growth of fibrous Al₂O₃ by treating Al with HgI₂, and the catalytic oxidation of coal gas by Cr₂O₃. E. S. H.

Priestley, Lavoisier, and Trudaine de Montigny. R. E. OESPER (J. Chem. Educ., 1936, 13, 403—412).—Historical. L. S. T.

Geochemistry.

Redetermination of the protium-deuterium ratio in water. N. F. HALL and T. O. JONES (J. Amer. Chem. Soc., 1936, 58, 1915—1919).—When allowance is made for ¹⁸O, the H/D ratio for surface lake H₂O is 6400 \pm 200. E. S. H.

Heavy water content of salt waters from petroleum springs. I. T. TITANI and K. OKABE (Bull. Chem. Soc. Japan, 1936, 11, 593—597).—The D₂O content of salt waters from ten Japanese petroleum springs depends not only on the depths of the springs but also on the geological formations. C. R. H.

Reaction of ground-water in Finland. A. E. SANDELIN (Suomen Kem., 1936, 9, A, 108—111).—The p_H of 95 samples of H₂O from dairies varied from 5.2 to $>$ 7.6. The acid reaction is due to H₂CO₃ and other acids. J. N. A.

Application of p_H to mineralogy and geology. M. DÉRIBÉRÉ (Ann. Chim. Analyt., 1936, [iii], 18, 262—263).—The rôle of p_H in determining the composition of sediments from mixed (e.g., siliceous and argillaceous) suspensions is indicated. The separability of mixed deposits by flotation depends on the p_H ; thus beryl and SiO₂ have the same floatability at p_H 9, and max. separability at p_H 6.4. J. S. A.

Colloidal silica in natural waters and the "silicomolybdate" colour test. A. R. TOURKY and D. H. BANGHAM (Nature, 1936, 138, 587—588).—The view that the colour intensity in the Diénert-Wandenbulcke reaction for SiO₂ is \propto the crystalloid

SiO₂ is incorrect. The SiO₂ which reacts with the NH₄ molybdate (I) is mainly colloidal, and approx. correct results for the total SiO₂ in natural H₂O are obtained when the SiO₂ has been held in solution for a sufficient time. Warming to 80° with NaOH improves the agreement with gravimetric results. The coloured substance obtained with SiO₂ and (I) is an adsorption complex, and not a true heteropolyacid. L. S. T.

Rapid sulphide deposition on organic residues at volcanic sulphur springs. F. BERNAUER (Zentr. Min., 1935, A, 343—344; Chem. Zentr., 1936, i, 530).—Plant material on the shore of Porto de Levante becomes coated with Fe sulphide in a few days. The deposit gives the X-ray diagram of marcasite. H. J. E.

Lake Ebeity. S. Z. MAKAROV and I. G. DRUSHININ (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 353—374).—The H₂O contains HCO₃' 0.089, Cl' 11.8, SO₄'' 7.57, Br' 0.025, Mg(HCO₃)₂ 0.016, Ca(HCO₃)₂ 0.101, KBr 0.037, KCl 0.026, MgCl₂ 2.96, Na₂SO₄ 12.13, NaCl 15.6 g. per litre. R. T.

Sulphide-carbonate equilibrium in mineral waters. P. N. PALEI (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 327—334).—A formula connecting [H₂S] with HS', S'', CO₂, HCO₃', CO₃'', and OH' concns. is derived. R. T.

Fluorides in the natural waters of Rhode Island.—See B., 1936, 1070.

Graphic representation of the mineral and curative springs of Switzerland. A. NUSSBERGER (Mitt. Lebensm. Hyg., 1936, 27, 201—203).

E. C. S.

(A) Geology of Swiss mineral and curative springs. (B) Geological characteristics of Swiss mineral and curative springs. J. CADISCH (Mitt. Lebensm. Hyg., 1936, 27, 216—243, 244—259).—

(A) The classification and mineralisation of springs and their regional grouping are discussed.

(B) The characteristics of the H₂O of individual spas are given.

E. C. S.

Surface markings on a diamond. W. H. GEORGE (Nature, 1936, 138, 616, 641).—The reproduced photomicrograph of the [111] face of a diamond shows triangular markings of the size predicted by the mosaic hypothesis of crystal structure.

L. S. T.

Mechanics of metasomatism. G. W. BAIN (Econ. Geol., 1936, 31, 505—526).

L. S. T.

Granodiorite laccolith of the Malka river (Caucasus) and its content of radium. S. P. SOLOVIEV (Amer. J. Sci., 1936, [v], 32, 380—391).—This laccolith of Palaeozoic age is intruded into schists. The mean of 52 determinations of Ra is 1.89×10^{-12} g. per g. The upper portion of the mass contains more Ra than the lower. A granodiorite from Mt. Elbrus contains 1.30×10^{-12} and 0.37×10^{-12} .

L. J. S.

Formula of aenigmatite. M. FLEISCHER (Amer. J. Sci., 1936, [v], 32, 343—348).—From published analyses the formula is deduced as X₄Y₁₃(Si₂O₇)₆, where X=Na, Ca, K, and Y=Fe^{II}, Fe^{III}, Ti, Mg, Mn, Al. A special case is Na₄Fe^{II}₉Fe^{III}₂Ti₂(Si₂O₇)₆. In rhönite part of the Si is replaced by Al, and Na by Ca (as in anorthite and albite). Chemically and crystallographically aenigmatite does not belong to the amphibole group.

L. J. S.

Paragenetic relations and mode of formation of minerals and pseudomorphs of the Wendelstein Höhenzug near Nürnberg. S. KLEIN (Zentr. Min., 1935, A, 257—266; Chem. Zentr., 1936, i, 738).

H. J. E.

Occurrence of platinum in the Far East. A. A. MENAJLOV and S. I. NABOKO (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 387—389).—The occurrence and genesis of Pt in far east Siberia are discussed. The paragenesis of sperrylite with sulphides was observed on the Khaikta river. The Amnunakt massif shows some analogy to the S. African Pt deposits, since, whilst the conen. of chromite in the dunites is low, the sulphides are mainly associated with autometamorphosed anorthosites.

O. D. S.

New occurrence of montmorillonite. H. JUNG (Naturwiss., 1936, 24, 667).—Montmorillonite occurs in faults in the basalt at Dolmar near Meiningen.

A. J. M.

Hydrothermal alteration of montmorillonite to feldspar at temperatures from 245° to 300°. J. W. GRUNER (Amer. Min., 1936, 21, 511—515).—Montmorillonite (I) heated in aq. KHCO₃ in Au-lined pressure bombs gives orthoclase after 7 days at 300°. X-Ray analysis showed the orthoclase to be adularia. At 272° or 245° longer heating is necessary. Muscovite is not formed, and 10% KCl solution had no

effect on (I) in 19 days at 300°. The probable reaction is $3[(OH)_2Al_2Si_4O_{10} \cdot 2H_2O] + 4KHCO_3 \rightarrow 4KAlSi_3O_8 + 2Al(OH)_3 + 8H_2O + 4CO_2$.

L. S. T.

Salt cupolas of the Ural-Emba region, and the possibilities of their industrial exploitation. N. I. BUJALOV and M. G. VALJASCHKO (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 335—352).—Geochemical data are recorded for the NaCl-KCl-MgCl₂ deposits.

R. T.

Halloysite and dolomite of Mártonhegy (Martinsberg), Budapest. G. VAVRINECZ (Magyar chem. Fol., 1935, 41, 70—77; Chem. Zentr., 1936, i, 306).—Analyses are recorded.

J. S. A.

Secondary removals and enrichments of gold in gold placers. G. BÜRG (Z. pr. Geol., 1935, 43, 134—139; Chem. Zentr., 1936, i, 34).—A mechanism is advanced for the process.

J. S. A.

X-Ray and optical investigation of the serpentine minerals. G. C. SELFRIDGE, jun. (Amer. Min., 1936, 21, 463—503).—The 100 specimens examined can be classified in two divisions each of which shows slight modifications in the intensities of certain lines. The first division consists of varieties the patterns of which are similar in at. spacing to that of serpentine, best represented by chrysotile, and the second to that of antigorite. Chemical analyses from the lit. are discussed. Many names indicating distinct mineral species should be abandoned in favour of the terms serpentine and antigorite, respectively.

L. S. T.

Minerals of Baveno granite: molybdenum glance. P. GALLITELLI (Rend. R. Ist. lombardo Sci. Lett., 1935, [ii], 68, 277—280; Chem. Zentr., 1936, i, 306).—The significance of the occurrence is discussed.

J. S. A.

Molybdenum glance in the magnetic iron ore deposit of Schwarzen Krux, Schmiedefeld, Thüringer Wald. H. MORITZ (Zentr. Min., 1935, A, 340—342; Chem. Zentr., 1936, i, 529).—The ore contains 0.001—0.05% of Mo. The zones with quartz, fluorspar, and granite are richest in Mo.

H. J. E.

Separation planes in magnetite. J. W. GREIG, H. E. MERWIN, and E. POSNJAK (Amer. Min., 1936, 21, 504—510).—Twinning is not the cause of the separation planes shown in the magnetites examined.

L. S. T.

Devitrified felsite dykes from Ascutney Mountain, Vermont. R. BALK and P. KRIEGER (Amer. Min., 1936, 21, 516—522).—Two analyses are given.

L. S. T.

Aguilarite from the Comstock Lode, Virginia City, Nevada. R. R. COATS (Amer. Min., 1936, 21, 532—534).—Ores from this lode contain aguilarite, Ag₂(S,Se).

L. S. T.

Comparative X-ray and morphological investigation of andalusite, (AlO)AlSiO₄, libethenite, (CuOH)CuPO₄, and adamine (ZnOH)ZnAsO₄. H. STRUNZ (Z. Krist., 1936, 94, 60—73).—Lattice constns. and probable space-groups for adamine and libethenite are determined; these substances are compared with andalusite, with which they are closely

related. The concepts of isomorphy and isotypy are discussed in regard to them. B. W. R.

Crystal form and molecular unit of nagyagite. B. GOSSNER (Zentr. Min., 1935, A, 321—327; Chem. Zentr., 1936, i, 528).—The crystals are tetragonal; a 12.5, c 30.25 Å.; 8 mols. of $6\text{Pb}(\text{S},\text{Te})_2\text{AuTe}_2$ in unit cell. H. J. E.

Origin of pyritic copper deposits of the mesothermal type. J. E. A. KANIA (Econ. Geol., 1936, 31, 453—471).—Fused, powdered Na_2S has been fused separately with pyrite, chalcopyrite, sphalerite, galena, and SiO_2 and the cooled melts extracted with H_2O . The behaviour of the resulting solutions and sols at temp. up to 90° in contact with marble, lime mud-rock, syenite porphyry, argillaceous quartzite, and carbonaceous shale and in presence or absence of CO_2 and/or H_2S is recorded. Marcasite forms from FeS_2 sols with little Na_2S present, and pyrite from Na_2S — FeS_2 solutions. Chalcopyrite crystals resulted from hot alkaline Na_2S — FeS_2 — CuFeS_2 sols as replacement in cryst. limestone. Certain mesothermal, pyritic Cu deposits are described and discussed in the light of the experimental results. L. S. T.

Greensands of Wisconsin. W. H. TWENHOFEL (Econ. Geol., 1936, 31, 472—487).—Analyses of glauconite from Wisconsin are recorded. L. S. T.

Ore deposition south of Ouray, Colorado. I, II. R. S. MOEHLMAN (Econ. Geol., 1936, 31, 377—397, 488—504).—Rock alteration and factors controlling ore deposition are described. Replacement, which has been important in the formation of the deposits, is discussed in detail. The order of deposition of minerals in the San Juan region is discussed. L. S. T.

Magnetic minerals and the practical applications of their magnetism. H. BRONDER (Tids.

Kjemi, 1936, 16, 124—125).—Magnetic separations are discussed. M. H. M. A.

Characteristic properties of palygorskites. H. LONGCHAMBON (Compt. rend., 1936, 203, 672—674).—The dehydration of palygorskites (I) in air saturated with H_2O at 15° has been studied at 20— 1000° . Three regions appear in the wt.—temp. curves, at 20— 100° , near 200° , and near 400° , separated by steps of approx. const. H_2O content. It is considered that (I) exists in two forms (a) and (b), stable up to 350° and at 500— 750° , respectively. With (a) a large proportion of H_2O is zeolitic and after heating at 350° the H_2O lost (7%) is rapidly absorbed from moist air at room temp. (a) passes irreversibly into (b) at 400° and the zeolitic absorption disappears. (I) are compared with the sepiolites (A., 1935, 842).

R. S. B.

Impregnation of North African phosphates by hydrocarbons, and its origin. L. CAYEUX (Compt. rend., 1936, 203, 639—642).—The phosphatic rocks are coloured by impregnations of hydrocarbons probably produced by the decomp. of org. matter; a bituminous liquid, and a solid and gaseous product are present. The origin, disposition, and relation to petroleum deposits are discussed. R. S. B.

Carbon dioxide eruptions from coal seams in Lower Silesia. O. STUTZER (Econ. Geol., 1936, 31, 441—452).—Eruptions of CO_2 , due to reduction of pressure by mining, from bituminous coal seams are described. Fragmentation of the coal appears to be a prerequisite for eruption. The CO_2 is a constituent foreign to the coal and is probably in solid solution with the vitrain. L. S. T.

Silica-sesquioxide ratio of clays in the characterisation of soils.—See B., 1936, 1114.

Iodine in Czechoslovakian soils.—See B., 1936, 1115.

Organic Chemistry.

Relations of carbon and its compounds. W. D. HARKINS (J. Org. Chem., 1936, 1, 52—64).—A review. R. S. C.

Form and formula in organic chemistry. Comparative morphology of carbon compounds. C. WEYGAND (Z. ges. Naturwiss., 1935, 1, 322—329; Chem. Zentr., 1936, i, 739).—A general discussion. H. N. R.

Contributions from a study of dipole moments to the problems of organic chemistry. C. P. SMYTH (J. Org. Chem., 1936, 1, 17—30).—A review. R. S. C.

Oxidation of organic compounds with perchloric acid. A. VIALARD-GOUDOU (Compt. rend., 1936, 203, 565—568).— H_2 is not and C is only slowly attacked by 65% HClO_4 at 200° to give, finally, CO and CO_2 . $\text{H}_2\text{C}_2\text{O}_4$ is oxidised at 155° to give an equimol. mixture of CO and CO_2 , which indicates that reaction occurs with $\text{H}_2\text{C}_2\text{O}_4$ and not its decomp. products. The paraffins are oxidised at 205— 210° , whereas C_2H_4 , C_6H_6 , and PhMe react at 130— 145° .

MeOH, EtOH, and AcOH are easily oxidised, but in no case is O_2 liberated, indicating that decomp. of HClO_4 does not precede oxidation. J. L. D.

Optical activity and chemical structure. P. A. LEVENE and A. ROTHEN (J. Org. Chem., 1936, 1, 76—133).—The configurative relationships of members of homologous series of the type $\text{R}\cdot[\text{CH}_2]_n\cdot\text{CHMe}\cdot[\text{CH}_2]_m\cdot\text{X}$ ($\text{X}=\text{Alk}$, Ar, OH, CO_2H , CN, CHO, OH, NH_2 , NH_3^+ , N_3 , Hal; $\text{R}=\text{Alk}'$ or, occasionally, Ar'; n =usually 0—2; $m=0, 1, 2$, etc.) are discussed; vals. of $[\text{M}]_D^{25}$ are given. The partial rotations of the chromophoric groups can be deduced by analysis of the rotatory dispersion curves (largely unpublished). Experimental observations for aliphatic carbinols are not explicable by the theories of Boys (A., 1934, 832) or Kuhn (this vol., 454); the direction of rotation is considered to be determined by the dissymmetry of the mol. as a whole. Born's model (A., 1935, 917) fails to predict a change of sign when the distance of the chromophoric group from the asymmetric C is changed by one CH_2 group. H. B.

Action of acetyl chloride and carbon monoxide on saturated hydrocarbons in presence of aluminium chloride. H. HOPFF, C. D. NENITZESCU, D. A. ISACESCU, and I. P. CANTUNIARI (Ber., 1936, 69, [B], 2244—2251; cf. A., 1932, 44, 514).—When AcCl and $n\text{-C}_4\text{H}_{10}$ react in the cold in presence of AlCl_3 the product is CH_2Ac_2 formed by autocondensation of AcCl . At $50\text{--}60^\circ$ the main product is COMeBu^β , also formed from $iso\text{-C}_4\text{H}_{10}$. In general CO , or HCOCl arising therefrom, reacts with saturated hydrocarbons in the same manner as the higher acid chlorides with the exception that it can react with the normal, unbranched chain (production of $\text{CHMeEt}\cdot\text{CO}_2\text{H}$ from $n\text{-C}_4\text{H}_{10}$), and addition at the double linking occurs in a different way. The intermediate formation of aldehydes with *tert.*-CHO explains the unusual intrusion of CO between the atoms of the C chain. The complex changes lead to homogeneous products in good yield. The following scheme is typical: $\text{CHMe}_3 (-2\text{H}) \rightarrow \text{CMe}_2\cdot\text{CH}_2$; $\text{CMe}_2\cdot\text{CHO} + \text{HCOCl} \rightarrow \text{CHO}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl} (+2\text{H} - \text{HCl}) \rightarrow \text{Bu}^\gamma\text{CHO} \rightarrow \text{COMePr}^\beta$. $\text{CMe}_2\cdot\text{CH}_2 + \text{HCl} \rightarrow \text{Bu}^\gamma\text{Cl} \rightarrow \text{Bu}^\gamma\text{COCl}$; $\text{CMe}_2\cdot\text{CH}_2 + \text{Bu}^\gamma\text{COCl} \rightarrow \text{COBu}^\gamma\cdot\text{CH}_2\cdot\text{CMe}_2\text{Cl} \rightarrow \text{COBu}^\gamma\cdot\text{CH}_2\text{Pr}^\beta$. If anhyd. AlCl_3 , HCl , and CO are heated in a Cu autoclave at about $80^\circ/100$ atm., a brisk absorption of the gases occurs with production of the stable adduct $\text{HCOCl}\cdot\text{AlCl}_3\cdot\text{CuCl}$, which is vigorously decomposed by H_2O into HCl and CO and with PhMe in presence of anhyd. AlCl_3 gives $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ in small yield. H. W.

Action of aluminium halides on *n*-pentane. A. L. GLASEBROOK, N. E. PHILLIPS, and W. G. LOVELL (J. Amer. Chem. Soc., 1936, 58, 1944—1948).—Dry $n\text{-C}_5\text{H}_{12}$ (liquid or gas + N_2) does not react with freshly sublimed AlCl_3 ; decomp. is initiated by addition of small amounts of H_2O , AlCl (not ArCl), hydrated AlCl_3 , HCl , or HBr (very effective). AlBr_3 alone causes decomp. and gives butanes (1.5—14.1%), isopentane (27.2—55.9%), and higher-boiling material (2.5—5.9%); added H_2O or HBr increases the reaction velocity. The extent of the decomp. depends on the concn. of AlBr_3 and the time of reaction. H. B.

Nitration of normal paraffins. T. URBANSKI and M. SLOŃ (Compt. rend., 1936, 203, 620—622).— C_3H_8 with N_2O_4 at about 100° affords $\text{Pr}^\gamma\text{NO}_2$ and $\text{CH}_2(\text{CH}_2\cdot\text{NO}_2)_2$ in 70% yield; aldehydes and fatty acids are by-products. CH_4 at about 200° gives a poor yield of MeNO_2 together with polynitro-compounds and products of oxidation. J. L. D.

Preparation of pure crystalline aliphatic hydrocarbons. J. STRATING and H. J. BACKER [with, in part, N. BENNINGA and J. Lolkema] (Rec. trav. chim., 1936, 55, 903—914).—The following series of compounds were prepared in a pure state by standard reactions. From undecenoic acid, b.p. $164.5\text{--}165.5^\circ$, undecic acid, b.p. $122\text{--}122.5^\circ/15$ mm., the Et ester, b.p. $89\text{--}89.5^\circ/1$ mm., di-*n*-decyl ketone, m.p. $64.3\text{--}64.5^\circ$, and *n*-heneicosane, m.p. $40.3\text{--}40.5^\circ$, b.p. $172\text{--}172.5^\circ/25$ mm. From lauric acid the Et ester, b.p. $141\text{--}141.5^\circ/8$ mm., di-*n*-undecyl ketone, m.p. $69.5\text{--}69.8^\circ$, and *n*-tricosane, m.p. $47.25\text{--}47.4^\circ$, b.p. $190\text{--}191^\circ/1.5$ mm. From lauryl alcohol, m.p. $24.0\text{--}24.2^\circ$, the bromide, b.p. $130.5^\circ/5$ mm., a mixture (by the Grignard reaction with EtOAc) of *v*-methyl- Δ^μ -

pentacosane, b.p. $218.5\text{--}219.5^\circ/3$ mm., and *v*-methyl-enepentacosane, b.p. $219.5\text{--}220.5^\circ/3$ mm., and *v*-methylpentacosane, m.p. $28.8\text{--}29.0^\circ$. From erucic acid the Me ester, b.p. $217\text{--}217.5^\circ/3$ mm., and (by MgMeI) β -methyl- Δ^β -tricosadiene, b.p. $210.5\text{--}211.5^\circ/3$ mm., which absorbs 1 H_2 (Pt-black; AcOH) at room temp. and a second H_2 at 50° giving β -methyl-*n*-tricosane, m.p. $38.0\text{--}38.5^\circ$ (lit. 42°), b.p. $207.5\text{--}208^\circ/3$ mm. From stearyl chloride, b.p. $195\text{--}195.5^\circ/2$ mm., m.p. $23.2\text{--}23.4^\circ$, *Bu* $^\gamma$ *n*-heptadecyl ketone, b.p. $202\text{--}203^\circ/4.5$ mm., m.p. $44.8\text{--}45.05^\circ$ (semicarbazone, m.p. $78.0\text{--}78.2^\circ$), which resists Clemmensen reduction and catalytic hydrogenation, presumably owing to steric hindrance, and with HI-P gives an impure product, m.p. $21.6\text{--}22.6^\circ$. From $(\text{CH}_2)_2\text{O}$ and $\text{MgBu}^\gamma\text{Cl}$ γ -methylisoamyl alcohol, b.p. $142.6\text{--}143.6^\circ$, the bromide [$\beta\beta$ -dimethyl-*n*-butyl bromide], b.p. $58.5\text{--}59^\circ/51$ mm., γ -methylisoamyl [$\beta\beta$ -dimethyl-*n*-butyl] *n*-heptadecyl ketone (by the Cd or Mg alkyl halide), m.p. $53.45\text{--}53.75^\circ$, b.p. $212.5\text{--}213.5^\circ/3.5$ mm., and $\beta\beta$ -dimethyl-*n*-docosane, m.p. $34.55\text{--}34.75^\circ$, b.p. $191\text{--}191.5^\circ/4$ mm. From Et nonoate, b.p. $226.5\text{--}227.5^\circ$, nonyl alcohol and bromide, b.p. $107.5^\circ/17.5$ mm., κ -*n*-nonyl-*n*- Δ^1 -nonadecene [from $\text{C}_9\text{H}_{19}\cdot\text{MgBr}$ and $\text{CH}(\text{OEt})_3$], b.p. $227.5\text{--}228.5^\circ/2.5$ mm., and κ -*n*-nonyl-*n*-nonadecane, b.p. $232.5\text{--}233^\circ/3$ mm., m.p. -6° to -5.5° . From cyclohexyl alcohol the bromide, b.p. $53^\circ/14$ mm., cyclohexyl *n*-heptadecyl ketone, b.p. $219\text{--}220^\circ/2.5$ mm., m.p. $42.6\text{--}42.85^\circ$ (semicarbazone, m.p. $82.2\text{--}82.5^\circ$), and α -cyclohexyl-*n*-octadecane, b.p. $207.5\text{--}208.5^\circ/3$ mm., m.p. $41.2\text{--}41.45^\circ$. R. S. C.

Polymerisation of unsaturated gaseous hydrocarbons at atmospheric pressure and ordinary temperature by the catalytic action of phosphoric oxide and stabilisation of the liquid polymerides by hydrogenation. E. DESPARMET (Bull. Soc. chim., 1936, [v], 3, 2047—2055).—After an induction period, C_2H_4 , *n*- and *iso*-butene are more or less rapidly and quantitatively adsorbed by P_2O_5 on porous earthenware at room temp. and atm. pressure, and when subsequently heated at 110° the polymeride (usually mainly dimeride) is evolved. In certain cases the two processes can be effected simultaneously and the reaction can be made continuous. The polymerides are unstable, but can be stabilised by hydrogenation under known conditions. Heavy residues, C, and H_2O are not produced.

H. W.

Thermal decomposition of olefinic hydrocarbons. B. M. MICHAÏLOV and J. A. ARBUSOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 423—426; cf. B., 1934, 792; this vol., 451).—Formation of condensation products during the pyrolysis of olefines is avoided by using a 0.5—1.0 sec. contact, and diluting to low partial pressure with steam. Δ^α -Pentene gave at 600° and 650° , respectively, H_2 2.6 and 3.1% (by vol.), CH_4 18.2 and 17.8%, C_2H_4 30.9 and 32.9%, C_2H_6 7.0 and 6.9%, propylene (I) 20.1 and 21.2%, C_3H_8 0.5 and 0.6%, butadiene (II) 13.0 and 11.9%, with 7.7 and 5.6% of Δ^α - and Δ^β -butene (III); Δ^β -pentene gave, at 600° and 650° , respectively, H_2 6.6 and 6.7%, CH_4 47.9 and 40.4%, C_2H_4 14.5 and 17.2%, C_2H_6 5.0 and 4.1%, (I) 5.4 and 10%, (II) 15.5 and 15.6%, (III) 5.1 and 6.0; Δ^α -hexene gave

at 650° and 700°, respectively, H_2 1.8 and 2.4%, CH_4 11.2 and 11.9%, C_2H_4 40.3 and 40.0%, C_2H_6 2.3 and 1.4%, (I) 30.2 and 28.0%, (II) 4.3 and 5.8%, (III) 9.9 and 10.5%; δ -methyl- Δ^2 -pentene at 550°, 600°, and 650°, respectively, H_2 6.2, 6.9, and 7.9%, CH_4 10.2, 9.3, and 8.0%, C_2H_4 14.7, 17.0, and 16.3%, C_2H_6 3.2, 1.2, and 0.9%, (I) 60.6, 59.3, and 58.4%, C_3H_8 0.0, 0.3, and 0.2%, (II) 0.6, 0.9, 1.9%, (III) 3.5, 4.1, and 5.3%, and *isobutene* 1.0, 1.0, and 1.1%.

R. C. M.

Resolution of $\alpha\gamma\gamma$ -trimethylallyl alcohol into optically active forms. D. I. DUVEEN and J. KENYON (J.C.S., 1936, 1451—1453).— $\alpha\gamma\gamma$ -Trimethylallyl alcohol was converted into its *p-xenylurethane*, m.p. 65°, and *H phthalate*, m.p. 81.5°; the *brucine* salt, m.p. 143—144°, $[\alpha]_{5893} -17.0^\circ$ in $CHCl_3$, of this was hydrolysed (HCl) to the *d-H phthalate*, m.p. 43—44°, $[\alpha]_{5893} +14.5^\circ$ in $CHCl_3$, converted (NaOH) into the *d-alcohol*, b.p. 129°, 43°/17 mm., $[\alpha]_{5893} +8.02^\circ$ in $CHCl_3$ (*Ac*, b.p. 51°/15 mm., and *Bz*, b.p. 139°/19 mm., derivatives), reduced (H_2 -Ni) to *d-CHMeBu β -OH*. The *l-H phthalate*, m.p. 44°, $[\alpha]_{5893} -12.8^\circ$ in CS_2 , obtained by HCl hydrolysis of its *strychnine* salt, m.p. 152° (decomp.), $[\alpha]_{5893} -20.64^\circ$ in $CHCl_3$, was hydrolysed (NaOH) to the *l-alcohol*, b.p. 129°, 43°/18 mm., $\alpha_{5893}^D -2.13^\circ$ (*l*, 0.5).

F. R. G.

Condensation of butan- β -one with aldehydes of the type, $CHRR\cdot CHO$. S. G. POWELL and M. M. BALDWIN (J. Amer. Chem. Soc., 1936, 58, 1871—1872).—The ketols obtained from COMeEt and CHMeEt \cdot CHO (obtained by dehydrogenation of CHMeEt \cdot CH $_2$ \cdot OH with a Cu-Cr-Ba oxide catalyst), CHEt $_2$ \cdot CHO, and CHEtBu a \cdot CHO (I) in dil. KOH are dehydrated and then reduced (methods: A., 1925, i, 7; 1933, 492) to ζ -methyl δ -octan- γ -ol, b.p. 81—83°/15 mm., ζ -ethyl δ -octan- γ -ol, b.p. 90—92°/20 mm., and ζ -ethyl δ -decan- γ -ol, b.p. 119—120°/18 mm., respectively, which are oxidised (*loc. cit.*) to β -methylvaleric, β -ethylvaleric, and β -ethylheptic acid (II), b.p. 135°/25 mm., 236°/760 mm., respectively (*piperazine* salts, m.p. 129°, 134°, and 100°, respectively). β -Ethylhexyl alcohol [prepared by addition of Na and AcOH to (I) in Et_2O +aq. $MgSO_4$ so that the mixture is slightly alkaline] and PBr_3 give the bromide (III), which with NaCN and subsequent hydrolysis affords (II). γ -Ethyl δ -octic acid, b.p. 253—256°/760 mm. (*piperazine* salt, m.p. 110°), is prepared (usual method) from (III) and $CH_2(CO_2Et)_2$. The *piperazine* salt of γ -methylhexic acid has m.p. 109°.

H. B.

Alkylation. V. Formation of ethyl ether from ethyl chloride and some theoretical deductions. V. A. ISMAILSKI and B. V. POPOV (Bull. Soc. chim., 1936, [v], 3, 2028—2037).—A solution of *m*- $NH_2\cdot C_6H_4\cdot SO_3H$ (1 mol.), NaOH (2 mols.), anhyd. Na_2CO_3 (1.57 mols.), and EtCl (4.08 mols.) in 96% EtOH is heated in an autoclave at 125° during 13 hr. and the EtCl used, $NHEt\cdot C_6H_4\cdot SO_3H$, $NEt_2\cdot C_6H_4\cdot SO_3H$, and Et_2O formed are determined in the mixture. Secondary changes involve 43.4% of the EtCl taken; of this, 56% is used in the production of Et_2O and 44% in that of EtOH. The schemes $EtCl + NaOH \rightleftharpoons NaOEt + H_2O$ and $EtCl + NaOEt \rightarrow Et_2O + NaCl$ are rejected, since in the aq-

alcoholic medium the equilibrium is almost completely displaced towards the left. More probably, the change involves the formation of oxonium compounds, transformed by NaOH into the oxonium bases, which decompose into $Et_2O + H_2O$ and $EtOH + H_2O$, respectively, and is thus analogous to Hofmann's reaction between amines and alkyl halides. The intermediate formation of oxonium compounds explains also the production of alkylenes from alkyl halides and alcohols and the prep. of Et_2SO_4 from Et_2O and $ClSO_3H$.

H. W.

Tertiary alkyl ethers. T. W. EVANS and K. R. EDLUND (Ind. Eng. Chem., 1936, 28, 1186—1188).—The direct addition of olefines to alcohols by the Reychler reaction (A., 1907, 275) has been elaborated. $CMe_2\cdot CHMe$ and EtOH with H_2SO_4 under pressure at 60° give an equilibrium mixture containing 40% of Et *tert.*-amyl ether, b.p. 101—102°. The following are thus prepared: Me, b.p. 55°, Et, b.p. 73°, Pr^β , b.p. 87—88°, Bu^a , b.p. 123—124°, Bu^β , b.p. 114°, *sec.*-*Bu*, b.p. 114—115°, Ph, b.p. 185—186°, and CH_2Ph , b.p. 82—83°/8 mm., *Bu γ* ether; *Bu γ* *isoamyl* ether, b.p. 138—140°: Me, b.p. 86—87°, and Pr^β , b.p. 114—115°, *tert.*-amyl ether; *Me tert.*-hexyl ether, b.p. 113°; ethylene glycol *Bu γ* , b.p. 153°, Bu_2^γ , b.p. 171°, *Me Bu γ* , b.p. 131—132°, *Et Bu γ* , b.p. 148°, $Bu^a Bu^\gamma$, b.p. 83°/20 mm., and *tert.*-amyl, b.p. 50—55°/3 mm., ether; $\alpha\beta$ -propylene glycol *Bu γ* ether, b.p. 151—153°; glycerol *Bu γ* , b.p. 93—94°/5 mm., and *Bu γ* ether, b.p. 80—82°/4 mm.; diethylene glycol *Bu γ* ether, b.p. 72°/2 mm. The equilibrium reached varies with the olefine used.

R. F. P.

Bromonitromethionic acid. H. J. BACKER (Rec. trav. chim., 1936, 55, 915—920).— K_2 nitromethionate (I) and $Br\cdot H_2O$ at 65° give bromonitromethionic acid, $+4H_2O$, m.p. about 65°, and $+2H_2O$ (retained in vac. over P_2O_5), m.p. 90—91° (decomp.) [*distrychnine*, $+H_2O$, *Ba*, $+3H_2O$, K_2 , Tl_2 , and *dibrucine*, $+6H_2O$, phototropic salts], which regenerates (I) with $K_2S_2O_3$. Dibrucine chloromethionate is also phototropic. Crystallographic data [P. TERPSTRA] are given for three of these salts.

R. S. C.

Addition of sodium hydrogen sulphite to alkylene oxides. W. M. LAUER and A. HILL (J. Amer. Chem. Soc., 1936, 58, 1873—1874; cf. Fromm *et al.*, A., 1928, 868).— $(CH_2)_2O$ with conc. aq. $NaHSO_3$ and $KHSO_3$ gives *Na* (I), m.p. 192—194°, and *K* (II), m.p. 191—193°, β -hydroxyethanesulphonate, respectively, acetylated (method: this vol., 316) to *Na* and *K*, m.p. 258—260°, β -acetoxyethanesulphonate, respectively. *Na* β -myristoyloxyethanesulphonate is prepared from (I) and myristoyl chloride. (I) and (II) with PCl_5 afford $CH_2Cl\cdot CH_2\cdot SO_2Cl$, b.p. 86—88°/13 mm. NH_4 β -chloroethanesulphonate and conc. aq. NH_3 at 105° give taurine, which with $KNO_2 + AcOH$ yields (II).

H. B.

Polysulphones from acetylenes and sulphur dioxide. L. L. RYDEN and C. S. MARVEL (J. Amer. Chem. Soc., 1936, 58, 2047—2050; cf. this vol., 186).— $CH:CR$ [$R=Me$, Et (I), Pr^a (II), Bu^a , *n*-amyl, and Ph (III)] with SO_2 in EtOH followed by paracet-aldehyde (must contain peroxide) give polysulphones, decomp. 250—260°, 210—215° (Ia), 203—208° (IIa),

195—205°, 164—170°, and 250—275° (IIIa), respectively. CMe:CR ($\text{R}=\text{Me, Pr, Ph}$), $(\text{:C}\cdot\text{CO}_2\text{Et})_2$, and allene do not similarly react. The presence of $\cdot\text{CR}\cdot\text{CH}\cdot\text{SO}_2\cdot$ in (Ia), (IIa), and (IIIa) is established by oxidation (aq. KMnO_4) to EtCO_2H , PrCO_2H , and BzOH , respectively. Hydrolysis (aq. NaOH) of (IIIa) affords COPhMe (trace), $\text{CH}_2\text{Ph}\cdot\text{SO}_2\text{Me}$ (IV) (8%), BzOH (20%) and Na_2SO_3 (50%) (the remainder of the S is in the tarry product formed); the formation of (IV) indicates that part of (IIIa) must be $[\cdot\text{SO}_2\cdot\text{CPh}\cdot\text{CH}\cdot\text{SO}_2\cdot\text{CPh}\cdot\text{CH}\cdot]_n$. (IIa) is similarly hydrolysed to COMePr^a (trace). (IIa) could not be reduced (H_2 , Pt, dioxan, room temp.). (IIa) heated to 200—215° gives 50—60% of SO_2 ; in boiling dioxan SO_2 (about 50%) and a little of a compound, $\text{C}_{10}\text{H}_{16}\text{O}_2\text{S}$, m.p. 88°, are formed. SO_2 (62.73%) is liberated when (IIIa) is heated at 140°/45 min.

H. B.

Chemistry of the Claisen condensation. F. ARNDT and B. EISTERT (Ber., 1936, 69, [B], 2381—2393).—The fundamental basis of the theoretical treatment of compounds with multiple linkings is the conception of the intermediate condition identical with that of resonance between electromeric limiting states and to which the term mesomerism has been applied. Also the inductive effect plays a part. The essentials for the Claisen reaction are the ester (amide) component (I) $\text{R}\cdot\text{CO}_2\text{Et}$ and the methylene component (II) $\text{CH}_2\text{R}\cdot\text{CO}\cdot\text{R}$, which must contain CH_2 vicinal to CO and in which CO may be present in CO_2Et . The alkaline condensing agent causes a possibly minute fraction of (II) to release a proton from CH_2 , thus giving EtOH , NH_3 , or H and forming the ionic alkali metal salt of (II). This conception agrees with that of Scheibler in so far as (II) [not (I)] is concerned in this preliminary stage, but differs in that it does not assume the production of an enolate, but of a compound in which Na functions as cation. Na is therefore not directly concerned with any of the subsequent reactions, and the question of the enolic structure of the anion is subsidiary. Such an anion is regarded as being in the intermediate condition between $[\text{CHR}\cdot\text{CO}\cdot\text{R}]'\text{Na}^+$ (III) and $[\text{CHR}\cdot\text{CO}\cdot\text{R}]'\text{Na}^+$. Reaction occurs between (I) and (III) which contains the unused pair of electrons at C. (I) is also capable of mesomerism and can react in the electromeric conditions $\text{R}\cdot\text{CO}\cdot\text{OEt}$ and $\text{OEt}\cdot\text{CR}\cdot\text{O}$ (IV). The initial step in the Claisen condensation therefore consists in the entry of the free pair of electrons of (III) into the octet vacancies of the CO-C atom of (I) in form (IV) giving the anionic product, $[\text{COR}\cdot\text{CHR}\cdot\text{CR}(\text{OEt})\cdot\text{O}]'\text{Na}^+$. The formation of this product is reversible and not detectable experimentally, and the equilibrium lies far on the left. Union of the second CO to the original $\text{CH}_2\cdot\text{C}$ atom of (II) causes this C atom to be placed under the influence of two pronouncedly positive vicinal C atoms, and consequently the remaining proton is much less firmly bound than was originally the case. It therefore unites with the anionic $[\text{OEt}]'$ to form EtOH , thereby giving the anion $[\text{COR}\cdot\text{CR}\cdot\text{CR}\cdot\text{O}]'\text{Na}^+$, which is almost completely enolic, since it thereby contains a conjugated system. The striving to build such a system must be regarded as the most important and controlling factor of the whole Claisen condensation,

since it brings the feature of irreversibility among a no. of reversible changes, many of which occur in only a small degree. This conception renders obvious the need of CH_2 as well as CO in (II) and the impossibility of the replacement of CO by SO_2 ; although the proton-loosening action of SO_2 is $>$ that of CO it cannot function as conjugation partner, since it does not contain true double linkings, but contains O atoms only in semipolar union. It also explains why (II) must contain at least two H attached to active C, since these are eliminated consecutively. Related reactions (aldol condensation, Perkin's and Knoevenagel's syntheses) are discussed. Other views of the course of ester and aldol condensation (enolisation hypothesis, the "intermediate substance" rule, and the hypothesis of the tautomerism, enolate \rightleftharpoons organo-metallic compound) are reviewed.

H. W.

Twitchell's reagent. I. Twitchell's reagent as promoter of esterification. J. N. ZAGANIARIS and G. A. VARVOGLIS (Ber., 1936, 69, [B], 2277—2282).—The hydrolytic and esterifying actions of Twitchell's reagent are in a dynamic equilibrium displaced towards the ester side. Reaction is usually effected with a three-fold excess of one component and 2.3 wt.-% of catalyst calc. on that of the mixture. Heating of the mixture is unnecessary and frequently disadvantageous. Aliphatic acids give good yields of esters with primary, *sec.*, and polyhydric aliphatic and fatty-aromatic alcohols, but not with *tert.* alcohols or phenols, with which little action takes place. Aromatic carboxylic, phenolic, and unsaturated fatty-aromatic acids do not react or give very moderate yields. The following interactions are described. AcOH with MeOH , EtOH , Pr^nOH , *iso.* (I) and *tert.* amyl alcohol, $(\text{CH}_2\cdot\text{OH})_2$, glycerol, $\text{CH}_2\text{Ph}\cdot\text{OH}$, PhOH ; $\text{CCl}_3\cdot\text{CO}_2\text{H}$ with EtOH ; $\text{Pr}^a\text{CO}_2\text{H}$ with EtOH and (I); EtOH with palmitic, oleic, and tartaric acid, $\text{H}_2\text{C}_2\text{O}_4$, BzOH , $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$, and *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$; PhOH and EtOH ; *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and MeOH .

H. W.

Basic acetates of lead.—See this vol., 1464.

Enzymic dehydration of trideuteroacetic acid.

—See this vol., 1418.

Reaction kinetics and the Walden inversion.

W. A. COWDREY, E. D. HUGHES, and C. K. INGOLD (Nature, 1936, 138, 759).—The hydrolysis of *l*- α -bromopropionic acid to give lactic acids of different optical sign is cited as an example connecting optical inversion with structure and conditions. The optical sign depends on whether conditions favour a uni- or a bi-mol. reaction.

L. S. T.

Effect of varying conditions in the catalytic hydrogenation of fatty oils on the nature of the reaction product. III. H. I. WATERMAN, C. VAN VLODROP, and J. A. PEZY (Rec. trav. chim., 1936, 55, 854—858; cf. A., 1933, 258).—Colloidal Ni, prepared by hydrogenation of $\text{Ni}(\text{CO})_4$ in oil, allows rapid hydrogenation of unsaturated aliphatic esters and fatty oils at 50°/1 atm., without destruction of vitamin-A. Hydrogenation follows the "homogeneous reaction scheme" (saturation first of the most unsaturated centres).

R. S. C.

Mechanism of the elaidinisation reaction. S. H. BERTRAM (Chem. Weekblad, 1936, 33, 637—638).—The isomerisation of oleic and elaidic acids in presence of 0.5% of Se at 150° is termol., the Se forming an intermediate complex, in accordance with the hypothesis put forward (this vol., 189). S. C.

Optical properties of fermentation lactic acids.—See this vol., 1419.

Enzymic racemisation of optically active lactic acid.—See this vol., 1560.

Polarographic analysis in the study of keto-enol tautomerism. G. SEMERANO and A. CHISINI (Gazzetta, 1936, 66, 504—509).—The different reduction potentials at a dropping Hg cathode of the keto- and enol forms of a substance can be used to determine the amounts of the two forms in a mixture. By this means the keto-enol tautomerism of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and of CH_2Ac_2 has been investigated.

O. J. W.

Doubly conjugated system in α - and β -licanic acids. R. S. MORRELL and W. R. DAVIS (J.C.S., 1936, 1481—1484).— α - and β -Licanic acids (Brown *et al.*, A., 1935, 607) present in oiticica oil combine with maleic anhydride in CO_2 at 85° to give, respectively, the α -additive compound (I), m.p. 79° [H_4 -derivative (Adams), m.p. 111°], and the β -additive compound (II), m.p. 97—98° (H_4 -derivative, m.p. 72—73°). Oxidation of (I) with 5% $\text{KMnO}_4\text{-Na}_2\text{CO}_3$ at 0° affords γ -ketoazelaic acid (III) (34% yield) and only a trace of valeric acid (IV) (p-bromophenacyl ester, m.p. 73°); ozonolysis of (II) gives mainly (IV) and a substance, m.p. 99—105°. As in the elaeostearic system the $\Delta^{\alpha,\beta}$ -double linkings are involved in the formation of (I) and the $\Delta^{\beta,\gamma}$ -linkings in (II), thus suggesting the *X-trans-trans-cis*-Y $\cdot\text{CO}_2\text{H}$ structure for α - and *X-cis-cis-trans*-Y $\cdot\text{CO}_2\text{H}$ for β -licanic acid. J. W. B.

Sensitive reaction for oxalic acid. O. CARLETTI (Boll. Chim. farm., 1936, 75, 498—499).—A reddish-violet colour, changing to blue, is given by $\text{H}_2\text{C}_2\text{O}_4$ (6.3×10^{-6} g.) with resorcinol in presence of glycerol (1 drop) and H_2SO_4 . F. O. H.

Resorcinol reaction of oxalic acid. M. PESEZ (Bull. Soc. chim., 1936, [v], 3, 2072—2074; cf. this vol., 745).—The oxalate solution is acidified with H_2SO_4 and reduced with sheet Zn in presence of CuSO_4 . A pale blue colour which becomes intense at 100° is developed when 4 drops of this solution are mixed with 2 c.c. of conc. H_2SO_4 and 2 drops of Denigès' resorcinol reagent. The reaction appears sp. for $\text{C}_2\text{O}_4'$ and is not affected by the presence of OCl' , ClO_3' , BrO_3' , NO_2' , NO_3' , or CrO_4'' . It is modified in presence of Br' or I' . $\text{C}_2\text{O}_4''$ interferes with the author's (*loc. cit.*) or Denigès' test for tartaric acid and is removed by pptn. as CaC_2O_4 in AcOH previously to the reduction. H. W.

[Activated form of oxalic acid.] E. SCHERÖER (Ber., 1936, 69, [B], 2243; cf. this vol., 1361; Krauss *et al.*, A., 1930, 577).— HCO_2H cannot be regarded as the "active form" of $\text{H}_2\text{C}_2\text{O}_4$, with which it has only the strongly reducing properties in common. It has not the more important ability to reduce mol. O_2 to H_2O_2 and to lose activity slowly.

H. W.

Oxalato complex compounds of tervalent manganese.—See this vol., 1477.

Diene syntheses and selenium dehydrogenation in their importance for the development of organic chemistry. O. DIELS (Ber., 1936, 59, [A], 195—208).—A lecture.

Condensation of ethyl α -bromoisobutyrate with *n*-alkylmalonic esters. Structure of the lupin alkaloids. H. N. RYDON (J.C.S., 1936, 1444—1448).—In the condensation of $\text{CMeR}'\text{Br}\cdot\text{CO}_2\text{Et}$ with $\text{CRNaX}\cdot\text{CO}_2\text{Et}$ to give $\text{CO}_2\text{Et}\cdot\text{CMeR}'\cdot\text{CRX}\cdot\text{CO}_2\text{Et}$ and $\text{CO}_2\text{Et}\cdot\text{CHR}'\cdot\text{CH}_2\cdot\text{CRX}\cdot\text{CO}_2\text{Et}$, the formation of the latter isomeride is greater when $\text{R}=\text{R}'=\text{Me}$ instead of H , is increased as X changes from Ac to CN and then CO_2Et , and decreased as R changes from H to Et , then Pr^a , Bu^a , and *n*-amyl. Hydrolysis of condensation products of the above type leads to *cis*- α -methyl- α' -ethyl-, m.p. 116°, and - α' -*n*-propylglutarimide, m.p. 78°; α -dimethyl- α' -*n*-butylsuccinic and -glutaric acid, oils; *cis*- α -methyl- α' -*n*-amylglutaric acid, m.p. 76°. In order to confirm the structure of the imide (I) on which the structure of anagyrene was based by Ing (A., 1933, 727), this was synthesised from $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, which with PBr_3 in CHCl_3 or PCl_5 yields respectively, *Et* β -bromo-, b.p. 91—93°/19 mm., and β -chloro-isobutyrate, b.p. 56—58°/10 mm., either of which with *Et* *n*-amylmalonate, NaI , and NaOEt in EtOH gives *Et* α' -carbethoxy- α -methyl- α' -*n*-amylglutarate, b.p. 140—145°/3 mm., hydrolysed to α -methyl- α' -*n*-amylglutaric acid, m.p. 74—75° [imide (II), m.p. 71—72°]. $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ with *n*- $\text{C}_5\text{H}_{11}\text{Br}$ and NaOEt in EtOH gives *Et* α -cyano- α' - α' -dimethyl- α' -*n*-amylsuccinate, b.p. 187—191°/22 mm., 137°/0.9 mm., hydrolysed (KOH) to α -dimethyl- α' -*n*-amylsuccinic acid, m.p. 119° [imide (III), m.p. 64—65°]. Ing's synthetic imide (*loc. cit.*) is a mixture of (II) and (III). (I) has the amended m.p. 58—60° and, although non-homogenous, is regarded as identical with (II), confirming the accepted structures of the lupin alkaloids. F. R. G.

Preparation in a high state of purity of long-chain compounds in view of the determination of their energy contents. II. Brassidic acid type. L. J. P. KEFFLER (J.S.C.I., 1936, 55, 331—333T).—Repeated crystallisations of brassidic acid (as well as other acids of the *trans*-type) do not remove certain impurities when the usual technique is followed. Systematic fractional crystallisation at one const. temp. should be carried out, starting with an amount of solvent many times that which would be just sufficient to dissolve completely the acid at a temp. not far removed from the b.p. of the pure solvent. This amount depends on the nature of the acid to be purified and on the nature and concn. of the impurities admixed with it.

Determination of ascorbic acid.—See this vol., 1567.

Reduction of inactivated *l*-ascorbic acid. I. A. GOLJANICKI and I. S. BELONOSOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 15—16).—*l*-Ascorbic acid, inactivated by heat and O_2 , is regenerated to the extent of 15—17% by addition of sugar and yeast

or, better, also of peroxidase, the necessary 2 H being derived from the change, $\text{CHAc}(\text{OH})_2 \rightarrow \text{AcCO}_2\text{H}$.

R. S. C.

Photochemical reactions of iron gluconates.—See this vol., 1473.

Colour reactions of keturonic acids and a colour test differentiating α - and β -glucosides. F. SHEPPARD and M. R. EVERETT (Proc. Soc. Exp. Biol. Med., 1936, 34, 7—9).—The results are given of the application of various colour tests to the products obtained by oxidising polyhydric alcohols, sugars, and sugar derivatives in 1% aq. solution with Br for 6 weeks at 25°.

W. O. K.

Pectin problem. F. EHRlich (Festschr. Techn. Hochsch. Breslau, 1935, 129—141; Chem. Zentr., 1936, i, 788—789).—Cold alkaline hydrolysis of citrus and apple pectin yields *gelpectolic acid*, $\text{C}_{24}\text{H}_{32}\text{O}_{24}$, which differs in many ways from pectolic acid, into which it is converted by long boiling with H_2O . A structure is suggested.

H. N. R.

Kinetics of sulphonium compounds.—See this vol., 1469.

α - and β -Sulphovaleric acids with a branched chain. H. J. BACKER and D. VAN DER VEEN (Rec. trav. chim., 1936, 55, 887—898).— $\text{CHPr}^\beta(\text{CO}_2\text{H})_2$, m.p. 93°, and SO_3 at <0° give an oily mixed *anhydride*, which on gentle warming decomposes exothermally to CO_2 and α -sulphoisovaleric acid, $+\text{H}_2\text{O}$, m.p. 68° [*Ba*, $+\text{H}_2\text{O}$, +6 and $+\text{8H}_2\text{O}$ (not obtained pure), *Ca*, $+\text{2H}_2\text{O}$, *Pb*, $+\text{2H}_2\text{O}$, *Tl*, *dibrucine*, and *distrychnine* salts], also obtained with $\text{OH}\cdot\text{CHPr}^\beta\text{CO}_2\text{H}$ from $\text{CHPr}^\beta\text{Br}\cdot\text{CO}_2\text{NH}_4$ and $(\text{NH}_4)_2\text{SO}_3$. The *brucine H* or *diquinine* salt leads to the *d-acid*, $[\text{M}]_D -3^\circ$ (*Ba* salt, $[\text{M}]_D +15^\circ$), racemised by NaOH slowly at 100° and more rapidly at 165° and by HCl at 165°. **α -Sulpho- α -methyl-*n*-butyric acid** (I), $+\text{H}_2\text{O}$, m.p. 83° (*Pb*, $+\text{2H}_2\text{O}$, *Ba*, $+\text{3H}_2\text{O}$, *Tl*, and *distrychnine* salts), is obtained in poor yield from SO_3 and $\text{CMeEt}(\text{CO}_2\text{H})_2$ by way of the mixed *anhydride* or with $\text{OH}\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$ from $\text{CMeEtBr}\cdot\text{CO}_2\text{NH}_4$ and in 34% yield from $\text{CHMeEt}\cdot\text{CO}_2\text{H}$ and SO_3 , and is resolved by the *brucine H*, $+\text{1.5H}_2\text{O}$, salt to the *l-acid*, $[\text{M}]_D -36^\circ$ (*Ba* salt, $[\text{M}]_D -27^\circ$), and by the *diquinine* salt, $+\text{5H}_2\text{O}$, to the *d-acid*. $\text{CMe}_2\text{CH}\cdot\text{CH}_2\text{M}$ ($\text{M}=\text{K}$ or NH_4) and $\text{K}_2\text{S}_2\text{O}_7$ at 90° give β -sulphoisovaleric acid (*Ba* and *Pb* salts, $+\text{H}_2\text{O}$). When $\text{CHMe}\cdot\text{CMe}\cdot\text{CHO}$ and SO_3 react at 0° and are then left with Br in light, β -sulpho- α -methyl-*n*-butyric acid (cf. lit.) (II) (*Ba*, $+\text{H}_2\text{O}$, *Pb*, *distrychnine*, $+\text{2H}_2\text{O}$, and *brucine H*, $+\text{3H}_2\text{O}$, salts) is obtained. $\text{OH}\cdot\text{CMeEt}\cdot\text{CN}$ and hot HCl give α -hydroxy- α -methylbutyric acid, m.p. 72—73°, which at 140—150° gives a mixture of angelic and tiglic acids. K tigliate and $\text{K}_2\text{S}_2\text{O}_7$ at 90° give the *stereoisomeride* (III) of (II) (*Ba*, $+\text{0.5H}_2\text{O}$, *Pb*, $+\text{H}_2\text{O}$, and *dibrucine*, $+\text{8H}_2\text{O}$, salts). The *diquinine* salt of (II) gives the *l-acid*, $[\text{M}]_D -26^\circ$ (*Ba* salt, $[\text{M}]_D -40.5^\circ$). The *diquinine* salt, $+\text{3H}_2\text{O}$, of (III) gives the *d-acid*, $[\text{M}]_D +37^\circ$ (*Ba* salt, $[\text{M}]_D -22^\circ$). $\text{CH}_2\cdot\text{CEt}\cdot\text{CO}_2\text{K}$ and $\text{K}_2\text{S}_2\text{O}_7$ at 90° give α -sulphomethyl-*n*-butyric acid (IV) (*Ba* and *Pb* salts, $+\text{H}_2\text{O}$), the *diquinine* salt, $+\text{4.5H}_2\text{O}$, of which gives the *d-acid*, $[\text{M}]_D +24^\circ$ (*Ba* salt, $[\text{M}]_D +7.5^\circ$). $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CO}_2\text{NH}_4$ and

$(\text{NH}_4)_2\text{SO}_3$ give β -sulphopivalic acid (*Ba* salt, $+\text{0.5H}_2\text{O}$). (II), (III), and (IV) resist racemisation, since the activity does not depend on a H adjacent to SO_3H .

R. S. C.

Trideuteroacetdeuter-aldehyde. J. E. ZANETTI and D. V. SICKMAN (J. Amer. Chem. Soc., 1936, 58, 2034—2035; cf. this vol., 316).— C_2D_2 passed into $\text{D}_2\text{O}-\text{D}_3\text{PO}_4-\text{HgSO}_4$ gives *trideuteroacetdeuter-aldehyde* (I), $\text{CD}_3\cdot\text{CDO}$, b.p. 20.5°/756 mm., m.p. —121.7°, v.p. 327 mm. at 0°, and *paratrideuteroacetdeuter-aldehyde* (II), b.p. 124—125°/753 mm., m.p. 13.7°. (I) polymerises fairly readily to (II) when kept in sealed tubes.

H. B.

Mechanism of carbohydrate oxidation. XXII. Preparation and reactions of glyceraldehyde diethyl mercaptal. H. W. ARNOLD and W. L. EVANS (J. Amer. Chem. Soc., 1936, 58, 1950—1952).—Glyceraldehyde, EtSH, and cold conc. HCl give *glyceraldehyde Et₂ mercaptal* (I), b.p. 156—158°/3 mm., and a little of a *compound*, m.p. 126—127.5° [probably formed by condensation of several mols. of (I)]. (I) and CPh_3Cl in $\text{C}_5\text{H}_5\text{N}$ afford the β -*CPh₃ ether*, m.p. 100—101° (α -*Ac*, m.p. 93—94°, and α -*Bz*, m.p. 90—91°, derivatives); the CPh_3 group could not be removed (various procedures) from these compounds. Acetylation ($\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$) of (I) and treatment of the resulting viscous oil with $\text{HgCl}_2+\text{CdCO}_3$ in aq. COMe_2 gives $\alpha\beta$ -diacetylglyceraldehyde, b.p. 154—156°/3 mm., which with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ in aq. EtOH-HCl affords (probably) β -*acetylglyceraldehyde-p-nitrophenylosazone*, m.p. 282—286° (block) (darkens at 235—240°) (all m.p. except this are corr.), and with $\text{MeOH}-\text{NH}_3$ followed by 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$, yields glyceraldehyde-2:4-dinitrophenylhydrazone.

H. B.

Mechanism of carbohydrate oxidation. XXI. Synthesis of glucosidoglyceraldehyde derivatives. H. W. ARNOLD and W. L. EVANS (J. Amer. Chem. Soc., 1936, 58, 1890—1894).—Glyceraldehyde benzylcycloacetal (I) (Fischer and Baer, A., 1932, 364), acetobromo-*d*-glucose, Ag_2CO_3 , and “Drierite” in C_6H_6 give 50% of β - β' -*d*-glucosidoglyceraldehyde benzylcycloacetal tetra-acetate, m.p. 172—173° (corr.), $[\alpha]_D^{25} -19.9^\circ$ in CHCl_3 , cleaved by H_2+Pd -black in MeOH to the amorphous β - β' -*d*-glucosidoglyceraldehyde tetra-acetate (II), m.p. 63°, $[\alpha]_D^{25} -15.5^\circ$ in CHCl_3 , which reduces cold Fehling's solution. Cryst. derivatives (*Ac*, *Bz*, phenylhydrazones) of (II) could not be prepared. (II) with $\text{C}_5\text{H}_5\text{N}$ at 135—140° (bath) followed by Ac_2O affords a syrup containing 8—9% of β -*d*-glucosidodihydroxyacetone penta-acetate (A., 1935, 477), determined as the *p*-nitrophenylhydrazone. β - β' -*l*-Arabinosidoglyceraldehyde benzylcycloacetal tri-acetate, m.p. 142—143° (corr.), $[\alpha]_D^{25} +4.2^\circ$ in CHCl_3 , is obtained (as above) in 7% yield from (I) and acetobromo-*l*-arabinose. Dimeric glyceraldehyde diacetate and TiCl_4 in CHCl_3 at room temp. give 81—87% of *acetochloroglyceraldehyde*, m.p. 174—175° (corr.), which with $\text{CH}_2\text{Ph}\cdot\text{OH}+\text{Ag}_2\text{CO}_3$ affords a mixture of isomeric glyceraldehyde benzylcycloacetal acetates, m.p. 109—110° (corr.) (small amount) and 141—142° (corr.) (Fischer and Baer, *loc. cit.*).

H. B.

Photochemical peroxide formation. IV. Oxidation of acetone by molecular oxygen in ultra-

violet light. Photochemical production of peracetone. R. CANTIENI (Ber., 1936, 69, [B], 2282—2285; cf. this vol., 1091).— COMe_2 is converted by O_2 in ultra-violet light, unfiltered or filtered through glass, into its peroxide (I), the formation of which is retarded by addition of H_2O . Since H is not produced by photolysis of COMe_2 and dry COMe_2 is transformable into (I), the production of H_2O_2 is excluded. (I) is unstable in ultra-violet light, its rate of decomp. increasing with its concn. The following scheme is therefore adopted, in which COMe_2 is its own O carrier. $\text{COMe}_2 + \text{CMe}_2 \xrightarrow{\text{O}} \text{(II)} \rightarrow \text{MeCHO} + \text{CH}_2\text{O} + \text{COMe}_2$; $\text{MeCHO}^* + \text{(II)} \rightarrow \text{AcOH} + \text{COMe}_2$; $\text{CH}_2\text{O}^* + \text{(II)} \rightarrow \text{HCO}_2\text{H} + \text{COMe}_2$. In the initial stages of the change the amounts of (I) formed in unit time are approx. const. but diminish with increasing period of irradiation. In ultra-violet light filtered through glass the formation of (I) is one fourth as fast as in unfiltered light.

H. W.

Condensation of acetone with formaldehyde.

L. A. GERMANN (Compt. rend., 1936, 203, 586—587).— CH_2O (1 mol.) in anhyd. EtOH containing K_2CO_3 with COMe_2 (2 mols.) below 30° affords $\text{CH}_2\text{Ac}\cdot\text{CH}_2\cdot\text{OH}$ and β -hydroxymethyl- Δ^a -buten- γ -one (cf. A., 1933, 1144).

J. L. D.

Alkylacetylenes and their additive compounds.

XVII. Synthesis of acetylenic ketones from acetylenic Grignard reagents. J. W. KROEGER and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1861—1863).— $\text{CR}:\text{C}:\text{COMe}$ are best prepared from $\text{CR}:\text{C}:\text{MgCl}$ (which are fairly insol. in Et_2O) and Ac_2O at $<-25^\circ$ in N_2 ; β -keto- Δ^y -octinene, b.p. $76-76.5^\circ/15$ mm., $-\Delta^y$ -noninene, b.p. $89-89.5^\circ/15$ mm., and $-\delta$ -phenyl- Δ^y -butinene, b.p. $101-102^\circ/3$ mm., are described. $\text{CR}:\text{C}:\text{MgBr}$ (I) similarly gives 10—20% of ketone and considerable amounts of $(\text{CR}:\text{C})_2\text{CMe}\cdot\text{OH}$; methyl-di- Δ^a -hexinenyl-, b.p. $123-125^\circ/2$ mm., $-\Delta^a$ -heptinenyl-, b.p. $134-136^\circ/2$ mm., and $-\text{phenylacetylenyl}$ -, m.p. $111.5-112^\circ$, $-\text{carbinols}$ are thus prepared. (I) do not react with MeCN or NH_2Ac . Little or no reaction occurs with $\text{CBu}:\text{C}:\text{MgBr}$ and dry O_2 at -30° .

H. B.

Chloromethylation of ketones and preparation of α -alkylvinyl ketones.

J. COLOGNE (Bull. Soc. chim., 1936, [v], 3, 2116—2121).—Certain ketones are condensed with 36% CH_2O in presence of HCl to β -chloroketones, transformed by NPhEt_2 to α -ethylenic ketones; $\text{CH}_2\text{O} + \text{HCl} \rightarrow \text{CH}_2\text{Cl}\cdot\text{OH}$ (I) and (I) + $\text{COMeR} \rightarrow \text{H}_2\text{O} + \text{COR}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$. Thus COMeBu^y gives β -chloroethyl Bu^y ketone, b.p. $69-70^\circ/9$ mm. (whence 5-tert.-butylpyrazoline-2-carboxylamide, m.p. 103°), which can be kept unchanged for a few weeks but is transformed by boiling NPhEt_2 into $\text{COBu}^y\cdot\text{CH}:\text{CH}_2$, b.p. $65-66^\circ/105$ mm., which appears to polymerise rapidly. COEt_2 yields α -chloro- β -methylpentan- γ -one, b.p. $64^\circ/9$ mm. [semicarbazone, m.p. about 115° (decomp.)], whence β -methyl- Δ^a -pentenone, b.p. $119^\circ/731$ mm. (semicarbazone, m.p. 161°). COBu^a_2 affords γ -chloromethylheptan- δ -one, b.p. $91-92^\circ/12$ mm. [semicarbazone, m.p. about 115° (decomp.)], whence γ -methylene- Δ^a -

heptenone, b.p. $157-159^\circ/742$ mm. (semicarbazone, m.p. 119°).

H. W.

Oxidation of 1:3-diketones by peracetic acid. J. BÖESEKEN and J. JACOBS (Rec. trav. chim., 1936, 55, 804—814).—Esters of β -keto-acids react in the enolic form with AcO_2H . In the aliphatic series the reaction is $\text{COR}\cdot\text{CHR}'\cdot\text{COR}'' + \text{O} + \text{H}_2\text{O} \rightarrow \text{CHRR}'\cdot\text{OH} + \text{HR}''\cdot\text{C}_2\text{O}_4$, in the aromatic $\text{COR}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + 3\text{O} \rightarrow \text{RCO}_2\text{H} + \text{EtHC}_2\text{O}_4$. This is proved for $\text{CHAcR}\cdot\text{CO}_2\text{Et}$ ($\text{R}=\text{H}$, Me, CH_2Ph , OMe, and OEt), $\text{CMe}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, $\text{COR}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ($\text{R}=\text{Et}$, C_6H_{11} , Ph, or $p\text{-NO}_2\cdot\text{C}_6\text{H}_4$), $\text{COMe}\cdot\text{CHR}\cdot\text{COMe}$ ($\text{R}=\text{H}$, Me, or CH_2Ph), and $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$. $(\text{COMe}\cdot\text{CH}_2)_2$ probably reacts at both enolic groupings, giving $\text{OH}\cdot\text{CMe}\cdot\text{CH}_2$ and thence $\text{H}_2\text{C}_2\text{O}_4 + 2\text{EtOH}$.

R. S. C.

Preparation of xylulose and ribulose. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1936, 115, 731—747).—The products of the action of $\text{C}_5\text{H}_5\text{N}$ on xylose and arabinose are best separated by way of the $:\text{CMe}_2$ derivatives, the prep. and hydrolysis of which are standardised. The ketopentose obtained from xylose is renamed *d*-xylulose (I). The equilibrium mixture from xylose yields *d*-xylose [$:\text{CMe}_2$ derivative, m.p. $44-45^\circ$, b.p. $78^\circ/0.1$ mm., $[\alpha]_D^{25} +19.5^\circ$ in COMe_2], (I) [$:\text{CMe}_2$ derivative, m.p. $70-71^\circ$ (lit. $50-52^\circ$), b.p. $110^\circ/0.1$ mm., $[\alpha]_D^{25} +1.7^\circ$ in COMe_2 , -6.5° in H_2O], and *d*-lyxose [$:\text{CMe}_2$ derivative, m.p. $79-80^\circ$, b.p. about $110^\circ/0.1$ mm., $[\alpha]_D^{25} +26^\circ$ in COMe_2 , $+19.7^\circ$ (final) in H_2O]. Arabinose [$:\text{CMe}_2$ derivative, $[\alpha]_D^{25} \pm 0.1^\circ$ in COMe_2] gives *d*-ribose [$:\text{CMe}_2$ derivative (II), an oily mixture of varying amounts of α - and β -forms, $[\alpha]_D^{25}$, e.g., -27.4° in COMe_2 ; *p*-bromophenylhydrazone, m.p. $164-165^\circ$, $[\alpha]_D^{25} +10.3^\circ$ in abs. EtOH, $-19.3^\circ \rightarrow +2.0^\circ$ in 67.5 hr. in dry $\text{C}_5\text{H}_5\text{N}$], *l*-ribulose, $[\alpha]_D^{27}$ (nearly pure) $+16.6^\circ$ (final) in H_2O [$:\text{CMe}_2$ derivative, m.p. 5° , $n_D^{25} 1.4422$, $[\alpha]_D^{27} +105.5^\circ$ in COMe_2], and unchanged material. Some anhydro-derivative, m.p. 61° , b.p. $50-57^\circ/0.1$ mm., $[\alpha]_D^{25} -64.7^\circ$ in COMe_2 , -59.4° in H_2O , of (II) is produced during the formation of (II).

R. S. C.

Determination of hexoses by fermentation.

O. MEYERHOF and W. SCHULZ (Biochem. Z., 1936, 287, 206—211).—During the fermentation of pure hexoses (glucose, fructose) with living yeast the quantity of CO_2 produced is equiv. to only 75—80% of the sugar decomposed, but is increased by addition of substances containing N [e.g., asparagine, $(\text{NH}_4)_2\text{SO}_4$, phenylalanine, protein-free extracts of tissues, yeast, urine, and serum] to the equiv. of 95% (fermentation in N_2) and 100% (in CO_2). These substances act by restricting the assimilation of sugar. W. McC.

Determination of glucose, galactose, and lactose in a mixture of the three sugars. M. SCOTT and E. S. WEST (Proc. Soc. Exp. Biol. Med., 1936, 34, 52—54).—The reducing vals. of solutions are determined before and after hydrolysis with acid under prescribed conditions and before and after fermentation with brewer's yeast. From the four figures so obtained the concns. of the three sugars originally present may be deduced with the help of formulæ which are given. W. O. K.

Determination of hydroxyl in carbohydrates by acetylation in pyridine. J. RABATÉ (Bull. Soc. chim., 1936, [v], 3, 2112—2116).—The substance (0.1—0.2 g.) is heated for 30 min. at 100° with Delaby's reagent (B., 1935, 1118) and cooled in ice; after addition of H₂O (10 c.c.) AcOH is titrated with *N*-NaOH using phenolphthalein as indicator. Results are generally accurate to within 3%, but the method fails with certain alcohols and phenols which contain CO or CHO. Among carbohydrates, the aldoses and their heterosides yield accurate results, but the process is invalid for ketoses (fructose, *d*-sorbitose) or for carbohydrates containing one or more mols. of these components. H. W.

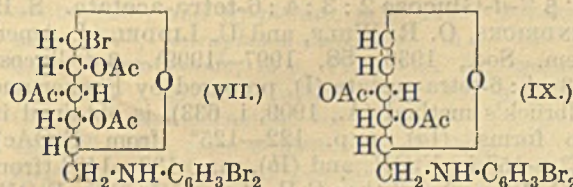
Mechanism of carbohydrate oxidation. XVIII. Oxidation of sugars with silver oxide in the presence of potassium hydroxide. K. G. A. BUSCH, J. W. CLARK, L. B. GENUNG, E. F. SCHROEDER, and W. L. EVANS (J. Org. Chem., 1936, 1, 1—16; cf. A., 1935, 476).—The CO₂, H₂C₂O₄, HCO₂H, and OH·CH₂·CO₂H formed by oxidation of glucose (I), mannose (II), galactose (III), and fructose (IV), and of the intermediates, arabinose (V), erythritol, glyceraldehyde, OH·CH₂·CHO (VI), and galacturonolactone by Ag₂O alone and with KOH at 50° are determined. (II) is oxidised first to CH₂O and (V), fructose either to (VI) (1 mol.) and erythrose (1 mol.) or 3 mols. of (VI). (I) is probably oxidised in several ways simultaneously. HCO₂H is derived from CH₂O, and H₂C₂O₄ and most of the CO₂ from CO-acids; ·CH₂·OH is stable under the reaction conditions, so that the survival of OH·CH₂·CO₂H is explained. Reaction probably occurs by enolisation and fission at OH·C·C·OH. R. S. C.

Oxidation of glucose in presence of insulin, glutathione, and other substances, and the probable mechanism of biological oxidations. C. C. PALIT and N. R. DHAR (J. Indian Chem. Soc., 1936, 13, 502—508).—Glutathione (I) and insulin (II), with or without phosphate or heavy-metal salts, usually accelerate but sometimes retard the oxidation by air of aq. solutions of glucose in presence of TiO₂, SiO₂, Ce(OH)₂, Fe(OH)₂, or Mn(OH)₂ (cf. A., 1934, 1314). (I) and (II) presumably act as O acceptors. E. W. W.

Structures of isopropylidene derivatives of galactose-, glucose-, and mannose-dibenzyl mercaptals. E. PACSU (J. Amer. Chem. Soc., 1936, 58, 2076).—Re-investigation of the compounds is being carried out (cf. Munro and Percival, this vol., 826) in view of previous work (A., 1932, 254). The supposed 2:3-isopropylidene-galactose dibenzyl mercaptal, m.p. 102—103° (A., 1930, 197), is a mixture of (probably) the 4:6-, m.p. 101.5°, [α]_D²⁰ +30.5° in CHCl₃, and 5:6-, m.p. 112.5°, [α]_D²⁰ +17.4° in CHCl₃, derivatives; neither reacts with CPh₃Cl. H. B.

Syntheses with 5:6-anhydroisopropylidene-glucose. IV. Derivatives of glucosyl-6-phenylamine (6-anilinochinovose). H. OHLE, H. FRIEDBERG, and G. HAESLER (Ber., 1936, 69, [B], 2311—2324; cf. this vol., 1094).—With amines of the hexose series with NH₂ at C₆, the relationship to the methylpentoses of similar configuration can be simply

expressed, e.g., glucosyl-6-amine=6-amino-6-deoxy-glucose=6-aminoisorhamnose. The use of prefixes such as *iso*- and *epi*- is regarded as undesirable, and it is considered advisable to choose for each sugar a short trivial name related, if possible, to its origin. The use of chinovose for *d*-isorhamnose is therefore advocated (cf. Freudenberg *et al.*, A., 1929, 427). Addition of NH₂Ph to 5:6-anhydroisopropylidene-glucose (I) gives 6-anilino-1:2-isopropylidene-*d*-chinofuranose (II), b.p. 220°/15 mm. (N·SO₂·C₆H₄Me derivative (III), m.p. 195.5°, [α]_D²⁰ −10.54° in CHCl₃, −7.16° in MeOH). (I) and NH₂Ph (1:2 mols.) at 80—100° yield non-cryst. *di*(isopropylidene-6-*d*-glucosyl)aniline, identified as the *tetra*-acetate, m.p. 194°, [α]_D²⁰ +19.4° in CHCl₃. From α- or β-C₁₀H₇·NH₂, tetrahydroquinoline, *ac*- or *ar*-tetrahydronaphthylamine only isopropylidene-6-*d*-glucosyl-*ar*-tetrahydro-β-naphthylamine, m.p. 187°, [α]_D²⁰ −1.6° in CHCl₃, could be obtained cryst. (III) is also obtained directly from (I) and *p*-C₆H₄Me·SO₂·NHPH at about 150° in presence of a little C₅H₅N, and the method is extended to the prep. of the following: *N*-*p*-toluenesulphonyl derivatives of isopropylidene-6-*d*-glucosyl-*p*-bromoaniline (IV), m.p. 224°, [α]_D²⁰ +12.09° in CHCl₃ (*p*-toluenesulphon-*p*'-bromoaniline, m.p. 147.5°), *p*-anisidine, m.p. 197°, [α]_D²⁰ +6.4° in CHCl₃, 2'-naphthylamine, m.p. 172°, [α]_D²⁰ +16.4° in CHCl₃, and to the *N*-α-, m.p. 223—225°, [α]_D²⁰ −14.2° in CHCl₃, and *N*-β-, m.p. 228—230°, [α]_D²⁰ ±0° in CHCl₃, *naphthalenesulphonyl* compounds of isopropylidene-6-*d*-glucosylaniline. If the amine component is not aromatic the change does not take place, or occurs so slowly that it is almost completely repressed by the autocondensation of (I). This appears also true of the amides of aliphatic and aromatic carboxylic acids, e.g., NH₂Ac, NHAc₂, NHPHAc, NH₂Bz, NHBz₂, and NHPHbz, but *o*-C₆H₄(CO)₂NH is exceptional. Mild treatment with alkali does not cause hydrolysis of the derivatives, whereas more drastic action involves removal of *p*-C₆H₄Me·SO₂·NHPH, hydrolysed to *p*-C₆H₄Me·SO₃H and NH₂Ph, and resinification of the sugar. (III) is readily converted by 50% AcOH into *N*-*p*-toluenesulphonyl-6-anilino-β-*d*-chinovose, m.p. 95—110°, or +1.5H₂O, m.p. 87—89°, [α]_D²⁰ −0.63° to +64.2° in COMe₂, [α]_D²⁰ +57.7° (const.) in C₅H₅N, converted by Ac₂O in C₅H₅N into *N*-*p*-toluenesulphonyl-6-anilino-β-*d*-chinopyranose 1:2:3:4-tetraacetate (V), m.p. 190°, [α]_D²⁰ +19.87° in CHCl₃, mixed with the α-variety, [α]_D²⁰ +64.3° in CHCl₃. The isomeric *N*-*p*-toluenesulphonyl-6-anilino-α-*d*-chinofuranose 1:2:3:5-tetraacetate (VII), m.p. 139—140°, [α]_D²⁰ +74.3° in CHCl₃, is obtained by hydrolysis of *N*-*p*-toluenesulphonylisopropylidene-6-anilino-chinofuranose 3:5-diacetate with 50% AcOH and acetylation of the product. (V) reacts abnormally



with HBr—AcOH, giving (C₆H₄Me)₂S and 6-2':4'-dibromoanilinochinopyranosyl 1-bromide 2:3:4-tri-

acetate (VII), m.p. 144—145°, $[\alpha]_D^{25} +135.6^\circ$ in CHCl_3 , accompanied by 6-2':4'-dibromoanilino-d-chinose hydrobromide, the yields of which are improved by pre-addition of Br. Under similar conditions, (VI) does not yield a cryst. material. The location of Br at C₁₁ in (VII) is established by the conversion of (VII) by Ag_2O and boiling abs. MeOH into 6-2':4'-dibromoanilino- β -methyl-d-chinopyranoside 2:3:4-triacetate (VIII), m.p. 139—140°, $[\alpha]_D^{25} +3.83^\circ$ in CHCl_3 , transformed by boiling Ac_2O , but not by acetylation in $\text{C}_5\text{H}_5\text{N}$, into N-acetyl-6-2':4'-dibromoanilino- β -methyl-d-chinopyranoside 2:3:4-triacetate, m.p. 158°, $[\alpha]_D^{25} +34.0^\circ$ in CHCl_3 , hydrolysed to the non-cryst. N-acetyl-6-2':4'-dibromoanilino- β -methyl-d-chinopyranoside. Hydrolysis of (VIII) by NaOMe gives 6-2':4'-dibromoanilino- β -methyl-d-chinopyranoside, m.p. 172°, $[\alpha]_D^{25} -4.82^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Further (VII) and AgOAc in AcOH afford 6-2':4'-dibromoanilino- β -d-chinopyranose 1:2:3:4-tetra-acetate, m.p. 168°, $[\alpha]_D^{25} +18.9^\circ$ in CHCl_3 , from which the cryst. sugar could not be obtained with NaOMe or $\text{NH}_3\text{-MeOH}$; it is transformed by boiling Ac_2O into N-acetyl-6-2':4'-dibromoanilino- β -d-chinopyranose 1:2:3:4-tetra-acetate, m.p. 148°, $[\alpha]_D^{25} +45.0^\circ$ in CHCl_3 . The position of the second Br in (VII) follows from the conversion of (IV) into (VII) by HBr-AcOH , reaction occurring slowly and with poor yield. For the elucidation of the position of the third Br direct synthesis fails owing to lack of additive capacity of 2:4- $\text{C}_6\text{H}_3\text{Br}_2\text{-NH}_2$. Reduction of (VII) with Zn dust and AcOH gives good yields of 6-2':4'-dibromoanilinochinoyal 3:4-diacetate (IX), m.p. 86—87°, $[\alpha]_D^{25} -2.3^\circ$ in CHCl_3 , readily hydrolysed (Zemplén) to 6-2':4'-dibromoanilino-d-chinoyal, m.p. about 142°, $[\alpha]_D^{25} +15.50^\circ$ in MeOH, which adds Br, is catalytically hydrogenated (Pd-BaSO_4), is degraded by O_3 , and resinified by mineral acids. Oxidation by KMnO_4 in COMe_2 destroys completely the sugar component but yields 2:4- $\text{C}_6\text{H}_3\text{Br}_2\text{-NH}_2$ and 2:4-dibromo-oxanilic acid. (V) is transformed by TiCl_4 in CHCl_3 into N-p-toluenesulphonyl-6-anilinochinopyranosyl 1-chloride 2:3:4-triacetate, m.p. 84—95°, $[\alpha]_D^{25} +114.9^\circ$ in CHCl_3 ; the yield is poor and the change is accompanied by formation of p- $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$. It is converted by Ag_2O in boiling MeOH into N-p-toluenesulphonyl-6-anilino- β -methyl-d-chinopyranoside 2:3:4-triacetate, m.p. 147°, $[\alpha]_D^{25} +5.0^\circ$ in CHCl_3 , hydrolysed (Zemplén) to N-p-toluenesulphonyl-6-anilino- β -d-methylchinopyranoside, m.p. 128°, $[\alpha]_D^{25} +2.62^\circ$. It is unusually stable towards alkalis so that p- $\text{C}_6\text{H}_4\text{Me-SO}_2$ cannot be removed in this manner. Under similar conditions (VI) gives cryst. products differing from those described above in amount too small for further investigation. H. W.

" β "-d-Glucose 2:3:4:6-tetra-acetate. S. B. HENDRICKS, O. R. WULF, and U. LIDDEL (J. Amer. Chem. Soc., 1936, 58, 1997—1999).— β -d-Glucose 2:3:4:6-tetra-acetate (I), prepared by Fischer and Delbrück's method (A., 1909, i, 633), is obtained in two forms, (Ia), m.p. 122—125° (from EtOAc), $[\alpha]_D^{25} +15^\circ$ in EtOH, and (Ib), m.p. 138—140° [from Et_2O (4 times) and then C_6H_6 (twice)], $[\alpha]_D^{25}$ (in EtOH) $-4.2^\circ \rightarrow +75^\circ$ (10 days), (in CHCl_3) $+18.8^\circ \rightarrow +78^\circ$ (10 days) (cf. Georg, A., 1932, 835). (Ib) is converted

into (Ia) when kept (2 years) or heated in CCl_4 or C_6H_6 for several days; subsequent recrystallisation of the (Ia) from Et_2O affords (Ib). Microscopical examination and X-ray powder diffraction patterns show that (Ia) and (Ib) are isomorphous. The above phenomenon is not shown by (I), m.p. 125—131°, prepared by Weizmann and Haskelberg's method (A., 1935, 1108). Infra-red absorption curves, showing characteristic OH-absorption, are given for (Ia), (Ib), β -d-galactose 2:3:4:6-tetra-acetate, and α -d-xylose 2:3:4-triacetate. H. B.

3:6-Dimethylglucose: methods of synthesis. D. J. BELL (J.C.S., 1936, 1553—1554).—3:5-isopropylidene-glucose 6-acetate with N_2O_5 in CHCl_3 gives isopropylidene-glucose 3:5-dinitrate 6-acetate, m.p. 81.5—82.5°, $[\alpha]_D^{25} -22.7^\circ$ in CHCl_3 , which with NHMe_2 in EtOH yields isopropylidene-glucose 5-nitrate, m.p. 86—87° and 106°, $[\alpha]_D^{25} -0.4^\circ$ in EtOH, and with MeI and Ag_2O gives 3:6-dimethylisopropylidene-glucose, a syrup, $[\alpha]_D^{25} -45.9^\circ$ in CHCl_3 (also obtained from 3-methylisopropylidene-glucose by successive treatment with p- $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$ and NaOMe), hydrolysed (HCl) to 3:6-dimethylglucose. F. R. G.

Photochemical peroxide formation. V. Oxidation of fructose by molecular oxygen in ultra-violet light. Photochemical formation of perfructose. R. CANTIENI (Ber., 1936, 69, [B], 2286—2288).—Fructose is converted by O_2 into a peroxide in ultra-violet light of long and short λ . Since photolysis of it affects almost exclusively the CO group it is assumed that photo-oxidation occurs thus:

$$\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R} \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CO}^*\cdot\text{R} \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$$

($\text{R} = [\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\cdot\text{OH}$). Perfructose is photochemically unstable whereby its oxidation is permitted. The final product is assumed to be CO_2 ; $\text{C}_6\text{H}_{12}\text{O}_6^* + 12(\text{C}_6\text{H}_{12}\text{O}_6)\text{O} \rightarrow 6\text{H}_2\text{CO}_3 + 12\text{C}_6\text{H}_{12}\text{O}_6$. H. W.

Ditriphenylmethylfructose. B. HELFERICH [with G. PYL, H. PAUKERT, and E. GUNTHER] (J. pr. Chem., 1936, [ii], 147, 60—63).—Fructose and CPh_3Cl (2 mol.) in abs. $\text{C}_5\text{H}_5\text{N}$ at room temp. give 1:6-ditriphenylmethyl-d-fructose, anhyd., amorphous, and +2 $\text{C}_5\text{H}_5\text{N}$, m.p. 96—97°, $[\alpha]_D^{25} +17.5^\circ$ in CHCl_3 , which gives an oxime, m.p. about 186° (decomp.), $[\alpha]_D^{25} -18^\circ$ in $\text{C}_5\text{H}_5\text{N}$, also obtained from fructose oxime and CPh_3Cl (2 mol.). R. S. C.

Convallamarin. W. VOSS and G. VOGT (Ber., 1936, 69, [B], 2333—2342).—Technical convallamarin is purified successively by distribution between BuOH and H_2O , fractional adsorption by active C, and fractional pptn. by Et_2O from MeOH, thereby giving an amorphous product for which the name convallamarin (I) is retained and which could not be separated into portions with differing physical consts. It retains an almost negligible cardiac activity and has a very low foam no. attributed to the presence of traces of convallatoxin and convallarin, respectively; it is considered to be about 99.5% pure. It does not give the Legal test and does not contain a lactone group or give a compound with cholesterol. It has $[\alpha]_D^{25} -66.5^\circ$ in Et_2O . Elementary analyses indicates the formula $\text{C}_{44}\text{H}_{70}\text{O}_{19}\cdot 3\text{H}_2\text{O}$, and the presence of one double

linking is established by hydrogenation. The sugar components are glucose (1 mol.) and *l*-rhamnose (2 mols.). Hydrolysis with aq. acids proceeds satisfactorily only in very dil. solution, and the use of 2% HCl-MeOH at 35° is preferable, whereby the sugars are quantitatively transformed into their methylglucosides and the aglucone is protected. The very ready alcoholysis of glucosides and the consequent danger of the use of possibly acidic EtOH in their extraction is stressed. *Convallamarctin*, m.p. 248.5—250.5° (decomp.), $[\alpha]_D^{20} -86.0^\circ$ in CHCl₃, contains one double linking, 2 OH (Zerevitinov determination at higher temp.), but not CO. Elementary analyses agree best with C₂₀H₄₀O₅, and harmonise with the hydrolysis, C₄₄H₇₀O₁₉ + 3H₂O → C₂₆H₄₀O₅ + C₆H₁₂O₆ + 2C₆H₁₂O₅. The presence of only two oxide rings is considered probable, whilst the remaining 3 O are present as 3 OH only two of which are affected by MgMeI. H. W.

Constituents of seeds of *Digitalis lanata* (Ehrh.).—See this vol., 1571.

Kinetics of the sulphite [cellulose] process.—See this vol., 1470.

[Preparation of] primary amines by reduction of oximes by aluminium amalgam. C. L. TSENG and C. CHANG (Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 3, 19—33).—The oximes of the following compounds with Al-Hg in 96% or aq. EtOH give the stated yields of primary base with, in some cases, small amounts of *sec.* amine: COMe₂ 17.3, PrⁿCHO 39.9, *n*-C₆H₁₃·CHO 48, COMe·C₆H₁₃-*n* 1.6, cyclohexanone 60.1, PhCHO 87.7, camphor 85, and furfuraldehyde 36.3%. Phenylhydrazones give similarly good yields of NH₂Ph and primary base, but the method is of val. only when the NH₂Ph and other base are readily separated. PhCN resists reduction by Al-Hg. Al foil of 0.1 mm. thickness or Al turnings give best results. The prep. of the Al-Hg, oximes, and phenylhydrazones used is described.

R. S. C.

Reineckates of organic bases. H. CARLSOHN and F. RATHMANN (J. pr. Chem., 1936, [ii], 147, 29—37).—Many reineckates are more sol. in H₂O-COMe₂ or -EtOAc than in either solvent alone. In general these salts are more sol. in H₂O, the less sol. they are in COMe₂. In EtOH the order of solubility is usually primary > *sec.* > *tert.* > quaternary aliphatic salts. The NPr₄ salt is least sol. in EtOH containing 2.2% of H₂O. R. S. C.

Carboxymethoxylamine [aminooxyacetic acid]. E. BOREK and H. T. CLARKE (J. Amer. Chem. Soc., 1936, 58, 2020—2021).—Crude CMe₂·N·O·CH₂·CO₂Et (from dry CMe₂·N·ONa and CH₂Cl·CO₂Et) is hydrolysed (11.4% NaOH at 100°) to CMe₂·N·O·CH₂·CO₂H, m.p. 76—76.5° [also prepared (cf. Hantzsch and Wild, A., 1896, i, 285) in smaller yield from CMe₂·N·OH and CH₂Cl·CO₂Na in aq. NaOH], further hydrolysed (boiling 6*N*-HCl) to NH₂·O·CH₂·CO₂H (I) (*hemihydrochloride*, m.p. 151°). *Acetophenoneoxime*, m.p. 97—97.5°, benzaldoxime, m.p. 96° (lit. 98°), and pyruvic acid oxime, m.p. 129° (lit. 130—132°), *O*-carboxymethyl ethers are prepared from (I) and the requisite CO-compound. H. B.

Action of amines on esters of the trichloro-nitrohydroxy-paraffins. F. D. CHATTAWAY, J. G. N. DREWITT, and G. D. PARKES (J.C.S., 1936, 1530—1532; cf. this vol., 595, 1362).—CRCl₂·CH(CH₂·NO₂)·O·COR' with NH₂R'' gives CRCl₂·CH(CH₂·NO₂)·NHR''. With NH₃ or the appropriate amine, CCl₃·CH(CH₂·NO₂)·OAc or its *p*-nitrobenzoate, m.p. 87°, yields $\gamma\gamma\gamma$ -trichloro- α -nitro- β -methyl-, b.p. 96°/3 mm. (*hydrochloride*, decomp. about 185°; *phenylcarbamyl* derivative, m.p. 130°), - β -ethyl-, b.p. 106°/2 mm. (*hydrochloride*, m.p. 146°; *phenylcarbamyl* derivative, m.p. 121°), and β -allyl-*amino*-propane, b.p. 106°/2 mm. [*hydrochloride*, m.p. 141° (decomp.); *phenylcarbamyl* derivative, m.p. 124°]; CHMeCl·CCl₂·CH(CH₂·NO₂)·OAc yields $\gamma\gamma\delta$ -trichloro- α -nitro- β -methyl-, b.p. 110°/2 mm. [*hydrochloride*, m.p. 172°; *phenylcarbamyl* derivative, m.p. 186° (decomp.)], - β -ethyl-, b.p. 115°/0.7 mm. (*hydrochloride*, m.p. 120°; *phenylcarbamyl* derivative, m.p. 140°), and - β -allyl-*amino*-*n*-pentane, b.p. 116°/0.5 mm. (decomp.) [*hydrochloride*, m.p. 140° (decomp.)]; CCl₃·CH(CHMe·NO₂)·OAc yields $\delta\delta\delta$ -trichloro- β -nitro- γ -methylamino-, b.p. 94°/0.5 mm. (*hydrochloride*, m.p. 194°), - γ -*p*-toluidino-, m.p. 99—100°, and - γ -*phenylhydrazino*-*n*-butane, m.p. 108—109°; CHMeCl·CCl₂·CH(CHMe·NO₂)·OAc yields $\delta\delta\epsilon$ -trichloro- β -nitro- γ -methylamino-, b.p. 109°/0.3 mm. (*hydrochloride*, m.p. about 200°), and - γ -*p*-toluidino-*n*-hexane, m.p. 82°; CCl₃·CH(CHPh·NO₂)·OAc yields $\gamma\gamma\gamma$ -trichloro- α -nitro- β -*p*-toluidino-, m.p. 121—122°, and - β -*phenylhydrazino*- α -*phenylpropane*, m.p. 155° (decomp.). F. R. G.

Polyamines. II. Preparation of $\beta\beta'$ -diamino-diethylamine and NN'-bis-(β -aminodiethyl)ethylenediamine. D. H. PEACOCK (J.C.S., 1936, 1518—1520; cf. A., 1934, 1207).—*p*-Toluenesulphon- β -chloroethylamide with (CH₂·NH₂)₂ in EtOH gives *N*-(β -*p*-toluenesulphonamidoethyl)ethylenediamine *dihydrochloride*, m.p. 182° {CuSO₄ complex, [(C₁₁H₁₉O₂N₃S)₂Cu(H₂O)₂]SO₄; NiSO₄ complex}, and the *dihydrochloride*, m.p. 246°, of NN'-bis-(β -*p*-toluenesulphonamidoethyl)ethylenediamine, m.p. 160°, hydrolysed (H₂SO₄) to NN'-bis-(β -aminoethyl)ethylenediamine {*tetrahydrochloride*, m.p. 266—270°; CuSO₄ and KPtCl₆ [Pt(C₆H₁₄N₄)]PtCl₄ (?), complexes}. NH(CH₂·CH₂Br)₂·HBr and NH₃ in EtOH give NH(CH₂·CH₂Br)₂ and piperazine, identified as their *p*-C₆H₄Me·SO₂ derivatives. F. R. G.

Aliphatic polyamines. III. J. VAN ALPHEN (Rec. trav. chim., 1936, 55, 835—840; cf. this vol., 1274).—Br·[CH₂]₃·Br and NH₂·[CH₂]₂·NH₂·H₂O in abs. EtOH, first alone and then with KOH, give NN'-*di*- β' -aminoethylpropylene- $\alpha\gamma$ -diamine (I), b.p. 185—186°/35 mm., 286—287°/760 mm. (*tetra*-, m.p. about 223°, and *tri*-*picrate*, m.p. 171°; *tetraoxalate*, m.p. 237°; *tetraphenyl-carbamide*, m.p. 145—155°, and -*thiocarbamide*, m.p. 179°, and Bz₄ derivative, m.p. 172°; gives a reddish-violet colour with aq. Cu salts), and a fraction, b.p. 274—276°/35 mm. (I) and PhCHO give a gum, which with Na-EtOH affords NN'-*di*- β' -benzylaminoethylpropylene- $\alpha\gamma$ -diamine (II), m.p. 44° [*tetra-hydrochloride*, m.p. 270—290° (decomp.)], -*picrate*, m.p. 201°, and -*oxalate*, m.p. 247°; (NO)₄-, m.p. 99°, and *tetraphenylthio*-

carbamide derivative, m.p. 130—135°]. (I) and CS₂ in EtOH give α -*di*-2-thiotetrahydroglyoxalinypropene, m.p. 156°. (II) with PhCHO or *p*-OMe·C₆H₄·CHO gives α -*di*-2-phenyl-, m.p. 123°, and -*p*-amisyl-, m.p. 110°, -3-benzyltetrahydro-1-glyoxalinypropene, m.p. 110°. R. S. C.

Alcoholysis in the reaction between triethanolamine and bivalent metal salts. IV. F. GARELLI and A. TETTAMANZI (Atti R. Accad. Sci. Torino [Cl. Sci. fis. mat.], 1934, 69, I, 89—96; Chem. Zentr., 1936, i, 535).—In presence of H₂O, N(CH₂·CH₂·OH)₃ reacts as the hydrate, NH(OH)(C₂H₄·OH)₃. Earlier results are summarised. H. N. R.

Production of methyl esters of difficultly esterified acids. V. PRELOG and M. PIANTANIDA (Z. physiol. Chem., 1936, 244, 56—58).—The acids, in MeOH, are converted into NMe₄ salts by titration with NMe₄·OH in MeOH avoiding excess, MeOH and any residual NMe₄·OH are removed by heating, and the salts are destructively distilled at 200—300° preferably in a vac., thus giving high yields of Me ester. Me esters of NH₂-acids may be prepared thus. W. McC.

Preparation of α -amino-acids from alkylcyanoacetic acids. A. DARAPSKY [with H. DECKER, E. STEUERNAGEL, and O. SCHIEDRUM] (J. pr. Chem., 1936, [ii], 146, 250—267; cf. A., 1916, i, 127).—CN·CHPr^a·CO₂Et and N₂H₄·H₂O at room temp. give the non-cryst. *n*-propylcyanoacetylhydrazide CN·CHPr^a·CO·NH·NH₂ (CMe₂ derivative, m.p. 98—100°), converted by NaNO₂ and HCl into the oily *n*-propylcyanoacetazide which with boiling EtOH·Et₂O affords *Et* α -cyano-*n*-butylcarbamate, transformed by boiling conc. HCl into α -amino-*n*-valeric acid, m.p. 291° (corr.; decomp.) in a sealed capillary [hydrochloride; Cu salt; Bz, m.p. 152°, and SO₂Ph, m.p. 150—152° (corr.), derivatives]. *Et* isobutylcyanoacetate is converted by N₂H₄·H₂O in boiling EtOH into diisobutylcyanoacetylhydrazide, (·NH·CO·CHBu ^{β} ·CN)₂, m.p. 198°, which does not condense with PhCHO. At room temp. in the absence of solvents the reactants yield the monohydrazidinedehydrazide, NH₂·NH·CO·CHBu ^{β} ·C(NH)·NH·NH₂, m.p. 101°, which condenses with PhCHO, whereas in presence of EtOH at room temp. they yield isobutylcyanoacetylhydrazide (CMe₂, m.p. 81—82°, CHPh, m.p. 95°, and *o*-hydroxybenzylidene, m.p. 115°, derivatives). Non-cryst. isobutylcyanoacetazide is transformed by NH₂Ph in Et₂O into isobutylcyanoacetanilide, m.p. 192°, and by boiling EtOH into *Et* α -cyanoisomylcarbamate, which with boiling conc. HCl affords α -aminoisohexoic acid, m.p. 293° in a sealed capillary (Cu salt; ·SO₂Ph derivative, m.p. 143°). *Et* isoamylcyanoacetate yields isoamylcyanoacetylhydrazide, m.p. 100° (unstable, hygroscopic hydrochloride, m.p. 107°; CMe₂, m.p. 81°, and CHPh, m.p. 85°, derivatives), converted by I in cold abs. EtOH into diisoamylcyanoacetylhydrazide, C₁₆H₂₆O₂N₄, m.p. 180° (decomp.). Non-cryst. isoamylcyanoacetazide yields isoamylcyanoacetanilide, m.p. 108°, and non-cryst. *Et* α -cyanoisohexylcarbamate, CH₂Bu ^{β} ·CH(CN)·NH·CO₂Et, hydrolysed by boiling 20% HCl to α -amino- δ -methyl-*n*-hexoic acid, m.p. 266° (decomp.) [hydrochloride, Cu salt, *Et* ester (I), b.p. 59°/19 mm., and its hydro-

chloride, m.p. 86°]. When kept in a sealed tube (I) slowly passes into 2:5-diketo-3:6-diisoamylpiperazine, m.p. 281° (decomp.). H. W.

Methylation of glycine. F. CHALLENGER (Chem. and Ind., 1936, 900—901).—The suggestion (A., 1935, 1027) that glycine (I), through its deamination products CHO·CO₂H and CH₂O, is the active agent in biological methylation (often a detoxication process) is supported by a review of relevant lit. The assumption of self-methylation explains the formation of sarcosine and betaine. The methylating action of (I) itself is exemplified by the conversion of nicotinic acid into trigonelline and nicotinuric acid. J. W. B.

Specificity of papain peptidase.—See this vol., 1557.

Spatial configuration of [natural] α -amino- β -hydroxy-*n*-butyric acid. C. E. MEYER and W. C. ROSE (J. Biol. Chem., 1936, 115, 721—729).—The α -amino- β -hydroxy-*n*-butyric acid isolated from proteins is shown to be (I); it is named *d*(or *D*)(-)-threonine. The dextro- (II) and lævo-rotatory (III) threodihydroxybutyric acids are the *l*(+)- and *d*(-)-compounds, respectively. (I) and HI-P at 150—155° give partly racemised *d*- α -amino-*n*-butyric acid with $[\alpha]_D^{25}$ +4.18° in H₂O. With chloramine-T it affords *l*-lactaldehyde (not isolated), oxidised to *l*-lactic acid. With Ba(NO₃)₂·H₂SO₄ at 0° (I) gives (III) (phenylhydrazide, m.p. 103.5—104°, $[\alpha]_D^{25}$ -16.25° in H₂O). The phenylhydrazides of (II) and the *dl*-form have m.p. 102—104° and 129.5—131°, respectively. R. S. C.

Polypeptidases of blood-serum and -plasma.—See this vol., 1556.

Hydrazino-acids. IV. A. DARAPSKY [with J. GERMSCHIED, C. KREUTER, E. ENGELMANN, W. ENGELS, and W. TRINIUS] (J. pr. Chem., 1936, [ii], 146, 219—249; cf. A., 1918, i, 506, 553; 1919, i, 601).—CHPr ^{β} Br·CO₂H and N₂H₄·H₂O in boiling EtOH give α -hydrazinoisovaleric acid, m.p. 230—235° [hydrochloride, m.p. 135.5°; *o*-hydroxybenzylidene, m.p. 124°, and cinnamylidene, m.p. 137—139°, derivatives; unstable *Me* ester and its hydrochloride (I), m.p. 112°; unstable *Et* ester and its hydrochloride (II), m.p. 104°], which is not converted by conc. aq. NH₃ into its NH₄ salt. (I) is transformed by aq. KCNO into *Me* α -carbamyllhydrazinoisovalerate, NH₂·CO·NH·NH·CHPr ^{β} ·CO₂Me, m.p. 126.5°, which does not condense with PhCHO or *o*-OH·C₆H₄·CHO and does not appear to yield a hydrochloride. *Et* α -carbamyllhydrazinoisovalerate, from (II), has m.p. 130°. (I) is converted by NaNO₂ in conc. aq. solution into *Me* α -nitrosohydrazinoisovalerate (III), NH₂·N(NO)·CHPr ^{β} ·CO₂Me, m.p. 35.5°, which readily decomposes when preserved, probably accompanied by *Me* α -hydroxyisovalerate. *Et* α -nitrosohydrazinoisovalerate is an unstable oil. (III) passes at 115—120° into N₂O and *Me* α -aminoisovalerate, b.p. 56°/14 mm. (hydrochloride, m.p. 116.5°; picrate, m.p. 145.5°), which decomposes when kept, probably giving diketodisopropylpiperazine. When distilled with steam in presence of 10% H₂SO₄ (III) affords

Me α -azidoisovalerate, b.p. 50°/15 mm., hydrolysed by aq. NaOH at room temp. to non-cryst. α -azidoisovaleric acid (NH_4 and Ag salts). The following substances are obtained by an analogous series of reactions: α -hydrazino-*n*-hexoic acid, m.p. 199—201° (very hygroscopic hydrochloride; $:CHPh$, m.p. 102—103°, *o*-hydroxybenzylidene, m.p. 123—124°, and Bz_2 , m.p. 157—158°, derivatives; *Et* ester hydrochloride, m.p. 75°; very hygroscopic *Me* ester hydrochloride); *Et* α -carbamyldiazino-*n*-hexoate, m.p. 102—103°; *Et* α -nitrosohydrazino-*n*-hexoate; *Et* α -amino-*n*-hexoate, b.p. 91—93°/11—12 mm., whence the corresponding acid, m.p. 299—303° in a sealed capillary, and its Cu salt; *Et* α -azido-*n*-hexoate, b.p. 93—95°/13—14 mm., also obtained from $CHBu^aBr \cdot CO_2Et$ and NaN_3 , whence non-cryst. α -azido-*n*-hexoic acid (non-cryst. NH_4 and Ag salts); α -hydrazinoisohexoic acid $CH_2Pr^b \cdot CH(NH \cdot NH_2) \cdot CO_2H$, m.p. 228° [hydrochloride, m.p. 170—177° (decomp.); $:CHPh$, m.p. 115.5°, *o*-hydroxybenzylidene, m.p. 139°, and $:CMe_2$, m.p. 99—101°, derivatives; *Me* ester hydrochloride, m.p. 99—102°; *Et* ester hydrochloride, m.p. 91—92°, and *o*-hydroxybenzylidene derivative, m.p. 212° of the *Et* ester); *Me* α -carbamyldiazinoisohexoate, m.p. 110°; *Et* α -nitrosohydrazinoisohexoate, m.p. 25—28°; *Et* α -aminoisohexoate, b.p. 88°/11 mm.; *Et* α -azidoisohexoate, b.p. 94°/14 mm., non-cryst. α -azidoisohexoic acid (NH_4 , m.p. 92—95° and Ag salts): α -hydrazino-*n*-heptoic acid, m.p. 205—206° (decomp.) [Cu salt, rapid decomp. 110° after darkening at 100°; hydrochloride, m.p. (indef.) 126—145°; $:CHPh$, m.p. 109°, and *o*-hydroxybenzylidene, m.p. 140°, derivatives; hydrochloride, m.p. 157°, and *o*-hydroxybenzylidene derivative, m.p. 203°, of the *Me* ester; non-cryst. *Et* ester and its hydrochloride, m.p. 99°, and *o*-hydroxybenzylidene derivative, m.p. 152°]; *Et* α -carbamyldiazino-*n*-heptoate, m.p. 94° (hydrochloride, m.p. 125°, immediately hydrolysed by H_2O), which does not condense with $PhCHO$ or *o*- $OH \cdot C_6H_4 \cdot CHO$; non-cryst. *Et* α -nitrosohydrazino-*n*-heptoate; *Et* α -amino-*n*-heptoate, b.p. 89°/12 mm., and its very hygroscopic hydrochloride; *Et* α -azido-*n*-heptoate, b.p. 104°/13 mm., also derived from $Me \cdot [CH_2]_4 \cdot CHBr \cdot CO_2Et$ and NaN_3 ; non-cryst. α -azido-*n*-heptoic acid (Ag salt): α -hydrazino-*n*-nonoic acid, m.p. 197° ($:CHPh$, m.p. 117°, and *o*-hydroxybenzylidene, m.p. 137°, derivatives; hydrochloride, m.p. 166° after some decomp., and *o*-hydroxybenzylidene derivative, m.p. 132°, of the *Me* ester; *Et* ester hydrochloride, m.p. 72°); *Et* α -carbamyldiazino-*n*-nonoate, m.p. 81°, which does not condense with $PhCHO$ or *o*- $OH \cdot C_6H_4 \cdot CHO$; *Et* α -nitrosohydrazino-*n*-nonoate; *Et* α -amino-*n*-nonoate, b.p. 132°/17 mm., α -amino-*n*-nonoic acid, sublimes at about 256° (Cu salt, also $+1H_2O$); *Et* α -azido-*n*-nonoate, b.p. 140—145°/15 mm.; non-cryst. α -azido-*n*-nonoic acid (Ag salt).

H. W.

Imidocarbonic esters, iminothio-, oximinothio-, and dithio-formic esters. J. HOUBEN and R. ZIVADNOVITSCH (Ber., 1936, 69, [B], 2352—2360).—Improvements in the prep. of Et_2N -chloroimidocarbonate (Sandmeyer, A., 1886, 611; Houben *et al.*, A., 1923, i, 1077) give the compound in 53.6—59% yield; it can be kept unchanged in light petrol-

eum. Et_2 imidocarbonate (I), b.p. 40°/12 mm., can be kept unchanged (sealed) over anhyd. CaO. When kept alone (sealed) even in the dark it is slowly converted into a solution of Et_3 isocyanurate in $EtOH$; under similar conditions, but in presence of granulated $CaCl_2$, Et_3 cyanurate results. It is converted by dil. aq. alkali or by prolonged warming with H_2O into $EtOH$ and $NH_2 \cdot CO_2Et$. With solid alkali it affords $EtOH$ or alkoxide and "isocyanate." An improved prep. of Et_2 di-imido-oxalate, b.p. 69—70°/18 mm., is described. (I) in Et_2O is transformed by $NH_2 \cdot CH_2 \cdot CO_2Et, HCl$ in H_2O into *Et* diethoxymethyleneaminoacetate, $(OEt)_2C=N \cdot CH_2 \cdot CO_2Et$, b.p. 108—109.5°/11 mm., in 66% yield. (I) and *p*- $C_6H_4Me \cdot NH_2, HCl$ in abs. $EtOH$ at room temp. afford *Et_2* *p*-tolylimido-carbonate, b.p. 135—136°/12 mm., but reaction does not occur with *o*- $C_6H_4Me \cdot NH_2, HCl$. KNO_2 and $CH_2(OEt)_2$ are produced by the action of solid KOH on (I) in Et_2O . Anhyd. HCN combines with mercaptans in presence of HCl, but the products are usually non-cryst. oils which cannot be transformed into the corresponding oximino-compounds; $CH_2Ph \cdot SH$, however, gives *CH_2Ph* imidothioformate hydrochloride (II), decomp. about 180°. Treatment of $EtSH$ and HCN with HCl in light petroleum affords a non-cryst. product, transformed by NH_2OH, HCl in Et_2O into *Et* thioformhydroxamate, $OH \cdot N \cdot CH \cdot SET$, m.p. 110—111°; the corresponding Bu^a , m.p. 90—91°, and CH_2Ph , m.p. 116—117°, esters are similarly obtained. *CH_2Ph* thioformate has b.p. 109—111°/26 mm. (II) is converted by the successive action of K_2CO_3 in H_2O-Et_2O and H_2S into *CH_2Ph* dithioformate, b.p. 161—162°/13 mm. $MeCN$ and $CH_2Ph \cdot SH$ give *CH_2Ph* imidothioacetate hydrochloride, m.p. 153—155°. $SH \cdot CH_2 \cdot CO_2Et$ and $MeCN$ afford *Et* α -imidoethylthiolacetate hydrochloride, m.p. 100—102°. $SH \cdot CH_2 \cdot CO_2H$ similarly gives α -iminoethylthiolacetic acid hydrochloride, m.p. 110—112° (decomp.), transformed by KOH into the corresponding (?) acid, m.p. 97—98°. NH_4 acetylthiolacetate, m.p. 68—70°, and acetylthiolacetamide, m.p. 78—80°, are incidentally described.

H. W.

Reaction of halogenoamines with ketens. G. H. COLEMAN, R. L. PETERSON, and G. E. GOHEEN (J. Amer. Chem. Soc., 1936, 58, 1874—1876).— NH_2Cl and $CH_2 \cdot CO$ in Et_2O at -60° and then at room temp. give 73% of acetchloroamide, m.p. 111—112°; $NHBr_2$ similarly affords 18% of bromoacetamide, m.p. 88—89° ($CH_2Br \cdot CO \cdot NHBr$ is probably first formed and then reacts with the HBr produced in the reaction), NCl_3 furnishes 14% of $CH_2Cl \cdot CO \cdot NH_2$, and NMe_2Cl yields (probably) chloroacetdimethylamide, b.p. 98—100°/11 mm. $CPh_2 \cdot CO$ (modified prep.; cf. Ritter and Wiedemann, A., 1930, 214) and NH_2Cl similarly give 51% of diphenylchloroacetamide, m.p. 116—117°; NMe_2Cl affords 95% of $CPh_2Cl \cdot CO \cdot NMe_2$, m.p. 122—123°, whilst NCl_3 furnishes (cf. A., 1928, 1362) (probably) diphenylchloroacetdichloroamide, m.p. 112° (Cu block).

H. B.

Monosodiocarbamide and its reactions. R. A. JACOBSON (J. Amer. Chem. Soc., 1936, 58, 1984—1986).—Na (1 equiv.) reacts readily with $CO(NH_2)_2$ in liquid NH_3 to give the Na_1 derivative (I), decomp. from 150—160°; reaction is slow with >1 equiv. of

Na and affords (I) + Na₂ derivative. Oleyl- (II), stearyl-, and benzoyl- (III) -carbamide are obtained from (I) and RCOCl; CH₂PhCl in liquid NH₃ gives benzylcarbamide. (II), (III), and NH₂·CO·NHAc are formed from (I) and Me oleate, MeOBz, and EtOAc, respectively, in COMe₂. (I) and CHR(CO₂Et)₂ in COMe₂ afford barbituric acid and its 5-Et, -Pr^β, and -Bu derivatives. (I) and Et glutarate similarly give a compound, probably [CH₂]₃(CO·NH·CO·NH₂)₂, m.p. 247—248°; Et pimelate affords a similar compound, m.p. 240—245°, and a little of (probably) the compound NH₂·CO·NH·CO[CH₂]₅·CO₂H, m.p. 205—206°. Mixed acylcarbamides are obtained from (I) and various oils (coconuts, linseed, China wood) in COMe₂. (I) does not react with BuI or dodecyl bromide. H. B.

Improved preparation of enolphosphopyruvic acid. W. KISSLING (Ber., 1936, 69, [B], 2331—2332; cf. A., 1935, 731).—Isolation is effected through the Ba salt. Ill-defined impurities containing P (probably phosphorylated products from condensed AcCO₂H) are removed as their Na salts in slightly alkaline solution (p_H 8.5) by treatment with EtOH, whilst P-free by-products are eliminated by taking advantage of the sparing solubility of Ba enolphosphopyruvate in hot solution and its fractional pptn. with EtOH from solution acid to litmus. H. W.

Constitution of complex metallic salts. IV. Bridged dipalladium derivatives. F. G. MANN and D. PURDIE (J.C.S., 1936, 873—890).—In the abstract of this paper (this vol., 1184) the following should have been recorded: *dichlorobis*(triethylphosphine)-μ-dichlorodipalladium, m.p. 230°, and the corresponding Pr^a, m.p. 189°, and Bu^a compound, m.p. 145°; *di-iodobis*(tri-n-butylphosphine)-μ-di-iodopalladium, m.p. 136° and the corresponding n-amyl compound, m.p. 127°; *dichlorobis*(trimethylarsine)-μ-dichloropalladium, decomp. 252—260° without melting, and the corresponding Et, m.p. 212°, Pr^a, m.p. 160°, Bu^a, m.p. 128°, and n-amyl compound, m.p. 108°; *dichloro-, dinitro-, and oxalato-dipyridylpalladium; oxalatobis*(n-butylphosphine)-μ-dichlorodipalladium, m.p. 185—186° (decomp.) in bath at 180°; *dinitritobis*-(n-butylphosphine)-μ-dinitritopalladium, m.p. 138° (decomp.), and its additive compound with NaNO₂; *oxalatobis*(n-butylphosphine)-μ-dinitritodipalladium, m.p. 201—204° (decomp.) in bath at 185°; *dinitritobis*(n-butylphosphine)palladium, m.p. 140°; *dichloro-*(I), m.p. 101° (corresponding Pr^a compound, m.p. 151°), and *dithiocyanato-bis*(n-butylarsine)-μ-dithiocyanatodipalladium (II), m.p. 111° (corresponding Pr^a compound, m.p. 142°); *dithiocyanatobis*(n-butylarsine)palladium (III), m.p. 75° (corresponding Pr^a compound, m.p. 90—91.5°); *dinitrito-*, m.p. 86—88°, and *dichloro-mono-p-toluidinomono-n-butylphosphinepalladium*, m.p. 75° (corresponding anilino-compound, m.p. 68°, and *arsine*, m.p. 87°); *dichloro-monoammino-*, m.p. 71°, and *triammino-n-butylphosphinepalladium dichloride; bis*(n-butylphosphine)-*bis*(ethylenediamino)-μ-dichlorodipalladium *dichloride; monochloro-n-butylphosphine-ethylenediaminopalladium monochloride; monochloroethylthiobis*(n-butylphosphine)-μ-dichlorodipalladium, m.p. 151°, and

dichlorobis-(n-octylsulphide)-μ-dichlorodipalladium, m.p. 61°. *Phosphines* corresponding with (I), (II), and (III) have m.p. 142°, 165°, and 112°, respectively. F. N. W.

Phenylcyclopentane and its behaviour towards catalytic hydrogenation. J. I. DENISENKO (J. Gen. Chem. Russ., 1936, 6, 922—924).—Contrary to the tension theory of Baeyer, the cyclopentane ring is broken by hydrogenation. Phenylcyclopentane, b.p. 216—218°/750 mm., when passed over Pt at 305—310° in H₂ yields a mixture of α-, β-, and γ-phenylpentane. J. J. B.

Action of bromine water on ethylenic compounds. Action on cyclohexene. F. SWARTS (Bull. Acad. roy. Belg., 1936, [v], 22, 924—932; cf. this vol., 712).—*cyclo*Hexene with Br in H₂O at <20° affords 1:2-dibromocyclohexane (I), m.p. 2.8°, 2-bromocyclohexanol (II), m.p. 27.5°, identified as the 2-NH₂-compound, and 2:2'-dibromodicyclohexyl ether (III), m.p. 70° (cf. A., 1925, i, 497). The ratio (II)/(I) is the greater the higher is the reaction temp. (cf. A., 1928, 505, 866). (I) when heated in vac. at 110° does not afford (III), which indicates that (III) does not arise from (II). Heat decomposes (III) but some cyclohexylcyclohexene is formed; when heated with PCl₃ and Br under pressure (III) affords some (I). J. L. D.

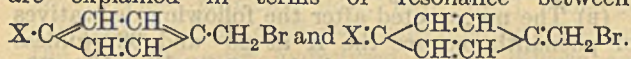
Oxidation of ααεε-tetraphenyl-Δ^{αδ}-pentadiene and ααζζ-tetraphenyl-Δ^{αε}-hexadiene. K. H. BAUER and H. HERZOG (J. pr. Chem., 1936, [ii], 147, 4—10).—CH₂(CH:CPh₂)₂ (I) with H₂-Pd-BaSO₄ in C₆H₆ gives CHPh₂·[CH₂]₃·CHPh₂ and with Br-CHCl₃ gives HBr and βδ-dibromo-ααεε-tetraphenyl-Δ^{αδ}-pentadiene, m.p. 141°. Bz·[CH₂]₄·Bz and MgPhBr in Et₂O give ααζζ-tetraphenylhexane-αζ-diol, m.p. 213°, dehydrated at 230° to give ααζζ-tetraphenyl-Δ^{αε}-hexadiene (II), m.p. 108—109°, which with H₂-Pd-BaSO₄ gives ααζζ-tetraphenylhexane, m.p. 123—124°; the tetrabromide, m.p. 146—147° (decomp.), of (II) in hot EtOH gives HBr and βε-dibromo-ααζζ-tetraphenyl-Δ^{αε}-hexadiene, m.p. 199°. With BzO₂H-CHCl₃ (II) yields ααζζ-tetraphenylhexane-αβεζ-tetraol, m.p. 193°. Owing to the presence of :C·CH₂·C· oxidation of (I) at 100° or in ultra-violet light at room temp. is faster than that of (II); in both cases COPh₂ is formed. R. S. C.

Colorimetric determination of carotenoids by a modified potassium dichromate method. A. KROGIS (Biochem. Z., 1936, 287, 226—234; cf. Jørgensen, A., 1927, 952).—The alterations which must be made in the p_H of aq. K₂Cr₂O₇ used as colour standard in determining various concns. of carotene (I) and xanthophyll (II) have been measured for layers 1—35 mm. thick at intervals of 1 mm. Consequently (I) and (II) can be determined with the help of buffered aq. K₂Cr₂O₇ as standard, the accuracy attainable being as great as that of the method of Kuhn *et al.* (A., 1932, 785), which is not applicable to the higher and lower concns. covered by the new method. For very low concns. the method of Connor (A., 1928, 786) should be applied. W. McC.

Carotenoids of purple bacteria.—See this vol., 1561.

Is the methyl group attached to the benzene nucleus positive or negative? W. HEROLD and K. W. ROSENMUND (J. pr. Chem., 1936, [ii], 146, 201—208; cf. this vol., 105).—In reply to Huntenburg (this vol., 1239) it is shown that conclusions based on Hund's theory (A., 1925, ii, 479), the results of absorption measurements of C_6H_6 derivatives, chemical evidence, and analyses of band spectra are in harmony with the view that Me acts as a positive substituent in the C_6H_6 nucleus. H. W.

Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. VIII. Polar effects of halogens. J. W. BAKER (J.C.S., 1936, 1448—1451; cf. this vol., 195).—The order for the velocity of interaction of the *m*-halogenobenzyl bromides with C_5H_5N in dry $COMe_2$ ($I > Br \approx Cl > F$) is in agreement with that of Bennett *et al.* (*ibid.*, 165) for the corresponding chlorides. The velocity order for the corresponding *p*-compounds ($F \approx I > Br > Cl$) differs from that of Bennett *et al.*, who used aq. $COMe_2$. These results are explained in terms of resonance between



The following were prepared from the appropriate halogenotoluene with Br: *m*-fluoro-, b.p. $87^\circ/17$ mm., *p*-fluoro-, b.p. $38^\circ/0.6$ mm., *m*-chloro-, b.p. $55^\circ/0.2$ mm., m.p. 17.5° , and *m*-iodo-, m.p. 50.8° , -benzyl bromide.

F. R. G.

Natural and synthetic rubber. XVI. Structure of polystyrene. T. MIDGLEY, jun., A. L. HENNE, and H. M. LEICESTER (J. Amer. Chem. Soc., 1936, 58, 1961—1963).—Contrary to Staudinger (cf. A., 1935, 740), polystyrene (I) is

$-CH_2 \cdot CHPh \cdot CHPh \cdot CH_2 \cdot CH_2 \cdot CHPh \cdot CHPh \cdot CH_2-$, since styrene+Na with EtOH give PhEt (74%) and $(CH_2Ph \cdot CH_2)_2$ (about 23%). This structure is the only one consistent with Mack's explanation (B., 1935, 196) of the elastic properties of (I). H. B.

Reactivity of the methyl group in some nitrodiphenylmethanes. G. D. PARKES and R. H. H. MORLEY (J.C.S., 1936, 1478—1479).—The influence of the position of NO_2 groups on the reaction between nitrodiphenylmethanes and *p*- $NO-C_6H_4-NMe_2$ (I) results in the formation of 4:4'-dinitro-, m.p. 155° , and 2:4:2':4'-tetranitro-benzophenone-*p*-dimethylaminoanil, m.p. 143° (decomp.), and of coloured products from 2:2'-dinitro- (II) and 2:4:6:2':4'-pentanitro-, m.p. 200° , obtained by nitration of 2:4:2':4'-tetranitro-diphenylmethane (III). The $(NO_2)_6$ -compound could not be prepared, and the 3:3'-(NO_2)₂-compound and CH_2Ph_2 do not react with (I). The anils of the (II) and (III) exceptionally resist hydrolysis. These nitrodiphenylmethanes do not couple with diazonium salts. F. R. G.

Reaction of sodium with triphenylmethyl chloride and triphenylmethyl in organic solvents. W. E. BACHMANN and F. Y. WISELOGLE (J. Amer. Chem. Soc., 1936, 58, 1943—1944).—Na (excess) reacts rapidly with CPh_3Cl in Et_2O or $Et_2O-C_6H_6$, and more slowly in C_6H_6 (cf. Morton and Stevens, A., 1932, 728), to give CPh_3 and thence $NaCPh_3$, if the metal surface is exposed throughout the reaction. When the complete reaction is slow (*e.g.*, use of 1

atom of Na) a little *p*-benzhydryltetraphenylmethane is also produced (cf. Schlenk and Marcus, A., 1914, i, 823). $NaCPh_3$ is oxidised (dry air) to $CPh_3 \cdot OH$ and a little $(CPh_3 \cdot O)_2$. H. B.

Allotropic forms of diphenyl sulphone and determination of their transition point. V. J. MIKESKA, N. T. FARINACCI, and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 1869—1871).—Crystallisation (any method) of Ph_2SO_2 at $>75^\circ$ gives a form, m.p. 128° (I); at $<75^\circ$ a form, m.p. 124° (II), results. (I) and (II) are reciprocally convertible allotropic forms; the transition temp. is 74.8° (determination described). Discrepancies in the lit. are thus explained. H. B.

Destructive catalysis of hydrindene and hydrindane. M. B. TUROVA-POLLAK (J. Gen. Chem. Russ., 1936, 6, 947—949).—Hydrogenation of hydrindene (I) at $360-380^\circ$ in presence of Pt affords mainly *o*- C_6H_4MeEt , converted by Br and $AlBr_3$ into C_6MeBr_5 . Hydrindane at $300-330^\circ$ gives chiefly (I). J. J. B.

Dipole moments and the fixation of aromatic double links: bromohydrindenes and bromotetralins. N. V. SIDGWICK and H. D. SPRINGALL (J.C.S., 1936, 1532—1537).—6-Bromo-5-aminohydrindene and 6-bromo-7-aminotetrahydronaphthalene with Cu_2Br_2 (Sandmeyer) yield respectively 5:6-dibromohydrindene (I), m.p. $76-77^\circ$, and 6:7-dibromotetrahydronaphthalene (II), m.p. $54-55^\circ$. The following dipole moments have been measured: hydrindene, 0.53D; 6-bromo-, 2.15D, and 5:6-dibromo-hydrindene, 2.48D; tetrahydronaphthalene, 0.52D; 7-bromo-, 2.23D, and 6:7-dibromo-tetrahydronaphthalene, 2.81D; 4-bromo-, 2.07D, and 4:5-dibromo-*o*-xylene, 2.86D; *o*- $C_6H_4Br_2$, 2.12D. Hence it is calc. that the moment of the aromatic Br·C·C·Br system is 2.12D; this val. is found for (I) but for (II) it is 1.78D owing to fixation of the double linkings (cf. Mills *et al.*, A., 1931, 83). F. R. G.

1-Vinylnaphthalene and certain of its derivatives. J. S. SALKIND and S. A. ZONIS (J. Gen. Chem. Russ., 1936, 6, 988—998).—The following 1-vinylnaphthalene (I) derivatives have been prepared by dehydrating the appropriate alcohols with $KHSO_3$ ($R = \alpha-C_{10}H_7$): (I), from $OH \cdot CH_2 \cdot CH_2R$; $CHR:CHMe$, from 1- α -hydroxy-*n*-propyl-, m.p. $58-59^\circ$, b.p. $139-140^\circ/4$ mm. (from EtCHO and MgRBr); $CRMe:CH_2$, from $OH \cdot CRMe_2$; 1- α -methyl- Δ^a -propenyl-, b.p. $113.5-115^\circ/5$ mm., from 1- α -hydroxy- α -methyl-*n*-propyl-, m.p. $49-50^\circ$, b.p. $146-147^\circ/4$ mm. (picrate, m.p. $138-139^\circ$) (from $COMeEt$ and MgRBr); 1- α -ethyl- Δ^a -propenyl-, b.p. $119-120.5^\circ/6$ mm., from 1- α -hydroxy- α -ethyl-*n*-propyl-, m.p. $42-43^\circ$, b.p. $145-146^\circ/3$ mm. (picrate, m.p. $131-132^\circ$) (from $COEt_2$ and MgRBr)-naphthalene. The velocity of polymerisation of the hydrocarbons falls in the order given, in presence or absence of catalysts (BzO_2H , floridin), and, except in the case of (I), the products consist chiefly of the dimerides. R. T.

cycloHexylnaphthalenes and related compounds. J. W. COOK and C. A. LAWRENCE (J.C.S., 1936, 1431—1434).—Hydrogenation (Adams) of 1-(1'-naphthyl)- Δ^1 -cyclohexene (I) takes place very

slowly owing to mutual saturation of free affinities at $C_{(2)}$ and $C_{(8)}$, to give 1-cyclohexylnaphthalene (II) (cf. Bodroux, A., 1929, 1050). 1-Keto-1:2:3:4-tetrahydronaphthalene with Mg cyclohexyl chloride gives (probably) 1-keto-2-(1'-tetrahydronaphthylidene)-1:2:3:4-tetrahydronaphthalene, m.p. 130—130.5° [2:4-dinitrophenylhydrazone, m.p. 249—250° (decomp.)], and 1-cyclohexyl-3:4-dihydronaphthalene, b.p. 140°/1 mm., 172°/10 mm., dehydrogenated to (II), b.p. 118—120°/0.3 mm. [picrate, m.p. 122—123.5°; styphnate, m.p. 150.5—151°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 116.5—117.5°]; the derivatives of (I) do not depress the m.p. of those of (II). (II) and its 2-isomeride are not dehydrogenated by Pt-black, whilst (II) remains unchanged with Se. The Li compound of 5-bromo-1:2:3:4-tetrahydronaphthalene with cyclohexene oxide gives 2-(5'-tetrahydronaphthyl)cyclohexanol, a gum (3:5-dinitrobenzoate, m.p. 163—164.5°), oxidised (H_2CrO_4 , AcOH) to the corresponding cyclohexanone [semicarbazone, m.p. 198—200° (decomp.)] and dehydrated (ZnCl_2) to 1-(5'-tetrahydronaphthyl)- Δ^1 -cyclohexene, b.p. 181°/15 mm., which was hydrogenated (Adams) rapidly [in contrast to (I)] to 5-cyclohexyl-1:2:3:4-tetrahydronaphthalene, b.p. 118°/0.2 mm. The carbinol from 2-methylcyclohexanone and $1\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ when dehydrated (KHSO_4) gives 1-(1'-naphthyl)-2-methyl- Δ^1 -cyclohexene, b.p. 125°/0.3 mm., dehydrogenated (Se) to 1-*o*-tolyl-naphthalene, m.p. 67.5—68.5°, and cyclised (AlCl_3 , CS_2) unlike (I) to a compound, b.p. 122—130°/0.3 mm., dehydrogenated (Se) to fluoranthene. n_D and d are recorded for some of the above compounds.

F. R. G.

Nitro-derivatives of fluorene. II. Colour reactions given by some derivatives of 2-nitrofluorene. C. CANDEA and E. MACOVSKI (Bull. Soc. chim., 1936, [v], 3, 1761—1767).—In presence of piperidine, 2-nitrofluorene and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ or piperonal give 2-nitro-9-*p*-tolylidene- and -9-piperonylidene-fluorene. With $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, the -9-*p*-hydroxybenzylidene compound (I), m.p. 207—208° (Bz derivative (II), m.p. 214—215°), is formed. The vanillylidene compound (A., 1935, 1488) is reduced ($\text{Zn}\text{-CaCl}_2$) to 2-amino-9-vanillylidene-fluorene (III), m.p. 190—191°. With KOH in EtOH or COMe_2 , (II) gives an intense red, (I) a feeble red, and (III) a pale yellow colour.

E. W. W.

2:3-cyclopentenonaphthalene. S. C. S. GUPTA (Current Sci., 1936, 5, 133).— γ -Keto- γ -5-hydrindyl-n-butyl-*butyric acid*, m.p. 123—124° [obtained by condensing $(\text{CH}_2\text{CO})_2\text{O}$ and hydrindine in presence of AlCl_3] is reduced (Clemmensen) to γ -5-hydrindyl-n-butyl-*butyric acid*, m.p. 56°; this on cyclisation (85% H_2SO_4) affords 1-keto-6:7-cyclopenteno-1:2:3:4-tetrahydronaphthalene, b.p. 167°/6 mm., which is reduced (Clemmensen) to 6:7-cyclopenteno-1:2:3:4-tetrahydronaphthalene, b.p. 125—126°/6 mm., and this in turn yields 2:3-cyclopentenonaphthalene, m.p. 94° (picrate, m.p. 120—121°), on dehydrogenation (Se; 300—340°).

F. N. W.

Retarding agents in the chlorination of anthracene. Influence of the nature of the solvent on the progress of the reaction. M. ILJINSKI and V. AFREMOV (Compt. rend. Acad. Sci. U.R.S.S., 1936,

3, 135—136).—The rate of chlorination of anthracene by SO_2Cl_2 is largely influenced by traces of impurity; the effect of the solvent (CCl_4 or xylene) varies with the purity of the sample of anthracene used.

A. J. E. W.

(A) **Phenanthrene-bromine addition reaction.** C. C. PRICE. (B) **Effect of substituents on phenanthrene-bromine addition reaction.** L. F. FIESER and C. C. PRICE (J. Amer. Chem. Soc., 1936, 58, 1834—1838, 1838—1843).—(A) The equilibrium consts. (K) for the reaction $\text{C}_{14}\text{H}_{10} + \text{Br}_2 \rightleftharpoons \text{C}_{14}\text{H}_{10}\text{Br}_2$ (in CCl_4 ; Br determined colorimetrically with a Keuffel and Esser spectrophotometer) are 340 ± 8 , 230 ± 6 , and 134 ± 2 at 15.7°, 25°, and 39°, respectively. O_2 , Bz_2O_2 , and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ have no effect but NHPh_2 , quinol, and tetrabromo-quinol and -pyrocatechol are effective inhibitors even in relatively small amounts. A chain mechanism and method for the determination of its length are discussed. Addition of phenanthrene (I) to Br in dioxan (II) (solution stable at room temp.) causes bromination of (II) ($\frac{2}{3}$) and addition to (I) ($\frac{1}{3}$).

(B) The nos. quoted after the following derivatives of phenanthrene are the K at 25° and 36° (unless stated otherwise), respectively: 2- CO_2Et -, 168, 88; 3- CO_2Et -, 93, 59; 2- CO_2Me -, 167, 81; 3- CO_2Me -, 129, 63; 2-Cl-, 159, 54; 3-Cl-, 170, 67; 2-Br-, 152, 59; 3-Br-, 152, 69; 2- Bu^γ -, 320, 262 (at 37.4°); 3- Bu^γ -, 467, 191 (at 37.4°). Hal and $\text{CO}_2\text{Me}(\text{Et})$ (more effective in 3- than 2-position), *i.e.*, groups which retard substitution in the C_6H_6 ring, decrease the free energy of the 9:10-addition of Br, whilst Bu^γ (which facilitates substitution) causes an increase; these results parallel those obtained (A., 1929, 1452) for the free energy of oxidation of 9:10-dihydroxyphenanthrenes. A sp. decrease in the reaction velocity is found for the 2-Hal (*i.e.*, *m*-position). Et, OMe, and NHAc substituents lead to irreversible absorption of >1 mol. of Br_2 .

PhBu^γ , $(\text{CH}_2\text{CO})_2\text{O}$, and AlCl_3 in CS_2 give β -*p*-tert-butylbenzoylpropionic acid, dimorphous, both m.p. 121—122° [oxidised (KOCl) to $p\text{-C}_6\text{H}_4\text{Bu}^\gamma\text{CO}_2\text{H}$ and thence (dil. HNO_3) to $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$], reduced (modified Clemmensen; this vol., 1249) to γ -*p*-tert-butylphenylbutyric acid, m.p. 59.5—60.5°, the Et ester, b.p. 145—147°/5 mm., of which with $\text{Et}_2\text{C}_2\text{O}_4$ (method: A., 1935, 1495) followed by 80% H_2SO_4 at 60° affords 7-tert-butyl-3:4-dihydronaphthalene-1:2-dicarboxylic anhydride (I), m.p. 143—145°, and a little of an isomeride, m.p. 174—175°. (I) is dehydrogenated (S at 330—340°) to 7-tert-butyl-naphthalene-1:2-dicarboxylic anhydride, m.p. 146.5—147.5°. $(\text{CH}_2\text{CH})_2$ and (I) at 150° give 6-tert-butyl-1:4:9:10:11:12-hexahydrophenanthrene-11:12-dicarboxylic anhydride, m.p. 85.5—86.5°, converted by KOH at 330—360° (method: this vol., 203) into a product which is dehydrogenated (Se) to 3-tert-butylphenanthrene, m.p. 54—55° (picrate, m.p. 142—143°; quinone, m.p. 186—187°). 2- $\text{C}_{10}\text{H}_7\text{Bu}^\gamma$, $(\text{CH}_2\text{CO})_2\text{O}$, and AlCl_3 in cold PhNO_2 afford β -6-tert-butyl-2-naphthylpropionic acid, m.p. 148—150°, reduced (as above) to γ -6-tert-butyl-2-naphthylbutyric acid, ? dimorphous, m.p. 87—95°, the chloride of which with AlCl_3 in cold CS_2 gives 1-keto-7-tert-butyl-1:2:3:4-tetrahydrophenanthrene (picrate,

m.p. 107—108°), converted by successive reduction and dehydrogenation (Se at 320—350°) into 2-*tert*-butylphenanthrene, m.p. 99—100° (*picrate*, m.p. 130—131°; *quinone*, m.p. 129—130°). 2-Acetylphenanthrene and MgMeI in Et₂O—C₆H₆ afford 2-phenanthryldimethylcarbinol, dimorphous, m.p. 90—92° (decomp.) and 97—99° (decomp.); recrystallisation of 3-phenanthryldimethylcarbinol *picrate*, m.p. 107—110° (decomp.), from EtOH gives (probably) 3-isopropenylphenanthrene *picrate*, m.p. 160—163° (decomp.). C₁₀H₈, Bu^γCl, and a little AlCl₃ afford (cf. Gump, A., 1931, 341) 2-C₁₀H₇Bu^γ and two C₁₀H₆Bu^γ₂, m.p. 86—90° (*picrate*, m.p. 155.5—156.5°) and 146—147° [oxidised (CrO₃, AcOH) to a *quinone*, C₁₈H₂₂O₂, m.p. 83.5—84.5°]. H. B.

Synthesis of an isomeride of retene: 1-methyl-9-isopropylphenanthrene. G. DARZENS and A. LÉVY (Compt. rend., 1936, 203, 669—671).—Condensation of 1:4-C₁₀H₆Pr^β-CH₂Cl with Et malonate yields *Et* 4-isopropyl-1-naphthylmethylmalonate (I), a viscid liquid (*acid*, decomp. 170° to 4-isopropyl-naphthalene-1-propionic acid, m.p. 136°). The Na derivative of (I) is condensed with allyl bromide, and the resulting ester hydrolysed to the dibasic acid which decomposes at 170°, giving β-(4-isopropyl-1-naphthyl)-α-allylpropionic acid, a viscid liquid. Cyclisation of this acid with H₂SO₄+AcOH for 3 days at 40° gives a mixture of 1-methyl-9-isopropyl-1:2:3:4-tetrahydrophenanthrene-3-carboxylic acid (II), m.p. 160° [*Me* ester (III), b.p. 192—193°/4 mm.], and the lactone, b.p. 195—197°/4 mm., of β-(4-isopropyl-1-naphthyl)-α-γ-hydroxypropylpropionic acid. (III) when heated with S at 240° gave the *Me* ester, b.p. 195—196°/4 mm., of 1-methyl-9-isopropylphenanthrene-3-carboxylic acid, m.p. 204°. Se and (II) at 340° gave 1-methyl-9-isopropylphenanthrene, b.p. 204—205°/14 mm. (*picrate*, m.p. 143°; *styphnate*, m.p. 156°). Oxidation with CrO₃ gives 1-methylphenanthraquinone with elimination of Pr^β. J. N. A.

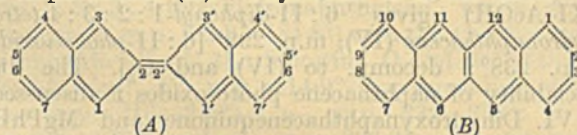
Constitution of hexahydropyrene. J. W. COOK and C. L. HEWETT (Chem. and Ind., 1936, 843—844).—Pestemer *et al.* (this vol., 1048) have overlooked the authors' earlier work (A., 1933, 601) on the isolation and structures of two hexahydropyrenes.

J. W. B.

Detection of 1:2-benzpyrene with the fluorescence spectrograph. G. MIESCHER, F. ALMASY, and K. KLÄUI (Biochem. Z., 1936, 287, 189—197; cf. Sannié, this vol., 664; Mayneord, *ibid.*).—Pure 1:2-benzpyrene (I) in C₆H₁₄ can be detected by its fluorescence spectrum in concns. <0.0025 mg. per litre; combination with other fluorescent polycyclic hydrocarbons (*e.g.*, chrysene, phenanthrene, pyrene, retene, 1:2:5:6-dibenzanthracene, anthracene, 2-methylanthracene, fluoranthrene) singly and together does not seriously interfere with the detection. (I) in tar fractions is detected in the same way in 0.0003% concn. if basic impurities are removed with H₂SO₄. W. McC.

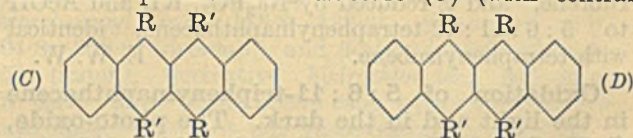
Naphthacene structure of rubenes. I. II. The new structure: mechanism of formation, constitutions, and formulæ with corrected nomenclature. C. DUFRAISSE. III. Historical review and discussion of naphthacenes, their syntheses,

and their photochemical characteristics. IV. Naphthacene the prototype of the rubenes. V. Synthesis of phenylnaphthacenes of rubene character. C. DUFRAISSE and R. HORCLOIS. VI. Synthesis of 5:6:11:12-tetraphenylnaphthacene: its identity with tetraphenylrubene (formerly known as rubrene). C. DUFRAISSE and L. VELLUZ (Bull. Soc. chim., 1936, [v], 3, 1847—1857, 1857—1872, 1872—1880, 1880—1893, 1894—1905, 1905—1913).—I. Theoretical. The name "rubene" is abandoned: rubenes have not the structure (A) previously attributed to them, but are derivatives of naphthacene (B). Objections to A are discussed.



That naphthacenes, with which rubenes are now identified, have not structure A is shown by absorption spectra, and by the formation of photo-oxides. The structure of ψ-rubene is discussed.

II. Three possible mechanisms of the formation of "rubenes" (tetra-substituted naphthacenes) from CPhRCl:C:CR' are discussed: the prior formation of structure (A) (above); the intermediate formation of dibenzocyclodecadiene; and direct condensation. That the product has structure (C) (with central



symmetry) and not the alternative (D) (with planar symmetry), is shown by the fact that if R' is replaced by Cl, HCl is lost by two stages; thus 6:12-dichloro-5:11-diphenylnaphthacene (the former "3:3'-dichloro-1:1'-diphenylrubene") yields first 12-chloro-11-phenyl-5:6-phenylenenaphthacene ("3'-chloro-3-phenyl-1:1'-phenylenrubene"), and then 5:6:11:12-diphenylenenaphthacene ("1:1':3:3'-diphenylenrubene"). Revised names of rubene derivatives are recorded.

III. A review.

IV. Naphthacene (I) (improved prep. from tetramethyleneanthraquinone by passage over Zn at 300—400°, followed by passage over Zn at 700° or PbO at 400°) gives an absorption spectrum similar to that from "tetra-arylrubenes"; when exposed, in CS₂ solution, to sunlight, it absorbs O₂ to give a non-fluorescent photo-oxide [decomp. 120°, to resinous products, with little (I)], which is reduced by KI, with formation of benzanthrone. With HI, or KOH in C₅H₁₁·OH or CH₂Ph·OH, (I) gives 5:12-dihydronaphthacene. (I) is not isomerised by H₂SO₄ or other acids.

V. Naphthacenequinone (new prep. from 2:3-tetramethyleneanthraquinone, using PbO) with MgPhBr yields 5:12-dihydroxy-5:12-diphenyl-5:12-dihydronaphthacene (II), m.p. 251—252°, with two diphenyltetrahydronaphthacenequinones (cf. this vol., 992). (II) with KI, Na₂PO₃, and AcOH, or 6:11-diphenyl-1:2:3:4-tetrahydronaphthacene dehydrogenated, gives 5:12-diphenylnaphthacene (III), m.p.

207—208° (+0.5Et₂O, m.p. 171—172°). Oxidation of (III) (heating in air, or action of H₂SO₄) gives violet 11-phenyl-5:6-phenylenenaphthacene, further oxidised by FeCl₃-H₂SO₄ to blue 5:6:11:12-diphenylenenaphthacene. With gaseous HI in CS₂, (III) gives 5:12-diphenyl-5:12-dihydronaphthacene, m.p. 206—207°, reconverted into (III) by heating. (III) is very sensitive to light, yielding the 5:12(or 6:11)-photodioxide, decomp. 160°. 2:3-Tetra-methyleneanthraquinone and MgPhBr furnish 6:11-dihydroxy-6:11-diphenyl-1:2:3:4:6:11-hexahydronaphthacene, m.p. 239—240°, which on attempted dehydration gives only (III), and on reduction (KI-AcOH) gives 6:11-diphenyl-1:2:3:4-tetrahydronaphthacene (IV), m.p. 298° [6:11-photodioxide, m.p. 238°; decomp. to (IV) and O₂]. The dissociability of naphthacene photo-oxides is discussed.

VI. Dihydroxynaphthacenequinone and MgPhBr give 5:6:11:12-tetrahydroxy-5:12-diphenyl-5:12-dihydronaphthacene (with some 6-hydroxy-11-phenylnaphthacene-5:12-quinone, m.p. 304—305°), converted on heating, alone or in AcOH, into 6:11-diphenylnaphthacene-5:12-quinone, m.p. 284—285°. This with MgPhBr yields 5:12-dihydroxy-5:6:11:12-tetraphenyl-5:12-dihydronaphthacene, m.p. 251° (+2C₆H₆, m.p. 185°), which when heated in AcOH loses H₂O, forming 5:12-diphenyl-5:6:11:12-diphenylene-5:12-dihydronaphthacene, identical with "dehydro-rubrene," and is reduced by Na₂PO₃, KI, and AcOH to 5:6:11:12-tetraphenylnaphthacene, identical with tetraphenylnaphthacene. E. W. W.

Oxidation of 5:6:11-triphenylnaphthacene in the light and in the dark. The photo-oxide, C₂₆H₂₄O₂. M. BADOCHÉ (Bull. Soc. chim., 1936, [v], 3, 2040—2046).—5:6:11-Triphenylnaphthacene (I) (formerly triphenylrubene) (prep. described) has m.p. 236—237°, or +1C₆H₆ which cannot be removed without decomp. of the mol., m.p. 177—178°. On exposure to sunlight in C₆H₆ it readily absorbs O₂ giving 5:6:11-triphenylnaphthacene 5:12-dioxide (II) (+1C₆H₆), m.p. about 176—177°, which evolves a small amount of gas containing 85—90% of O₂ when heated at 140°/vac., and a larger proportion when heated rapidly over a naked flame. Little gas is evolved when it is heated progressively by itself or mixed with vaseline or sand. The constitution of (II) is advanced with reserve and is based mainly on its differing behaviour from 5:6:11:12-tetraphenylnaphthacene 5:12-dioxide and the analogous difference between the photo-oxides of anthracene and 9:10-diphenylanthracene. A conc. solution of (I) in C₆H₆ over Hg slowly absorbs O₂ in the dark giving an oxide which does not appear identical with (II). H. W.

Isotopic exchange between aniline hydrochloride and heavy water.—See this vol., 1339.

Rearrangement of N-iodoformanilide in anisole solution.—See this vol., 1471.

Additive product of basic copper trichloroacetate with benzylamine. A. ABLOV (Bull. Soc. chim., 1936, [v], 3, 1915).—The compound, (CCl₃·CO₂)₂ $\left[\begin{array}{c} A \\ \diagdown \quad \diagup \\ \text{Cu} \quad \text{OH} \\ \diagup \quad \diagdown \\ A \end{array} \right]_2 \text{H}_2\text{O}$, where A =

CH₂Ph·NH₂, is prepared by treating Cu(O·CO·CCl₃)₂ with A in EtOH. E. W. W.

Derivatives of 2:4-di- and 2:4:5-tri-methylaniline. G. VAN KLEEF (Rec. trav. chim., 1936, 55, 765—785).—Acet-*m*-4-xylylide, m.p. 130° (best prepared by boiling the base with AcOH), with HNO₃ (best, *d* 1.42) at 0° gives the 5-NO₂- (Me:Me:NH₂=1:3:4), m.p. 172° (cf. lit.), and with abs. HNO₃ the 5:6-(NO₂)₂-derivative, m.p. 220° (lit. 117°). *Me m*-4-xylylcarbamate [prep. from *as*-*m*-xylidine (I) and ClCO₂Me in H₂O at 0°], m.p. 79°, affords similarly the 5-NO₂-, m.p. 134° [hydrolysed to 5-nitro-*m*-4-xylidine (II) by conc. H₂SO₄ at 100°], and 5:6-(NO₂)₂- (III) -derivative, m.p. 218° (resistant to hydrolysis). Similarly are obtained Et *m*-4-xylylcarbamate, m.p. 59° (lit. 58°), and its 5-NO₂-, m.p. 134° (lit. 125—126°) [hydrolysed by conc. H₂SO₄ at 125—130° to (II)], and 5:6-(NO₂)₂-derivative (IV), m.p. 150° (hydrolysed similarly to 5:6-dinitro-*m*-4-xylidine). *N*-*m*-4-Xylyl-*N'*-methylcarbamide (prep. in C₆H₆), m.p. 170°, with HNO₃ (*d* 1.4) affords the 5-NO₂-derivative, m.p. 230° [also obtained from (II) and PhNCO], and with abs. HNO₃ *N*-nitro-*N*-5:6-dinitro-*m*-4-xylyl-*N'*-methylcarbamide, unstable, which with hot abs. EtOH gives (IV), also obtained from (III). Similarly are prepared *N*-*m*-4-xylyl-*N'*-ethylcarbamide, m.p. 188°, and its 5-NO₂-, m.p. 220°, and 5:6:*N'*-(NO₂)₃-derivative. *Me m*-4-xylyloxamate [prep. with some ox-*m*-4-xylylide (V) by boiling Me₂C₂O₄], m.p. 77°, gives similarly the 5-NO₂-, m.p. 145°, and 5:6-(NO₂)₂-derivative, m.p. 169°, both stable to hydrolysis. (V), m.p. 214° (lit. 210°), gives the 5:5'-(NO₂)₂-, m.p. 220°, and 5:6:5':6'-(NO₂)₄-derivative, amorphous, both stable to hydrolysis. Similarly are obtained acet-*ψ*-cumidide (prep. by Ac₂O), m.p. 165° (cf. lit.), and its 6-NO₂- (Me:Me:Me:NH₂=1:2:4:5), m.p. 198° (cf. lit.), and 3:6-(NO₂)₂-derivative, m.p. 288° (cf. lit.), *Me*, m.p. 115° [6-NO₂-, m.p. 155°, and 3:6-(NO₂)₂-derivative, m.p. 211°], and Et *ψ*-cumyl-5-carbamate, m.p. 105° [6-NO₂-, *cryst.*, and 3:6-(NO₂)₂-derivative, m.p. 221°], *N*-*ψ*-5-cumyl-*N'*-methyl-, m.p. 212° [6-NO₂-, m.p. 268°, and *N'*:3:6-(NO₂)₃-derivative], and -ethyl-carbamide, m.p. 213° [6-NO₂-, m.p. 246°, and 3:6:*N'*-(NO₂)₃-derivative], *Me*, m.p. 75° [6-NO₂-, m.p. 206°, and 3:6-(NO₂)₂-derivative, m.p. 192°], and Et *ψ*-5-cumyloxamate, m.p. 78° [6-NO₂-, m.p. 162°, and 3:6-(NO₂)₂-derivative, m.p. 171°], *s*-ox-*ψ*-5-cumidide, m.p. 237° (lit. 230°) [6:6'-(NO₂)₂-derivative, m.p. 317° (block), and 3:6:3':6'-(NO₂)₄-derivative, m.p. 340° (block)]. N₂H₄·H₂O and (I) in EtOH give rapidly *m*-4-xylyloxamhydrizide (VI), m.p. 165° (lit. 160°). 5-*ψ*-Cumyloxamhydrizide (VII), m.p. 212°, is similarly prepared. (VI) in H₂O containing a little EtOH and (VII) in 50% EtOH, respectively, give substituted hydrazones [oxamazones] with the following aldehydes: CH₂O, m.p. 196°, about 219°, MeCHO, m.p. 205°, 238°, EtCHO, m.p. 186°, 214°, PrCHO, m.p. 168°, 198°, BuCHO, m.p. 173°, 194°, *o*-, m.p. 248°, 252°, and *p*-OH·C₆H₄·CHO, m.p. 265°, 267°, *p*-OMe·C₆H₄·CHO, m.p. 220°, 245°, vanillin, m.p. 240°, 241°, piperonal, m.p. 261°, 226°, *p*-C₆H₄·Me·CHO, m.p. 212°, 245°, *p*-C₆H₄·Pr^β·CHO, m.p. 209°, 205°, *o*-, m.p. 275°,

271°, *m*-, m.p. 211°, 239°, and *p*-NO₂·C₆H₄·CHO, 271°, 277°, furfuraldehyde, m.p. 206°, 228° (decomp.), 5-methyl-, m.p. 182°, 180° (decomp.), and 5-hydroxymethyl-furfuraldehyde, m.p. 200°, 174°. R. S. C.

New diphenylamine derivatives. J. S. JOFFE, S. D. SUDAKOV, and S. G. KUZNETZOV (J. Gen. Chem. Russ., 1936, 6, 983—987).—3-Chloro-6-nitroaniline-4-sulphonic acid, NH₂Ph, and MgCO₃ in 60% EtOH (16 hr.; 160—180°) yield the Mg salt of 4-nitro-5-aminodiphenylamine-2-sulphonic acid, from which the internal salt of the corresponding diazonium compound is obtained. This yields a red *azo-dye* when coupled with β-C₁₀H₇·OH, 4-nitro-5-hydroxydiphenylamine-2-sulphonic acid with boiling H₂O, and 4-nitro-5-chlorodiphenylamine-2-sulphonic acid by the Sandmeyer reaction. R. T.

Nitration of benzyaniline and its derivatives. P. VAN DEN BERG (Rec. trav. chim., 1936, 55, 841—853).—Unless otherwise stated, nitrations given below were effected by abs. HNO₃ and acetylations by Ac₂O and a little H₂SO₄ (Ac₂O alone usually being ineffective). *p*-Nitrobenzyl-2:4:6-trinitrophenylnitroamine (I) [previously considered to be the (NO₂)₄-base], m.p. 142° (decomp.), is obtained from *p*'-nitrobenzyl-*p*- and -*o*-nitroaniline, m.p. 140° (cf. lit.) (*Ac* derivative, m.p. 157°), benzyl-2:4-di-, m.p. 116.5°, and -2:4:6-tri-nitroaniline, *p*-nitrobenzyl-2:4-di-, m.p. 186°, and -2:4:6-tri-nitroaniline, m.p. 191°. With NH₃-EtOH it gives picramide and with hot aq. Na₂CO₃ picric acid. 2':4'-Dinitrobenzyl-2:4:6-trinitrophenylnitroamine (II), m.p. 151° (decomp.), is obtained from *p*'-nitrobenzyl-aniline (H₂SO₄-HNO₃, *d* 1.4), benzyl-*p*-nitroaniline, m.p. 147° [*Ac* derivative, m.p. 111° (lit. 108—109°); H₂SO₄-abs. HNO₃], and (I) (H₂SO₄-abs. HNO₃). *o*'-Nitrobenzyl-*p*-, m.p. 202° (*Ac* derivative, m.p. 178°), or -*o*-nitroaniline, m.p. 138° (*Ac* derivative, m.p. 137°), with HNO₃ (*d* 1.46) gives *o*-nitrobenzyl-2:4:6-trinitrophenylnitroamine (III), m.p. 149° (decomp.), and with abs. HNO₃ yields (II). *m*- and *p*-Nitration of the CH₂Ph of NHPh·CH₂Ph by a little abs. HNO₃ in H₂SO₄ is confirmed. R. S. C.

Nitrous acid as a nitrating and oxidising agent. III. Nitration of 4-dimethylaminoaceto-1-naphthalide, of 4-chloro-1-naphthylidimethylamine, and of β-naphthylidimethylamine. H. H. HODGSON and J. H. CROOK (J.C.S., 1936, 1500—1503).—By coupling α-C₁₀H₇·NMe₂ (*picrate*, m.p. 145°) with diazotised *p*-NH₂·C₆H₄·SO₃H and reductive fission (SnCl₂-HCl) of the azo-compound is obtained 1:4-NH₂·C₁₀H₆·NMe₂ [*dihydrochloride* (I)], converted by Ac₂O into 1:4-NHAc·C₁₀H₆·NMe₂ (II) [*picrate*, m.p. 201° (decomp.)]. (I) is converted (Sandmeyer) into the *hydrochloride*, m.p. 215° (decomp.), of 4-chloro-1-naphthylidimethylamine (III) (*picrate*, m.p. 146°). (II) with NaNO₂-HCl at 0° is oxidised to α-naphthaquinone, but (III) affords a 2-NO₂-derivative, (IV), m.p. 58°, synthesised as follows: 2-nitroaceto-1-naphthalide with Cl₂-AcOH at 100° gives its 2-*Cl*-derivative, m.p. 219°, hydrolysed to 4-chloro-2-nitro-α-naphthylamine, m.p. 202°, converted (Sandmeyer) into 1:4-dichloro-2-nitronaphthalene, m.p. 116.5° (1-chloro-4-iodo-3-nitronaphthalene, m.p. 107°, is obtained similarly), converted by heat-

ing with NHMe₂-EtOH into (IV), and by NH₂Me, HCl-NaOAc-EtOH into 4-chloro-2-nitro-1-naphthylmethylamine, m.p. 175°. β-C₁₀H₇·NMe₂ [*picrate*, m.p. 200° (decomp.)] and NaNO₂-HCl at 0° afford 1-nitro-2-naphthylidimethylamine, m.p. 76—77°, synthesised from 2:1-C₁₀H₆Cl·NO₂ and NHMe₂-EtOH. J. W. B.

Local anæsthetics containing the ac-tetrahydro-β-naphthylamine pressor group. H. W. COLES and W. A. LOTT (J. Amer. Chem. Soc., 1936, 58, 1989—1990).—*ac*-Tetrahydro-β-naphthylamine (I) (2 mols.) and CH₂Cl·CH₂·OH (1 mol.) in xylene and N₂ at 110—115° give 2-β-hydroxyethylamino-1:2:3:4-tetrahydronaphthalene, which (as *hydrochloride*, m.p. 183.8—184.8°) with the appropriate acyl chloride affords the following *O*-acyl derivative *hydrochlorides*: *Bz*, m.p. 214.9° (corresponding *sulphate*, m.p. 216—218°); *o*-, m.p. 232—233°, *m*-, m.p. 216—217°, and *p*-, m.p. 236.2°, -*nitrobenzoyl* [reduced (Fe, HCl) to the aminobenzoyl derivatives (*dihydrochlorides*, m.p. 150°, 205—206°, and 223.3°, respectively)]; *p*-chloro-, m.p. 219—220°, and *p*-iodo-, m.p. 232°, -*benzoyl*; *cinnamoyl*, m.p. 194—195.8°; *phthaloyl*, m.p. 185—186°. 2-γ-Hydroxypropylamino-1:2:3:4-tetrahydronaphthalene (*hydrochloride*, m.p. 161°), from (I) and CH₂Cl·CH₂·CH₂·OH, similarly affords *Bz*, m.p. 195.6° (corresponding *picrate*, m.p. 83.86°), *m*-, m.p. 173.4—177.4°, and *p*-, m.p. 228—229°, -*nitrobenzoyl*, *p*-chlorobenzoyl, m.p. 188.8—189.8°, *cinnamoyl*, m.p. 204.8—206.8° (decomp.), and β-phenylpropionyl, m.p. 95° (indef.), derivative *hydrochlorides*. All m.p. are corr. Most of the above ester hydrochlorides are local anæsthetics but not vasopressors. H. B.

Reaction of *p*-phenylenediamine and its derivatives with diazonium salts. J. S. JOFFE and V. J. SOLOVEJTSCHUK (J. Gen. Chem. Russ., 1936, 6, 977—982).—*p*-C₆H₄(NHPh)₂ (I) in EtOH-HCl and diazotised metanilic acid at 0° yield 2:5-dianilino-diphenyl-3'-sulphonic acid. An analogous reaction takes place when *p*-C₆H₄(NH₂)₂ or *p*-NHPh·C₆H₄·NH·C₆H₄·NH₂ is used in place of (I). R. T.

Preparation of 2:6-dinitro-*p*-phenylenediamine, 2:6-dinitrotetramethyl-*p*-phenylenediamine, and 4-chloro-2:3-dinitroanisole. H. H. HODGSON and J. H. CROOK (J.C.S., 1936, 1570).—When heated with an excess of NHMe₂-EtOH, 2:6-dinitrodimethyl-*p*-anisidine affords 2:6-dinitrotetramethyl-*p*-phenylenediamine, m.p. 176°; 2:6-dinitro-*p*-phenylenediamine is obtained similarly. 4-Chloro-2:3-dinitroanisole, m.p. 133°, is obtained by the Sandmeyer reaction from 2:3-dinitro-*p*-anisidine. J. W. B.

NN'-Dibenzylethylenediamine. G. LOB (Rec. trav. chim., 1936, 55, 859—873).—NN'-Dibenzylethylenediamine (I), b.p. 212—213°/12 mm., *d*₄²⁰ 1.024, *n*_D²⁰ 1.5624, best obtained by reduction of the Schiff's base with Na-EtOH, gives the following derivatives: *hydrochloride*, m.p. 160—170° (block), *nitrate*, m.p. 180—190° (block), *picrate*, m.p. 200—210° (block), *carbamate* (from 1 mol. of CO₂), decomp. 90—95° (open tube), *dinitroso*-, m.p. 87°, *Ac*₂, m.p. 139°, *di-propionyl*, m.p. 69°, -*n*-butyryl, m.p.

72—73°, -*n*-valeryl, m.p. 91°, -*n*-hexoyl, m.p. 92°, -stearyl, m.p. 67°, -*o*-, m.p. 198—202°, -*m*-, m.p. 136—147°, and -*p*-nitrobenzoyl, m.p. 178°, *Bz*₂ (II), m.p. 183°, *di*-benzenesulphonyl, m.p. 228°; *dicarbonyl*, m.p. 176°, *di*-ethyl-, m.p. 168°, -phenyl-, m.p. 178—179°, -*o*-, m.p. 183—184°, -*m*-, m.p. 171—172°, and -*p*-nitrophenyl-, m.p. 231°, and -2:4-dinitrophenyl-*dicarbonyl*, m.p. 225° (decomp.), *di*-*α*-naphthyl-*dicarbonyl*, m.p. 229° (decomp.), and *diphenyldithiocarbonyl*, m.p. 184°. 2-Phenyl-1:3-dibenzyl-tetrahydroglyoxaline gives (I) and PhCHO with dry or 10% aq. HCl, picric acid, or 10% H₂SO₄, but is stable to CO₂, 10% aq. NaOH, Na-EtOH, or MeI; with KMnO₄ it gives BzOH and NH₂Bz, with abs. HNO₃ at -10° NN'-*di*-*α*-nitrobenzylethylenediamine, and with I-EtOH N-iodo-NN'-*di*-benzylethylenediamine di-iodide (III), +2EtOH, m.p. 165—166°, and PhCHO. The structure of (III) follows because it contains 2 reactive I (giving with Na₂S₂O₃ N-iodo-NN'-*di*-benzylethylenediamine, +C₆H₆, m.p. 142°), with 10% H₂SO₄ and subsequent benzylation affords (II), and is obtained also from (I) and I-Et₂O. (I) with aliphatic aldehydes alone or with aromatic aldehydes in abs. EtOH gives 2-substituted 1:3-dibenzyltetrahydroglyoxalines in which the 2-substituent is H, m.p. 27°, Me, m.p. 34°, Et, m.p. 32°, Pr^α, m.p. 11°, Pr^β, m.p. 33°, Bu, m.p. 13°, amyl, an oil, n_D²⁰ 1.5448, hexyl, an oil, n_D²⁰ 1.5406, *p*-tolyl, m.p. 88°, *p*-anisyl, m.p. 90°, *o*-, m.p. 91°, *m*-, m.p. 95—96°, and *p*-nitro-, 101—102°, *o*-, m.p. 96—97°, *m*-, m.p. 93°, and *p*-chloro-, m.p. 110°, *o*-, m.p. 108°, and *p*-hydroxy-, m.p. 139°, *p*-isopropyl-, m.p. 63°, 3-methoxy-4-hydroxy-, m.p. 84—85°, and 3:4-methylenedioxy-phenyl, m.p. 111—112°, benzyl, m.p. 66—67°, furyl, m.p. 74°, 2-5-methyl-, m.p. 77—78°, and 2-5-hydroxymethyl-furyl, m.p. 127°, all hydrolysed by dil HCl. However, (I) does not react with COMe₂ at 200—210°, CMe₂Cl₂-K₂CO₃ at 100°, CPh₂Cl₂, or PhI. With COCl₂ (I) gives a *s*-dichloroformyl derivative, m.p. 83°, which decomposes at 230°/12 mm. into CO₂ and 2-*keto*-1:3-dibenzyltetrahydroglyoxaline, m.p. 93°. With CS₂ (I) gives 2-*thio*-1:3-dibenzyltetrahydroglyoxaline, m.p. 90°, stable to hot 10% acid or alkali, with (COCl)₂ in C₆H₆ gives 1:4-dibenzyl-2:3-diketopiperazine, amorphous, m.p. 120—140°, with 2:4-C₆H₄Cl(NO₂)₂ or picryl chloride in NaOAc-EtOH affords NN'-*di*-2:4-*di*-, m.p. 178°, and -2:4:6-*tri*-nitrophenyl-NN'-*di*-benzylethylenediamine, m.p. 202° (decomp. from 190°), respectively, and with CH₂PhCl-K₂CO₃ or EtBr-K₂CO₃ (100°), or C₂H₄Br₂-K₂CO₃ (130—140°) yields NNN'N'-*tetra*benzyl-, m.p. 95° [*di*hydrochloride, m.p. 140—150° (block), +*z*EtOH, m.p. 80—90° (block) (resolidifies and remelts at 140—150°), hydrolysed by cold H₂O], and NN'-*di*-benzyl-NN'-*di*ethyl-ethylenediamine, b.p. about 250°/20 mm. (*di*-carbonate, -hydrochloride, solid, and -picrate, m.p. 202—206°), and 1:4-dibenzylpiperazine, m.p. 91°, respectively.

R. S. C.

Diaryls and their derivatives. XII. Selective sorption by vegetable fibres of azo-dyes prepared from dihydroxynaphthalenes and polyhydroxydinaphthyls. J. S. JOFFE and M. A. TSCHEGROV (J. Gen. Chem. Russ., 1936, 6, 1014—1021).—The following azo- and bisazo-dyes, prepared from the appropriate diazonium salts and polyhydroxy-naph-

thalenes and -dinaphthyls, are only very feebly substantive for cotton: 1-*p*-sulphobenzeneazo-2:6- and -2:7-dihydroxynaphthalene, 1-*p*-nitrobenzeneazo-8-*p*-sulphobenzeneazo-2:7-dihydroxynaphthalene, 1-*p*-nitrobenzeneazo-5-*p*-sulphobenzeneazo-2:6-dihydroxynaphthalene, 8-*p*-sulphobenzeneazo-2:7:2':7'-tetrahydroxy-1:1'-dinaphthyl, 5-*p*-sulphobenzeneazo-2:6:2'-*tri*- and -2:6:2':6'-*tetra*-hydroxy-1:1'-dinaphthyl, and 5-*p*-nitrobenzeneazo-5'-*p*-sulphobenzeneazo-2:6:6'-*tri*-hydroxy-1:1'-dinaphthyl.

R. T.

Diazotisation of weakly basic and insoluble amines. Use of pyridine, quinoline, and *iso*-quinoline as solvents for the amines. C. DEMILT and G. VAN ZANDT (J. Amer. Chem. Soc., 1936, 58, 2044—2046).—3-Nitro-4-aminodiphenyl, 2:6-dichloro-4-nitroaniline, picramide (I), and 3-aminophenanthrene (II) are completely diazotised by slow addition of a solution in C₅H₅N to nitrosylsulphuric acid (III) in H₂SO₄ at <10°; the mixture is stirred for 30 min. and finally freed from HNO₂ with CO(NH₂)₂. 4:6-Dibromo-2-nitroaniline and (I) are similarly diazotised using solutions in quinoline and *iso*quinoline, respectively. Diazotisation also occurs when (II) (in C₅H₅N) and aq. NaNO₂ are added alternately to 40% HBr at <4°. The org. base releases HNO₂ from (III). 2-Nitro-4-phenyl-, m.p. 228°, and 4:6-dibromo-2-nitro-, m.p. 250°, -benzeneazo-β-naphthols are new.

H. B.

Potentiometric measurements of the transformation of the diazo- into the azo-group. V. KŘEPELKA and M. BLABOLIL (Coll. Czech. Chem. Comm., 1936, 8, 408—418).—The tetrazotisation of benzidine (I) can be followed potentiometrically. The coupling at 3° of tetrazotised (I) with Na 8-amino-α-naphthol-3:6-disulphonate (1 mol.), and the coupling of the product with *m*-C₆H₄(NH₂)₂ in Na₂CO₃ solution were followed by determining, at intervals, the % of diazo-N and azo-N. Diazo-N was measured by boiling an aliquot part with 50% aq. H₂SO₄ and measuring the evolved N₂. Azo-N was determined, after removing diazo-N by boiling with H₂SO₄, by adding excess of Ti₂(SO₄)₃ in an atm. of CO₂ and back-titrating electrometrically with approx. 50 c.c. of 0.05N-FeNH₄(SO₄)₂. The first coupling is rapid at first, but requires >40 hr. for completion. The acidity of the medium has little effect. The second coupling is complete in 2 hr. Tetrazotised (I) is stable at 3° whether in acid, neutral, or alkaline (Na₂CO₃) solution.

J. G. A. G.

Manufacture of alkylated phenols.—See B., 1936, 1083.

Action of hexamethylenetetramine on alkyl halides in presence of monohydric phenols. I. P. BOUCHEREAU (J. Pharm. Chim., 1936, [viii], 24, 352—362).—By heating (CH₂)₆N₄ (I) with RX and ArOH in CHCl₃ or EtOH are obtained crystalline compounds of the general type (CH₂)₆N₄(RX)(ArOH) in which the halogen remains united to the alkyl. When heated the halogen migrates to the phenol to give halogenated phenol-CH₂O resins. Thus are obtained the compounds from (I), PhOH, and: EtBr, loses NH₃ at 85—90°, resinifies at 130—150°; CH₂PhCl, m.p. 79—80°; EtI, m.p. 118—120°,

resinifies at 140—150°; and (I), $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, and EtBr , m.p. 85°, resinifies at 130—140°. These compounds are antiseptic and non-toxic when injected intravenously and their therapeutic uses are briefly described.

J. W. B.

Mills-Nixon effect. L. F. FIESER and W. C. LOTHROP (J. Amer. Chem. Soc., 1936, 58, 2050—2054).—The coupling of 5-hydroxy-4:7-dimethylhydrindene and the non-coupling of 5-hydroxy-6-methylhydrindene with diazotised $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ indicate, in agreement

with Mills and Nixon (A., 1931, 83), that hydrindene has the rigid structure (I). Contrary to these authors, 1:2:3:4-tetrahydronaphthalene can

react in both Kekulé forms, since its 6-hydroxy-5:8-dimethyl derivative undergoes coupling (cf. this vol., 835).

β -3-Amino-4-methylphenylpropionic acid, m.p. 140—141° [obtained by reduction (H_2 , PtO_2 , 95% EtOH) of 3-nitro-4-methylcinnamic acid], is converted (diazo-method) into the 3-OH-acid, m.p. 156—157°, methylated (Me_2SO_4) to β -3-methoxy-4-methylphenylpropionic acid, m.p. 82—83°. The chloride of this with AlCl_3 in CS_2 gives 5-methoxy-6-methyl-1-hydrindone, m.p. 114—115° [attempted demethylation (48% HBr , AcOH) gave a dimeride, $\text{C}_{22}\text{H}_{24}\text{O}_4$, m.p. 237—240°], which when reduced (modified Clemmensen) and then demethylated (48% HBr +45% HI in AcOH and N_2) affords 5-hydroxy-6-methylhydrindene, m.p. 83—84° (*Bz* derivative, m.p. 111—112°). 4:7-Dimethyl-1-hydrindone (Mayer and Müller, A., 1928, 65) is reduced (Clemmensen) to 4:7-dimethylhydrindene, b.p. 223—225°, m.p. -1.5° [5:6-(NO_2)₂-derivative, m.p. 191—192°], which with conc. H_2SO_4 at 100° (bath) gives the 5-sulphonic acid [*p*-toluidine salt, m.p. 248—249° (decomp.)] (KOH -fusion of the Na salt gives tars). Methoxy-*p*-xylene added to $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COCl}$ and AlCl_3 in cold CS_2 affords 2-methoxy-5- β -chloropropionyl-*p*-xylene, m.p. 85—86°, converted by $\text{NPh}\cdot\text{NH}_2$ in EtOH into 1-phenyl-3-3'-methoxy-2':5'-dimethylphenyl- Δ^2 -pyrazoline, m.p. 171—172°, and by AcOH -conc. H_2SO_4 at 100° (bath) into 5-methoxy-4:7-dimethyl-1-hydrindone, m.p. 163—165°. This is reduced (Clemmensen) to the hydrindene, m.p. 25—26°, demethylated (48% HBr in AcOH and N_2) to 5-hydroxy-4:7-dimethylhydrindene, m.p. 111—112° [*Bz*, m.p. 72—73°, and 6-*p*-nitrobenzeneazo-, m.p. 220—222° (decomp.), derivatives].

1-Keto-7-methoxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene (improved prep.; cf. Cleme *et al.*, A., 1929, 1454) is reduced (Clemmensen) to 6-methoxy-, m.p. 38—39°, which is demethylated (45% HI , AcOH) to 6-hydroxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene, m.p. 104—105° (*Bz*, m.p. 119—120°, and 7-*p*-nitrobenzeneazo-, m.p. 229—231°, derivatives).

H. B.

Synthesis of 6:7-methylenedioxy-1:1-dimethyl-1:2:3:4-tetrahydronaphthalene. R. M. ORCUTT and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 2055—2056).—The *Et* ester, b.p. 184—185°/14 mm., of piperonylacetic acid, m.p. 87—90° (lit. 84°) [prepared by reduction (Na-Hg) of piperonylideneacetic acid (I)], is reduced (Na , Bu°OH) to

β -piperonylethyl alcohol (II), b.p. 170—172°/8 mm., 184—186°/16 mm. (lit. 149—150°/6 mm.), m.p. 28—29° (*phenylcarbamate*, m.p. 98—99°), also obtained by reduction (Na powder, Bu°OH , PhMe) of the *Et* ester of (I). (II) and PBr_3 at \approx about 28° give the bromide, b.p. 163—165°/7.5 mm., the Grignard reagent from which with COMe_2 gives δ -piperonyl- β -methylbutan- β -ol (III), b.p. 145—148°/2 mm., and $\alpha\delta$ -dipiperonylbutane, m.p. 78°. (III) is converted by 85% H_2SO_4 at \approx 10° into 6:7-methylenedioxy-1:1-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. 148—149°/10 mm., dehydrogenated (S) to 6:7-methylenedioxy-1-methylnaphthalene (*picrate*, m.p. 134—136°).

H. B.

Synthesis of 5:6-methylenedioxy-1:1:2-trimethylindane from safrole. R. M. ORCUTT and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 2057—2059; cf. A., 1934, 292).—Safrole and 69% HBr at about 0° give 75% of α -bromo- α -piperonylethane [β -bromo- α -3:4-methylenedioxyphenylpropane], b.p. 145°/9 mm., the Grignard reagent (I) from which reacts readily with atm. O_2 . Hydrolysis (H_2O) of (I) affords α -piperonylethyl alcohol (II), b.p. 127—129°/3 mm. (*phenylcarbamate*, m.p. 93—94°), and some β - γ -dipiperonylbutane (III), m.p. 74°. (I) and COMe_2 in N_2 give (III) and γ -piperonyl- β -methylbutan- β -ol (IV), b.p. 142—144°/3 mm., m.p. 49° (softens at 43°); in presence of air (II) (main product), (III), and (IV) result. (IV) is converted by cold 85% H_2SO_4 into 5:6-methylenedioxy-1:1:2-trimethylindane (V), b.p. 137°/11 mm., and (occasionally) some γ -piperonyl- β -methyl- Δ^{β} -butene, b.p. 120°/7 mm., which with H_2SO_4 also gives (V). *iso*Safrole and 69% HBr at 0° afford the unstable α -bromo- α -3:4-methylenedioxyphenylpropane, decomp. on attempted distillation at 2 mm. 3:4-Methylenedioxyphenylethylcarbinol, b.p. 126—127°/3 mm. (cf. Marnett, A., 1904, i, 1023) (from piperonal and MgEtBr), could not be converted into the bromide (PBr_3); when kept it gives the carbinyl ether, m.p. 85° (lit. 88°).

H. B.

Diaryls and their derivatives. IX. Sulphonation. J. S. JOFFE, S. G. KUZNETZOV, and A. A. PANOV. X. Nitration of 2:2'-dihydroxy-1:1'-dinaphthyl. J. S. JOFFE (J. Gen. Chem. Russ., 1936, 6, 999—1002, 1003—1005).—IX. Sulphonation of 2:2'-dihydroxy-1:1'-dinaphthyl (I) at 100° yields the 6-mono- and the 6:6'-di-sulphonic acids. The former, when fused with NaOH , affords 2:6:2'-trihydroxy-1:1'-dinaphthyl, m.p. 305—307°, giving a red azo-dye, m.p. 138—140°, when coupled with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$.

X. (I) and HNO_3 in AcOH at 100° yield 6:6'-dinitro-2:2'-dihydroxy-1:1'-dinaphthyl, m.p. >300° (decomp.), reduced by NaHSO_3 to the 6:6'-(NH_2)₂-compound, m.p. >300°. This is readily converted by HNO_2 into the bisdiazocompound [compound with 2:3:6-OH· $\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$].

R. T.

Alkylphenols. I. 4-n-Alkylpyrogallols. M. C. HART and E. H. WOODRUFF (J. Amer. Chem. Soc., 1936, 58, 1957—1959).—1:2:3- $\text{C}_6\text{H}_3(\text{OH})_3$, the appropriate AlkCO_2H , and ZnCl_2 at 130—140° give 2:3:4-trihydroxyphenyl Me, m.p. 170°, Et, m.p. 128—129°, Pr^a , m.p. 101—102°, Bu^a , m.p. 84—84.5°, *n*-amyl, m.p. 86.5—87°, and *n*-hexyl, m.p.

78—78.5°, *ketones*, reduced (Clemmensen) to 4-ethyl-, m.p. 108.5° (1, 2.3), 4-*n-propyl*-, m.p. 110—111° (2.5, 4.4), 4-*n-butyl*-, m.p. 88—89° (5, 12.6), 4-*n-amyl*-, m.p. 90—91° (19, 25), 4-*n-hexyl*-, m.p. 104—105° (44, 38), and 4-*n-heptyl-pyrogallol*, m.p. 116—117° (50, 26), respectively. The nos. in parentheses are the PhOH-coeffs. towards *S. aureus* and *B. coli*, respectively. The alkylpyrogallols, which show quasi-specificity (cf. Klarmann *et al.*, A., 1933, 817), are less effective germicides than alkyl-phenols and -resorcinols. H. B.

Molecular rearrangement of N-sulphenanilides in alkaline solution. IV. M. L. MOORE and T. B. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 1960—1961; cf. this vol., 200).—4-Chloro-2-nitrobenzenesulphenanilide, -*o*-toluidide, and -*o*-chloroanilide, m.p. 112° (from 2 : 4-NO₂·C₆H₃Cl·S·Cl and *o*-C₆H₄Cl·NH₂), and *o*-NO₂·C₆H₄·S·NH·C₆H₄Cl-*o* rearrange when heated with aq. EtOH-NaOH and give 4'-chloro-2'-nitro-2-thiol-, a chloronitrothiomethyl-, a dichloronitrothiol-, and a chloronitrothiol-diphenylamine (as Na salts; *S-Me* ethers, m.p. 135—136°, 164—165°, 158—158.5°, and 144.5—145°, respectively), respectively. The formation of thiodiphenylamines is not observed (cf. Moore and Smiles, A., 1935, 1511). *p*-NO₂·C₆H₄·S·NHAr (Ar=Ph, *o*-C₆H₄Me, and *o*-C₆H₄Cl) do not similarly rearrange. H. B.

Molecular transformations in the cyclane series. M. TIEFFENEAU (Bull. Soc. chim., 1936, [v], 3, 1942—1974).—A lecture.

Reduction of acid chlorides and anhydrides by chromous hydroxide. R. GRAF [with M. TATZEL] (J. pr. Chem., 1936, [ii], 146, 198—200).—Simultaneous addition of BzCl and 50% KOH to an aq. suspension of Cr(OAc)₂ at 0° gives >30% yield of CH₂Ph·OH, also obtained from Bz₂O. H. W.

Preparation of amino-alcohols. II. J. T. ABRAMS and F. S. KIPPING (J.C.S., 1936, 1480—1481).—Condensation of CH₂Bz·CO₂Et-NaOEt-EtOH with the appropriate alkyl iodide affords *Et* α-benzoyl-*isovalerate* (*amide*, m.p. 179—180°), -*γ*-methylvalerate [*amide* (I), m.p. 157—158°], and -*δ*-methyl-*n*-hexoate, b.p. 169—170°/6 mm. [*amide* (II), m.p. 156—157°]. Reduction of (I) with Al-Hg-aq. EtOH affords α-hydroxybenzyl-*γ*-methylvaleramide, m.p. 136—137°, and the *pinacol*, [NH₂·CO·CHBu^β·CPh(OH)]₂, m.p. 169°, separated by fractional crystallisation from EtOAc-C₆H₆. Similar reduction of (II) affords α-hydroxybenzyl-*δ*-methylhexoamide, m.p. 137—138°, together with the *pinacol*, m.p. 159° (not analysed). α-Hydroxybenzylbutyramide (A., 1935, 209) with Br-aq. NaOH affords β-amino-α-phenylbutyl alcohol, m.p. 79—80° (*hydrochloride*, m.p. 195—196°), probably a diastereoisomeride of the base obtained by Hartung *et al.* (A., 1930, 1286). J. W. B.

Phenanthrene series. XIII. 9 : 10-Dihydrophenanthrene and amino-alcohols derived from it. A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1936, 58, 1857—1860).—Phenanthrene is reduced [H₂ (136—218 atm.), Cu-Cr-Ba oxide, EtOH, 220°] to the 9 : 10-H₂-derivative (I) (80% yield); anthracene is similarly reduced more quickly at 160°. (I) and AcCl (1.2 mols.) with AlCl₃ (2 mols.) in cold

PhNO₂ give 2-acetyl-9 : 10-dihydrophenanthrene (II) [(I) thus reacts as a diphenyl], which is oxidised by CrO₃-aq. AcOH to 2-acetyl-9 : 10-phenanthraquinone, and by dil. NaOCl to an acid, the Me ester of which with Se at 280—300° affords phenanthrene-2-carboxylic acid. (I) and EtCOCl similarly yield 2-propionyl-9 : 10-dihydrophenanthrene (III), m.p. 62—63° (*semicarbazone*, m.p. 213—214°), oxidised (CrO₃) to 2-propionyl-9 : 10-phenanthraquinone, m.p. 215—217° (decomp.). 2-Bromoacetyl-9 : 10-dihydrophenanthrene [from (II) and Br in Et₂O; the 2-chloroacetyl derivative, m.p. 100—101°, is obtained in poor yield by the Friedel-Crafts reaction] and the appropriate NHR₂ in C₆H₆ give 2-dimethylamino- [*hydrochloride*, m.p. 213—215° (decomp.)], 2-diethylamino- [*hydrochloride*, m.p. 173—176° (decomp.)], 2-piperidino-, m.p. 86—87° [*hydrochloride*, m.p. 240—252° (decomp.)], and 2-1' : 2' : 3' : 4'-tetrahydroisoquinolino- (IV) [*hydrochloride*, m.p. 238—239° (decomp.)], -acetyl-9 : 10-dihydrophenanthrenes, which are reduced (H₂, PtO₂, 90% EtOH or MeOH, using salts) to 2-β-dimethylamino-α-hydroxy- [*hydrochloride*, m.p. 170—172° (decomp.)], O-Ac derivative *hydrochloride*, m.p. 216—217° (decomp.)], 2-β-diethylamino-α-hydroxy- [*hydrochloride*, m.p. 184—186° (decomp.)], O-Ac derivative *hydrochloride*, m.p. 145—150° (decomp.)], 2-β-piperidino-α-hydroxy-, m.p. 124° [*hydrochloride*, m.p. 242° (decomp.)], O-Ac derivative *hydrochloride*, m.p. 212—213° (decomp.)], and 2-β-1' : 2' : 3' : 4'-tetrahydroisoquinolino-α-hydroxy-, m.p. 101—102° [*hydrochloride*, m.p. 244—246° (decomp.)], O-Ac derivative *hydrochloride*, m.p. 197—199° (decomp.)], -ethyl-9 : 10-dihydrophenanthrene, respectively. 2-α-Bromopropionyl-9 : 10-dihydrophenanthrene, m.p. 85—86° [from (III) and Br in Et₂O], similarly gives 2-α-dimethylamino- [*hydrochloride*, m.p. 210—214° (decomp.)], 2-α-diethylamino- (*perchlorate*, m.p. 138—140°), 2-α-piperidino- [*hydrochloride*, m.p. 208—213° (decomp.)], and 2-α-1' : 2' : 3' : 4'-tetrahydroisoquinolino- (*perchlorate*, m.p. 230—231°), -propionyl-9 : 10-dihydrophenanthrenes, reduced to 2-β-dimethylamino-α-hydroxy-, m.p. 90—91° [*hydrochloride*, m.p. 225—227° (decomp.)], O-Ac derivative *hydrochloride*, m.p. 210—211° (decomp.)], 2-β-diethylamino-α-hydroxy- [*hydrochloride*, m.p. 209—210° (decomp.)], O-Ac derivative *hydrochloride*, m.p. 189—190° (decomp.)], 2-β-piperidino-α-hydroxy-, m.p. 104—106° [*hydrochloride*, m.p. 249—250° (decomp.)], O-Ac derivative *hydrochloride*, m.p. 192—194° (decomp.)], and 2-β-1' : 2' : 3' : 4'-tetrahydroisoquinolino-α-hydroxy-, m.p. 136—138° [*hydrochloride*, m.p. 226—228° (decomp.)], O-Ac derivative *hydrochloride*, m.p. 190—192° (decomp.)], -propyl-9 : 10-dihydrophenanthrene, respectively. (IV) is accompanied by resinous material which with dil. alkali gives 9 : 10-dihydrophenanthrene-2-carboxylic acid. H. B.

Lignin. XII. Action of hydrogen sulphite solutions on aromatic alcohols. S. HEDÉN and B. HOLMBERG (Svensk Kem. Tidskr., 1936, 48, 207—211).—Many aromatic alcohols resemble lignin in that when boiled with NaHSO₃, OH is replaced by SO₃H. M. H. M. A.

Synthesis of *p*-methoxybenzyl alcohol. R. QUELET and J. ALLARD (Bull. Soc. chim., 1936, [v],

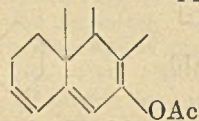
3, 1794—1800).—Previous work (A., 1934, 290) is repeated in the light of that of Ofner (A., 1935, 1120), which is confirmed. *p*- (with *o*-)CH₂Cl·C₆H₄·OMe, obtained as before (method improved), is converted into *p*- (with *o*-)OAc·CH₂·C₆H₄·OMe (I). Hydrolysis (aq. KOH) then gives *p*-OMe·C₆H₄·CH₂·OH and (*p*-OMe·C₆H₄·CH₂)₂O, which decomposes on distillation, giving *p*-C₆H₄Me·OMe and *p*-OMe·C₆H₄·CHO. Hydrolysis of (I) by KOH-EtOH yields 90% of *p*- and 10% of *o*-OMe·C₆H₄·CH₂·OH. E. W. W.

Derivatives of phenyldihydroxypropylamine. H. OHLE and G. HAESLER (Ber., 1936, 69, [B], 2324—2327; cf. this vol., 1491).—Epichlorohydrin and *p*-C₆H₄Me·SO₂·NPh in presence of a little C₅H₅N at 120—150° give *p*-toluenesulphonphenyl-*γ*-chloro-*β*-hydroxypropylamine C₆H₄Me·SO₂·NPh·CH₂·CH(OH)·CH₂Cl, m.p. 96—97°, transformed by cautious addition of NaOH to its solution in EtOH at 100° into *p*-toluenesulphonphenyl-*βγ*-oxidopropylamide (I), m.p. 77°, in 92% yield. Addition of a drop of C₅H₅N to (I) and BzOH at 120° affords *p*-toluenesulphonphenyl-*β*-hydroxy-*γ*-benzoyloxypropylamide, m.p. 117—118°, transformed by BzCl in C₅H₅N into *p*-toluenesulphonphenyl-*βγ*-dibenzoyloxypropylamide (II), m.p. 135—136°. (II) and HBr-AcOH yield 2:4-dibromophenyl-*βγ*-dibenzoyloxypropylamine (III) m.p. 122.5°, and (C₆H₄Me)₂S₂ (III) (hydrobromide, m.p. 176—178°) gives a non-cryst. nitrosoamine and N-Ac derivative. It is hydrolysed and then oxidised by KMnO₄ in C₆H₅CO₂ to 2:4-C₆H₃Br₂·NH₂ and 2:4-dibromo-oxanilic acid. H. W.

Isomeride of lutein from furze (*Ulex europaeus*).—See this vol., 1571.

Sterol group. XXVII. Oxidation of cholesterol hydrogen phthalate with potassium permanganate: *β*-7-hydroxycholesterol and tetrahydrocholestanone. T. BARR, I. M. HEILBRON, E. G. PARRY, and F. S. SPRING (J.C.S., 1936, 1437—1440).—Cholesteryl H phthalate with 0.25N-KMnO₄-N-Na₂CO₃ at room temp. affords the following three products: the *H* phthalate, m.p. 199—201° (insol. in CHCl₃-Et₂O), of *β*-7-hydroxycholesterol, m.p. 184—185°, [α]_D²⁰ -86.4° [Ac₂, m.p. 121—122°, [α]_D¹⁹ -174.6°, and Bz₂ (I), m.p. 150—151°, [α]_D¹⁹ -105.3°, derivatives; oxide, m.p. 173—175° (Ac₂ derivative, m.p. 203—204°)], which is a stereoisomeride of the (now designated) *α*-7-hydroxycholesterol of Windaus *et al.* (A., 1935, 1363) since thermal decomp. of (I) affords 7-dehydrocholesteryl benzoate; from the CHCl₃-Et₂O extract is obtained the *H* phthalate, m.p. 236—237°, of 3:5:6:7- or 3:4:5:6-tetrahydrocholestanone, +H₂O, m.p. 235—236°, and anhyd., m.p. 230—231° (Ac₃, m.p. 219—220°, [α]_D¹⁹ +23.1°, and Bz₃, m.p. 271—272°, [α]_D¹⁹ +114.0°, derivatives), whilst KOH-EtOH hydrolysis of the resin from the CHCl₃-Et₂O mother-liquor affords the hydroxyketo-acid C₂₇H₄₆O₄ obtained by oxidation of cholesteryl acetate with CrO₃ (Windaus *et al.*, A., 1915, i, 677), identified by thermal decomp. to the diene, C₂₆H₄₂, m.p. 76° (Lettré, A., 1933, 1047). All [α]_D vals. are in CHCl₃. J. W. B.

Enolisation of oxysterilene. V. A. PETROW (Nature, 1936, 138, 645).—Acetylation of 7-ketocholesterol removes the C₆₃-OH, yielding oxysterilene and its acetate, m.p. 90—92°, [α]_D -222°, [α]₅₄₆₁ -283°, which has the appended structure.

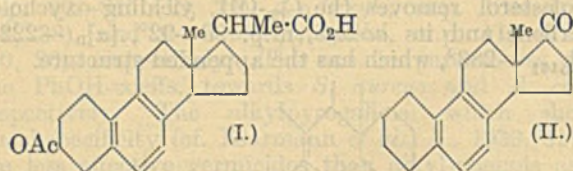


L. S. T.

Lanosterol. I. C. DORÉE and V. A. PETROW (J.C.S., 1936, 1562—1567).—Dehydrogenation of lanosterol (I) with Pd-C at 330—360° affords an oily hydrocarbon, C₁₈H₂₀ [C₆H₃(NO₃)₃ adduct, m.p. 147—148°]. The presence of one reactive and one unreactive double linking in (I) is proved by the following data: titration with BzO₂H gives an O₂ absorption never >1.5 atoms, but lanosteryl acetate (II) with BzO₂H-CHCl₃ at 0° affords its oxide, m.p. 178°, hydrolysed to lanosterol oxide, m.p. 139—140°. (II) with H₂O₂-AcOH and subsequent hydrolysis gives oxylanostanetriol, m.p. 120—121° (Ac₁ derivative, m.p. 162—163°). The ultra-violet absorption spectrum shows that lanostenone (III) (improved prep.) is not an *αβ*-unsaturated ketone, and with NPh-NH₂-AcOH it gives a tetrahydrocarbazole derivative, m.p. 201—202° (picrate, m.p. 201°), which surface film measurements suggest must be an *ang*-derivative. The monohydrochloride of (II), m.p. 126—127°, is hydrolysed by KOH-EtOH to isolanosterol (IV), m.p. 131—132° (Ac derivative, m.p. 130—131°), oxidised to isolanostenone (V), m.p. 138—139° (tetrahydrocarbazole derivative, m.p. 224—225°), the semicarbazone, m.p. 210°, of which is reduced by Na-EtOH at 180° to isolanostene, m.p. 80—81°; lanostene, similarly prepared, has m.p. 76—77°. (V) with Na-boiling EtOH gives isolanosterol-A, m.p. 130—131° (Ac derivative, m.p. 138°), which depresses the m.p. of (IV). Attempted oxidation of (II) with CrO₃-66% AcOH affords the Ac derivative, m.p. 164°, of lanosterol-D, m.p. 137—138°, which is obtained on hydrolysis, and is a OH-spatial isomeride of (I) since it is oxidised to (III). Surface film measurements of the above derivatives are recorded and support the conclusion that (I) has an amyryn type of structure. J. W. B.

Artificial production of oestrogenic substances from sterols. I. Synthesis of the oestrogenic substance from animal sterols. I. REMESOV and N. TAVASTSTJERNA. II. Synthesis of an isomeride of the follicular hormone from vegetable sterols. I. REMESOV (Rec. trav. chim., 1936, 55, 791—797, 797—803).—I. Agnosterol (modified prep.), C₃₀H₄₇·OH (acetate), contains 3 ethylenic linkings (BzO₂H), resists complete hydrogenation, and resembles theelin in absorption spectrum. A mixture with CH₂Br·CO₂Na, when heated with Br-Ac₂O, gives the crude acetate dibromide, m.p. 130—131°, [α]_D¹⁹ -79° in CHCl₃, which with maleic anhydride in C₆H₆ at 133—135° affords the adduct, m.p. (crude) 196—204°; oxidation by CrO₃ and subsequent debromination gives gums, but the final product shows oestrogenic activity by the Allen-Doisy test and towards monkeys.

II. Neergosterol (prep. in 22–26% yield from ergosterol), m.p. 152.5°, gives the *acetate dibromide*,



m.p. 180–181°, which with O_3 in AcOH affords $CHMePr^{\beta}\cdot CHO$ and the *acid* (I), m.p. 210–212°, the *Me* ester, m.p. 144–145°, of which by the $MgPhBr$ method is degraded to a *substance*, $C_{13}H_{22}O_2$, m.p. 225–226°, sublimes at 210°/0.001 mm., believed to have structure (II) and to be isomeric with the follicular hormone. 1 g. of (II) corresponds with $8\text{--}10 \times 10^6$ mouse units of theelin. R. S. C.

Sterols. VII. *cis*- and *trans*-Androstanone-3-carboxylic acid, an œstrus-producing male hormone derivative, and epicholesterol. R. E. MARKER, O. KAMM, T. S. OAKWOOD, and J. F. LAUCIUS (J. Amer. Chem. Soc., 1936, 58, 1948–1950).—Oxidation (CrO_3 , AcOH) of Me (*cis*+*trans*)-cholestane-3-carboxylate (this vol., 604) gives a little Me (*cis*+*trans*)-androstanone-3-carboxylate [purified through the semicarbazone, m.p. 250–260° (decomp.)], hydrolysed (MeOH-KOH) to the (*cis*+*trans*)-*acid*, m.p. 253°, which is readily esterified; $5\text{--}10 \times 10^6$ g. of the *Et* ester, m.p. 108–110°, which is more active than the *acid*, causes an œstrus response in rats but is inactive in the cock's comb test. Unsaturation is not necessary for œstrus production. *epi*Cholesterol (I) is separated from cholesterol (cf. *loc. cit.*) by purification of the mixture through the H succinates, fractional crystallisation of the mixed acetates from EtOH, hydrolysis (EtOH-NaOH) of the more sol. material, and final fractionation of the mixed benzoates [containing about 90% of that of (I)]. The acetate of (I) and Br in $Et_2O\text{--}AcOH$ give a *tetra-bromocholestane*, m.p. 110°, which differs from that obtained from cholesterylene (II) and Br. (I) is dehydrated by EtOH-HCl to (II). Ultra-violet irradiation of (I) does not give antirachitic products.

H. B.

2:4-Dimethylphenylacetic [*m*-4-xylylacetic] acid and its derivatives. J. V. HARISPE (Ann. Chim., 1936, [xi], 6, 249–347).—Re-examination of the conversion of pinonic acid (I) into *m*-4-xylylacetic acid (II) (Barbier and Grignard, A., 1909, i, 301) by $Br\text{--}H_2O$ shows that in the first phase, the duration of which is a function of the homogeneity of the medium, H attached to C probably vicinal to CO is replaced by Br. Substitution causes production of HBr, under the influence of which (or of HCl added before commencement of the change) the bromopinic acid becomes isomerised to the compound $CHBrAc\cdot CH_2\cdot CH\left\langle \begin{array}{l} CMe_2\cdot O \\ CH_2\text{--}CO \end{array} \right.$ (III), which slowly in the cold, but very rapidly when heated, loses HBr with formation of an ethylenic linking, eliminates 1 mol. of H_2O between CO and a terminal Me with production of a second ethylenic linking and of a six-membered ring, and suffers hydrolysis of the lactonic function immediately followed by dehydr-

ation of the corresponding *tert*-alcohol with appearance of the third ethylenic linking, and hence of the benzenoid nucleus. The yield of (II) is >70%; the remaining 30% is a brownish-red resin containing esterifiable CO_2H . The heats of combustion of (I), (II), and (III) have been determined. (II) has m.p. 105.5–106° (block), b.p. 300–302°(corr.)/760 mm. Its physiological properties are described. The *K* ($+H_2O$), *Ba* ($+H_2O$), *Ca* ($+4.5H_2O$), m.p. 120°, *Ag* ($+H_2O$), m.p. <100°, and *Na* ($+1H_2O$) salts have been prepared. (II) gives the following esters; Me, b.p. 138°(corr.)/20 mm.; *Et*, b.p. 146.5°(corr.)/18 mm.; *Pr*^a, b.p. 155°(corr.)/18 mm.; *Bu*^a, b.p. 164°(corr.)/17 mm.; *CH_2Ph*, b.p. 214°(corr.)/20 mm. *m*-4-*Xylylacetyl chloride* (IV), b.p. 116°(corr.)/11 mm., from (II) and $SOCl_2$, is converted in the usual manner into the corresponding amide, m.p. 184° (block), *anilide*, m.p. 144.5° (block), *o-toluidide*, m.p. 172° (block), *p-toluidide*, m.p. 145° (block), 1-, m.p. 209°, and 2-, m.p. 183°, *-naphthylamide*, and by $C_6H_3Me_2\cdot CH_2\cdot CO_2Ag$ into *m*-4-*xylylacetic anhydride*, m.p. 86–87°. *Ph m*-4-*xylylacetate*, m.p. 39°, is derived from (IV), $PhOH$, and K_2CO_3 in boiling C_6H_6 . (IV) and C_6H_6 in presence of $AlCl_3$ afford 2:4-*dimethyldeoxybenzoin*, m.p. 108.5° (block) (*oxime*, m.p. 114.5°). From the esters by means of the appropriate Grignard reagents the following *carbinols* are obtained: 2:4-*dimethylbenzyl-dimethyl-*, b.p. 139°(corr.)/20 mm.; *-diethyl-*, b.p. 162°(corr.)/18 mm.; *-di-n-propyl-*, b.p. 179°(corr.)/19 mm.; *-di-n-butyl-*, b.p. 203°(corr.)/24 mm.; *-diphenyl-*, m.p. 99° (block); *-dibenzyl-*, m.p. 87–88° (block). Dehydration of the *tert*. alcohols is effected with $Ac_2O+AcCl$, $Ac_2O+H_2SO_4$, or by H_2SO_4 giving the unsaturated hydrocarbon which is oxidised by CrO_3 in AcOH at 100° or by alkaline $KMnO_4$ at room temp. to 2:4- $C_6H_3Me_2\cdot CO_2H$ and the corresponding ketone. α -*m*-4-*Xylyl*- β -*methyl*- Δ^{α} -*propene* has b.p. about 108–109°(corr.)/16 mm.; α -*m*-4-*xylyl*- β -*ethyl*- Δ^{α} -*butene*, b.p. 242°(corr.)/760 mm.; 122–123°/10–11 mm.; α -*m*-4-*xylyl*- β -*propyl*- Δ^{α} -*pentene*, b.p. 137–138°(corr.)/13 mm.; α -*m*-4-*xylyl*- β -*n-butyl*- Δ^{α} -*hexene*, b.p. 286–288°/760 mm., 173°(corr.)/20 mm.; $\beta\beta$ -*diphenyl*- β -*m*-4-*xylylethylene*, m.p. 69–70° (block); γ -*phenyl*- α -*m*-4-*xylyl*- β -*benzyl*- Δ^{α} -*propene*, b.p. 246°/13 mm. Reduction of the Me ester by Na and EtOH leads to β -*m*-4-*xylylethyl alcohol*, (V), b.p. 101–102°/3 mm.; 125°(corr.)/10 mm. [*phenylurethane*, m.p. 124.5–125° (block); *allophanate*, m.p. 222° (block)] transformed by $SOCl_2$ and C_5H_5N into the corresponding *chloride* (VI), b.p. 111.5°(corr.)/11 mm., by PBr_3 into the *bromide*, b.p. 132°(corr.)/18 mm.; the *iodide* from (VI) and NaI in $COMe_2$, has b.p. 136–137°/12 mm. The corresponding normal *sulphite*, b.p. 216–217°/2 mm., passes when heated into the alcohol, SO_2 , and *m*-4-*xylylethylene*, b.p. 81–85°/14 mm. The *acetate*, b.p. 135°/14 mm., normal *oxalate*, m.p. 73–73.5° (block), and *benzoate*, b.p. 182°/12 mm., of (V) are described. (V) is transformed by $NaHSO_4$ at 160–170° into *di*- β -*m*-4-*xylylethyl ether*, m.p. 38°. H. W.

Alkylene- and alkylidene-phenylacetoneitriles and derivatives. 1-Cyano-1-phenyl-2-ethyl-cyclopropane and α -phenyl- β -ethyl- and β -*iso*-propyl-acrylonitriles. J. V. MURRAY and J. B.

CLOKE (J. Amer. Chem. Soc., 1936, 58, 2014—2018; cf. A., 1932, 739).— $\text{CH}_2\text{Ph}\cdot\text{CN}$ (I) is treated with NaNH_2 (2 mols.) in liquid NH_3 (which is then replaced by Et_2O) followed by $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Et}$, thus giving 40% of 1-cyano-1-phenyl-2-ethylcyclopropane, b.p. 93—94°/ < 1 mm., which is hydrolysed ($\text{AcOH}\text{--}\text{H}_2\text{SO}_4$ or $\text{EtOH}\text{--}\text{KOH}$) to 1-phenyl-2-ethylcyclopropane-1-carboxylamide, m.p. 84°, and thence ($\text{EtOH}\text{--}\text{KOH}$) to the acid, m.p. 105—105.5° (corr.). (I) and $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\text{Cl}$ similarly afford 38% of α -phenyl- β -isopropylacrylonitrile (II), b.p. 95—95.2°/ < 1 mm., probably formed by rearrangement of the intermediate $\text{CMe}_2\cdot\text{CH}\cdot\text{CHPh}\cdot\text{CN}$. (II), also obtained in 85% yield from (I) and $\text{Pr}^\beta\text{CHO}$ in $\text{EtOH}\text{--}\text{NaOEt}$ at $< -5^\circ$, is hydrolysed ($\text{AcOH}\text{--}\text{H}_2\text{SO}_4$) to α -phenyl- β -isopropylacrylamide, m.p. 123—124° (corr.) [free acid, m.p. 133—134° (corr.)], and converted by alkaline H_2O_2 in COMe_2 (cf. A., 1935, 212) into $\alpha\beta$ -oxido- α -phenylisohexoamide, m.p. 148—149° (corr.). Oxidation (KMnO_4 , aq. Na_2CO_3) of (II) gives BzOH , $\text{Pr}^\beta\text{CO}_2\text{H}$, and HCN . (I) and EtCHO in $\text{EtOH}\text{--}\text{NaOEt}$ similarly afford α -phenyl- β -ethylacrylonitrile [α -phenyl- Δ^2 -pentenonitrile], b.p. 112—112.5°/3 mm. (55% yield), converted [as for (II)] into α -phenyl- Δ^2 -pentenoamide, m.p. 130° (corr.) (free acid, m.p. 67.5—68.5°), and $\alpha\beta$ -oxido- α -phenylvaleramide, m.p. 155° (corr.). H. B.

[Preparation of ethyl cyclopentanone-2-carboxylate.]—See this vol., 1482.

Compounds $\text{LiCl}\cdot\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{LiCl}\cdot\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. K. SANDVED and R. VEIMO (Tids. Kjem., 1936, 16, 115—116).—Phase-rule studies show the existence of these two compounds, which have been isolated together with the compound $2\text{LiCl}\cdot\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. M. H. M. A.

Hydrazino-acids. V. A. DARAPSKY [with J. LOEVENICH, O. CREIFELDS, W. BELLINGEN, E. KÖSTER, V. BINET, H. WASSERFUHR, and H. BECK] (J. pr. Chem., 1936, [ii], 146, 268—306; cf. this vol., 1494).—Cautious addition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ in EtOH gives the hydrazine salt (I), m.p. 123°, of phenylpyruvic acid hydrazone, converted by dil. HCl into $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$. (I) is reduced by $\text{Na}\text{--}\text{Hg}$ in H_2O to α -hydrazino- β -phenylpropionic acid, m.p. 196° [:CHPh derivative, m.p. 154—158°]. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ in C_6H_6 and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH give the hydrazine salt, m.p. 134—135°, of p -tolylglyoxylic acid hydrazone, which does not yield a :CHPh derivative; it is converted by dil. HCl into p -tolylglyoxylic acid azine, [$\text{:N:C}(\text{CO}_2\text{H})\cdot\text{C}_6\text{H}_4\text{Me}\text{--}p$] $_2$, m.p. 183° (decomp.), also obtained from $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ in $\text{EtOH}\text{--}\text{H}_2\text{O}$, which is reduced by $\text{Na}\text{--}\text{Hg}$ to hydrazo- p -tolylacetic acid, m.p. 149° (non-cryst. *Et* ester). $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ is transformed by successive treatment with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in $\text{EtOH}\text{--}\text{H}_2\text{O}$ at room temp. and $\text{Na}\text{--}\text{Hg}$ into hydrazino- p -tolylacetic acid, m.p. 174—176° (hydrochloride, m.p. 143—145° (decomp.)); :CHPh , m.p. 130°, and *o*-hydroxybenzylidene, m.p. 150°, derivative; *Et* ester hydrochloride, m.p. 141—143° (decomp.); *Et* carbonamidohydrazino- p -tolylacetate, m.p. 130°. *Et* nitrosohydrazino- p -tolylacetate, m.p. 70°, passes when heated above its m.p. into N_2O and *Et* amino- p -tolylacetate, b.p. 136—139°/12

mm., hydrolysed to amino- p -tolylacetic acid, sublimes at 228° (*Cu* salt). The phenylhydrazone of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ is reduced by $\text{Na}\text{--}\text{Hg}$ to phenylhydrazino- p -tolylacetic acid, m.p. 148°. *Et* azido- p -tolylacetate, b.p. 155°/18 mm., from the *NO*-ester and 10% H_2SO_4 , is hydrolysed to azido- p -tolylacetic acid, m.p. 100° (NH_4 and *Ag* salts). $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in abs. EtOH give benzylpyruvic acid hydrazone, m.p. 133—134° (decomp.), the N_2H_4 salt (II), m.p. 141°, of which is converted by dil. HCl into the azine, m.p. 114°, of benzylpyruvic acid (*Ca* salt), reduced by $\text{Na}\text{--}\text{Hg}$ to hydrazo- γ -phenyl-*n*-butyric acid, decomp. 220—230°. (II) is reduced by $\text{Na}\text{--}\text{Hg}$ to α -hydrazino- γ -phenyl-*n*-butyric acid (III), m.p. 215—217° (decomp.) [NH_4 , m.p. 203—204° (decomp.)], and *Cu*, decomp. 115° after becoming red at 60—70°, salts; hydrochloride, m.p. 187° (decomp.); :CHPh derivative, m.p. 158° (decomp.); *Et* ester hydrochloride, m.p. 108°. (III) is transformed by $\text{HBr}\text{--}\text{Br}$ at 0° into α -bromo- γ -phenyl-*n*-butyric acid, reconverted into (III) by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling EtOH . *Et* α -nitrosohydrazino- γ -phenyl-*n*-butyrate, m.p. 48°, passes at 115—120° into *Et* α -amino- γ -phenyl-*n*-butyrate, b.p. 161—162°/16 mm. [hydrochloride, m.p. 121—123° (decomp.)], hydrolysed to α -amino- γ -phenyl-*n*-butyric acid, m.p. 292—293° when rapidly heated. *Et* α -azido- γ -phenyl-*n*-butyrate, b.p. 172—173°/16 mm., gives the non-cryst. α -azido- γ -phenyl-*n*-butyric acid (NH_4 , m.p. 118—120°, and *Ag* salt). $\text{CHPhMe}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling EtOH give α -hydrazino- β -phenyl-*n*-butyric acid, m.p. 216° [NH_4 salt; hydrochloride, m.p. 172—173° (decomp.)]; unstable :CHPh , m.p. 107° (indef.), and *o*-hydroxybenzylidene, m.p. 133° (decomp.), derivatives; *Me*, m.p. 58—60°, and non-cryst. *Et* ester hydrochloride]. *Me* α -nitrosohydrazino- β -phenyl-*n*-butyrate passes at 120—130° into *Me* α -amino- β -phenyl-*n*-butyrate, b.p. 145—155°/13 mm. (hydrochloride, decomp. 170°), whence α -amino- β -phenyl-*n*-butyric acid, m.p. 239° (lit. m.p. 247—252°) (hydrochloride, m.p. 198°), and is transformed by steam-distillation in presence of 10% H_2SO_4 into α -azido- β -phenyl-*n*-butyric acid (NH_4 , m.p. 144°, and *Ag* salt). $\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ affords α -hydrazino- β -phenyl-*n*-butyric acid, m.p. 169—172° (decomp.) [hydrochloride, m.p. 132—135°; :CHPh , m.p. 109—112°, and *o*-hydroxybenzylidene, m.p. 112—113°, derivatives; *Ac* $_2$, m.p. 155° (decomp.), and *Bz* $_2$, m.p. 139—141°, compounds; non-cryst. *Me* and *Et* ester hydrochlorides]. $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling EtOH give benzylidenepyruvic acid hydrazone, m.p. 84° (decomp.), the N_2H_4 salt, m.p. 92°, of which could not be transformed into the corresponding azine, but is reduced by $\text{Na}\text{--}\text{Hg}$ to α -hydrazino- γ -phenyl-*n*-butyric acid, m.p. 215—217°. $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ gives the N_2H_4 salt, m.p. 125° (decomp.), of cinnamylidenepyruvic acid hydrazone, which yields an impure azine and is reduced to α -hydrazino- ϵ -phenyl-*n*-hexoic acid, m.p. 157° [:CHPh , m.p. 124° (decomp.)], and *o*-hydroxybenzylidene, m.p. 120°, derivatives; *Ac* $_2$, m.p. 127°, and *Bz* $_2$, m.p. 65°, compounds; non-cryst. *Me* and *Et* ester hydrochlorides]. *Et* α -nitrosohydrazino- ϵ -phenyl-*n*-hexoate gives α -amino- ϵ -phenyl-*n*-hexoic acid, m.p. 233—236°, and α -azido- ϵ -phenyl-*n*-hexoic acid (*Ag* salt, m.p. 111—112°). $1\text{-C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{CO}_2\text{H}$

affords the N_2H_4 salt, m.p. 188° after becoming discoloured, of 1-naphthylglyoxylic acid hydrazone whence the corresponding *azine*, $[N:C(C_{10}H_7) \cdot CO_2H]_2$, m.p. 160—162° (decomp.), reduced to *hydrazo- α -naphthylacetic acid*, m.p. 186—188° (decomp.) (non-cryst. *Et* ester). *Hydrazino-1-naphthylacetic acid*, m.p. 181° after darkening at 175—176°, gives a *hydrochloride*, m.p. 194°, a *CHPh*·, m.p. 124° (decomp.) after darkening at about 110°, and *o-hydroxybenzylidene*, m.p. 70° (decomp.) after darkening at 50°, derivatives. It does not condense with $COMe_2$ or give a cryst. Ac derivative and is not esterified by HCl-MeOH or HCl-EtOH. H. W.

Diaryls and their derivatives. XI. Structure and composition of the complex compound of iron with β -naphthol-3-carboxylic acid. J. S. JOFFE and M. I. KRILOVA (J. Gen. Chem. Russ., 1936, 6, 1006—1013).—Addition of aq. $FeCl_3$ to aq. 2 : 3- $OH \cdot C_{10}H_6 \cdot CO_2Na$ leads to the production of a complex salt, $[(O \cdot C_{10}H_5 \cdot CO_2)_2Fe]_3 \cdot 18H_2O$, which is oxidised by excess of $FeCl_3$ to yield a salt of Fe with 2 : 2'-dihydroxy-1 : 1'-dinaphthyl-2 : 2'-dicarboxylic acid, $[(O \cdot C_{10}H_5 \cdot CO_2)_2Fe]$. R. T.

Condensation of phenylpyruvic acid with acetophenone. P. CORDIER (J. Pharm. Chim., 1936, [viii], 24, 345—352).— $CH_2Ph \cdot CO \cdot CO_2Na$ with $COPhMe$ in aq. EtOH-KOH at room temp. affords the Na salt of α -hydroxy- α -phenacyl- β -phenylpropionic acid (liberated by acidification), dehydrated by HCl-AcOH at 100° or by heat alone to give 2-keto-5-phenyl-3-benzylidene-2 : 3-dihydrofuran, $O \begin{matrix} \diagup CO \cdot C \cdot CHPh \\ \diagdown CPh : CH \end{matrix}$ (I), m.p. 150° (insol. in Na_2CO_3), and α -phenacyl- β -phenylacrylic acid (or β -benzoyl- α -benzylacrylic acid), decomp. 160°, also obtained by the action of boiling alkali on (I). J. W. B.

Synthesis of pharmacologically important carboxylic acids. II. Synthesis of substituted phenylacetic acids from aromatic aldehydes. K. KINDLER and E. GEHLHAAR (Arch. Pharm., 1936, 274, 377—388; cf. A., 1933, 1293).—*p*-Methylmandelonitrile *O*-benzoate reduced by Pd-black (I) and boiling tetrahydronaphthalene (II) and subsequently hydrolysed (aq. KOH, EtOH) gives *p*-tolylacetic acid, m.p. 91 (60% yield). *p*-isoPropylphenylacetic acid was similarly obtained. Hydrogenation [(I) and boiling (II) at 2 atm.; (I) and AcOH] of mandelamide *O*-benzoate yields BzOH and $CH_2Ph \cdot CO \cdot NH_2$ (75% yield). Mandelonitrile *O*-benzoate in aq. MeOH with HCl yields *Me benzoyl-mandelate*, m.p. 78°, which by the above methods of hydrogenation and subsequent hydrolysis gives $CH_2Ph \cdot CO_2H$ (84% yield). By the action of HCl in aq. MeOH on the corresponding nitriles are obtained *Me O-acetyl-3 : 4-dimethoxymandelate*, b.p. 186—196°/14 mm., *-4-methoxymandelate*, b.p. 164—174°/15 mm., and *-mandelate*, b.p. 144°/15 mm., which by hydrogenation [2 atm.; (I) and AcOH] and hydrolysis yield homoveratric acid (III), *p*- $OMe \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$, and $CH_2Ph \cdot CO_2H$, respectively, in good yield. 3 : 4-(OEt) $_2C_6H_3 \cdot CHO$ in aq. MeOH hydrogenated by (I) yields 3 : 4-(OEt) $_2C_6H_3 \cdot CH_2 \cdot OH$, which with SO_2Cl_2 gives 3 : 4-(OEt) $_2C_6H_3 \cdot CH_2Cl$, and this in C_6H_6 with KCN in H_2O yields 3 : 4-diethoxyphenylacetoneitrile,

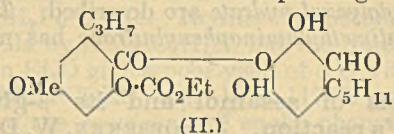
b.p. 175—180°/14 mm., m.p. 37°, hydrolysed (KOH; aq. EtOH) to 3 : 4-diethoxyphenylacetic acid, m.p. 79—80°, all obtained in good yields. A good yield of (III) was similarly obtained from 3 : 4-(OMe) $_2C_6H_3 \cdot CHO$. F. R. G.

2 : 2-Disubstituted indandiones. G. N. GHEORGHIU (J. pr. Chem., 1936, [ii], 146, 193—197).—*Me 2-methylindandione-2-acetate*, m.p. 163—164°, obtained by the successive action of KOH-EtOH and $CH_2Br \cdot CO_2Me$ on 2-methylindandione, is hydrolysed by 20% H_2SO_4 -AcOH at 150° to the corresponding acid, m.p. 190°. $CH_2Br \cdot CO_2Et$ similarly gives *Et 2-methylindandione-2-acetate*, m.p. 159—161°, and, after re-solidification, m.p. 161—162°. The following -2-methylindandiones are obtained analogously: 2-benzyl-, m.p. 78—79°; 2-acetonyl-, m.p. 136—137°. 2-Phenylindandione yields 2-acetonyl-, m.p. 152—153° [accompanied by the compound (?) $CO(CH_2 \cdot CPh \begin{matrix} \diagup CO \\ \diagdown CO \end{matrix} C_6H_4)_2$, m.p. 208—210°, arising from $CO(CH_2Br)_2$ present in CH_2BrAc], and 2-allyl-, m.p. 76°, 2-phenylindandione, and *Et 2-phenylindandione-2- β -propionate*, m.p. 72—74°. H. W.

Lichen substances. LXXI. Synthesis of diplo-schistessic acid. Y. ASAHINA and M. YASUE (Ber., 1936, 69, [B], 2327—2330; cf. Koller *et al.*, A., 1935, 748).—Treatment of gallaldehyde Me_3 ether with $N_2H_4 \cdot H_2O$ in boiling EtOH and of the residue with KOH at 120° gives 5-methylpyrogallol Me_3 ether, b.p. 117—118°/5 mm., demethylated by boiling HI (*d* 1.7) to 5-methylpyrogallol (I). 2 : 3 : 4-Trihydroxy-6-methylbenzaldehyde, m.p. 182—183° or, $+1H_2O$, m.p. 182—183° after softening at about 120°, obtained from (I), $Zn(CN)_2$, and HCl in abs. Et_2O , is converted by $ClCO_2Et$ and C_5H_5N in $COMe_2$ at 0° into 2 : 3 : 4-triethylcarbonato-6-methylbenzaldehyde, m.p. 66—68°, oxidised by $KMnO_4$ in $COMe_2-H_2O$ at 45° to 2 : 3 : 4-triethylcarbonato-6-methylbenzoic acid (II), m.p. 109°. (II) is converted by successive treatments with $SOCl_2$ and orcyaldehyde into *tricarbethoxydiploschistess-aldehyde*, m.p. 136—138°, which is condensed with $ClCO_2Et$ in C_5H_5N and then oxidised to *tetracarbethoxydiploschistessic acid*, m.p. 131—132°, hydrolysed by NaOH in $COMe_2-H_2O$ to diploschistessic acid (4-2' : 3' : 4'-trimethoxy-6'-methylbenzoyl-3-hydroxy-5-methylbenzoic acid), m.p. 174° (decomp.) (tetraacetate, m.p. 164—165°, and its Me ester, m.p. 169°). H. W.

Lichen substances. LXX. Synthesis of ram-alinolic acid. Y. ASAHINA and T. KUSAKA (Ber., 1936, 69, [B], 1896—1899).—3 : 4 : 5-Trimethoxyvalerophenone is reduced by Zn-Hg and boiling 5*N*-HCl to 5-*n*-amylpyrogallol Me_3 ether, b.p. 166°/6 mm., converted by red P and boiling HI (*d* 1.7) into 5-*n*-amylpyrogallol, b.p. 179—182°/3 mm., m.p. 67°. Treatment of (I) and $Zn(CN)_2$ in Et_2O with HCl and of the product with boiling H_2O yields 2 : 3 : 4-trihydroxy-6-*n*-amylbenzaldehyde (I), m.p. 116—117°, transformed by $ClCO_2Et$ in C_5H_5N at -15° and then oxidised by $KMnO_4$ in $COMe_2$ to 2 : 3 : 4-triethylcarbonato-6-*n*-amylbenzoic acid, m.p. 81°, whence 2 : 3 : 4-trihydroxy-6-*n*-amylbenzoic acid, m.p. 163°. Treatment of (I) with carbethoxydivaricatyl chloride gives the *depside aldehyde* (II),

which, after protection of the free OH groups by CO_2Et , is oxidised to the corresponding acid; this,



after decarboxylation, gives a product identical with natural ramalinic acid (III). (I) in COMe_2 is transformed by BzCl and $N\text{-KOH}$ into 2:4-dihydroxy-3-benzoyloxy-6-n-amylobenzaldehyde (V), m.p. 123°, the dicarboxy-derivative of which is oxidised and then decarboxylated to 2:4-dihydroxy-3-benzoyloxy-6-n-amyloxybenzoic acid, m.p. 173°. (IV) in COMe_2 is converted by MeI and anhyd. K_2CO_3 into an oil, oxidised by KMnO_4 to 2:4-dimethoxy-3-benzoyloxy-6-n-amyloxybenzoic acid, m.p. 162—163°; the corresponding Me ester is hydrolysed by KOH-MeOH to the substance $\text{C}_{15}\text{H}_{22}\text{O}_5$, m.p. 73—74°, identical with that obtained by hydrolysis of permethylated (III). H. W.

Elimination of the aldehydic group as formic acid from aromatic aldehydes. IV. 2-Chloro-6-fluoro- and 2:6-difluoro-benzaldehyde. G. LOCK (Ber., 1936, 69, [B], 2253—2258; cf. A., 1935, 1238).—With di-ortho-substituted benzaldehydes the behaviour of F resembles that of other halogens. 2:6- $\text{C}_6\text{H}_3\text{MeClF}$ is converted by gradual treatment with Br at 180—200° and of the product with conc. H_2SO_4 at 50—60° followed by distillation with steam into 2-chloro-6-fluorobenzaldehyde (I), m.p. 38.5° [semicarbazone, m.p. 213° (corr.); oxime, m.p. 134° (corr.)], oxidised by $\text{Ag}_2\text{O-H}_2\text{O}$ at 100° to 2-chloro-6-fluorobenzoic acid (II), m.p. 159° (corr.). (I) and 50% $\text{KOH-H}_2\text{O}$ at 100° afford HCO_2H , a little (II), and m-chlorofluorobenzene, b.p. 127—128°/761 mm., also obtained from $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$. 2:6- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$ is converted into the corresponding diazonium borofluoride, decomp. 118°, which when heated with sand at 150—250°/vac. affords 2-fluoro-6-nitrotoluene (III), b.p. 97°/11 mm., m.p. 6.5—7°. (III) is reduced (SnCl_2 and conc. HCl) to 6-fluoro-o-toluidine, b.p. 89.5—90.5°/15 mm., m.p. 7° [*Ac* derivative, m.p. 132° (corr.)], transformed through the diazonium borofluoride into 2:6-difluorotoluene (IV), b.p. 112°(corr.)/742 mm. [2-fluoro-6-hydroxytoluene, b.p. 186—188°(corr.)/748 mm., m.p. 56.5°]. The direct prep. of (IV) from 2:6- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$ appears impossible. (IV) is brominated at its b.p. to 2:6-difluorobenzylidene bromide, m.p. 45°, converted by H_2SO_4 into 2:6-difluorobenzaldehyde (V), b.p. 82—84°/15 mm., 190—195°/743 mm., m.p. about 15—17° [semicarbazone, m.p. 226° (corr.); 2:6-difluorobenzoic acid, m.p. 157.5° (corr.)], also obtained from (IV) by Etard's reaction. (V) and 50% KOH yield HCO_2H and $m\text{-C}_6\text{H}_4\text{F}_2$. H. W.

Condensation of 5-chloro-2-nitrobenzaldehyde with aniline. I. TANASESCU and (MLLE.) M. SUCIU (Bull. Soc. chim., 1936, [v], 3, 1753—1761).—2:5- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CHO}$ and $(\text{NH}_2\text{Ph})_2\cdot\text{H}_2\text{SO}_4$ —condense (ZnCl_2) to form 5-chloro-2-nitro-4':4''-diaminotriphenylmethane (I), m.p. 164° (hydrochloride; *Ac*, m.p. 209°, and *Bz*, m.p. 253°, derivatives), which with $\text{Zn-NH}_4\text{Cl-EtOH}$ gives 5-chloro-2:4':4''-tri-

aminotriphenylmethane, m.p. 98° (*Bz* derivative, m.p. 260°). As by-product with (I), 5-chloro-3-p-aminophenylanthranil, m.p. 208° (*Ac*, m.p. 222°, *Bz*, m.p. 242°, benzylidene, m.p. 149°, and 5''-chloro-2''-nitrobenzylidene, m.p. 245°, derivatives), is formed, which with $\text{Zn-NH}_4\text{Cl-EtOH}$ gives 5-chloro-2:4'-diaminobenzophenone, m.p. 149° (*Bz* derivative, m.p. 207°). E. W. W.

Action of aniline on o-nitrobenzaldehyde in acetic acid. S. SECAREANU and A. SILBERG (Bull. Soc. chim., 1936, [v], 3, 1777—1782).—These substances condense in AcOH to give a product, converted by conc. HCl in EtOH into a mixture of 3-p-aminophenylanthranil, $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and 5-chloro-

3-p-aminophenylanthranil (cf. preceding abstract). E. W. W.

Formation of polyene chains. Preparation of unsaturated aldehydes. G. WITIG and R. KETHUR [with, in part, A. KLEIN and R. WIETBROCK] (Ber., 1936, 69, [B], 2078—2087).—The syntheses follow the course $\text{R}\cdot\text{CHO} + \text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{CHR}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{H} \rightarrow \text{CHR}\cdot\text{CH}\cdot\text{CN} \rightarrow \text{CHR}\cdot\text{CH}\cdot\text{CH}\cdot\text{NH} \rightarrow \text{CHR}\cdot\text{CH}\cdot\text{CHO}$. $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in boiling AcOH afford cinnamylideneacyanoacetic acid, which loses CO_2 when heated with Cu powder at 180—185° giving cinnamylideneacetonitrile (I), b.p. 158—160°/11 mm., converted by HCl in abs. Et_2O followed by treatment of the hydrochloride with H_2O into the solid isomeride (II), m.p. 40—41.5°. (I) and (II) give the same cinnamylideneacetamide, m.p. 185.5—186.5°, and -acetic acid, m.p. 163—164°, when subjected to short and protracted hydrolysis with KOH-EtOH , respectively. Reduction of (I) or (II) to the corresponding aldehyde by $\text{SnCl}_2\text{-SnCl}_2\cdot 2\text{H}_2\text{O}$ and HCl in Et_2O is unsatisfactory by reason of the sparing solubility of the intermediate adducts and the best yields of δ -phenyl- $\Delta^{\alpha\gamma}$ -pentadienal (phenylhydrazone, m.p. 173.5—174°) are secured in dioxan at 55°. Cinnamylideneacetaldehyde and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ give α -cyano- ζ -phenyl- $\Delta^{\alpha\gamma\epsilon}$ -heptatrienoic acid, m.p. 227—228°, converted by Cu powder at about 190° into CO_2 and ζ -phenyl- $\Delta^{\alpha\gamma\epsilon}$ -heptatrienonitrile, b.p. 195—197°/12 mm., m.p. 50—55°, a mixture of stereoisomerides from which a form, m.p. 111—112°, is obtained by the action of HCl in Et_2O ; this is also produced when the mixture is reduced by SnCl_2 and HCl in Et_2O or dioxan.

$\text{CPh}_2\text{Me}\cdot\text{OH}$ is transformed by HBr in boiling AcOH into $\text{CPh}_2\cdot\text{CH}_2$; Br in AcOH is added to the cooled solution, which is again heated, whereby the intermediate $\text{CPh}_2\text{Br}\cdot\text{CH}_2\text{Br}$ is transformed into $\text{CPh}_2\cdot\text{CHBr}$ in 66% yield. The Grignard compound from the latter substance and $\text{HCO}\cdot\text{NPhMe}$ afford β -phenylcinnamaldehyde (III), m.p. 44—45° (semicarbazone, m.p. 217—219°; anilide, m.p. 98—98.8°, azine, m.p. 199—199.5°), in 41% yield. (III) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in boiling AcOH yield γ -phenylcinnamylideneacyanoacetic acid, m.p. 217—218° (decomp.), whence γ -phenylcinnamylideneacetonitrile, m.p. 68—69°, and $\delta\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadienal, m.p. 69.5—71° (corresponding azine, m.p. 183—184°). H. W.

Condensation reactions of 2:4-dinitrophenylhydrazine. F. L. RODUTA and G. QUIBILAN (Rev. Filipina Med. Farm., 1936, 27, 123—130).—A summary of the known 2:4-dinitrophenylhydrazones of aldehydes and ketones is given and 2:4-dinitrophenylhydrazones of the following have been prepared: citral, m.p. 103°; $\text{CCl}_3\cdot\text{CHO}$, m.p. 131°; hydrocinnamaldehyde, m.p. 147°; furfuraldehyde, m.p. 218°; protocatechualdehyde, m.p. 226°; COPh_2 , m.p. 228°; *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. 232°; PhCHO , m.p. 235°; α -naphthaquinone, m.p. 278° (decomp.); and isatin. F. R. S.

[Halogeno-cinnamaldehydes.]—See this vol., 1463.

Enol-betaines. II. α -Ketoaldonitrone and a new preparation of α -ketoaldehydes. F. KRÖHNKE and E. BÖRNER (Ber., 1936, 69, [B], 2006—2016; cf. A., 1935, 987).—Addition of *N*-NaOH to phenacylpyridinium bromide (I) and PhNO in aq. EtOH at -10° to -5° affords *benzoyl-N-phenylnitrone* (II), $\text{CHBz}\cdot\text{NPh}\cdot\text{O}$, m.p. 109—110°, which gradually decomposes when kept and yields mandelic acid when treated with alkali. *Benzoylphenylnitrone hydrate* (III) $\text{OH}\cdot\text{CHBz}\cdot\text{NPh}\cdot\text{OH}$, m.p. 90°, is derived from (I) and 0.1*N*- H_2SO_4 in EtOH. (II) or (III) is transformed by $\text{NPh}\cdot\text{NH}_2$ (1 mol.) into a mixture of α - and β -glyoxalphenylhydrazone and by excess of the reagent into the corresponding osazone. (II) and NH_2OH (1 mol.) yield oximinoacetophenone, whereas with 2 mols. *anti*-phenylglyoxime is produced. With NH_2Ph in hot EtOH (II) gives *phenylglyoxaldianil hydrate*, $\text{C}_{20}\text{H}_{18}\text{ON}_2$, m.p. 97° (corresponding *di-p-tolil hydrate*, m.p. 118—119°). The *p*-dimethylaminoanil of phenylglyoxal has m.p. 88°, and the *p*-dimethylaminoanilides of cinnamylideneacetic acid and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ have m.p. 205—207° and 174°, respectively. Analogous reactions between PhNO and phenacylquinolinium, -isoquinolinium, and -triethylammonium bromide and between phenacylpiperidinium bromide and *p*- $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ are described. *Benzoyl-N-p-dimethylaminophenylnitrone*, m.p. 110—111°, obtained as above or from the enolbetaine of (I) in absence of NaOH, is converted by 5*N*- H_2SO_4 into phenylglyoxal, m.p. 73°. (A compound, 2-*p*- $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{p-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, m.p. 50—51° after softening at 48°, is described.) The oxime of phenacylpyridinium perchlorate and PhNO give the compound, $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$, m.p. 156° (decomp.). The following -*benzoyl-N-p-dimethylaminophenylnitrone*s are described; *p*-iodo-, m.p. 97°, whence *p*-iodophenylglyoxal hydrate, m.p. 137—138°; 3:4-dichloro-, m.p. 136—137°, whence 3:4-dichlorophenylglyoxal hydrate, m.p. 82—84°; 3:4-dichloro-2-nitro-, decomp. about 140°. *p*-Phenylphenacylpyridinium bromide (IV) and PhNO afford *p*-phenylbenzoyl-N-phenylnitrone, m.p. 144°. Treatment of (IV) with *p*- $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ and alkali and of the product with warm, dil. H_2SO_4 gives *p*-xenylglyoxal hydrate, m.p. 117—121°, also obtained by hydrolysis of *p*-phenyl-*p*-bromophenacylpyridinium bromide, m.p. 206° (decomp.), derived from (IV) and Br in AcOH; *p*-xenylquinoxaline has m.p. 128°. β -Naphthacylpyridinium bromide gives β -naphthoyl-N-phenylnitrone, m.p. 101—101.5°, and β -naphthylglyoxal hydrate,

m.p. 106—109°. *Keto-2-thiophenonyl-N-p-dimethylaminophenylnitrone*, m.p. 123°, and non-homogeneous 2-thiophenylglyoxal hydrate are described. *Trimethylacetyl-N-p-dimethylaminophenylnitrone* has m.p. 87—88°. H. W.

Synthesis of sesamol and its β -glucoside. Baudouin's reaction. J. BÖESEKEN, W. D. COHEN, and C. J. KIP (Rec. trav. chim., 1936, 55, 815—820).—Piperonaldehyde (I) and 20% AcO_2H (prep. free from Ac_2O_2 described) in AcOH with 2 drops of H_2SO_4 or, better, a trace of *p*- $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{SO}_3\text{H}$ at $<30^\circ$ give 50 and 60% yields, respectively, of sesamol (II) and 0.7 mol. of HCO_2H . Larger amounts of acid cause resinification and very poor yields. (II), tetra-acetylglucosidyl bromide, 2*N*-KOH, and Et_2O , when shaken, give sesamol β -glucoside tetra-acetate, cryst. (10%), hydrolysed by $\text{Ba}(\text{OH})_2$ to sesamol β -glucoside, m.p. 168—169°, which gives Baudouin's reaction slowly as does sesame oil; the reaction of the oil is thus proved to be due to hydrolysis of sesamoline to (II). Pure (II) colours rapidly in air, but this is prevented by a little (I). R. S. C.

Reduction of benzophenone at the dropping mercury cathode. H. SCHWEITZER and E. LAQUEUR (Rec. trav. chim., 1936, 55, 959—962).—Reduction of COPh_2 at the dropping Hg cathode occurs in one stage in neutral solution, but in two stages in presence of HCl, particularly of an excess. Whereas reduction of the pinacone or its half-radical is possible, it is preferable to regard the reduction in acid solution as that of $[\text{CPh}_2\cdot\text{OH}]^+\text{Cl}^-$. R. S. C.

Hydrogen linking formation between hydroxyl groups and nitrogen atoms in organic compounds. S. B. HENDRICKS, O. R. WULF, G. E. HILBERT, and U. LIDDEL (J. Amer. Chem. Soc., 1936, 58, 1991—1996; cf. this vol., 703).—The existence of chelation between OH and N in compounds of the type *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{X}\cdot\text{NR}$ (X=CH or N) is indicated by the absence of infra-red absorption characteristic of the OH group; such chelation requires the OH to be *trans* to R. Thus, the following show no absorption: (*anti*-)2-hydroxy-, m.p. 95°, and 2-hydroxy-5-methyl-, m.p. 114°, -benzophenoneoxime acetates (cf. Blatt, this vol., 1511), salicylaldehyde-anil, hydrazone, -dimethylhydrazone, -phenylhydrazone, -phenylmethylhydrazone, and -azine; *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OAc}$; 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{CMe}_2$; 1-benzeneazo- and 2:5-dichlorobenzeneazo- β -naphthols; 2:2'-dihydroxy- and 2:5:5'-trichloro-2'-hydroxy-4-methyl-azobenzenes. Absorption is shown by *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ (probably due to $\text{N}\cdot\text{OH}$), 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}_2$ (m.p. 157°), *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$, α - and β -benzoinphenylhydrazones, 2:2'-dihydroxybenzophenone-oxime acetate and -phenylmethylhydrazone, and *syn*-2-hydroxybenzophenoneoxime acetate; in some cases, partial chelation probably occurs. Structural formulæ (showing probable interat. distances) for several of the above compounds are discussed. H. B.

Oxidation of the ethylenic linking adjacent to a carbonyl group by peracids. J. BÖESEKEN and J. JACOBS (Rec. trav. chim., 1936, 55, 786—790).— $\text{CHPh}\cdot\text{CMe}\cdot\text{COMe}$ is oxidised by AcO_2H in AcOH at $<30^\circ$ to (?) *cis*- and *trans*-forms, (I), m.p. 131°, and

(II), b.p. 100—103°/3 mm., n_D 1.5503, of the acetate of enolic benzyl Me ketone, hydrolysed by conc. HCl to $\text{CH}_2\text{Ph}\cdot\text{COMe}$. Neither is obtained from $\text{CH}_2\text{Ph}\cdot\text{COMe}$ by $\text{Ac}_2\text{O}\cdot\text{C}_6\text{H}_5\text{N}$, but the Na derivative and AcCl in Et_2O give a poor yield of (II) with a little (I). $\text{CHPh}\cdot\text{CH}\cdot\text{COEt}$, b.p. 109—117°/3 mm., and AcO_2H give the propionate of enolic phenylacetaldehyde (III), b.p. 90—92°/1—3 mm., n_D^{20} 1.5541, hydrolysed by conc. HCl to $\text{CH}_2\text{Ph}\cdot\text{CHO}$. The aldehyde and $(\text{EtCO})_2\text{O}\cdot\text{C}_6\text{H}_5\text{N}$ give an isomeride (IV), b.p. 92—96°/high vac., n_D^{20} 1.5371, of (III). Both (III) and (II) may be mixtures of isomerides. The action of AcO_2H is to insert O between the systems $\cdot\text{C}\cdot\text{C}\cdot$ and CO.

R. S. C.

Autoxidation phenomena in the indone series. A. SCHÖNBERG and R. MICHAELIS (*Naturwiss.*, 1936, 24, 620; cf. A., 1935, 1369).—2-*p*-Dimethylamino-anilino-3-phenylindone is autoxidised in solution by addition of O_2 to the free radical form.

J. L. D.

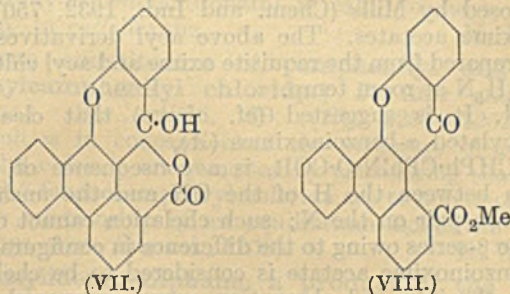
Synthesis of hexahydrophenanthrene derivatives. J. C. BARDHAN (*Chem. and Ind.*, 1936, 879—880).—The *cis*-structure assigned by van de Kamp and Mosettig (this vol., 1062) to liquid octahydrophenanthrene is uncertain.

$\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{Et}$, b.p. 155°/1 mm., with $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$ and NaOEt give *Et* β -keto- α - β' -phenylethylpimelate, b.p. 175°/1 mm., which with cold, conc. H_2SO_4 affords *Et*₂ 3:4-dihydronaphthalene-2-carboxylate-1- γ -butyrate, b.p. 177°/1 mm. This undergoes ring-closure with Na and then yields by hydrolysis 1-keto-1:2:3:4:9:10-hexahydrophenanthrene, the semicarbazone, m.p. 254—255°, of which yields (NaOEt) a hydrocarbon, smoothly dehydrogenated to phenanthrene.

R. S. C.

Alkylation and arylation of benzanthrone by Grignard reagents. Oxidative degradation of 6-phenylbenzanthrone. G. CHARRIER and E. CHIGI (*Ber.*, 1936, 69, [B], 2211—2232; cf. A., 1933, 160).—Addition of benzanthrone (I) in Et_2O to MgPrI in Et_2O gives 6-propylbenzanthrone, m.p. 83—84°, oxidised by CrO_3 in AcOH to 4-propylanthraquinone-1-carboxylic acid, m.p. 180—181°. Similarly (I) and MgBuI afford 6-*n*-butylbenzanthrone, m.p. 99° [the *Bz*-3-*n*-butylbenzanthrone of Nakanishi (A., 1934, 191)], oxidised by CrO_3 in AcOH to 4-*n*-butylanthraquinone-1-carboxylic acid, m.p. 175°, and thence by HNO_3 under pressure to anthraquinone-1:4-dicarboxylic acid, m.p. about 315°. Oxidation of 6-phenylbenzanthrone (II) with KMnO_4 in boiling dil. alkali affords 4-phenylanthraquinone-1-carboxylic acid (III), m.p. 288—290° [*Na* ($3\text{H}_2\text{O}$) salt], diphenyl-3:4-dicarboxylic-2-glyoxylic acid (IV), m.p. 256—257° (decomp.), and $\text{H}_2\text{C}_2\text{O}_4$. Oxidation of (IV) with KMnO_4 and 33% H_2SO_4 yields diphenyl-2:3:4-tricarboxylic acid (V), m.p. 210—212°, which readily passes into an anhydride. Conc. H_2SO_4 at 100° converts (IV) or (V) into fluorenone-1:2-dicarboxylic acid (VI), m.p. 330° (*Me*₂ ester, m.p. 199°; *Me* ester, m.p. about 230° and m.p. 315—320° after resolidification at 235—240°; anhydride, m.p. 315—320°), decarboxylated by Cu powder in quinoline at 150—160° and then at 200—210° to fluorenone-2-

carboxylic acid, m.p. 330° (*Me* ester, m.p. 186°). For purposes of comparison, diphenyl-2:3:2'-tricarboxylic acid (VI) is converted by conc. H_2SO_4 at 150—160° into fluorenone-1:5-dicarboxylic acid, decarboxylated to fluorenone-1-carboxylic acid, m.p. 191—192° (*Me* ester, m.p. 89°). (V) and $\text{NHPh}\cdot\text{NH}_2$ in boiling EtOH gave the corresponding phenylhydrazone, m.p. 305—307° (corresponding anhydride, m.p. 315°), and the phenylhydrazone of fluorenone-1:2-dicarboxyanilinoimide, m.p. 276° (decomp.). Oxidation of (IV) with alkaline KMnO_4 gives (III), which is reduced by Zn in ammoniacal solution to 4-phenylanthracene-1-carboxylic acid, m.p. 246—247°, decarboxylated by Cu in quinoline at 140—160° to 1-phenylanthracene, m.p. 110—112°. Oxidation of (II) with CrO_3 in $\text{AcOH}\cdot\text{H}_2\text{SO}_4$ gives a product, $\text{C}_{23}\text{H}_{14}\text{O}\cdot\text{CrO}_3$, decomp. about 150°. Satisfactory oxidation of (II) by CrO_3 in AcOH is secured if H_2SO_4 is omitted and the change is allowed to proceed very vigorously, whereby small amounts of (III) and, mainly, 1:2-3:4-dibenzoxanthonecarboxylic acid (VII), m.p. 296—305° (decomp.), are produced. (VII) is neutral in cold solution, but readily yields the *Na*



salt ($+3\text{H}_2\text{O}$) with boiling alkali or alkali carbonate. The *Me* ester (VIII) has m.p. 217°. (VII) is unattacked by boiling conc. H_2SO_4 but is transformed by a large excess of boiling 20% NaOH into 9-*o*-hydroxybenzoylfluorene-1:9-dicarboxylic acid, m.p. 210—212° (decomp.), which gives a red colour with FeCl_3 . Oxidation of (VII) with KMnO_4 of differing concn. usually gives (VI) but under certain conditions *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is isolable. Distillation of (VII) with Zn powder affords phenanthrene and 1:2-3:4-dibenzoxanthone (IX), m.p. 207—209°, together with C_6H_6 and traces of Ph_2 and PhOH . (IX) is very resistant towards oxidation but, under drastic conditions, is transformed by KMnO_4 into diphenic acid. Distillation of (IX) over Zn powder affords mainly phenanthrene. Treatment of (IX) with $\text{KOH}\cdot\text{EtOH}$ at 180° gives 9-hydroxy-10-*o*-hydroxybenzoylphenanthrene, m.p. 152°, readily re-converted into (VIII), whilst molten KOH at 250—280° gives *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and 9-hydroxyphenanthrene.

H. W.

Action of alkali on acylated ketoximes. II. Steric hindrance to alkaline hydrolysis. A. H. BLATT and R. P. BARNES. **III. Hydrogen bond formation in derivatives of *o*-hydroxybenzophenoneoximes.** A. H. BLATT and L. A. RUSSELL (*J. Amer. Chem. Soc.*, 1936, 58, 1900—1902, 1903—1908; cf. A., 1935, 1125).—II. Under conditions causing hydrolysis of $\text{CPh}_2\cdot\text{N}\cdot\text{OBz}$, and α -*p*-chloro-, m.p. 114—115°, α -*p*-methoxy-, m.p. 115—116°, and

β -*p*-methoxy-, m.p. 85—86°, -benzophenoneoxime benzoates to oxime (and EtOBz), benzophenone-, m.p. 136—137°, and α -*p*-chloro-, m.p. 101—102°, α -*p*-methoxy-, m.p. 102—103°, and β -*p*-methoxy-, probably dimorphous, m.p. 75° and 120—121°, -benzophenoneoxime 2 : 4 : 6-trimethylbenzoates are unaffected (by cold aq. EtOH-NaOH), owing to steric hindrance effects; the latter esters are hydrolysed by EtOH-conc. HCl to *s*-C₆H₂Me₃·CO₂H and the original COAr₂. The above production of EtOBz is due to the preliminary addition of EtOH, viz., CAr₂:N·OBz → CAr₂:N·O·CPh(OH)(OEt) → CAr₂:N·OH + EtOBz; this view is confirmed by the formation of *p*-C₆H₄Ph·CO₂Me from acetoxime *p*-phenylbenzoate, m.p. 132—133°, and cold aq. MeOH-NaOH. α -Benzoinoxime 2 : 4 : 6-trimethylbenzoate, m.p. about 92° (unstable), is cleaved by aq. 5% NaOH or aq. EtOH-Na₂CO₃ to PhCHO, PhCN, and *s*-C₆H₂Me₃·CO₂H; β -benzoinoxime 2 : 4 : 6-trimethylbenzoate, m.p. 151°, is similarly unaffected, but with aq. EtOH-NaOH the same fission products result. The mechanism of the cleavage process, which is unaffected by steric hindrance, is discussed; it is a modification of that proposed by Mills (Chem. and Ind., 1932, 750) for aldoxime acetates. The above acyl derivatives are all prepared from the requisite oxime and acyl chloride in C₅H₅N at room temp.

III. It is suggested (cf. above) that cleavage of acylated α -benzoinoximes (A), OH·CPh·CPh·N·O·COR, is a consequence of chelation between the H of the OH and the unshared electron pair on the N; such chelation cannot occur in the β -series owing to the difference in configuration. α -Benzoinoxime acetate is considered to be chelated since the infra-red absorption curve, compared with that of the β -acetate, shows marked suppression of OH absorption (cf. Hilbert *et al.*, this vol., 703). Examination of the acetates of *o*-hydroxy- and 2-hydroxy-5-methyl-benzophenoneoximes shows that chelation can take place; its occurrence is accompanied by reactions comparable with those of (A). The acetates, m.p. 96—97° (I) and 156° (II), of *syn*-(III) and *anti*-(IV) *o*-hydroxybenzophenoneoximes (modified prep.; cf. Kohler and Bruce, A., 1931, 732) are hydrolysed by an excess of cold 5% NaOH to (III) and (IV), respectively; with aq. EtOH-Na₂CO₃, (I) gives 1-phenylbenzoxazole (V) [*i.e.*, a reaction equiv. to cleavage of (A)], whilst (II) affords (IV). Pyrolysis of (I) in a vac. occurs smoothly and gives 2-phenylbenzisooxazole (VI); (II) similarly undergoes much charring and yields (probably) a little of (V) and (VI) (isolable). The acetate (VII), m.p. 125—126°, of *syn*-2-hydroxy-5-methylbenzophenoneoxime (VIII) (modified prep.) is converted by (a) 5% NaOH into (VIII), (b) aq. EtOH-Na₂CO₃ into 1-phenyl-4-methylbenzoxazole (IX), and (c) pyrolysis into 2-phenyl-4-methylbenzisooxazole (X), m.p. 92—93°, the acetate (XI), m.p. 157—158°, of *anti*-2-hydroxy-5-methylbenzophenoneoxime (XII), m.p. 136—137°, similarly gives (a) (XII), (b) (XII), and (c) a little of (IX) and (X) (isolable). (XII) is formed when (VIII) is heated with 40% NaOH, whilst (X) is also obtained by successive oximation and action of alkali on the mixture of 2-chloro-5-methyl- and 5-chloro-2-methylbenzophenones prepared (method: Heller, A., 1913,

i, 631) from *p*-C₆H₄MeCl. (XII) and PCl₅ in Et₂O give 5 : 2-OH·C₆H₃Me·CO·NHPH.

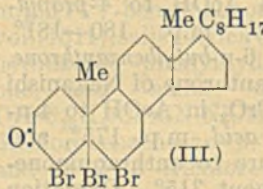
The infra-red absorption curves for (I) and (VII), unlike those for (II) and (XI) (data now given), do not show OH absorption. (I) and (VII) are much more sol. in CCl₄, and much less sol. in EtOH, than (II) and (XI). These data show that (I) and (VII) are chelated.

H. B.

Interconversion of mixed benzoinoximes. H. H. WEINSTOCK, jun., and R. C. FUSON (J. Amer. Chem. Soc., 1936, 58, 1986—1988).—A difficultly separable equilibrium mixture of 2 : 4 : 6- (I) and 2' : 4' : 6'- (II) -trimethylbenzoinoximes [mesitylphenyl- and benzoyl-mesityl-carbinol, respectively] is obtained when either (I) or (II) is heated with aq. EtOH-NaOAc. Interconversion probably occurs through the intermediate $\alpha\alpha'$ -dihydroxy-2 : 4 : 6-trimethylstilbene, *i.e.*, the enediol; this view is supported by the following results. (I) and (II) with BzCl in C₅H₅N at 80° give a single benzoate, m.p. 127—127.5° [probably that of (I)], hydrolysed (EtOH-KOH) to 2 : 4 : 6-trimethylbenzil (III). The Na₂ derivative (IV) from (III) with BzCl affords $\alpha\alpha'$ -dibenzoyloxy-2 : 4 : 6-trimethylstilbene, two forms, m.p. 138.5—139° (V) and 169.5—170° (VI); (V) heated above its m.p. undergoes quant. conversion into (VI), whilst hydrolysis (EtOH-KOH) of (VI) gives (I) and (III). (I) and Ac₂O-NaOAc for 5 hr. yield the acetate, m.p. 73—73.5°; the same treatment of (II) [and more prolonged treatment of (I)] affords $\alpha\alpha'$ -diacetoxy-2 : 4 : 6-trimethylstilbene, m.p. 104—104.5°, also prepared from (IV) and AcCl. (I) and (II) heated with a little I at 200—220° or in AcOH undergo disproportionation to (III) and Ph 2 : 4 : 6-trimethylbenzyl ketone. All reactions are carried out in N₂. (I) and (II) react with MgMeI in the enediol form to the extent of 78 and 30%, respectively.

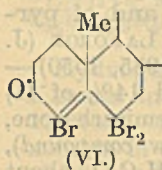
H. B.

Bromination of Δ^5 -cholestenone dibromide. A. BUTENANDT and G. SCHRAMM (Ber., 1936, 69, [B], 2289—2299).—Cautious oxidation of cholesterol dibromide (I) with CrO₃ affords Δ^5 -cholestenone dibromide (II), m.p. 80°, converted by Br₂ (1 mol.) in AcOH into 4 : 5 : 6-tri-bromo- (III), m.p. 106° (decomp.), which is brominated further to 4 : 4 : 5 : 6-tetra-bromo-cholestanone (IV), m.p. 128° (decomp.), also obtained directly from (II). Generally it appears that 3-keto-sterol



derivatives in which rings A and B are united in the same manner as in *cis*-decahydronaphthalene are brominated at 4, and those in which the arrangement is as in *trans*-decahydronaphthalene react at 2. It is assumed that the rule can be applied to the determination of configuration, and that rings A and B in (I) are probably united in the *cis*-position. The constitution of (III) rests on the following observations. It is debrominated by Zn and AcOH to Δ^4 -cholestenone and by NaI in EtOH to a non-cryst. heterogeneous product containing >1 Br per mol. and converted by KOAc in AcOH at 200° into cholestane-3 : 6-dione. When treated with NaI in EtOH-C₆H₆ (conc. solu-

tion) (III) gives cholestenedione Et ether; it is therefore stereoisomeric with the Br_3 -ketone (V) of Inhoffen (this vol., 854, 1104). The structure of (IV) follows from its transformation by KOAc in BuOH into Δ^5 -cholestene-3:4-dione, m.p. 159° (quinoxaline derivative, m.p. 175°), the constitution of which (cf. Inhoffen, *loc. cit.*) is confirmed by its oxidation to the 7-keto-dicarboxylic acid, $C_{27}H_{42}O_5$, m.p. 215—216°. The possibility of confirming the constitution



of (IV) by its production by bromination of (V) is excluded by Br in AcOH or Et_2O into an $\alpha\beta$ -unsaturated Br_3 -ketone (VI), m.p. 163°, also obtained from (IV) in warm EtOH. Further proof of the structure of (IV) is afforded by its transformation by NaI in boiling abs. EtOH into 4-bromo-6-ethoxy- Δ^4 -cholesten-3-one, m.p. 110—111° (decomp.), and thence by KOAc in boiling BuOH into cholestenedione Et ether. H. W.

Constitution of benzoylformoin. R. SCHOLL (Ber., 1936, 69, [B], 2288; cf. this vol., 606).—The lactol ether formula of benzoylformoin has been advanced previously by Blatt (A., 1935, 982).

H. W.

So-called "valency tautomerism" of unsaturated systems. B. EISTERT (Ber., 1936, 69, [B], 2393—2398).—An explanation of the constitution of tetraphenyldimethylenediphenoquinone, tetraaryldiquinodimethanes, and 4:4'-disubstituted dipyrindyls along the lines of mesomerism is advanced; this harmonises with Müller's magneto-chemical observations.

H. W.

Reduction potential of some naphthaquinones.—See this vol., 1467.

Preparation of fluoroaminoanthraquinone.—See B., 1936, 1083.

Linear pentacene. C. MARSCHALK (Bull. Soc. chim., 1936, [v], 3, 2155—2158; cf. this vol., 1256).—6:13-Dihydroxypentacene-5:14:7:12-diquinone (I) is obtained by cyclisation of 1:4-dihydroxy-2-benzoylanthraquinone-3-carboxylic acid (obtained by condensation of 1:4-dihydroxyanthraquinone-2:3-dicarboxylic anhydride with C_6H_6 and $AlCl_3$), by cautious oxidation of the substance (II) obtained (*loc. cit.*) from o - $C_6H_4(CO)_2O$ and leucoquinizarin, and by oxidation of the Ac derivative of (II) with PbO_2 or CrO_3 in boiling AcOH and hydrolysis of the product. (II) is therefore 5:6:13:14-tetrahydroxypentacene-7:12-quinone. The relationship between (I) and (II) is similar to that between quinone and quinol. Oxidation of (I) or (II) by $Pb(OAc)_4$ in AcOH at 50—60° gives pentacene-5:14:6:13:7:12-triquinone, reduced by N_2H_4 or $Na_2S_2O_4$ to (II), by SO_4 to (II) and then to (I) by KI in cold AcOH to (I). H. W.

Comparison of the rate of racemisation with the rate of enolisation [of *l*-menthyl *d*- α -phenylacetoacetate]. R. H. KIMBALL (J. Amer. Chem. Soc., 1936, 58, 1963—1970; cf. Rupe *et al.*, A., 1913, i, 266, 884).—The pseudo-unimol. velocity coeffs. for (i) the racemisation (of C α) and (ii) the enolisation of *l*-menthyl *d*- α -phenylacetoacetate (I) in cyclohexane (in which enolisation is 71% complete at

equilibrium containing 8—12 p.p.m. of piperidine are determined polarimetrically and by direct Br-titration, respectively; (i) proceeds several times as fast as (ii). Polarimetric determination of the rate for *d*-keto \rightarrow enol gives a val. $>$ that obtained by titration, indicating that enolisation proceeds through an intermediate (II) (which subsequently changes partly to the enol and partly to the *dl*-keto-form). (II) may be the intermediate anion which has lost its asymmetry; alternatively, reversible formation of a little open-chain enol, followed by a slower accumulation of chelated enol, may occur.

(I), prepared from *l*-menthol and $CHPhAc-CO_2Et$ (improved prep.) at 150—160° followed by distillation and slow evaporation of a MeOH-solution of the resulting oil, has m.p. 77—78.3° (in Pyrex glass) (lit. 69°), $[\alpha]_D^{25}$ (in cyclohexane) $-15.84^\circ \rightarrow -59.83^\circ$, $[\alpha]_{D401}^{25} + 21.9^\circ$ in MeOH (cf. *loc. cit.*). Equilibration of (I) with a trace of $Ba(OH)_2$ and subsequent slow distillation (Hickman mol. still) at 85—95° gives a product (64% enol), which on repeated fractionation in absence of catalyst affords a const.-boiling mixture containing 93.8% of enol. The pure enol (*i.e.*, menthyl β -hydroxy- α -phenylcrotonate) is calc. to have $[\alpha]_D^{25} -56.5^\circ$ in cyclohexane. H. B.

[True constitution of camphenilyl and 4-methylcamphenilyl chloride.] P. LIPP and J. DANIELS (Ber., 1936, 69, [B], 2251—2252).—Difficulties in conception of the structure of camphenilyl chloride are removed by considering that it, α - and β -fenchocamphoryl chloride are to one another in the relationship of an equilibrium isomerism (cf. Komppa *et al.*, this vol., 1258). H. W.

Benzylidenecamphane, a product of the dehydration of tertiary benzylbornyl alcohol. S. S. NAMETKIN and M. K. STRUGAZKI (Ber., 1936, 69, [B], 2272—2277).—The main product of the dehydration of benzylbornyl alcohol by $KHSO_4$, aq. and anhyd. $H_2C_2O_4$, HCO_2H , 50% H_2SO_4 , or anhyd. $CuSO_4$ is the cryst. hydrocarbon, m.p. 25°, which, contrary to Haller and Bauer (A., 1906, i, 440), is identified as *benzylidenecamphane*,

$C_8H_{14} \begin{matrix} \leftarrow CH_2 \\ C:CHPh \end{matrix}$, since it is oxidised by $KMnO_4$ to camphor, camphoric acid, and BzOH. It is indifferent towards AcOH and CCl_3CO_2H . It is obtained synthetically from *phenylbornylcarbinol*, b.p. 169—170°/15 mm. (prep. from Mg bornyl chloride and PhCHO), which is treated with K in dry PhMe followed successively by CS_2 and MeI and decomp. of the ester so produced. H. W.

Stereoisomerism in the fenchol series. H. SCHMIDT and L. SCHULZ (Ber. Schimmel, 1935, 97—99; Chem. Zentr., 1936, i, 350—351).—As in the borneol series there are two stereoisomeric optically inactive fenchyl alcohols which, on oxidation, give rise to only one *dl*-fenchone. Hydrogenation (Ni) of *dl*-fenchone yields *dl*- β -fenchyl alcohol, b.p. 200.5°/750 mm., f.p. 6.3° (*formate*; *acetate*; *phenylurethane*, m.p. 90—90.5°; *H phthalate*, m.p. 153—153.5°). *dl*- α -Fenchyl alcohol, prepared by reduction of *dl*-fenchone with Na-EtOH, has m.p. 38°, b.p. 199.5°/750 mm. (*phenylurethane*, m.p. 104°; *H phthalate*, m.p. 169°). The following are obtained

similarly: *l*- α -fenchyl alcohol (from *d*-fenchone), m.p. 48°, $[\alpha]_D^{20}$ -11° in EtOH; *d*- α -fenchyl alcohol (from *l*-fenchone), m.p. 47°, $[\alpha]_D^{20}$ +11.5° in EtOH (*phenylurethane*, m.p. 81°; *H phthalate*, m.p. 145.5°); *l*- β -fenchyl alcohol (from *d*-fenchone), m.p. 5–6°, b.p. 200.5°/750 mm., $[\alpha]_D^{20}$ -21.7° in EtOH (*phenylurethane*, m.p. 89–90°); *d*- β -fenchyl alcohol (from *l*-fenchone), $[\alpha]_D^{20}$ +21.8° in EtOH (*phenylurethane*, m.p. 89°; *H phthalate*, m.p. 151°). By analogy with borneol, α -fenchyl alcohol is assigned the *exo*- and β -fenchyl alcohol the *endo*-configuration.

H. N. R.

Degradation of fenchone in the animal organism. F. REINARTZ and W. ZANKE (Ber., 1936, 69, [B], 2259–2262).—*d*-Fenchone is administered to dogs and the paired glycuronic acid is separated from the urine as the Pb salt, which is treated with 15% H₂SO₄; the filtrate from the PbSO₄ is boiled with H₂O, thereby giving a mixture (I) of hydroxyfenchones which could not be separated into its components by crystallisation or through the *p*-nitrobenzoates. (I) is therefore oxidised with CrO₃ followed by KMnO₄, thus giving 5-ketofenchone, m.p. 36°, Rimini's 4-hydroxyfenchone, m.p. 79–80° (3:5-dinitrobenzoate, m.p. 144–146.5°), and π -apofenchone-3-carboxylic acid, m.p. 120.5–122° (*Ag* salt), decarboxylated to fenchosantenone. 5-Ketofenchonedisemicarbazone has m.p. 243.5°.

H. W.

β -Myrcene. Reduction with sodium and alcohol. G. DUPONT and V. DESREUX (Compt. rend., 1936, 203, 623–625).— β -Myrcene, b.p. 72–73°/25 mm., free from α -myrcene, with Na in EtOH affords a H₂-derivative (I), b.p. 62–63°/18–20 mm. (cf. A., 1901, i, 732), apparently identical with a reduction product (II) of β -geraniol. The Raman spectrum of (I) exhibits a line of frequency 1648 cm.⁻¹, not shown by (II), probably due to a terminal double linking. It is probable that reduction at the linking outside the conjugated system in β -myrcene is a less marked subsidiary reaction and may account for the marked differences in the physical consts. of (I) and (II) (cf. A., 1929, 538).

J. L. D.

Polyterpenes and polyterpenoids. CVII. Transformation of gypsogenin (alsapogenin) into oleanolic acid. L. RUZICKA and G. GIACOMELLO (Helv. Chim. Acta, 1936, 19, 1136–1140).—Fractional crystallisation of crude gypsogenin gives a product, m.p. about 270°, which does not appear homogeneous under the fluorescence microscope and gives analytical data in harmony with a C₃₀ formula. It is converted by boiling Ac₂O and NaOAc into a more freely sol. acetate (I), C₃₂H₄₈O₅, m.p. 176–177°, $[\alpha]_D^{20}$ +78° in CHCl₃, and a more sparingly sol. acetate, C₃₂H₄₈O₅, m.p. 262°, $[\alpha]_D^{20}$ +65° in CHCl₃, (I) gives a yellow colour with C(NO₂)₄, is converted by CH₂N₂ in Et₂O into the *Me* ester, C₃₃H₅₀O₅, m.p. 186°, and by Br in MeOH-CCl₄ into the *Br*-lactone, C₃₂H₄₇O₅Br, m.p. 180–181° (decomp.). The semicarbazone, m.p. (indef.) 140–160° and m.p. 274° (decomp.) after re-solidification, is transformed by NaOEt in EtOH at 160–170° into oleanolic acid, m.p. 304–306°, $[\alpha]_D^{20}$ +76.9° in CHCl₃.

H. W.

Helénalin. I. Helénalin, the bitter sternutative substance occurring in *Helenium autumnale*.

E. P. CLARK (J. Amer. Chem. Soc., 1936, 58, 1982–1983).—Details are given for the isolation of *helenalin*, C₁₅H₁₈O₄, m.p. 167°, $[\alpha]_D^{20}$ -101.9° in 95% EtOH (*Ac*, m.p. 184°, and *methoxyacetyl*, m.p. 135°, derivatives; *dibromide*, m.p. 161°), which is reduced (H₂, PtO₂, EtOAc) to *tetrahydrohelenalin*, m.p. 176° (*Ac* derivative, m.p. 145°).

H. B.

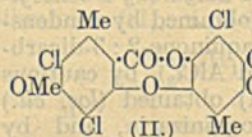
Constituents of pyrethrum flowers. IV. Semicarbazones of pyrethrins I and II and of pyrethrolone. H. L. HALLER and F. B. LAForge (J. Org. Chem., 1936, 1, 38–51; cf. A., 1935, 1550).—Pyrethrin I concentrate (45% of I and 14% of II) gives, best in C₅H₅N, the nearly pure I-semicarbazone, m.p. about 118° (in CCl₄ gives a new compound), which affords by hydrolysis with aq. H₂C₂O₄ about 30% of pyrethrin I, partly changed by distillation at 175–180°/2 mm. A pyrethrin II concentrate (81% of II) gives, best in C₅H₅N, the II-semicarbazone, m.p. 164–165°, hydrolysed by aq. H₂C₂O₄ to free II (30% yield), which is highly toxic to flies and decomposes when distilled in a vac., giving thereafter a poor yield of a different semicarbazone. Pyrethrolonesemicarbazone (*A*), C₁₂H₁₇O₂N₃ (lit. H₁₉), m.p. 208° (decomp.), is obtained from pyrethrolone (*B*) or the I- or II-semicarbazones and NaOMe. The II-semicarbazone with H₂-PtO₂ in EtOAc gives a *tetrahydro-semicarbazone*, C₂₃H₃₅₍₃₇₎O₅N₃, m.p. 141–142° (also obtained by hydrogenation of free II), which with NaOMe affords tetrahydropyrethrolone-semicarbazone, C₁₂H₂₁O₂N₃, m.p. 196° (decomp.), also obtained by hydrogenation (4 H absorbed) of (*A*). The formula of (*B*) thus is revised. Chrysanthemum acid is best characterised by its *p*-phenylphenacyl, m.p. 65°, chrysanthemumdicarboxylic acid by its *di*-*p*-phenylphenacyl ester, m.p. 154°.

R. S. C.

Constituents of lichens found in Ireland. *Buellia canescens*. II. P. A. SPILLANE, J. KEANE, and T. J. NOLAN (Sci. Proc. Roy. Dublin Soc., 1936, 21, 333–343; cf. A., 1935, 133).—A compound, C₁₅H₈O₅Cl₃·OMe, m.p. 257°, is isolated in small amount from *B. canescens* (I). The ratio of chlorinated to unchlorinated atranorin varies in different lichens, being 9:1 in (I), 4:1 in *Lecanora gangaleoides*, and 35:65 in *L. sordida*. The difficulty of determining OMe in lichen products is confirmed. Diploicin (II), OH·C₁₅H₆O₃Cl₄·OMe (*K* salt), with CH₂N₂ gives an ether, C₁₅H₆O₃Cl₄(OMe)₂, m.p. 220°, which with KOH-MeOH gives the phenolic ester, OH·C₁₄H₆OCl₄(OMe)₂·CO₂Me, m.p. 143°, sol. in 2% aq. KOH. With KOH-MeOH (II) affords the phenolic ester, OMe·C₁₄H₆OCl₄(OH)₂·CO₂Me, m.p. 200°, which with CH₂N₂ gives the ether, C₁₄H₆OCl₄(OMe)₃·CO₂Me, m.p. 97°, hydrolysed by 15% KOH-MeOH to the acid, C₁₄H₆OCl₄(OMe)₃·CO₂H, m.p. 160–161°. (II) is probably as annexed.

R. S. C.

Yellow pigment from Saké-Kasu (saké grains). T. HIGASI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 1060–1076).—*Flazine* (I), C₁₈H₁₆O₅N₂, m.p. 218–220° (decomp.) [*hydrochloride*, +H₂O; *hydr-*



iodide, unstable; (?) NO_2 -derivative, $C_{17}H_{13}O_5N_2 \cdot NO_2 + H_2O$, is isolated in 0.001% yield from saké grains. In EtOH, $COMe_2$, or acid it shows a strong yellow-green fluorescence, destroyed by alkali. (I) resinifies in air and resembles lactoflavin, but has less vitamin- B_2 activity. Absorption spectra, reduction potential, and fluorescence indicate phenazine structure. On oxidation (I) gives a *substance*, $C_{17}H_{12}O_5N_2$, and on dehydration a *substance*, $C_{36}H_{30}O_9N_4$. R. F. P.

Hydrogenation value of violaxanthin. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1936, 19, 1024—1025).—Hydrogenation of purified violaxanthin in AcOH or EtOH—AcOH causes absorption of 9.5—10 H_2 . It therefore contains 10 rather than 11 double linkings. This harmonises with spectroscopic evidence which is compatible with the presence of 11 double linkings only if two ethylenic linkings are assumed to be outside conjugation. H. W.

Bitter principles of Colombo root. IV. **Hydrogenation of columbin and isocolumbin.** F. WESSELY, A. MÜNSTER, and K. SCHÖNOL [with, in part, W. ISEMAN] (Monatsh., 1936, 68, 313—325; cf. this vol., 610, 995).—Columbin (I) (improved isolation), $[\alpha]_D +52.2^\circ$, is $C_{10}H_{22}O_6$; decarboxycolumbin (II), $C_{19}H_{22}O_4$, has m.p. 148—149°. Hydrogenation (Pd-sponge in MeOH) of (I) gives a product in which the second group of (I) which reacts with hot alkali is not present. Reaction is not accompanied by loss of CO_2 , and gives mainly a mixture of stereoisomeric octahydrocolumbic acids (III) which could not be obtained *cryst.*, but from which after treatment with CH_2N_2 a *cryst. Me ester*, m.p. 124—131°, $[\alpha]_D -18.7^\circ$, is isolated and a neutral *product*, $C_{20}H_{28}O_6$, probably a mixture of saturated lactones. The view that 2 O of the 6 O of (I) are present in a normal lactone ring containing at least one double linking is confirmed, but the hypothetical presence of a second lactone ring is discarded, particularly in view of the behaviour of (III) towards Zerevitinov's reagent. Hydrogenation of (II) gives a mixture of stereoisomeric octahydrodecaboxycolumbic acids. Hydrogenation establishes that (I) contains three double linkings, whereas in (III) 2 O and O are present in CO_2H and OH, respectively, and the function of the remaining 3 O is unknown. *isoColumbin* is hydrogenated to a non-*cryst.* mixture of stereoisomeric acids from which a non-homogeneous, *cryst. Me ester* is isolated which contains 1 OH (Zerevitinov). H. W.

Reaction of lignin and vanillin. P. FOURMENT and H. ROQUES (Bull. Sci. pharmacol., 1935, 42, 449—451; Chem. Zentr., 1936, i, 601).—Vanillin, in addition to plant tissues containing lignin, gives a red coloration with benzidine in AcOH solution. H. N. R.

Lignin. VIII. **Thioglycollic acid as a reagent for lignin.** B. HOLMBERG (Ing. Vet. Akad. Handl. No. 131, 81 pp.); Chem. Zentr., 1936, i, 93—94).—In presence of acid lignin combines with thioglycollic to give a sparingly sol. compound. Application of this reaction to a no. of plant species is described. A. G. P.

Hydroxyfurans. II. **3-Hydroxy-2:5-diphenylfuran.** E. P. KOHLER and D. W. WOODWARD (J. Amer. Chem. Soc., 1936, 58, 1933—1936).—Successive treatment of 3-acetoxy-2:5-diphenylfuran (I) (Lutz, A., 1927, 61) with $MgMeI$ and cold dil. H_2SO_4 gives 3-hydroxy-2:5-diphenylfuran (II) (not isolable), which resembles the 2:4:5- Ph_3 derivative (this vol., 479). (II) (in Et_2O) and O_2 afford the 2:3-*peroxide*, explodes about 100° , which is reduced by AcOH—KI to 3:3'-*diketo*-2:5:2':5'-*tetraphenyl*-2:3:2':3'-*tetrahydro*-2:2'-*difuryl*, m.p. 255° , and catalytically to $\alpha\beta\delta$ -*triketo*- $\alpha\delta$ -*diphenylbutane* (Lutz *et al.*, A., 1934, 1222). Hydrolysis (dil. H_2SO_4 in AcOH and N_2) of (I) gives the unstable 3-*keto*-2:5-*diphenyl*-2:3-*dihydrofuran*, m.p. 93° , *i.e.*, the ketonic form of (II). (I) and Cl_2 or PCl_5 afford 2-*chloro*-3-*keto*-2:5-*diphenyl*-2:3-*dihydrofuran* (III), m.p. 133° (the 2-*Br*-derivative has m.p. 135°), converted by boiling MeOH and EtOH into the 2-*OMe*- and 2-*OEt*-derivatives [cf. Lutz *et al.* (*loc. cit.*), who formulate these as open-chain compounds]. Maleic anhydride, PhBr, and $AlBr_3$ in $C_2H_2Br_4$ at $<50^\circ$ give β -*p-bromobenzoylacrylic acid*, m.p. 161° , the *chloride*, m.p. 103° , of which with C_6H_6 and $AlCl_3$ in N_2 affords α -*benzoyl*- β -*p-bromobenzoylethylene*, m.p. 127° , also obtained from $COPh \cdot CHO$ and $p-C_6H_4Br \cdot COMe$ in Ac_2O . This and Br in $CHCl_3$ yields *dibromides*, m.p. 116—119° and 170—175° (decomp.), a mixture of which is converted by MeOH—KOH, followed by MeOH—HCl, into 3-*keto*-2-*methoxy*-2-*phenyl*-5-*p-bromophenyl*- (IV), m.p. 158° , and 5-*phenyl*-2-*p-bromophenyl*- (V), m.p. 102° , -2:3-*dihydrofuran*s. (IV) (ozonolysis products, $p-C_6H_4Br \cdot CO_2H$ and MeOBz) is hydrolysed (MeOH—KOH) to $\alpha\beta\delta$ -*triketo*- α -*phenyl*- δ -*p-bromophenylbutane*, m.p. 100—101° [oxidised (30% H_2O_2 , MeOH—KOH) to $p-C_6H_4Br \cdot COMe$, $p-C_6H_4Br \cdot CO_2H$, and BzOH], whilst (V) (ozonolysis products ($p-C_6H_4Br \cdot CO_2Me$ and BzOH) similarly gives $\alpha\beta\delta$ -*triketo*- δ -*phenyl*- α -*p-bromophenylbutane*, m.p. 88—90° (oxidised to $COPhMe$, BzOH, and $p-C_6H_4Br \cdot CO_2H$). The 3:4-*diacetoxy*- and 3-*chloro*-4-*acetoxy*-2:5-*diphenylfurans* of Lutz *et al.* (*loc. cit.*) are 3-*keto*-2-*acetoxy*-2:5-*diphenyl*-2:3-*dihydrofuran*, m.p. 140° , and (III), respectively; the α -*chloro*- $\gamma\delta$ -*diketo*- $\alpha\delta$ -*diphenyl*- Δ^2 -*butene* of Lutz and Wilder (A., 1934, 1361) is also (III). H. B.

Hydrazide and azide of 3:4-dihydroxyfuran-2:5-dicarboxylic acid. A. DARAPSKY and M. STAUBER (J. pr. Chem., 1936, [ii], 146, 209—218).—Treatment of Me_2 3:4-dihydroxyfuran-2:5-dicarboxylate (I) with $N_2H_4 \cdot H_2O$ in EtOH gives the *dihydrazine salt*, $C_8H_8O_7 \cdot N_2H_4$, m.p. (indef.) 168° (decomp.). With boiling $N_2H_4 \cdot H_2O$ (I) yields the *monohydrazine salt*, decomp. $>200^\circ$, of 3:4-*dihydroxyfuran*-2:5-*dicarbonyldihydrazide*, m.p. $>260^\circ$ after darkening at 200° [*dihydrochloride*, blackens at 260° after becoming discoloured at 170 — 220° ; *dipicrate*, gradual decomp. at about 205° after becoming brown at 180° ; *dibenzylidene*, m.p. 258° (decomp.), *di-o-hydroxybenzylidene*, m.p. $>270^\circ$, *dicinnamylidene*, m.p. 240° (decomp.), and *düsopropylidene*, blackens at 260° after darkening at 170 — 220° , derivatives]. 3:4-*Dihydroxyfuran*-2:5-*dicarbonylazide* (II), explodes at 148 — 149° , is transformed by NH_2Ph in

boiling Et₂O into the salt, C₆H₂O₅N₆NH₂Ph, and by NH₂Ph at 150° into the dianilide, m.p. >260°. The azide is converted by boiling EtOH into 3:4-dihydroxyfuran-2:5-diurethane, m.p. 147, which could not be transformed by heat into the desired dilactone

$\text{CO} \begin{array}{c} \diagup \text{O} \text{---} \text{C} \text{---} \text{C} \text{---} \text{O} \diagdown \\ \text{NH} \text{---} \text{C} \text{---} \text{O} \text{---} \text{C} \text{---} \text{NH} \end{array} \text{CO}$. When warmed in indifferent media (II) evolves N₂ and yields a solid tile-red compound which could not be purified; analyses indicate the presence of the dicarbimide but the material is odourless and does not react with EtOH so that possibly (III) is present. Attempts to hydrogenate (I) by H₂-colloidal Pd, Na-Hg, Al-Hg, or Na in boiling EtOH were unsuccessful. H. W.

Electrolysis of aromatic acids. II. Electrolysis of opianic acid. V. M. RODIONOV and V. C. ZVORYKINA (Bull. Soc. chim., 1936, [v], 3, 1836—1841; cf. this vol., 722).—Electrolysis of K opianate yields meconine, a mixture of dimeconyls, m.p. 215—230°, and resins. In a cell with diaphragm the reduction products are obtained in the cathodic division in better yield; opianic acid under the same conditions gives less impure products, without resins. Reduction by Na-Hg gives meconine and a trace of α-dimeconyl. Mixed dimeconyls electrolysed, or reduced by Na-Hg, give a substance, m.p. 170—172°. E. W. W.

Synthesis of dehydracetic acid from ethyl acetoacetate. F. ARNDT, B. EISTERT, H. SCHOLZ, and E. ARON (Ber., 1936, 59, [B], 2373—2380).—Irregularities in the conversion of CH₂Ac·CO₂Et into dehydracetic acid (I) (Arndt *et al.*, A., 1924, i, 1223) are traced to the influence of the containing vessel. The initial stage is the formation of EtOH and CO₂Et·CH:CMe·O·CO·CH₂Ac the progress of which depends on the continuous removal of EtOH [very little (I) is produced when CH₂Ac·CO₂Et is heated (sealed) at < its b.p.]; this is followed by an irreversible Claisen condensation for which the presence of alkali is required. This is provided uncertainly by the alkali of the glass, and is best supplied by NaHCO₃ in controlled amount, since the decomp. of CH₂Ac·CO₂Et into COMe₂ is also accelerated thereby. The best yields are obtained with minute amounts of catalyst if the process is interrupted when about 25% of the possible EtOH has distilled; unchanged ester is distilled from the product and worked up as a fresh charge. At 300—600° the streaming vapours of CH₂Ac·CO₂Et are remarkably stable in presence of SiO₂, Al, Cu, or V2A steel. Fe accelerates decomp. into COMe₂, CO₂, gaseous and resinous products. In absence of Fe, glass or porcelain, preferably in tubes of the same material, gives good yields of pure (I) if the temp. is >400°. The operation may be extended over long periods and 25% conversion is secured. The process appears generally applicable for the production of "dehydroacids" from β-CO-esters. Thus CH₂Bz·CO₂Et gives dehydrobenzoylacetic acid, CPh<math display="block">\begin{array}{c} \text{CH} \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{array} \text{CHAc}, m.p. 171°, converted by H₂SO₄ at 138—140° into BzOH and 6-phenylpyronone, decomp. 245—246°, which with

NH₃-H₂O at 120° affords 2:4-dihydroxy-6-phenylpyridine, decomp. 315—318°. An improved prep. of 2:6-dimethylpyrone from (I) is described. Short treatment of (I) with 90% H₂SO₄ at 135° gives 6-methylpyronone or 6-methyl-4-hydroxy-2-pyrone (II), converted by NH₂Me-H₂O at 130° into 4-hydroxy-1:6-dimethyl-2-pyridone, decomp. 225—226°; 4-hydroxy-6-methyl-1-ethyl-2-pyridone, decomp. 198°, is obtained with NH₂Et. 4-Hydroxy-1-cyclohexyl-6-methyl-2-pyridone has m.p. 108°. (II), boiling 10N-NaOH, and *p*-NMe₂·C₆H₄·NH₂·H₂SO₄ yield 4-hydroxy-1-*p*-dimethylaminophenyl-6-methyl-2-pyridone, decomp. 270—275°, whereas NH₂Ph yields a substance, m.p. 199—200°, of undetermined structure. H. W.

Geometrical inversion in the acids derived from the coumarins. III. Trans- to cis-. T. R. SESHADRI and P. S. RAO (Proc. Indian Acad. Sci., 1936, 4, A, 157—161; cf. A., 1935, 211).—HgO lowers the temp. of decomp. of coumaric (I), 4-methyl (II) and 5-nitro-coumaric acid (III) to give the coumarin in >50% yield. Similarly, with HgCl₂ coumarins are formed in excellent yield; in each case the coumarin mercurichloride is isolated. (I) and (II) with conc. H₂SO₄ at 100° give poor yields of the coumarin due to sulphonation, whereas (III) gives a 95% yield; boiling EtOH containing dry HCl decarboxylates (I) and (II) and esterifies (III). J. L. D.

Reactivity of the double linking in coumarins and related αβ-unsaturated carbonyl compounds. II. Action of mercury salts on coumarins. T. R. SESHADRI and P. S. RAO (Proc. Indian Acad. Sci., 1936, 4, A, 162—169; cf. A., 1928, 298).—Coumarin with boiling MeOH containing Hg(OAc)₂ in excess affords 3:6:8-triacetoxymercuri-4-methoxymelilotic anhydride, converted by H₂S in NaOH into β-methoxymelilotic acid, m.p. 122—123° (cf. A., 1912, i, 461), and with Br in AcOH gives 3:6:8-tribromocoumarin. Similarly, 7-methylcoumarin affords 3:6:8-triacetoxymercuri-4-methoxy-7-methylmelilotic anhydride, decomp. at 265°, converted by H₂S in NaOH into 4-methylcoumaric acid, and with Br in AcOH affords 3:6:8-tribromo-7-methylcoumarin, m.p. 207—208°. 6-Nitrocoumarin similarly yields 3:8-diacetoxymercuri-6-nitro-4-methoxymelilotic anhydride, converted by H₂S in NaOH into 5-nitrocoumaric acid, and by Br in AcOH into 3:8-dibromo-6-nitrocoumarin (cf. J.C.S., 1923, 123, 3380). Coumarin and 7-methylcoumarin with HgCl₂ in COMe₂ afford 3-chloromercuri-4-chloro- (cf. *ibid.*, 1908, 93, 524) and 7-methyl-melilotic anhydride, respectively, decomposed by H₂S in NaOH into coumaric and 4-methylcoumaric acid, respectively. 6-Nitrocoumarin does not react with HgCl₂. J. L. D.

Separation of natural mixtures of anthocyanins by chromatographic adsorption analysis. II. "Althæin." P. KARRER and H. M. WEBER (Helv. Chim. Acta, 1936, 19, 1025—1027; cf. this vol., 341).—Chromatographic analysis, using CaSO₄·2H₂O, shows that althæin (Willstätter *et al.*, A., 1915, i, 287) is a mixture of monoglucosides of delphinidin 3':5'-Me₂ ether (syningidin), delphinidin 3'-Me ether, and delphinidin. H. W.

Pigment of the corn poppy (*Papaver rhæas*, L.). See this vol., 1572.

Anthocyanin pigment of the winesap apple.—See this vol., 1435.

Constituents of the Chinese drug lei-kung-teng.—See this vol., 1572.

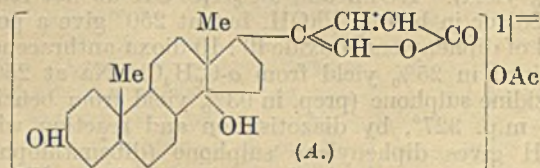
Constitution of cubebin. R. D. HAWORTH and W. KELLY (Chem. and Ind., 1936, 901—902).—The structure $\begin{matrix} \text{CHX}-\text{R} \\ \text{CHX}\cdot\text{CH}_2 \end{matrix} \text{O}$ (X=3:4-CH₂O₂:C₆H₃:CH₂; R=CH·OH) for cubebin (Ishiguro, this vol., 1247) is confirmed by the presence of 1 OH (Zerevitinov), semicarbazone formation, and facile oxidation to cubebinolide (R=CO). J. W. B.

Vegetable heart poisons. XI. Constitution of thevetin. R. TSCHESCHE (Ber., 1936, 69, [B], 2368—2372).—Thevetin (I), gradual decomp. >195°, obtained from be-still nuts (Chen *et al.*, A., 1934, 820) when dried at 100°/10 mm. has the composition C₄₂H₆₆O₁₈·0.5H₂O, which becomes C₄₂H₆₆O₁₈·3H₂O when the product is exposed to air. It is converted by boiling 0.1N-KOH-MeOH into *isothevetin*, C₄₂H₆₆O₁₈·2H₂O, m.p. 236—238°. Complete hydrolysis of (I) is difficult, and energetic treatment with acids causes separation of 2 mols. of glucose originally present as gentiobiose, since the octa-acetate is obtained when (I) is treated with Ac₂O and ZnCl₂ at 70°. A third sugar mol., probably digitalose, is present as a Me ether, but its separation from the aglucone requires so drastic treatment that the mol. is disrupted. Cautious hydrolysis of (I) with 2N-HCl in H₂O-EtOH, hydrogenation of the residue (PtO₂ in AcOH), and renewed hydrolysis of the product leads to tetrahydroanhydrothevetigenin (II), oxidised by CrO₃ to tetrahydroanhydrodigitoxigenone, m.p. 245—248°, [α]_D²⁰ +35.8° in CHCl₃. The identity of (II) with digitoxigenin is excluded by the differing physiological action of (I) and digitoxin (III), and the possibility of isomerisation due to differing position of OH at C₃₀ is confirmed by the ability of thevetigenin (IV) to give an

additive product with (III) from which *anhydrothevetigenin*, C₂₃H₃₂O₃, m.p. 218—220°, [α]_D¹⁸ +40.0° in CHCl₃, is isolated; it is cautiously oxidised to anhydrodigitoxigenone. (IV) is therefore (A). Chen's kokilphin (*loc. cit.*) is identical with sucrose. H. W.

Toad poisons. II. Cino- and marino-bufagin. R. TSCHESCHE and H. A. OFFE (Ber., 1936, 69, [B], 2361—2367; cf. this vol., 81).—In agreement with Crowfoot (A., 1935, 921), but contrary to Kotake (A., 1928, 1138) and Jensen *et al.* (A., 1934, 412), fresh analyses of cinobufagin (I) agree with C₂₆H₃₄O₆. (I) therefore contains three double linkings, confirmed by quant. micro-hydrogenation. In the presence of a large amount of catalyst a slow further absorption of 4 H₂ is observed; this cannot be attributed to saturation of double linkings and is not shown by certain derivatives of (I) or by marino-bufagin (II). The ultra-violet absorption spectrum

of (I) and (II) agrees only with the presence of a conjugation of two C:C linkings with the C:O of the lactone group. The similarity of the absorption spectra of (I), (II), scillaren, and $\text{CO} \begin{matrix} \text{CH:CH} \\ \text{O}-\text{CH} \end{matrix} \text{C}\cdot\text{CO}_2\text{Me}$, the production of a free or latent ·CHO group when (I) is cautiously hydrolysed, and the formation of HCO₂H by ozonolysis of (I) indicate the presence of $\cdot\text{C} \begin{matrix} \text{CH:CH} \\ \text{CH}-\text{O} \end{matrix} \text{CO}$ as found by Wieland *et al.* (this vol., 1252) in bufotalin and the subsidiary poisons. Hydrogenation of cinobufagin monoacetate, m.p. 202°, gives α-, m.p. 238°, and β-, m.p. 250° (decomp.), *hexahydrocinobufagin monoacetate*, which differ probably only by the steric arrangement of a H and are identical with the two perhydrogenated cinobufagin acetates of Kotake (*loc. cit.*). These are cautiously hydrolysed to *α-deacetylhexahydrocinobufagic acid* (III), C₂₄H₃₈O₅·0.5H₂O, m.p. (indef.) 160°, which does not absorb H or give a colour with C(NO₂)₄, and the corresponding β-compound, m.p. (indef.) 180°; the analytical data are complicated by the presence of H₂O of crystallisation which is very firmly retained, and the production of an O₅ acid involves the elimination of H₂O with production of a double linking, the presence of which could not be detected. Cautious oxidation of (III) with CrO₃-AcOH at 0° gives *deacetylhexahydrocinobufagonic acid*, C₂₄H₃₄O₅, m.p. 205°. It is monobasic even in hot solution, and hence contains only the original CO₂H. It affords only a *monosemicarbazone*, decomp. 217°, and hence contains only 1 CO unless another is present at the non-reactive or sluggishly reactive C₍₁₁₎ position



of the cholane skeleton. It has no appreciable absorption in the ultra-violet. (A) appears the most probable structure of (I). H. W.

Mol. wt. of cinobufagin. D. CROWFOOT and H. JENSEN (J. Amer. Chem. Soc., 1936, 58, 2018—2019; cf. A., 1935, 921).—X-Ray crystallographic data for cinobufagin (I), acetylcinobufagin, and cinobufagone indicate that (I) is C₂₆H₃₄O₆; previous analytical data (A., 1934, 412) are in agreement. H. B.

Steric hindrance to the hydrogenation of the ethylenic linking in butadiene sulphones. C. C. BOLT and H. J. BACKER (Rec. trav. chim., 1936, 55, 898—903).—3:4-Ditert.-butyl-2:5-dihydrothiophen 1:1-dioxide (I) resists hydrogenation by H₂-PtO₂, but with H₂-Pd-black in AcOH (1.4 atm.) gives 3:4-ditert.-butyltetrahydrothiophen 1:1-dioxide (II), b.p. 171—171.5°/14 mm., m.p. 76—76.5°. 3:4-Diphenyl-2:5-dihydrothiophen 1:1-dioxide (III) resists hydrogenation at 1 atm., but at 1.4 atm. (PtO₂) gives 3:4-dicyclohexyltetrahydrothiophen 1:1-dioxide (IV), b.p. 210—212°/12 mm., m.p. 143—143.5°, whilst cessation of the reaction after absorption of 1 or 4 H₂ gives mixtures. However, 2:3-4:5-

ditetramethylene-2:5-dihydrothiophen 1:1-dioxide (V) (from di- Δ^1 -cyclohexenyl and SO_2), m.p. 77.5—78°, with H_2 -Pt-black, $-\text{PtO}_2$, or $-\text{Pd}$ -black at 1 atm. gives 2:3-4:5-*ditetramethylenetetrahydrothiophen 1:1-dioxide* (VI), m.p. 85.5—86°, b.p. 173—175°/6 mm. The H_2 -compounds readily lose SO_2 to regenerate the butadiene, decomp. temp. being (I) 116—118°, (III) 188—190°, and (V) 115°. The H_4 -compounds decompose only at the b.p./760 mm., namely, (II) 270—275°, (IV) 350—360°, and (VI) 310°, but with KMnO_4 or CrO_3 at 50° give 1 mol. of H_2SO_4 . R. S. C.

Substitution derivatives of diphenylene sulphide and diphenylene sulphone. N. M. CULLINANE, C. G. DAVIES, and G. I. DAVIES (J.C.S., 1936, 1435—1437).—Nitration (HNO_3 -AcOH) of diphenylene sulphide (I) gives the 3- NO_2 -derivative, m.p. 186°, also obtained by reduction and deamination of 2:4-dinitrophenyl sulphide. The NO_2 -compound on reduction, followed by CuBr, forms 3-*bromodiphenylene sulphide*, m.p. 127°, obtained by bromination of (I). Nitration (HNO_3 - H_2SO_4) of diphenylene sulphone (II) affords the 2:7-(NO_2)-derivative, m.p. 290° (slight decomp.), reduced (Fe) to the 2:7-(NH_2)₂, which yields the 2:7- Br_2 -compound, m.p. 312°, also derived by bromination of (II). 3-Nitrodiphenylene sulphide is oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$) to the sulphone. F. R. S.

Synthesis of heterocyclic compounds. N. M. CULLINANE and (in part) C. G. DAVIES (Rec. trav. chim., 1936, 55, 881—886).—Dibenzfuran is obtained when 2:2'-dihydroxydiphenyl is boiled for 50 hr. (90% yield) or heated with P_2O_5 at 300° for 26 hr. (95% yield). KOPh and $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OK}$ do not react at 120° or in boiling PhOH, but at 250° give a poor yield of diphenylene dioxide (9:10-dioxanthracene), obtained in 25% yield from $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{ONa}$ at 250°. Benzidine sulphone (prep. in 93% yield from benzidine), m.p. 327°, by diazotisation and reaction with EtOH gives diphenylene sulphone (dibenzthiophen 1:1-dioxide), m.p. 235°, converted into dibenzthiophen, m.p. 99°, by S at 350°. PhSH, $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, and KOH at 190—195° give Ph *o*-nitrophenyl sulphide, m.p. 82° (cf. lit.; 85% yield), reduced by Fe- FeCl_3 (trace)- H_2O to Ph 2-aminophenyl sulphide, m.p. 35°, the diazonium compound from which with Na xanthate or $\text{K}_3\text{Cr}(\text{SCN})_6$ gives thianthren. R. S. C.

Oxidation of thianthren and its oxides by peracetic acid. J. BÖESEKEN and (MLLE.) A. T. H. VAN DER MEULEN (Rec. trav. chim., 1936, 55, 925—934).—*E* and *B* in the equation, $\log K = B - E / 2 \cdot 303RT$, for oxidation by AcO_2H are for thianthren (I) 16,750 and 8.9, its monosulphoxide 14,200 and 5.3, *trans*- 15,100 and 5.1, and *cis*-disulphoxide 13,600 and 3.5, respectively. The prep. of (I) (66.5% yield) is modified. The monosulphone could not be obtained by Fries and Vogt's method (A., 1911, i, 555) or modifications thereof. (I) has a dipole moment, but gives only two dioxides and one monosulphoxide; thus the two forms are labile. The rate of oxidation of S in (I) is decreased when the other S becomes SO. R. S. C.

Indigoid dyes. IX. Absorption spectra of isomeric thioindigoid dyes. P. C. DUTTA (Ber.,

1936, 69, [B], 2343—2346; cf. A., 1935, 1249).—Measurement of the absorption spectrum of 36 dyes of this series in PhNO_2 confirms the conclusions reached previously (*loc. cit.*). H. W.

Action of ammonia and amines on aryl chlorosulphates and the *N*-chlorosulphonylsulphonamides. L. DENEVILLE (Bull. Soc. chim., 1936, [v], 3, 2143—2152).—Aryl chlorosulphates behave as chlorosulphonating agents towards NH_3 , primary and *sec.* aliphatic and heterocyclic amines, giving *N*-chlorosulphonyl derivatives which, if sufficiently stable, give aminosulphonamides with excess of the amine. Under the same conditions, primary and *sec.* aromatic amines do not yield the corresponding amidosulphonamides; at a higher temp. they suffer oxidation. *tert.*-Aromatic amines give additive products at room temp. *N*-Chlorosulphonylsulphonamides resemble aryl chlorosulphates in their behaviour towards amines. PhSO_3Cl , $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{SO}_3\text{Cl}$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Cl}$, and *o*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Cl}$ behave similarly except with regard to rate of reaction. Gradual addition of PhSO_3Cl to piperidine (I) in C_6H_6 at room temp. affords PhOH, piperidine hydrochloride, and di-1:1'-piperidyl sulphone, m.p. 92°. (I) and SO_2Cl_2 in PhMe at 0° give 1-*chlorosulphonylpiperidine* (II), b.p. 120°/14 mm., which is completely decomposed at about 150° and converted by a suspension of NaOph in boiling C_6H_6 into *Ph sulphonpiperidamate*, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{SO}_3\text{Ph}$, m.p. 59—60°. (II) is also formed when (I) is added gradually to PhSO_3Cl in PhMe at 0°. PhSO_3Cl and NH_2Et_2 (3 mols.) yield *sulphtetraethylamide*, $\text{SO}_2(\text{NEt}_2)_2$, b.p. 101—102°/1 mm., or *chlorosulphondiethylamide*, b.p. 209°/atm. pressure, if the ester is in excess. NH_2Me gives $\text{SO}_2(\text{NHMe})_2$, m.p. 78°, and *sulphdibenzylidamide*, m.p. 181—182°, is derived from $\text{CH}_2\text{Ph}\cdot\text{NH}_2$. PhSO_3Cl and NH_3 react: $\text{PhSO}_3\text{Cl} + \text{NH}_3 \rightarrow \text{PhOH} + \text{NH}_2\cdot\text{SO}_2\text{Cl}$ (III) and $3(\text{III}) \rightarrow (\text{SO}_2\cdot\text{NH})_3 + 3\text{HCl}$. PhSO_3Cl oxidises NH_2Ph and NHPhMe with evolution of SO_2 ; with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ diaminophenazine is produced. NPhMe_2 and PhSO_3Cl in cold C_6H_6 yield the non-cryst. compound, $\text{C}_6\text{H}_5\text{O}_3\text{S}\cdot\text{Cl}\cdot\text{C}_8\text{H}_{11}\text{N}$. H. W.

4-Keto-3:5-dialkylpiperidines. C. MANNICH and P. SCHUMANN (Ber., 1936, 69, [B], 2299—2305).—4-Keto-3:5-dialkylpiperidines are obtained by condensing $\alpha\alpha'$ -dialkylacetonedicarboxylic esters with NH_2Me and CH_2O (which cannot be replaced by other aldehydes) at room temp. followed by hydrolysis of the esters so produced and decarboxylation of the acids. Thus Et_2 diethylacetonedicarboxylate, NH_2Me , and 35% CH_2O in EtOH- H_2O afford *Et*₂ 4-keto-1-methyl-3:5(*cis*)-diethylpiperidine-3:5-dicarboxylate (I), b.p. 176°/13 mm. (*perchlorate*, m.p. 166°; *hydrochloride*, m.p. 147°; *picrate*, m.p. 143°; *methiodide*, decomp. 164—165°). (I) is converted by boiling 25% HCl into 4-keto-1-methyl-3:5(*cis*)-diethylpiperidine, b.p. 93°/11 mm. [*hydrobromide* (II), m.p. 168—169°; *hydrochloride*, m.p. 133—135°; *methiodide*, m.p. 254° (decomp.); *oxime*, m.p. 196°]. (II) is reduced by Na-Hg in dil. AcOH to 4-hydroxy-1-methyl-*cis*-3:5-diethylpiperidine, $\alpha(\psi)$ -form (III), m.p. 99° (*hydrochloride*, m.p. 188—189° after softening; *perchlorate*, m.p. 154—156°; *methiodide*, m.p.

251—252.5°; benzoate and its methiodide, m.p. 220° after softening at 210°, and β -variety, b.p. 118—122°/13 mm. (methiodide, m.p. 250—251°; benzoate and its methiodide, m.p. about 260°). (III) is not isomerised by 10% NaOEt at 175°. Et_2 4-keto-1-methyl-cis-3:5-diallylpiperidine-3:5-dicarboxylate, b.p. 183—184°/11 mm. (hydrochloride, m.p. 131°), is converted by HBr in AcOH at room temp. into Et_2 4-keto-1-methyl-3:5-di- β -bromopropylpiperidine-3:5-dicarboxylate (hydrobromide, m.p. 160° when slowly heated), and reduced (PtO₂ in EtOH) to Et_2 4-keto-1-methyl-cis-3:5-dipropylpiperidine-3:5-dicarboxylate, b.p. 185—186°/12 mm. [hydrochloride (III), m.p. 138°]. (III) is hydrolysed and decarboxylated by boiling 25% HCl to 4-keto-1-methyl-cis-3:5-dipropylpiperidine (IV), b.p. 120°/11 mm. (*H* tartrate, m.p. 81—82°; oxime, m.p. 93—94°, and its hydrochloride, decomp. 225°), the methiodide, m.p. 165—166° after darkening when rapidly heated, of which is transformed by hot 15% KOH followed by MeI into the methiodide (V), CH₂:CPr^a:CO·CHPr^a:CH₂:NMe₃I, m.p. 148° after softening at 145—147°. Treatment of (V) with KOH affords α' -dipropyldivinyl ketone, b.p. 84—85°/12 mm., hydrogenated (PtO₂ in MeOH) to α' -dimethyl-dibutyl ketone, b.p. 86°/13 mm. (IV) is reduced to 4-hydroxy-1-methyl-cis-3:5-dipropylpiperidine, α (ψ)-form, m.p. 112—113° (perchlorate, m.p. 113—115°; nitrate, m.p. 137—138°; sulphate, m.p. 170—171°; non-cryst. benzoate and its hydrochloride, m.p. 109—111°, picrate, m.p. 190—193°, and methiodide, m.p. 270—272°), and β -variety, m.p. 63—65° (methiodide, m.p. 225—227°; benzoate and its picrate, m.p. 205—209°, and methiodide, m.p. about 295°). Na amyloxyde in boiling NH₂Ph isomerises the β - to the α -form, but is without action on the latter. H. W.

Tricyclic oxetone derivatives. C. MANNICH and P. SCHUMANN (Ber., 1936, 69, [B], 2306—2310).—Treatment of Et_2 4-keto-1-methyl-3:5-diallylpiperidine-3:5-dicarboxylate hydrochloride with boiling 25% HCl gives 1:5':5''-trimethyl-3':2'-3:4-2'':3''-4:5-ditetrahydrofuranopiperidine (I), b.p. 113°/11 mm. $\begin{matrix} CHMe-CH_2 \\ O \\ \diagdown \\ C \\ \diagup \\ CHMe-CH_2 \end{matrix} \begin{matrix} CH_2-CH_2 \\ | \\ CH-CH_2 \\ | \\ CH-CH_2 \end{matrix} NMe$ (I). [hydrochloride, m.p. 220—221°; methiodide (II), m.p. 238°], which does not contain CO or active H (Zerevitinov) and does not add Br or H. The base obtained from (II) and Ag₂O passes when heated into $\beta\epsilon$ - $\epsilon\theta$ -dioxido- δ -dimethylaminomethyl- ζ -methylenenonane, $\begin{matrix} CH_2-CHMe-O \\ | \\ CH(CH_2\cdot NMe_2) \end{matrix} \begin{matrix} O \\ | \\ C \\ | \\ C(CH_2)\cdot CH_2 \end{matrix}$, b.p. 115°/11 mm. (hygroscopic hydrochloride; picrate, m.p. 147°), the methiodide (II), m.p. 207—208°, of which is hydrogenated (PtO₂) to $\beta\epsilon$ - $\epsilon\theta$ -dioxido- ζ -methyl- δ -dimethylaminomethylnonane methiodide (III), m.p. 195—197°. (III) is degraded to NMe₃ and $\beta\epsilon$ - $\epsilon\theta$ -dioxido- $\delta\zeta$ -dimethylenenonane (IV), b.p. 86—87°/13 mm., whilst (III) yields $\beta\epsilon$ - $\epsilon\theta$ -dioxido- ζ -methyl- δ -methylenenonane (V), b.p. 84—88°/13 mm.; hydrogenation of (IV) or (V) (PtO₂ in MeOH) leads to $\beta\epsilon$ - $\epsilon\theta$ -dioxido- $\delta\zeta$ -dimethylnonane, b.p. 88—92°/13 mm. (I) is transformed by HBr·AcOH at 75° into the non-cryst., unstable 4-keto-1-methyl-cis-3:5-di- β -bromopropylpiperidine [hydrobromide (VI), m.p. 164—165° (decomp.)], quantitatively reconverted into (I) by

H₂O at 100°]. (VI) is reduced (PtO₂ in EtOH) to 4-hydroxy-1-methyl-cis-3:5-di- β -bromopropylpiperidine, m.p. 125—126°. 2:6-Diallylcyclohexanone is converted by HBr·AcOH at room temp. into the unstable 2:6-di- β -bromopropylcyclohexanone, m.p. 94—95°, transformed by boiling H₂O containing KHCO₃ into 5':5''-dimethyl-3':2'-2'':3''-dietetrahydrofuranol:2-2:3-cyclohexane, b.p. 115—117°/14 mm.

H. W.

2-Aminopyridine series. IV. Reactivity of the methyl group in 6-amino-2-picoline. K. FEIST, W. AWE, and M. KUKLINSKI. V. Reactivity of the amino-group in 6-amino-2-picoline. K. FEIST and M. KUKLINSKI (Arch. Pharm., 1936, 274, 418—425, 425—435).—IV. Unlike that of 2-picoline the Me of 6-amino-2-methylpyridine (I) (benzyl, m.p. 66°, and formylbenzyl, m.p. 76°, derivatives) or its *N*-Me derivatives does not react with *o*- or *p*-NO₂·C₆H₄·CHO to give stilbazoles (cf. Shaw *et al.*, A., 1933, 282). 6-Dimethylamino-2-methylpyridine with Ac₂O gives the Ac derivative, b.p. 264°, of 6-methylamino-2-methylpyridine, b.p. 209—210° (picrate, m.p. 192°); attempted condensation of this in Ac₂O with *o*-NO₂·C₆H₄·CHO gives β -hydroxy- β -2-nitrophenylpropionic acid, b.p. 175—185°/14 mm., m.p. 87°. Picrates of 2-stilbazole, m.p. 207°, and 2-dihydrostilbazole, m.p. 128°, were also prepared.

V. (I) forms Schiff's bases with many aromatic aldehydes, but with *o*-OH·C₆H₄·CHO and *o*-NO₂·C₆H₄·CHO reacts slowly to give yellow products regarded as Me·C₅H₃N·NH·N:CH< $\begin{matrix} CH:CH \\ CO:CH \end{matrix}$ >CH. Such are 6-*o*-methoxy-, m.p. 84°, and 6-*o*-hydroxy-benzylideneamino-2-methylpyridine, m.p. 68°, hydrogenated (Pd-black) to 6-*o*-methoxy-, m.p. 69° [also from (I) and *o*-OMe·C₆H₄·CHO in anhyd. HCO₂H], and 6-*o*-hydroxy-benzylamino-2-methylpyridine, m.p. 97°. The following were similarly prepared: 6-*o*-, m.p. 114.5°, and 6-*p*-nitro-, m.p. 161°, 6-6'-nitro-3:4-dimethoxy-, m.p. 139°, and 6-3':4'-methylenedioxy-benzylideneamino-2-methylpyridine, m.p. 118°; 6-3':4'-methylenedioxybenzylamino-2-methylpyridine, m.p. 80°, also from (I) with piperonal in anhyd. HCO₂H. (I) with S in CS₂ and EtOH yields NN-bis-(2-methylpyridine)-6-thiocarbamide, m.p. 209°, and 6-thiourethano-2-methylpyridine, m.p. 113°. (I) with CH₂:CH·CH₂·NCS yields 2-methylpyridine-6-allylthiocarbamide, m.p. 170°, which with 2*N*-NaOH, EtOH, and 10% Pb(OAc)₂ gives the corresponding carbamide, m.p. 139°. Similarly PhNCS gives phenyl-2-methylpyridine-6-thiocarbamide, m.p. 196°, and carbamide, m.p. 186°. 2-Aminopyridine (II) and CO(NH₂)₂ with butylchloral yield respectively 2-(di- $\beta\beta$ -trichloro- α -hydroxybutylamino)pyridine, m.p. 109°, and $\beta\beta$ -trichloro- α -hydroxybutylcarbamide, m.p. 156°. C₅H₅N with ω -chloro-3:4-dihydroxyacetophenone yields an additive compound with pyridine (hydrate, m.p. 269°; picrate, m.p. 190°). 2-(β -Hydroxy- β -3':4'-dihydroxyphenylethylamino)pyridine hydrochloride (A., 1934, 417) gives a picrate, m.p. 199°. F. R. G.

Reduction products of nicotinamide methiodide. II. P. KARRER and F. BENZ (Helv. Chim. Acta, 1936, 19, 1028—1029; cf. this vol., 1121).—The orange-coloured intermediate product formed during the reduction of nicotinamide methiodide by

$\text{Na}_2\text{S}_2\text{O}_4$ in aq. NaHCO_3 or Na_2CO_3 cannot be removed by CHCl_3 . A similar effect is observed with many other quaternary pyridinium salts and appears characteristic of reduction to the *o*- H_2 -stage. The yellow colorations have nothing in common with those produced by the reduction of cozymase in strongly alkaline solution. 1-Methyldihydropyridinamide has been obtained cryst. H. W.

Manufacture of heterocyclic compounds. [Pyridines and pyrrolidines.]—See B., 1936, 1083.

Manufacture of carboxylic acids or derivatives thereof containing the pyridine nucleus.—See B., 1936, 1084.

Interaction of tetraphenyl glycol and pyridinium chloride. A. SCHÖNBERG and R. MICHAELIS (J.C.S., 1936, 1571).—Tetraphenyl glycol, $\text{C}_6\text{H}_5\text{N}$, and HCl give a substance, m.p. 185—190° (decomp.), probably $\text{OH}\cdot\text{CPh}_2\cdot\text{CPh}_2\cdot\text{OH}\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$, decomposed by alkali into its components. F. R. S.

Nitrogenous substances analogous to tetraphenyl [2:5-diphenylpyridines]. M. COLONNA (Gazzetta, 1936, 66, 528—532).— $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, *o*-, *m*-, or *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, and AcCO_2H yield respectively 2-*o*- (cf. A., 1907, i, 853), 2-*m*-, m.p. 282° (decomp.), and 2-*p*-nitrophenyl-5:6- $\alpha\beta$ -naphthoquinoline-4-carboxylic acid, m.p. 262°, with *o*-, *m*-, or *p*-nitrobenzyl- β -naphthylamine. The above acids are oxidised by $\text{NaOH}\text{-KMnO}_4$ to 6-(2'-nitrophenyl)-3-(2''-carboxyphenyl)-, m.p. 287° (decomp.), 6-(3'-nitrophenyl)-3-(3''-carboxyphenyl)-, m.p. 115° (decomp.), and 6-(4'-nitrophenyl)-3-(4''-carboxyphenyl)-pyridine-2:4-dicarboxylic acid, m.p. 170°. E. W. W.

Condensation of aromatic formamido-derivatives with pyruvic acid. A. SILBERG (Bull. Soc. chim., 1936, [v], 3, 1767—1776).—This condensation does not follow the mechanism proposed by van Schelven (B., 1933, 341). Formanilides and AcCO_2H (I) in EtOH yield 2-methylquinoline-4-carboxylic acids (II), apparently by the stages $\text{NHR}\cdot\text{CHO} \rightarrow \text{NH}_2\text{R} \rightarrow \text{NR}\cdot\text{CHMe} \rightarrow \text{NHR}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{H} \rightarrow$ (II); secondary products are also formed. Thus $\text{NHPh}\cdot\text{CHO}$ and (I) give (in EtOH at the b.p.) 2-methylquinoline-4-carboxylic acid [also obtained from NH_2Ph and (I)] and (especially in the cold) β -anilinoacrylanilide, m.p. 236°. Form-*p*-anisidide (III) in EtOH gives 6-methoxy-2-methylquinoline-4-carboxylic acid (*Cu* salt); with (I) alone at 120° (III) yields γ -*p*-anisidino- α -ketovaleric acid (?), m.p. 200°. $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OME}$ and (I) in EtOH yield pyrotartrodip-anisidide. Form-*o*- and -*p*-toluidide give 2:8-, m.p. 153°, and 2:6-dimethylquinoline-4-carboxylic acid, m.p. 263° (decomp.), respectively. Form- α - and - β -naphthylamide condense to 2-methyl- α -naphthoquinoline-4-carboxylic acid, m.p. 245°, and 3-methyl- β -naphthoquinoline-1-carboxylic acid, m.p. 290°. *m*-Bromoformanilide gives 7(or 5)-bromo-2-methylquinoline-4-carboxylic acid, m.p. 187° (decomp.). *p*-Bromoformanilide and (I) in EtOH at the b.p. furnish a neutral substance, $\text{C}_{17}\text{H}_{15}\text{N}_2\text{Br}_3$, m.p. 222°; in the cold a substance, $\text{C}_9\text{H}_8\text{ONBr}$, is obtained. *o*-Bromoformanilide gives a substance, $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2\text{Br}$, m.p. 204—205°. E. W. W.

Manufacture of derivatives of anthraquinone series. Manufacture of 3-hydroxy-2-methylquinoline-4-carboxylic acid and derivatives.—See B., 1936, 976.

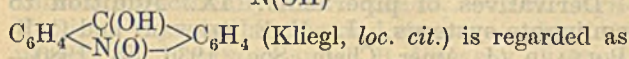
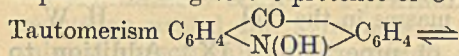
Addition of benzene to 2- and 4-styrylquinolines. R. C. FUSON, L. L. ALEXANDER, E. ELLINGBOE, and A. HOFFMAN (J. Amer. Chem. Soc., 1936, 58, 1979—1980).—4-*p*-Chlorostyrylquinoline, m.p. 127—128° (from 4-methylquinoline, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$, and a little ZnCl_2 at 125°), and 4-styrylquinoline (I) with C_6H_6 (excess), AlCl_3 , and HCl both give 4- $\beta\beta$ -diphenylethylquinoline, m.p. 130—131°. MgPhBr and (I) afford 2-phenyl-4-styrylquinoline, m.p. 102.5—103.5°. 2- $\beta\beta$ -Diphenylethylquinoline (A., 1933, 721) is also prepared by reduction of 2- $\beta\beta$ -diphenylvinylquinoline (II) with (i) $\text{H}_2 + \text{PtO}_2$, and (ii) C_6H_6 , AlCl_3 , and HCl . 2- β -Hydroxy- β -phenyl- β -*p*-chlorophenylethylquinoline, m.p. 140.5—141° (which could not be dehydrated), and (II) are obtained by Ziegler and Zeiser's method (A., 1931, 364). H. B.

Synthesis of substituted 5:6-benzocinchonic acids by the Doebner and Pfitzinger reactions. E. A. ROBINSON and M. T. BOGERT (J. Org. Chem., 1936, 1, 65—75).— $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, various aldehydes, and AcCO_2H or $\text{CH}_2\text{Bz}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ give 3-substituted 5:6-benzocinchonic acids (A) and their Bz derivatives, respectively (with *N*-substituted naphthylamines formed by oxidation of the dihydrocinchonic acids at the expense of the anils which are primary products), which by decarboxylation or soda fusion, respectively, lead to 3-substituted benzoquinolines. (A) are also obtained by the Pfitzinger reaction from β -naphthistatin and acetophenones. Identity of the compounds obtained by the various methods is rigorously proved and structures are thereby confirmed. The following appear to be new. 3-*p*-Anisyl-5:6-benzoquinoline, m.p. 190—191° (lit. 184°) (picrate, m.p. 224°). 5:6-Benzocinchonic acid, m.p. 302° (uncorr.). 3-Methyl-5:6-benzoquinoline picrate, m.p. 228—230° (decomp.) (lit. 220—221°). 2-Benzoyl-5:6-benzocinchonic acid, decomp. 247° (chloride, m.p. 197—199°; *Et* ester, m.p. 146.5—147°), and its 3-*Me*, decomp. 271° (decomp.), -*Ph*, decomp. 249° [chloride, m.p. 205—206°; *Et* ester, m.p. 144° (sinters at 137—140°)], -*p*-anisyl, decomp. 237° (chloride, m.p. 181—183°; *Et*, m.p. 160—161°, and *Me* ester, m.p. 175—176°), and -piperonyl derivative, decomp. 259° (chloride, m.p. 188—189°; *Et* ester, m.p. 158—159°). *N*-*p*-Anisyl, m.p. 104.5° (lit. 98°) (hydrochloride, m.p. 195°), and -piperonyl- β -naphthylamine, m.p. 119° (hydrochloride, m.p. 192°). 2-Benzoyl-3-methyl-, m.p. 132—133° (oxime, m.p. 242°; picrate, m.p. 216—217°), -phenyl-, m.p. 189° (lit. 185°) (picrate, m.p. 243—244°), -*p*-anisyl-, m.p. 186° (picrate, m.p. 199.5—200°), and -piperonyl-5:6-benzoquinoline, m.p. 210.5—211° [oxime, m.p. 262° (decomp.)]. M.p. are corr.

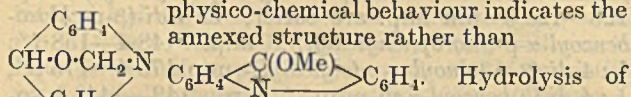
R. S. C.

Acridones. VIII. 10-Keto- and 10-keto-5-hydroxy-acridine. I. TANASESCU and E. RAMON-TIANU (Bull. Soc. chim., 1936, [v], 3, 2009—2018; cf. A., 1934, 1010).—In consequence of the somewhat divergent views of Lehmsstedt (A., 1935, 1251) and Kliegl *et al.* (this vol., 343) proof is adduced that "10-hydroxyacridone" is 5-hydroxyacridine 10-oxide.

5-Chloroacridine is oxidised by BzO_2H in CHCl_3 to 5-chloroacridine 10-oxide (II), m.p. 209° (additive complex with HgCl_2), hydrolysed by aq. alkali to 5-hydroxyacridine 10-oxide identical with that derived from $o\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$, C_6H_6 , and conc. H_2SO_4 . It is also obtained from (I) and NaOMe . This synthesis is decisive and also establishes that "acridol" is intermediately produced by the action of alkali on 5-chloroacridine and then becomes isomerised to acridone. In the present case the isomerisation is impossible owing to the presence of O attached to N.



is regarded as excluded since the absorption spectra in EtOH are closely similar in absence or presence of alkali. Reduction of the "5-methoxyacridine" of Lehmstedt (loc. cit.) with Zn dust in boiling EtOH containing CaCl_2 gives a basic substance ($\text{C}_{15}\text{H}_9\text{N}$)_n, m.p. 388° , of undetermined constitution with some acridone; its physico-chemical behaviour indicates the annexed structure rather than



5-benzoyloxyacridine 10-oxide with conc. HCl in $\text{EtOH-H}_2\text{O}$ gives 3-chloroacridone, identified by conversion into 3-chloro-5-*p*-dimethylaminophenylacridine, m.p. 230° . Similar hydrolysis of 3-chloro-5-benzoyloxyacridine 10-oxide gives a substance, $\text{C}_{13}\text{H}_7\text{ONCl}_2$, m.p. $<360^\circ$. H. W.

Acridine. XV. Relationship between basicity and radical formation during the action of alkali metal on bases of the acridine series. K. LEHMSTEDT, W. BRUNS, and H. KLEE (Ber., 1936, 69, [B], 2399—2405; cf. this vol., 999).—K-Na reacts initially with acridine (I) with production of

the radical $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH} \\ \text{NK} \end{array} \right\rangle \text{C}_6\text{H}_4$, which may become

saturated by reaction with a further K to produce $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CHK} \\ \text{NK} \end{array} \right\rangle \text{C}_6\text{H}_4$ (II), may become disproportion-

ated to (I) and (II), or may afford $(\text{NH} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \right\rangle \text{CH})_2$

by union of two radicals. Interaction of various acridine bases with Na-K in Et_2O and decomp. of the products with EtOH invariably yields mixtures of *ms*-dihydroacridines with *ms*-tetrahydrodiacridyls, the proportion of the latter being the greater as the base is weaker. 4'-Methoxydiphenylamine-2'-carboxylic acid is converted by PCl_5 in C_6H_6 into 3-methoxyacridone (I), m.p. 278° , transformed into 3-methoxyacridine (II), m.p. 104° [hydrochloride (+2H₂O)]. *meri*Quinonoid salts,

$\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}, \text{C}_{14}\text{H}_{11}\text{ON}, \text{HCl}, 2\text{H}_2\text{O}$ and $\text{C}_{14}\text{H}_{11}\text{ON}, \text{C}_{15}\text{H}_{13}\text{O}_2\text{N}, \text{HCl}$, are derived from (I) and (II) and from (II) and 3-methoxy-10-methylacridone, respectively. 2-Methyldiphenylamine-2'-carboxylic acid (improved prep. from $o\text{-C}_6\text{H}_4\text{ClCO}_2\text{H}$, K_2CO_3 , $o\text{-C}_6\text{H}_4\text{MeNH}_2$, and Cu powder) is almost quantitatively converted by PCl_5 in C_6H_6 followed by distillation with steam into 4-methylacridone, reduced by Na-Hg, and then dehydrogenated by PhNO_2 to 4-methylacridine, m.p. 88° (hydrochloride, +2H₂O).

3:7-Dimethylacridine hydrochloride (+2H₂O) is described. The following are obtained from the products of the action of Na-K on the bases: *ms*-tetrahydro-5:5'-di-3-methoxyacridyl, m.p. 204° in bath at 185° ; -5:5'-di-3:7-dimethylacridyl, m.p. $228\text{--}229^\circ$ in bath at 210° ; -5:5'-di-4-methylacridyl, m.p. 193° in bath at 175° ; -5:5'-di-3:4-benzoyloxyacridyl, m.p. $165\text{--}168^\circ$ in bath at 150° . *ms*-Dihydro-3:4-benzoyloxyacridine has m.p. 158° . H. W.

Preparation and therapeutic properties of certain acridine derivatives. I. Anil and styryl derivatives of 2:8-diaminoacridine and acridine-5-aldehyde respectively. W. L. GLEN, M. M. J. SUTHERLAND, and F. J. WILSON (J.C.S., 1484—1487).

—The following anils have been prepared but are too insol. in H_2O for biological tests: 2:8-bis-benzylidene-, m.p. 220° , -cinnamylidene-, m.p. 252° , -*p*-dimethylaminobenzylidene-, m.p. 230° , -anisylidene-, m.p. $241\text{--}242^\circ$, and -salicylidene-aminoacridine, m.p. 282° . The styryl compounds have been prepared by condensing acridine-5-aldehyde with α -picoline or quinoline alkylidene with $\text{C}_5\text{H}_{11}\text{N}$ as catalyst, and some therapeutic properties examined and recorded: 5-(2-pyridyl methiodide)-5-acridylethene, decomp. $220\text{--}225^\circ$ (hydrochloride); *s*-2-pyridyl-5-acridylethene dimethiodide; *s*-(2-pyridyl ethiodide)-5-acridylethene and -(5-acridyl methiodide)ethene; *s*-(2-quinolyl methiodide)-5-acridylethene, m.p. $220\text{--}225^\circ$ (decomp.) (hydrochloride); *s*-2-quinolyl-5-acridylethene dimethosulphate, dimethochloride, and dimethiodide; and *s*-(2-quinolyl ethiodide)-(5-acridyl methiodide)-ethene. F. R. S.

Attempts to find new antimalarials. XV. Synthesis of acridine compounds related to atebirin. R. R. GOODALL and W. O. KERMACK (J.C.S., 1936, 1546—1550).—5-Phenoxy-3-methoxyacridine, m.p. $146\text{--}147^\circ$, obtained from PhOH and the 5-Cl-compound, condenses with the appropriate amine to give: 5-(β -diethylaminoethyl-methylamino)-(dihydrobromide), m.p. $239\text{--}240^\circ$, -*n*-propylamino)-(dihydrobromide), m.p. $142\text{--}143^\circ$, and -amino-3-methoxyacridine (dihydrobromide), and 5-(γ -diethylamino-*n*-propylamino)-3-methoxyacridine dihydrobromide, m.p. $242\text{--}245^\circ$. 1:3:5-Trichloroacridine, m.p. 175° , obtained from 2:4-dichlorodiphenylamine-2'-carboxylic acid and POCl_3 , with PhOH gives 1:3-dichloro-5-phenoxyacridine, m.p. 171° , which condenses with amines to form 1:3-dichloro-5-(β -diethylaminoethylamino)-, m.p. $121\text{--}122^\circ$, and -(γ -diethylamino-*n*-propylamino)-acridine (dihydrobromide, decomp. 200°). 5-Chloro-1-bromo-, m.p. $159\text{--}161^\circ$, is converted into 1-bromo-5-phenoxy-3-methylacridine, m.p. 145° , which affords 1-bromo-5-(β -diethylaminoethylamino)-, m.p. 114° , and -(γ -diethylamino-*n*-propylamino)-3-methylacridine (dihydrobromide, decomp. about 230°). 1:3:7-Trichloro-5-(γ -diethylamino-*n*-propylamino)-, m.p. 155° , and 7-chloro-1-bromo-5-(γ -diethylamino-*n*-propylamino)-3-methylacridine, m.p. $130\text{--}131^\circ$, and 1:4-dichloro-5-(γ -diethylamino-*n*-propylamino)acridine dihydrobromide, decomp. about $225\text{--}230^\circ$, are also described.

F. R. S.

Manufacture of acridinium compounds.—See B., 1936, 1018.

Constitution of Knoevenagel's "acetone-anil." K. VON AUWERS (Ber., 1936, 69, [B], 2351—2352).—The structure assigned to the compound by Kalnin (this vol., 1123) is not in agreement with spectrochemical behaviour, which harmonises with that adopted by Reddelien (A., 1932, 1142). H. W.

Manufacture of cyclohexenylalkylhydantoins.—See B., 1936, 1018.

Action of phenylcarbimide on insulin.—See this vol., 1564.

Sensitisation of photographic silver halide emulsions. Preparation of pyrazolone and other derivatives.—See B., 1936, 1020.

Oxidation of 1-phenyl-3-methyl-5-pyrazolone. II. G. PERRONCITO (Gazzetta, 1936, 66, 563—565).—The product, m.p. 180°, of oxidising 1-phenyl-3-methyl-5-pyrazolone with dry H_3AsO_4 (this vol., 614) is methenylbis-4-(1-phenyl-3-methyl-5-pyrazolone). $NHPh \cdot NHAc$ is also formed, supporting the view that $NHAc \cdot NPh \cdot CO \cdot CHO$ is an intermediate product. E. W. W.

N-Arylbarbituric acids. II. J. S. BUCK (J. Amer. Chem. Soc., 1936, 58, 2059—2061).—The following are prepared from $NH_2 \cdot CO \cdot NHAr$ and $CEtR(CO_2Et)_2$ (method: this vol., 1125): 1-phenyl-, m.p. 149°, 1-o-, m.p. 134°, -m-, m.p. 138.5°, and -p-, m.p. 149.5°, -tolyl-, 1-o-, m.p. 176—177°, -m-, m.p. 139.5°, and -p-, m.p. 149°, -anisyl-, 1-o-, m.p. 142—143°, -m-, m.p. 125.5°, and -p-, m.p. 145°, -phenetyl-, and 1- α -, m.p. 158°, and - β -, m.p. 161—162°, -naphthyl-5-ethyl-5-isobutylbarbituric acids; 1-phenyl-, m.p. 129°, 1-o-, m.p. 119°, -m-, m.p. 113—114°, and -p-, m.p. 115°, -tolyl-, 1-o-, m.p. 134°, -m-, m.p. 115—116°, and -p-, m.p. 120°, -anisyl-, 1-o-, m.p. 162—163°, -m-, m.p. 72—74°, and -p-, m.p. 100—101°, -phenetyl-, and 1- α -, m.p. 193—194°, and - β -, m.p. 138°, -naphthyl-5-ethyl-5-isoamylbarbituric acids; 1-p-dimethylaminophenyl-5:5-diethyl-, m.p. 182°, -5-ethyl-5-n-, m.p. 157°, and -iso-, m.p. 153°, -butyl-, -5-ethyl-5-isoamyl-, m.p. 130°, and 1-p-diethylaminophenyl-5:5-diethyl-, m.p. 175°, -5-ethyl-5-n-, m.p. 125.5°, and -iso-, m.p. 140—141°, -butyl-, and -5-ethyl-5-isoamyl-, m.p. 125°, -barbituric acids. p-Dimethyl-, m.p. 183°, and p-diethyl-, m.p. 136.5°, -aminophenylcarbamides are described. All m.p. are corr. H. B.

Isomerisation of acylated pyrazolines. K. VON AUWERS and H. LUDEWIG (Ber., 1936, 69, [B], 2347—2351).—Repeated attempts to re-obtain 5-methylpyrazoline-1-carboxylamide, m.p. 167—168°, from 5-methylpyrazoline (I) and $HCNO$ (von Auwers, A., 1927, 1203) give only an isomeride, m.p. 119°, whereas ring-closure from $CH_2Cl \cdot CH_2 \cdot CMe \cdot N \cdot NH \cdot CO \cdot NH_2$ (Maire, A., 1908, i, 290) and condensation of 3-methylpyrazoline (II) with $HCNO$ give exclusively the product of m.p. 167—168°. Acyl migration occurred therefore during the original experiment but its cause has not been traced. The incidence of accidental influences in similar changes is illustrated by the behaviour of (I) towards boiling $ClCO_2Me$; in one experiment the main product was *Me* 3-methylpyrazoline-1-carboxylate, b.p. 135°/14 mm. [decarboxylated to (II) and identified as the picrate, m.p. 149°], whereas in other experiments

Me 5-methylpyrazoline-1-carboxylate, b.p. 124—132°/14 mm., was mainly produced. Benzoylation of (II) proceeds normally and yields 1-benzoyl-3-methylpyrazoline, m.p. 98.5—99°, differing from the 5-Me isomeride, m.p. 156°. The possibility of isomerisation during the nitrosation of (I) could not be investigated owing to the instability of the product. The occurrence of isomerisation with alkylpyrazolines proves that the phenomenon is not caused by a tendency towards the production of conjugated systems and indicates that it is due to a striving towards a uniform distribution of masses in the mol. H. W.

Derivatives of piperazine. IX. Addition to conjugate systems. I. V. E. STEWART and C. B. POLLARD (J. Amer. Chem. Soc., 1936, 58, 1980—1981).—Piperazine (1 mol.) and $COAr \cdot CH \cdot CHAr$ (2 mols.) in boiling PhMe give almost quant. yields of 1:4-di-(β -aroyl- α -arylethyl)piperazines, which are decomposed by dil. HCl (not H_2O) or HCl in $CHCl_3$ or PhMe to the original components. The following are described: 1:4-di-(β -benzoyl- α -phenylethyl)-, m.p. 128—128.3° (all m.p. are corr.); 1:4-di-(β -p-chlorobenzoyl- α -p-chlorophenylethyl)-, m.p. 148.4—158.7°; 1:4-di-(β -p-toluoyl- α -p-tolylolethyl)-, m.p. 175.4—175.8°; 1:4-di-(β -benzoyl- α -m-nitro-, m.p. 143—144°, -o-chloro-, m.p. 110.9—111.3°, -p-chloro-, m.p. 146.8—147°, -p-methyl-, m.p. 145.5—146°, and -p-methoxy-, m.p. 109.5—110.1°, -phenylethyl-); 1:4-di-(β -p-chloro-, m.p. 117.7—118.1°, -p-bromo-, m.p. 116.3—117.3°, and -p-methyl-, m.p. 132—132.5°, -benzoyl- α -phenylethyl-), and 1:4-di-(β -p-toluoyl- α -p-anisylethyl)-, m.p. 149.8—150.2°, -piperazines. H. B.

Manufacture of derivative of pyrazinemono-carboxylic acid.—See B., 1936, 1130.

Pyrrolidine derivatives. III. Catalytic hydrogenation under pressure of pyridylpyrrole derivatives. E. OCHIAI, K. TSUDA, and S. IKUMA (Ber., 1936, 69, [B], 2238—2242).—With pyridylpyrrole derivatives catalytic hydrogenation (PtO_2) under pressure first affects the C_5H_5N nucleus. The influence of substituents in the pyrrole nucleus is pronounced. Whereas Me has little effect, CO_2Alk markedly inhibits reaction as does Ac until it has been reduced to $\cdot CHMe \cdot OH$ or Et. The following transitions are described: 4-2'-pyridyl-2-methylpyrrole to 4-2'-piperidyl-2-methylpyrrole, m.p. 113—114° [hydrochloride, m.p. 228° (decomp.); p-nitrobenzoyl derivative, m.p. 140—141°], and 4-2'-piperidyl-2-methylpyrrolidine, b.p. 110°(bath)/6 mm. (di-3:5-dinitrobenzoyl derivative, m.p. 180°); 4-3'-pyridyl-2-methylpyrrole to 4-3'-piperidyl-2-methylpyrrolidine, b.p. 120—130°(bath)/6 mm. (aurichloride, decomp. 230°; di-3:5-dinitrobenzoyl derivative, m.p. 237°); 3-acetyl-4-2'-pyridyl-2-methylpyrrole to a base, b.p. 200°(bath)/0.03 mm., converted by HI (*d* 1.7) and red P at 130° into 4-2'-piperidyl-2-methyl-3-ethylpyrrole (hydrochloride, m.p. 214°) or into a base, b.p. 150—170°(bath)/0.03 mm., and thence into 4-2'-piperidyl-2-methyl-3-ethylpyrrolidine (di-p-nitrobenzoyl derivative, m.p. 239—240°); 3-acetyl-4-3'-pyridyl-2-methylpyrrole to 3-acetyl-4-3'-piperidyl-2-methylpyrrole, m.p. 184° (p-nitrobenzoyl, m.p. 198°, and Ac, m.p. 216°, derivatives); Et 4-3'-pyridyl-2-methylpyrrole-3-carboxylate to Et 4-3'-piperidyl-2-methylpyrrole-3-carboxylate, m.p. 137°

(*Bz* derivative, m.p. 174°); Et_2 4-2'-pyridyl-2-methylpyrrole-3:5-dicarboxylate is hydrolysed to 3-carbethoxy-4-2'-pyridyl-2-methylpyrrole-5-carboxylic acid, decomp. 218°, decarboxylated at 220°/3 mm. to *Et* 4-2'-pyridyl-2-methylpyrrole-3-carboxylate, m.p. 120° (perchlorate, m.p. 205°; methiodide, m.p. 207°; ethiodide, m.p. 179°), which is hydrogenated to *Et* 4-2'-piperidyl-2-methylpyrrole-3-carboxylate (*p*-nitrobenzoyl, m.p. 210°, and *Ac*, m.p. 142°, derivatives).

H. W.

Pyrimidines. CLIV. Pyrimidine side-chain reactions useful for synthesis of 1:3-diazines related structurally to vitamin- B_1 . **CLV.** Synthesis of thymine and its conversion into uracil. A. LITZINGER and T. B. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 1936—1939, 1940—1942).—**CLIV** (cf. A., 1935, 991). 6-Hydroxy-2-ethylthiolpyrimidine-5-acetylhydrazide, m.p. 207—208° (decomp.) (from the *Et* ester and $\text{EtOH-N}_2\text{H}_4\cdot\text{H}_2\text{O}$), is converted into the azide (I), m.p. 175—180° (decomp., after evolution of N_2 at 75—80°), and thence (in *PhMe*) into 6-hydroxy-2-ethylthiol-5-carbimidomethylpyrimidine (II), m.p. 189—191° (decomp.). (II) with warm H_2O gives mainly *s-di*-(6-hydroxy-2-ethylthiolpyrimidine-5-methyl)carbamide, m.p. 270—272° (decomp.), and a little 6-hydroxy-2-ethylthiol-5-aminomethylpyrimidine, m.p. 221—222° (decomp.) [*N-CO_2Et*- (III), m.p. 148.5—149.5°, and *N-CO_2CH_2Ph*- (IV), m.p. 159—160°, derivatives, obtained from (I) or (II) with *EtOH* and $\text{CH}_3\text{Ph}\cdot\text{OH}$, respectively]. (II) with aq. NH_3 and NH_2Ph (in dioxan) affords 6-hydroxy-2-ethylthiol-5-carbamido-, m.p. 190—192° (decomp.), and 5-phenylcarbamido-, m.p. 223—224° (decomp.), -methylpyrimidine, respectively. *Uracil-5-acetylhydrazide*, decomp. about 326° (darkens at 285°), is similarly converted through the azide, m.p. 275—276° (decomp., after evolution of N_2 at 75—80°), into thyminecarbamide [5-carbimidomethyluracil] (V), $\text{CO} \begin{array}{l} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CH} \end{array} \text{C}\cdot\text{CH}_2\cdot\text{NCO}$, m.p. 273—275° (decomp.), and thence (boiling H_2O) into *s-dithyminecarbamide*, decomp. 315°. *Et* (VI), m.p. 256—257°, and *benzyl*, m.p. 261—263° (decomp.), thyminecarbamates are obtained by hydrolysis (warm *EtOH*-conc. *HCl*) of (III) and (IV), respectively.

CLV. Partly a more detailed account of work previously reviewed (this vol., 1126). Thyminecarbamide [5-aminomethyluracil] (VII), m.p. 260—270° (decomp.) [hydrochloride (+0.5 H_2O), m.p. 242—243° (decomp.); sulphate (+ H_2O) (VIII), m.p. 245—246° (decomp.)], is obtained (not absolutely pure) by hydrolysis (*HCl* or H_2SO_4) of the above (II), (III), (V), and (VI). (VII) is further hydrolysed (conc. *HCl* and to some extent by boiling H_2O) to uracil (IX), CH_2O , and NH_3 . (VII) with $\text{Ba}(\text{NO}_3)_2$ and 0.2*M*- H_2SO_4 gives impure thymine alcohol [5-hydroxymethyluracil], m.p. 190—200° [also hydrolysed to (IX)], which could not be synthesised from (IX) and CH_2O . (VII) and *N* oxides in H_2O give the compound, $\text{CO-N}\cdot\text{C}\cdot\text{O}$ $\text{NH}\cdot\text{CH}\cdot\text{C}\cdot\text{CH}_2$, m.p. 195—200°. Thyminecarbamide, m.p. 204—205°, is prepared from (VIII) and NH_4NCS .

H. B.

Synthesis of benzimidazole derivatives. R. WEIDENHAGEN (Ber., 1936, 69, [B], 2263—2272).—

The author's glyoxaline synthesis (A., 1935, 1380, 1507) is extended to benzimidazoles. $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, $\text{Cu}(\text{OAc})_2$, and MeCHO in H_2O afford the *Cu* derivatives of 2-methylbenzimidazole, whence the parent compound, m.p. 175—176°, in 75% yield. The following benzimidazoles and the corresponding *Cu* derivatives are analogously obtained: 2-ethyl-, m.p. 174—175°; 2-*n*-propyl-, m.p. 157—159°; 2-*iso*-propyl-, m.p. 228°; 2-*n*-butyl-, m.p. 149—151°; 2-*iso*-butyl-, m.p. 186—187°; 2-*n*-amyl-, m.p. 159—161°; 2-*n*-hexyl-, m.p. 136—138°; 2- β -dimethyl- Δ^{α} -heptadienyl- (from citral), m.p. (indef.) 102°; 2-phenyl-, m.p. 290°; 2-*o*-nitrophenyl-hydrochloride, m.p. 291° (decomp.); 2-*m*-nitrophenyl- (+ H_2O), m.p. 204°; 2-*p*-nitrophenyl-hydrochloride, m.p. 310° (decomp.); 2-4'-hydroxy-3'-methoxyphenyl-, m.p. 221—222°; 2-*p*-methoxyphenyl-, m.p. 228—230°; 2-3':4'-methylene-dioxyphenyl-, m.p. 249°; 2-styryl-, m.p. 201—202°; 2-furyl-, m.p. 285—286°. *Et* 2-ethylbenzimidazole-5-carboxylate, m.p. 151°, and *Et* 2-hexylbenzimidazole-5-carboxylate hydrochloride, m.p. 238—240°, are derived from $(\text{NH}_2)_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{Et}$. 2-*iso*Propyl-, m.p. 239—240°, and 2-*n*-hexyl-, m.p. 199—202°, -1':2'-naphthimidazole are described.

H. W.

Complex benzylation products of indigotin. Höchst Yellow U. E. HOPE and J. S. ANDERSON (J.C.S., 1936, 1474—1478).—Methylation (Me_2SO_4 -*NaOH*) of the "monohydrate of Höchst Yellow U" (cf. Posner *et al.*, A., 1929, 1313) gives a *Me_2*, m.p. 167—168°, and a *Me* derivative, m.p. 238—240° (decomp.). Höchst Yellow U (I) and 15% *NaOH* at 215° afford an *NH_2*-acid, m.p. 232° (efferv.) [(+ $2\text{H}_2\text{O}$), m.p. 182° (efferv.); NH_4 salt; *Bz* derivative, m.p. 212—213°, and (+ H_2O), m.p. 265—267° (efferv.); *Ac* derivative, m.p. 272°; *Me_2* derivative, m.p. 238—239°, converted by *HCl* into an acid (+ $2\text{H}_2\text{O}$), m.p. 308—310° (decomp.)], which when heated forms a product, m.p. 230—231°; at the same time, an acid (+ H_2O), m.p. 206—208° (methylation product, m.p. 247—249°), is also obtained. These results are not in agreement with the formula of de Diesbach *et al.* (A., 1934, 306) for (I) and the alternative

$\text{CO} \begin{array}{l} \text{C}_6\text{H}_4 \\ \text{N} \end{array} \begin{array}{l} \text{C}=\text{C}\cdot\text{CO} \\ \text{C}_6\text{H}_4\cdot\text{C}=\text{N} \end{array} \text{C}_6\text{H}_4$ is suggested.

F. R. S.

Manufacture of heterocyclic hydroxy-compounds.—See B., 1936, 977.

C-Aminophthalazone and N-aminophthalimidine. A. DARAPSKY and P. HEINRICH (J. pr. Chem., 1936, [ii], 146, 307—318).—Phthalazonecarboxylic acid (I), m.p. 232° (NH_3 , m.p. 237°, and N_2H_4 , m.p. 249—250°, salts), obtained by the direct action of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ on the product of the oxidation of C_{10}H_8 , is esterified by *HCl*-*MeOH* and *HCl*-*EtOH* to the *Me*, m.p. 211°, and *Et*, m.p. 169°, ester. The latter is transformed by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling abs. *EtOH* into phthalazonecarbohydrazide, m.p. 234° (hydrochloride; :CHPh , m.p. >390°, *o*-hydroxybenzylidene-, m.p. >290°, and anisylidene-, m.p. >290°, derivatives), whence phthalazonecarboazide, transformed by warm NH_2Ph into the corresponding anilide, m.p. 288°, and by boiling *EtOH* into *Et* phthalazonecarbamate, m.p. 207°, whence 4-aminophthalazone (II), m.p. 257—258° (hydrochloride, m.p.

240°; perchlorate, m.p. 209°). (II) is transformed by NaNO_2 into phthalhydrazide. Reduction of (I) with Zn dust and conc. HCl at 100° yields *phthalimidine-carboxylic acid*, $\text{CO} \langle \text{NH} \rangle_{\text{C}_6\text{H}_4} \text{CH} \cdot \text{CO}_2\text{H}$, m.p. 146—147°, which loses CO_2 when heated above its m.p. and yields phthalimidine. With Zn dust in alkaline solution reduction occurs without loss of N, and gives rise to *aminophthalimidinecarboxylic acid*,

$\text{CO} \langle \text{N}(\text{NH}_2) \rangle_{\text{C}_6\text{H}_4} \text{CH} \cdot \text{CO}_2\text{H}$, m.p. 140° [*hydrochloride*, m.p. 188°; *:CHPh*, m.p. 106°, *o*-hydroxybenzylidene, m.p. 276°, and Bz, m.p. 141—142° (decomp.), derivatives]. Similarly phthalazone is reduced to *aminophthalimidine* (*:CHPh*, m.p. 206°, and *o*-hydroxybenzylidene, m.p. 276°, derivatives). Attempts to reduce (I) (Pd or Pt in alkaline or AcOH solution) without altering the structure of the six-membered pyridazine ring were unsuccessful. H. W.

Hydroxyketones. III. Benzoylformoin.

A. H. BLATT (J. Amer. Chem. Soc., 1936, 58, 1894—1899).—Benzoylformoin (I) and its open-chain Alk_1 derivatives (cf. A., 1935, 982) react either as ene-diols or hydroxyketodihydrofurans; the cyclic Alk_1 and Alk_2 derivatives are ketoalkoxydihydrofurans. Distillation of (I) at about 240°/0.5 mm. gives an unstable red liquid, probably $\text{CPh} \cdot \text{C}(\text{OH}) \cdot \text{CBz}$ (dotted line indicates chelation), which gradually reverts to the stable, yellow cryst. form (2:4-dihydroxy-3-keto-2:5-diphenyl-2:3-dihydrofuran). (I) and $\text{Cu}(\text{OAc})_2$ in Et_2O afford a brown Cu derivative, $\text{C}_{16}\text{H}_{10}\text{O}_4\text{Cu}$, which is thus derived from an ene-diol. (I) heated with SOCl_2 gives $(\text{CO} \cdot \text{COPh})_2$, which, like (I) and benzoin, is oxidised by $\text{Cu}(\text{OAc})_2$ in aq. AcOH to benzil [$(s\text{-C}_6\text{H}_2\text{Me}_3 \cdot \text{CO})_2$ is similarly obtained from mesitoylformoin]. (I) and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in MeOH afford 2-phenyl-3- α -hydroxy- β -keto- β -phenylethylquinoxaline (II), m.p. 187—188°, converted by MgPhBr into 2-phenyl-3- $\alpha\beta$ -dihydroxy- $\beta\beta$ -diphenylethylquinoxaline, m.p. 163—164°, which is oxidised (CrO_3 , AcOH) to 3-phenylquinoxaline-2-carboxylic acid and thence to 2-hydroxy-3-phenylquinoxaline (III). Acetylation of (I) with Ac_2O , $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$, AcCl , or $\text{AcCl}-\text{C}_5\text{H}_5\text{N}$ gives 3-keto-2:4-diacetoxy-2:5-diphenyl-2:3-dihydrofuran (IV) (cf. Abenius, A., 1894, i, 286), converted by *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in C_6H_6 into the 4-hydroxy-2-acetoxy-derivative, m.p. 198°, which is reacylated to (IV) and with $\text{MeOH}-\text{HCl}$ affords the 4-hydroxy-2-methoxy-derivative (*loc. cit.*), also obtained from the 4-acetoxy-2-methoxy-derivative (Abenius, *loc. cit.*) and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$. Acetylation of (I) with Ac_2O in aq. AcOH yields the open-chain acetate, $\text{OAc} \cdot \text{CHBz} \cdot \text{COBz}$, m.p. 109—110° (or its enol), converted by $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ into (IV) and by *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ into (III). *s*- $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{COCl}$ and (I) in $\text{C}_5\text{H}_5\text{N}$ give the *di*-(2:4:6-trimethylbenzoate) (V), $\text{OR} \cdot \text{CPh} \cdot \text{C}(\text{OR}) \cdot \text{COBz}$ ($\text{R} = s\text{-C}_6\text{H}_2\text{Me}_3 \cdot \text{CO}$), m.p. 145°, which with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in MeOH affords 2-phenyl-3- $\alpha\beta$ -*di*-(2:4:6-trimethylbenzoyloxy)styrylquinoxaline, m.p. 182—183°, oxidised (CrO_3 , AcOH) to (III). (V) is converted by MeOH -conc. HCl into an isomeride, m.p. 189° [isolated once during prep. of (V)], which does not react with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$. 3-Keto-2:4-

dimethoxy-2:5-diphenyl-2:3-dihydrofuran with $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ gives the 2-acetoxy-4-methoxy-derivative, m.p. 164—165° [also obtained by acetylation of $\text{OH} \cdot \text{CPh} \cdot \text{C}(\text{OMe}) \cdot \text{COBz}$ (*loc. cit.*)], unaffected by *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$; the 2-acetoxy-4-ethoxy-derivative, m.p. 133°, is prepared by the same methods. Any of the above furans containing the 4-alkoxy-group is converted by $\text{AcOH}-\text{HBr}$ into a mixture of 2-bromo-4-alkoxy-derivative (VI) (not isolable in pure condition) and 3:3'-diketo-4:4'-dialkoxy-2:5:2':5'-tetraphenyl-2:3:2':3'-tetrahydro-2:2'-difuryl (VII) (the 4:4'-dimethoxy-, m.p. 226—227°, and 4:4'-diethoxy-, m.p. 218—219°, derivatives are described). (VI) is converted by heat or acidified KI in COMe_2 into (VII). The Et ether, $\text{OH} \cdot \text{CPh} \cdot \text{C}(\text{OEt}) \cdot \text{COBz}$ (VIII) (*loc. cit.*), unlike the Me ether, gives (III) with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$; it is brominated to $\text{COPh} \cdot \text{CBr}(\text{OEt}) \cdot \text{COBz}$ (Abenius, *loc. cit.*), which with acidified KI and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ affords (VIII) and (III), respectively.

2-Phenyl-3- β -keto- α -methoxy- β -phenylethylquinoxaline is cleaved by $\text{MeOH}-\text{NaOMe}$ to MeOBz , BzOH , (III), and 3-phenyl-2-methoxymethylquinoxaline (IX), m.p. 78—79°; (II) similarly gives (III) and 3-phenyl-2-hydroxymethylquinoxaline, m.p. 140—141°, which is methylated (MeI, solid NaOH) to (IX) and oxidised (CrO_3 , AcOH) to 3-phenylquinoxaline-2-carboxylic acid. H. B.

$\alpha\delta$ -Diphenylbutane- $\alpha\beta\delta$ -trione enol; alkylation and benzoylation. R. E. LUTZ and A. H. STUART (J. Amer. Chem. Soc., 1936, 58, 1885—1890; cf. Kohler and Woodward, this vol., 1515).—Partly a correction and amplification of previous work (A., 1934, 1222, 1361). α -Hydroxy- $\alpha\beta$ -dibenzoylethylene (I) with BzCl and a trace of conc. H_2SO_4 gives 2-chloro-3-keto-2:5-diphenyl-2:3-dihydrofuran (II), hydrolysed ($\text{MeOH}-\text{NaOH}$) to (I) and converted by $\text{MeOH}-\text{NaOMe}$ into the 2-OMe-derivative (III). (II) and AgOBz in Pr^2_2O afford 3-keto-2-benzoyloxy-2:5-diphenyl-2:3-dihydrofuran (IV), m.p. 162—163° [also obtained from (I), Bz_2O , and a little conc. H_2SO_4], readily hydrolysed (NaOH or NaOMe) to (I). (I) and BzCl in aq. NaOH give $\approx 50\%$ of α -benzoyloxy- $\alpha\beta$ -dibenzoylethylene (or $\gamma\delta$ -diketo- α -benzoyloxy- $\alpha\delta$ -diphenyl- Δ^a -butene) (V), m.p. 139°, converted by $\text{MeOH}-\text{HCl}$ into (III) and by $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ and $\text{AcCl}-\text{H}_2\text{SO}_4$ into 3:4-diacetoxy- (VI) and 3-chloro-4-acetoxy- (VII) -2:5-diphenylfuran, respectively. (I), (II), (IV), and (VII) react immediately with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in boiling EtOH yielding 2-phenyl-3-phenacylquinoxaline, m.p. 169—170° [oxidised (CrO_3 , AcOH) to 3-hydroxy-2-phenylquinoxaline and a little 2-phenylquinoxaline-3-carboxylic acid], also obtained (on prolonged action) from α -methoxy- and α -amino- $\alpha\beta$ -dibenzoylethylene, but not from (III), (IV), (VI), and *trans*- α -chloro- $\alpha\beta$ -dibenzoylethylene. Evidence is given indicating that methylation of (I) gives the stable $\text{COPh} \cdot \text{C}(\text{OMe}) \cdot \text{CH} \cdot \text{COPh}$ and the unstable $\text{COPh} \cdot \text{CO} \cdot \text{CH} \cdot \text{CPh} \cdot \text{OMe}$. It is unlikely that the colourless and yellow forms of (I) are *cis-trans* isomerides; the former is probably 2-hydroxy-3-keto-2:5-diphenyl-2:3-dihydrofuran. $\text{CPhCl} \cdot \text{CH} \cdot \text{CO} \cdot \text{COPh}$ is (II).

The Ag salt of (I) with AlkI in Pr^2_2O gives (mainly)

2-hydroxy-3-keto-2 : 5-diphenyl-4-alkyl-2 : 3-dihydrofuran [4-Me, m.p. 143—144°, 4-Et, m.p. 113°, and 4-Pr^a, m.p. 137.5°, derivatives, hydrolysed by aq. Ba(OH)₂ to BzCO₂H and COPhEt, COPhPr, and COPhBu, respectively], and 0—20% of the α-alkoxy-αβ-dibenzoyl ethylene. The Na and Ag salts of (I) with Me₂SO₄ in MeOH and EtOH afford (III) and the 2-OEt-derivative, respectively. (I) and 2-hydroxy-1 : 4-naphthaquinone react in similar manners. All m.p. are corr.

H. B.

Heteropolar combinations. II. Coloured "carbenium" salts of halogen acids with 4-hydroxy-2-thion-(or -oxo-)tetrahydroquinazoline and with the corresponding halogenomercuri-compounds. C. V. GHEORGHIU and (MLLE.) L. MANOLESCU (Bull. Soc. chim., 1936, [v], 3, 1830—1836; cf. this vol., 1126).—4-Ethoxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazol-2-one with halogen acids in Ac₂O gives the *hydrochloride*, decomp. >300°, and *hydriodide*, m.p. 225°, of the 4-OH-compound, and the *hydrobromide*, m.p. 253° (decomp.), of the 4-OAc-compound; all these are yellow and therefore presumably in the carbonium state. 2-Thion-4-ethoxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline (I) similarly yields the *hydrochloride*, m.p. 225—226°, and *hydriodide*, m.p. 193—194° (red), of its 4-OH-compound, and the *hydrobromide*, m.p. 231—234° (orange), of its 4-OAc-compound. The HgCl₂, HgBr₂, and HgI₂ compounds of (I), with HBr or HI in Ac₂O, give the *dihydrobromides*, m.p. 200—217°, 221°, and 207°, and the *dihydriodides*, m.p. 145°, 109—110°, and 104—105°, respectively, of 2-thiol-3-hydroxy-3-phenyl-3 : 4-dihydroquinazolinium-*S*-mercuri-dichloride, -dibromide, and -di-iodide; these salts are all red in colour.

E. W. W.

Formation of cyclic azo-compounds from 2 : 2'-diaminodiphenyls. R. B. SANDIN and T. L. CAIRNS (J. Amer. Chem. Soc., 1936, 58, 2019—2020).—Tetrazotised 2 : 2'-diaminodiphenyl with Na₃AsO₃ in aq. Na₂CO₃+CuSO₄ gives 45% of the cyclic 2 : 2'-azodiphenyl, m.p. 155° [the *o*-diphenyleneazone of Täuber (A., 1892, 183)]. 2 : 2'-Azo-4 : 4'-dimethyldiphenyl, m.p. 184—185°, is similarly obtained from the 2 : 2'-(NH₂)₂-derivative and also by reduction (Na-Hg, MeOH) of the 2 : 2'-(NO₂)₂-derivative.

H. B.

Manufacture of halogenoamino-1 : 9-anthra-pyrimidines.—See B., 1936, 1084.

Nitrogenous heterocyclic rings. XXIV. Benzodipyrroles. IV. Ring-closure with a *m*-phenylenedihydrazone. P. RUGGLI and C. PETITJEAN (Helv. Chim. Acta, 1936, 19, 928—930; cf. this vol., 866).—Treatment of deoxybenzoin with *m*-C₆H₄(NH·NH₂)₂ in boiling EtOH affords *dideoxybenzoin-m-phenylenedihydrazone*, *m*-C₆H₄(NH·N:CPh·CH₂Ph)₂, m.p. 164°, which resinifies when heated with ZnCl₂ but is transformed by short treatment with boiling H₂SO₄-EtOH into tetraphenylbenzodipyrrole [2 : 3 : 2' : 3'-tetraphenylpyrrolo-4' : 5'-5 : 6-indole], m.p. 279°.

H. W.

Relationship of the tricyanomelamines to polymerised dicyanoamides. J. BIECHLER (Compt. rend., 1936, 203, 568—570; cf. A., 1935, 482).—

Alkyl or aryl K cyanamides (I) with CNCl afford tricyanomelamines (cf. A., 1922, i, 438), stable at 170°. The following are prepared: *tri-phenyl-* (II), m.p. 210°, *-o-tolyl-*, m.p. 203°, *-o-*, m.p. 110°, and *-p-anisyl-*, m.p. 201°, *-p-phenetyl-*, m.p. 151°, *-naphthyl-*, m.p. 271°, *-2 : 4-xyllyl-*, m.p. 193°, *-benzyl-*, m.p. 158°, and *-methyl-tricyanomelamine*, m.p. 241°. Deficiency of (I) in the above reaction yields chlorotriazines. The following are prepared: 4 : 6-dichloro-2-cyanoanilino-, m.p. 138—183°, and 6-chloro-2 : 4-dicyanoanilino-1 : 3 : 5-triazine, m.p. 181°, converted into 1-phenyl-3 : 5-di-*p-phenetyl-*, m.p. 115—120°, and 1 : 3-diphenyl-5-*p-phenetyl-tricyanomelamine*, m.p. 98—104°, respectively. From measurements of the heat of polymerisation of NPh(CN)₂ and (II), the structure of the polymeride is deduced.

J. L. D.

Aminoflavin, 9-β'-aminoethylisoalloxazine. P. KARRER and R. NAEF (Helv. Chim. Acta, 1936, 19, 1029—1033).—*o*-C₆H₄Cl·NO₂ and OH·CH₂·CH₂·NH₂ in boiling C₅H₅N give β-*o-nitro-anilinoethyl alcohol*, m.p. 76° [Ac derivative (? acetate), m.p. 67°], transformed by PCl₅ in CHCl₃ at room temp. into *o-nitro-β-chloroethylaniline*, m.p. 59°, which with *o*-C₆H₄(CO)₂NK at 170° gives *o-nitro-β-phthalimidoethylaniline* (I), m.p. 184°. (I) is reduced by Na₂S₂O₄ in 50% EtOH to *o-amino-β-phthalimidoethylaniline*, m.p. 124°, the *hydrochloride* of which condenses with alloxantin to 9-β-*phthalimidoethylisoalloxazine*, decomp. about 285°, hydrolysed by conc. HCl-AcOH at 100° to 9-β-*aminoethylisoalloxazine hydrochloride* (II), decomp. >300°. The alkaline solution of (II) darkens in sunlight but does not form a pigment sol. in CHCl₃; in neutral solution or in presence of AcOH (II) gradually darkens without formation of > a trace of lumichrome. Photolysis of (II) therefore occurs in a more complex and incomplete manner than that of the OH-flavins.

H. W.

Synthesis of flavins. P. KARRER and T. H. QUTBELL (Helv. Chim. Acta, 1936, 19, 1034—1042).—*Et p-ethylphenylcarbamate*, from *p*-C₆H₄Et·NH₂ and ClCO₂Et in dil. COMe₂, is converted by HNO₃ (*d* 1.42) and conc. H₂SO₄ at -3° to -8° into *Et 2-nitro-4-ethylphenylcarbamate*, m.p. 40.5°, which is reduced (Pt in EtOH) to *Et 2-amino-4-ethylphenylcarbamate*, m.p. 63°. The latter is transformed by *d*-ribose in boiling MeOH followed by reduction with Ni and H₂ at 95°/25 atm. into 2-carbethoxyamino-5-ethylphenyl-*d*-ribamine, m.p. 169°, which is hydrolysed and then converted by alloxan and H₃BO₃ in AcOH containing NaOAc into 7-ethyl-9-*d*-1'-ribitylisoalloxazine (I), m.p. 220° after softening at 215°. 3 : 4-C₆H₃MeEt·NH₂ and *l*-arabinose yield 3-methyl-4-ethylphenyl-1-arabamine hydrochloride, m.p. 198°, whence 2-benzeneazo-5-methyl-4-ethylphenyl-1-arabamine, m.p. 185—186°, reduced (Ni or, preferably, Na₂S₂O₄) to 7-methyl-6-ethyl-9-1-1'-arabitylisoalloxazine, decomp. 243—244°. 3 : 4-C₆H₃MeEt·NH₂ and *d*-ribose give 3-methyl-4-ethylphenyl-*d*-ribamine hydrochloride, whence 2-benzeneazo-5-methyl-4-ethylphenyl-*d*-ribamine, m.p. 152°, and 7-methyl-6-ethyl-9-*d*-1'-ribitylisoalloxazine (II), m.p. 238—240° after incipient decomp. when heated rapidly. β-Naphthyl-1-arabamine, m.p. 156°, obtained by reduction of the condensation product,

$C_{15}H_{17}O_4N$, decomp. 163—164°, of the sugar and β - $C_{10}H_7 \cdot NH_2$ in boiling MeOH, is transformed into 1-benzeneazo-2-arabitylaminonaphthalene, m.p. 193°, and 5:6-benzo-9-1'-arabitylisoalloxazine, decomp. about 275°. β -Naphthyl-d-ribamine, m.p. 157°, affords 1-benzeneazo-2-d-ribitylaminonaphthalene, m.p. 195°, whence 5:6-benzo-9-d-1'-ribitylisoalloxazine (III), decomp. about 290°. The action of (I) on animals on a vitamin-B₂-free diet is stimulating but not prolonged, whereas (II) and (III) are physiologically inactive. H. W.

Optical absorption of porphyrins.—See this vol., 1444.

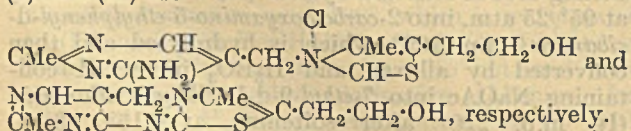
Manufacture of dialkyl-substituted amides of isooxazolecarboxylic acids.—See B., 1936, 1084.

Hydroxyquinolines. II. Synthesis of quino-linoisooxazines. F. PIRRONI (Gazzetta, 1936, 66, 518—524).—8-Hydroxyquinoline, PhCHO, and excess of NH_3 in EtOH give a substance, $C_{23}H_{25}ON_2$, m.p. 156—157°. This is decomposed by boiling dil. HCl with liberation of PhCHO and formation of a (A) cryst. substance, forms a picrate, m.p. 220—221°, and Ac, m.p. 208—209°, and Bz, m.p. 196—197°, derivatives, but gives no metallic compounds or reactions of 8-hydroxyquinoline; it is therefore probably 2:4-diphenyl-5:6-(7':8'-quinolino)-1:3-isooxazine (A). E. W. W.

Manufacture of sulpheneamides.—See B., 1936, 1083.

1-Methyl- $\beta\beta'$ -naphthathiazole and substitution products.—See B., 1936, 977.

Constitution of oryzanin (vitamin-B₁). T. IMAI (Z. physiol. Chem., 1936, 243, II; cf. this vol., 487).—Aneurin (I) and thiochrome (II) contain two CMe groups and in (I) there is a CH_2 bridge between the thiazole and pyrimidine nuclei. KSH with 8-chloro- or 8-bromo-theophylline gives 8-thiotheophylline, which with $CH_2Cl \cdot COMe$ gives the compound $NMe \cdot CO \cdot C \begin{array}{l} \diagup N \cdot CMe \\ \diagdown S \end{array} \cdot CH$, which exhibits no blue fluorescence. (I) is almost quantitatively converted by H_2SO_3 into 4-amino-2-methyl-5-pyrimidylsulphonic acid and 4-methyl-5- β -hydroxyethylthiazole. Hence (I) and (II) are



W. McC.

Aneurin. III. Methyl α -chloro- γ -hydroxypropyl ketone and its application to thiazole synthesis. A. R. TODD, F. BERGEL, and (Miss) A. JACOB. **IV. 5-Thioformamidopyrimidines.** A. R. TODD, F. BERGEL, and KARIMULLAH. **V. Synthesis of 3-pyrimidylthiazolium salts, including an isomeride of aneurin.** A. R. TODD and F. BERGEL (J.C.S., 1936, 1555—1557, 1557—1559, 1559—1562).—III. $OAc \cdot [CH_2]_2 \cdot CHAc \cdot CO_2Et$ with SO_2Cl_2 gives *Et* α -chloro- α - β' -acetoxylethylacetoacetate, b.p. 120—121°/2 mm., which with H_2SO_4 -AcOH

forms *Me* α -chloro- γ -acetoxypopyl ketone, b.p. 85—92°/16 mm. The ketone with thioformamide is converted into 4-methyl-5- β -hydroxyethylthiazole, the *picrate*, m.p. 162—163°, of which is identical with that obtained from aneurin (vitamin-B₁). *Et* α - β' -phenoxyethylacetoacetate, b.p. 148°/4 mm., prepared from $OPh \cdot CH_2 \cdot CH_2Br$ and *Et* sodioacetoacetate, with SO_2Cl_2 affords *Et* α -chloro- α -2-phenoxyethylacetoacetate, b.p. 135—140°/3 mm., hydrolysed to *Me* α -chloro- γ -phenoxypropyl ketone, b.p. 168—172°/12 mm., which with $NH_2 \cdot CSMe$ gives 2:4-dimethyl-5- β -phenoxyethylthiazole (*picrate*, m.p. 122°).

IV. 5-Amino- with dithioacetic acid yields 5-thioacetamido-, m.p. 265—267°, and with dithioformic acid affords 5-thioformamido-4-methyluracil, m.p. 260—262°, which with $CH_2Cl \cdot COMe$ gives 3-(2':6'-dihydroxy-4'-methylpyrimidyl-5')-4-methylthiazolium chloride, m.p. 306° (decomp.). 6-Amino-5-thioformamido-4-methylpyrimidine gives 4-methylpurine at its m.p. 168°. 2-Amino-6-hydroxy-4-ethylpyrimidine, m.p. 247—248°, prepared from *Et* propionylacetate and guanidine carbonate, with PCl_5 gives 6-chloro-2-amino-, m.p. 120—121°, converted (NH_3) into 2:6-diamino-4-ethylpyrimidine, m.p. 160—161°. Thioformylation (K dithioformate) affords 6-amino-, m.p. 178°, and 2:6-diamino-5-thioformamido-4-methylpyrimidine, m.p. 255°, which is converted ($CH_2Cl \cdot COMe$) into 3-(2':6'-diamino-4'-methylpyrimidyl-5')-4-methylthiazolium chloride hydrochloride (+3H₂O), m.p. 255°.

V. 6-Amino-5-thioformamido-4-ethylpyrimidine and *Me* α -chloro- γ -hydroxypropyl ketone give 3-(6'-amino-4'-ethylpyrimidyl-5')-4-methyl-5- β -hydroxyethylthiazolium chloride hydrochloride (+H₂O), m.p. 220° (decomp.), which is not identical with aneurin hydrochloride, and shows no measurable physiological activity, in common with the following: 3-(6'-amino-4'-ethylpyrimidyl-5')-4-methylthiazolium chloride hydrochloride, m.p. 252—253° (decomp.), 3-(6'-amino-4'-methylpyrimidyl-5')-4-methyl-5- β -hydroxyethylthiazolium chloride hydrochloride (+H₂O), m.p. 250° (decomp.), and 4-methylthiazolium chloride hydrochloride (+2H₂O), m.p. 254—255° (decomp.). 2:6-Dihydroxy-8-thiopurine with $CH_2Cl \cdot COMe$ yields 2:6-dihydroxy-4'-methylthiazolo-(2':3':8:7)-purine, m.p. >250°, but 8-thio-6-ethylpurine, m.p. >300°, does not condense satisfactorily with chloroketones. The structure of aneurin is discussed. F. R. S.

Lupin alkaloids. XI. Octahydropyridocoline-norlupinane relationship. G. R. CLEMO, T. P. METCALFE, and R. RAPER (J.C.S., 1936, 1429—1431).—*Et* 2-methylpyrrolidine-5-acetate, $CH_2Cl \cdot CH_2 \cdot CO_2Et$, and NaOAc give *Et* 2-methylpyrrolidine-5-acetate-1- β -propionate, b.p. 168—169°/14 mm., which is cyclised (K) to 7-keto-3-methyloctahydropyrrocoline, b.p. 72—75°/1 mm. (*picrate*, m.p. 204°), reduced (Wolff) to 3-methyloctahydropyrrocoline and a substance, b.p. 95°/1 mm. [*picrolonate*, m.p. 245° (decomp.)]. *Me* piperidine-2-acetate, $CH_2Cl \cdot CH_2 \cdot CO_2Me$, and NaOAc afford *Me* piperidine-2-acetate-1- β -propionate, b.p. 170—172°/1 mm., cyclised (K) to 2-keto-octahydropyridocoline, b.p. 70—72°/1 mm. (*picrate*, m.p. 211°), which is reduced (Zn-Hg) to norlupinane, also obtained by reduction (Wolff) of 1-keto-octahydropyridocoline.

These results support the *cis-trans* formulation of octahydropyridocoline and norlupinane.

F. R. S.

Electrolytic reduction of vasicine. K. S. NARANG and J. N. RAY (J.C.S., 1936, 1570).—The substances reported (this vol., 869) to be dissimilar are now shown to be identical.

F. R. S.

Ambaline, a new alkaloid from *Pycnarrhena manillensis*, Vidal. G. Q. QUIBILAN and A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1933, 3, 353—364).—*Ambaline*, $C_{38}H_{42}O_{10}N_2$, m.p. 123°, $[\alpha]_D^{25} +143.2^\circ$ in $CHCl_3$ [*aurichloride*, m.p. 185° (decomp.); *platinichloride*, m.p. 260°; *dihydrochloride*, m.p. 265°; *dihydrobromide*, m.p. 195—197° (decomp.); *dihydriodide*, m.p. 245° (decomp.); *methiodide*, m.p. 263°; *oxime*, m.p. 197° (decomp.); 2:4-dinitrophenylhydrazone, m.p. 96°], has been isolated and its colour reactions determined. It contains $\cdot CH_2O_2$, CO, 3 OMe, and 2 NMe, and is toxic.

F. R. S.

Ambalinine, a new non-phenolic alkaloid from *Pycnarrhena manillensis*, Vidal. I. VILLANOS and A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1935, 4, 338—341).—A non-phenolic alkaloid, *ambalinine*, $C_{15}H_{12}O(OMe)_2 \cdot NMe$, m.p. 203—204° [*platinichloride*, m.p. 240° (decomp.); *aurichloride*, m.p. 170° (decomp.); *picrate*, m.p. 238° (decomp.)], has been isolated.

F. R. S.

Alkaloids of *Corydalis ambigua* of China, Cham et Sch. (Yen-hu-So). VI. Identification of *corydalis D* and *M*. T. Q. CHOU (Chinese J. Pharmacy, 1936, 10, 507—511).—*Corydalis D* (I), $C_{19}H_{17}O_4N$, $[\alpha]_D^{25} -305^\circ$, was oxidised by I in EtOH to a quaternary iodide, m.p. $>300^\circ$, reduced by Zn- H_2SO_4 to *dl*-tetrahydrocoptisine, m.p. 220°. (I) is therefore the *l*-isomeride of this substance. *Corydalis M*, $C_{21}H_{23}O_5N$, m.p. 160°, optically inactive, contains 2 OMe and 1 CH_2O_2 , and is probably identical with β -homochelidonine.

P. W. C.

Microscopic investigation of alkaloids in ergot.

I. Ergotamine and ergotaminine. A. KOFLER (Arch. Pharm., 1936, 274, 398—414).—The compound of ergotamine with $2COMe_2 \cdot 2H_2O$ (cf. Stoll, A., 1923, i, 127), m.p. 172—174°, and compounds with H_2O , m.p. 174—176°, C_5H_5N , m.p. 172—176°, MeOH, m.p. 208—210° (decomp.), and EtOH, m.p. 208—210°, form monoclinic crystals; compounds with C_6H_6 , m.p. 168—172°, and $(CH_2Cl)_2$, m.p. 182—186°, are rhombic. Compound with Et_2O , m.p. 183—185°. n_D for the axes of these compounds and ergotaminine are recorded.

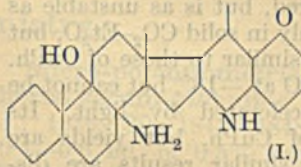
F. R. G.

Alkaloids of ergot. VII. isoErgine and isolysergic acids. S. SMITH and G. M. TIMMIS (J.C.S., 1936, 1440—1444).—The levorotatory physiologically active ergot alkaloids can be transformed readily into alkaloids of high dextrorotation with weak physiological action and the change is readily reversed. Ergine can be converted ($EtOH-H_3PO_4$) into *isoergine* (I), m.p. 242° (decomp.), $[\alpha]_{5461}^{20} +25^\circ$ in C_5H_5N [*hydrochloride*, m.p. 269° (decomp.)]. (I) is hydrolysed to lysergic acid (II), which is converted by hot H_2O into *isolysergic acid* ($+2H_2O$), m.p. 218° (decomp.) $[\alpha]_{5461}^{20} +368^\circ$ in C_5H_5N [*nitrate* ($+H_2O$), m.p.

185° (decomp.); *Me* ester, m.p. 170° (decomp.), $[\alpha]_{5461}^{20} +236^\circ$ in $CHCl_3$], reconverted into (II) by aq. KOH. (II) with $Ba(OH)_2$ yields *inactive lysergic acid* ($+2H_2O$), m.p. 250° (decomp.) [*Me* ester, m.p. about 160° (decomp.)], which cannot be reconverted into (II).

F. R. S.

Alkaloids from *Solanum pseudocapsicum*, L. G. BARGER and H. L. FRAENKEL-CONRAT (J.C.S., 1936, 1537—1542).—*Solanocapsine* (I), $C_{26}H_{44}O_2N_2 \cdot H_2O$, m.p. 222°, $[\alpha]_D +25.5^\circ$ [*dihydrochloride* ($+H_2O$), m.p. $>280^\circ$; *Ac_2* derivative, m.p. 150—160°] is dehydrated to *aposalanocapsine*, with HNO_2 forms a *NO*-compound (II), m.p. 194° (H_2 -derivative, m.p. 211—212°), and with $COMe_2$ yields a compound, m.p. 233°, which with Ac_2O affords *monoacetylsolanocapsine*, m.p. 238°. Oxidation of (II) gives an acid, m.p. 226—227°, and a neutral substance, m.p. 218°. *Solanocapsidine*, $C_{26}H_{42}O_4N_2$, m.p. about 305°, is dehydrogenated (Se) to methylcyclopentenphenanthrene, 2-methyl-5-ethylpyridine (*picrate*, m.p. 163°), and 4-methyl-2-ethylpyridine (?) (*picrate*, m.p. about 125°). On the basis of the reactions the formula for (I) is suggested.



The two bases may be secondary products, formed during isolation.

F. R. S.

Anodic oxidation of brucine and nicotine. F. FICHTER and H. STENZL (Helv. Chim. Acta, 1936, 19, 1171—1175).—Electrolytic oxidation of brucine in H_2SO_4 at a PbO_2 anode affords dehydrobisapomethylbrucine, $C_{21}H_{22}O_4N_2$, or, if reaction is prolonged, a red-brown base. Electrolytic chlorination of brucine yields a mixture of substances, $C_{21}H_{27}O_7N_2Cl_7$. Nicotinic acid is obtained by electrochemical oxidation of nicotine in H_2SO_4 at a Pt anode. The products are therefore identical with those obtained by purely chemical methods.

H. W.

Manufacture of deoxymorphine-C and dihydromorphine-D.—See B., 1936, 1018.

Structure and toxicity of arsinic acids of the diphenylamine series. V. A. ISMAILSKI and A. M. SIMONOV (Bull. Soc. chim., 1936, [v], 3, 1739—1753).—The introduction of OH or NHAc at 4' in 2-nitro- or 2-amino-diphenylamine-4-arsinic acid (A., 1934, 1118) reduces the toxicity, and a similar and greater effect (especially of OH) is produced at 3'. Reduction of toxicity is less with 4'-OMe than with 4'-OH, and still less with 4'-OEt. The use of the effect of substituents to reduce toxicity of arsinic acids for pharmacological use is suggested, and the electronic transmission of the effect to the AsO_3H_2 group is discussed. The following are prepared. From 4-chloro-3-nitrophenylarsinic acid (I) and NH_2R : 2-nitro-3'- (II) and 4'-acetamido- (III), 4'-hydroxy- (IV), 4'-ethoxy- (V), 3'-hydroxy- (VI), 4'-methoxy-, and 2'-methoxy-diphenylamine-4-arsinic acid. From (II), (III), (IV), and (V), using $Na_2S_2O_4$: 2-amino-3'- and 4'-acetamido-, 4'-hydroxy-, and 4'-ethoxy-diphenylamine-4-arsinic acid. [The NH_2 -compound from (VI) could not be isolated.] From 2-nitro-diphenylamine-4-arsinic acid, the 2-amino-acid. 6-Chloro-3-nitro-

phenylarsinic acid (obtained from 6-chloro-3-nitro-aniline) gives resinous condensation products. (I) and benzidine yield 3-nitro-4-benzidinophenylarsinic acid. E. W. W.

Manufacture of arsenobenzenesulphoxylates.—See B., 1936, 1018.

Manufacture of arsenic compounds of the naphthaquinone series.—See B., 1936, 1018.

Relative activities of organo-metallic compounds. XIII. Copper and silver. H. GILMAN and J. M. STRALEY (Rec. trav. chim., 1936, 55, 821—834; cf. this vol., 1279).—MgPhI and CuI in Et₂O at 0° give 86% of CuPh, which, besides the known reactions, with AcCl gives 66% of CPhMe, with BzCl 55% of CPh₂, with CH₂:CH:CH₂Br 31% of CH₂Ph:CH:CH₂, with H₂O 36% of C₆H₆, and with PhNCO 14% of NHPhBz with, in most cases, much Ph₂. With other reagents only Ph₂ is obtained. *Cu p-anisyl* was also prepared, but is as unstable as CuPh. *Cu ethyl* is stable only in solid CO₂-Et₂O, but the solution gives reactions similar to those of CuPh. *Ag phenyl* is prepared in Et₂O at -18°, but cannot be isolated; its prep. is accelerated by light. Its reactions resemble those of CuPh, but yields are usually lower. These and similar results are discussed. The order of stability and of decreasing reactivity of MR is M=Cu>Ag>Au, R=aryl>alkyl, and of decreasing reactivity ZnR₂>CuPh>HgR₂. R. S. C.

Phenylmercury nitrate and some other phenylmercury salts. T. B. GRAVE, S. E. HARRIS, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1936, 25, 752—756).—Hg Ph nitrate, from the acetate and NaNO₂, is HgPh·OH, HgPh·NO₃; in presence of C₅H₅N, a compound, HgPh·NO₃·C₅H₅N, m.p. 182—183°, is formed. Aq. Hg Ph hydroxide with the appropriate acid affords *Hg Ph lactate*, m.p. 160—161°, *basic gluconate*, m.p. 171—172° (decomp.), *phenolsulphonate*, m.p. 162—164° (decomp.), and *hydroxybutyrate*, m.p. 149—149.5° (decomp.).

F. O. H.

Mercury compounds containing nitrogen [bactericides and fungicides].—See B., 1936, 1019.

Relative reactivities of organometallic compounds. XIV. Orientation in metalation. H. GILMAN and R. H. KIRBY (J. Amer. Chem. Soc., 1936, 58, 2074—2075).—Prolonged interaction of HgEt₂ (0.02 g.-mol.) and K (0.08 g.-atom) in C₆H₆ (35—75 c.c.) gives C₂H₆ (with small amounts of H₂ and C₂H₄), KPh, and *o*- and *p*-C₆H₄K₂, since subsequent treatment with CO₂ affords BzOH (33—45%) and *o*- and *p*- (14—17%) -C₆H₄(CO₂H)₂; KPh appears to be formed thus: C₂H₆+KEt→KPh+C₂H₆. KPh is *o-p* orienting. The order of reactivity KEt>NaEt>LiEt (no reaction), has been established. H. B.

[Organic compounds of tin.] M. K. KOZESCHKOV (Bull. Soc. chim., 1936, [v], 3, 2069—2070).—A claim for priority against Lesbre (A., 1935, 966).

H. W.

Arylstannonic acids and their halogenated derivatives. M. LESBRE (Bull. Soc. chim., 1936, [v],

3, 2071—2072).—A reply to Kozeschkov (preceding abstract). H. W.

Separation of amino-acids by means of their copper salts. II. Investigation of the methyl alcohol-soluble copper salt fraction, and the yield of protein from gliadin. B. W. TOWN (Biochem. J., 1936, 30, 1837—1844).—The Cu salts of NH₂-acids from proteins can be separated into three fractions: (a) those sol. in MeOH and H₂O, (b) those insol. in MeOH, sol. in H₂O, (c) those insol. in MeOH or H₂O. From gliadin 97% of the total N is accounted for in these fractions. The CdCl₂ ppt. from (a) contains mainly proline; the amount corresponds with a proline content in gliadin of 10.3%. This val. is > that obtained by isolation, but < that corresponding with total non-NH₂-N; this is due to the presence of diketopiperazines. F. A. A.

Micro-determination of glycine in protein hydrolysates. B. W. TOWN (Biochem. J., 1936, 30, 1833—1836).—3 : 6-Dinitro-2 : 5-dihydroxy-*p*-benzoquinone (I) (prep. given) is a sp. precipitant for glycine, in the absence of inorg. cations. Using (I) the glycine content of gelatin is found as 25.5%, but the data for caseinogen indicate a glycine content of 3.4—3.7%. F. A. A.

Spectrophotometry of proteins. I. Absorption spectra of tyrosine, tryptophan, and their mixtures. II. Determination of tyrosine and tryptophan in proteins. E. R. HOLIDAY (Biochem. J., 1936, 30, 1795—1803).—The absorption curves of tyrosine (I) and tryptophan (II) are determined between 260 and 305 mμ in acid, neutral, or alkaline solution, and a method for determination of their concns. in mixtures of the two is described. Determination of (I) and (II) in 5 mg. of protein by this method is described and the results are compared with those by chemical analysis. The errors of the method and a means of correcting for pigment impurities are discussed. P. W. C.

Diazotization of proteins. H. EAGLE (Proc. Soc. Exp. Biol. Med., 1936, 34, 39—40).—The colour which many proteins give when treated with HNO₂ and coupled with aromatic amines or phenols in presence of alkali is probably due in part to the presence of tryptophan. W. O. K.

Iodine [in protein]. E. NOLTE (Arch. Pharm., 1936, 274, 415—418).—Hydrolysis of iodoprotein with Sr(OH)₂ gives an active product (14% I) resembling that given by Ba(OH)₂ (cf. Mattis, A., 1931, 1463). Ca(OH)₂ and superheated steam do not give an active product. F. R. G.

Hydrogen bond and the structure of proteins. D. M. WRINCH and D. J. LLOYD (Nature, 1936, 138, 758—759; cf. this vol., 619).—Possible structural formulæ using the H linking as the mechanism whereby laminar protein mols. are formed from closed polypeptides are elaborated. L. S. T.

Semi-micro-determination of carbon in organic compounds. J. A. SANCHEZ (J. Pharm. Chim., 1936, [viii], 24, 297—310).—The compound is heated with solid KMnO₄ in a sealed tube and the CO₂, collected initially in NaOH, is liberated quantitatively

with 25% H_3PO_4 and distilled into standard NaOH containing $BaCl_2$. J. L. D.

Determination of carbon and hydrogen by semi-micro-combustion. E. V. ZAPPI and R. LABRIOLA (Anal. Asoc. Quím. Argentina, 1936, 24, 47—50).—Satisfactory results are obtained in the combustion of 20—30 mg. of material using the method of Berger (A., 1932, 410). F. R. G.

Selective combustion of hydrogen, carbon monoxide, and methane by palladium catalysts.—See this vol., 1472.

Determination of vanillin with 2:4-dinitrophenylhydrazine. N. RUBIN and A. BLOOM (Amer. J. Pharm., 1936, 108, 387—388).—Contrary to Iddles *et al.* (A., 1935, 101) a technique is described whereby vanillin may be accurately determined (99.44%)

gravimetrically as its 2:4-dinitrophenylhydrazone even in presence of 10% EtOH. J. W. B.

Extremely sensitive reaction for some nitrogenous bases. H. WACHSMUTH (J. Pharm. Belg., 1935, 17, 795—798; Chem. Zentr., 1936, i, 379).—Morphine, pyramidone, apomorphine, and adrenaline give sensitive colour reactions (described) with $CuSO_4$ and CN' , SCN' , $Fe(CN)_6'''$, or nitroprussides. H. N. R.

Determination of nicotine. W. HAMMERLE and W. WEBER (Mitt. Lebensm. Hyg., 1936, 27, 46—48).—The silicotungstic acid method is preferred, but the nicotine should be liberated originally from 2 g. of sample in 40 c.c. of H_2O with 5 c.c. of 30% NaOH; 2 c.c. of 10% reagent per 250 c.c. of distillate should be used for pptn., which is complete after 5 min. at 80° and 3 hr. in the cold. J. G.

Biochemistry.

Rôle of the vagus in the automatic regulation of respiration. W. HESS (Pflüger's Arch., 1936, 237, 24—39).—Disagreement between the author's previous results and those of ter Braak and van Niekerk is explained. M. A. B.

Physiological effects of high pressures. L. A. SHAW (J. Ind. Hyg., 1936, 18, 486—496).—Pulmonary emboli can be absorbed by breathing O_2 under 3 atm. pressure without harmful effect. "Compressed air disease" is caused by the accumulation of N_2 bubbles in the venous circulation following exposure to high pressures. P. G. M.

Biological importance of phosphate esters of red corpuscles. E. FREUDENBERG (Z. Kinderheilk., 57, 427—441; Chem. Zentr., 1936, i, 100).—Arterialisation of blood inhibits phosphatolysis. P esters of erythrocytes in conjunction with phosphatase control the level of blood-P, and form a P reserve which in acidosis serves to eliminate H' . P ester content of erythrocytes is lowered in rickets but increases after sp. therapy. A. G. P.

Secretin XI: its effect on the reticulocytes of the circulating blood. J. FERGUSON (Endocrinol., 1936, 20, 683—684). R. N. C.

Physico-chemical properties of hæmocyanins. IV. Variation in the osmotic pressure of hæmocyanin during prolonged inanition. A. ROCHE and J. ROCHE (Bull. Soc. Chim. biol., 1936, 18, 1503—1512).—Determinations of osmotic pressure show that during hibernation of *Helix pomatia* and aestivation of *H. pisana* the mol. wt. of the hæmocyanin considerably decreases. The physiological significance of this is discussed. A. L.

Serum-bilirubin content of the blood of rats consuming a ration deficient in inorganic salts. J. M. ORTEN and A. H. SMITH (Proc. Soc. Exp. Biol. Med., 1936, 34, 72—74).—The bilirubin content of the blood of rats on a diet deficient in inorg. salts, and in consequence exhibiting a polycythæmia, does not differ significantly from that of controls. The polycythæmia is therefore not the result of abnormally slow erythrocyte destruction. W. O. K.

Micro-potentiometric titrations of normal horse serum-globulins. A. G. OGSTON (Biochem. J., 1936, 30, 1845—1848).—A method using only 0.4—0.6 ml. of 0.5% protein solution is described. The titres of horse serum-pseudoglobulins (I) are < those of the euglobulins (II). The variation between individual samples is greater for (II). Both proteins after drying, and (II) after $(NH_4)_2SO_4$ pptn., give abnormal curves and indicate increased polydispersion in solution. CH_2O titration indicates that any new groups so formed are not NH_2 , and that the greater titre of (II) is not due to NH_2 . There is no apparent correlation between the titres and the tyrosine content. F. A. A.

Constituents of acid globulins. Protein C. M. DOLADILHE (Ann. Inst. Pasteur, 1936, 57, 443—462).—Flocculation of sera produced by dilution with acidulated H_2O is mainly due to the effect of the p_H on the acid globulin fraction rather than to lowered salt concn.; the flocculation frequently produced by distilled H_2O is effected by dissolved CO_2 , the ppt. consisting of acid globulins. The application of these facts to the flocculation of syphilitic sera is considered. Details of the prep. and the effect of heat on the physical properties of protein C are given (cf. this vol., 875). P. G. M.

Biochemistry of serum irradiated with artificial light. VIII. Analysis of serum-protein. M. MURAYAMA (J. Orient. Med., 1936, 24, 79—80).—Irradiation with ultra-violet light or with X-rays caused a small decrease in the total N and albumin-N, but an increase in the globulin-N in human serum. NUTR. ABS. (m)

Limits of the reaction for determination of the tyrosine index of serum-polypeptides. V. CIOCALTEU and G. TANASESCO (Compt. rend. Soc. Biol., 1936, 123, 49—50).—A modified method utilising the Folin-Ciocalteu reagent (A., 1927, 892) is proposed since that of Goiffon and Spacy (A., 1935, 374) is accurate over only a narrow range. H. G. R.

Nucleotide-nitrogen content of human leucocytes. F. W. ALLEN, S. P. LUCIA, and J. J. EILER

(Proc. Soc. Exp. Biol. Med., 1936, 34, 609—611).—In cases of myeloid leucæmia with high leucocyte counts the nucleotide-N of the leucocytes is >50% of the total. The nucleotide content of whole blood decreases with a regression of the leucocyte count, when the erythrocyte count is const. P. G. M.

Quantitative isolation of histamine and tyramine from plasma and serum. A. SCHWARTZ and A. RIEGERT (Compt. rend. Soc. Biol., 1936, 123, 219—223).—Adsorption on Permutit is followed by elution with saturated aq. NaCl. H. G. R.

Determination of the urea content of blood-serum. P. SORGDRAGER (Pharm. Tijds. Nederl.-Indië, 1935, 12, 241—243; Chem. Zentr., 1936, i, 125).—An improved apparatus for, and corrections to be applied to results obtained by, van Assenraad's method (A., 1929, 1326) are described. H. N. R.

Normal phenol content of blood. M. CASTEX and A. ARNAUDO (Publ. méd., 1935, 1, No. 3).—In normal blood vals. were: free phenols (I) 1—1.3, total (I) 1.1—1.4, conjugated (I) 0—0.3 mg. per 100 c.c. Normal variations are small even when large amounts of (I) are eliminated in urine.

CH. ABS. (p)

Determination of fat in 0.1 c.c. of blood or serum. G. SURÁNYI and P. VÉGHÉLYI (Magyar orvosi Arch., 1935, 36, 169—175; Chem. Zentr., 1936, i, 391—382).—Total fat is extracted with 15 c.c. of EtOH, and total fat without lecithin with COME₂, each from 0.05 c.c. of blood. The solutions are brought to 10 c.c., and 2 c.c. are slowly treated with 5 c.c. of 10% HCl+1% of BuOH. The turbidity produced is measured photometrically. J. S. A.

Partition of reduced ascorbic acid in blood. D. J. STEPHENS and E. E. HAWLEY (J. Biol. Chem., 1936, 115, 653—658).—The content in human white blood cells is > that in whole blood, plasma, or red cells. Abnormally high vals. in the whole blood of leucæmic patients are due to the high leucocyte count. F. O. H.

Determination of reduced ascorbic acid in small amounts of blood. C. J. FARMER and A. F. ABT (Proc. Soc. Exp. Biol. Med., 1936, 34, 146—150).—The method enables the ascorbic acid content of 0.3 ml. of blood to be determined by titration from a special micro-burette, with 2:6-dichlorophenol-indophenol. HPO₃ is used for deproteinisation.

W. McC.

Influence of muscular action on blood-sugar and -catalase. H. KOEPPE (Klin. Woch., 1935, 14, 667—670; Chem. Zentr., 1936, i, 372).—Blood-sugar and -catalase contents are changed simultaneously and in opposite directions after carbohydrate feeding, during fasting, and during muscular activity.

A. G. P.

Hyperglycæmia and augmentation of the undetermined carbohydrate of the plasma following experimental shock in the dog. O. LAMBRET, G. BIZARD, and J. DRIESSENS (Compt. rend. Soc. Biol., 1936, 123, 413—415).—The phenomena appear to be connected with the adrenal gland. H. G. R.

Effect of hypophysectomy on blood-sugar in Rhesus monkeys. P. E. SMITH, L. DOTTI, H. H.

TYNDALE, and E. T. ENGLE (Proc. Soc. Exp. Biol. Med., 1936, 34, 247—249).—After fasting, hypophysectomy reduced the sugar content of the blood from 90—100 to 20—90 mg. per 100 c.c.

W. McC.

Determination of small amounts of carbon monoxide in blood. H. BURESCH and V. LUNIATSCHEK (Arch. Gewerbepath. Gewerbebyg., 1936, 7, 182—191).—An improved apparatus (cf. A., 1934, 1241) is described. M. A. B.

Residual nitrogen of the blood and its principal components. I. Normal distribution. P. LARIZZA (Arch. exp. Path. Pharm., 1936, 182, 617—632).—Data for the total residual (*i.e.*, non-protein) N (I) and its distribution in human blood are tabulated. The average distribution-ratios between corpuscles and serum are: total (I) 1.75, urea-N 0.70, NH₂-N 1.71, total creatinine-N 1.67; that of uric acid-N is irregular. The undetermined (I) in serum was 15% and in corpuscles 44% of the total (I). F. O. H.

Calcium and inorganic phosphorus content of blood-serum of swine. E. H. HUGHES (J. Agric. Res., 1936, 53, 267—279).—Serum-Ca and -inorg. P in young pigs were > in older ones. Immediately before and after farrowing Ca vals. increased and those of P declined, in comparison with those for non-pregnant sows. Ingestion of Ca increased serum-Ca temporarily, a prolonged increase (with simultaneous decrease in inorg. P) following continuous feeding of large proportions of CaCO₃. Continuous feeding of a Ca-deficient diet lowered serum-Ca, the -inorg. P being increased in mature but decreased in young animals. Low serum-Ca caused Ca tetany.

A. G. P.

Copper and iron in human blood. IV. Normal children. A. SACHS, V. E. LEVINE, and A. A. FABIAN (Arch. Int. Med., 1936, 58, 523—530).—Cu varies inversely as Fe in the blood of normal children. The blood of the new-born contains Fe, 51.79 mg., Cu, 83×10⁻⁶ g. per 100 c.c.; in an age group 1½ months—15 years the figures were Fe, 40.51 mg., Cu, 171×10⁻⁶ g.

P. G. M.

Effect of boiler-makers' work on the composition and properties of their blood. Water shift between blood and tissues and between serum and cells. MEER S. MISCHKIS and MARIA S. MISCHKIS (Ukrain. Biochem. J., 1936, 9, 369—380).—The H₂O content of blood cells of workers in all branches of the trade increases by 0.7—1.4% towards the end of the day. No increase in H₂O content of serum is found. The H₂O content of whole blood, serum, and blood cells of boiler sweeps is > that of other boiler workers. These effects are contrary to those observed during short periods of strained work. F. A. A.

Determination of blood-p_H by the glass electrode. V. Glass micro-electrode and the p_H of arterial, venous, and capillary blood. H. YOSHIMURA (J. Biochem. Japan, 1936, 23, 335—350; cf. this vol., 682).—A glass electrode, applicable to 0.07 c.c. and accurate to 0.02 p_H, is described. Direct measurements on rabbits and examination of blood removed from men show that the p_H of arterial blood

equals that of capillary but is $>$ that of venous blood by approx. 0.03. F. O. H.

Preservation of sera by desiccation in the frozen state without the use of refrigerants. R. I. N. GREAVES and M. E. ADAIR (J. Hyg., 1936, 36, 507—513).—Antisera are desiccated after freezing by rapid evaporation in a high vac. over P_2O_5 . Preliminary evacuation of the sera in the absence of the drying agent overcomes violent frothing. The method can be applied to the drying of bacteria. W. L. D.

Food allergy. A. W. OELGOETZ, P. A. OELGOETZ, and J. WITTEKIND (Amer. J. Digest. Dis. Nutrition, 1934, 1, 730—737).—Hypersensitiveness to foods is probably caused by excess of free food (free from enzymes) in the blood-serum, this excess being due to a low pancreatic threshold. CH. ABS. (p)

Blood-groups and -radiation. W. W. SIEBER and H. SEFFERT (Biochem. Z., 1936, 287, 109—112).—The blood of a normal healthy man is strongly mitogenetic. When the same amount of blood of two individuals is mixed *in vitro*, the mixed blood is mitogenetic only when it results from a combination of definite blood-groups. Mixtures of bloods from the same blood-groups, of group *O* with another group, and of group *AB* with another group, remain active, but those of group *A* with group *B* are inactive. P. W. C.

Hæmolysis produced by small variations in p_H . R. VAVRA (Compt. rend. Soc. Biol., 1936, 123, 161—163).—The phenomenon is peculiar to red cells and is observed only when they are fresh. H. G. R.

Influence of the plasma on the hæmolysis produced by small variations in p_H . R. VAVRA (Compt. rend. Soc. Biol., 1936, 123, 163—165).—When produced in presence of plasma, hæmolysis is probably caused by the plasma itself. H. G. R.

Influence of trisodium citrate on hæmolysis of red cells by alcohol. J. VIGNATI and M. RAUCHENBERG (Compt. rend. Soc. Biol., 1936, 123, 165—166).—Hæmolysis is inhibited by EtOH up to 50% concn. H. G. R.

Production of fibrinolysin *in vivo*. E. NETER (Proc. Soc. Exp. Biol. Med., 1936, 34, 735—736).—The abdominal washings of mice killed by injection of saline suspensions of various strains of hæmolytic streptococci (but not pneumococci) contained fibrinolysin. P. G. M.

Decalcifying anticoagulants. J. H. FERGUSON (Proc. Soc. Exp. Biol. Med., 1936, 34, 797—798).—Incubation of a thrombin solution with 50—100 equivs. of oxalate or citrate for varying times produces both an immediate retardation and a progressive inactivation of clotting. P. G. M.

Effect of sulphur compounds on blood coagulation. J. H. STERNER and G. MEDES (Proc. Soc. Exp. Biol. Med., 1936, 34, 597—599).—Addition of cystine to the coagulation system before thrombin formation has a marked inhibitory effect. Inhibition is only slight in the presence of thrombin. Methionine has an inhibitory effect *in vivo* but not *in vitro*. P. G. M.

Kinetics of thrombin action. E. WÖHLISCH, W. DIEBOLD, and O. KIDERLEN (Pflüger's Arch., 1935, 237, 599—608).—With increasing fibrinogen (I) concn. up to 0.3—0.4% the rate of clotting increased, but decreased again above his concn.; the max. rate occurred at the blood concn. of (I). The influence of temp. on rate of clotting became progressively less with decreasing concn. of (I) and finally disappeared. M. A. B.

Blood in hæmophilia. A. J. PATEK, jun., and F. H. L. TAYLOR (Science, 1936, 84, 271—272).—The difference between normal and hæmophilic blood appears to be due either to a qual. difference of their prothrombins or to other substances probably associated with them. L. S. T.

Venom of *Lachesis (Bothrops)* snakes. IV. Action of the coagulatory principle *in vivo*. D. VON KLOBUSITZKY and P. KÖNIG (Arch. exp. Path. Pharm., 1936, 182, 577—583; cf. this vol., 1010).—The activity of preps. free from protein, of low toxicity, and effective in doses of 5×10^{-10} g. per c.c. of blood, depends on the time between administration (pigeons) and removal of blood and on concn. F. O. H.

Rapid process for macroscopic agglutination after centrifuging. R. LE GUYON (Compt. rend. Soc. Biol., 1936, 123, 239—240).—After centrifuging the mixture of serum and bacterial emulsion, the clot is redispersed by shaking, when agglutination can be observed. H. G. R.

Relation between complement and prothrombin. A. J. QUICK (J. Immunol., 1935, 29, 87—97).—A close relation in respect of chemical and physiological properties is indicated. Complement and prothrombin are not identical. CH. ABS. (p)

General properties of vegetable agglutinins and precipitins. T. FRÉMONT (Compt. rend. Soc. Biol., 1936, 123, 417—418).—Sp. agglutinins are more readily detected in infected plants than precipitins. H. G. R.

Distribution of precipitin in serum-globulins of different species. B. F. CHOW (Proc. Soc. Exp. Biol. Med., 34, 651—653).—The antibody in the pseudoglobulin (I) of antipneumococcus horse serum (sol. at p_H 5.5) is completely pptd. at 7.6; no such pptn. occurs in rabbit (I), the main portion of the antibody being conc. in the euglobulin fraction. P. G. M.

Albuminous precipitins. M. BORNAND (Mitt. Lebensm. Hyg., 1936, 27, 24—26).—Precipitin reactions given by antiserum, prepared by immunisation of a rabbit with the muscle-albumin of a chamois or cow, with albuminous substances extracted from the blood or flesh of various animals are described. J. G.

Distribution of antibody to crystalline ovalbumin in rabbit serum. M. E. ADAIR and G. L. TAYLOR (J. Hyg., 1936, 36, 564—569).—Pooled antisera from rabbits injected with ovalbumin were fractionated with $(NH_4)_2SO_4$ to investigate the distribution of the antibody (I) in the serum-proteins. Albumin contained no (I), but all the globulin fractions contained (I) at a fairly uniform concn. W. L. D.

Specificity of the complement fixation test for amoebiasis. E. WEISS and L. ARNOLD (Amer. J. Digest. Dis. Nutrition, 1934, 1, 548—552).—EtOH and COMe₂ extracts of *E. histolytica* yield a sp. antigen, by injection of which a sp. anti-amoebic serum can be produced. Ox heart lipin antigens used in the Wassermann and the Kahn tests give non-sp. reactions with serum from amoebic dysentery patients and that from various protozoa. The lipins produce antisera containing non-sp. antibodies.

CH. ABS. (p)

Union with complement as a surface reaction. II. Changes of surface activity of serum after heat-inactivation of complement function. III. Cause of the dependence of the amount of protein for union on the degree of sensitisation of antigen cells. F. SEELICH (Biochem. Z., 1936, 287, 1—8, 9—17; cf. this vol., 1335).—II. A series of curves shows the σ of fresh and heat-inactivated guinea-pig's serum, both undiluted and at varying dilutions with 0.9% NaCl, against paraffin oil as measured by du Noüy's interfacial tensiometer. The σ of fresh serum is always about 30% < that of inactivated serum, the surface activity greatly increasing during inactivation. At greater dilutions the σ -time curves of normal and heat-treated serum tend to cross. The cause of this increase in surface-active material is discussed.

III. The changes occurring when antigen cells unite with sp. antibody in which the amount of complement protein bound is greater the greater is the degree of sensitisation, are explained in terms of an increase in σ at the absorbing surface, σ progressively increasing with increasing sensitisation.

P. W. C.

Ultrafiltration of type I antipneumococcal sera. K. GOODNER, F. L. HORSEFALL, jun., and J. H. BAUER (Proc. Soc. Exp. Biol. Med., 1936, 34, 617—619).—The smallest sp. antibody of antipneumococcal rabbit serum corresponds with a pore-size of 11 m μ and of horse serum to 44 m μ ; the mass of the latter is 64 times that of the former. The antibody of conc. horse serum requires a pore-size of 176 m μ .

P. G. M.

New preparation of type-specific polysaccharide from pneumococcus, type I. B. F. CHOW (Proc. Soc. Exp. Biol. Med., 1936, 34, 667—669).—By a method of prep. minimising hydrolysis, a polysaccharide (I) was obtained which reacted with homologous immune-rabbit serum, previously absorbed with the acetylpolysaccharide (II), but not *vice versa*. (I) produced active immunity in mice, and may be the precursor of (II).

P. G. M.

Precipitation of diphtheria anatoxin by alum. F. FARAGÓ (Magyar orvosi Arch., 1935, 36, 176—182; Chem. Zentr., 1936, i, 366).—Conditions for obtaining the best prep. are examined.

A. G. P.

Urea as solvent for antigen extracts. E. M. MACKAY and R. W. LAMSON (Proc. Soc. Exp. Biol. Med., 1936, 34, 123—125).—Conc. aq. solutions of urea are suitable solvents for antigens which are only slightly or not at all changed on dissolution.

W. McC.

Antigenic properties of proteins linked through ureide or azo-groups to aromatic nuclei. W. MUTSAARS and P. E. GRÉGOIRE (Compt. rend. Soc. Biol., 1936, 123, 144—148). H. G. R.

Histochemical detection of mineral constituents of tissues. L. LISON (Bull. Acad. roy. Belg., 1936, [v], 22, 951—967).—An account of difficulties in determining the distribution of Cl and K in animal tissues by histochemical methods. Cl, which exists only in the diffusible form, cannot be accurately demonstrated; non-diffusible K can be shown if the tissue is previously fixed.

J. L. D.

Determination of small amounts of iodine in organs, particularly in ox thyroid. W. RUFF (Biochem. Z., 1936, 287, 40—49).—A modification of the Fellenberg method, designed to prevent loss of I on ashing, is described. Right and left sides of the thyroid and the glands of male and female animals have the same I content. The I content varies considerably with the time of the year, having the highest vals. in winter and the lowest in summer. Glands of animals living on the coast are richer in I than those of animals from inland. The thyroxine contents of the glands are independent of the total I content. The pituitary of female animals contains more I than that of male animals and the anterior lobes are richer in I than the posterior.

P. W. C.

Fractional iodine determinations in human organs. Biological function of tissue-iodine. A. STURM and L. ROCKMANN (Biochem. Z., 1936, 287, 50—60).—Tables summarise the I contents of human liver, spleen, skeletal and heart muscle, and lung after fractionation with H₂O and COMe₂. The total [I], particularly the sol. protein- (thyrogenic) I (I) is decreased in cases of decreased cellular activity (aged people, liver cirrhosis, necrotic liver and lung carcinomatous tissue, tubercular lung tissue). Tissues in cases of abnormally increased metabolic activity are richer in I, particularly in (I). The functional condition of the central nervous system appears to control the distribution of I, particularly of (I), in the organs. The H₂O-insol. I fraction increases in age and in necrotic tumour tissue at the expense of the (I) fraction.

P. W. C.

(A) Sodium contents, (B) chloride contents, of aqueous and vitreous humour and serum. P. W. SALIT (Amer. J. Ophthalmol., 1934, 17, 706—708, 818—819).—(A) Age has little effect on the Na content of aq. or vitreous humour. Vals. for serum were > those for humour and those for calves > those of adult cattle.

(B) The Cl' contents of aq. and vitreous humour were similar and > that of serum. Vals. were the same for calves and adult oxen.

CH. ABS. (p)

Analysis of tissues for metallic content. H. RAMAGE (Nature, 1936, 138, 762—763).—Before spectrographic determination, tissues must first be extracted. After 18 to 24 hr. at room temp., N-HCl extracts from sheep's liver, spleen, and heart the alkalis, Mg, Zn, Mn, Ni, etc., with only a little org. matter: Ca, Cu, and Fe are only partly extracted. Healthy liver contains more Zn than is commonly realised.

L. S. T.

Copper in the liver of the calf embryo. Z. GRUZEWSKA and G. ROUSSEL (Compt. rend. Soc. Biol., 1936, 123, 377—379).—The liver of the embryo contains 20—40 times as much Cu as the foetal spleen, and it appears to be in complex combination since it is not liberated by prolonged dialysis. Cu in rabbit liver is very variable.
H. G. R.

Silica content of lungs of infants and of placental tissue. W. D. McNALLY and W. L. BERGMAN (J. Ind. Hyg., 1935, 17, 171—173).—SiO₂ contents determined were, infants to 3 years 0.34, placenta 0.294, blood 0.13, placental blood 0.32, umbilical cord 0.33 mg. per g. of dried tissue.

CH. ABS. (p)

Carbonate content of inorganic bone material and its synthesis. R. KLEMENT (Ber., 1936, 69, [B], 2232—2238).—The content of inorg. bone material does not correspond with an equilibrium between the hydroxyapatite (I) contained therein and the CO₃" of the serum. Probably CaCO₃ is carried down by induced pptn. during the formation of (I). The artificial prep. of a product closely resembling natural bone material is described.

H. W.

Inorganic structure of teeth. W. F. BALE, M. L. LEFEVRE, and H. C. HODGE (Naturwiss., 1936, 24, 636—637).—Changes in the X-ray diagram of dentine on heating to 900° agree with the view of Klement *et al.* (A., 1933, 296) that the principal constituent is a hydroxyapatite (I), with included or adsorbed carbonates. The X-ray diffraction diagram of commercial Ca₃(PO₄)₂ changes on heating to 900°, like that of (I), to the diagram of β-Ca₃(PO₄)₂. Samples of tooth-substance gave, after the above heating, few diagrams showing a similar change, but after 5 hr. heating of dentine from certain teeth, the diagram of β-Ca₃(PO₄)₂ was obtained in many cases. Powdered dentine after extraction for 1½ hr. with (CH₂·OH)₂ and 3% KOH showed no such transformation. The differences observable in the tooth-substance of different teeth can be ascribed to the extent of adsorption of PO₄" on the surface of the small (I) crystals.
A. J. M.

X-Ray absorption coefficients of coronal and root dentine. F. HOLLANDER and E. VESELY (Proc. Soc. Exp. Biol. Med., 1936, 34, 158—159).—The coeffs. were different in different parts of the dentine of the same specimen and there were differences of >20% between different specimens. In any one specimen there is a uniform decrease in the coeff. from crown to apex of the root, the gradient being parallel to the age gradient of the dentine.
W. McC.

X-Ray diffraction patterns from reprecipitated connective tissue. R. W. G. WYCKOFF and R. B. COREY (Proc. Soc. Exp. Biol. Med., 1936, 34, 285—287).—The part of the freshly excised tendon of the tail of the adult rat which dissolves in dil. AcOH and is repptd. by 5% aq. NaCl is cryst. and has the same X-ray diffraction pattern as has the original tendon.
W. McC.

Mechanism of hexose monophosphate formation in muscle and isolation of a new phosphate ester. C. F. CORI and G. T. CORI (Proc. Soc. Exp.

Biol. Med., 1936, 34, 702—705).—Glucose-1-phosphoric acid was isolated as the brucine salt from minced frog muscle incubated with adenylic acid in phosphate buffer. It is readily converted into hexose monophosphate.
P. G. M.

Comparative biochemistry of muscle. I. Phosphagen in sea- and fresh-water Teleostei and Ganoidei. L. E. ROZENFELD and G. J. BAGDASARJANTZ. II. Nature of phosphagen in the Selachii. G. J. BAGDASARJANTZ (Ukrain. Biochem. J., 1936, 9, 321—332, 333—340).—I. The skeletal muscles of *Acanthopterygii* and *Lophobranchii* contain 0.007—0.015% of creatinephosphoric acid (I). The P of (I) amounts to 3—8% of the inorg. and acid-labile P, significantly < that in the lower vertebrates. The creatine content of muscle of salt-water fish is < that of fresh-water fish. Sturgeon muscle does not differ from that of bony fish in creatine or (I) content.

II. Muscle of the shark and ray contains 0.013—0.035% of (I). An acid-labile P compound, probably argininephosphoric acid (II), is also present. The total amount of (I) and (II) in the shark is > that in the ray.
F. A. A.

Biochemistry of carbohydrates. XIV. Modified Zuckerkandl-Klebermass method for determination of glucosamine. Distribution of glucosamine in ox tissue. XV. Determination of N-acetylglucosamine and its application to biochemical analysis. K. WATANABE (J. Biochem. Japan, 1936, 23, 365—369, 371—376; cf. A., 1935, 402).—XIV. The method (A., 1931, 1081) indicates that glucosaminase occurs in liver, lung, pancreas, and kidney but not significantly in spleen, thyroid gland, muscle, and adrenal cortex.

XV. The above method is applicable to the determination of N-acetylglucosamine in tissue, blood, or urine.
F. O. H.

Glycogen content of fresh-water mussels during prolonged starvation. M. M. ELLIS and D. B. CALVIN (Proc. Soc. Exp. Biol. Med., 1936, 34, 222—225).—The dried hepatopancreas and pedal muscle of several species of thick-shelled mussel contained 25—61% of glycogen (I). The (I) content decreased slowly during starvation; in many cases it remained >30% after 180—338 days. After 536 days the average (I) content of one species was 1.1%. The (I) content of thin-shelled was < that of thick-shelled mussels and decreased more rapidly during starvation.
W. McC.

Chemical and histochemical determination of the glycogen contents of white and red muscle. A. NOLL and M. BECKER (Biochem. Z., 1936, 287, 88—91).—In rabbits and hens, red muscle contains 66—80% of the amount of glycogen (I) of white muscle. Histochemical determination gave in general a lower (I) content for red muscle, the vals., especially with rabbit's muscle, agreeing closely with those by chemical methods. In hens, the red muscle of the legs must be used whole in chemical determinations, since (I) is not evenly distributed therein.
P. W. C.

Fats of Japanese birds. XVII. Fat from *Oreocincla dauma*, Holandre [White's ground

thrush]. R. KOYAMA (J. Chem. Soc. Japan, 1935, 56, 596—599).—Data are recorded. CH. ABS. (e)

Oil extracted by pressure from the male silk-worm butterfly. M. BONICATTI (Annali Chim. Appl., 1936, 26, 306—309).—The oil, obtained in 20% yield, has I val. 110—116, acid val. 22—38, solid fatty acids 27.1—33.2%; it differs little from the chrysalis oil. L. A. O'N.

Inversion point of cholesterol in aqueous suspension by calcium chloride. H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 154—156).—The $[\text{CaCl}_2]$ corresponding with the inversion of cholesterol is 2.8N. H. G. R.

Chemical composition of various divisions of the nervous system. A. V. PALLADIN, E. J. RASCHBA, and R. M. GELMAN (Ukrain. Biochem. J., 1936, 9, 169—192).—In the peripheral nervous system of cows, the roots of the spinal cord contain a relatively large amount of cholesterol (I) (17—18% of the dry matter). The anterior and posterior roots are similar to each other in composition, per unit of dry matter. Lipins, N, creatine, P, and H_2O are lower in the peripheral nerve than in the other divisions (possibly owing to a high fat content), whilst the sympathetic trunk is relatively rich in N and creatine. The ganglia of the posterior roots differ from other ganglia in having high (I) and unsaturated phosphatide content. Phylogenetically, the peripheral nervous system resembles the central nervous system in that the older divisions are rich in (I) and unsaturated phosphatides, while the younger divisions are richer in H_2O and proteins. F. A. A.

Chemistry of vitreous humour. III. Lipins. A. C. KRAUSE (Arch. Ophthalmol., 1935, 13, 1022—1025; cf. A., 1935, 511).—In bovine humour parts of the lipin and cholesterol (I) contents are bound to protein. No cholesteryl fatty acid esters are present. Particles of (I) and Ca soaps in the humour probably arise from liberation of lipins of leucocytes.

CH. ABS. (p)

Biochemistry of the lens. IV. Origin of pigment. J. G. BELLOW (Arch. Ophthalmol., 1935, 14, 99—107).—The lens contains histone and protamine. The latter reacts with cysteine (I) to form a black dye. A normal hydrolysed lens becomes pigmented when placed in a slightly alkaline solution of (I). CH. ABS. (p)

Cellular hæmatins and cytochromes. J. ROCHE and M. T. BÉNEVENT (Compt. rend. Soc. Biol., 1936, 123, 20—22; cf. this vol., 1287).—The hæmatins (I) of cytochrome-A and -A₁ are similar if not identical, whilst those of -A₂ are very different, the hæmochromogens absorbing in the orange-red. Pigments B, B₁, and C and Keilin's intracellular (I) yield, with $\text{C}_5\text{H}_5\text{N}$, a mixture of (I)-C and proto-hæmatin in varying proportions. H. G. R.

Hæmatin- and cytochrome-C. Mobility of iron and combinations of hæmatins with a globin. J. ROCHE and M. T. BÉNEVENT (Compt. rend. Soc. Biol., 1936, 123, 18—19).—The absorption spectra of the products of condensation of proto-hæmatin with $\text{C}_5\text{H}_5\text{N}$ and with $\text{NH}_2\text{CH}_2\text{CO}_2\text{Me}$ are identical. Hæmatin-C (I), obtained from the proto-

hæmatin by alternate oxidation and reduction, will not combine with horse globin and when boiled in MeOH with 1% HCl yields a porphyrin and Fe^{+++} , in contrast to Zeile's (I), that of cytochrome-C, and of blood. H. G. R.

Chemical studies on bioluminescence. III. Reversible reaction of *Cypridina* luciferin with oxidising agents and its relations to the luminescent reaction. R. S. ANDERSON (J. Cell. Comp. Physiol., 1936, 8, 261—276; cf. this vol., 360).—Oxidation of luciferin (I) by $\text{K}_3\text{Fe}(\text{CN})_6$, unlike that by O_2 in the presence of luciferase, is reversible, as (I) is re-formed largely in the former, but only to a slight extent in the latter, case on addition of $\text{Na}_2\text{S}_2\text{O}_4$. The end products of the two reactions are therefore different. Abnormal reaction curves obtained may be due to mixtures of (I) and reversibly oxidised (I). A preliminary val. for the apparent oxidation-reduction potential of the (I) system is given. Possible chemical characteristics of (I) are discussed. E. A. H. R.

Influence of starvation on the content of plant-auxin-like substances in the larva of *DiscoGLOSSUS pictus*, Otth. H. BERRIER (Compt. rend., 1936, 203, 522—524; cf. A., 1935, 1289).—The auxin-like activity of *D. pictus* persists during the normal larval stage but disappears on starving the larvæ for 15 days. F. O. H.

Nettle poisons. Poison of sea anemones. I. R. SONDERHOFF (Annalen, 1936, 525, 138—150).—*Anemonia sulcata* yields to EtOH a highly active substance, containing C, H, O, N, and S, having a mol. wt. about 2000 (determined by dialysis), and probably of albumin (histone) type. The isolation, physiological properties, method of testing (*Rana esculenta*, not *temporaria*), and colour reactions are detailed. R. S. C.

Isolation of the anti-anæmic principle of the liver. P. LALAND, A. KLEM, B. STRANDELL, L. POULSSON, and H. SCHARTUM-HANSEN (Acta med. scand., 1936, 88, 620—623, 624—625).—The method of isolation depends on extraction with PhOH which removes much of the inactive substances. Several fractions isolated by variations of this method had an anti-anæmic effect. A fraction isolated by a combination of the $(\text{NH}_4)_2\text{SO}_4$ process of Dakin and West and the PhOH extraction method gave 0.35 mg. of dry material per 100 g. of liver. 0.7 mg. of this material produced an excellent response in four cases of pernicious anæmia. NUTR. ABS. (m)

Physical and chemical properties of desiccated stomach. J. KYER, F. P. BROOKS, and R. ISAACS (Proc. Soc. Exp. Biol. Med., 1936, 34, 677—680).—A H_2O extract of desiccated hog's stomach (p_{H} 4.5) is effective in treatment of pernicious anæmia. The active principle is alkali-stable and is not ultra-filterable; it contains two factors, one heat-stable and the other heat-labile. Incubation of an acid extract yields a hæmatopoietic substance sol. in 70% EtOH. P. G. M.

Heparin. IV. Chemistry of heparin. A. F. CHARLES and D. A. SCOTT (Biochem. J., 1936, 30, 1927—1933).—A very active prep. of heparin (I) is

obtained from ox lung (cf. A., 1935, 632). Analyses of the Ba and benzidine salts indicate the empirical formula $C_{25}H_{65}O_{50}N_2S_5$ for (I). The S is present as $\cdot SO_3H$ and is removed by MeOH-HCl as SO_4^{2-} with loss of activity. Part of the N is present as $\cdot NH_2$ groups and these are associated with the physiological activity. Colour tests indicate the presence of a carbohydrate complex and the absence of pentoses and glycuronic acid. The cryst. prep. is 22 times as active as the commercial product. Analyses do not support the view that (I) is a chondroitinpolysulphuric acid.

P. W. C.

Progesterin content of human placenta. D. A. MCGINTY, N. B. McCULLOUGH, and J. G. WOLTER (Proc. Soc. Exp. Biol. Med., 1936, 34, 176—178).—Fresh full-term human placenta contains approx. 7 rabbit units of progesterin per kg.

W. McC.

Organic bases, especially spermine, in the muscle of higher animals. II. K. YOSHIMURA, Y. HIWATASHI, and T. SAKOMOTO (J. Chem. Soc. Japan, 1935, 56, 582—587).—Freshly ground muscle of rabbit and of wild boar contains creatine 10.8, 0.30, hypoxanthine hydrochloride 0.6, 2.05, methylguanidine 1.2, 0.30, creatinine 1.7, 2.05, carnitine 1.8, 6.0, and spermine 0.0, 0.0 g. per 5 kg., respectively.

CH. ABS. (p)

Brain-creatine during the ontogenetic development of vertebrates. A. PALLADIN and H. RASCHBA (Ukrain. Biochem. J., 1936, 9, No. 1, 5—42).—In various mammals the creatine and total N content of the brain decreases during development. In chicks a less marked fall takes place.

W. O. K.

Creatine content of human hearts. G. HERRMANN, G. M. DECHERD, jun., and T. OLIVER (Proc. Soc. Exp. Biol. Med., 1936, 34, 827—829).—The creatine content of hearts from patients who died of infectious disease is lowered, as is that of hearts showing myocardial change consequent on coronary sclerosis; in hypertrophied hearts the content is raised if they have not failed, and *vice versa*.

P. G. M.

Tissue-acetylcholine. IV. Cytology of chorioc villous epithelium of the human placenta. I. C. WEN, H. C. CHANG, and A. WONG (Chinese J. Physiol., 1936, 10, 559—569).—Fixation with NH_4 reineckate preps. is used to indicate the liberation of choline granules in various histological elements of placental tissue, the results being correlated with the acetylcholine activity of different types of placenta.

P. W. C.

Structure of proteins and of certain physiologically active compounds. D. M. WRINCH (Nature, 1936, 138, 651—652).—The cyclol theory of protein structure and the part played by the cyclol pattern in the structure of carcinogenic substances is discussed.

L. S. T.

Digestion products formed by the action of papain on ovalbumin. M. ANNETTS (Biochem. J., 1936, 30, 1807—1814).—Under the action of papain the ovalbumin (I) mol. is split up into two groups of substances, both heterogeneous, a light fraction consisting of particles of the order of magnitude of the NH_2 -acids and lower polypeptides and a heavy fraction containing no unchanged (I) and having an

average sedimentation const. of 3.3 and diffusion const. of 8.27 sq. cm. per sec. Ultracentrifuge, *n*, diffusion, cataphoresis, and light absorption measurements all lead to the view that first a change occurs in all the mols. of (I), probably a loosening of bonds within the mol., followed by a gradual splitting off of small pieces from these modified mols.

P. W. C.

Swelling of the vitreous gel and intraocular pressure. M. COHEN, J. M. NEWELL, and J. A. KILLIAN (Arch. Ophthalmol., 1934, 12, 352—358).— H_2O and solutions of acids, alkalis, and NaCNS, separated from the vitreous gel by a porous alundum disc, produced no swelling of the gel. Pressure ultrafiltration through Cellophane removed >99% of protein-free liquid from the gel. The residue swelled when placed in the H_2O . A true swelling of vitreous gel is impossible.

CH. ABS. (p)

Protein content of human aqueous [humour]. E. SELINGER (Amer. J. Ophthalmol., 1934, 17, 1130—1137).—A method for determining protein is based on treatment with CCl_3CO_2H and comparison of turbidity. Vals. for normal and pathological conditions are given.

CH. ABS. (p)

Inversion point of autocomplex coacervates of phosphatides by calcium chloride as a function of p_H . H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 149—154).—Between p_H 4 and 9 the $[CaCl_2]$ necessary to cause inversion of the electro-capillary charge is practically const. On the acid side the val. falls rapidly to zero (p_H 1.82) and increases rapidly when alkaline.

H. G. R.

X-Ray diffraction studies of chitin, chitosan, and derivatives.—See this vol., 1451.

Adsorption of benzene derivatives by serum colloids and organ pulps.—See this vol., 1462.

Elastoïdin fibres.—See this vol., 1462.

Milk of the merino ewe. A. W. PEIRCE (Austral. J. Exp. Biol., 1936, 14, 187—192).—Colostrum differed from milk principally in its higher proportions of casein, lactalbumin, globulins, and lactose. Seasonal variations in two typical breeds are examined.

A. G. P.

Copper, zinc, and manganese content of cows' milk. A. BROEK and L. K. WOLFF (Acta brev. neerl. Physiol., 1935, 5, 80—81; Chem. Zentr., 1936, i, 461).—The Cu content was $15-50 \times 10^{-6}$ g. per litre, and was uninfluenced by season or diet. The Zn was 1.94—4.96 mg. per litre. Mn averaged 10^{-5} g. per litre; this val. was influenced much more by org. than by inorg. Mn in the feed.

H. J. E.

Determination of vitamin-C content of fresh milk. W. LOJANDER (Suomen Kem., 1936, 9, A, 111—114).—Several 20-c.c. samples of milk are treated respectively with increasing amounts of a standard solution of dichlorophenol-indophenol, and after 10 min. in the dark, the -C content corresponds with that amount of indicator between the last white and the first coloured test. The method fails with milk containing many bacteria.

J. N. A.

Occurrence and possible significance of some minor components of cow-milk fat. T. P. HIL-

DITCH and H. PAUL (Biochem. J., 1936, 30, 1905—1914).—Results of analyses of the component acids of milk fat are calc. (a) on the assumption that no unsaturated acids of lower mol. wt. than oleic acid (I) are present, and (b) allowing for the presence of decenoic (II), tetra- (III) and hexa-decenoic (IV) acids. Comparison of these results with those for the similar analysis of completely hydrogenated butter indicates the presence of lower unsaturated acids. In addition to traces of (II) and <1% of (III), there must be present about 4—5% of (IV). By applying the correction, the palmitic acid val. is increased by 2% and the (I) val. decreased by 5%. There is no detectable amount of any unsaturated acid of lower mol. wt. than $\Delta^{9:10}$ -(II) in butter fat. The minor lower unsaturated components are probably degradation products of oleo-glycerides which have escaped complete saturation. P. W. C.

Variation of the fat content of milk with the time of day. Z. CZUKÁS (Mezőg.-Kutat., 1935, 8, 270—279; Chem. Zentr., 1936, i, 461).—Tests with 8 cows on 94 days showed that morning milk had a 40%, and evening milk a 29%, lower fat content than midday milk. H. J. E.

Hydrogen-ion concentration of tears: relation to certain ocular symptoms and to conjunctival and corneal lesions. G. N. HOSFORD and A. M. HICKS (Arch. Ophthalmol., 1935, 13, 14—25).—Tears are sufficiently buffered to permit sufficient dilution for practicable determinations of p_H . Vals. for normal eyes averaged 7.35. Protein and salt errors and the relation of tears to certain bacteria are discussed. CH. ABS. (p)

Influence of the nature of the stimulant on the quantity, chloride content, and p_H of the salivary secretion. E. J. BIENKA and C. SZCZEPANSKI (Compt. rend. Soc. Biol., 1936, 123, 32—34).—The secretion is affected less by mechanical than by chemical stimulation. When stimulation is rapid or the medium alkaline, the Cl' content is > and the p_H < that on slow stimulation or in acid medium. H. G. R.

Bile-sugar. G. BALTAČEANO and C. VASILIU (Compt. rend. Soc. Biol., 1936, 123, 54—55).—In bile the free sugar is glucose and the protein-bound sugar lactose. H. G. R.

Method of determining total pigment in bile applicable to "biliverdin" biles. C. R. SCHMIDT, K. K. JONES, and A. C. IVY (Proc. Soc. Exp. Biol. Med., 1936, 34, 17—21).—The bile-pigments are oxidised to yellow compounds by $(NH_4)_2S_2O_8$ in presence of AcOH-EtOH (1 : 1) and then determined colorimetrically. W. O. K.

Determination of cholic acid in bile and in duodenal drainage. H. DOUBILET (Proc. Soc. Exp. Biol. Med., 1936, 34, 84—86).—The Gregory-Pascoe reaction (cf. A., 1929, 1114) is applied to the determination of cholic acid in bile. W. O. K.

Influence of diet on formation of hepatic and renal calculi. IV. Histological study of liver, gall-bladder, and kidneys. V. Changes of hydrogen-ion concentration and the buffer action of the bile. K. USUKI (Japan. J. Gastro-

enterol., 1934, 6, 94—104, 105—111).—V. In young rabbits receiving a diet deficient in fat-sol. vitamins, the liver and gall-bladder biles showed lowered p_H and buffer action, with which is associated the formation of calculi. CH. ABS. (p)

Quantitative studies of the normal human gastric secretion. S. WANG (Chinese J. Physiol., 1936, 10, 493—506).—The HCl, neutral Cl', and non-Cl' alkaline (base+mucus+pepsin) components of gastric juice of four normal human subjects were investigated, histamine being used as stimulant. The HCl and neutral Cl' were secreted in proportional vols. at const. concn. in the order approximating to the electrolyte concn. of the blood. Both vals. were numerically < those in dogs. During active secretion, the vol. of the alkaline component is small. The total base and Cl' concn. of the serum is remarkably const. P. W. C.

Gastric secretion during the night. A. WINKELSTEIN (Amer. J. Digest. Dis. Nutrition, 1934, 1, 778—782).—Normal curves of gastric secretion show little HCl during the night. In cases of gastric or intestinal ulcers, secretion and HCl content are high. Nocturnal hyperchlorhydria is not controlled by alkalis, olive oil, atropine, or aspiration. CH. ABS. (p)

Influence of the pylorus on the regulation of the acidity of gastric secretion. W. W. LERMANN and L. M. NELSON, jun. (Amer. J. Digest. Dis. Nutrition, 1934, 1, 245—247).—Regurgitation of bile and trypsin and lowered acidity in the digesting stomach were observed, the pylorus being held open during the test. CH. ABS. (p)

Dry natural digestive juices: properties and use. W. N. BOLDYREFF (Amer. J. Digest. Dis. Nutrition, 1935, 2, 33—36).—The dry residue from vac. evaporation of freshly collected and cooled juice may be preserved without an antiseptic. Technique of prep. is described. CH. ABS. (p)

Relations between hæmoglobin and gastric acidity. W. C. ALVAREZ and F. R. VANZANT (Proc. Staff Meetings Mayo Clin., 1936, 11, 385—391).—There was a marked rise in the incidence of achlorhydria in man as the hæmoglobin (I) vals. fell below 12 g. per 100 ml., and the mean gastric acidity decreased rapidly below this (I) level. With (I) levels >18 g. per 100 ml., mean gastric acidity decreased slightly, and the incidence of achlorhydria was normal. Severe anæmia is not incompatible with the presence of excess of acid, and the presence of great excess of hæmoglobin is compatible with achlorhydria. NUTR. ABS. (m)

Gastro-intestinal studies. V. Gastric juice in anæmias other than pernicious anæmia. P. J. FOUTS, O. M. HELMER, and L. G. ZERTAS (Amer. J. Digest. Dis. Nutrition, 1934, 1, 677—684).—No enzymes were found in gastric juice having p_H <7.0. No improvement in gastric secretion was found when the gastric contents, after histamine stimulation, had p_H >7.0 and contained no enzymes. CH. ABS. (p)

Anti-pernicious anæmia principle in gastric juice. A. W. C. G. KAMERLING and W. GROTEPASS

(Nederland. Tijds. Geneesk., 1936, 80, II, 1991).—The effect of liver is increased by incubation with normal gastric juice, but not with the gastric juice of pernicious anæmia patients. Pepsin-HCl digestion does not increase the activity of liver. After removal of the enzymes of gastric juice the ultrafiltrate from active liver digests was equally active, even after heating at 80° for 30 min. NUTR. ABS. (m)

Buffer capacity of pancreatic juice. M. T. HOERNER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 300—302).—Protein diets induced a greater flow of secretion than did other test meals. The buffer capacity of the juice reached max. 1—3 hr. after ingestion of food and gradually diminished as the acidity of the duodenum declined. The secretion was always alkaline and possessed slight buffer capacity even during fasting. CH. ABS. (p)

Effect of exclusion of pancreatic secretion by evulsion of the pancreatic ducts on reaction of duodenal contents. M. T. HOERNER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 295—297).—The p_{H} of the contents during fasting was 7.00—7.81, after a meat meal 6.40—3.50, after a carbohydrate meal 6.75—4.26, and after a fat meal 6.80—5.20. In the absence of pancreatic juice the total buffer secretions are smaller but the bile and succus entericus maintain a normal p_{H} except when gastric matter of high acidity enters the duodenum. CH. ABS. (p)

Effect of exclusion of pancreatic secretion by a pancreatic fistula on reaction of gastric, duodenal, and jejunal contents. M. T. HOERNER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 298—300).—Production of a pancreatic fistula caused no change in the p_{H} of gastric contents during fasting or after test meals. The p_{H} of duodenal contents was normal during fasting, but protein and carbohydrate meals caused a more rapid and prolonged decline in p_{H} than when pancreatic secretion was present. Similar changes occurred in the jejunal contents, but only after a protein diet. CH. ABS. (p)

Reaction of the contents of the isolated duodenum. P. R. IMES (Amer. J. Digest. Dis. Nutrition, 1935, 2, 285—288).—The alkalinity of the contents (p_{H} 7.10—8.15) is caused by weak alkalis or buffer substances, fluctuations in which depend on the relative proportions of pancreatic juice, bile, and duodenal secretion present. The alkalinity of pancreatic juice is approx. double that of bile. CH. ABS. (p)

Capacity of duodenum to neutralise, to buffer, and to dilute acid. G. A. STEVENS (Amer. J. Digest. Dis. Nutrition, 1935, 2, 288—293).—The increase in neutralising capacity after a fat meal and the decrease after a protein meal are attributed to inhibition and stimulation, respectively, of the gastric juice. HCl introduced continuously in small amounts is neutralised, buffered, and diluted; little is absorbed in the duodenum. A large single injection of acid is swept through the duodenum by peristalsis. CH. ABS. (p)

Reaction of duodenal content after exclusion of bile from duodenum. J. W. McROBERTS (Amer. J. Digest. Dis. Nutrition, 1935, 2, 293—294).—Loss

of bile did not materially affect the p_{H} of duodenal contents in dogs. CH. ABS. (p)

Determination of ketones in urine. J. TROTZKI and R. MENDELSON (Ukrain. Biochem. J., 1936, 9, No. 1, 157—163).—The urine is treated first with $\text{Pb}(\text{OAc})_2$ and aq. NH_3 and then with $\text{Pb}(\text{OAc})_2$ and NaOH . The COMe_2 in a portion of the filtrate acidified with AcOH is distilled into aq. NaOI , $\text{K}_2\text{Cr}_2\text{O}_7$, and H_2SO_4 being added to the distillation flask at intervals. W. O. K.

Detection of pyruvic acid in urine. A. PISUNER and M. FARRAN (Biochem. Z., 1936, 287, 113—114; 288, 294).— AcCO_2H is isolated as the dinitrophenylhydrazone, m.p. 216°. P. W. C.

Methylmalonic acid from rat urine. E. BOYLAND and A. A. LEVI (Biochem. J., 1936, 30, 2007—2008; cf. this vol., 234).—Methylmalonic acid (I) was isolated in yields >0.5 g. per litre from rats' urine, but could not be found in human and rabbits' urine. (I) separates from H_2O as monohydrate. Thymine is a possible precursor of (I) in the organism. The Na salt of (I) does not inhibit respiration and acetoacetate breakdown in liver slices. W. McC.

Origin of trimethylamine in human and animal urine. S. V. FOMIN (Ukrain. Biochem. J., 1936, 9, No. 1, 143—155).— NMe_3 in human or pig urine is of exogenous origin. W. O. K.

Phenols or glyoxalines in urine. A. D. MARENZI and R. F. BANFI (Compt. rend. Soc. Biol., 1936, 123, 73—74).—The diazo-reaction of urine is principally due to phenols. H. G. R.

Excretion of ammonia and uric acid by larvæ of muscoid flies. A. W. A. BROWN (J. Exp. Biol., 1936, 13, 131—139).—Small amounts of uric acid (I) were found in tissues and excreta of *Calliphora erythrocephala*, *Mg.*, and *Wohlfahrtia vigil*, *Wlk.* NH_3 excretion increased with rise in body-wt. of *Calliphora* larvæ, but there was a lag of 1 day in *Wohlfahrtia*. (I) excretion increased in a similar manner but the amount was very much less. In *Calliphora* a diet of caseinogen proved adequate and ovalbumin inadequate. The caseinogen diet brought about an excretion of NH_3 and (I) about twice as great as that on a normal meat diet. NUTR. ABS. (m)

Determination of veronal [in urine]. G. SACK (Arch. exp. Path. Pharm., 1936, 183, 71—76).—Urine (10—20 c.c.) is treated with $\text{Pb}(\text{OAc})_2$ - AcOH and filtered and the material extracted from the filtrate by Et_2O is purified by treatment with $\text{K}_2\text{Cr}_2\text{O}_7$ - H_2SO_4 followed by H_2O_2 and freed from fat by successive treatments with EtOH and H_2O . The final Et_2O extract of the aq. solution is evaporated to dryness and weighed. The accuracy is $\pm 5\%$. A qual. test is given. F. O. H.

Colour reaction for the urine of pregnancy. P. E. SEMOLA (Suomen Kem., 1936, 9, B, 20).—I is added, the solution boiled, and shaken with amyl alcohol. The alcohol layer assumes a red-violet colour in 70% of the cases examined. A. L.

Losses of nitrogen and carbon in drying the fæces of cattle. M. KLEIBER, R. W. CALDWELL, and H. JOHNSON (Proc. Soc. Exp. Biol. Med., 1936,

34, 128—130).—N determinations in faeces should be made with fresh samples immediately after defecation since storage and drying result in N losses of $4.48-7.19 \pm 0.049\%$. C is best determined by combustion of dried faeces in O_2 at 25 atm. The loss of C on drying ($1.36 \pm 0.08\%$) is determined in a special apparatus. 35—55% of the lost C occurs as pre-formed CO_2 . W. McC.

Elimination by sweat in an ozonised atmosphere. THIODET and RIBÈRE (Compt. rend. Soc. Biol., 1936, 123, 329—330).—An analysis of the sweat is given, an increase in the elimination of toxic substances being apparent. H. G. R.

Pathogenesis of oil acne. N. S. VEDROV and A. P. DOLGOV (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 428—436).—Compounds of the type of naphthene, in naphtha oil, can cause skin affections of the type of oil acne. Purification of the oil does not render it completely harmless. Sulphonated and unsulphonated oils have the same effect. M. A. B.

Serum electrolytes and mineral metabolism in a case of Addison's disease. Use of adrenal cortical extract (Eschatin). S. K. CHOU, K. C. CHEN, S. H. LIU, and S. S. FANG (Chinese Med. J., 1936, 50, 1013—1024).—A case is reported of Addison's disease accompanied by pulmonary tuberculosis. Low plasma vol., low total base, serum-Na and -Cl vals. were found, which were temporarily relieved by Eschatin. Later doses were ineffective, owing to mineral loss by tissue destruction as a result of active pulmonary tuberculosis. G. H. B.

Anæmia caused by deaminised caseinogen. A. G. HOGAN, R. E. GUERRANT, and W. S. RITCHIE (J. Biol. Chem., 1936, 115, 659—672; cf. A., 1934, 1387).—For a given diet, a ration of approx. 5% of caseinogen (I) prevents, whilst a min. of 5—10% of deaminised (I) produces, an anæmia in rats which is not alleviated by milk, egg yolk, wheat germ oil, muscle, or liver or stomach preps. Laboratory preps. of lactalbumin do not prevent the anæmia and those of ovalbumin have a variable effect; commercial preps. of both proteins, however, prevent anæmia, as does dried yeast (aq. extracts of which are inactive). Autoclaved (I) or yeast has no curative action. The anæmia and anti-anæmia factors occur in the 25% H_2SO_4 hydrolysate of deaminised and normal (I), respectively. F. O. H.

Origin of the anti-anæmic factor. IX. Action of the liver in pernicious anæmia. F. REIMANN, H. BIEDERMANN, and L. ZWILLIGER (Z. Klin. Med., 1935, 128, 205—212; Chem. Zentr., 1936, i, 585).

Basal metabolism in experimental anæmias. K. C. CHEN and H. C. CHANG (Proc. Soc. Exp. Biol. Med., 1936, 34, 646—648).—In NH_2Ph anæmia there is only a fleeting increase in basal metabolic rate, and the immature blood cells contribute little to the total O_2 consumption. There is no strict relation between O_2 consumption and reticulocyte count. P. G. M.

Myohæmoglobin content of the hypertrophied heart of the anæmic rat. D. W. COWAN and L. C. BAUGUESS (Proc. Soc. Exp. Biol. Med., 1936, 34, 636—637).—In spite of severe anæmia rats are able to

maintain normal muscle-hæmoglobin concn. during development of abnormal hypertrophy. P. G. M.

Changes in the protein equilibrium of blood during asthma. AUBRY, THIODET, and RIBÈRE (Compt. rend. Soc. Biol., 1936, 123, 327—328).—During an attack the albumin:globulin ratio and the albumin content decrease and the globulin content increases. H. G. R.

Chemistry of carcinoma. II. A. VON CHRISTIAN (Z. Krebsforsch., 1935, 42, 25—29; Chem. Zentr., 1936, i, 360).—Cytolysis of carcinoma by serum is inhibited by cholesteryl *n*-butyrate, isovalerate, and palmitate. A. G. P.

Glycolysis in cancer. II. C. FRISCH and R. WILLHEIM (Biochem. Z., 1936, 287, 198—202; cf. A., 1935, 885).—The inhibition of glycolysis in muscle extract by benzoquinone is not counteracted by extracts of healthy kidney, spleen, muscle, embryonal tissue (hen), or by ascorbic acid and hence the counter-acting effect of tumour extract is sp. W. McC.

(A) **Lysine as a factor in malignant growth.** C. VOEGTLIN and J. W. THOMPSON. (B) **Effect of gliadin diet on malignant growth.** C. VOEGTLIN and M. E. MAVER (U.S. Publ. Health Repts., 1936, 51, 1429—1436, 1436—1444).—(A) A diet of 70% wheat meal and 30% whole milk powder gives normal growth in rats and rapid growth of mammary carcinoma in mice. Heating the milk powder renders it inadequate for normal and inhibitory to malignant growth. Administration of lysine removes the inhibition of normal and malignant growth and an adequate supply is necessary for rapid growth of malignant tumour.

(B) Normal growth of young mice and growth of spontaneous mammary carcinoma in adult mice are inhibited by diets containing gliadin (I) as the only protein source, but the addition of lysine makes the diet adequate for both forms of growth. The effect of glutenin (II) is different from that of (I) in that growth is not inhibited. (II) is a complete protein and (I) is deficient in lysine. Lysine is necessary for the growth of mammary carcinoma. W. L. D.

Diagnosis of cancer. P. MENDELÉEFF (Compt. rend. Soc. Biol., 1936, 123, 135—137).—The pituitary in cancer secretes a substance detectable in the blood, cerebrospinal fluid, saliva, and urine by the coagulating action on plasma *in vitro*. H. G. R.

Calcium and protein of blood and blister fluid in malignant disease. R. O. BOWMAN, H. C. PRITS, P. H. MITCHELL, and E. EWERTZ (Canad. Med. Assoc. J., 1936, 34, 527—532).—K, P, Ca, and total protein were determined in the blood-serum and fluid from artificially raised blisters of 50 cancerous and 22 non-cancerous subjects. Since the average Ca of the fluid in the cancerous was < in the non-cancerous group malignancy may be related to a Ca deficiency not evident in the blood-serum but appearing in the blister fluid. Corresponding differences were noted in respect of P and (especially) protein, which was significantly lower in the blood and fluid of cancerous individuals. NUTR. ABS. (m)

Total sulphur of tissue in normal and abnormal growth (mouse carcinoma). H. BROWN and J. V. KLAUDER (J. Lab. Clin. Med., 1935, 20, 1143—

1150).—The S content of the skin of rabbits decreases with the falling rate of growth from birth to maturity. After maintenance on a low-cystine diet the S content of normal organs of mice declines, and the no. of infections and rate of growth of inoculated tumours are reduced. Rapidly growing tumours contain more S than slow-growing ones. CH. ABS. (p)

Paraffin and mineral oil cancer. WELWART (Seifensieder-Ztg., 1935, 62, 792—793; Chem. Zentr., 1936, i, 360).—The carcinogenic action of mineral oils is associated with the unsaturated hydrocarbons, notably 1:2:5:6-dibenzanthracene and 1:2-benzopyrene, and textile spinning oils. A. G. P.

Prophylaxis of benzpyrene cancer with organic peroxides. J. MAISIN and F. ROBERT (Compt. rend. Soc. Biol. 1936, 123, 156—159).—Diformaldehyde peroxide (A., 1935, 1526) and HCO_3H have a prophylactic action on benzpyrene cancer. H. G. R.

Carcinogenic power of methylcholanthrene. J. MAISIN and M. L. COOLEN (Compt. rend. Soc. Biol., 1936, 123, 159—160).—Methylcholanthrene is particularly active in producing cancerous tumours. H. G. R.

Differentiation of tumours (carcinomata and sarcomata) of varying origin and investigation of the relationship between primary tumours and their metastases by the protective proteinase reaction. E. ABDERHALDEN (Fermentforsch., 1936, 15, 245—250). E. A. H. R.

Action of tumour tissue on hexosediphosphoric acid. K. TSUZUKI (J. Biochem. Japan, 1936, 23, 421—435).—In rabbits' spindle-cell sarcoma, hexosediphosphoric acid yields triosephosphoric acid which does not form (from 2 mols.) phosphoglyceric (I) (1 mol.) and glycerophosphoric acid (1 mol.). The tumour tissue converts (I) into phosphopyruvic acid but not AcCO_2H except in presence of adenosinetriphosphoric or adenylic acid or phosphatase. The conversion of AcCO_2H into lactic acid (II) was not observed, but small amounts of (II) are always produced. The metabolism of the tumour is compared with that of muscle. F. O. H.

(A) **Copper content of human tumours in relation to that of the liver.** W. GERLACH. (B) **Copper content of Jensen sarcoma in relation to that of the organs.** S. EDLBACHER and W. GERLACH (Z. Krebsforsch., 1935, 42, 290—294, 272—289; Chem. Zentr., 1936, i, 574).—(A) Spectrographic determinations show the Cu content of tumours to vary within wide limits (0.5 — 20×10^{-6} g. per g. fresh wt.). Liver contains 4 — 19×10^{-6} g. per g.

(B) Rat livers contained 1—6, spleen 0.3, and kidneys 3.4×10^{-6} g. per g. fresh wt. Necrotic and healthy areas of Jensen tumour contained 0.73 and 0.32×10^{-6} g. per g., respectively. A. G. P.

Intermediary fat and carbohydrate metabolism of sarcomatous rats. B. PURJESZ and S. LAJOS (Magyar orvosi Arch., 1936, 37, 69—74).—The development of Jensen sarcoma in rats was associated with a fall in blood-sugar from 99 mg. per 100 ml. before inoculation to 60 mg. at 3—4 weeks. Liver-glycogen declined, on the average, from 1.58 to 0.43% and total carbohydrate of the liver from 3.5 to 2.1%.

The corresponding average figures for muscle were: glycogen 0.88 to 0.68%, total carbohydrate 2.0 to 1.5%. Neutral fat increased in the liver from 0.57 to 1.3, sterols from 0.35 to 0.54, and phosphatides from 2.7 to 3.1%. The I val. of liver fat was not significantly altered. NUTR. ABS. (m)

Celiac disease. I. Carbohydrate metabolism. E. BADENOCH and N. MORRIS (Quart. J. Med., 1936, 5, 227—250).—The flat blood-sugar curve was found only in active stages of celiac disease in children (7 cases). In convalescent periods the normal type of curve was approached. The curve was low in normal children of < 4 years, in marasmic children, and in cretins. The absorption and excretion of urea in celiac cases, and the absorption of sugar given with fat in normal children, indicate that fermentation of carbohydrate in the intestine is an important factor in the production of the flat curve in celiac disease. After 4 units of insulin injected subcutaneously in the fasting state in celiac disease, the blood-sugar fell to a mean val. of 33 mg. per 100 ml. in 1 hr. as compared with 67 mg. in normal children, but there were no clinical signs of hypoglycemia. Injection of anterior pituitary extract in cases of the disease caused a rise in the fasting blood-sugar and an increase in the height of the curve. Injections of extract of anterior pituitary improved the utilization of fat in 3 cases of the disease. It is suggested that in the disease there is a deficiency of the contrainular pituitary hormone. NUTR. ABS. (m)

Mechanism of increased oxygen consumption in patients with cardiac disease. H. RESNIK, jun., and B. FRIEDMAN (J. Clin. Invest., 1935, 14, 551—562). CH. ABS. (p)

Nutritional factors which produce cataract and dermatitis. A. F. MORGAN and B. B. COOK (Proc. Soc. Exp. Biol. Med., 1936, 34, 281—285).—In rats a diet containing 70% of lactose caused development of cataract in every case when the vitamin- B_2 content of the diet was low and in 85% of the cases when it was high. In no case was there development of dermatitis. A diet containing 68% of maize starch caused severe dermatitis when the $-B_2$ content was low but not when it was high. Administration of flavin cured the dermatitis. W. McC.

Effects of excessive ingestion of sodium and potassium salts on carbohydrate metabolism and blood pressure in diabetic children. I. MCQUARRIE, W. H. THOMPSON, and J. A. ANDERSON (J. Nutrition, 1936, 11, 77—101).—Daily ingestion of 1—2 g. of NaCl per kg. body-wt. had a favourable effect on the carbohydrate metabolism of diabetic children receiving a simplified low-K diet. Other Na salts have similar though less marked effects. KCl has the reverse action on glycosuria and blood pressure. K completely antagonises the effects of Na when given simultaneously in amounts corresponding with 1/3 of the equiv. of Na ingested. A. G. P.

Products of carbohydrate metabolism in the blood of diabetics. Residual chromic index. H. WAREMBOURG (Ann. Méd., 1936, 39, 342—356).—The difference between the total chromic index and the glucose chromic index (I.C.G.) is called the

residual chromic index (I.C.R.) The I.C.R. represents chiefly carbohydrate degradation products such as lactic acid and AcCO_2H . The ratio I.C.G. : I.C.R. was normally 0.18—0.4. The I.C.R. was increased in untreated diabetes and the increase was not due to blood-ketones. I.C.R. was increased in diabetic blood after sugar ingestion and decreased by 75% after insulin (I) injection. No alteration took place in the normal individual. It is concluded that there is an increase in the intermediary products of carbohydrate metabolism in diabetes. Dietetic treatment and (I) therapy resulted in a decrease in I.C.R.

NUTR. ABS. (m)

Serum-lipins in diabetes. E. B. MAN and J. P. PETERS (J. Clin. Invest., 1935, 14, 579—594).—Cholesterolaemia (I) and phospholipinaemia were closely correlated in diabetics. Relation between (I) and the serum-fatty acids was less definite. Serum-cholesterol was unrelated to the severity of diabetes. Hypocholesterolaemia was associated with malnutrition and with hypoproteinaemia.

CH. ABS. (p)

Cholesterol content of blood in diabetic patients on fat-rich diets. R. H. FREYBERG, L. H. NEWBURGH, and W. A. MURRILL (Arch. Int. Med., 1936, 58, 589—597).—In 21 patients with controlled diabetes fed on diets rich in fat for periods of 2 months to 8 years, the cholesterol (I) vals. during fasting were 0.126—0.223% (average 0.176%). With normal controls the vals. were 0.130—0.186%, average 0.156%. These was no correlation between the amount of fat in the diet and blood-(I). Lack of control of the disease is the main factor in causation of hypercholesterolaemia in diabetics.

J. N. A.

Exercise in diabetes mellitus. A. MARBLE and R. M. SMITH (Arch. Int. Med., 1936, 58, 577—588).—Exercise of short duration producing only mild fatigue markedly increased the blood-sugar of young diabetics (severe or moderate) who had not received food or insulin for several hr. Exercise probably causes glycogenolysis in the liver.

J. N. A.

Eczema in nickel platers. N. S. VEDROV (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 179—196).

M. A. B.

Composition and changes in blood and spinal fluid in epilepsy. I. I. BAN (Curierul farm., 1935, 5, No. 8, 1—17; Chem. Zentr., 1936, i, 584—585).—A relation is established between carbohydrate metabolism and the onset of epilepsy.

A. G. P.

Fluorine in the bones and teeth in fluorosis. J. M. MUNOZ (Compt. rend. Soc. Biol., 1936, 123, 74—75).—In rat fluorosis a diminution in the ash of the teeth and bones together with a three-fold increase in F was observed. Treatment with Ca, vitamin-D, and parathyroid hormone had no effect on the dental lesions.

H. G. R.

Influence of blood-serum of goitre patients on tissue respiration. K. MUNE (Folia Endocrinol. Japon., 1934, 10, 69—70).—Serum contains a substance (I) which accelerates O_2 consumption in surviving rat tissue. The (I) content of serum increases in hyper- and decreases in hypo-thyroidism and approaches normal vals. with thyroid correction.

CH. ABS. (p)

Relation between the occurrence of endemic goitre and the presence of traces of silver and barium in drinking-water. C. H. BOISSEVAIN and W. F. DREA (Endocrinol., 1936, 20, 686—687).—Ag is present in traces in drinking- H_2O from both goitrous and non-goitrous areas. H_2O from the Swiss goitrous area shows an unusually high Ba content, but neither Ag nor Ba affects development of goitre when fed to rats.

R. N. C.

Oxygen utilisation, cardiac output, and related circulatory functions in Graves' disease. S. A. GLADSTONE (Proc. Soc. Exp. Biol. Med., 1936, 34, 587—591).—In 4 cases with basal metabolic rates of +33%, the arterio-venous O_2 difference was decreased by 37%, whilst cardiac output increased by 93%.

P. G. M.

Blood-sugar tolerance test in hypertension. K. MAEHARA (Folia Endocrinol. Japon., 1934, 10, 52).—Hyperglycaemia following administration of glucose was higher and of longer duration in hypertensive cases.

CH. ABS. (p)

Hermaphroditism with growth disturbance. M. SAKOMOTO, S. ITO, and H. HATTORI (Folia Endocrinol. Japon., 1934, 10, 59—60).—Growth disturbances are attributed to functional derangement of thyroid and sex glands. Blood-sugar was normal but tolerance was lowered. Basal metabolism was normal but the sp. dynamic protein metabolism was low.

CH. ABS. (p)

Hermaphroditism. K. NISHIDA and J. MATSUI (Folia Endocrinol. Japon., 1934, 10, 60—61).—In the case described sugar tolerance and blood-sugar were almost normal; basal metabolism and sp. dynamic action were somewhat lowered.

CH. ABS. (p)

Pathological physiology of infarcts. IV. Arginase in necrosis. H. BAYERLE, G. BORGER, and T. MAYR (Z. physiol. Chem., 1936, 243, 227—236).—The arginase (I) content of experimental anaemia-infarct of rabbit's kidney is < that of the healthy tissue and decreases progressively to zero in 10—14 days. At first the (I) content is raised by activation with Fe^{++} and Mn^{++} but these have no effect later. During autolysis the (I) content of healthy tissue decreases in the same way and is similarly affected by Fe^{++} and Mn^{++} .

W. McC.

(A) Cholesterol fractions in acute infections of infants with and without eczema. (B) Iodine value of serum-fatty acids in acute infections of infants with and without eczema. A. V. STOEISSER (Proc. Soc. Exp. Biol. Med., 1936, 34, 10—11, 12—14).—(A) In fasting infants, the cholesteryl ester of the blood during acute infection of the respiratory tract was < during convalescence, but the free cholesterol underwent little change except in cases of pneumonia.

(B) During the febrile period, the amount and I val. of the serum-fatty acids decreased.

W. O. K.

Significance of carbohydrate metabolism and local acidosis in inflammation. V. MENKIN and C. R. WARNER (Proc. Soc. Exp. Biol. Med., 1936, 34, 594—596).—The cytological picture in inflammation is conditioned by p_{H} , which is influenced by

increased glycolysis and local depletion of the alkali reserve. P. G. M.

Hyperproteinæmia with reversal of the albumin-globulin ratio in lymphogranuloma inguinale. R. D. WILLIAMS and A. B. GUTMAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 91—94).—Ten out of 12 cases of lymphogranuloma inguinale showed a hyperproteinæmia. There was an abs. and relative increase in serum-globulin in 11 cases.

W. O. K.

Serum reaction in leprosy. (A) Flocculation reaction. (B) Kephalin as flocculation reagent. I. SAKAKIBARA (J. Biochem. Japan, 1936, 23, 377—420, 437—448).—(A) The use of preps. containing lecithin as antigen in serological reactions for leprosy is discussed. The principal antigenic factor in nerve extracts, lecithin preps., etc. is kephalin (I).

(B) The antigenic action (which is due to the β - and not the α -form) of (I) is unchanged by heating at 37° or 56° for 1 hr. or at 100° for $\frac{1}{2}$ hr., by the presence of small amounts of Et_2O , by oxidation (KMnO_4) or reduction (Pt-H_2). The (I) from ox brain, ox liver, or hens' eggs contains 81, 76, and 79% of β -(I), respectively.

F. O. H.

Cholesterol fractions in leprosy plasma. G. G. VILLELA and A. CASTRO (Compt. rend. Soc. Biol., 1936, 123, 433—435).—Variations in the cholesterol fractions in the different clinical forms are discussed.

H. G. R.

Multiple myeloma. IX. Crystalline and amorphous Bence-Jones protein. A. MAGNUS-LEVY (Z. physiol. Chem., 1936, 243, 173—188).—The cryst. form of the protein (I) from 3 new cases was identical with that of (I) from 8 previous cases. It is not yet certain that (I) is a chemical entity.

W. McC.

Myotonia. W. R. RUSSELL and E. STEDMAN (Lancet, 1936, 231, 742—743).—Myotonia may be due to excessive production or accumulation of acetylcholine at the motor nerve-endings. It is increased by administration of prostigmine or a K salt, and temporarily relieved by EtOH .

L. S. T.

Investigation of the origin of urinary protein in nephritis by the protective proteinase reaction. H. HARTMANN (Fermentforsch., 1936, 15, 183—190).

E. A. H. R.

Amino-nitrogen of nephritic transudates. H. A. BULGER (Proc. Soc. Exp. Biol. Med., 1936, 34, 221—222).—The average $\text{NH}_2\text{-N}$ contents of serum and transudates of patients with nephritis do not differ appreciably from those of non-nephritic persons, showing that rapid extravascular proteolysis does not occur in nephritis.

W. McC.

Sodium chloride restriction and urea clearance in renal insufficiency. E. M. LANDIS, K. A. ELSOM, P. A. BOTT, and E. SHIELS (J. Clin. Invest., 1935, 14, 525—541).—On a const. diet and fluid intake restricted intake of NaCl was accompanied by slightly diminished urea clearance (24 hr.). Administration of NaCl lowered plasma-urea (I) and increased the clearance. In advanced renal insufficiency (I) decreased markedly on administration of NaCl ; acute NaCl restriction produced hypochlor-

æmia with temporary retention of urea, creatinine, and PO_4''' .

CH. ABS. (p)

Kidney function in children. I. Urea clearance values (a) with no evidence of kidney disease, (b) after acute hæmaturic nephritis, (c) in the acute stage of the nephritis. G. E. CULLEN, W. E. NELSON, and F. E. HOLMES (J. Clin. Invest., 1935, 14, 563—574).—Vals. for normal children and adults and nephritic children show no fundamental differences.

CH. ABS. (p)

Rôle of certain inorganic elements in the cause and prevention of perosis. H. S. WILGUS, jun., L. C. NORRIS, and G. F. HEUSER (Science, 1936, 84, 252—253).—Perosis is due to lack of certain elements, especially Mn, and is aggravated by excess of Ca and probably of P. Al and Zn have a less effective preventive action than Mn.

L. S. T.

Alteration in content of alkaline-earth metals in pathological body-fluids. S. TOMISAWA (Mitt. med. Akad. Kioto, 1936, 17, 340—341).—The Ca and Mg contents of exudates, transudates, and sera from patients had some relationship to the course of their illnesses. In many cases during recovery, Ca increased and the Mg decreased, whilst when the condition became worse, Ca usually decreased and Mg increased.

NUTR. ABS. (m)

Ascorbic acid excretion in pneumonia and other pathological conditions. J. G. M. BULLOWA, I. A. ROTHSTEIN, H. D. RATISH, and E. HARDE (Proc. Soc. Exp. Biol. Med., 1936, 34, 1—7).—In pneumonia and other fevers urinary excretion of ascorbic acid following administration of large doses of vitamin-C is abnormally low.

W. O. K.

Nervous system during pregnancy. H. RASCHBA (Ukrain. Biochem. J., 1936, 9, No. 1, 55—68).—During pregnancy the creatine and H_2O content of the brain of rabbits is normal but the total N appears to be slightly reduced. In guinea-pigs' brain pregnancy produces no change in creatine, total N, or H_2O content.

W. O. K.

Glutathione. I. Total and reduced glutathione, oxygen content and capacity, and cell volume of blood in non-pregnant and pregnant women with special reference to toxæmias of pregnancy. F. W. OBERST and E. B. WOODS (Amer. J. Obstet. Gynecol., 1935, 30, 232—236; cf. A., 1935, 1392).—No essential differences were found in the total or reduced glutathione (I) or % O_2 saturation of normal, pregnant, or parturient women. In the puerperium total (I) decreased slightly. Vals. were unaffected by late pregnancy toxæmias. The % O_2 saturation was increased by use of anæsthetics containing O_2 and was somewhat higher in non-convulsive toxæmias.

CH. ABS. (p)

Diagnosis of pregnancy by the S. African clawed toad (*Xenopus laevis*). H. A. SHAPIRO and H. ZWARENSTEIN (S. African Med. J., 1935, 9, 202—205).—The Et_2O extract of acidified urine is treated with EtOH and the centrifuged and washed ppt. is dissolved in H_2O and injected into toads.

CH. ABS. (p)

Aschheim-Zondek [pregnancy] test. J. B. DAWSON (New Zealand Med. J., 1935, 34, 22—25).—Urines for this test may be preserved by addition of H_3BO_3 (20 grains per oz.). CH. ABS. (p)

Kidney function during normal pregnancy. M. NICE (J. Clin. Invest., 1935, 14, 575—578).—Urea (I) clearance during pregnancy is $>$ normal and is not affected by increasing the blood-(I) by feeding (I). CH. ABS. (p)

Fasting ketosis in the pregnant rat as influenced by adrenalectomy. E. M. MACKAY and R. H. BARNES (Proc. Soc. Exp. Biol. Med., 1936, 34, 682—683).—Pregnant rats develop a ketosis $>$ that in non-pregnant animals. It is abolished by adrenalectomy. P. G. M.

Respiration and glycolysis in normal and pathological skin with special reference to psoriasis. A. BUHMANN (Biochem. Z., 1936, 247, 145—152).—Anaerobic glycolysis in healthy human skin is relatively vigorous and the O_2 consumption is low. Glycolysis probably occurs under aerobic conditions also. In psoriasis the O_2 consumption increases on the average about 27% and the glycolysis about 68%. The age of the diseased skin has no effect on O_2 consumption or glycolysis. Aerobic glycolysis occurs in psoriatic skin. Increases in O_2 consumption and glycolysis $<$ those observed in psoriasis are observed in other pathological affections of the skin. W. MCC.

Dust in Mansfeld lung affections. W. GEISLER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 87—116).—The dust from the Mansfeld cupriferous slate workings contains much quartz (I) and mica (II), that from the overlying sandstone-shale mixture much (I) and feldspar (III). Affected lung tissue showed much (I) and (III), a little (II) and rutile, and very little sericite (IV). It is improbable that (IV) is the main causal agent of these affections. In studies on the individual cell (various bacteria) dusts of Si compounds showed no toxic effect; sol. Si compounds showed only low toxicity, decreasing in the order K silicate, Na silicate, aq. SiO_2 sol, glycol silicate. True solubility in H_2O at p_H 7.6 is shown only with clay and asbestos but not with any of the constituents of the Mansfeld slate. M. A. B.

Dust-affected lungs. II. Silica and titanium contents of lungs from 100 cases of dust affection. G. GERSTEL (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 304—348).—The intensity of the lung affections did not appear to depend only on the TiO_2 , SiO_2 , or ash content of the lung, although the heaviest deposits were found in the more severe cases. M. A. B.

Asbestosis bodies. P. J. BEGER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 349—392).—The capsule of asbestosis bodies consists of protein and not SiO_2 (cf. Koppenhofer, A., 1935, 1022). The n of the Fe-free capsule is \gg that of SiO_2 gels and is practically the same as that of the blood corpuscles and tissue particles in microscopic preps. The capsule shows similar solubility in acids and alkalis to blood corpuscles and tissue particles, and is combustible. Koppenhofer's technique is criticised and the unreliability of the I-azide reaction for protein is pointed

out. The mechanism of the deposition of the protein capsule on the asbestos needle is discussed. M. A. B.

Idiopathic steatorrhœa with multiple nutritional deficiencies. H. W. FULLERTON and J. A. INNES (Lancet, 1936, 231, 790—792).—A case report with evidence of a deficiency of Ca, Fe, anti-anæmic factor, vitamin-B complex, and -C and -D. A possible deficiency of -A and -E is discussed. L. S. T.

Differential glycæmia in pulmonary tuberculosis following administration of glucose-insulin. R. DEL ZOPPO (Arch. Farm. sperim., 1936, 62, 1—16).—Mild forms of the disease do not affect carbohydrate metabolism in man. Initially the venous and capillary blood-sugar levels differ both during fasting and after administration of glucose. The non-occurrence of this difference in advanced cases excepting after injection of insulin and the prolonged alimentary glycæmia curve indicate hypofunction of the pancreas. F. O. H.

Ascorbic acid metabolism in tuberculosis. F. H. HEISE and G. J. MARTIN (Proc. Soc. Exp. Biol. Med., 1936, 34, 642—644).—55—138 mg. of ascorbic acid daily are required to bring a tuberculous patient into equilibrium as regards vitamin-C nutrition (normal is 15—20 mg.). P. G. M.

Euglobulin in human serum in different forms of pulmonary tuberculosis. J. VIGNATI and M. RAUCHENBERG (Compt. rend. Soc. Biol., 1936, 123, 167—168).—The val. is independent of that of the other protein fractions of the serum. H. G. R.

Peptic ulcer following loss of pancreatic secretion through a fistula. M. T. HOERNER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 302—305).—Following the production of a pancreatic fistula, the p_H of gastric contents was unchanged but that of the duodenum after fasting varied somewhat, and reached a low level after ingestion of protein or carbohydrate. CH. ABS. (p)

Influence of chemical thought on biology. (SR) F. G. HOPKINS (Science, 1936, 84, 255—260).—A lecture. L. S. T.

Carbon dioxide diffusion through human skin. H. HAEUSSLER (Pflüger's Arch., 1935, 237, 448—453). M. A. B.

Effect of oxygen inhalation on gaseous distension of the stomach and small intestine. J. FINE, J. B. SEARS, and B. M. BANKS (Amer. J. Digest. Dis. Nutrition, 1935, 2, 361—367).— H_2 is much more readily absorbed from the gastro-intestinal tract than is N_2 . Pure O_2 inhalation does not increase absorption of H_2 . The efficiency of O_2 for absorption of intestinal gases $\propto [O_2]$. CH. ABS. (p)

Ultracentrifugation and oxygen consumption of the eggs of *Ascaris suum*. Goeze. G. C. HUFF and E. J. BOELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 626—628).—Respiration in *Ascaris* eggs is lowered by centrifuging. Respiratory and cleavage processes are not associated. P. G. M.

Gaseous metabolism of the mammalian heart in sufficiency and insufficiency. K. GOLLWITZER-MEIER, K. KRAMER, and E. KRÜGER (Pflüger's Arch.,

1936, 237, 68—92).—The gaseous metabolism of the heart increases with increased load whether due to increased resistance (aortic pressure) or increased inflow, but differs in the two cases. In both, the efficiency increases to a max. and then decreases. In spontaneous insufficiency the O_2 utilisation increases for a given load, whilst the efficiency decreases; the optimum efficiency shifts towards the region of lighter load. The arterial O_2 tension varies with the magnitude of the heart minute-vol. and the ventilation of the lungs, decreasing with decreased ventilation and *vice versa*. Increased resistance first decreases and then increases the capillary O_2 utilisation in the heart-muscle. M. A. B.

Effect of training on the respiration of muscle-tissue. E. T. SORENI (Ukrain. Biochem. J., 1936, 9, 193—203).—The semitendinosus and biceps femoris muscles of rabbits, after short faradic stimulation for 15 min. daily for 15 days, show a large increase in respiratory activity compared with control muscles. The effect with the red muscle is < with the white muscle. F. A. A.

Fasting and realimentation in the ruminant.
I. **Effect of food and fasting on certain blood constituents.** II. **Calcium and phosphorus metabolism during fasting, and during realimentation followed by fasting.** F. X. AYLWARD and J. H. BLACKWOOD (Biochem. J., 1936, 30, 1819—1824, 1824—1832).—I. Lipin-P decreases, and acid-sol. inorg. and org. P increase, in the blood of cows during fasting. Other blood constituents remain practically const., in contrast with the effects observed with single-stomached animals.

II. During prolonged fasting (12 days) Ca and P continue to be excreted by cows, and the data indicate that they are derived from both bone and phosphoprotein. F. A. A.

Effect of excessive dietary sodium chloride on liver- and muscle-glycogen in the rat. D. G. CRABTREE and B. B. LONGWELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 705—707).—High NaCl content of the diet causes a large increase in liver- but has little effect on muscle-glycogen. P. G. M.

Calcium content of the body in relation to the calcium and phosphorus content of the food. L. B. WHITCHER, L. E. BOOHER, and H. C. SHERMAN (J. Biol. Chem., 1936, 115, 679—684).—Diets containing 0.42% of P and with Ca:P=1.2—2.4 or containing 0.73% of P and with Ca:P=0.7—1.4 do not increase the rate of calcification in rats; this effect is opposite to that found with diets containing 0.42% of P and with low Ca:P ratios (0.16—0.5) (A., 1931, 1326). F. A. A.

Effect of liberal intakes of calcium or calcium and phosphorus on growth and body-calcium. E. W. TOEFFER and H. C. SHERMAN (J. Biol. Chem., 1936, 115, 685—694).—Increasing the Ca or Ca+P contents of adequate diets results in more rapid growth and rate of calcification in rats, including those of the second generation. The max. effect is obtained at about 0.64% of Ca. F. A. A.

Protein intake in relation to growth and rate of calcification. R. T. CONNER and H. C. SHERMAN

(J. Biol. Chem., 1936, 115, 695—706).—With diets of approx. min. adequate Ca content (0.2%), raising the protein (I) level from 14% to 28% promotes growth and calcification in young rats. At higher Ca levels, increasing (I) to 25% gives a further increase in growth; further increase of (I) in the diet to 40% does not enhance this effect.

F. A. A.

Effect of digestibility on the availability of iron in whole wheat. E. McC. VAHLTEICH, M. S. ROSE, and G. MACLEOD (J. Nutrition, 1936, 11, 31—36).—Hæmoglobin regeneration in depleted rats receiving a whole milk diet was influenced by supplements in the order predigested wheat > natural fine-ground wheat > minerals ($FeCl_3$, $CuSO_4$). Ease of digestion contributed largely to the val. of predigested wheat. A. G. P.

Protein utilisation as affected by the presence of small amounts of bran or its fibre. E. H. FUNNELL, E. McC. VAHLTEICH, S. O. MORRIS, G. MACLEOD, and M. S. ROSE (J. Nutrition, 1936, 11, 37—45).—Of the total N intake of human subjects the proportion excreted when prepared bran was added to the diet was > when the fibre from the same amount of bran was used and, in turn > when no supplement was given. Feeding of vitamin-B with the fibre did not affect these results. Bran decreased the digestibility coeff. of the ration, the difference being attributable to excretion of bran protein. A. G. P.

Specific dynamic action of carbohydrate and of protein in human hypothyroidism after total ablation of the normal thyroid gland. M. LANDOWNE (J. Clin. Invest., 1935, 14, 595—603).—Ingestion of carbohydrate (I) or of protein (II) after complete removal of the thyroid is followed by an increased O_2 consumption, thus demonstrating sp. dynamic effects of (I) and (II). CH. ABS. (p)

Effect of high-protein diets on the kidney function in dogs. L. K. CAMPBELL (J. Lab. Clin. Med., 1935, 20, 1162—1163).—No disturbance followed prolonged use of a diet containing 5 g. of protein per kg. live wt. with adequate supplies of other nutrients. CH. ABS. (p)

Absorption of undigested proteins in man.
IV. **Absorption of unaltered egg-protein in infants and in children.** S. J. WILSON and M. WALZER (Amer. J. Dis. Children, 1935, 50, 49—54).—Absorption of unchanged egg-protein is a normal function in infants, children, and adults. CH. ABS. (p)

Protein with sulphur-containing amino-acids suitable for feeding experiments. Y. KOTAKE, jun., H. NAKATA and F. FUJIKAWA (Z. physiol. Chem., 1936, 243, 270—271).—The failure of *Pisum sativum*, L., to maintain growth is counteracted by addition of 0.5% of *l*-cystine or 0.625% of *l*-methionine. The proteins of the bean, legumin (I), vicilin, and legumelin, contain respectively 0.46, 0.26, and 1.1% of S. (I) and its acid hydrolysate contain insufficient S for maintenance of growth. The hydrolysate is rendered capable of maintaining growth by addition of *l*-cystine but not by that of *l*-tryptophan. W. McC.

Amino-acid contents of eggs and chicks. Relation to diet and to incidence of chondrodystrophy. A. R. PATTON and L. S. PALMER (J. Nutrition, 1936, 11, 129—134).—The glycine (I) content of chondrodystrophic embryos was < normal. Synthesis of (I) occurs during embryonic development. Feeding (I) to hens did not affect the (I) content of eggs. Large doses were toxic. The NH_2 -acid distribution in eggs from hens receiving optimum or deficient diets revealed no significant influence of diet on the composition of egg-proteins.

A. G. P.

Intermediary metabolism of tryptophan. XVIII. Mechanism of kynurenine production from tryptophan. I. Y. KOTAKE and T. MASAYAMA [with C. ITAGAKI]. XIX. *d*-Indolyl-lactic acid. K. ICHIHARA and H. NAKATA. XX. Production of indole from tryptophan derivatives by *B. coli*. XXI. Biological production of *d*-tryptophan. S. MAJIMA. XXII. Difference between rats and mice in the utilisation of tryptophan and its derivatives. Y. KOTAKE, K. ICHIHARA, and H. NAKATA. XXIII. Production of kynurenine acid by various animals. K. ICHIHARA and S. GOTO. XXIV. Hæmatopoietic action of tryptophan. T. HAMADA (Z. physiol. Chem., 1936, 243, 237—244, 244—246, 247—250, 250—253, 253—256, 256—258, 258—265).—XVIII. Fresh rat's and rabbit's liver and liver extracts convert *l*-tryptophan (I) into kynurenine (II) and prokynurenine (III), whilst the boiled extracts convert *l*-(I) into (III) only. *d*-(I) yields (III) but not (II). (II) yields aminoacetophenone (IV) on heating in solutions slightly alkaline with $\text{Ba}(\text{OH})_2$ but (III) gives (IV) only when heated with conc. aq. K_2CO_3 . Hence the power of liver and liver extracts to convert (III) into (II) is destroyed by heating. Optimal conditions for the production of (II) and (III) from *l*-(I) by liver are: temp. 37.5° , p_{H} 6.5, concn. of *l*-(I) 0.04*M*, and an O_2 atm. (III) is probably the lactam corresponding to (II) and is produced from the first decomp. product of *l*-(I), namely 2-hydroxytryptophan.

XIX (cf. A., 1931, 513). *dl*-Indolyl-lactic acid (V) with quinine in MeOH gives a salt, $[\alpha]_{\text{D}}$ approx. -104.5° in MeOH, which on decomp. with HCl and extraction with Et_2O yields *d*-(V), m.p. $97-100^\circ$, $[\alpha]_{\text{D}} +5.18^\circ$ in H_2O . *d*-(V) replaces (I) in the diet of rats, being about twice as effective for growth as *sdl*-(V).

XX. *B. coli* convert *l*-(I) quantitatively and *d*-(V) almost quantitatively into indole, which is not produced from *l*-(V) and only slightly from indolepyruvic acid.

XXI. When *dl*-(I) is treated with *B. coli* at p_{H} 7.2 the *l*-form is converted into indole which is removed with Et_2O and a 66% yield of *d*-(I) is obtained. Similarly *d*-2-methyltryptophan, m.p. 231° , $[\alpha]_{\text{D}} +18.78^\circ$ in H_2O , is obtained in 72% yield from the *dl*-form.

XXII. In rats *d*- and *dl*-(I) and *l*-(V) are utilised almost equally well, the utilisation of *dl*-(V) being poor, whereas in mice *l*-(I) and *l*-(V) are utilised whilst *d*-(I) and *d*-(V) are not. Probably the power of the rat to convert (V) into indolepyruvic acid is > that of the mouse. When the diet is poor in cystine, rats utilise methionine much better than do mice.

XXIII. After administration of (I), kynurenine acid (VI) occurs in human urine but not in the urine and bile of the cat and hen or in human bile. (VI) is found in small amounts in the urine and bile of rats and mice and in very small amounts in the bile of guinea-pigs after administration of (I).

XXIV. A diet free from (I) produces, in rats and mice, anæmia which is readily cured by subcutaneous administration of *l*-, but not *d*-, (I) which also stimulates growth. *l*-(I) given orally also cures the anæmia, but is more effective in stimulating growth. The effect of *l*-(I) given in successive small doses is \gg that observed when one large dose is given. W. McC.

Comparison of glycine and guanidinoacetic acid as precursors of creatine. M. BODANSKY [with V. B. DUFF and C. L. HERRMANN] (J. Biol. Chem., 1936, 115, 641—652).—Creatine (I) fed to rats transiently increases the (I) level of muscle, liver, and kidney; the guanidinoacetic acid (II) (traces of which normally occur in kidney and alimentary tract but not heart, muscle, and liver) levels remain unchanged. Following administration of (II), considerable amounts of (II) appear in liver and kidney (but not in muscle), up to 50% is excreted unchanged, whilst kidney- and urine-(I) increase. Methylation of (II) possibly occurs in the kidneys. No evidence of glycine being a precursor of (I) was obtained (cf. this vol., 369).

F. O. H.

Synthesis of creatine during protein inanition. G. MOUROT (Bull. Soc. Chim. biol., 1936, 18, 1513—1523).—The sum of the amounts of creatine-N in the excreta of rats during, and in the bodies of rats after, periods of total or protein inanition is > that originally present.

A. L.

Origin of urinary creatinine. A. GOUDSMIT, jun. (J. Biol. Chem., 1936, 115, 613—625).—The "apparent" creatinine (I) content of venous blood of dogs is consistently < that of arterial blood, the difference agreeing with the theory that the substance in blood responsible for Jaffe's reaction is the precursor of urinary (I). The excretion of this chromogenic substance is probably similar in the first stages to that of ingested (I).

F. O. H.

Fate of protamines in the fertilised egg. K. FELIX, L. BAUMER, and E. SCHÖRNER (Z. physiol. Chem., 1936, 243, 43—56). The spermatozoa and eggs of herrings and the eggs of the rainbow trout contain dipeptidase (I) and arginase (II) and the spermatozoa of the trout contain (II). Trypsin, cathepsin, and polypeptidase are absent. Trout's eggs, 18 hr. after fertilisation, contain (I) which disappears in about 7 days and (II) which first decreases in amount and then increases as the egg develops. On fertilisation and during development the arginine (III), tyrosine, cystine (IV), and histidine (V) contents of the eggs remain almost const. whilst the tryptophan (VI) and lysine (VII) contents decrease. The protamine (VIII) of trout's eggs closely resembles clupeine, its chief constituent being (III). The spermatozoa contain, in addition to (VIII), (IV)—(VII), and other NH_2 -acids.

W. McC.

Fat metabolism in fishes. X. Hydrogenation in the fat depôts of the tunny. J. A. LOVERN

(Biochem. J., 1936, 30, 2023—2026).—The component fatty acids of the fats from the flesh, liver, pyloric caeca, heart, and spleen of the tunny, *Thunnus thynnus*, exhibit peculiarities probably characteristic of the tunny family such as lack of C_{14} acids, low palmitoleic (I) and high palmitic (II) and stearic acid (III) contents. The content of (III) of the different fats inversely \propto the degree of unsaturation of the remaining C_{18} acids and simultaneous hydrogenation of oleic acid and polyethylenic acids (C_{18}) is suggested as the explanation. Hydrogenation of (I) to (II) and of unsaturated C_{20} acids to arachidic acid also occurs. It is suggested that by hydrogenation the content of saturated acids is maintained roughly const. and at a higher level than is usual for fish fats, possibly because of the warm habitat of the tunny and of the fact that its body-temp. is somewhat $>$ that of the H_2O . P. W. C.

Rôle of the liver in fat metabolism. Lipase action. J. BENEDIOT (Arch. exp. Path. Pharm., 1936, 182, 537—549).—The serum-lipase activity of normal and diseased men is practically const. for each individual. The activity is increased by ingestion of fat (the increase being due to liver-lipase) and diminished by that of carbohydrate, whilst that of fat + carbohydrate has no significant effect, indicating antagonism between their hepatic catabolisms. F. O. H.

Metabolism of ethyl esters of fatty acids. H. J. DEUEL, jun., L. HALLMAN, J. S. BUTTS, and S. MURRAY (Proc. Soc. Exp. Biol. Med., 1936, 34, 669—671).—When the Et esters of odd C chain acids were fed, only small amounts of ketones are excreted. Acetonuria after administration of esters of acids with $< 8 C$ is $>$ that of $CH_2Ac \cdot CO_2'$ controls. P. G. M.

Effects of increased metabolism on the ketone body excretion of depancreatized dogs. S. B. BARKER (Proc. Soc. Exp. Biol. Med., 1936, 34, 893—897).—Increased metabolism always takes place at the expense of fat oxidation and ketone formation. P. G. M.

Rôle of phosphorus in carbohydrate and fat absorption processes. S. E. EPELBAUM (Ukrain. Biochem. J., 1936, 9, 409—420).—A review. F. A. A.

Carbohydrate metabolism. H. WEIL-MALHERBE (Nature, 1936, 138, 551; cf. this vol., 1412).—Succinic acid is formed from $AcCO_2H$, $AcOH$, and α -ketoglutaric acid (I) both anaerobically in minced brain and aerobically in minced brain poisoned with malonic acid. The decarboxylation of (I) by brain-tissue under anaerobic conditions depends on the presence of suitable H acceptors. Evolution of CO_2 is increased by addition of brilliant-cresyl-blue and reduced to normal when the dye is decolorised. The mechanism of decarboxylation is discussed. L. S. T.

Carbohydrate metabolism. G. K. MCGOWAN and R. A. PETERS (Nature, 1936, 138, 552).—Using avitaminous pigeon's brain tissue, no increased or decreased vitamin- B_2 effect was observed by adding α -ketoglutaric (I) to pyruvic acid (II). The extra O_2 uptake catalysed by $-B_1$ in presence of (II) in

these brain systems does not follow the equation (cf. this vol., 1412) $(I) + \text{ketonic acid} + H_2O \rightarrow \text{succinic acid} + CO_2 + \text{"OH"-acid}$. L. S. T.

Carbohydrate metabolism of the isolated cat liver. E. LUNDGAARD, N. A. NIELSEN, and S. L. ØRSKOV (Skand. Arch. Physiol., 1936, 73, 296—313).—Although the perfused rabbit liver stores glycogen (I) from glucose (II) that of the cat does not; as with the rabbit liver addition of insulin has no effect. Fructose (III) and lactic acid (IV) are stored as (I) in perfused liver from normal cats or from cats depancreatized 48 hr. previously. It is supposed that hexoses must be first converted into (IV) before giving rise to (I) in the mammalian liver, and that the inability of the isolated cat liver to form (I) from (II) is due to its lack of power to convert (II), but not (III), into (IV). NUTR. ABS. (m)

Carbohydrate metabolism of kidney. M. J. LAWSON (Biochem. J., 1936, 30, 1996—2003).—In excised rabbit's kidney added $0.5M$ - NaF inhibits production of lactic acid (I) but does not affect liberation of PO_4''' and $0.01M$ - KCN at p_H 7.0 does not affect production of (I) or PO_4''' liberation. At p_H 7.0 0.01 — $0.02M$ - $CH_2I \cdot CO_2Na$ inhibits (I) production in the cortex and in 3 hr. at 37.5° decreases the (I) content but does not affect PO_4''' liberation. Large amounts of (I) are produced by the cortex from glucose, smaller amounts from glycogen (II), still less from fructose, and none from galactose and mannose; from hexose mono- and di-phosphate a little (I) is sometimes produced. (II) of the cortex is insufficient to account for the (I) produced in 2 hr. at 37.5° . Glycolysis in the cortex is not accelerated by $0.002M$ - AsO_4''' . The cortex readily reduces $AcCO_2H$ to (I) and $AcCO_2H$ may be an intermediate in glycolysis. W. McC.

Carbohydrate metabolism of warm-blooded animals during muscular work. E. JOKL (Klin. Woch., 1935, 14, 1139—1143; Chem. Zentr., 1936, i, 101—102).—In rats moderate muscular work lowered the lactic acid content of the muscle and liver and increased that in blood. Exhaustive work lowered all vals., which increased again during rest (without food). The depôt-glycogen content of organs decreased during work; blood-sugar was unchanged by moderate exercise but declined with exhaustion. The phosphagen content increased in exhausted animals. A. G. P.

Significance of histotrophy in the carbohydrate metabolism of the foetus within the uterus. B. SZENDI and G. PAPP (Orvosi Het., 1935, 79, 890—895).—The decidua of man, rats, and rabbits contain relatively large amounts of glycogen, which diminish during pregnancy. Nutrition of the foetus depends on the combined effects of histotrophy and hæmotrophy. CH. ABS. (p)

Carbohydrate oxidation in hypophysectomised rats. R. E. FISHER and R. I. PENCHARZ (Proc. Soc. Exp. Biol. Med., 1936, 34, 106—107).—As compared with normal rats hypophysectomised rats continue to oxidise carbohydrate (I) for a longer time during fasting with a slightly higher R.Q., and they

derive a larger proportion of their energy from (I) after glucose feeding. W. O. K.

Glycogen of frog's liver and muscle after subcutaneous injection of sugars. A. MOSCHINI (Compt. rend. Soc. Biol., 1936, 123, 119—121).—Injection of glucose, fructose, galactose, or maltose increases glycogen, whilst sucrose or lactose has little effect. H. G. R.

Mechanism of glycogenolysis. J. K. PARNAS and P. OSTERN (Bull. Soc. Chim. biol., 1936, 18, 1471—1492).—Theoretical. A. L.

Site of formation of conjugated glycuronates in the organism. F. SCHMID (Compt. rend. Soc. Biol., 1936, 123, 223—226).—The liver is the chief site. H. G. R.

Respiratory exchange in children following administration of various carbohydrates: relation to curves for blood-sugar. J. L. LAW and H. GAY (Amer. J. Dis. Children, 1935, 50, 375—384).—The increase in R.Q. in the first 30 min. after ingestion of carbohydrates was highest for sucrose, followed, in descending order, by galactose, glucose, lactose, fructose, and dextri-maltose. The max. increase in heat production in this period appeared simultaneously with the peak of the blood-sugar curve. No parallelism was apparent between the max. vals. for R.Q. and blood-sugar.

CH. ABS. (p)

Metabolism of galactose. III. (1) Lactose synthesis from (a) a glucose-galactose mixture, (b) phosphoric esters, by slices of the active mammary gland *in vitro*. (2) Effect of prolactin on lactose synthesis by the mammary gland. G. A. GRANT (Biochem. J., 1936, 30, 2027—2035).—When glucose (I)-galactose (II) mixtures are used as substrates for lactating mammary tissue *in vitro*, lactose (III) synthesis is not noticeably increased beyond that for (I) alone and direct coupling of (I) and (II) does not appear to be the mechanism of (III) formation. An active β -galactosidase could not be detected in preps. of the lactating gland. (I) 6-phosphate, fructose 6-phosphate or 1:6-diphosphate, (II) 6-phosphate, and phosphoglyceric acid also did not give increased (III) synthesis, although the slices were active when (I) was substrate. NaF (0.04M) and $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Na}$ (0.02M) inhibit almost completely both (I) utilisation and (III) synthesis by slices of lactating tissue. The *in vivo* synthesis of (III) was re-established to a limited extent in the inactive regressing mammary glands of guinea-pigs by prolactin. The induced secretion resembled milk in appearance but had a low (III) content (0.04—0.24%). P. W. C.

Intravenous galactose liver-function test. I. R. JANKELSON and H. H. LERNER (Amer. J. Digest. Dis. Nutrition, 1934, 1, 310—312).—The rate of utilisation of galactose (I) by the liver may be ascertained by periodic measurements of blood-(I) following intravenous injection. In cases of demonstrable liver damage (I) is metabolised more slowly.

CH. ABS. (p)

Absorption of glucose and water from chronic isolated loops of the colon. P. H. MOORE and G. E. BURGET (Amer. J. Digest. Dis. Nutrition, 1934,

1, 376—382).—Optimal absorption of glucose (I) occurs with 5—10% solutions. Small amounts of NaCl do not affect, but NaHCO_3 retards, absorption of (I). Optimal absorption of H_2O takes place from 0.9% aq. NaCl; it is inhibited by 2.5% aq. (I) and with 10% solutions there is a definite H_2O influx. Small quantities of NaHCO_3 in an isotonic solution of (I) cause an influx of fluid into the intestine. Blood-sugar is not a true index of sugar absorption from the intestine when the amount absorbed is small.

CH. ABS. (p)

Absorption of glucose and galactose from dog's intestine. F. A. CAJORI and W. G. KARR (Amer. J. Med. Sci., 1935, 189, 880—881).—When both sugars were inserted into loops of the jejunum glucose (I) was absorbed more rapidly than galactose (II), the total carbohydrate absorption remaining about the same as when either sugar was given separately. Absorption rates were the same for each sugar administered alone. PO_4''' did not accelerate absorption of (I), (II), or fructose. CH. ABS. (p)

Oxidation of glucose in presence of insulin etc. and probable mechanism of biological oxidations.—See this vol., 1491.

Relations between liver function and metabolism of fructose. I—VI. Y. IIDA (Japan. J. Gastroenterol., 1934, 6, 61—93).—Impaired liver function is examined by means of blood-fructose curves after parenteral administration of fructose (I). Intestinal absorption of (I) is inhibited by hepatic disturbances. CH. ABS. (p)

Metabolism of fructose. IX. Effect of endocrine dysfunction on tolerance. A. W. ROWE, M. A. McMANUS, A. J. PLUMMER, and G. A. RILEY (Endocrinol., 1936, 20, 648—656).—The deviations of fructose tolerance from the normal vary considerably with the endocrine disturbance. The extent of agreement with the deviations of galactose tolerance also shows wide variations. R. N. C.

Production of hexose monophosphate and its conversion into fructose diphosphate in muscle. P. OSTERN, J. A. GUTHKE, and J. TERSZAKOWEC (Z. physiol. Chem., 1936, 243, 9—37).—Dialysed extract of autolysed rabbit's muscle even when 8 days old produces large yields of hexose monophosphate (I) from glycogen (II) and inorg. PO_4 (but not from glucose and inorg. PO_4), the process not being dependent on the presence of co-enzyme. When excess of (II) is present all the inorg. PO_4''' is consumed and when excess of inorg. PO_4''' is present all the (II) is consumed. In extracts inactivated with $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ and NaF deamination of adenosinetriphosphoric acid (III) is greatly accelerated by (I) and (II) [but not by fructose diphosphate (IV)], which act as PO_4 acceptors. In fresh or reactivated extracts which produce lactic acid (V) the deamination of (III) is inhibited by (IV) > (I) > (II) because phosphopyruvic acid, the sp. PO_4''' donor for rephosphorylation of adenylic acid, is produced. (I) is converted by (III) into (IV), probably by direct transfer of PO_4''' from (III) to (I). (I) is not phosphorylated by inorg. PO_4''' . Phosphorylation of (II) by PO_4''' and the transfer of the P-containing residue from (III) to (II) are inhibited

by 0.01M-phloridzin, which also greatly checks hydrolysis of (III) to adenylic acid (VI) and H_3PO_4 but scarcely checks the transfer of PO_4''' from (III) to (I). Hence deamination of (III) is much more rapid when (I) is present than when it is replaced by (II). In the degradation of (II) to (V) the first stages are (II) + H_3PO_4 yielding (I) followed by (I) + (III) + H_2O giving (IV) + H_3PO_4 + (VI), no H_3PO_4 being liberated at any stage. In the degradation of (I) to (V) 0.5 mol. and in the degradation of (IV) to (V) 1 mol. of H_3PO_4 per mol. of (V) are liberated, respectively.

W. MCC.

Action of pilocarpine and potassium on phosphorylation in muscle. J. WAJZER and R. LIPPMANN (Bull. Soc. Chim. biol., 1936, 18, 1428—1435).—Whilst pilocarpine and K⁺ increase the decomp. of phosphagen (I) in normal frog's muscle, the contents of adenosinetriphosphoric acid and hexose esters remain const. In the presence of $CH_3I \cdot CO_2H$, however, the (I) content is affected only by K⁺.

A. L.

Carbohydrate resynthesis in the liver. H. VON EULER and G. GÜNTHER (Z. physiol. Chem., 1936, 243, 1—8).—About 50% of cozymase (I) added to sliced rat's liver is inactivated in 4 hr. Lactate (II) and pyruvate (III) added together with (I) to slices of rat's and guinea-pig's liver in O_2 disappear and the carbohydrate (IV) content increases in parallel or the consumption of (IV) which normally occurs when nothing is added is decreased. [No consumption of (IV) occurs when the (IV) content of the slices is very low.] When the amount of added (I) is increased the amount of (IV) synthesised and the amount of (II) which disappears increase. Probably (II) is converted by (I) into (III).

W. MCC.

Deuterium as an indicator in the study of intermediary metabolism. VII. **Bile acid formation.** R. SCHOENHEIMER, D. RITTENBERG, B. N. BERG, and L. ROUSSELOT (J. Biol. Chem., 1936, 115, 635—640; cf. A., 1935, 1407).—Following intravenous injection of 4:5-dideuterocoprostanone (I) into dogs with biliary fistulae, a D-containing unsaponifiable substance [probably (I)] occurs in the bile whilst cholic acid (II) from the bile is free from D. Hence coprostanone is probably not an intermediary in the hypothetical conversion of cholesterol into (II).

F. O. H.

Lactic acid metabolism of the heart in spontaneous insufficiency and in poisoning by sodium fluoride, iodoacetic acid, and euphylline. F. GOTTDENKER and C. J. ROTHBERGER (Pflüger's Arch., 1936, 237, 59—67).—In spontaneous insufficiency, in spite of coronary dilatation, the heart-muscle takes up less lactic acid (I) than normally and may even liberate it into the blood. In NaF poisoning, although (I) formation is inhibited, utilisation of the preformed (I) is not increased but often sinks to zero. With $CH_3I \cdot CO_2H$ and euphylline there is a marked, protracted dilatation of the coronary vessels, but (I) uptake is increased only for a short time, after which it decreases until liberation into the blood takes place.

M. A. B.

Rôle of the 4-carbon dicarboxylic acids in muscle respiration. J. M. INNES (Biochem. J.,

1936, 30, 2040—2048).—Methods for determination of fumaric (I), succinic (II), malic (III), oxaloacetic (IV), and pyruvic acid (V) are worked out. Addition of 2 mg. of (I) to 0.4 g. of minced pigeon breast muscle suspended in PO_4''' buffer (p_H 7) caused an increase in respiration during which some of the added (I) disappeared and was not found again either as (II) or (IV). During incubation of the muscle with (I) in O_2 , (IV) and (V) show a slight increase. The amount of (III) accumulating depended on the degree of oxygenation, none being obtained in O_2 but appreciable amounts in air. The latter amounts appeared, however, to have no fixed relationship to the amount of (I) present. The entire O uptake was never > could be accounted for by oxidation of some of the (I) disappearing. In experiments with washed tissue, (I) is oxidised in preference to lactic acid in equiv. concn. The results suggest that (I) is being utilised as a substrate for respiration and not as a catalyst for transference of O to other substrates in the muscle.

P. W. C.

Ketogenesis-antiketogenesis. III. **Metabolism of aldehydes and dicarboxylic acids.** IV. **Substrate competition in liver.** N. L. EDSON (Biochem. J., 1936, 30, 1855—1861, 1862—1869).—III. Rat liver slices are able anaerobically to form acid probably by dismutation from $MeCHO$, $EtCHO$, $PrCHO$, Bu^cCHO , and Bu^pCHO but not from hex-, hept-, and oct-aldehydes. Under aerobic conditions all these aldehydes are ketogenic except $EtCHO$, the ketone formation being of the same order as that with the corresponding fatty acids. With dicarboxylic acids and their derivatives there is increased O_2 consumption and the acids are neither ketogenic in livers of well nourished nor antiketogenic in livers of starved animals. Exceptions to this rule are malonic, hydroxymalonic, and mesoxalic acids which are strongly, and tartaric and oxalic acids which are weakly, ketogenic.

IV. Antiketogenesis is studied in liver slices of starved and well nourished rats in presence of added fatty acids. The rate of ketone formation is the outcome of competition between fatty acids and other oxidisable substrates for the oxidising systems of liver. Carbohydrates and their derivatives, e.g., lactate, pyruvate, $CO(CH_2 \cdot OH)_2$, alcohols, certain NH_2 -acids, and particularly glycerol and sorbitol are antiketogenic substances. The fatty acids also compete amongst themselves.

P. W. C.

Degradation of fenchone in the animal organism.—See this vol., 1514.

Active water and salt transport through the frog's skin. E. HUF (Pflüger's Arch., 1936, 237, 143—166).—Identical salt solutions separated by a frog's skin soon show differences in salt concn. which are increased when Na lactate or pyruvate is added to the solutions. When KCN is added the effect is either inhibited or reversed. Transport of H_2O and salts through the skin by an "active" energy-consuming process is probable.

M. A. B.

Permeability to ions of the isolated frog's heart. G. ORZECOWSKI (Arch. exp. Path. Pharm., 1936, 183, 77—86).—Washing of the heart with

normal (frogs) Ringer's solution after a period of washing with K-free Ringer's solution temporarily depresses cardiac activity due to action of K^+ which diffuses from perfusion fluid to heart-muscle or *vice versa*. Diffusion of Ca^{++} from salt solutions to heart-muscle does not occur. The "threshold" val. of $[K^+]$ of perfusing fluids at which K^+ is neither given up to nor taken from frog's heart-muscle is approx. 0.009%. The K content of dried frog's heart-muscle is 1.4—1.7%. F. O. H.

Phosphates and work. E. ATZLER, K. BERGMANN, O. GRAF, H. KRAUT, G. LEHMANN, and A. SZAKÁLL (Arbeitsphysiol., 1935, 8, 621—694; Chem. Zentr., 1936, i, 372).—Daily variations in the P balance in man and in dogs are examined. The min. P requirement of dogs is controlled by the metabolic level and not by body-wt. During exercise the P balance declines relative to the N balance for a time. Subsequent feeding of P lowers the N balance relative to that of P. Ca and P metabolism shows a similar relationship. The relative efficiency of org. and inorg. P is examined. In pregnancy with a levelled N balance, the P balance is negative during the first 19 weeks. Subsequently the P balance is positive and inorg. P is readily retained. A. G. P.

Sodium-potassium antagonism and its significance in water metabolism. C. DIENST (Arch. exp. Path. Pharm., 1936, 182, 567—576).—Examination of the urine of salt-treated men shows that Na^+ displaces K^+ from the organism and *vice versa* but whilst Na^+ produces retention, K^+ enhances excretion of H_2O . Administration of large doses of K^+ to normal and ascitic men temporarily increases serum-K and subsequently urine-K and produces diuresis. F. O. H.

Rate of water loss by man at rest. I. Constant-temperature and -humidity room. II. Spontaneous diuresis during prolonged rest. P. D'A. HART and E. B. VERNEY (Clin. Sci., 1935, 1, 367—380, 380—396).—I. Experimental equipment is described.

II. During rest and fasting, spontaneous diuresis, commencing within 3—6 hr., is characterised by decreased urinary N and Cl and is inhibited by posterior pituitary extract. Relations between diuresis and the concn. of extract in the plasma are examined. CH. ABS. (p)

Oxidation-reduction potential, action of fuadin, and duration of life in *Opisthorchis*, *in vitro*. W. KOLLATH and A. ERHARDT (Biochem. Z., 1936, 287, 287—288; cf. Klin. Woch., 1935, 14, 1809).—The duration of life of the intestinal worm, *Opisthorchis tenuicollis felinus*, *in vitro* at 37° is maximal when the oxidation-reduction potential is -0.081 (in neutral Ringer's solution diluted 1:50,000) and at this potential the sp. toxic effect of fuadin is maximal. The effect is minimal at a potential of $+0.011$. W. McC.

Fate [in the organism] of complexes of citric acid with salts of heavy metals. H. LANGECKER (Arch. exp. Path. Pharm., 1936, 182, 642—653).—The complexes [with citrate (I) in anionic form] of Fe^{III} and Co^{II} are less readily oxidised by O_2 than is Na citrate. Liver or kidney pulp decomposes Fe^{III} ,

Mn^{II} , or Co^{II} complex but not that of Ni^{II} or Cu^{II} . Following intravenous injection into rabbits of Fe^{III} , Co^{II} , or Ni^{II} complex, a part of the metal appears in the urine; this occurs only slightly with Mn^{III} whilst with Fe^{III} , the Fe excretion is equivalently $>$ that of (I) and (I) does not appear in the intestine. Absorption of (I) from enterally administered Fe^{III} complex occurs only very slowly. F. O. H.

Fate of senna drugs in the organism. H. GEBHARDT (Arch. exp. Path. Pharm., 1936, 182, 521—526).—Injection of senna glucosides (I) into cats is followed by urinary excretion of (I) and conjugated (sulphate and glycuronate) emodin (II); with continuous intravenous injection of (I) or (II), the excretion is mainly of conjugated (II). Ingestion of (I) by men is followed by excretion of conjugated (II) with traces of free (II) and of free and conjugated anthranol. F. O. H.

Effect of X-radiation on the blood. H. L. BROSE and E. B. JONES (Nature, 1936, 138, 687—688).—Irradiation by X-rays or Ra reduces the ratio erythrocyte-P: plasma-P in man. This change may serve as a measure of the effect of X-ray dosages. L. S. T.

(A) Detection of mitogenetic rays with the help of a physical differential method. (B) Biological detection. W. W. STEBERT and H. SEFFERT (Biochem. Z., 1936, 287, 92—103, 104—108).—(A). Further experiments (cf. A., 1933, 336) are described using two light quanta enumerating tubes, one registering the variation in the effect of cosmic rays, the other of cosmic + mitogenetic rays. Curves are given showing differences due to a no. of mitogenetic effects. The mitogenetic effect of normal blood is destroyed by the presence of KCN.

(B). The method depends on the inhibition by mitogenetic radiation of the rate of elimination of gas by a fluid yeast culture. The results by the method compare favourably with those by the above physical method. P. W. C.

Influence of work and training on the oxidation-reduction potential of muscle-tissue. R. TSCHAGOVETZ (Ukrain. Biochem. J., 1936, 9, 273—307; cf. A., 1935, 1522).—The biceps femoris muscle of rabbits, fatigued by electrical stimulation *in vivo* for 45 min., and similar muscles after training (similar stimulation for 20 min. daily for 15 days) yield extracts showing differences in oxidation-reduction potential compared with control muscles of the same animals. With fatigued muscle the initial val. of potential is more positive, and the fall to the same final val. takes longer, than with unfatigued muscle. Training results in a diminution of positive potential and a quicker attainment of the stable val. The p_H of extracts from fatigued muscles is $>$, and that of trained muscle $<$, those of their respective controls. F. A. A.

Effect of acid and basic fodder on oxidative processes in muscles during work and training. M. F. GULI (Ukrain. Biochem. J., 1936, 9, 309—320).—Comparison is made between the rates of decolorisation of methylene-blue by the muscles of rabbits fed on acid and basic diets, and the effects of fatigue, training, and of training followed by fatigue, on these

muscles. In all cases the rate of decolorisation in the acid-fed animals is $>$ that in the basic-fed, and the difference is greater in trained than in fatigued muscles.

F. A. A.

Influence of the acid-base ratio of foods on some physico-chemical properties and the capacity for work of isolated muscle. G. BENETATO and N. MUNTEANU (Compt. rend. Soc. Biol., 1936, 123, 201—203).—The p_{H} , buffering power, and capacity for work are only slightly affected by the diet.

H. G. R.

Oxidation-reduction potential of muscle-tissue *in vivo*, *in situ*, and its functional variations. V. V. KOVALSKI and O. M. GLEZINA (Ukrain. Biochem. J., 1936, 9, 205—271).—The oxidation-reduction potential of leg muscles of rabbits, determined directly *in situ*, shows small irregular fluctuations and long periodic asymmetrical fluctuations. The val. of E_h differs between right and left legs of the same animal, due to unequal distribution of glutathione. E_h of muscles trained by continuous electrical stimulation is \ll that of normal muscle. Fatigue raises E_h of normal muscle, but lowers that of trained muscle. Further complex phenomena are discussed.

F. A. A.

Osmotic pressure and muscular contraction. I. CHAO (Chinese J. Physiol., 1936, 10, 547—558).—Parallel determinations of the contraction due to const. submaximal stimuli and of the wt. of the muscle preps. used (toad's sartorius) were made in solutions of varying osmotic pressure. The wt. of the muscle, after correcting for the wt. of osmotically inactive materials, is inversely \propto the osmotic pressure. A temporary increase in contraction occurs on increasing the osmotic pressure and *vice versa*. The contraction at osmotic equilibrium is max. in a slightly hypotonic solution. Within the limits of 4.3—8.5 atm., the contraction is a linear function of osmotic pressure.

P. W. C.

Chemical mediation of impulses in certain fibres of the splanchnic nerves. G. V. RUDD and F. M. KINROSS (Austral. J. Exp. Biol., 1936, 14, 193—198).—The pressor response to splanchnic stimulation in ergotoxinised dogs shows periodical alternations in character. It is influenced by the discharge of adrenaline from the gland and by the release of a pressor substance from some and of a depressor substance from other visceral terminations of the splanchnic nerve, not the adrenal.

A. G. P.

Effects of heat and humidity on the human body. C. K. DRINKER (J. Ind. Hyg., 1936, 18, 471—485).—A summary of the effects of exposure to high temp. (periodic or continuous). The importance of controlling NaCl and H₂O intake in cases of heat cramp and other conditions is stressed. Neither humidity nor sunlight is a prime factor; they merely intensify the effects of heat.

P. G. M.

Gastric motility under low oxygen pressures. E. J. VAN LIERE (Amer. J. Digest. Dis. Nutrition, 1934, 1, 373—376).—Anoxæmia decreased motility.

CH. ABS. (p)

Action of the gases issuing from fire-damp pockets. F. FLURY (Arch. Gewerbepath. Gewerbe-

hyg., 1935, 6, 257—269).—A discussion. Although none of the constituents of fire-damp is of high toxicity, long-continued exposure to them, together with the relative O₂ shortage occurring in mines, is probably responsible for the characteristic symptoms developed by coal-miners.

M. A. B.

Central-nervous regulation of the heart minute volume during breathing of air containing carbon dioxide. O. DIEBOLD and O. MERTENS (Pflüger's Arch., 1935, 237, 585—589).

M. A. B.

Influence of water administration on oxygen consumption rate in shock. H. A. DAVIS (Proc. Soc. Exp. Biol. Med., 1936, 34, 21—23).—In anæsthetised dogs in which shock had been induced by various means, intravenous administration of isotonic NaCl solution produced a rise in metabolism, less prolonged than that observed in normal anæsthetised animals. Whereas the latter tolerated isotonic NaCl solution up to 25% of the total body-wt., amounts equal to 5—12% of the body-wt. caused a fall in O₂ consumption in the shocked animals.

W. O. K.

Comparative action of mineral waters on the autonomous contraction of the ureter. P. TESTONI (Annali Chim. Appl., 1936, 26, 370—384).—The action of various Italian mineral waters on the contraction of the guinea-pig's ureter was determined. Analytical data indicate that generally stimulation is due to CO₂ and Ca⁺⁺ and inhibition to NO₃⁻, Br⁻, H₂S, and high concns. of Na⁺ and Cl⁻.

L. A. O'N.

Presence of sterols in the mud of the salt lake of Tékirghiol (Dobrodgea) [Roumania]. N. L. COSMOVICI and J. S. ATANASIU (Bull. Soc. Chim. biol., 1936, 18, 1425—1427).—Extracts of the black mud give reactions for sterols. The therapeutic action is probably due to the sterol content.

A. L.

Pharmacology of the mineral water of Valleverde. P. TESTONI (Annali Chim. Appl., 1936, 26, 283—290; cf. A., 1935, 1023).—The H₂O stimulates the germination of lupin seeds and the development of the plant, inhibits the movement of the epithelial cilia of the cesophagus of the frog, and stimulates the contraction of the ureter of the guinea-pig, and increases the tonus.

L. A. O'N.

Therapeutic effects of mineral waters. A. KELLER (Mitt. Lebensm. Hyg., 1936, 27, 204—215).—A review.

E. C. S.

Feeding deuterium oxide to rats. SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (Kong. Norske Vidensk. Selsk. Forhandl. 1935, 8, 27—28; Chem. Zentr., 1936, i, 360).—Apart from an initial period of increased thirst, D₂O had no appreciable effect on growth or sexual development of the animals.

A. G. P.

Occurrence of acidosis after experimental ammonia poisoning. N. ALWALL and E. GEIGER (Arch. exp. Path. Pharm., 1936, 183, 123—126).—Diminution of alkali reserve occurs in rabbits after introduction of aq. NH₃ into the stomach but not intestine. Hence the acidosis is not due to absorption of NH₃ (cf. Fazekas, this vol., 223).

F. O. H.

Methæmoglobin-producing action of sodium nitrite. S. RAPPEPORT-LEWEY (Arch. Farm. sperim.,

1936, 62, 17—36).—Intravenous injection of lethal doses (>0.12 g. per kg.) of NaNO_2 into rabbits causes death during which methaemoglobin formation occurs to the extent of 67.5—99%. Differences in rate of formation between cats and rabbits are discussed.

F. O. H.

Action of calcium salts on living tissue. L. I. WEBER (Cernauti Med., 1, No. 1, 57—59; Chem. Zentr., 1936, i, 373).—The influence of Ca salts of org. and inorg. acids on the swelling of gelatin gels is examined and the special action of Ca gluconate (I) is observed. The effects of injecting (I) on the natural gel of living muscle are explained on this basis.

A. G. P.

Determination of cardio-analeptic activity by means of the potassium-paralysed Straub frog's heart preparation. F. HENDRYCH (Arch. exp. Path. Pharm., 1936, 182, 738—748).—Heart preps. paralysed with 0.1% KCl solution are suitable for testing drugs owing to the paralysis being readily removed by washing with Ringer's solution. In restoring cardiac activity, adrenaline and caffeine and, to a smaller extent, "cardiazol" are effective; camphor, "coramin," ephedrine, and sympathol are not stimulatory but, at certain concns., paralytic.

F. O. H.

Liberation of acetylcholine from perfused human placenta. H. C. CHANG (Proc. Soc. Exp. Biol. Med., 1936, 34, 665—666).—K⁺ causes a transfer of acetylcholine (I) from tissue to fluid, whilst eserine and heat stimulate the formation of (I) by some unknown mechanism.

P. G. M.

Magnesium sulphate and catharsis. J. FERGUSON and A. C. IVY (Proc. Soc. Exp. Biol. Med., 1936, 34, 720—722). Subcutaneous injection of aq. 25% MgSO_4 does not cause catharsis by absorption into the blood followed by excretion into the colon, nor does it increase the excretion of Mg by the mucosa.

P. G. M.

Influence of magnesium oxide on antipyretic action and toxicity of aspirin in rabbits. D. R. CLIMENKO (Proc. Soc. Exp. Biol. Med., 1936, 34, 807—812).—The toxicity of aspirin (I) is unaffected by simultaneous administration of MgO . (I) and MgO are synergic as regards their antipyretic action.

P. G. M.

Influence of ethyl alcohol on energy metabolism of the mammalian heart. H. C. PETERS, C. E. REA, and J. W. GROSSMAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 61—64).—The total energy output of the isolated mammalian heart, working at const. diastolic vol., diminishes under the influence of EtOH.

W. O. K.

Liver-lipins of the white rat following chloroform poisoning, insulin administration, and fungus infection. P. L. MACLACHLAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 31—33).— CHCl_3 poisoning, insulin administration, or *Aspergillus* or *Sporothrix* infection produces no change in the lipin content of the livers of rats or in the ratio of phospholipin to neutral fat.

W. O. K.

Physiological action of methylglyoxal. E. MARTINI (Arch. ital. Biol., 91, 173—184; Chem. Zentr., 1936, i, 103).

A. G. P.

Toxicology of the organic solvents. 1:4-Dioxan. W. WIRTH and O. KLIMMER (Arch. Gewerbepath. Gewerbehyg., 1936, 7, 192—206).—Dioxan, absorbed through the respiratory tract, is about as toxic as MeOH but considerably less toxic than $(\text{CH}_2)_2\text{O}$.

M. A. B.

Oxidation-reduction processes in the inflammatory focus of the mucous membrane. V. V. KOVALSKI, M. M. BUGAEVA, and O. M. GLEZINA (Ukrain. Biochem. J., 1936, 9, 381—386).—Inflammation of the mucous membrane of the lip of a rabbit is accompanied by a change in oxidation-reduction processes, measured directly as E_h . Application of mustard gas to this membrane is accompanied by a fall in E_h , followed by a slow rise towards normal. This differs from the clinical picture.

F. A. A.

Microscopy of fat absorption in the normal gut and inhibition by iodoacetic acid and phloridzin. L. JEKER (Pflüger's Arch., 1936, 237, 1—13).—Free fatty acids give positive staining reactions with Fischler's $\text{Cu}(\text{OAc})_2$ -haematoxylin reagent and with Sudan III, neutral fats with Sudan III only. In the normal gut the first stage of absorption is the penetration of free fatty acids into the epithelial cells; later, synthesis of neutral fat occurs. In the poisoned gut penetration of fatty acids occurs but conversion into neutral fat is inhibited.

M. A. B.

Effect of dinitrophenol on the metabolism of frog muscle. E. RONZONI and E. EHRENFEST (J. Biol. Chem., 1936, 115, 749—768).—2:4-Dinitrophenol (I) ($5 \times 10^{-5}\%$) accelerates the O_2 consumption of frog's muscle 6—10 times, glycogen being consumed. Caffeine has a similar effect, only slightly enhanced by (I). Treatment with $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ reduces the effect of (I), which is partially restored by lactic acid (II). Anaerobic (II) production is accelerated 8—10 times, and continues until phosphocreatine (III) and adenosine phosphate are completely decomposed. O_2 prevents (II) accumulation. (I) accelerates the rate of hydrolysis of (III), and the data indicate inhibition of its resynthesis. In muscle extracts, (I) increases the rate of O_2 consumption, but does not affect the rates of production of (II) or of hydrolysis of (III). (I) appears to act by allowing a max. mobilisation of carbohydrate.

F. A. A.

Action of 2:4-dinitrophenol on the oxidation-reduction potential of the aqueous humour and crystalline lens of the rabbit. J. NORDMANN and P. REISS (Compt. rend. Soc. Biol., 1936, 123, 233—234).—Injections increase the potential to vals. similar to that of C_{10}H_8 cataract, no signs of which, however, are visible.

H. G. R.

Increase in blood-polypeptides in phenylhydrazine-poisoned dogs. A. VON JENEY and L. SOKORAY (Arch. exp. Path. Pharm., 1936, 182, 560—566).—The normal level of blood-polypeptide-N of 0.0024—0.0060% rises to 0.0054—0.0082%, whilst the erythrocyte count diminishes.

F. O. H.

Toxic effects of neutral diaminoacridine methochloride. H. WAREMBOURG, J. DRIESSENS, and G. LABENNE (Compt. rend. Soc. Biol., 1936, 123, 13—14).—Intravenous injection into the rabbit results in lesions in the lungs, adrenals, liver, kidneys,

and bone marrow, together with an increase in blood-urea and -polypeptides, and anæmia. Elimination appears to be through the liver and kidneys.

H. G. R.

Preparation and therapeutic properties of certain acridine derivatives.—See this vol., 1521.

Helenalin, the bitter sternutative substance occurring in *Helenium autumnale*.—See this vol., 1514.

***dl*-Methionine in developmental growth.** F. S. HAMMETT and K. PADIS (Proc. Soc. Exp. Biol. Med., 1936, 34, 181—183).—The early growth of *Obelia geniculata* is stimulated by very low concns. of *dl*-methionine (I). In the living organism (I) is possibly converted into cystine.

W. McC.

Pressor effects of some new alkyl derivatives of β -phenylethylamine. W. E. HAMBOURGER and R. B. JAMIESON, jun. (J. Pharm. Exp. Ther., 1936, 58, 53—61).—Me and Et derivatives are all less active than the parent substance, *p*-substitution reducing the duration of action. With *N*-Me a second *o*-Me or *p*-Et reduces the activity greatly, the latter sometimes showing a depressor action. The NH_2Et derivatives are depressor whatever the position of the substituted Me.

H. G. R.

Vasomotor interference in the vascular network of the muscles during experimental hyperæmia produced by vaso-dilator substances. F. GROSSE-BROCKHOFF, M. SCHNEIDER, and W. SCHOEDEL (Pflüger's Arch., 1936, 237, 178—189).—Adrenaline injected intravenously produced constriction in muscular blood vessels dilated by adenosine, adenylic acid, histamine, and glucose, but not after acetylcholine (I) dilatation. Resistance to vasoconstriction in the working muscle is probably due to the liberation of a substance [possibly (I)] as a result of the increased muscular activity.

M. A. B.

Influence of vaso-dilator substances on the output of work and the blood supply, during work, in the skeletal muscles. W. SCHOEDEL (Pflüger's Arch., 1936, 237, 190—212).—Acetylcholine, histamine, and adenylic acid all produced a further increase in blood supply in muscular vessels already showing hyperæmia due to work, but in no case did the increased blood supply result in a better output of work by the muscle. Probably none of these substances is involved in the hyperæmia of work.

M. A. B.

Physiology and pharmacology of sterols. I. Cholesterol and sterol economy. E. STARKENSTEIN. **II. Significance of cholesterol in permeability and absorption.** E. STARKENSTEIN and F. HENDRYCH. **III. Influence of sterols on the cutaneous absorption of drugs from unguents.** H. MATSCHAK. **IV. Influence of cholesterol on the action of hypnotics and narcotics.** **V. Influence of cholesterol mobilisation by saponin on the action of soporifics.** E. STARKENSTEIN and H. WEDEN (Arch. exp. Path. Pharm., 1936, 182, 654—663, 664—687, 688—699, 700—714, 715—719).—I. The physiological importance of sterols, especially cholesterol (I), is discussed.

II. The rôle of sterols, especially (I), in the influence

of cellular lipins on absorption of H_2O - and lipin-sol. substances and on cell permeability is discussed.

III. The theory that cutaneous absorption of drugs occurs more readily from salves of fat or lipin than from those of vaseline or paraffin could not be fully confirmed. The absorption of H and Na salicylate from lanoline and vaseline indicates that, in addition to the lipin- or H_2O -solubility of the drug, reactions with the base (e.g., esterification with sterol alcohols) or with cellular sterols influence the rate of absorption. Other factors include acidity of the salve and the sterol contents of salve and skin.

IV. Intraperitoneal injection of aq. emulsions of (I) or its esters into mice, rabbits, or guinea-pigs enhances the narcotic action of inspired Et_2O or CHCl_3 or subcutaneously injected Et_2O and the soporific action of veronal etc. Orally administered (I) is ineffective. Oils and fats resemble (I) but are often more active enterally owing to increased absorption of the narcotic. The action of (I) in increasing localisation of lipin-sol. dyes in the brain of injected animals indicates that (I) aids in the transport of narcotics to the nervous tissues.

V. The enhancement of the soporific action of veronal by prior intravenous injection of aq. saponin (II) is due to mobilisation of body-(I) by (II). That bees' poison acts similarly to (II) indicates that it contains a (II)-like substance.

F. O. H.

Inulin and its suitability for intravenous administration in man. W. GOLDRING and H. W. SMITH (Proc. Soc. Exp. Biol. Med., 1936, 34, 67—68).—Certain purified samples of dahlia and chicory inulin (I), administered intravenously to man, produced marked toxic symptoms. This action is probably the result of overheating (I) during drying.

W. O. K.

Effect of varying p_{H} on toxic effect of bile salts on the normal gall-bladder. H. G. ARONSOHN and E. ANDREWS (Proc. Soc. Exp. Biol. Med., 1936, 34, 763—765).—The toxic action of bile salts on the normal gall-bladder is unaffected by change of p_{H} within the normal range of the bile.

P. G. M.

Relative toxicity of different bile salts on the normal gall-bladder. E. ANDREWS and H. G. ARONSOHN (Proc. Soc. Exp. Biol. Med., 1936, 34, 765—767).—Deoxycholic acid is the most toxic to the gall-bladder wall.

P. G. M.

Effect of methylene-blue on respiration of blocked and developing embryonic cells. J. H. BODINE and E. J. BOELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 629—630).—Methylene-blue may act as a substitute for the part of the respiratory process impaired either naturally or by HCN.

P. G. M.

Action of hæmatoporphyrin on blood-calcium and -phosphorus. P. MABIQUE and G. MELOT (Compt. rend. Soc. Biol., 1936, 123, 280—283).—Ca is slightly lowered whilst changes in P are negligible.

H. G. R.

Tissue response to subcutaneous injection of cod-liver oil. J. DAVSON (Lancet, 1936, 231, 737—738).—Subcutaneous injection of fish-liver oils into rabbits produces a marked stimulation of phagocytes, fibroblasts, and young capillaries. Liquid

paraffin and olive oil are comparatively inert. The vitamin-A of the oils is not responsible for the reaction.
L. S. T.

Growth inhibitor in liver. A. M. BRUES, E. B. JACKSON, and J. C. AUB (Proc. Soc. Exp. Biol. Med., 1936, 34, 270—273).—The growth of explants of embryonic and sarcomatous tissue is inhibited by the solution obtained when fresh, sterile liver is shaken with 2 vols. of Tyrode's solution. The inhibiting agent does not dialyse and is fairly stable to O₂ but not to heat.
W. McC.

Supplement to Steenbock diet 2965. W. J. NIJVELD (Z. Vitaminforsch., 1936, 5, 257—262).—Addition of liver or liver extract to the diet prevented the unsatisfactory growth of rats, for there was a steady increase in wt. corresponding with an increased food intake. The deaths which frequently occurred after approx. 10 days on the ordinary diet were also prevented. The active factor of the liver is not in the ash, and it is not destroyed by heating dry powdered liver at 130° for 6 hr. Heating of liver extract in an autoclave at 120° did not completely remove the activity.
J. N. A.

Rôle of lactoflavin and flavinphosphoric acid in adrenal cortex deficiency and iodoacetic acid poisoning. F. VERZÁR and L. LASZT (Z. Vitaminforsch., 1936, 5, 265—275).—Adrenalectomised rats can be kept alive for > 2 months with yeast concentrates containing flavinphosphoric acid. Lactoflavin alone does not have this effect, and is unable, even in daily doses of 2×10^{-4} g., to cause growth in rats poisoned with CH₂I-CO₂H (I). Growth can take place as a result of refection in rats suffering from chronic (I) poisoning.
J. N. A.

Chemical factors governing gastric motility. J. P. QUIGLEY (Amer. J. Digest. Dis. Nutrition, 1934, 1, 425—426).—Fats and carbohydrates liberate humoral factors from the mucosa of the upper intestine which resemble an inhibitory hormone.
CH. ABS. (p)

Anæsthetic activity of butanes and pentanes. R. W. STOUGHTON and P. D. LAMSON (J. Pharm. Exp. Ther., 1936, 58, 74—77).—The activity and lethality of C₄H₁₀ are < those of C₅H₁₂ and those of the straight chain > those of the isomerides with branched chains.
H. G. R.

Local anæsthetic activity of quinoline compounds. H. K. SINHA (J. Pharm. Exp. Ther., 1936, 58, 62—67).—Activity, both when applied to the mucous membranes and on intradermal injection, is observed on introducing a basic side-chain at 8.
H. G. R.

Influence of the anæsthetic on the results of digitalis assay by the cat method of Hatcher and Brody. C. C. HASKELL (J. Pharm. Exp. Ther., 1936, 58, 111—117).—The cat unit with dial-urethane anæsthetic is > that with Et₂O.
H. G. R.

Detoxication of local anæsthetics by "cardiazol." K. ZIPF and H. HOPPE (Arch. exp. Path. Pharm., 1936, 183, 67—70).—The toxic effects of novocaine and larocaine in mice and cats are diminished by simultaneous injection of "cardiazol."
F. O. H.

Local anæsthetics containing the α -tetrahydro- β -naphthylamine pressor group.—See this vol., 1501.

Plasticity of skeletal muscle before and during deep narcosis. A. HEINRICH (Pflüger's Arch., 1936, 237, 19—23).
M. A. B.

Blood-ammonia during ether narcosis in man. L. STANOYEVITCH and S. PETKOVITCH (Compt. rend. Soc. Biol., 1936, 123, 430—432).—The increase is greater when the initial val. is high and after the anæsthesia remains at an increased level.
H. G. R.

Atropine-morphine-ether narcosis. F. HENDRYCH (Arch. exp. Path. Pharm., 1936, 182, 732—737).—The narcotic action of Et₂O on mice is enhanced by prior injection of morphine + atropine (I); (I) thus resembles scopolamine. The mechanism of the phenomenon is discussed.
F. O. H.

Sedative action of valerian. H. DRUCKREY and G. KÖHLER (Arch. exp. Path. Pharm., 1936, 183, 106—109).—The narcotic effect of different types of extract of valerian from various sources was determined by the action on the head movements of mice. Infusions are most, and Et₂O extracts least, active (cf. Kochmann and Kunz, this vol., 1022).
F. O. H.

Distribution of atebtrin in the organism. G. HECHT (Arch. exp. Path. Pharm., 1936, 183, 87—105).—Data for the distribution of atebtrin (I) in cats and rabbits following administration by various routes are tabulated. The general tendency is for (I) to be most conc. in liver, lungs, heart, kidneys, and spleen and, to a smaller extent, in intestines, heart, pancreas, and reproductive organs. Intramuscularly injected (I) is detectable in the blood for only 1 hr. after injection.
F. O. H.

Effect of drugs on the Schlesinger reaction for urobilin. J. J. HOFMAN (Pharm. Weekblad, 1936, 73, 1417—1421).—Acriflavine (I) when administered orally gives a positive Schlesinger test for urobilin in the urine [fluorescence when treated with EtOH-Zn(OAc)₂ suspension]. (I) is detected by treatment with NaOCl or KI-I solution, when a black ppt. is formed and the filtrate no longer fluoresces. Several precipitants for (I) are noted, the sensitivity being given in parentheses: 10% Na salicylate (1:10⁴), K₃Fe(CN)₆ (1:10⁵), K₄Fe(CN)₆ (1:10⁴), K₂Cr₂O₇ (1:10⁴), Na tungstate (1:10⁴), NH₄ molybdate (1:10⁴), HgCl₂ (1:10⁵).
S. C.

Endocrine localisation of medicinal and toxic substances. R. FABRE (Ukrain. Biochem. J., 1936, 9, No. 1, 125—141).—Various toxic substances including CHCl₃, C₂H₂Cl₄, veronal, quinine, F₂, and Cr are retained by the endocrine glands, on which they probably exercise a profound effect.
W. O. K.

Experimental hypertrophy with and without digitalisation on creatine content of rabbit hearts. G. M. DECHERD, jun., G. HERRMANN, and E. H. SCHWAB (Proc. Soc. Exp. Biol. Med., 1936, 34, 864—866).—There is an abs. increase in the creatine content of hypertrophied hearts which is further increased by administration of digitalis.
P. G. M.

Disturbance of protein metabolism following liver injury by salvarsan. A. WIEDMANN (Wien. klin. Woch., 1935, 48, 1539—1543; Chem. Zentr., 1936, i, 803).—Metabolism of protein but not carbohydrate is affected.

A. G. P.

Neuromuscular junction. II. Antagonism between calcium and curarising agencies. T. P. FENG (Chinese J. Physiol., 1936, 10, 513—527).—With nerve-sartorius preps. of the toad, Ca antagonises the curarising action of curare, eserine, veratrine, nicotine, atropine, ergotoxine, strychnine, pilocarpine, and novocaine, of fatigue and long survival, of Sr, Ba, and Mg, and of extreme temp. The immediate and reversible cause of curarisation appears to be an electrolytic disturbance involving the loss of Ca from the neuromuscular junction.

P. W. C.

Effect of calcium and curare on muscular contraction and neuromuscular transmission. I. CHAO (Chinese J. Physiol., 1936, 10, 545—546).—With sciatic-sartorius preps. of toad, excess of Ca decreases muscular contraction, whilst Ca antagonises the effect of curare and facilitates neuromuscular transmission.

P. W. C.

Action of ergometrine. K. K. CHEN, E. E. SWANSON, and C. C. HARGREAVES (Proc. Soc. Exp. Biol. Med., 1936, 34, 183—185).—Ergometrine nitrate (I) in a concn. of about 1:30,000 slightly stimulates the isolated rabbit uterus, having about 0.01% of the oxytocic activity of ergometrine (II). The action of (I) on the cock's comb is about 0.7% of that of (II). (I) relaxes isolated rabbit intestine and produces prolonged reduction of blood pressure in the cat.

W. McC.

Physico-chemical processes in nerve tissue. I. Oxidation-reduction potential in rabbit brain during strychnine and cocaine poisoning. S. V. FOMIN and D. N. STRAJESKO (Ukrain. Biochem. J., 1936, 9, No. 1, 43—54). The oxidation-reduction potential of rabbit brain tissue becomes stable more rapidly when from an animal poisoned with strychnine (I) or cocaine (II) than when normal. The potential of boiled brain tissue extract from rabbits poisoned with (I) is < that of a similar extract of normal tissue, but under anaërobic conditions the potentials of both boiled and unboiled extracts are higher from the poisoned than from normal animals. (II) poisoning also produces changes in the oxidation potentials of the extracts.

W. O. K.

Comparative action of cobra venom and morphine on the autoxidation of cerebral and other tissues. D. I. MACHT and H. F. BRYAN (Compt. rend. Soc. Biol., 1936, 123, 385—388).—The inhibition with venom is more prolonged than with morphine, since a modification of the alkaloid is observed if the time of contact is long.

H. G. R.

Poisons of animal origin. The venins. M. T. REGNIER (J. Pharm. Chim., 1936, [viii], 24, 368—375, 413—429).—A review.

Heart poisons and saponins of the cholane series. K. BOHLE (Chem.-Ztg., 1936, 60, 893—896).—A review.

Seeds of the Madagascar anthelmintic Combrataceæ. J. MAHEU and R. WEITZ (Bull. Sci. pharmacol., 1935, 42, 202—210; Chem. Zentr., 1936, i, 805).—The leaves of *Quisqualis indica*, L., and the fruits of *Q. madagascariensis*, Boj., and their application as anthelmintics are described.

H. N. R.

Physico-chemical mechanisms in convulsive reactivity. E. SPIEGEL and M. SPIEGEL-ADOLF (Proc. Soc. Exp. Biol. Med., 1936, 34, 799—800).—Epileptogenous agents act on the nervous system (a) by a change in ion concn. on the surface of the nerve cells and (b) by diminution of the cellular surface films.

P. G. M.

Chronic nicotine toxicity. I. Feeding of nicotine sulphate and tannate and bentonite. II. Effect of nicotine-containing diets on blood-sugar concentration in the rat. R. H. WILSON and F. DE EDS (J. Ind. Hyg., 1936, 18, 553—564, 565—570).—I. The growth of rats fed on a diet containing >0.006% of nicotine (I) was retarded; this retardation was largely due to diminished food intake and, in lesser degree, to the toxic effect of (I). (I) sulphate was approx. twice as toxic as the tannate or bentonite.

II. Chronic (I) poisoning produces an initial hypoglycæmia and acute intoxication a transient hyperglycæmia followed by a return to normal.

P. G. M.

Acute toxicities of rotenone and mixed pyrethrins in mammals. M. B. SHIMKIN and H. H. ANDERSON (Proc. Soc. Exp. Biol. Med., 1936, 34, 135—138).—The min. lethal doses of rotenone for guinea-pigs, rats, and mice were 7—10 mg. per kg. (intraperitoneally) and 75—100 mg. (orally). The corresponding vals. for mixed pyrethrins were 100—150 mg. and <1500 mg.

W. McC.

Toxicity of *d*- and *l*- α -tolylpyrrolidine to *Aphis rumicis*. Toxic constituents of derris root.—See B., 1936, 1117.

Acute intraperitoneal toxicity of plant growth-substances for mice. H. H. ANDERSON, M. B. SHIMKIN, and C. D. LEAKE (Proc. Soc. Exp. Biol. Med., 1936, 34, 138—139).—The min. lethal doses for mice of indolyl-propionic and -butyric acid and phenyl-, α -naphthyl-, and indolyl-acetic acid were respectively 100, 100, 300, 100, and 25 mg. per kg. The toxicities of these substances to plants are approx. in the same relative order.

W. McC.

Alleged toxicity to rats of maize germ and its ethereal extract. E. CASERIO (Z. Vitaminforsch., 1936, 5, 263—265).—Maize germ and its ethereal extract have no action on rats, and they actually show favourable somatic effects. The contrary results of Randoin and Simonnet may be explained either by fermentation of the extracts or by contamination with toxic material.

J. N. A.

Pathomorphological changes in the internal organs and endocrine glands in dinitrophenol poisoning. I. PEISSAKOVITSOH and P. KOSTENKO (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 160—170).

M. A. B.

Morphological and chemical investigations in a case of death from acute benzene poisoning.

G. F. KOPPENHÖFER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 417—427).— C_6H_6 was demonstrated in the blood and organs by distilling these with H_2O acidified with H_2SO_4 , nitrating the distilled C_6H_6 , and identifying the *o*- and *m*- $C_6H_4(NO_2)_2$ by the intense violet colour with fructose. M. A. B.

Permeability of the cerebrospinal barrier and blood variations in experimental benzene poisoning. S. B. SCHACHNOVSKAJA (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 144—156). M. A. B.

Toxicity of propylene glycol. H. A. BRAUN and G. F. CARLAND (J. Amer. Pharm. Assoc., 1936, 25, 746—749).—The min. lethal dose in rats is 15.7 and 23.1 g. per kg. for intramuscular and subcutaneous injection, respectively: corresponding vals. for glycerol are 7.6 and 15.1. The oral lethal dose of the glycol in rabbits is 20 g. per kg. but daily ingestion of 8 c.c. for 50 days has no cumulative effect.

F. O. H.

Chronic carbon tetrachloride poisoning. J. Löwy (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 157—159). M. A. B.

Chronic iodoacetic acid poisoning and its relation to the Gee-Herter disease. L. LASZT and F. VERZAR (Pflüger's Arch., 1936, 237, 483—493).—Chronic $CH_2I \cdot CO_2H$ poisoning produces in rats symptoms similar to those of the Gee-Herter disease. In the poisoned rats the symptoms can be removed by feeding dried yeast or vitamin- B_2 (flavin phosphate) but not by flavin. It is suggested that the symptoms are due, in both cases, to inhibition of $-B_2$ formation from flavin. M. A. B.

Mechanism of methylene-blue in carbon monoxide poisoning. M. M. BROOKS (Proc. Soc. Exp. Biol. Med., 1936, 34, 48—49).—In rabbits poisoned with CO, the conversion of CO-hæmoglobin into oxy-hæmoglobin is definitely accelerated by intravenous administration of methylene-blue (1 c.c. of 0.03% solution per kg. body-wt.). W. O. K.

Influence of liver poisons on action of parathyroid extract. D. M. GREENBERG (Proc. Soc. Exp. Biol. Med., 1936, 34, 622—626).—Poisoning with P inhibits, and with N_2H_4 markedly reduces, the serum-Ca rise following injection of parathyroid extract; CCl_4 has no effect. N_2H_4 and P do not act *via* the bone cells. P. G. M.

Cyanide poisoning. K. K. CHEN, C. L. ROSE, and G. H. A. CLOWES (Metal Ind., N.Y., 1936, 34, 346).—First-aid treatment with amyl nitrate and 1% aq. $Na_2S_2O_3$ is described. L. S. T.

Combined action of lead and nicotine. R. M. SKLIANSKAJA (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 270—274).—The combined toxic effect of Pb and nicotine (I) on the isolated frog's heart is < the sum of the toxic effects of Pb and (I) separately. M. A. B.

Toxicity of selenium-containing plants to aphids. A. M. HURD-KARRER and F. W. POOS (Science, 1936, 84, 252).—*Rhopalosiphum prunifoliae* (Fitch) is killed by the Se taken up by plants (wheat, rye, oats, and barley) from small amounts of Na_2SeO_4 added to cultures or soils. L. S. T.

Poisoning by sodium nitrite. A. SCHOLES (Analyst, 1936, 61, 685—686).—The $NaNO_2$ had been mistaken for NaCl. The amounts present in the stomachs of the deceased and in the unconsumed food are recorded. E. C. S.

Structure and toxicity of arsinic acids of the diphenylamine series.—See this vol., 1527.

Enzymes in relation to cancer. A. PURR (Current Sci., 1936, 5, 194—196).—A review.

Effect of irradiation with short waves on enzymes. I. Diastase. K. KOSIERADSKI (Biochem. Z., 1936, 287, 265—270).—The saccharifying action of diastase alone or mixed with starch is not affected by irradiation with short waves (2, 4, 10, and 15 m.). W. McC.

Keilin's cytochrome-c and the respiratory mechanism of Warburg and Christian. H. THEORELL (Nature, 1936, 138, 687).—Cytochrome-c, like O_2 and methylene-blue, does not oxidise the dihydroco-enzyme directly. It rapidly oxidises the leuco-form of the yellow enzyme. L. S. T.

Action of cyanides on the purine dehydrogenase of milk. E. J. BIGWOOD, J. THOMAS, and H. HERBO (Compt. rend. Soc. Biol., 1936, 123, 87—90).—The inhibiting effect of KCN is not observed under anaërobic conditions. H. G. R.

Storch reaction [for peroxidase in milk]. L. C. JANSE (Chem. Weekblad, 1936, 33, 638—640).—Milk containing traces of Cu gives a positive Storch reaction [colour with $p\text{-}C_6H_4(NH_2)_2$, HCl, and H_2O_2] even when pasteurised at $> 85^\circ$. The adverse effect of Cu is corr. by preliminary addition of 1 c.c. of 0.25% aq. KCN to 5 c.c. of milk. S. C.

Behaviour of the amylase of silkworms living under unfavourable conditions. K. YAMAFUJI (Biochem. Z., 1936, 287, 23—25).—The amylase contents of the blood and digestive juices of silkworms kept for a time under unfavourable conditions of aëration and moisture decrease considerably without obvious change in the appearance of the worms and do not regain their original vals. when the worms are replaced under favourable conditions. The amylase contents of the blood and juices of their offspring are also subnormal. P. W. C.

Action of the lysin of pneumococcus on certain tissue-polysaccharides. K. MEYER, R. DUBOS, and E. M. SMYTH (Proc. Soc. Exp. Biol. Med., 1936, 34, 816—818).—The same enzyme from pneumococci is capable of hydrolysing the carbohydrate complex (acetylglucosamine-glycuronic acid) from bovine vitreous humour or human umbilical cord, and heat-killed pneumococci. The optimum p_H is 5—6 and the enzyme is reversibly inactivated by I. P. G. M.

Enzymic fission of difficultly hydrolysable glucoside of senna leaves. E. TRIENDL (Arch. exp. Path. Pharm., 1936, 182, 527—532).—The glucoside (I) (Straub and Gebhardt, this vol., 1021) is hydrolysed (with formation of emodin; optimum p_H 5.0) by mucous membrane of large and small intestine and by liver-tissue of dogs and cats, bitter almond preps., and emulsin. (I) is therefore a

β -glucoside. With animal enzyme preps., enzymic oxidation of intermediary anthranol to anthraquinone occurs.

F. O. H.

Relations between vitamin-C and enzymic fission of carbohydrates. I. R. WEIDENHAGEN and P. LU. II. R. WEIDENHAGEN (Z. Wirts. Zuckerind., 1936, 86, 240—253, 482—494).—I. Ascorbic acid (I) in 0.005M concn. reduced by 60—80% the rate of hydrolysis of sucrose by β -*h*-fructosidase [invertase (II), from yeast] in solutions buffered at p_H 4.7 and 6.9, and its effect was detectable at 0.0001M. Even at 0.005M, however, the inhibition was entirely annulled by the presence of cysteine (10⁻⁶M), glutathione (III) (0.0001M), certain other S compounds or NH₂-acids at higher concn., or even by citric acid or H₂C₂O₄ (0.005M). The opposite actions of (I) and (III) suggest a possible means by which (II) action may be controlled in plant life.

II. (I) produces inhibitory effects equal to or > those observed with invertase on β -glucosidase (highly purified emulsin from bitter almonds) and on the amylases of pancreas, wheat, barley, and malt. The amylases were purified by tannin pptn., followed by pptn. by COMe₂. In all cases (III) at the same equiv. concn. as (I) partly or entirely prevented the inhibitory action of (I).

J. H. L.

Separation of β -*h*-fructosidase [invertase] from yeast autolysates. R. WEIDENHAGEN [with A. RENNER] (Z. Wirts. Zuckerind., 1936, 86, 473—481).—If a slightly acid yeast autolysate is adjusted to p_H 8 with Sr(OH)₂ the ppt. formed contains the whole of the invertase present; if Ca(OH)₂ or Ba(OH)₂ is used pptn. is not complete. The invertase may be dissolved from the washed ppt. by means of NH₄H₂PO₄ or Na₂SO₄. Practical details of the method are given.

J. H. L.

Changes in the curve of enzymic hydrolysis of sucrose by the action of heat on the enzyme. A. CHAUDIN (Bull. Soc. Chim. biol., 1936, 18, 1467—1470).—Invertase heated for 3 hr. at 55° hydrolyses sucrose less rapidly, but at the same time the angular point of the reaction curve is displaced so that the amount of enzyme appears to have increased. A similar effect has been observed with alkali, EtOH, and MeCHO.

A. L.

Lacto-mannitic enzymes. III. Products of fermentation of glucose. V. BOLCATO (Annali Chim. Appl., 1936, 26, 356—361; cf. this vol., 638).—The enzymes which produce mannitol from fructose produce only lactic acid (I), EtOH, CO₂, and a little AcOH from glucose. The productions of (I) and EtOH are independent, and the ratio (I)/EtOH is not const. The mechanisms of the fermentation of glucose and fructose are compared.

L. A. O'N.

Recent researches on cell-free alcoholic fermentation. O. MEYERHOF (Naturwiss., 1936, 24, 689—692).—A lecture.

Pasteur and Meyerhof's reaction. C. FRISCH and R. WILLHEIM (Biochem. Z., 1936, 287, 203—205).—Glycolysis in muscle extract is diminished by Warburg's respiratory enzyme but increased by lactoflavin, which also partly counteracts the inhibition caused by benzoquinone.

W. McC.

Rôle of the adenylic acid system and of cozymase in alcoholic fermentation. P. OHLMEYER (Biochem. Z., 1936, 287, 212—225).—Although purified cozymase (I) and the adenylic acid (II) system do not differ as regards their effects on liberation of PO₄''' from phosphopyruvic acid (III) and transfer of PO₄''' to glucose (IV) from (III), (I) cannot be replaced by (II) in the conversion of hexose diphosphate [with or without (IV)] in presence of NaF into phosphoglyceric and glycerophosphoric acid and in the interaction of (IV) and MeCHO in presence of inorg. PO₄'''. Hence in the system (III) + (IV) fermentation ceases when the CO₂ equiv. of (III) has been liberated when (II) replaces (I) but continues if (I) is not so replaced.

W. McC.

Inhibition of glycolysis by heavy metals and reversal of this inhibition. T. WAGNER-JAUREGG and H. W. RZEPPA (Z. physiol. Chem., 1936, 243, 166—172; cf. this vol., 895).—The amount of CuSO₄ required to inhibit glycolysis in muscle extract from *Rana esculenta* is 5—10 times that necessary with extract from *R. temporaria* and no inhibition is produced in rabbit muscle extract by 0.00017M-CuSO₄. Pure and impure cozymase (I) and Warburg's co-enzyme (II) (but not KCN and ascorbic acid) and, to a much smaller extent, cysteine and glutathione reverse the inhibition whilst muscle-adenylic acid acts indefinitely. (I) and (II), which reactivate in the mol. ratio of >5 to 1 of metal, probably act by producing complexes or difficultly sol. salts with Cu. Fe^{II} inhibits \ll does Cu whilst Fe^{III}, Zn, and Cd have little or no effect and Mn stimulates glycolysis.

W. McC.

Inactivation of cozymase in an apozymase system poisoned with fluoride. A. LENNERSTRAND (Biochem. Z., 1936, 287, 172—188; cf. this vol., 380).—In the system apozymase + cozymase (I) + glucose (II) + hexose diphosphate (III) + PO₄''' buffer phosphorylation and O₂ consumption occur to a small extent in presence of NaF but soon cease. Methylene-blue added after the cessation is decolorised only very slowly. Pyocyanine (IV) increases phosphorylation and O₂ consumption to an extent which diminishes to zero as the interval of time which elapses before the addition increases. The duration of O₂ consumption and phosphorylation \propto the concn. of (III). After O₂ consumption and phosphorylation have ceased they are re-started by addition of (I) [but not by that of (III), muscle-adenylic acid (V), adenosinetriphosphoric acid (VI), or Warburg's co-enzyme]; the O₂ consumption, within limits, then \propto the amount of (I) added. If NaF + (IV) + (II) are added to the system vigorous O₂ consumption occurs even if liberation of CO₂ has almost ceased. These findings indicate that cessation of O₂ consumption and phosphorylation are due to the inhibitory action of NaF on some mechanism which protects (I). The extent of inhibition is measured by the effect of (IV). In the enzyme system of yeast (I) alone can act as PO₄''' carrier whilst (V) accelerates the process but cannot act alone. During fermentation (I) continuously phosphorylated by phosphopyruvic acid (VII) transfers PO₄''' directly or by way of (V) and (VI) to

(II). NaF prevents dephosphorylation of (VII) and hence (I) cannot act. W. McC.

Cozymase and dihydrocozymase in living cells. E. ADLER and H. VON EULER (Svensk Kem. Tidsskr., 1936, 48, 221—226; cf. this vol., 246).—Cozymase (I) and dihydrocozymase (II) exist in the living cell as intermediates in fermentation and muscular activity enzyme systems. The stability of (I) to acids and of (II) to alkalis enables the (I)/(II) ratio to be determined. M. H. M. A.

Zymohexase. III. Determination [of activity]. E. BAUER (Z. physiol. Chem., 1936, 243, 202—206; cf. this vol., 1299).—The activity of zymohexase (I) (with and without HCN activation) is max. at p_H 9.5—10.0 but most stable at p_H 7—8. At $p_H > 10$ irreversible inactivation occurs. The stability decreases more rapidly in the acid than in the alkaline zone. The activity is independent of substrate [hexose diphosphate (II)] concn. Until the amount of P converted into alkali-hydrolysable form reaches 0.003%, the amount of (II) decomposed \propto the (I) concn. The unit of (I) is defined as the amount which converts 0.01 mg. of P into alkali-hydrolysable form in 1 hr. Fe^{III} activates (I) at p_H 9.1 but inactivates it in slightly acid media. (II) forms with Fe a very stable complex salt which possibly is partly responsible for the activating effect of Fe. The affinities of (I) for (II) and this complex are probably different. W. McC.

Choline esterase. H. KWIAŃSKI (Fermentforsch., 1936, 15, 138—151).—Choline esterase (I) was detected in lymph, bile, and skin dialysate. (I) is not adsorbed by bolus alba and animal C, is not destroyed by X-rays, and is inhibited by pituglandol, padutin, NaF, and prostigmine (II), but not by histamine. The synthesis of acetylcholine from choline and NaOAc in fluids containing (I) depends on the amount of (I) present and is inhibited by physostigmine, (II), and NaF. E. A. H. R.

Action of the stereoisomerides of leucylglycylglycine on pancreas- and liver-esterase. W. GERTLER (Fermentforsch., 1936, 15, 171—176).—All stereoisomerides of leucylglycylglycine (I), especially the *l*-form, strongly activate the hydrolysis of tributyrin (II) by pancreatic lipase. The effect is less marked with $PrCO_2Me$ (III). (I) has no effect on the hydrolysis of (II) and (III) by liver-esterase, or on the enzymic hydrolysis of acetylcholine. E. A. H. R.

***In vitro* hydrolysis of fats by lipase and bile salts.** J. E. DAVIS (Proc. Soc. Exp. Biol. Med., 1936, 34, 772—775).—A method is evolved for *in vitro* hydrolysis of fats by lipase and bile salts, by means of which equilibrium is reached in 24 hr. at 24% hydrolysis. P. G. M.

Enzymic hydrolysis of nucleotides and nucleosides. I. Hydrolysis of purine ribonucleotides. H. ISHIKAWA and Y. KOMITA (J. Biochem. Japan, 1936, 23, 351—363; cf. this vol., 433).—Dog's pancreas preps. hydrolyse guanylic (I) and xanthylic acid to give ribose phosphate (II) (optimum p_H 7.5), small amounts of NH_3 being liberated from (I) when crude enzyme preps. are used. Dog's pancreas

also contains a nucleosidase. Cat's pancreas yields (II) from nucleotides and also contains nucleosidase and deaminase which are absent from ox and pig's pancreas. Nucleotidase and nucleosidase occur in rabbit's liver, kidney, muscle, and small intestine. Nucleotides are hydrolysed both by primary dephosphorylation and by splitting of the pentose linking followed by hydrolysis of (II). F. O. H.

Tyrosinase. II. Action of potato-tyrosinase on phenols and the influence of amino-compounds on the tyrosinase system. F. NOBUTANI (J. Biochem. Japan, 1936, 23, 455—485).—Tyrosinase (I) produces pigments only from those phenolic substances which yield *o*-quinones on oxidation. The O_2 uptake by *p*-cresol or pyrocatechol in presence of (I) is 1 atom $>$ that corresponding with formation of *o*-benzoquinone. NH_2 -acids accelerate the action of (I) but do not affect the O_2 consumption, whilst NH_2OH accelerates the action but depresses O_2 consumption. The mechanism of these phenomena is discussed. F. O. H.

Polypeptidases excreted in the urine of health and disease. P. STEINBRÜCK (Fermentforsch., 1936, 15, 121—133). E. A. H. R.

Polypeptidases of blood-serum and -plasma. R. ABDERHALDEN (Fermentforsch., 1936, 15, 157—170).—Protection of the CO_2H of polypeptides inhibits the action of the carboxypolypeptidase in trypsin (I), for it hydrolyses neither *dl*-leucylglycylmethylamine (II), m.p. 76—78°, nor *dl*-leucylglycylglycylbenzylamine (III), m.p. 130—131°. (II) and (III) are hydrolysed by erepsin (IV) and serum to a greater extent than the corresponding polypeptides, perhaps because of a greater ease of attachment of the NH_2 to the enzyme surface when the CO_2H is blocked. *dl*-(*N*)Benzyl-leucylglycylbenzylamine, m.p. 70—71°, is not hydrolysed by (I), (IV), or serum, and can be recovered unchanged 10 days after injection into a rabbit. The aminopolypeptidase content of foetal blood is the same as, but the dipeptidase content is $<$, that of the mother. E. A. H. R.

Fibrinolysis. V. M. ROSENMAN (Biochem. Z., 1936, 287, 26—32).—A substance is present in serum which is inactivated by heating for $\frac{1}{2}$ hr. at 50° and is identical with thrombolysin (I) (Å., 1922, i, 596). The p_H optimum for fibrinolysis by autolysate-(I) is between 7.8 and 8.4 and for serum-(I) between 8 and 8.4, whilst the material is active over the range p_H 5.8—10. The p_H optimum is not displaced by addition of thromboligin. P. W. C.

Autodigestion. VI. Digestion of living tissues by trypsin. H. NECHELES, P. LEVITSKY, and M. MASKIN (Proc. Soc. Exp. Biol. Med., 1936, 34, 768—772).—Tryptic digestion of living frogs' legs can take place following immersion in HCl or pepsin-HCl. P. G. M.

Influence of high temperatures on the trypsin of warm- and cold-blooded vertebrates. P. A. KORSCHUJEFF (Fermentforsch., 1936, 15, 152—156).—The higher is the body-temp. of a vertebrate, the greater is the thermostability of its trypsin. E. A. H. R.

Enzymic digestion of lactalbumin and caseinogen *in vitro*. M. C. KIK (Proc. Soc. Exp. Biol. Med., 1936, 34, 194—196).—Lactalbumin is less readily digested *in vitro* by trypsin and erepsin than is caseinogen. W. McC.

Determination of antitrypsin. K. L. BURDON and C. LAFFERTY (Proc. Soc. Exp. Biol. Med., 1936, 34, 787—790).—Opaque photographic film is used for titration of antitrypsin; the amount of trypsin required to produce complete transparency of the film is determined. P. G. M.

Enzymes of snake venom. I. Their action on hæmoglobin and on protein solutions of different p_H . B. N. GHOSH (J. Indian Chem. Soc., 1936, 13, 450—455).—Proteolytic activity of cobra venom to gelatin and ovalbumin is a max. at p_H 7.8—8.0 and to casein at p_H 6.6. The protease of this venom thus resembles trypsin. This venom and that of Russell's viper cause oxidation of hæmoglobin to methæmoglobin. R. S. C.

Tissue proteinases (cathepsin) in protein-free and low-protein feeding. B. GOLDSTEIN and M. GINZBURG (Ukrain. Biochem. J., 1936, 9, 341—354).—Protein-starved and gelatin-fed rabbits show an increase of cathepsin (I) concn. in the kidney and, more especially, in the liver, the difference between H_2S -non-activated and H_2S -activated (I) being also raised. Predominance of protein synthesis in the organ appears to be accompanied by strong activation of (I) by $\cdot SH$. Protein synthesis is increased in the livers of rabbits on restricted protein diets. F. A. A.

Intracellular proteinases. XVIII. Effect of co-enzyme and cozymase on proteinases reversibly inactivated by heavy metals. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1936, 243, 207—208; cf. A., 1935, 1538).—The inactivating effect of Cu on the degradation of gelatin by papain (I) and cathepsin (II) is not reversed by addition of Warburg's co-enzyme (III) or Euler's cozymase (IV). The action of (I) but not that of (II) is appreciably restricted by (III) and (IV). W. McC.

Proteolytic enzymes. XI. Specificity of papain peptidase I. M. BERGMANN, L. ZERVAS, and J. S. FRUTON (J. Biol. Chem., 1936, 115, 593—611; cf. this vol., 1152).—The hydrolysis by peptidase I of compounds of the type $NHR''\cdot CO\cdot CHR'\cdot NH\cdot CO\cdot R$ ($R=Ph$ or $O\cdot CH_2Ph$) was investigated. Hippurylamide (I) ($R=Ph$, $R'=H$, $R''=H$) is readily hydrolysed whilst derivatives ($R''=Me$, *isoamyl*, or *Ph*) under the same conditions were only slightly hydrolysed. Carbobenzyloxyglycylglycine (II) and -di- and -tri-glycylglycine are hydrolysed with increasing velocity as R'' increases in length. Hydrolysis of (I), hippurymethylamide, and (II) indicates an inhibitory influence of *Me* but not CO_2H . *Benzoylglycylglycine piperidide*, m.p. 134°, is hydrolysed more rapidly than is (II). The splitting of carbobenzyloxyglutamyl- α -amide is $>$ that of derivatives where $R''=isoamyl$ or, to a greater extent, $R''=Me$. In order to demonstrate the marked effect of slight structural changes on the rate of hydrolysis, the hydrolysis of, amongst others, the

following compounds was studied: *benzoyl-l-leucyl-l-leucylglycine*, m.p. 161°, *carbobenzyloxy-l-glutamyl-glycylglycine*, m.p. 142° (*Et* ester, m.p. 139—140°), *benzoyl-l-lysine amide* (III), m.p. 187° [*d-isomeride* (IV), m.p. 187°]. The linking ' is more readily attacked than ". The peptidase hydrolyses a variety of peptide linkings with widely different velocities. The fission of free polypeptides by papain is due to peptidase I. (III) but not (IV) is hydrolysed. The antipodal specificity of peptidase I is discussed (cf. A., 1935, 1416). The following compounds were prepared: *l-leucyl-l-leucylglycine* (*carbobenzyloxy-methyl* ester, m.p. 108°), *carbobenzyloxy-piperidide*, m.p. 78°, *hippuryl-anilide*, m.p. 214°, and *isoamylamide*, m.p. 98°, *carbobenzyloxy-l-glutamyl-methylamide*, m.p. 178°, and *isoamylamide*, m.p. 135°.

F. O. H.

Proteases and proteolytic processes in muscle tissue. III. Activity of muscle proteases in B- and C-avitaminosis. S. V. FOMIN and N. M. ROMANTSCHUK (Ukrain. Biochem. J., 1936, 9, 355—368).—The protease activity on caseinogen of muscle extracts from B-avitaminotic pigeons or C-avitaminotic guinea-pigs is $<$ that of extracts from normal animals. F. A. A.

Influence of phloridzin on renal phosphatase *in vitro*. A. LAMBRECHTS (Compt. rend. Soc. Biol., 1936, 123, 311—313).—There is no parallelism between the diabetogenic and inhibitory actions.

H. G. R.

Phosphatase of human milk. K. V. GIRI (Z. physiol. Chem., 1936, 243, 57—62).—Human milk contains phosphatases exhibiting optimal activity at p_H 9.2 and 5.1, respectively, with Na glycerophosphate (I) as substrate. The first is activated by Mg^{++} ; the second is not. Na hexose diphosphate (II) is more readily hydrolysed by the phosphatases than is (I), and $Na_4P_2O_7$ is much more readily hydrolysed than are (I) and (II). The amount of the phosphatases in the milk 3 days *post partum* is $>$ that in the milk of later stages of lactation and they are activated to a greater extent by Mg^{++} . W. McC.

Fermentation enzymes. VI. Dephosphorylating enzymes of yeast. A. SCHÄFFNER and F. KRUMEY (Z. physiol. Chem., 1936, 243, 149—165).—Although the action of α -glycerophosphatase, phosphatase from top yeast, and phosphatases exhibiting optimal effects at p_H 9 and 7, respectively, is inhibited by AsO_4''' and that of pyrophosphatase is unaffected, the dephosphorylation of hexose diphosphate (I) by crude yeast maceration juice is very greatly accelerated. Since dephosphorylation of phosphopyruvic acid (II) by the juice is greatly accelerated by added adenylic acid (III), it is possible that an early stage in fermentation consists in interaction of (II) and (III) to give adenosinetriphosphoric acid (IV) and $AcCO_2H$. AsO_4''' accelerates the dephosphorylation of (IV) by the juice. The phosphatase exhibiting optimal action at p_H 7 does not attack (IV). AsO_4''' inhibits phosphorylation by (I) and (IV). If sufficient org. PO_4''' is present fermentation can proceed without the consumption of inorg. PO_4''' , (II) from (I) reacting as described and (IV) with glucose yield-

ing (I) and (III) so that a closed system, capable of acting for a long time, is formed. W. McC.

Glucosidases of *Schizosaccharomyces*. E. HOFMANN (Biochem. Z., 1936, 287, 271—275; cf. this vol., 1024).—*S. octosporus*, *S. Pombe*, and *S. mellacei* contain maltase and α -methylglucosidase both exhibiting optimal activity at p_H 4.5. Invertase is also present and hydrolyses raffinose to fructose and melibiose (I) but does not attack (I). W. McC.

Fermentation of phosphogluconic acid. F. LIPMANN (Nature, 1936, 138, 588—589).—Curves for the aerobic and anaerobic fermentation of phosphogluconic acid (in yeast macerate) show that in absence of O_2 the formation of CO_2 is slow. Behaviour in presence of $CH_2Br\cdot CO_2'$ (I) suggests that a primary oxidation and decarboxylation, unaffected by (I), is followed by a reaction which may be of an enzymic nature. Fluoride inhibits O_2 absorption and CO_2 formation more strongly than (I). L. S. T.

Importance of "pantothenic acid" in fermentation, respiration, and glycogen storage. R. J. WILLIAMS, W. A. MOSHER, and E. ROHRMAN (Biochem. J., 1936, 30, 2036—2039).—Yeast having an extremely low pantothenic acid (I) content (2% of the normal amount) is almost lacking in fermenting power but fermentation is increased on adding a minute amount of (I). Aerobic respiration is also very low and is only slightly increased when (I) is added after the yeast is grown. Yeast grown with a good supply of (I) respire much more rapidly than does the deficient yeast. Most samples of maltose (II) contain (I), which is removed completely only by electrolytic transport. The promotion of glycogen storage in yeast by (II) (McAnally and MacLean, A., 1935, 1164) is due to the (I) content. (I) thus plays a fundamental rôle in carbohydrate anabolism and catabolism whether the latter is aerobic or anaerobic. P. W. C.

Effect of α -keto-acids other than pyruvic acid on the synthesis of amino-acids by yeast. C. FROMAGEOT and G. MINARD (Bull. Soc. Chim. biol., 1936, 18, 1454—1466).— α -Keto-acids (e.g., $COPr^2\cdot CO_2H$ and $CHMeEt\cdot CO\cdot CO_2H$) capable of decarboxylation by decarboxylase, when added to sucrose solutions undergoing fermentation by yeast, are converted into alanine (I). Addition of $COBu^v\cdot CO_2H$ does not increase the yield of (I). A. L.

Thermal analysis and action on fermentation of mixtures of antiseptics. A. MOSSINI (Boll. Chim. farm., 1936, 75, 493—494).—Mixtures of Me or Pr *p*-hydroxybenzoate with camphor (I) have eutectic points at 59.9° [70% of (I)] and 32° [60% of (I)], respectively. The respective actions on yeast fermentation, however, are additive with respect to those of the components. F. O. H.

Increase of diamagnetic susceptibility on the death of living cells. E. BAUER and A. RASKIN (Nature, 1936, 138, 801).—The increase observed in the case of yeast and *B. coli* and *B. proteus* supports the theory that the lack of equilibrium in living systems is due to an excited state of protein mols. of the protoplasm. Denaturation of native protein does not affect magnetic susceptibility. L. S. T.

Strains of yeast which produce alcoholic fermentation at low temperatures. B. PORCHET (Mitt. Lebensm. Hyg., 1936, 27, 42—45).—Yeasts responsible for the spontaneous fermentation of grape musts and apple juice at -3° to 0° are indistinguishable morphologically from other forms of *S. ellipsoideus*; they form white colonies with irregular edges and a central crater on gelatin at room temp., without producing liquefaction. They develop a fine bouquet and are suitable for wine and cider production, being superior to ordinary yeasts in fermentations at 6° . J. G.

Gum and glycogen of yeast. F. STOCKHAUSEN and K. SILBEREISEN (Biochem. Z., 1936, 287, 276—286).—The amounts of the gum in brewer's, wine, and baker's yeast are respectively 4—6, 7.5—8.5, and up to 13%. The glycogen and gum of yeast exist as such in the cells and are not produced by the action of the hot 65% KOH solution used in extraction. W. McC.

Determination of hexoses by fermentation.—See this vol., 1490.

Formation of oxalic and citric acids by fungi. V. S. BUTKEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 427—430).—Polemical against Chrzaszcz *et al.* (A., 1935, 254; this vol., 1026, 1027). E. A. H. R.

Pharmacodynamic action of iron in general metabolism. O. KAUFFMANN-COSLA and R. BRÜLL (Bull. Soc. Chim. biol., 1936, 18, 1493—1502).—The monose content of *Aspergillus niger* grown in media containing no Fe is $>$ normal. The cellulose content is normal, but the lipin content $<$ normal. Fe is therefore necessary for normal carbohydrate and lipin synthesis. A. L.

Assimilation of nitrites by fungi. III. Y. WANG (J. Agric. Chem. Soc. Japan, 1936, 12, 877—884).—Assimilation of NO_2' -N by various species of *Aspergillus* does not depend on the previous mode of culture of the fungus but is largely conditioned by the nature of the sources of C. W. O. K.

Production of acids from sugar by *Aspergillus niger*. VII. Importance of nitrogen source for citric acid production. K. BERNHAUER and A. IGLAUER (Biochem. Z., 1936, 287, 153—166; cf. A., 1936, 1026).—Citric acid (I) production by *A. niger* is optimal when the N concn. of the medium is 0.07—0.875%. The rate of (I) production and the amount of (I) produced vary with the N source employed, the highest rate and yield (80—90%) being obtained with NH_4NO_3 and $Mg(NO_3)_2$ and sugar concn. 17.5—20%. (I) production with NH_4NO_3 as N source is very greatly accelerated by addition of $MgCl_2$, especially when the sugar concn. is high. The yield and rate of production of (I) are affected by the purity of the sugar used. W. McC.

Production of citric acid from lactic acid and from alcohol. T. CHRZASZCZ and K. LEONHARD (Biochem. J., 1936, 30, 1947—1952).—On media containing $CaCO_3$ *Botrytis cinerea* partially converted Ca and NH_4 lactates into citric acid (I), $H_2C_2O_4$ (II), and CO_2 with small amounts of malic acid (III), fumaric acid (IV), AcOH, Et CO_2H (V), $AcCO_2H$

(VI), and MeCHO. Without CaCO₃, the utilisation of NH₄ lactate was greater but (II) was not obtained. On a medium containing CaCO₃, EtOH was utilised yielding (I), (III), HCO₂H, AcOH, (II), and CO₂. Lactic acid (VII) is first converted into (VI) which is decarboxylated to MeCHO. This is either oxidised to AcOH or with a mol. of (VII) undergoes dismutation into (V) + AcOH. The AcOH formed is converted *via* succinic acid, (IV), and (III) into (I) or is oxidised *via* OH·CH₂·CO₂H, (II), and HCO₂H to CO₂ + H₂O. In older cultures the (I) formed possibly also undergoes decomp. P. W. C.

Production of acids by *Rhizopus*. I. Production of malic acid in fumaric acid fermentation. K. BERNHAUER and H. THOLE (Biochem. Z., 1936, 287, 167—171).—The variation in the yield of fumaric acid (I) produced from glucose in presence of CaCO₃ by strains of *Rhizopus* is due to the conversion of (I) into malic acid, the amount of which continues to increase while that of (I) after reaching a max. is decreasing. W. McC.

Low concentrations of deuterium oxide and the growth of marine diatoms. D. L. FOX, E. E. CUPP, and G. F. MCEWEN (Proc. Soc. Exp. Biol. Med., 1936, 34, 575—581).—The growth rate of *Nitzschia bilobata* shows a tendency to lag in dil. D₂O. P. G. M.

Detection of hormones in unicellular animals. I. Choline and acetylcholine in *Paramecium*. II. Adrenaline in *Paramecium*. G. BAYER and T. WENSE (Pflüger's Arch., 1936, 237, 417—422, 651—654).—I. Choline was demonstrated in *Paramecium* by the effect of a Ringerextract of the organism on the eserinated dorsal muscles of the leech, the effect being considerably increased on acetylation. The presence of acetylcholine (I) in the original extract was also shown. *Paramecium* contains less (I) at low temp. at which the esterase is more active.

II. Adrenaline was demonstrated in *Paramecium*. M. A. B.

Isolation of *Glaucoma ficaria*, Kahl, in bacteria-free cultures: growth in relation to the p_H of the medium. D. F. JOHNSON (Arch. Protistenk., 1935, 86, 262—277).—The growth range of *G. ficaria* is p_H 4.9—9.5 and that of *G. piriformis*, 4.0—8.9. The latter has the lower p_H optimum. A. G. P.

Physiology of euglenoid flagellates. V. Effect of certain carbohydrates on growth of *Euglena gracilis*, Klebs. VI. Effects of temperature and of acetate on *E. gracilis* cultures in the dark. VII. Effects of salts of certain organic acids on growth of *E. gracilis*. T. L. JAHN (Arch. Protistenk., 1935, 86, 238—250, 251—257, 258—262).—V. Transference of *E. gracilis* from an inorg. medium to one to which carbohydrates are added may result in encystment or modification of the rate of division. Effects vary with the carbohydrate used and probably also with the physiological condition of the stock, with temp., light intensity, and p_H .

VI. Addition of NaOAc to peptone media increased the rate of division and raised the optimum growth temp.

VII. In daylight the rate of division was accelerated by addition to media of PrCO₂Na (I), NaOAc, Na₂C₂O₄, and Na lactate (II) (in descending order), unaffected by NaCl, HCO₂Na, Na tartrate and citrate, and retarded by Na succinate (III). In darkness, the order of acceleration was (I) > NaOAc > (II) > (III) and HCO₂Na caused some deceleration. A. G. P.

Oxidation-reduction potential of protozoan cultures. II. Reduction potential of cultures of *Chilomonas paramecium*. T. L. JAHN (Arch. Protistenk., 1935, 86, 225—237; cf. A., 1934, 329).—Changes in the E_h of cultures in different media are determined by means of special apparatus described. These changes are largely attributable to removal of O₂ from the medium during growth although the possibility of the production of reducing substances by the organism is not eliminated. Variations in E_h may be a causative factor in allelocatalysis. A. G. P.

Utilisation of sugars by *Leishmania tropica*. A. DUBOIS (Compt. rend. Soc. Biol., 1936, 123, 141—144).—Carbohydrates most readily utilised include glucose, fructose, mannose, galactose, sucrose, inulin, and glycerol. H. G. R.

Resistance of Leishman-Donovan bodies to various physical, chemical, and biological agents. I. Physical agents. H. L. CHUNG (Chinese Med. J., 1936, 50, 1039—1050).—Leishman-Donovan bodies were tested for viability (by injection into hamsters) after various treatments. The bodies were resistant to X-rays, to temp. of 40—43° for 30 min., and to -25° for 48 hr., but succumbed to drying for 1½ hr. G. H. B.

Metabolism of bacteria in exhausted media and media containing vaccines. A. DAMBOVICANU and H. ROTH (Compt. rend. Soc. Biol., 1936, 123, 61—63).—Cessation of growth of streptococci in a liquid medium is due to consumption of the sugar, no evidence being obtained of the production of inhibiting substances. H. G. R.

Physiology of *Rhizobium*. VI. Accessory factors. D. W. THORNE and R. H. WALKER (Soil Sci., 1936, 42, 231—240; cf. this vol., 114).—Small quantities of Fe added to a NO₃'-sucrose medium increased the growth of *R. trifolii* and *R. meliloti*, Fe⁺⁺⁺ being more active than Fe⁺⁺. Repeated subculturing in mineral salt-sucrose media with KNO₃ as N source led to growth failure, but with NH₄Cl or asparagine full activity was retained. Growth and O₂ consumption in highly purified media may be improved by addition of cysteine or thioglycollic acid. The organisms do not require any complex or unidentified substances for growth, although many substances have stimulatory effects. A. G. P.

Association of characters among dissociates from *Staphylococcus aureus*. M. DOUDOROFF (Proc. Soc. Exp. Biol. Med., 1936, 34, 216—217).—In the dissociates relatively high power to produce hæmolysin, to liquefy gelatin, and to produce fibrinolysin are each associated with relatively low production of orange pigment and relatively high production of white pigment. The violet reaction and the

production of coagulase apparently remain const. despite variations in the amount of pigment produced.

W. McC.

Relation of so-called *Streptococcus apis* to certain lactic acid streptococci. J. G. DAVIS and H. L. A. TARR (Nature, 1936, 138, 763).—The two kinds of *S. apis* previously reported (this vol., 763) are morphologically, culturally, and biochemically indistinguishable from *S. glycerinaceus* and *S. liquefaciens*.

L. S. T.

Enzymic racemisation of optically active lactic acid. E. L. TATUM, W. H. PETERSON, and E. B. FRED (Biochem. J., 1936, 30, 1892—1897).—Associated growth of *Strep. lactis* or *Lactobacillus delbrückii* with the PrCO_2H organisms *Cl. acetobutylicum* or *Cl. butylicum* leads to the formation of inactive lactic acid (I) due to the racemising action of the latter bacteria. In the absence of lactic acid bacteria, both PrCO_2H organisms partly ferment active (I) and racemise the remainder. Cultures of these PrCO_2H organisms convert either *d*- or *l*-(I) quantitatively into the *dl*-acid in presence of antiseptics. The racemising system consists of extracellular heat-labile (10 min. at 87°) and intracellular heat-stable components. Neither cell suspensions nor cell-free media of *Cl. butylicum* can racemise active (I) but the two are effective in combination.

P. W. C.

Butyl alcohol and acetone fermentations. II. Intermediate products of the butyl alcohol-acetone fermentation. K. BERNHAUER, A. IGLAUER, W. GROAG, and R. KÖTTIG (Biochem. Z., 1936, 287, 61—64).—Further experiments (cf. A., 1935, 1541) on the intermediate products of this fermentation are described. When the fermentations are carried out in presence of CaCO_3 , PrCHO gives 80% yields of Bu°OH , whilst crotonic acid gives 66—80% and AcCO_2H and lactic acid 70% yields of AcOH . In each case considerably more Bu products (PrCO_2H , BuOH) and correspondingly less COMe_2 products (COMe_2 , AcOH , EtOH) are obtained in the absence than in the presence of CaCO_3 .

P. W. C.

Metabolism of strict anaerobes (genus *Clostridium*). V. Coupled reactions between pairs of amino-acids induced by *Cl. sporogenes*. D. D. WOODS (Biochem. J., 1936, 30, 1934—1946).—In the linked oxidation and reduction of pairs of NH_2 -acids by washed cells of *Cl. sporogenes l*-cysteine (I) can act as a H donor and also is partly deaminated in the absence of other acids. Glycollic acid, β -alanine, and taurine are not attacked, whilst *d*-ornithine (II) and *d*-arginine (III) are both activated as H acceptors and partly deaminated in the absence of H donors. When (II) reacts with alanine, it accepts 2 H and undergoes reductive deamination to δ -aminovaleric acid. Simple NH_2 -acids (with the exception of glycine) appear to act only as H donors. When there is another substituent group in the chain in addition to the α - NH_2 , the acids are broken down in the absence of other NH_2 -acids. If this extra group is not NH_2 [(I), serine] the substance also acts as a H donor but if it is or contains NH_2 [(II), (III)] the substance also acts as a H acceptor (cf. A., 1935, 537, 664).

P. W. C.

Mechanism of oxidation processes. XLV. Anaerobic fermentation of fumaric acid. H. WIELAND, M. CRAWFORD, and H. WALCH. XLVI. Anaerobic fermentation of citric acid. R. SONDERHOFF and M. DEFFNER (Annalen, 1936, 525, 119—131, 132—138; cf. this vol., 893).—XLV. Cultures of bacteria occurring in certain impoverished yeasts, if < 24 hr. old, or yeasts containing them, change Na fumarate (I) anaerobically into $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ (II) 0.5, CO_2 0.7—0.75, EtOH 0.1, AcOH 0.4, and HCO_2H 0.2 mol. The primary reaction is $(\text{I}) + \text{H}_2\text{O} \rightarrow \text{malic acid (III)}$; $(\text{III}) + (\text{I}) \rightarrow (\text{II}) + \text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (IV); $(\text{IV}) \rightarrow \text{CO}_2 + \text{AcCO}_2\text{H} \rightarrow \text{CO}_2 + \text{MeCHO}$; $2\text{MeCHO} \rightarrow \text{EtOH} + \text{AcOH}$. This is, however, complicated by the side reactions, $(\text{IV}) \rightarrow \text{HCO}_2\text{H} + \text{CH}_2(\text{CO}_2\text{H})_2$, and $\text{AcCO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{AcOH} + \text{HCO}_2\text{H}$, both of which are caused by the bacteria in neutral solution. This is confirmed by the rapid anaerobic production of (II), CO_2 , EtOH , AcOH , and HCO_2H from *l*-(-)-(III) by the bacteria; *dl*-(III) is less quickly fermented, owing to the slower reaction of the *d*-form (which accumulates in the solution), and to its negative catalytic effect on fermentation of the *l*-form. The bacteria also ferment (IV) anaerobically, giving 25% of (II), the reaction being $(\text{IV}) + \text{CHMe}(\text{OH})_2 \rightarrow \text{AcOH} + (\text{III})$, etc. Formation of HCO_2H and $\text{H}_2\text{C}_2\text{O}_4$ during various fermentations probably occurs by way of (IV). Sterile yeast does not act on (I).

XLVI. The anaerobic fermentation of citric acid (V) by yeast is due to bacteria (cf. A., 1933, 865; 1935, 1539), similar to those described above. The presence of aq. yeast extract is necessary for the production of much H_2 . Sterile yeast, however, produces (V) and (II) from $\text{Ba}(\text{OAc})_2$ and ferments (V) anaerobically.

R. S. C.

Aerobic breakdown of glucose by *Bact. suboxydans*. K. R. BULLIN (Biochem. J., 1936, 30, 1870—1877).—Washed suspensions of *B. suboxydans* from maize wort-agar without CaCO_3 are dirty white and oxidise glucose (I) at p_{H} 5.5 but only to gluconic acid (II) and give no CO_2 . Similar suspensions from wort-agar containing CaCO_3 are pink, give a much larger and more rapid O_2 uptake with (I), oxidising (I) to (II) and then probably to 5-ketogluconic acid; the CO_2 evolved equals the O_2 absorbed. No synthesis of hexose phosphates by suspensions or air-dried or COMe_2 preps. of either type was detected but cultures obtained on media containing CaCO_3 had a much greater capacity for hydrolysing Na hexose diphosphate than the corresponding preps. without CaCO_3 . The modification in enzymic properties by CaCO_3 is a temporary variation.

P. W. C.

Growth factors for bacteria. V. Vitamin- B_{11} , a growth stimulant for propionic acid bacteria. E. L. TATUM, H. G. WOOD, and W. H. PETERSON (Biochem. J., 1936, 30, 1898—1904).—The stimulating action of protein hydrolysates on acid production by EtCO_2H bacteria is partly due to a factor which can be separated from unhydrolysed caseinogen, ovalbumin, yeast extract, and milk powder by extraction with COMe_2 or EtOH and is active in a concn. of 0.15×10^{-6} g. per mol. The factor is most active in presence of NH_2 -acids, and is not replaced by

inositol, panthothenic acid, ascorbic acid, hepato-flavin, nicotinamide, or indolylacetic acid, but is replaceable by 0.5×10^{-6} g. of cryst. vitamin- B_1 per 100 ml.

P. W. C.

Effect of sulphur compounds on the fermentation of glucose by propionic bacteria. P. CHAIX and C. FROMAGEOT (Bull. Soc. Chim. biol., 1936, 18, 1436—1453; cf. this vol., 760).—The max. stimulating action of S compounds on the fermenting activity of propionic bacteria is obtained with >0.1 mg. of S per 5 c.c. and is dependent on p_H . Ascorbic acid, glycine, and alanine have no activating effect.

A. L.

Combined action of succinodihydrogenase and aspartase in *Bacterium coli*. M. MICHAELIS (Z. physiol. Chem., 1936, 243, I).—The no. of cu. mm. of H_2 transferred from 1 mg. of dry *B. coli* to methylene-blue in 1 hr. at p_H 7.6 is increased from 2.5 to 7.3 by addition of 0.1N-Na succinate (I) and to 10.0 by addition of (I) + $M-(NH_4)_2SO_4$. The acceleration occurs because the rate of production of fumarate (II) from (I) by succinodihydrogenase is $<$ the rate of conversion of (II) + NH_3 into aspartic acid by aspartase.

W. McC.

Fermentation of pyruvic acid by colon-aerogenes bacteria. M. MICKELSON, H. REYNOLDS, and C. H. WERKMAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 748—750).—*Escherichia coli* and *Citrobacter freundii* decompose $AcCO_2H$ by a similar mechanism, $AcOH$ being largely produced along with lactic acid, HCO_2H , CO_2 , and H_2 . *Aerobacter indologenes* can also reduce the $AcOH$ to $(\cdot CHMe \cdot OH)_2$.

P. G. M.

Hydrogen donators for *B. prodigiosus*. D. BACH and J. LAMBERT (Compt. rend. Soc. Biol., 1936, 123, 358—361).—Of 128 org. substances examined 94 were donators.

H. G. R.

Biology of the pullorum-gallinarum group. Differentiation of types of pullorum by maltose fermentation. C. RODRIGUES and G. PACHECO (Compt. rend. Soc. Biol., 1936, 123, 438—440).—The maltose of normal serum, if used in the medium, will vitiate results.

H. G. R.

Hydrogen donators for Friedlander's pneumobacillus. D. BACH and J. LAMBERT (Compt. rend. Soc. Biol., 1936, 123, 361—364).—Of 125 substances examined 68 were active.

H. G. R.

Soluble specific substances of pneumococcus type III possessing properties distinct from SSS III. G. J. P. HORNUS and J. F. ENDERS (Proc. Soc. Exp. Biol. Med., 1936, 34, 102—104).—A carbohydrate, isolated from type III pneumococcus by a method which avoids the use as far as possible of strong acid, reacts with type III antipneumococcus serum but is different from the sol. sp. substance III of Heidelberg *et al.* (cf. A., 1926, 545).

W. O. K.

Ultrafiltration in the concentration and purification of pneumococcus specific polysaccharides. R. BROWN (Proc. Soc. Exp. Biol. Med., 1936, 34, 832—833).—A 16 hr. culture of pneumococcus (type VII) was centrifuged and the fluid ultrafiltered and washed on a 4% cellulose nitrate

membrane. 100-fold concn. resulted, with removal of 98.26% of the N. An initial concn. with aq. $(NH_4)_2SO_4$, prior to ultrafiltration, is also useful.

P. G. M.

Ash of bacteria (*Vibrio cholerae*). A. DAMBOVICIANU and C. VASILESCO (Compt. rend. Soc. Biol., 1936, 123, 65—68).—The ash of *V. cholerae* is considerably influenced by the mineral content of the medium, particularly when the normal ash content of the organism is low.

H. G. R.

Ash of bacteria (*Vibrio cholerae*). C. BARBER (Compt. rend. Soc. Biol., 1936, 123, 64—65).—Species with a high ash content generally contain more K, Na, and P and less Ca than those with a low ash. In all species Ca is low compared with other bacteria.

H. G. R.

Carotenoids of purple bacteria. III. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1936, 19, 1019—1024; cf. this vol., 248, 340).—Further examination of the *Rhodovibrio* carotenoids shows that rhodopin contains probably 1 OH and 12 double linkings. In accordance with its position in the chromatogram rhodovibrin is a polyene alcohol. Rhodoviolasene, $C_{42}H_{60}O_2$, contains 2 OMe, 13 double linkings, and $>1 Pr^{\beta}$; it is probably $COMe_2 \cdot CH \cdot C(OMe) \cdot CH \cdot CMe \cdot [CH \cdot CH \cdot CH \cdot CMe]_2 \cdot CH \cdot CH \cdot [CH \cdot CH \cdot CMe \cdot CH]_2 \cdot CH \cdot CH \cdot C(OMe) \cdot CH_2 \cdot CHB_{10}O_2 \cdot OMe$. Rhodopurpurene is a hydrocarbon resembling lycopene spectroscopically, but its identity therewith is doubtful. The presence of β -carotene is occasionally observed. Flavorhodin is probably a hydrocarbon but certainly not a polyene with free OH.

H. W.

Pigment of *B. violaceus*. II. Pyrrolic nucleus of violacein. W. C. TOBIE (Proc. Soc. Exp. Biol. Med., 1936, 34, 620—622).—Violacein contains C 69.28, H 6.79, O 16.45, N 4.83, and ash 2.65%. The ash contains Fe. The mol. contains one or more pyrrolic nuclei, probably with hydrocarbon side-chains. It is sol. in Et_2O and light petroleum, but insol. in EtOH, and is similar to the pigment of *B. prodigiosus*.

P. G. M.

Chemical composition of *B. tumefaciens*. E. CHARGAFF and M. LEVINE (Proc. Soc. Exp. Biol. Med., 1936, 34, 675—677).—The $COMe_2$ -sol. fat has I val. 95.0, sap. val. 201.2, acid val. 53.2, ester val. 148.0; it contains 9% of non-saponifiable matter, 10% of which consists of a sterol mixture. The phosphatide has N 2.2, P 3.4%; it stimulates growth. The defatted bacteria contain 3.5% of a polysaccharide.

P. G. M.

Polysaccharides of *Amylobacter* strains. H. MEISEL (Compt. rend. Soc. Biol., 1936, 123, 173—176).—The polysaccharide obtained by acid extraction in some cases gives protein reactions depending on the medium in which the organism is grown.

H. G. R.

Sonic extraction of labile bacterial constituents. L. A. CHAMBERS and E. W. FLOSDORF (Proc. Soc. Exp. Biol. Med., 1936, 34, 631—636).—Suspensions of *Eberthella typhi* and *S. haemolyticus*, after subjection at $<15^\circ$ to intense magnetic vibrations of 8900 cycles per sec., yield supernatant fluids on centrifuging which will combine with the antibody

responsible for phagocytosis. These antigens lose their activity in 3 days at 2—4°, but may be stored after rapid drying from the frozen state. P. G. M.

Properties of different streptococcal fibrinolysins. E. WITEBSKY and E. NETER (Proc. Soc. Exp. Biol. Med., 1936, **34**, 858—863).—Human hæmolytic streptococci tested for lysin formation in 0.05 and 2.0% glucose broth may fall into one of four groups: (1) production in 2% only, (2) in 0.05% only, (3) in both, (4) in neither. *S. viridans* behaves similarly to *S. hæmolyticus*, which produces lysin in 2% broth. P. G. M.

Preparation of a soluble dysentery toxin by grinding and extraction of the bacteria. A. HANSEN (Biochem. Z., 1936, **287**, 35—39).—A method is described for the prep. from the finely ground dysentery bacilli (Shiga) by adsorption on $\text{Al}(\text{OH})_3$, elution, and pptn. of a readily sol. toxin in purified condition. The CH_2O toxoid prep. therefrom possesses strong immunising power. P. W. C.

Phytochemical reduction with *Thermobacterium mobile* (*Pseudomonas Lindneri*). W. M. CAHILL (Fermentforsch., 1936, **15**, 134—137).—Phytochemical reduction of Bu^nCHO by *P. Lindneri* gives $\text{C}_5\text{H}_{11}\cdot\text{OH}$, and that of COAc_2 by yeast gives $\text{OH}\cdot\text{CMe}(\text{CHMe}\cdot\text{OH})_2$. E. A. H. R.

Precipitating action of basic dyes on bacteriophage and bacterial proteolytic enzymes. A. W. WALKER (Proc. Soc. Exp. Biol. Med., 1936, **34**, 726—728).—*B. coli* bacteriophage and the proteolytic enzymes of *B. pyocyaneus* are completely pptd. by azine and thiazine dyes, but not by oxazines, xanthanes, or CHPh_3 dyes. P. G. M.

Variation in animal viruses. G. M. FINDLAY (J. Roy. Microscop. Soc., 1936, [iii], **56**, 213—299).—A comprehensive review.

Tobacco-mosaic virus. VII. Preparation of crystalline tobacco-mosaic virus protein. W. M. STANLEY (J. Biol. Chem., 1936, **115**, 673—678; cf. this vol., 1156).—A method for the prep. of the cryst. protein by fractional pptn. with $(\text{NH}_4)_2\text{SO}_4$, CaO , etc. is described. The yield from crude globulin preps. is approx. 80%. F. O. H.

Sedimentation and electrophoresis of the tobacco-mosaic virus protein. I. B. ERIKSSON-QUENSEL and T. SVEDBERG (J. Amer. Chem. Soc., 1936, **58**, 1863—1867).—Mol. wt. determinations by sedimentation methods indicate that the protein (I) (Stanley, A., 1935, 1181) is not homogeneous; at p_H 6.8 about 65% has M 15—20 $\times 10^6$ provided the dissymmetry const. is the same as for other proteins of high mol. wt. (I) is more polydisperse at $p_H >$ or $<$ 6.8. Electrophoresis measurements indicate that (I) is practically homogeneous; the isoelectric point is p_H 3.49. H. B.

Nature of factor-V. A. Lvov and M. Lvov (Compt. rend., 1936, **203**, 520—522).—Factor-V (I), a principle promoting bacterial growth, is pptd. by EtOH and $\text{Pb}(\text{OAc})_2$ at p_H 9.5 but not by $\text{Pb}(\text{OAc})_2$ at p_H 6.8 or $\text{Hg}(\text{NO}_3)_2$ at p_H 7.0, and resists desiccation in a vac. These and biological properties indicate similarity to or identity with the codehydrogenases

(Warburg-Christian co-enzyme and Harden-Young cozymase). F. O. H.

Activation of silver by acids. F. LIEB (Arch. Hyg. Bakt., 1936, **116**, 317—320).—The oligodynamic activation of Ag can be promoted only by acids which form insol. or slightly sol. Ag salts, e.g., HCl , H_2CrO_4 . W. L. D.

Bactericidal power of metals (zinc). A. BERNI and G. RÈSTIVO (Boll. sez. Ital., 1936, **8**, 123—125).—Strips of various metals were immersed in nutrient agar and various organisms grown in the agar. Halos free from growth appeared around strips of Fe, Cu, Zn, and Mg but not around Au, Ag, Pb, Sn, Al, or Ni. Zn as sheet, powder, or in solution after contact with distilled H_2O for 24 hr. was toxic to *B. coli*. The decreasing order of toxicity to bacteria of metals is: Zn, Cu, Ag, Mg. Other metals are inactive. W. L. D.

Bactericidal power of the stomach: some influential factors. A. HANSEN (Amer. J. Digest. Dis. Nutrition, 1934, **1**, 723—727).—The bactericidal power of the stomach is increased by feeding 1 hr. prior to ingestion of infected fluids. Foods of high buffer power retain and subsequently release acid. To ensure effective bactericidal action the p_H of the stomach contents should reach >2 . CH. ABS. (p)

Properties acquired by plant extracts after inoculation with bacteria or toxins pathogenic to animals. T. FRÉMONT (Compt. rend. Soc. Biol., 1936, **123**, 418—420).—The development of antibodies increases or decreases the virulence of the bacteria when injected, depending on whether they are lytic or coagulating. H. G. R.

Bactericidal action of sea-water. C. E. ZOBELL (Proc. Soc. Exp. Biol. Med., 1936, **34**, 113—116).—Although fresh- H_2O bacteria may be acclimatised to grow in sea- H_2O unacclimatised strains as well as sewage and other bacteria are killed by natural, autoclaved, and Berkefeld-filtered sea- H_2O . Sea- H_2O probably contains a bactericidal agent, other than salts. Its potency is diminished by autoclaving and by addition of org. matter. Survival of sewage bacteria is favoured by water containing 5 and 10% of sea- H_2O . W. McC.

4-n-Alkylpyrogallols.—See this vol., 1503.

Cardiac tonus under the influence of adrenaline and acetylcholine. W. TOMASZEWSKI (Pflüger's Arch., 1936, **237**, 260—272). M. A. B.

Similarity of action of the adrenal medulla hormone and synthetic adrenaline. G. KAHLSON and O. MERTENS (Pflüger's Arch., 1936, **237**, 699—709).—Injection of synthetic adrenaline produced exactly the same effects on blood distribution, mobilisation of the blood reserves, minute-vol., etc. in the dog as did the hormone liberated by stimulation of the secretory nerves of the left adrenal. M. A. B.

Effect of adrenaline on the activity of the heart. K. GOLLWITZER-MEIER, K. KRAMER, and E. KRÜGER (Pflüger's Arch., 1935, **237**, 639—650). M. A. B.

Effect of adrenaline on the blood-vessels in resting and working muscles. O. MERTENS, H.

REIN, and F. G. VALDECASAS (Pflüger's Arch., 1935, 237, 454—475).
M. A. B.

Weight changes following the use of glycerol extract of adrenal cortex. R. G. HOSKINS and H. FREEMAN (Endocrinol., 1936, 20, 565—566).
R. N. C.

Influence of adrenaline and cortin on oxidised and reduced glutathione in the blood. E. ZUNZ and O. VESSELOVSKY (Compt. rend. Soc. Biol., 1936, 123, 114—116).—Intravenous injection of adrenaline or cortin increases the reduced and total glutathione in the red cells.
H. G. R.

Adrenaline hyperglycæmia and variations in hile-sugar. G. BALTACEANO, C. VASILIU, and T. BUDEANU (Compt. rend. Soc. Biol., 1936, 123, 56—58).—Parallel with the increase in blood-sugar there is an increase in both free and protein-sugar in the bile.
H. G. R.

Fat absorption after adrenalectomy. F. VERZAR and L. JEKER (Pflüger's Arch., 1936, 237, 14—18). Adrenalectomised rats showed no synthesis of neutral fat in the cells of the intestine although penetration of free fatty acids was not inhibited. Injection of adrenal cortical hormone restored normal fat synthesis.
M. A. B.

Potassium in adrenal deficiency. C. I. URECHIA, G. BENETATO, and RETEZEANU (Compt. rend. Soc. Biol., 1936, 123, 197—200).—After adrenalectomy, K is diminished in the kidney, spleen, muscles, heart, and liver and increased in the brain of the frog.
H. G. R.

Glucose absorption and glycogen production in the hypophysectomised rat. L. L. BENNETT (Proc. Soc. Exp. Biol. Med., 1936, 34, 277—279).—In hypophysectomised rats the rate of absorption of glucose (I) is about 35% < that in normal rats, the glycogen (II) contents of the liver and muscle are abnormally low, and the increase in the (II) contents following consumption of (I) is < that in normal rats.
W. McC.

Carbohydrate levels in fasted and fed hypophysectomised rats. J. A. RUSSELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 279—281).—Liver- and muscle-glycogen and blood-sugar vals. are normal in fully fed but low in fasted hypophysectomised rats. The low vals. are raised to normal but not maintained by giving carbohydrates.
W. McC.

Pituitary-thyroid-gonad relationship. S. L. LEONARD (Proc. Soc. Exp. Biol. Med., 1936, 34, 599—600).—Follicle-stimulating hormone from either pituitary or urinary sources is more effective in the absence of the thyroid; the luteinising hormone is unaffected.
P. G. M.

Relationship of the anterior pituitary gland to thyroid and ovary. L. LOEB, J. SAXTON, and S. J. HAYWARD (Endocrinol., 1936, 20, 511—519).—The anterior pituitary gland of cattle, sheep, and pigs contains a substance, "atresin" (I), that destroys follicles in guinea-pig ovaries. It appears possible to obtain extracts from cattle glands that contain (I) in effective concn. with little or no thyroid-stimulating (II) or luteinising hormone (III). (I), (II), and (III) are usually in association with one another,

but can be separated. (II) is associated with the follicular growth-maturation hormone in some human glands, and is not essential for activation of (III). A method of demonstrating the active substances *in situ* is described.
R. N. C.

Ovaries after administration of a gonadotropic principle of anterior pituitary. E. C. HAMBLEN (Endocrinol., 1936, 20, 321—328).
R. N. C.

Fat storage in the liver by treatment with the fat-metabolism hormone of the anterior lobe of the pituitary. K. J. ANSELMINO, F. HOFFMANN, and E. RHODEN (Pflüger's Arch., 1936, 237, 515—516).
M. A. B.

Action of hormones and of maintenance in the dark on the content of pressor and oxytocic factors in the posterior pituitary gland. A. SIMON (Arch. exp. Path. Pharm., 1936, 182, 584—588).—Administration of pituitary, thyroid, and pituitary thyrotropic extracts and of insulin to guinea-pigs, or keeping the animals in the dark, is without effect.
F. O. H.

Effect of posterior pituitary extracts on sodium balance in health and in diabetes insipidus. F. M. SMITH and E. M. MACKAY (Proc. Soc. Exp. Biol. Med., 1936, 34, 116—118).—Excretion of Na and Cl was increased and the Na and Cl balance rendered negative without change in urinary vols. by administration of the extract to a healthy subject. In diabetes insipidus the same dose caused no increase in NaCl excretion.
W. McC.

Sex hormones. J. FREUD (Chem. Weekblad, 1936, 33, 632—637).—A summary of the chemistry and action of the various sex hormones.
S. C.

Analyses of urine of the chimpanzee for œstrogenic content during various stages of the menstrual cycle. E. ALLEN, A. W. DIDDLE, T. H. BURFORD, and J. H. ELDER (Endocrinol., 1936, 20, 546—549).—The content is max. at the time of max. genital swelling.
R. N. C.

Extraction of both the gonadotropic and (free or total) œstrogenic hormones from a single urine sample. S. C. FREED and O. HECHTER (Endocrinol., 1936, 20, 396—397; cf. this vol., 902).—The gonadotropic hormone is pptd. from the urine with H₂WO₄ and, after removal of adsorbed œstrin (I), is separated from impurities by fractional pptn. with alkaline aq. COMe₂. Free (I) is extracted from the urine filtrate by the H₂WO₄ method, whilst combined (I) is liberated by boiling the urine with HCl and neutralising before extraction.
R. N. C.

Isolation from ovarian tissue of a crystalline substance possessing high œstrogenic properties. R. H. ANDREW and F. FENGER (Endocrinol., 1936, 20, 563—564).—After rapid saponification of the fatty portion of whole ovaries with KOH-EtOH at low temp., the unsaponifiable material is extracted from the dil. solution, and the extract evaporated. Cholesterol is removed by boiling with EtOH and chilling, and other impurities by repeated pptn. with dil. aq. NaOH. Subsequent extraction with Et₂O and crystallisation from EtOH affords a substance, C₂₀H₄₁O₂N (?), m.p. 95.1° (uncorr.), mol. wt. 320, active in doses of 10⁻⁵ mg. in rats.
R. N. C.

Presence of oestrogenic hormones in the ova and ovaries of fish. A. I. WEISMAN, C. W. COATES, and R. L. MOSES (Endocrinol., 1936, 20, 561—562).—The hormones, if present at all in whitefish ova and herring ovaries, are not in sufficient concn. to produce oestrus in mice. R. N. C.

Oestrin-deprivation theory of menstruation. C. F. FLUHMANN (Endocrinol., 1936, 20, 318—320). R. N. C.

Effect of injection of residual ovarian extracts. H. W. MARLOW (Endocrinol., 1936, 20, 339—341). R. N. C.

Structural changes induced in the anterior pituitary by injections of oestrin. J. M. WOLFE and C. S. CHADWICK (Endocrinol., 1936, 20, 503—510). R. N. C.

Modification of the Frank-Goldberger blood-oestrin test. T. NEUSTAEDTER (Endocrinol., 1936, 20, 639—642). R. N. C.

Tube-locking of ova by oestrogenic substances. R. WHITNEY and H. O. BURDICK (Endocrinol., 1936, 20, 643—647). R. N. C.

Oestrogenic substances of hypertrophied prostatic tissue and urine. J. B. HAMILTON, C. L. DEMING, and E. ALLAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 193—194).—Hypertrophied prostatic tissues and urine from patients of 60—80 years contained no oestrogenic substances before or after prostatectomy. W. McC.

Effect of combined administration of oestrone and progesterone in adult ovariectomised rats. H. SELYE, J. S. L. BROWNE, and J. B. COLLIP (Proc. Soc. Exp. Biol. Med., 1936, 34, 198—200).—In ovariectomised rats the effect of administration of daily doses of 0.03 mg. of oestrone (I) is modified by simultaneous administration of 0.4 mg. of progesterone (II). (I) and (II) together cause mucification of the vaginal epithelium and second-stage progestational proliferation of the uterus, the vaginal effect being modified even in cases in which the uterine effect is unchanged. W. McC.

Epithelial regeneration by the action of the oestrogenic hormone and in avitaminosis-A. W. SCHMIDT (Beitr. Path. Anat. allg. Path., 1935, 96, 129—146; Chem. Zentr., 1936, i, 370).—No relation was apparent between epithelial growth and the level of vitamin-A in rats. A. G. P.

Concentration of gonadotropic substance from pregnancy urine. H. L. FEVOLD and F. L. HISAW (Proc. Soc. Exp. Biol. Med., 1936, 34, 712—714).—Pregnancy urine is extracted with cresol and the hormone is pptd. by addition of 2 vols. of COMe₂. The method is more efficient than tannic acid or BzOH adsorption. P. G. M.

Water-soluble pregnandiol complex from human pregnancy urine. E. M. VENNING and J. S. L. BROWNE (Proc. Soc. Exp. Biol. Med., 1936, 34, 792—793).—Pregnandiol-glycuronic acid as thin plates, m.p. 268—271° (decomp.), has been isolated from human pregnancy urine (9th month) by extraction with BuOH, dissolution of the residue in 0.5*N*-NaOH, re-extraction with BuOH, and crystall-

isation of the residue from H₂O and EtOH. The yield is 40—50 mg. per litre. P. G. M.

Relative effectiveness of progestin in hypophysectomised and normal rabbits. S. R. M. REYNOLDS, W. M. FIROR, and W. M. ALLEN (Endocrinol., 1936, 20, 681—682). R. N. C.

Effect of testosterone on the growth of the comb in *Triton cristatus*. W. FLEISCHMANN and S. KANN (Pflüger's Arch., 1936, 237, 517—518). M. A. B.

Effect of testosterone on the mammary gland. H. SELYE, C. S. McEVEN, and J. B. COLLIP (Proc. Soc. Exp. Biol. Med., 1936, 34, 201—203).—Slight development of the mammary tissue and marked secretion of milk are induced in immature male and female rats in presence and absence of the gonad by administration of 0.2 mg. of testosterone benzoate. W. McC.

Presence of an excess of "male" (comb-growth and prostate-stimulating) hormone in virilism and pseudo-hermaphroditism. S. L. SIMPSON, P. DE FREMERY, and A. MACBETH (Endocrinol., 1936, 20, 372). R. N. C.

cis- and *trans*-Androstanone-3-carboxylic acid, an oestrus-producing male hormone derivative, and *epicholesterol*.—See this vol., 1506.

Artificial production of oestrogenic substances from sterols.—See this vol., 1505.

Crystalline insulin. VIII. Standardisation by the "area of activity" method. H. KOHL (Arch. exp. Path. Pharm., 1936, 182, 550—559).—Assays in rabbits by determination of the "area of activity" (A., 1934, 223) are applicable only with intravenous injection. The method indicates cryst. insulin to have an activity of approx. 16 international units per mg. F. O. H.

Measurement of insulin action. P. O. GREELEY H. C. BERGMAN, D. B. TYLER, and D. R. DOURY (Proc. Soc. Exp. Biol. Med., 1936, 34, 121—123).—In order to maintain nearly sugar-free urine and a normal blood-sugar level in depancreatised dogs, 0.0094—0.014 unit of insulin per kg. of body-wt. must be administered. W. McC.

Action of phenylcarbimide on insulin. II. Chemistry of insulin and its phosphate-lowering power. W. E. GAUNT and A. WORMALL (Biochem. J., 1936, 30, 1915—1926; cf. A., 1935, 441).—The inactivation by PhNCO (I) and *p*-C₆H₄Br·NCO (II) of the hypoglycaemic activity of insulin (III) in rabbits is accompanied by a parallel inactivation of the hypophosphatæmic power. Inactivation in both cases appears to be due to interaction with the free NH₂ groups of (III). (I) does not react, under conditions similar to those maintained in the prep. of phenylcarbamidoprotein derivatives, with the OH of tyrosine, the CO·NH₂ of asparagine (IV) and glutamine (V), or the glyoxaline group of histidine (VI) nor is there any significant change in the S·S linking. The SH of cysteine (VII) reacts but (VII) is not present in (III). (I) also reacts with the pyrrolidine group of proline (VIII) and to some extent with the guanidino-group of arginine (IX). The following compounds

were prepared: (I) derivatives of (VII), m.p. 139—140° (decomp.), in which both SH and NH₂ are blocked; of α -thiolpropionic acid, m.p. 140—141° (decomp.); of thiolacetic acid, m.p. 144—146° (decomp.); of (IV), m.p. 163° (decomp.) (*hydantoin*, m.p. 231—233°); of (V), m.p. 161° (decomp.) (*hydantoin*, m.p. 160—161°); (II) derivatives of (VIII), m.p. 169° (decomp.); of (VI), m.p. 177—178° (decomp.); of (IV), m.p. 175—176° (decomp.) (*hydantoin*, m.p. 220°); of (V), m.p. 189° (*hydantoin*, m.p. 200—201°). With (IX) mixtures of mono- and di-derivatives were obtained with both (I) and (II).
P. W. C.

Effect of various substances on the action of insulin. A. M. FISHER and D. A. SCOTT (J. Pharm. Exp. Ther., 1936, 58, 93—104).—The effect of insulin (I) is prolonged by admixture with spermine + Zn or an ox thymus prep. + Zn, the presence of Zn being essential in both cases. Suspensions of (I) containing no potency in solution do not differ in activity from a solution of the same (I).
H. G. R.

Insulin with protamine. D. A. SCOTT and A. M. FISHER (J. Pharm. Exp. Ther., 1936, 58, 78—92).—The action of insulin (I) is prolonged when administered in conjunction with protamine (prep. from fish testes described), this being further enhanced if traces of Zn are first added to (I), especially when a low-ash prep. is used. A method of assay on rabbits is described.
H. G. R.

Treatment of diabetes mellitus with insoluble insulin compounds. P. A. GRAY (Endocrinol., 1936, 20, 461—472).—Insulin (I) tannate shows a hypoglycaemic action > that of commercial (I) but approx. equal to that of protamine insulinate. It can control diabetes when administered alone or with (I). Its relative insolubility delays absorption and hence decreases the rate of liberation of free (I).
R. N. C.

Cutaneous absorption of insulin. R. H. MAJOR (Proc. Soc. Exp. Biol. Med., 1936, 34, 775—778).—Insulin in OH·[CH₂]₂·OEt is absorbed through the skin of the rabbit, producing a definite fall in blood-sugar.
P. G. M.

Response of normal and hypophysectomised Rhesus monkeys to insulin. P. E. SMITH, H. H. TYNDALE, L. DOTI, and E. T. ENGLE (Proc. Soc. Exp. Biol. Med., 1936, 34, 250—251).—Injection of insulin in doses of 0.0625 unit per kg. reduced the blood-sugar in normal monkeys by 14% and in hypophysectomised monkeys by 35% in 30 min.
W. McC.

Fate of the sugar disappearing under the influence of insulin. V. VENDEG (Pflüger's Arch., 1936, 237, 683—698).—Insulin causes conversion of sugar into glycogen (I) and then into fat in the liver. The final result may be an increase or decrease of (I) accompanied by a decrease or increase of fat, respectively. More sugar disappears in the former case. Occasionally where the initial fat content of the liver is high, insulin may decrease both (I) and fat. Decrease in fat is due to translocation to the fat depôts.
M. A. B.

Diuresis during insulin hypoglycaemia. V. LE CLERC (Compt. rend. Soc. Biol., 1936, 123, 273—275).—The diuresis, which diminishes and may become

total when the blood-sugar is very low, does not appear to be due to a blockage of H₂O absorption in the region of the stomach.
H. G. R.

Sensitivity of blood-sugar to insulin after pancreatectomy in dogs. E. S. PANAYOTOPOULOS (Compt. rend. Soc. Biol., 1936, 123, 403—404).—An abnormal sensitivity was noted during the 48 hr. following the operation.
H. G. R.

Diminution of the hyperpolypeptidæmia, secondary to cellular destruction, by insulin with or without glucose. O. LAMBRET, J. DRIESSENS, and H. MALATRAY (Compt. rend. Soc. Biol., 1936, 123, 12—13).
H. G. R.

Biologically active calcium of the aqueous humour in hyperparathyroidism and acute and latent tetany. F. MATHIEU (Compt. rend. Soc. Biol., 1936, 123, 112—114).—Variations in plasma-Ca during hypo- and hyper-parathyroidism are accompanied by corresponding variations in the humour.
H. G. R.

Metabolic effects of human thyroglobulin and its proteolytic cleavage products. W. T. SALTER and J. LERMAN (J. Clin. Invest., 1935, 14, 691—695).—Clinical assay of the metabolic potency of thyroglobulin (I) in terms of I showed that (I) from "colloid adenomatous" glands and iodised toxic glands, thyroxine (II), peptone from either type of gland, and synthetic racemic glycythyroxine were equiv. All preps. approximated to natural (II) polypeptide when assayed in human myxoedema. Di-iodopeptone produced no effect.
CH. ABS. (p)

Iodine tolerance test for the investigation of thyroid function. E. M. WATSON (Endocrinol., 1936, 20, 358—362).—The rate of disappearance of I from the blood-stream of patients injected intravenously with Lugol's solution is increased in thyrotoxicosis and reduced in hyperthyroidism.
R. N. C.

Assay of blood and urine for thyrotropic hormone in thyrotoxicosis and myxoedema. S. HERTZ and E. G. OASTLER (Endocrinol., 1936, 20, 520—525).
R. N. C.

Similarity of the iodine remission in experimental anterior hypophyseal hyperthyroidism, the hyperthyroidism of acromegaly, and that of exophthalmic goitre. H. B. FRIEDGOOD (Endocrinol., 1936, 20, 526—536).—The depressions of metabolic rate produced by NaI in all three conditions are of the same order.
R. N. C.

Effect of pregnancy on resistance to thyroxine; creatine content of the maternal and foetal myocardium. M. BODANSKY and V. B. DUFF (Endocrinol., 1936, 20, 537—540).—Tolerance to thyroxine is increased in pregnancy in the rat. Creatine falls in the maternal but not the foetal myocardium in hyperthyroidism.
R. N. C.

Age as a factor in the resistance of rats to thyroxine. Creatine content of the tissues in experimental hyperthyroidism. M. BODANSKY and V. B. DUFF (Endocrinol., 1936, 20, 541—545).—Resistance to thyroxine is high in immature rats. Myocardial creatine (I) is reduced in young and old

hyperthyroid rats, but young rats withstand greater depletion than do old rats. (I) falls in skeletal muscle and rises in the testes of hyperthyroid rats. Cessation of thyroxine treatment brings ventricular (I) to normal levels in 7—14 days. R. N. C.

Relation between insensible water loss and heat production in hyperthyroidism. D. R. GILLIGAN and G. EDSALL (*J. Clin. Invest.*, 1935, **14**, 659—664).—In hyperthyroidism the insensible H₂O loss and the % of total heat lost by evaporation decreased. The decline in H₂O loss through the lungs but not that through the skin \propto the decreased metabolism. CH. ABS. (*p*)

Rôle of vitamins in fat and lipin metabolism. T. KALAJA (*Suomen Kem.*, 1936, **9**, B, 21—22; cf. this vol., 389).—The I val. and the total fatty acid (I), phosphatide, free cholesterol (II), and cholesteryl ester contents of the heart-muscle of vitamin-A-deficient rats were equal to those of control animals, but in the brain (II) was reduced. Deficiency of the vitamin-B complex or of -B factors except -B₁ lowered the I val. and (I) content in the skin and blood. Deficiency of -C and inanition caused no change in the above vals. in guinea-pigs. A. L.

Utilisation by the rat of vitamin-A and carotene administered in different media. K. H. COWARD (*Biochem. J.*, 1936, **30**, 1878—1882).—Responses of large nos. of rats to the vitamin-A of cod-liver oil (true -A), of plant tissues [probably wholly carotene (I)], of butters (largely true -A), and of margarines containing vitamin concentrates (-A in different solvents, mostly vegetable oils) showed no significant differences. Differences in results obtained by dissolution of (I) in various oils cannot be due to differences in utilisation of -A or (I) contained in them. P. W. C.

Relative vitamin-A potency of carotene fed in butter fat and cottonseed oil. H. R. KRAYBILL and C. H. SHREWSBURY (*J. Nutrition*, 1936, **11**, 103—110).—Treatment of melted butter fat with Lloyd's reagent removes natural yellow pigments and vitamin-A without removal or destruction of the natural antioxidants. Quinol (up to 100 mg. per 100 g. of oil) does not seriously interfere with the utilisation of carotene (I) from cottonseed oil (II). (I) in butter fat decolorised with Lloyd's reagent is less readily utilised than when dissolved in (II). A. G. P.

Vitamin-A reserve of embryo and baby chicks. A. D. HOLMES, F. TRIPP, and P. A. CAMPBELL (*J. Nutrition*, 1936, **11**, 119—128).—The -A contents of egg yolks during hatching and of livers of young chicks are recorded. The rapid increase of -A in livers after hatching is derived from yolk reserves. A. G. P.

Microscopical observation of the fluorescence produced during reversible production of vitamin-A in the retina during visual perception. N. VON JANCÓS and H. VON JANCÓS (*Biochem. Z.*, 1936, **287**, 289—290).—Microscopical examination in filtered ultra-violet light of the retina of rats shows that after max. light adaptation there is strong fluorescence due to vitamin-A, whilst after max. dark adaptation there is no fluorescence, -A having dis-

appeared. The light destroys -A in 1—4 min. with disappearance of the fluorescence. Power to exhibit strong fluorescence is conferred on rat's liver by giving 7 mg. of carotene daily and by feeding Vogan for 3—4 weeks. At max. dark adaptation -A of the retina is converted into visual purple and stored in the rods, whilst on adaptation to light the carotenoid produced by photochemical decomp. of the purple reappears as -A, which is stored in the pigment cells. W. McC.

Accuracy of vitamin-A determinations. Starting point of the test period. K. H. COWARD (*Biochem. J.*, 1936, **30**, 2009—2011).—The greatest accuracy is obtained in determinations of vitamin-A by the "increase in wt." method when the test period is counted from the first day of dosing. P. W. C.

Influence of the vitamin-B complex on keto-acid metabolism. P. E. SIMOLA (*Suomen Kem.*, 1936, **9**, B, 20—21; cf. this vol., 646).— α -Ketoglutaric acid is excreted in the urine of rats during avitaminosis-B and when only vitamin-B₁ is included in the diet. No AcCO₂H or AcCHO was detectable. A. L.

Influence of the length of the test period on the accuracy obtainable in a vitamin-B₁ test. K. H. COWARD (*Biochem. J.*, 1936, **30**, 2012—2015).—The average variance in response of rats to doses of vitamin-B₁ is determined in tests lasting 1, 2, and 3 weeks, and the slopes of curves of response relating increase in wt. and the dose are measured. The probable errors of determinations of -B₁ potency of a substance by comparison with the International standard tested simultaneously, when 10 animals are used on each substance and when the tests are carried on for 1, 2, and 3 weeks, are about 18, 12.5, and 10%, respectively. Thus the accuracy is much > with -A determinations and is only very slightly increased by extending the tests from 2 to 3 weeks. The curve of response of bucks is only a very little steeper than for does and it is not necessary to have equal nos. of each in each group. P. W. C.

Assay of League of Nations standard preparation of vitamin-B₁. B. C. P. JANSEN (*Z. Vitaminforsch.*, 1936, **5**, 254—256).—1 g. of the standard prep. contains approx. 0.3 mg. of -B₁ hydrochloride. J. N. A.

Crystallisation of vitamin-B₁. L. ROSENTHALER (*Z. Vitaminforsch.*, 1936, **5**, 276—277).—Vitamin-B₁ can be pptd. in cryst. condition by K tetranitrodiamminocobaltiate and by Reinecke salt. Most alkaloid precipitants give only amorphous ppts. J. N. A.

Constitution of oryzanin (vitamin-B₁).—See this vol., 1526.

Aneurin. III. Methyl α -chloro- γ -hydroxypropyl ketone and its application to thiazole synthesis.—See this vol., 1526.

Constitution of aneurin (vitamin-B₁). R. GREWE (*Naturwiss.*, 1936, **24**, 657—662)—A lecture.

Vitamin-B₁ (oryzanin, torulin, aneurin). R. A. PETERS (*Current. Sci.*, 1936, **5**, 207—214).—A discussion of the chemistry and mode of action.

Vitamin-B₂ and its relation to canine black tongue. C. J. KOEHN, jun., and C. A. ELVEHJEM (J. Nutrition, 1936, 11, 67—76).—Black tongue was cured by liver extracts rich in -B₂ but freed from peptoflavin (I). (I) obtained from the extracts was without effect.
A. G. P.

Relation between vitamin-B₂ and the hormone of the adrenal cortex. F. VERZAR and L. LASZT (Pflüger's Arch., 1936, 237, 476—482).—In rats the adrenal cortical hormone (I) was effective only when the diet contained flavin (II) (provitamin-B₂). Adrenalectomised animals could be kept alive with flavin phosphate (III) in place of (I) but (II) itself was inactive. From the similarity of action between (I) and (II) it is concluded that (I) promotes the production of (III) from (II), so that (III) is vitamin-B₂.
M. A. B.

Synthesis of flavins.—See this vol., 1525.

Influence of ascorbic acid on the glycogen content of the liver of hyperthyroidised guinea-pigs. L. HIRSON (Biochem. Z., 1936, 287, 126—129).—Intraperitoneal injection of 25 mg. of ascorbic acid (I) per day causes in 12 days a 60% increase of liver-glycogen (II). The decrease of (II) brought about by intraperitoneal injection of thyroxine (0.1 mg. per day) is inhibited by (I) or by "cebion." "Cortidyn" injected with (I) did not increase the action of (I).
P. W. C.

Stabilisation of vitamin-C by adrenaline. M. YAMAMOTO (Z. physiol. Chem., 1936, 243, 266—269; cf. Abderhalden, A., 1934, 1138).—The oxidation of ascorbic acid (I) (0.602 mg. in 3 c.c.) at p_{H} 7.38 in the dark is prevented to the extent of 93% by addition of 0.7 mg. of *l*-adrenaline (II) but when *dl*-(II) is used the max. extent is only 43%. No oxidation of (II) occurs while (I) is present. Since *dl*-(II) exerts its max. effect when the ratio (I) : *dl*-(II) is 1 : 1 and since the bis-2 : 4-dinitrophenylhydrazone of (I) is much more slowly produced when (II) [especially *l*-(II)] is present than when it is absent it is possible that (II) combines with (I).
W. McC.

Divergent physiological effects of synthetic and "natural" ascorbic acids. L. HAVAS and I. GÁL (Nature, 1936, 138, 586—587; cf. A., 1935, 1430).—Vitamin-C from paprika still stimulates growth in wheat seedlings at a concn. of 0.1%. The inhibitory effect at 0.5% concn. is < that produced by the same concn. of synthetic ascorbic acid (I). With synthetic (I) inhibition appears at a concn. of 0.1%, and may be due to an impurity.
L. S. T.

Ascorbic acid content of the organs of rats in vitamin-B deficiency. J. MELKA (Pflüger's Arch., 1936, 238, 74—77).—On a vitamin-B-free diet ascorbic acid (I) synthesis was decreased. The content of (I) was decreased most in the liver, less in the brain, the ileum wall, and the testicles, and very little in the adrenals.
M. A. B.

Ascorbic acid content of different parts of the central nervous system and of the peripheral nerves. J. MELKA (Pflüger's Arch., 1936, 237, 210—221).—The following decreasing order of ascorbic acid content was established in man and various animals: pituitary body, cortex cerebelli, cerebral

cortex, basal ganglia, medulla oblongata, medulla spinalis, white matter of the central nervous system.
M. A. B.

Excretion of vitamin-C in normal individuals following a comparable quantitative administration in the form of orange juice, ascorbic acid by mouth, and ascorbic acid intravenously. E. E. HAWLEY, D. J. STEPHENS, and G. ANDERSON (J. Nutrition, 1936, 11, 135—145).—Excretion of -C remained at normal levels for several days after changing to a -C-deficient diet. Comparable amounts of -C given as orange juice or as ascorbic acid (I) produced similar changes in urinary excretion. Intravenously administered (I) was excreted more rapidly and more completely than when given by mouth. Variations in the intake of -C had no influence on the (I) content of whole blood.
A. G. P.

Blood-cell count and ascorbic acid content in guinea-pigs. H. VON EULER and M. MALMBERG (Z. physiol. Chem., 1936, 243, 121—143).—Anæmia is not regularly produced in guinea-pigs by a vitamin-C-free but otherwise adequate diet, but -C-free milk diet produces anæmia and reduction in the leucocyte content of the blood. This content is also greatly (66%) reduced in scurvy produced by other -C-free diets; the accompanying diminished immunity is possibly due to lack of -C. Diminution of leucocytes does not occur if ascorbic acid is added to the -C-free diet.
W. McC.

Vitamin-C in vegetables. III. Oxidation of ascorbic acid by metallic catalysts. G. L. MACK and Z. I. KERTESZ (Food Res., 1936, 1, 377—382).—The catalytic activity of Cu is considerably increased by the addition of small amounts of Fe, which by itself has no such activity. 2% of HPO₃ in the acid used to extract ascorbic acid retards oxidation sufficiently to allow analysis to be carried out. Only a small amount of the Cu in many vegetables appears in the extract in an active form.
E. C. S.

Determination of ascorbic acid. P. MANCEAU, A. A. POLICARD, and M. FERRAND (Bull. Soc. Chim. biol., 1936, 18, 1369—1386).—The sulphotungstate method of Fujita *et al.* (A., 1935, 793) for the determination of ascorbic acid (I) is modified by the introduction of a titrimetric determination of the reduced tungstate using K₃Fe(CN)₆. The method, however, is not sp. for (I), and other substances, particularly adrenaline, interfere. 2 : 6-Dichlorophenol-indophenol is more sp. and in presence of phenols gives better results.
A. L.

Determination of ascorbic acid by titration. H. CHEFTEL and M. L. PIGEAUD (Nature, 1936, 138, 799).—Increased accuracy is obtained in the Harris-Ray method by cooling the reactants to 0°, at which temp. oxidation of ascorbic acid is retarded.
L. S. T.

Determination of ascorbic acid by titration. I. GÁL (Nature, 1936, 138, 799).—Ascorbic acid is extracted with HPO₃ and allowed to react with methylene-blue, excess of which is titrated with 0.5% TiCl₃.
L. S. T.

Identity of the indophenol-reducing substances in brain tissue. F. G. YOUNG (Biochem. J., 1936,

30, 1883—1885).—The properties of the indophenol-reducing substance (I) in crude brain extracts differ in some respects from those of ascorbic acid (II). The reducing properties of (II) are, however, greatly modified by the presence of glutathione and other substances present in the extracts. (I) added to "inactivated" crude brain extract re-establishes the properties of the normal crude extract. (I) is probably (II).
P. W. C.

Strongly reducing substance accompanying ascorbic acid in the adrenals of the ox. E. OTT, K. KRÄMER, and W. FAUST (Z. physiol. Chem., 1936, 243, 199—201).—The MeOH extract of 1 kg. of the adrenals after treatment in N_2 with $Ba(OAc)_2$, filtration, addition of $Pb(OAc)_2$, and subsequent purification yields 0.15—0.20 g. of an amorphous, hygroscopic, H_2O -sol., reducing substance (I) (N 5.21, P 0.544—0.554%), which is very sensitive to the action of O_2 , reduces 4.6% of the amount of 2:6-dichlorophenol-indophenol reduced by an equal wt. of ascorbic acid, reduces hot but not cold Fehling's solution, and has only slight or no antiscorbutic action. W. McC.

Antirachitic activity of sterol derivatives. W. GRAB (Z. physiol. Chem., 1936, 243, 63—89).—The antirachitic activity of the crude and cryst. (vitamin- D_3) ultra-violet irradiation product of 7-dehydrocholesterol (I) and that of the crude ultra-violet irradiation products of 22-dihydroergosterol (II), 7-dehydrositosterol (III), and 7-dehydrostigma-sterol (IV) was compared with the activity of cryst. - D_2 (V), halibut-liver oil and concentrate, and cryst. material from the liver oil of the tunny by preventive and curative experiments on rats (experimental error $\pm 30\%$) and chickens ($\pm 50\%$). With rats the amounts of (V), crude irradiation product of (I), of (II), and of (III) required to produce the same result as the active dose of tunny-liver oil concentrate taken as unity are 32, 0.6—0.8, 2.5—10.0, >13 , respectively, and with chickens the corresponding vals for (V), crude and cryst. irradiation product of (I), and crude irradiation product of (II) are 32—80, 0.4, 0.6, and 1.6—2.5; crude irradiation product of (IV) has a relatively very low activity. The cryst. product from tunny-liver oil has activity indistinguishable from that of cryst. irradiation product of (I) and hence is identical with cryst. irradiation product of (I) which is therefore provitamin- D_3 . Probably the irradiation product of (II) is closely related to that of (I). Sterols of the C_{25} series cannot serve as provitamin- D .
W. McC.

Antirachitic values of irradiated yeast and of cod-liver oil. E. L. COMPERE, T. E. PORTER, and L. J. ROBERTS (Amer. J. Dis. Children, 1935, 50, 55—76).—The curative dose of irradiated dried yeast is 1.1—3.3 times that of cod-liver oil (rat units).
CH. ABS. (*p*)

Colorimetric determination of vitamin-D. H. TZONI (Biochem. Z., 1936, 287, 18—22).—The method described depends on the production of a red-violet colour on heating with $AlCl_3$ and pyrogallol. The reaction is sp. and is not given by phytosterol, cholesterol, ergosterol, or lumisterol. Suprasterol II gives a feeble colour.
P. W. C.

Chilean fish oils. Vitamin-D content of cod-liver oil.—See B., 1936, 1054.

Vitamin-E. P. SCHOORL (Z. Vitaminforsch., 1936, 5, 246—253).—An improved vitamin- E deficiency diet which contains casein and a high % of potato starch and dextrin, but no lard, is described. Royal jelly (the food of the larva of the honey bee destined to be a queen) shows no - E activity. Daily doses of 0.2 c.c. of wheat-germ oil during pregnancy are sufficient for fertility in rats. The - E concentrate Vibeta shows no anti-sterility activity. J. N. A.

Vitamin-E. V. Eutropic and anti-sterility activity of wheat-germ oil in comparison with other vegetable oils. L. SCHIOPPA (Z. Vitaminforsch., 1936, 5, 241—246; see this vol. 392).—Only wheat-germ oil possesses the activities described.
J. N. A.

Vitamin-E in cacao embryo. H. LABRÉ and F. H. DE BALSAC (Compt. rend., 1936, 203, 587—589).—Vitamin- E -deficient rats bear litters when cacao germ, but not when a fatty extract presumed rich in - E , is added to the diet. If germ or extract is incorporated in an - E -deficient diet sterility does not occur.
J. L. D.

New essential dietary factor. C. A. ELVEHJEM, C. J. KOEHN, jun., and J. J. OLESON (J. Biol. Chem., 1936, 115, 707—719).—A dietary factor essential for the growth of rats, not identical with any of the known factors, is present in liver, yeast extracts, and milk. The factor is H_2O -sol., pptd. from aq. solution by $EtOH-Et_2O$ or $COMe_2$, adsorbed by C, and thermolabile. It is not identical with arginine, cystine, or the NH_2 -acids from blood-fibrin or caseinogen. Rats deficient in this factor shown no sp. symptoms other than lack of growth.
F. A. A.

Influence of temperature on the carbohydrate metabolism, respiration, and morphological development of the tulip. I. L. ALGERA (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 846—855).—The effects of temp. during the later growth stages, during storage of lifted bulbs, and after subsequent planting out are examined. In general, the reducing sugar content declines during late growth, remains at a low level during storage, and increases rapidly some weeks after planting out. Non-reducing sugars begin to increase soon after lifting and continue to do so until nearly the end of the growth period. The starch content rises towards the end of growth, remains high after lifting and during early growth, and declines towards maturity. No optimum temp. for any individual stage is apparent. Optimum conditions for growth are those in which the temp. of successive stages is suitably balanced. A. G. P.

Electrometric determination of quality of potato tubers. Redox potential of pulped tuber tissue. H. WARTENBERG and A. HEY (Planta, 1936, 25, 258—281).—The melanin (I) system and its influence in maintaining anaërobic conditions in the tissue are discussed. Addition of electrolytes (notably PO_4''' buffers of $p_H >$ that of the pulp) favours (I) formation. The redox potential is an index of the vitality of tubers.
A. G. P.

Relation of hydrogen-ion concentration to the growth and distribution of mosses. G. J. IKENBERRY (Amer. J. Bot., 1936, 23, 271—279).—The distribution of 46 species of mosses was unrelated to the p_H of their natural substrates, although closely related species develop best on soils of similar p_H , and show optimum spore germination in culture solutions of almost identical reaction. The p_H of soil in which a species becomes dominant bears no relation to that of the culture solution most favourable to germination and development. A. G. P.

Relation of temperature to the effect of hydrogen- and hydroxyl-ion concentration on *Sclerotinia fructicola* and *Fomes annosus*. Spore germination and growth. P. E. TILFORD (Ohio Agric. Exp. Sta. Bull., 1936, No. 567, 27 pp.).—The p_H optimum for spore germination of *S. fructicola* is largely influenced by temp. At every temp. examined germination- p_H curves show two max. with a min. at 6.0. Growth injury by H^+ was \ll that by OH^- . H^+ was more toxic at higher than at lower temp. The reverse was the case with OH^- . The optimum p_H for mycelial extension at a higher temp. was $>$ that at a lower temp. A. G. P.

Chemistry of cell growth. I, II. O. RAHN (Cold Spring Harbor Symp., 1934, 2, 57—62, 63—69).—I. Energy exchange in certain plant and bacterial processes is examined. The vitamin requirements of rats for protein synthesis are discussed.

II. Nutritional factors affecting growth rates of bacteria, yeasts, and animals are considered.

CH. ABS. (p)

Respiration of potato tissue in relation to hydrogen-ion concentration of a surrounding solution. P. LEMMON (Amer. J. Bot., 1936, 23, 296—302).—The gaseous exchange of potato tissue in various buffer solutions over a p_H range of 1.5—9.5 is examined. A. G. P.

Variations in imbibition caused by reciprocal displacement of fixed cations on dead tissues of *Laminaria flexicaulis*. D. KOHLER (Compt. rend. Soc. Biol., 1936, 123, 394—396).—Ions fixed from immersion in one solution are partly replaced when the solute is changed, with corresponding modification in the imbibition. H. G. R.

Water and salt content of East African mangroves. H. WALTER (Ber. deut. bot. Ges., 1936, 54, 76—79).—The difference in osmotic pressure of sap and soil solution is considered in relation to salt intake. A. G. P.

Effect of nutrients on the water relationships of tomato plants. Influence of light on development, sugar formation, and nutrient absorption of the sugar beet.—See B., 1936, 1116.

Significance of the physiological antagonism between calcium and magnesium for plant growth.—See B., 1936, 1060.

Uptake of minerals by pineapple plants at different stages of growth.—See B., 1936, 1115.

Effect of transpiration on absorption and distribution of mineral salts in plants. R. O. FREELAND (Amer. J. Bot., 1936, 23, 355—362).—In plants grown under conditions of high transpiration the ash,

Ca, P, K, and dry matter contents were $>$ when transpiration was low, the Ca and K contents being the most affected. In high-transpiration plants, mineral contents increased more in leaves and roots than in stems; Ca and K showed the greatest differences. No correlation was apparent between the mineral content and the dry matter of leaves, stems, and roots. A. G. P.

Nitrogen losses in green plants. W. H. PEARSALL and M. C. BILLIMORIA (Nature, 1936, 138, 801—802).—Pure cultures of *Chlorella vulgaris* growing in a medium containing NO_3^- lose much N, presumably as N_2 . Similar losses occur with daffodil leaves floated on glucose media containing NO_3^- , but not with org. N. Large losses of N are always associated with low NH_2-N content of the leaf tissues. L. S. T.

Fat metabolism of germinating pumpkins. U. WEBER (Ber. deut. bot. Ges., 1936, 54, 70—75).—The I val. of fat in cotyledons of germinating walnuts increases in the early stages and subsequently declines with the rapid development of the seedlings. Similar changes occur in pumpkins except that a double max. occurs in the I val.-time curve. Formation of unsaturated fatty acids is an intermediate step in the utilisation of fats by the seedlings. Addition of KOAc increases the rate of development of seedlings, accelerates the consumption of unsaturated acids, and increases their % utilisation. A. G. P.

Glutamine metabolism of beet. H. B. VICKERY, G. W. PUCHER, and H. E. CLARK (Plant Physiol., 1936, 11, 413—420).—Treatment of soil with $(NH_4)_2SO_4$ increased the glutamine (I) content of root tissue without affecting the asparagine level. (I) acts as a detoxicating agent for NH_3 in the plant, probably through the intermediate formation of glutamic acid and subsequent dehydration of the NH_4 salt to form the amide. A. G. P.

Diurnal variations in the carbohydrate content of leaves. C. BÉGUIN (Bull. Soc. Chim. biol., 1936, 18, 1387—1395).—In the leaves of *Lonicera alpigena*, L., the amounts of sucrose and glucosides hydrolysed by emulsin increase during the day and decrease during the night. This variation is the reverse of that of the reducing sugars present. In bruised leaves (half leaf method) the glucosides diminish steadily. A. L.

Thymonucleic acid content of hyperchromatic somatic cell nuclei. P. F. MILOVIDOV (Planta, 1936, 25, 197—205).—Certain "stimulated" cell nuclei, e.g., mycorrhiza cells of *Neottia nidus avis*, cells of *Heteroda* galls, trichocytes of *Stratiotes aloides* and *Trianea bogotensis*, contain relatively high proportions of thymonucleic acid. A. G. P.

Production of mucus during decomposition of plant materials. III. Effect of partly aerobic and anaerobic conditions. J. G. SHRIKHANDE (Biochem. J., 1936, 30, 1789—1794).—The conditions necessary for the production of stickiness in manures (A., 1933, 1334) are further investigated using ragi straw (*Eleusine covacana*) which was decomposed under partly aerobic conditions in presence of different sources of available N, the C:N ratio being adjusted to 30:1 and 10:1. Strong acidities

prevent, whilst high concns. of N and final adjustment of the p_H to 9 have no effect on, the development of stickiness during fermentation. P. W. C.

Daily variations in products of photosynthesis, water content, and acidity of leaves towards the end of the vegetative period. P. P. STANESCU (Amer. J. Bot., 1936, 23, 374—379).—Rhythmic variations in the carbohydrate content of leaves continues until the last days of vegetative growth. Curves for hexoses frequently take an opposite course to those for sucrose (I) and starch (II), especially during the day. (II) accumulation begins later in the morning during the late vegetative period than during the summer. Monosaccharides predominate in petioles, followed in descending order by (II) and (I). No uniform relation exists between carbohydrate and H_2O contents or the acidity of the tissue. The course of H_2O absorption is paralleled by that of the synthesis of org. materials. A. G. P.

Effects of light on carotenoid formation in tomato fruits. O. SMITH (Cornell Univ. Agric. Exp. Sta. Mem., 1936, No. 187, 26 pp.).—The carotenoid content of greenhouse-grown fruit is > of that grown outdoors; that of the skin is higher in winter-grown and of the flesh in summer-grown fruit. Strong light favours the production of carotene (I); less intense light produces more lycopene (II). Fruit grown in complete darkness contains more (II) and less (I) than that grown in light. (I) in granular form occurs in plastids and remains after the decomp. of plastids. (II) is not found in plastids but crystals are numerous in the epidermal, plastid-free layer. A. G. P.

Determination of photosynthetic and respiratory ratios. B. S. HEYER and D. S. RADER (Plant Physiol., 1936, 11, 437—443).—Appropriate apparatus is described. A. G. P.

Fluorescence curves of living leaves. H. KAUTSKY and R. HORMUTH (Naturwiss., 1936, 24, 650—651).—Photographic registration of the fluorescence curves of living leaves indicates the occurrence of four part reactions, all connected with free or combined O. The velocities of the reactions can be calc. from the slopes of the curves. The fluorescence curve is best investigated when the atm. surrounding the leaf is so poor in O_2 that the amount of O_2 dissolved in the chloroplasts is negligible. A. J. M.

Fluorescent substance present in plants. I. Production of the substance as a result of virus infection: some applications of the phenomenon. R. J. BEST (Austral. J. Exp. Biol., 1936, 14, 199—213).—In tobacco leaves showing primary lesions of tomato spotted wilt, fluorescent material appears in filtered ultra-violet light. This is caused by a H_2O -sol., relatively stable org. substance, small amounts of which occur normally in healthy tissue, but which increases in proportion as invasion by the virus proceeds. A. G. P.

Metastable oxygen and assimilation of carbon dioxide. H. GAFFRON (Biochem. Z., 1936, 287, 130—139).—The formation of metastable O_2 in photo-oxidations sensitised by chlorophyll could not be demonstrated. P. W. C.

Yield of green plants in relation to oxygen content of surrounding atmospheres.—See B., 1936, 1061.

Growth hormones and development of plants. N. G. CHOLODNI (Nature, 1936, 138, 586).—Oat seeds soaked in a dil. solution of β -indolylacetic acid before planting produced stronger plants and 55% more grain than untreated seeds. L. S. T.

Hormonal theory of plant development. M. C. TSCHAILLACHIAN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 443—447).—The processes leading to the sexual development of plants are not determined by the processes of growth and nutrition but are sp. and due to a flowering hormone elaborated in the leaves. E. A. H. R.

Hormonisation of grains. N. G. CHOLODNI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 439—442).—The effect on the normal course of grain crop growth of increasing the hormone content of the embryonic tissue at the commencement of germination is examined. Hormonisation was effected by soaking the dry grain in a solution of β -indolylacetic acid or thrusting it into moist ground with maize endosperm, which is a potent source of auxin. E. A. H. R.

Plant growth-substances. XXII. Occurrence of biotin in the animal organism. F. KÖGL and W. VAN HASSELT (Z. physiol. Chem., 1936, 243, 189—194; cf. this vol., 1305).—The biotin (I) contents of the organs of the dog, cow, calf, and hen are tabulated. (I) occurs in all the organs examined (except the vitreous humour) in amounts varying from 0.0001 to 1.025 mg. per 100 g. of fresh tissue. The organs of hens contain 3—5 times as much (I) as do those of cattle and dogs. W. McC.

Effect of crown rust on composition of oats. H. C. MURPHY (Phytopath., 1936, 26, 220—234).—Infected plants contained larger proportions of insol. solids, ash, N (notably amides, NH_3 , NO_3 , and NO_2), and acid-hydrolysable matter, and less sol. solids, sugar, and dextrin. A. G. P.

Variations in chief ash constituents of apples affected with blotchy cork. W. A. DE LONG (Plant Physiol., 1936, 11, 453—456).—The Ca content of affected fruit was > that of healthy controls. A. G. P.

Comparison of total nitrogen in wheat seeds by the Gunning (modified Kjeldahl) and Dumas methods. W. Z. HASSID (J. Amer. Chem. Soc., 1936, 58, 2075).—Contrary to Smyth and Wilson (this vol., 121), the Gunning and Dumas methods give the same val. Results (lit.) showing N-fixation by wheat plants are thus not invalidated (cf. *loc. cit.*). H. B.

Relative distribution of phosphorus and phosphatase activity in the floral parts of *Nicotiana affinis*, *Petunia*, *Salpiglossis*, and *Gladiolus*. V. IGNATIEFF (Biochem. J., 1936, 30, 1815—1818).—Phosphatase activity is higher in the sex organs as a whole than in other floral parts. It is particularly marked with *Gladiolus* in the anthers. With the floral parts of *Gladiolus* the total P of the sex organs is also high and is highest in the anthers. P. W. C.

Biose/monose ratio as a biochemical varietal character in the onion. B. A. RUBIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 431—434).—Both in gross sugar content and in the biose/monose ratio differences between varieties of onions are great. Monoses predominate in annual onions and bioses in biennials.
E. A. H. R.

Oil of American black walnut.—See B., 1936, 1054.

Rice oil. Soya bean oil foots. Oiticica oil. Kapok seed oil. Seed oils of Cucurbitaceæ. Seed fat of "Yabunikukei," *Cinnamomum pedunculatum*.—See B., 1936, 1105, 1106.

Chemical composition of *Hibiscus sabdariffa*, L., and its cultivation in Eritrea. A. CASTIGLIONI (Atti R. Accad. Sci. Torino, 1934, 69, I, 97—105; Chem. Zentr., 1936, i, 93).—The calyx contains citric and not (as previously stated) tartaric acid. A. G. P.

Constituents of the seeds of *Digitalis lanata*, Ehrh. K. SZÄHLENDER (Arch. Pharm., 1936, 274, 446—449).—The ground seeds on cold pressing yield 16% of an oil having d_4^{20} 0.922, butyro-refractometer no. 76.0, acid val. 8.0, sap. val. 187, I val. 130. The residue yields digitonin and a bitter *glucoside*, hydrolysed (HCl, EtOH) to a *genin*, m.p. about 245°.
F. R. G.

Hemicellulose constituents of lucerne roots. B. A. BURKHART (Plant Physiol., 1936, 11, 421—428).—Separation and fractionation of the hemicelluloses of xylem and phloem of the roots is described. The principal sugars in all fractions were *d*-xylose (I) and *d*-glucose. Some *d*-glycuronic acid (II) was also present. The (I) content was higher in xylem tissue and that of (II) in the phloem.
A. G. P.

Carbohydrates in *Iridæa laminaroides* (Rhodophyceæ). W. Z. HASSID (Plant Physiol., 1936, 11, 461—463; cf. this vol., 193).—Further examination of *I. laminaroides* showed the presence of starch and a sulphuric ester of galactan, but no cellulose.
A. G. P.

Biochemical study of Salicaceæ. J. RABATÉ (J. Pharm. Chim., 1936, [viii], 24, 363—367).—The isolation of salicoside from the leaves (0.23 g. per 100 g. of fresh leaves; sucrose is also present), bark, and twigs (0.8 g. per 100 g.) of *S. pentandra* is described; populoside is also isolated from the twigs, and the presence of a levorotatory, hydrolysable, glucosidic substance, partly pptd. by Saturne's extract and completely pptd. by Mg or Ca defecation, is indicated.
J. W. B.

Glucosides of the Salicaceæ. Analytical method. J. RABATÉ (J. Pharm. Chim., 1936, [viii], 24, 311—325).—H₂O removes the glucoside (I) and tannins from an EtOH extract. Hydrolysis (invertase, emulsin) of (I) is followed polarimetrically after removal of tannins with Pb, Mg, or Ca(OH)₂. By determining the reducing sugar present, the concn. of (I) is calc. Details are given for the quant. extraction of glucosides from many species.
J. L. D.

Heterosides and essential oils in the Primulaceæ. A. GORIS and H. CANAL (Bull. Soc. Chim. biol., 1936, 18, 1405—1424; cf. A., 1935, 268, 1041; this vol., 911).
A. L.

Thioglycollic acid as reagent for lignin.—See this vol., 1515.

Colorimetric determination of naringin. E. M. HARVEY and G. L. RYGG (Plant Physiol., 1936, 11, 463—465).—The method is based on the colour produced by FeCl₃ with naringin. H₂O extracts of fruit tissue are utilised for the determination. Experimental conditions must be carefully standardised.
A. G. P.

New saponins. F. BOAS and R. STEUDE (Angew. Bot., 1936, 18, 16—21).—The nature and function of saponins in plants are discussed. The isolation of a saponin from *Avena sativa* and a hæmolytic saponin from *Medicago falcata* is recorded.
A. G. P.

***Alhagi camelorum* (Dshantak) manna.** N. F. IVANOVA (J. Appl. Chem. Russ., 1936, 9, 1661—1663).—The manna contains H₂O 5.08, ash 5.8, melezitose 47.07, invert sugar 11.64, and sucrose 26.44%.
R. T.

Carotenoids. III. Isomeride of lutein from furze (*Ulex europæus*). K. SCHÖN. IV. Carotenoids of *Genista tridentata*. K. SCHÖN and B. MESQUITA (Biochem. J., 1936, 30, 1960—1965, 1966—1969).—III. From the flowers of *U. europæus* and *U. galli* there have been isolated α - and β -carotene, violaxanthin (I), taraxanthin, hentriacontane, sitosterol, a *sterol* (II), C₃₀H₅₀O, m.p. 152—153°, a carotenoid similar to flavoxanthin (III), and an *isomeride* (IV) of lutein (V), m.p. 205—206° (corr.). (IV) combines with MeOH, changing to a substance, m.p. 199—200°. The flowers of *U. galli* probably contain (III).

IV. The flowers of *G. tridentata* yielded β -carotene (VI), α -carotene in very small amount, (V) (present as esters; at least 3 esters in the plant), sitosterol, and a *sterol*, possibly (II). Probably other carotenoids are also present. In furze (I), but in *G. tridentata* (V), is the predominating xanthophyll. In the plant (V) may be related to (VI).
W. McC.

Carotenoids of fresh-water algæ. II. Carotenoids and production of ionone in *Trentepohlia*. Erythritol content of the algæ. J. FISCHER (Z. physiol. Chem., 1936, 243, 103—118; cf. this vol., 912).—The pigment of *Trentepohlia* (*iolithus*, *umbrina*, *aurea*) consists chiefly of α - and β -carotene in the ratio 3 : 7 together with small amounts of the xanthophylls, lutein, zeaxanthin, and an unidentified pigment resembling fucoxanthin. The yield of carotene from dried algæ was about 0.5%. The algæ contain free erythritol (1.3% in dried *T. iolithus* and *aurea*). The dry algæ contain also small amounts of ionone (I) and produce (I) from carotene.
W. McC.

Carotenoids of the cranberry. H. WILLSTAEDT (Svensk Kem. Tidskr., 1936, 48, 212—213).—Cranberries (*Vaccinium vitis idæa*, L.) have a total carotenoid content of only 27×10^{-6} g. per litre of berries, in keeping with their low vitamin-A content.
M. H. M. A.

Colorimetric determination of carotenoids.—See this vol., 1496.

Pigments of the oat coleoptile. G. WARD and H. G. DU BUX (Science, 1936, 84, 247).—The coleoptile of *Avena sativa* possesses the same pigments as the

leaf, but in lower concns. The photosensitive system is associated with the presence of carotenoids.

L. S. T.

Pigment of the corn poppy (*Papaver rhoeas*, L.). L. SCHMID and H. KÖRPERTH (Monatsh., 1936, 68, 290—295; cf. A., 1931, 738; 1932, 934).—The fresh blossoms are extracted with 2% HCl-MeOH; the ppt. obtained by addition of Et₂O to the extract is treated with EtOH to remove mecocyanin, and the residue is purified by repeated pptn. from MeOH by Et₂O or dil. HCl, thereby giving the *glucoside* (I) as a dark, reddish-violet powder. (I) is hydrolysed by acid or, preferably, by dil. alkali to *p*-OH·C₆H₄·CO₂H; the presence of hexose but no pentose (*loc. cit.*) is indicated. Hydrolysis with HCl gives two products differing in colour and solubility in MeOH; when dried in a high vac. each loses halogen and leaves *aglucone*-A and -B, C₁₅H₁₂O₆ [not C₁₅H₁₁O₄Cl (*loc. cit.*)], -B being derived from -A by the action of acid. Alkaline degradation affords *p*-OH·C₆H₄·CO₂H and possibly protocatechuic acid, but a homogeneous phenolic compound could not be prepared. 1:3:5-C₆H₃(OH)₃ does not appear present. Oxidation with HNO₃ affords picric acid and H₂C₂O₄. (I) is probably a complex pelargonidin glucoside with firmly retained H₂O of crystallisation; the name *mecopelargonin* is therefore proposed.

H. W.

Investigations of extracts of blossoms. L. SCHMID and M. KÖRPERTH (Monatsh., 1936, 68, 296—300).—Robinson's scheme (A., 1932, 1296) for the detection of anthocyanidins is extended to the hydrolysates of the crude extracts of blossoms, and to the examination of the extracts with regard to colour, solubility in C₅H₁₁·OH, and coloration with NaOAc or Na₂CO₃.

H. W.

Constituents of the Chinese drug lei-kung-têng [of the plant] *Tripterygium wilfordii*, Hook. I. Colouring matter and sugar. T. Q. CHOU and P. F. MEI (Chinese J. Physiol., 1936, 10, 529—533).—The drug (used as an insecticide) on extraction with Et₂O gave a red cryst. substance, *tripterin*, C₂₅H₃₇O₃, m.p. 195° (decomp.), and the residue on extraction with EtOH gave glucose, fructose, and dulcitol.

P. W. C.

Active fish poison from the bark of *Piscidia erythrina*. F. HAUSCHILD (Arch. Pharm., 1936, 274, 388—392).—The bark contains a *substance*, m.p. 72°, not identical with those isolated by Danckwortt *et al.* (A., 1934, 1046). It can be hydrolysed (KOH, EtOH) and in its toxicity to fish resembles rotenone, of which it is probably a derivative.

F. R. G.

Yellow pigment from Saké-Kasu (saké grains).—See this vol., 1514.

Semicarbazones of pyrethrias I and II and of pyrethrolone.—See this vol., 1514.

Constituents of *Buellia canescens*.—See this vol., 1514.

Alkaloids of *Corydalis ambigua*.—See this vol., 1527.

Ambaline and ambalinine, new alkaloids from *Pycnarrhena manillensis*, Vidal.—See this vol., 1527.

isoErgine and isolysergic acids.—See this vol., 1527.

Alkaloids from *Solanum pseudocapsicum*, L.—See this vol., 1527.

Improved Feulgen staining technique. J. A. DE TOMASI (Stain Tech., 1936, 11, 137—144).—Since different samples of fuchsin vary considerably, the use of pure pararosaniline is suggested. K₂S₂O₅ is substituted for NaHSO₃ for decolorising. Fast-green is recommended as a counterstain for plant and orange-G for animal tissue.

E. M. W.

Stable, high-contrast mordant for hæmatoxylin staining. A. G. LANG (Stain Tech., 1936, 11, 149—151).—The use of Fe₂(NH₄)₂(SO₄)₄ with H₂SO₄ and AcOH is recommended.

E. M. W.

Colloidal silver method for nerve cells and processes, neuroglia, and microglia. R. STAGE (Stain. Tech., 1936, 11, 155—160).—A method of staining brain tissue with argyrol or silvol is described, the Ag being replaced with Au before reduction.

E. M. W.

Pinacyanol as supra-vital mitochondrial stain for blood. D. C. HETHERINGTON (Stain Tech., 1936, 11, 153—154).—Pinacyanol stains mitochondria selectively and almost permanently.

E. M. W.

Large quartz spectrograph for examination of biological material.—See this vol., 1480.

Microcolorimetric apparatus and a method for determination of total blood volume. J. C. SOMOGYI (Nature, 1936, 138, 763—764).—An arrangement for determining the concn. of weakly coloured solutions contained in a capillary is applied to estimating the total blood vol. of white rats.

L. S. T.

Open gas-analysis method for metabolic determinations [on animals]. M. ADANT, P. SPEHL, and R. MINNE (Compt. rend. Soc. Biol., 1936, 123, 313—316).

H. G. R.

Biochemical gravimetric methods. V. Determination of sodium with the torsion balance. L. JENDRASSIK and L. DZIOBEK (Biochem. Z., 1936, 287, 262—264).—The ppt. obtained in the method of Barber *et al.* (A., 1928, 859) is collected on suitable filter-paper and weighed on a torsion balance. Na in blood-serum and in other biological material may be determined with an average error of about ±1%. The normal K content of blood-serum does not interfere. The serum should be deproteinised with CCl₃·CO₂H; when UO₂(OAc)₂ is used the results are inaccurate.

W. McC.

Determination of residual nitrogen and of its fractions and of blood-phenols in the Folin-Wu filtrate by the step photometer. F. BÖHM and G. GRÜNER (Biochem. Z., 1936, 287, 65—70).—Modifications of older methods for determination by the step photometer of uric acid, NH₂-acids, and creatinine and new methods for determination of urea and blood-phenols are described.

P. W. C.

