BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1931.

General, Physical, and Inorganic Chemistry.

Relative intensities of the Balmer and Paschen lines. U. Doi (Sci. Rep. Tokyo Bunrika Daigaku, 1931, 1, 97—103).

Reversal-like phenomenon of the Balmer lines of hydrogen. H. Nagashima (Sci. Rep. Tokyo Bunrika Daigaku, 1931, 1, 133—143).—The H_β, but not the H_α and H_γ, lines were reversed in the spectra of the explosion in water vapour or in H_2 or under water of metallic wires (Pb, Al, Cu).
N. M. Bligh.

Spectrum of H_2. Bands ending on $2p^3$ II. levels. O. W. Richardson and P. M. Davidson (Proc. Roy. Soc., 1931, A, 131, 658—683).—A full description of the bands is given. The value of ν_e'' is estimated to be 29,307, in fair agreement with the value 29,503 extrapolated from the Rydberg–Ritz formula for the α, β, γ bands (A., 1927, 1).
L. L. Bircumshaw.

Intensity variations of the helium lines with voltage. J. Razek (Physical Rev., 1931, [ii], 37, 1252—1262).—Direct measurements were made by a new method. N. M. Bligh.

Anomalous dispersion of lithium vapour. A. Filippov (Z. Physik, 1931, 69, 526—547).—Anomalous dispersion of Li vapour in the visible and ultraviolet gives the relative transition probabilities for the first 12 terms of the principal series; the results agree with theory (cf. A., 1929, 1129). A. B. D. Cassie.

Spectrum of the cathode glow in nitrogen and other gases. K. G. Emeléus and (Miss) O. Hall (Proc. Roy. Irish Acad., 1931, 40, *A*, 1—10; cf. A., 1930, 835).—The appearance of the arc spectrum of N in the light from the cathode glow of a low-voltage d.c. glow discharge from a cold cathode is confirmed, and an explanation suggested which accounts for the cathode glow spectra in a number of polyat. gases and gas mixtures. Local plasma-type discharges were observed. N. M. Bligh.

Large displacements in the spectrum of singly-ionised oxygen. K. Asagoe (Sci. Rep. Tokyo Bunrika Daigaku, 1931, 1, 105—125).—The modes of appearance and displacements are tabulated for 82 lines of the doublet, 67 lines of the quadruplet, and 138 unclassified lines of O II for pressures of 3 cm., 7 cm., and 1 atm. N. M. Bligh.

Difference in the self-reversal of neon lines excited by direct and alternating currents. H. Nagaoka and T. Mishima (Proc. Imp. Acad. Tokyo, 1931, 7, 140—141).—The reversal is greater for d.c. than for a.c. W. E. Downey.

Origin of the light from the negative glow. R. H. Sloane and K. G. Emeléus (Phil. Mag., 1931, [vii], 12, 73—80).—The view of Druyvesteyn that the negative glow of the normal discharge in Ne and A gives an excitation light (cf. A., 1930, 1076) is in agreement with the similarity of the intensity distribution for A I lines in the negative glow and positive column, and with the electrical analysis of the negative glow. N. M. Bligh.

Oscillating arc: elements of group VI. E. Z. Stowell (Physical Rev., 1931, [ii], 37, 1452—1457; cf. this vol., 1).—The behaviour of S, Se, Te, Cr, Mo, W, and U as cathodes in an arc in H_2 was investigated.
N. M. Bligh.

Structure of the Cr I spectrum. M. A. Catalán and P. M. Sancho (Anal. Fís. Quím., 1931, 29, 327—366).—Existing data are summarised and reviewed, and more than 700 lines are classified in 202 levels belonging to triplet, quintuplet, and septet systems. The principal ionisation potential is 6·74 volts.
H. F. Gillbe.

Hyperfine structure in the spectrum of copper. J. B. Green and J. Wulff (Nature, 1931, 127, 891—892).—Each line of the doublet at 3248 and 3275 Å. consists of a sharp, narrow doublet of separation 0·043±0·001 Å. L. S. Theobald.

Absolute wave-lengths of the copper and chromium *K*-series. J. A. Bearden (Physical Rev., 1931, [ii], 37, 1210—1229).—In measurements by ruled gratings the periodic error of the grating and the geometrical divergence of the *X*-ray beam are corrected by a study of the intensities of the optical ghost lines, and by the disposition of apparatus, respectively. Satisfactory agreement among results from 5 glass gratings and with a calcite crystal are obtained, and values of e/m, N, Planck's constant, and the calcite crystal grating space are calc. N. M. Bligh.

Fine structure in the arc spectra of bromine and iodine. S. Tolansky (Nature, 1931, 127, 855).—Fine structure measurements have been extended for I (4700—8000 Å.) and Br. The most probable values of nuclear spin are F $\frac{1}{2}$, Cl 5/2, Br 3/2, and I 9/2; the isotopes of Br, 79 and 81, appear to possess the same nuclear spin. L. S. Theobald.

Hyperfine structure in the rubidium spectrum. D. A. Jackson (Nature, 1931, 128, 34).—Effects due to the isotopes Rb 85 and 87 are described and discussed. L. S. Theobald.

Near infra-red spectrum of iodine. T. Iwama (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 163—165).—Results of an examination of the I spectrum, obtained by discharge in a narrow quartz Geissler tube, are given. W. Good.

Absorption spectra of salt solutions. Metallic ions. S. Kato (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 161—162).—The absorption corresponding to the third term $^3P_2$ in $Tl^{\cdot}$ and $Pb^{\cdot\cdot}$ ions appears respectively at λ 1710 and λ 1570 Å. W. Good.

Nuclear moments of cæsium, rubidium, and indium. D. A. Jackson (Nature, 1931, **127**, 924—925).—The probable values of i (the quantum no. of the nuclear rotation) for Cs, Rb, and In are 9/2 or more, $\frac{1}{2}$ to 3/2, and 7/2, respectively. L. S. Theobald.

Effect of other metals on the secondary emission from platinum. T. I. Campan (Bul. Fac. Stiinte Cernauti, 1929, **3**, 245—247; Chem. Zentr., 1931, i, 1570).

Hyperfine structure of the principal components of mercury lines 5770, 5791, 5461, and 4358 Å. H. Nagaoka and S. Mishima (Proc. Imp. Acad. Tokyo, 1931, **7**, 137—139). W. E. Downey.

Isotope effect and hyperfine structure of the mercury resonance line. S. Mrozowski (Nature, 1931, **127**, 890—891).—A discussion. L. S. Theobald.

Emission bands in the mercury spectrum under low excitation. (Lord) Rayleigh (Nature, 1931, **127**, 854).—The "core effect" (this vol., 780) includes a band series identical with that obtained in electrically stimulated vapour (A., 1927, 1122). L. S. Theobald.

Molecular spectra of mercury, zinc, cadmium, magnesium, and thallium. H. Hamada (Phil. Mag., 1931, [vii], **12**, 50—67).—Full details of work previously noted (this vol., 664) are given.

[Absorption of resonance lines by mercury vapour containing foreign gases.] E. A. Neumann (Z. Physik, 1931, **69**, 701—702).—A reply to Kunze (this vol., 541). A. B. D. Cassie.

Displacement effect in the hyperfine structure terms of thallium isotopes. H. Schüler and J. E. Keyston (Z. Physik, 1931, **70**, 1—9).—The hyperfine structure of some Tl I and Tl II lines is consistent with two isotopes of nuclear spin $\frac{1}{2}$, and with masses 205 and 203 in the ratio of 2·3 to 1; the two isotopes have different nuclear fields. A. B. D. Cassie.

Resonance potential of trebly-ionised bismuth. S. Smith (Nature, 1931, **127**, 855).—A discussion. L. S. Theobald.

High-frequency behaviour of a plasma. L. Tonks (Physical Rev., 1931, [ii], **37**, 1458—1483; cf. A., 1929, 1359).—The formula for the sp. inductive capacity of a uniformly ionised gas is extended to two cases of non-uniform ionisation. Formulæ are derived for the conductivity and sp. inductive capacity of a cylindrical plasma (positive column of an arc). N. M. Bligh.

Repulsive energy levels in band spectra. J. Kaplan (Physical Rev., 1931, [ii], **37**, 1406—1411).—Theoretical. N. M. Bligh.

Statistical equilibrium in the positive branch of the gas discharge. H. Kopfermann and R. Ladenburg (Naturwiss., 1931, **19**, 513—515).—The relatively simple optical phenomena noticed in the positive branch of the electric discharge through rare gases are investigated, A. J. Mee.

Temperature of the arc light. L. S. Ornstein (Physikal. Z., 1931, **32**, 517—520).—A spectral method is used. In arc-light gas the temp. is very high, being highest in the centre and lowest at the edge. A. J. Mee.

Semi-silvering of interferometer plates by distillation in a high vacuum. R. Ritschel (Z. Physik, 1931, **69**, 578—585).—A means is described of depositing Ag simultaneously and at the same rate on to two plates, by distillation of the Ag in a high vac.; any density can be obtained. A. B. D. Cassie.

$K\alpha$ lines of the light elements. E. Rudberg (Phil. Mag., 1931, [vii], **11**, 1248—1250).—A comparison with, and discussion of, the results of Söderman (cf. A., 1930, 1502). N. M. Bligh.

Absorption of the $K\alpha$ line of carbon in various gases and its dependence on atomic number. E. Dershem and M. Schein (Physical Rev., 1931, [ii], **37**, 1238—1245).—Absorption coeffs. in the elementary gases, CO_2, and Au leaf for the $K\alpha$ line of C were determined photographically, and values of some at. absorption coeffs. (μ_a) are deduced. Log μ_a is a linear function of log Z (where Z is the at. no.). N. M. Bligh.

Reflexion of the $K\alpha$ line of carbon from quartz and its relation to refractive index and absorption coefficient. E. Dershem and M. Schein (Physical Rev., 1931, [ii], **37**, 1246—1251; cf. preceding abstract). N. M. Bligh.

Fine structure of absorption edges of the Röntgen K series of elements with a medium atomic number. H. T. Meyer (Wiss. Veröff. Siemens-Konz., 1931, **10**, [2], 95—98).—Absorption spectra of the K series have been examined in Rb_2CO_3, $Sr(NO_3)_2$, $ZrOCl_2$, $Zr(NO_3)_4$, Y_2O_3, K_2NbF_7, Nb_2O_5, and MoO_3. The results are in agreement with the assumption that fine structure at the edges of the absorption bands in the Röntgen spectra are observed only in the higher valency states of those elements which have more than one valency. Thus fine structure is particularly well marked in bromates, selenates, and arsenates, but not in bromides or in salts of Rb and Sr. $ZrOCl_2$, K_2NbF_7, and Mo^{VI} compounds all have fine structure. A. R. Powell.

Investigations of Röntgen spectra. I. X-Ray spark lines. II. X-Ray spectra and chemical combination. Sulphur. III. Fine structure of K-absorption edge of SiO_2. G. B. Deodhar (Proc. Roy. Soc., 1931, A, **131**, 633—647, 647—653, 654—658).—I. A study of the $K\alpha$ and $K\beta$ satellites of Si, P, S, and Cl indicates that the structure of the satellites is complex and their nature highly dependent on the state of chemical combination of the atom which emits them.

II. Many S compounds have been studied. Considerable changes are found in the relative intensities of β_1 and β_x lines for different compounds, and new lines are obtained for some compounds. The influence of the anticathode material is investigated. It appears that the substance of the anticathode reacts under cathodic bombardment on the mol. of the S compound, causing alteration in the electron distribution of the peripheral levels of the S atom.

III. The fine structure has been measured by using quartz as the analysing and absorbing crystal. The fact that the difference between the principal edge and the limit of the fine structure K_{m-2} is only 5·17 volts precludes the possibility of double ionisation.

L. L. Bircumshaw.

Complexity of the *L* series of barium. V. Dolejšek and J. Kubiček (Compt. rend., 1931, **192**, 1369—1370; cf. A., 1929, 376).—Emission bands, $L\alpha_3$, $L\beta_2'$, and $L\gamma'$, similar to $K\beta'$, occur near $L\alpha_1$, $L\beta_2$, and $L\gamma_1$ of Ba. For BaO the centres are at 2767·6, 2398·6, and 2235·4 X, respectively.

C. A. Silberrad.

Natural widths of the *X*-ray lines in the *L* series spectrum of uranium. J. H. Williams (Physical Rev., 1931, [ii], **37**, 1431—1442).—The half widths at half max. of the rocking curves in parallel positions of the double *X*-ray spectrometer are a linear function of the wave-lengths. N. M. Bligh.

Plane grating spectroscopy in the ultra-soft *X*-ray region. J. A. Prins (Z. Physik, 1931, **69**, 618—636).—Measurement of wave-lengths between 20 and 50 Å. with a grating of 50 lines per mm. is discussed theoretically and practically; wave-lengths are given for *K* lines due to O, N, C, B, Be, and *M* and *N* lines due to W. A. B. D. Cassie.

Breadth of the Compton modified line with the double-crystal spectrometer. A. Hoyt and J. Du Mond (Physical Rev., 1931, [ii], **37**, 1443—1451; cf. A., 1929, 747).—Using similar apparatus, the narrow structure reported by Davis (A., 1928, 1168), Bearden (A., 1930, 1491), and Gingrich (*ibid.*) is not confirmed. Concordant results are obtained by the single-, double-, and multi-crystal spectrometer.

N. M. Bligh.

Atomic scattering factors. R. W. James and G. W. Brindley (Phil. Mag., 1931, [vii], **12**, 81—112).—A general account of the nature of, and methods of calculating, the scattering factors of atoms for *X*-rays is given. Two methods of calculating the factor for the atom at rest, with sufficient accuracy for use in crystal analysis, are discussed, and values are tabulated for many atoms and ions. N. M. Bligh.

Photo-electric properties of gold. L. W. Morris (Physical Rev., 1931, [ii], **37**, 1263—1268).—Variations in photo-electric properties of Au filaments were investigated with regard to rise of temp. and progress of out-gassing up to a stable state.

N. M. Bligh.

Photo-electric properties of silver. R. P. Winch (Physical Rev., 1931, [ii], **37**, 1269—1275).—Investigations were made during out-gassing, and in the resulting stable state, of photo-emission as a function of temp. for fixed wave-lengths. N. M. Bligh.

Recoil atoms in rare gases. L. Goldstein (Compt. rend., 1931, **192**, 1373—1376; cf. this vol., 279).—The yield of activation for voltages giving the saturation current is identical for A, He, and Ne, and independent of the ionisation potential. Results at both electrodes and at varying pressures are discussed. C. A. Silberrad.

Electron polarisation. G. O. Langstroth (Nature, 1931, **137**, 891).

Interference of electron spin in crystals. H. Hellmann (Z. Physik, 1931, **69**, 495—506).—Theoretical. Reflexion of electrons at crystal surfaces is governed by a potential barrier of finite thickness.

A. B. D. Cassie.

Behaviour of electrons in homogeneous electromagnetic fields according to Dirac's relativistic theory. F. Sauter (Z. Physik, 1931, **69**, 742—764).—Mathematical.

Angular distribution of photo-electrons ejected by polarised ultra-violet light in potassium vapour. M. A. Chaffee (Physical Rev., 1931, [ii], **37**, 1233—1237; cf. Anderson, A., 1930, 972).—The most probable direction of ejection was found to be that of the electric vector; results are in accord with wave-mechanical predictions for a spherically symmetrical atom. N. M. Bligh.

Specific heat of quasi-free electrons. E. C. G. Stueckelberg and P. M. Morse (Z. Physik, 1931, **69**, 666—677).—Theoretical. Sommerfeld's conductivity law may be considerably modified for quasi-free electrons. A. B. D. Cassie.

Microscopical determination of the position of an electron. K. F. von Weizsäcker (Z. Physik, 1931, **70**, 114—130).—Mathematical.

A. B. D. Cassie.

Pictorial representations of the electron cloud for hydrogen-like atoms. H. E. White (Physical Rev., 1931, [ii], **37**, 1416—1424).—The wave-equation probability density factors are represented graphically and discussed. N. M. Bligh.

Elucidation of the wave nature of H particles by scattering measurements in hydrogen. C. Gerthsen (Ann. Physik, 1931, [v], **9**, 769—786).—The scattering of H particles by H_2 has been observed for angles between 15° and 35°. The scattering of He^+ particles by He has also been studied.

W. R. Angus.

Mobility of aged ions in air in relation to the nature of gaseous ions. N. E. Bradbury (Physical Rev., 1931, [ii], **37**, 1311—1319).—The change in mobility with age of ions formed under the conditions of recombination measurements was investigated, and results are discussed. N. M. Bligh.

Relation between range of rapid protons in air and the ionisation produced: artificial disintegration of the elements. L. Leprince-Ringuet (Compt. rend., 1931, **192**, 1543—1545).—The range of protons arising from the transmutation of Al by α-rays of Po in air at 15° and 760 mm. is about 60 cm., those of longest range forming a definite monokinetic group. The max. ionisation produced by such a proton is about one fourth the max. produced by an α-ray, and during the last 50 cm. of its range is about 2800 ions per cm. C. A. Silberrad.

Ionic and electronic collisions. E. Friedländer, H. Kallmann, and B. Rosen (Naturwiss., 1931, **19**, 510—512).—Multiply-charged ions can be formed directly by electronic collision, and have been produced in CO_2 and CO. The decomp. of mol. ions by collision with a gas mol., or with a surface such as the walls of a containing vessel, is also shown.

A. J. Mee.

Residual ionisation in air at new high pressures, and its relation to the cosmic penetrating radiation. J. W. Broxon (Physical Rev., 1931, [ii], **37**, 1320—1337).—The ionisation-pressure curve slope (up to 170 atm.) gradually decreased to zero. N. M. Bligh.

Influence of bromine vapour on the mobility of positive and negative ions in hydrogen and oxygen. H. Mayer (Bul. Fac. Stiinte Cernauti, 1928, **2**, 65—82; Chem. Zentr., 1931, i, 1573—1574).

Effective cross-sections of molecules on the basis of gas theory. H. E. Binkele (Ann. Physik, 1931, [v], **9**, 839—852).—Theoretical. Consts. calc. from viscosity measurements agree well with the value of b in van der Waals' equation. W. R. Angus.

Effective cross-section of extinction of light emitted from sodium by iodine molecules and atoms. A. Terenin and N. Prileshaeva (Z. physikal. Chem., 1931, **B**, **13**, 72—92; cf. A., 1930, 520).—The extinction by I mols. of the D lines emitted by excited Na atoms formed by optical dissociation of NaI is attributed to the reaction $Na'+I_2=NaI+I$, the effective cross-section in the collision between the Na atom and the I mol. falling from 7×10^{-14} to $1{\cdot}5\times10^{-14}$ sq. cm. as the speed of the Na atom is increased from 1×10^5 to 3×10^5 cm. per sec. The extinction by I atoms is ascribed to the reaction $Na'+I=NaI+h\nu$; the effective cross-section is $1{\cdot}5\times10^{-14}$ sq. cm. and does not vary with the speed of the Na atom. R. Cuthill.

Periodic classification of the elements. S. K. Mitra (Phil. Mag., 1931, [vii], **11**, 1201—1214).—The periodic table is modified and extended to show electron configurations. N. M. Bligh.

Spectrographic search for element 61. S. Takvorian (Compt. rend., 1931, **192**, 1372—1373; cf. this vol., 783).—Spectrographic examination of the fractions previously referred to showed nothing but Nd and Sm, of which some 50 and 40 new lines respectively were measured between 3150 and 3200 Å.

C. A. Silberrad.

Existence of the stable element of at. no. 84. J. Proszt and M. Vendl (Mitt. Berg- Hüttenmänn. Abt. Sopron, 1930, 21 pp.; Chem. Zentr., 1931, i, 1893).—Attempts to obtain the element from tetradymite, crude Te, and a metallurgical Bi residue were unsuccessful. A. A. Eldridge.

At. wt. of xenon. R. Whytlaw-Gray, H. S. Patterson, and W. Cawood (Nature, 1931, **127**, 970—971).—The extrapolated limiting density of Xe obtained from measurements of the pressures at which O_2 and Xe are equal in density is 4·1020, giving an at. wt. 131·26(4) ±0·005 in agreement with Aston's value of 131·27±0·04. L. S. Theobald.

Radioactive disintegration according to the relativity wave equation. S. Gupta (Z. Physik, 1931, **69**, 686—698).—Mathematical.

A. B. D. Cassie.

New applications of the emanation method. F. Strassmann (Naturwiss., 1931, **19**, 502—504; cf. Hahn, A., 1929, 737).—The method is used to show the marked difference in emanation properties of a dry and a moist sample of $BaSO_4$, and its dependence on temp. The method was also used to show the different emanation properties of Ba glasses with different life histories, and their dependence on temp. The emanation power of org. Ba salts in relation to their mol. structure is also investigated. A. J. Mee.

Grouping of radioactive atoms in gases. (Mlle.) C. Chamié and L. Goldstein (J. Chim. phys., 1931, **50**, 228—232).—The formation of groups of radioactive atoms is probably due to ionisation of traces of gas in the emanation tube, forming centres for condensation of radioactive atoms.

E. S. Hedges.

Actinium problem. II. G. Elsen (Chem. Weekblad, 1931, **28**, 342—348).—A survey of the problem of the origin of the actinium family, in the light of recent work on isotopes. H. F. Gillbe.

Range of α-rays of polonium in different gases. Nahmias (Compt. rend., 1931, **192**, 1451—1452).—Using Curie's method (cf. A., 1925, ii, 834) the value of $\varphi=l/\alpha$, where l is the most probable range and α varies directly with l and inversely as the density of the gas, is for air, O_2, A, and CO_2, respectively, 0·0200, 0·0250, 0·0190, and 0·0280. l_{ThC}/l_{P_0} in air at 15° and 760 mm. is 1·20—1·21. Short-range α-particles of Th-C form a notable percentage of the total emitted. C. A. Silberrad.

Analysis of the long-range α-particles from Ra-*C*. (Lord) Rutherford, F. A. B. Ward, and W. B. Lewis (Proc. Roy. Soc., 1931, **A**, **131**, 684—703).—The new counting methods (A, 1930, 1338) have been used to analyse the distribution of the long-range α-particles from Ra-C (7—12 cm. in air). Nine homogeneous groups have been detected varying in energy between 8·30 and $10{\cdot}62\times10^6$ volts. The mean range of the strongest group is 9·04 cm. The velocities and energies of the α-particles are deduced from the measured ranges. The emission of α-rays from Ra-C appears to be closely connected with the long-range α-particles. It is concluded that the γ-rays arise from transitions of the α-particle between the excited levels and the ground level.

L. L. Bircumshaw.

Nuclear deflexions of β-rays. J. M. Nuttall and H. S. Barlow (Mem. Manchester Phil. Soc., 1929—1930, **74**, 35—40).—Stereoscopic photographs of more than 900 tracks of β-rays deviated by passage close to the nucleus in O_2 and N_2 were examined. The variation in the no. of deflexions with scattering angle, and the calc. value of the at. no. of the scattering nucleus were in accordance with the simple Rutherford theory of nuclear deflexion. N. M. Bligh.

γ-Rays of potassium. F. Běhounek (Z. Physik, 1931, **69**, 654—663; cf. A., 1930, 1233).—Ionisation due to 96 kg. of KCl suggests that γ-radiation due to

K is homogeneous and of wave-length 13·3 X; its intensity is $1 \cdot 3 \times 10^{-10}$ times that of the hardest Ra-*C* γ-radiation. A. B. D. CASSIE.

Decay constant of uranium II. C. H. COLLIE (Proc. Roy. Soc., 1931, A, 131, 541—553).—The half-life period of U II is shown to be not less than 10^6 years. L. L. BIRCUMSHAW.

Experimental technique preparatory to atom disintegration by means of high potentials. A. BRASCH and F. LANGE (Z. Physik, 1931, 70, 10—37).—Apparatus necessary for utilising atm. p.d. of 8000—15,000 kv. is described. Using an impulse generator, discharge tubes were tested to 2000 kv., and *X*-rays, β-rays, and H canal rays were produced. A. B. D. CASSIE.

Ionisation probability for inner levels through rapid corpuscular radiation and a method for its proof. L. MEITNER (Naturwiss., 1931, 19, 497—499).—The question of how far it is possible for rapid corpuscular radiation—electrons or α-rays—to ionise from the inner shell is discussed, and investigated for light elements in the gaseous state. A. J. MEE.

Conditions on Schrödinger's ψ. E. H. KENNARD (Nature, 1931, 127, 892—893).—Theoretical. L. S. THEOBALD.

Transformation of light into heat in solids. II. J. FRENKEL (Physical Rev., 1931, [ii], 37, 1276—1294; cf. this vol., 282).—Previous results are generalised for diatomic crystals. N. M. BLIGH.

Application of quantum mechanics to chemical kinetics. L. GOLDSTEIN (Compt. rend., 1931, 192, 1536—1539; cf. this vol., 666).—A qual. study of the combination of two H atoms to H_2, all being in the fundamental state, and neglecting proton spin and rotation of the atoms, based on a Schrödinger equation, shows that for this to occur a de Broglie wave must affect the system while it is experiencing a collision of the second kind. C. A. SILBERRAD.

Formation of elements and cosmic radiation. M. VON LAUE (Naturwiss., 1931, 19, 530—531).—Theoretical. A. J. MEE.

Identification of the Raffety spectrum. H. GRENAT (Compt. rend., 1931, 192, 1553—1555).—Measurements of 20 lines, with their intensities, of the Raffety spectrum, observed in the pointed flame of an O_2-C_2H_2 blowpipe, show this spectrum to belong definitely to the hydrocarbon group. C. A. SILBERRAD.

Raffety bands and cometary spectra. F. BALDET (Compt. rend., 1931, 192, 1531—1533).—Comparison between the lines of the Raffety band (cf. preceding abstract) and those of cometary spectra shows definitely that there is no connexion. C. A. SILBERRAD.

Transparency of sodium fluoride and lithium fluoride in the extreme ultra-violet. E. H. MELVIN (Physical Rev., 1931, [ii], 37, 1230—1232).—Artificially prepared single crystals of NaF and LiF were transparent to 1320 and 1083 Å. (132 Å. below the limit of fluorite), respectively. N. M. BLIGH.

Visible halogen bands, with special reference to ICl. R. S. MULLIKEN (Physical Rev., 1931, [ii], 37, 1412—1415; cf. A., 1930, 1328; this vol., 1).—Dissociation into normal atoms of excited ICl mols., after absorption of light in the visible bands, agrees with theory. The probable classification of these bands is discussed; previous views on the behaviour of the I_2 bands in magnetic fields are revised. N. M. BLIGH.

Vibrational levels of the iodine monochloride molecule. W E. CURTIS and O. DARBYSHIRE (Trans. Faraday Soc., 1931, 27, 77—87).—The effect of temp., up to 200°, on the intensities of the vibrational progressions of ICl has been investigated. F. G. TRYHORN.

Ultra-violet absorption spectrum of sulphur dioxide. W. W. WATSON and A. E. PARKER (Physical Rev., 1931, [ii], 37, 1484—1492; cf. A., 1930, 1090).—Band assignments to the fundamental vibrational series are tabulated. The process $SO_2 \longrightarrow S+O_2$ for the two symmetrical vibrations and $SO_2 \longrightarrow SO+O$ for the asymmetrical vibration are indicated. N. M. BLIGH.

Ultra-violet absorption spectrum of hydrazine vapour. S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 166—167).—A brief account of results obtained with small dispersion. W. GOOD.

Absorption spectra of complex salts of Fe, Co, Ni, Pd, and Pt. R. SAMUEL (Z. Physik, 1931, 70, 43—73).—With a H_2 discharge tube absorption spectra were measured in the region 200—600 mμ for $[Co(NH_3)_6]Cl_3$, $[Co(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3]Cl_3$, $[Co(NH_3)_6]Cl_3$ to $[Co(NH_3)_3(NO_2)_3]$, $Na_3[Co(NO_2)_6]$, $Na_2[Fe(CN)_5(NO)]$, $[Co(NH_3)_6]Cl_3$ to $[Co(NH_3)_4Cl_2]Cl$, $[Co\,en_2Cl_2]Cl$, K_3 and $K_4[Fe(CN)_6]$, K_3 and $K_4[Co(CN)_6]$, $K_2[Ni(CN_4)]$, $K_2[Ni(CN)_4]$, $K_2[Pd(CN)_4]$, and $K_2[Pt(CN)_4]$. The results are inconsistent with a purely electrostatic theory of co-ordination, only the long-wave limit of absorption being influenced by the degree of ionisation of the metal atom. Observed bands do not belong to radicals such as NH_3, but are characteristic of the co-ordination group. A. B. D. CASSIE.

Organic acid iron solutions. I. Concentrations and colours. N. J. HARRAR and F. E. E. GERMANN (J. Physical Chem., 1931, 35, 1666—1673).—The concentrations, colours, colours on dilution, and relative colour intensities of the solutions obtained by dissolving freshly-precipitated $Fe(OH)_3$ in HCl, H_2SO_4, and the commoner org. acids (mainly aliphatic, and approx. *N* where possible) are recorded. Colour is mainly determined by the strength of the acid concerned, strong acids giving green, and weak acids red, solutions. L. S. THEOBALD.

Absorption spectra of crystals at low temperatures as references in the measurement of stellar velocities. S. FREED (Nature, 1931, 128, 33).—The absorption spectrum of dysprosium ethyl sulphate at the temp. of liquid N contains sharp lines between 4000 and 4800 Å., and, together with spectra of other rare earths at this temp., is suggested as reference for stellar velocities. L. S. THEOBALD.

Simple relations between molecular spectra and structure. H. DESLANDRES (Compt. rend., 1931, 192, 1417—1421; cf. this vol., 544).—Further examples are given, the submultiples of the fundamental frequency (1062·5) being 3, 6, 7, 8, and 9.

C. A. Silberrad.

Simple relations between molecular spectra and structure. H. Deslandres (Compt. rend., 1931, **192**, 1606—1610; cf. preceding abstract).—Similar relations are shown to exist as regards many infra-red bands of CO_2 and NH_3, the submultiples of the fundamental frequency 1062·5 varying from 2 to 108. C. A. Silberrad.

Spectroscopy and chemical reactions. M. de Hemptinne (Bull. Soc. chim. Belg., 1931, **40**, 220—233).—A lecture. H. F. Gillbe.

Spectroscopic and photochemical research on the diazo-compounds. I. Fukushima and M. Horio (Mem. Coll. Eng. Kyoto, 1931, **6**, 179—238).—The absorption spectra of C_6H_6, NH_2Ph,HCl, and diazobenzene chloride are similar, but different from NH_2Ph. This relationship persists if the groups NO_2, SO_3H, CO_2H, Me, and Cl are introduced into the nucleus, and suggests that diazobenzene chloride and its derivatives are structurally similar to NH_2Ph,HCl and its derivatives, the first N atom being quinquevalent in each case, The spectra of the diazo-compounds are radically changed by the introduction of the groups OH, OMe, and OEt.

Absorption spectra of 1 : 2 : 4-diazonaphtholsulphonic acid and diazobenzenesulphonic acid were obtained. The rate of photolysis of both compounds is independent of the concentration, and that of diazonaphtholsulphonic acid is independent of the temp., but reduced by addition of quinine sulphate. The rate of decomp. of diazobenzenesulphonic acid varies with the temp., for the photolysis is accompanied by a thermal reaction, the rate of which is proportional to the concentration of reactant. The two reactions are not entirely independent, but the effect of the thermal reaction is not perceptible below about 40°. The quantum efficiency of the photolysis of diazobenzenesulphonic acid by light of wave-length 366 mμ is 0·16. R. Cuthill.

Absorption spectra of plumbagin and naphthoquinones. N. Gómez (Anal. Fís. Quím., 1931, **29**, 367—368).—The ultra-violet absorption spectra of naphthoquinone and 2-methylnaphthoquinone are almost identical, and it is not possible to ascertain the position of the OH group of plumbagin spectroscopically. H. F. Gillbe.

Absorption spectra and constitution of azoxy-derivatives and analogous compounds. L. Szegö and P. Ostinelli (Atti III Cong. Naz. Chim. pura appl., 1929, 395—401; Chem. Zentr., 1931, i, 1444).—Ultra-violet absorption spectra of the following compounds were studied : deoxybenzoin, m. p. 56°; *p*-nitro- ; *p*-amino-, m. p. 95°; β-*p*-hydroxy- ; α-*p*-methyl- ; β-*p*-chloro-, m. p. 102°, -deoxybenzoin; oxime, m. p. 117°. The singular behaviour of the β-compounds is discussed. A. A. Eldridge.

Absorption of infra-red radiation by water vapour. E. K. Plyler and W. W. Sleator (Physical Rev., 1931, [ii], **37**, 1493—1507).—Using increased resolution, new lines of the 4 absorption bands of water vapour have been measured, and existing data for the strong lines corrected.

N. M. Bligh.

Reflecting power of water and ice for infra-red radiation. M. Weingeroff (Z. Physik, 1931, **70**, 104—108).—The reflecting power of liquid water was measured for the wave-lengths 11—18 μ, and of ice for 6—16 μ; the latter suggests a residual-ray frequency in this region. A. B. D. Cassie.

Obtaining Raman spectra with small quantities of liquid. W. Dekeyser (Natuurwetensch. Tijds., 1931, **13**, 230—231).—About 13 c.c. are enclosed in a small vessel covered with a microscope cover glass; the time of exposure in the spectrograph is reduced to about one seventh by using an Al electrically-heated plate holder. H. F. Gillbe.

Monochromatic excitation of Raman spectra in the ultra-violet. H. Hulubei and (Mlle.) Y. Cauchois (Compt. rend., 1931, **192**, 1640—1643; cf. this vol., 667).—By interposing a quartz tube containing Cl under pressure and an arrangement for cooling in the apparatus previously described, the resonance line, λ 2535·32, is isolated, accompanied only by λ 4358 slightly diminished and the green and yellow lines. The blue Raman H_2O band (cf. A., 1930, 1091) is double, whilst that with max. at 2780—2782 Å. is simple (cf. this vol., 408). Six other bands were observed corresponding with Δν 7729, 8243, 8703, 9223, 10,151, 11,264 cm.$^{-1}$ EtOH showed lines corresponding with Δν 506, 880, 1038, 2741, 2876, 2929, and 2980, and two bands with Δν 9870 and 10,551 cm.$^{-1}$

C. A. Silberrad.

Raman effect and polymerisation of water at various temperatures. O. Specchia (Atti R. Accad. Lincei, 1930, [vi], **12**, 659—662).—Raman spectra of water in the region 4108—5790 Å. have been measured at 17—91°. The results indicate changes in the state of polymerisation of water with temp. O. J. Walker.

Raman spectra of some substances containing SO or SO_2 group. H. Nisi (Japan. J. Phys., 1930, **6**, 1—15; cf. A., 1930, 662).—Raman lines and wave-no. shifts are tabulated for SO_2 (liquid), H_2SO_4, $SO_2\cdot OH\cdot Cl$, SO_2Cl_2, $PhSO_3H$, $PhSO_2Cl$, $C_6H_4Me\cdot SO_3H$ (*p*), C_6H_6, PhMe, $SOCl_2$, S_2Cl_2, $POCl_3$, PCl_3, $SO(OEt)_2$, EtOH, and H_2SO_3. The structure of the last (non-ionised) is indicated as $H\cdot SO_2\cdot OH$. The polarisation states of the various lines are described.

N. M. Bligh.

Raman effect in the ultra-violet region. J. C. Ghosh and B. C. Kar (J. Physical Chem., 1931, **35**, 1735—1744).—The Raman effects produced by ultra-violet light are recorded for a number of simple org. compounds. The frequency shifts between 1340 and 1405 given by $H\cdot CO_2H$, $H\cdot CO_2Na$, and NaOBz may be due to a C—(OH) vibration. Acids, except $CCl_3\cdot CO_2H$, but not the corresponding Na salts, give frequency shifts 1600—1700. The shifts diminish in passing from $CH_2Cl\cdot CO_2H$ and $CCl_3\cdot CO_2H$ to their Na salts. Formic acid undergoes decomp. and the halogeno-acids undergo hydrolysis when exposed to ultra-violet light of wave-length 2000—3000 A.

L. S. Theobald.

Spectrum of radiation scattered by some simple open and closed hydrocarbon rings. J. Weiler (Z. Physik, 1931, 69, 586—596).—Raman spectra due to C_5H_{12}, amylene, *cyclo*pentane, *cyclo*hexane, *cyclo*hexene, and C_6H_6 are given in full, and are shown to be consistent with an intense line near 900 cm.$^{-1}$ characteristic of a closed ring, and with a line near 3000 cm.$^{-1}$ due to CH groups.

A. B. D. Cassie.

Ionic nature of the hydrogen linking. C. Kasper (J. Amer. Chem. Soc., 1931, **53**, 2424—2425; cf. this vol., 670).—Raman effect data for hydrates and solutions afford strong evidence that the H linking is not of the extreme electron-pair type.

J. G. A. Griffiths.

The carbon–halogen linking as related to Raman spectra. W. D. Harkins and H. E. Bowers (J. Amer. Chem. Soc., 1931, **53**, 2425—2427).—The frequency corresponding with the C–Br linking in MeBr is $1{\cdot}808\times10^{13}$ per sec., but with longer normal chains or with sufficiently remote *iso*-groups, the const. value $1{\cdot}688\times10^{13}$ is found. An adjacent double linking or side-chain or direct attachment of the Br to a *sec.* or *tert.* C atom decreases the frequency to $1{\cdot}61\times10^{13}$, except in the case of $Bu^{\beta}Br$. The results indicate that the CH_2 group, and not the whole org. radical linked to the Br atom, vibrates with respect to the Br, but the effective mass of the CH_2 is increased by constraints due to its union with the rest of the hydrocarbon chain. J. G. A. Griffiths.

Raman spectra of formaldehyde, trioxymethylene, ethylene glycol, and some viscous liquids. J. H. Hibben (J. Amer. Chem. Soc., 1931, **53**, 2418—2419).—The similarity of the Raman spectra of 37% aq. CH_2O and ethylene glycol indicates the formation of methylene glycol by CH_2O in aq. solution. Lines typical of the C:O linking are absent, but that of C·O is strong in these spectra and in that of trioxymethylene.

Na silicate, H_3PO_4, potassium hydrogen phosphite, and glycol solutions afford strong continuous Raman spectra which decrease on dilution and on raising the temp., indicating that this property is probably common to viscous liquids (cf. A., 1928, 1170, 1306).

J. G. A. Griffiths.

Raman effect of some amino-compounds. A. S. Ganesan and V. N. Thatte (Z. Physik, 1931, **70**, 131—139).—The Raman effect due to NHPhMe, $NPhMe_2$, and $NPhEt_2$, *o*-, *p*-, and *m*-toluidine and xylidine has been investigated. The displacement 3432 cm.$^{-1}$ is characteristic of the N–H linking.

A. B. D. Cassie.

Intensity and polarisation of Raman radiation due to polyatomic molecules. G. Placzek (Z. Physik, 1931, **70**, 84—103).—Intensity and polarisation of Raman radiation is determined by variation of mol. polarisability with nuclear separations, whereas infra-red absorption depends on the effective permanent electric moment. This explains differences between the two, and indicates that the intensity of Raman lines increases from zero for ionic mols., where the resultant polarisability tends to be independent of nuclear separation, to a max. for homopolar mols. Symmetry properties lead to the selection rule that no normal frequency can appear as Raman radiation if a symmetry operator of the mol. (such as rotation of a symmetrical linear mol. through 180°) when applied to the corresponding normal co-ordinate changes its sign but not its magnitude. These results are applied to the spectra of CCl_4, CO_2, N_2O, CS_2, C_2H_2, and C_2H_4. A. B. D. Cassie.

Fluorescence and absorption of phosphorus vapour. A. Jakowlewa (Z. Physik, 1931, **69**, 548—563).—Fluorescence and absorption spectra of P vapour indicate a 5·2 volt dissociation energy for the P_2 molecule. A. B. D. Cassie.

Phosphorescent substances. IV. Calcium, strontium, and barium sulphides. N. F. Shirov (Ukrain. Chem. J., 1930, **5**, [Sci.], 365—382).—The intensivity and duration of phosphorescence of mixtures containing alkaline-earth sulphides are increased by ignition with MgO and, to a smaller extent, with BeO, CdS, or tungstates; BaO, CaO, SrO, and Al_2O_3 are unsuitable. The best activation temp. is 900—1000° for mixtures containing alkaline-earth carbonate, MgO, Mg tungstate, S, sugar, borax, Li_2O_3, K_2SO_4, CaF_2, and $Bi(NO)_3$.

R. Truszkowski.

Quenching of some alkali-halide phosphors and the quantum efficiency of quenching for the potassium chloride phosphor with admixed thallium. W. Bunger and W. Flechsig (Z. Physik, 1931, **69**, 637—653).—Spectral distribution of radiation effective in quenching light from KCl, KBr, and NaCl phosphors was found to give a max. at the frequency equal to the difference between positions of absorption and emission max.; the abs. efficiency for the KCl–Tl phosphor suggests that quenching by irradiation is a quantum process. A. B. D. Cassie.

Connexion between photo-current and light intensity for gas-filled alkali cells. G. Kortüm (Physikal. Z., 1931, **32**, 417—425).—The relationship $i^z=cj+\text{const.}$ holds to a fair degree of accuracy for the cells investigated. The cell const., z, is rarely unity, and is then independent of charge and wave-length. In other cases it differs considerably from unity and varies with the intensity and the wave-length. A. J. Mee.

Photo-electric cells and formation of photo-electrons. S. E. Sheppard and W. Vanselow (Physikal. Z., 1931, **32**, 454—455).—The mechanism of the photo-electric effect and formation of photo-electrons is discussed for Ag–AgBr–KBr cell.

A. J. Mee.

Spectral sensitivity of unidirectional layer photo-cells. B. Lange (Naturwiss., 1931, **19**, 525—530).—The spectral sensitivity of several Cu_2O unidirectional photo-cells was determined. The cells differ markedly among themselves in their sensitivity, but in all cases the photo-current started at about 575 mμ, and reached a very sharp max. at about 630 mμ. The infra-red wave-length limit for all cells was about 1400 mμ. The course of the sensitivity curve appears to depend on the thickness of the Cu_2O layer. The very sharp increase in spectral sensitivity at the red end of the spectrum is explained by the considerable transparency of Cu_2O for light of this wave-length. A. J. Mee.

Photo-electric emission of thin films. N. R. Campbell (Phil. Mag., 1931, [vii], 12, 173—185).—The nature of the film formed and the changes in emission during the heating of oxidised Ag in Cs vapour are described. The reaction is concluded to be $2Cs+Ag_2O=Cs_2O+2Ag$. The support for the Cs film is probably a mol. mixture of Cs_2O and Ag formed from an alloy of Cs and Ag. N. M. Bligh.

External photo-electric effects in phosphors and its dependence on the state of excitation. H. Göthel (Ann. Physik, 1931, [v], 9, 865—886).—Curves are reproduced showing the effects produced by modifications of experimental procedure using Ca–Bi–Na, Sr–Bi–Na, and Ba–Bi–K sulphide phosphors; the effects are discussed. W. R. Angus.

Electrical discharge in rock-salt. L. Inge and A. Walther (Naturwiss., 1931, 19, 595).—The direction in which the electrical discharge takes place in rock-salt is investigated. A. J. Mee.

Conductivity of pure liquids [hexane]. A. Nikuradse (Z. physikal. Chem., 1931, 155, 59—64).—An apparatus is described in which by drying with P_2O_5, filtration through sintered glass, cataphoresis, and fractional distillation, commercially pure hexane is purified until its conductivity is reduced from its original value of 10^{-12} to 10^{-13} mho to a limiting value of 10^{-19} mho. N. H. Hartshorne.

Electrical conductivity of single aluminium crystals in directions inclined at various angles to the crystal axes. M. Fraser (Phil. Mag., 1931, [vii], 12, 112—129).—The sp. resistance of a single crystal was independent of the orientation relative to the crystal axes, and was about 1% greater than for the annealed metal. N. M. Bligh.

Conductance of zirconium oxide. H. Schweitzer (Z. angew. Chem., 1931, 44, 151—152).—The conductance of ZrO_2 has been measured over the range 200—800°. Slight differences appear in measurements made during heating or cooling. Traces of MgO considerably increase the conductance. Ohm's law is obeyed up to a potential gradient of 1500 volts per cm. F. G. Tryhorn.

Electrical conductivity of liquid hydrocarbons. L. Bruninghaus (Ann. Office Nat. Combust. liq., 1929, 4, 515—527; Chem. Zentr., 1931, i, 1705).—The fact that benzine, when filtered through metal filings, becomes negatively, and the metal positively, charged is discussed theoretically.

A. A. Eldridge.

Magnetic and electric moments of Dirac's electrons. T. Tanaka (Z. Physik, 1931, 69, 810—821).—Mathematical.

Experimental and theoretical foundations of the swarm theory. L. S. Ornstein (Z. Krist., 1931, 79, 90—121).—A critical account of the theory.

C. A. Silberrad.

Oscillation method for determining the dielectric constants of conducting liquids. W. Graffunder and R. Weber (Ann. Physik, 1931, [v], 9, 887—904).—A more detailed account of work already noted (this vol., 23). W. R. Angus.

Dipole moments of some inorganic compounds and a method for determining atomic distances and radii. E. Bergmann and L. Engel (Physikal. Z., 1931, 32, 507—509).—Inorg. halides of the type AX_3 have a finite dipole moment. Hence the atoms cannot all be arranged in one plane, but must be arranged as a three-sided pyramid. The same conclusion is reached by considering the Raman effect. A calculation based on the work of Hund on the H_2O and NH_3 models shows that the plane model would be less stable than the pyramidal. In the series BCl_3–PCl_3–$AsCl_3$–$SbCl_3$ the radius of the central atom increases, and there is a gradually increasing distance between the central atom and the halogen atoms. Compounds of the type AX_4, such as $SnCl_4$, have also a finite moment. Hence the atoms must be arranged in the form of a four-sided pyramid. For $SiCl_4$ and $TiCl_4$ (as for CCl_4) the moment is zero, and the arrangement is tetrahedral. Compounds of the type AX_5 have also a finite moment. The moments of $SbCl_5$ and $Fe(CO)_5$ exclude the two configurations, plane (a regular pentagon with the central atom at the centre of gravity), and trigonal bipyramid, but allow the five-sided pyramid, and the four-sided pyramid with four atoms at the base and one atom at the point, and a central atom inside. The tetragonal cryst. structure of PCl_5 and $TaCl_5$ as well as the chemical properties are in favour of the latter. A. J. Mee.

Dielectric constant of air at high pressures. J. W. Broxon (Physical Rev., 1931, [ii], 37, 1338—1344).—The dielectric const. of aged, dry, dust-free air, measured up to 170 atm., increased linearly with the pressure. N. M. Bligh.

Dielectric properties of methylamines. O. Steiger (Physikal. Z., 1931, 32, 425—434).—The dielectric consts. of gaseous NH_2Me, $NHMe_2$, and NMe_3 have been determined. Several other consts. for these substances are also found. A. J. Mee.

Dielectric constant and chemical constitution: method. A. Chrétien (Compt. rend., 1931, 192, 1385—1387).—The method is Nernst's (cf. A., 1894, ii, 437) modified by using condensers with quartz plates, an indirectly excited oscillating circuit, a galvanometer in place of telephone, and a vertical condenser for the liquid under examination. Et_2O is the standard liquid. ε at 25° for C_6H_6, $CHCl_3$, hexane, and acetal is respectively 2·270—2·274, 4·721—4·726, 1·910—1·014, and 4·791—3·798 (cf. A., 1930, 729).

C. A. Silberrad.

Electric moments and molecular constitution. G. Allard (Compt. rend., 1931, 192, 1455—1457).—The principle of additivity of electric moments (cf. A., 1929, 980) is extended by assigning different moments to atoms attached to a C atom according as this latter is attached to another by a single or double linking. The results indicate three ethylenic linkings for C_6H_6, and a quinonoid structure for *p*-chlorophenol (cf. Smyth and Dornte, this vol., 669).

C. A. Silberrad.

Dielectric constants [of mesomorphic substances]. W. Kast (Z. Krist., 79, 146—160).—A crit. summary of recent work. C. A. Silberrad.

Dipole moments and structure of organic compounds. VII. Electric moments of stereo-

isomeric hydrobenzoins. A. Weissberger and R. Sängewald. **VIII. Nature of simple linkings.** A. Weissberger (Z. physikal. Chem., 1931, B, **12**, 399—407, 408—412; cf A., 1930, 1093).—VII. The dipole moments of hydrobenzoin and *iso*hydrobenzoin, measured in C_6H_6 solution at 25°, are respectively 2·1 and $2{\cdot}7 \times 10^{-18}$ e.s.u. Owing to small solubility, supersaturated solutions were used. The Me_2 esters of *d*-tartaric and racemic acid were examined in both unsaturated and supersaturated solution, and the same dipole moment, $2{\cdot}9 \times 10^{-18}$, was obtained in both cases and for both substances.

VIII. A general discussion of results. Reasons are given for believing that groups inclined at an angle to a single linking do not assume a rigid position of low symmetry. F. L. Usher.

Electric moment and molecular structure. IV. Glycols. C. P. Smyth and W. S. Walls (J. Amer. Chem. Soc., 1931, **53**, 2115—2122).—Density and dielectric const. data at 25° and 50° have been determined for solutions of BuOH and the glycols in 1 : 4-dioxan (cf. A., 1930, 849). The following electric moments at 25° are recorded: BuOH $1{\cdot}81 \times 10^{-18}$ e.s.u.; $HO{\cdot}[CH_2]_2{\cdot}OH$ 2·28; $OH{\cdot}CHMe{\cdot}CH_2{\cdot}OH$ 2·25; $HO{\cdot}[CH_2]_3{\cdot}OH$ 2·5; $HO{\cdot}[CH_2]_6{\cdot}OH$ 2·48; $HO{\cdot}[CH_2]_{10}{\cdot}OH$ 2·52. The results are discussed and indicate the absence of any pronounced bending of the C chain. J. G. A. Griffiths.

Dielectric constant of formic, acetic, and propionic acids, and the electric moment of complex molecules. C. T. Zahn (Physical Rev., 1931, [ii], **37**, 1516—1526; cf. A., 1930, 841).—The temp. and pressure variations of the dielectric const. of formic and propionic acids are similar to those for AcOH. For formic acid the amount of association into double mols. is calc.; values for the electric moment of the single and double mol. are $1{\cdot}51 \times 10^{-18}$ and $0{\cdot}99 \times 10^{-18}$ e.s.u., and for the single mol. of acetic and propionic acids $1{\cdot}73 \times 10^{\ 18}$ and $1{\cdot}74 \times 10^{-18}$ e.s.u., respectively. The electric moment of complex mols. is discussed and interpreted, and a structure for the double mol. of formic acid is suggested. N. M. Bligh.

Electric moments of the fixed vegetable oils. W. N. Stoops (J. Physical Chem., 1931, **35**, 1704—1711).—The densities and dielectric consts. of tung, linseed, and castor oils have been measured at temp. between −70° and 100° and the polarisations at infinite dilution calc. from the Debye equation. L. S. Theobald.

Optical activity dependent on co-ordinated nickel. G. T. Morgan and F. H. Burstall (Nature, 1931, **127**, 854).—Pink, complex nickelous salts $[Ni3R]X_2,6H_2O$, where R is dipyridyl and X is Cl, Br, I, or NO_3, and $[Ni3R](CNS)_2,3H_2O$ have been prepared. Ammonium *d*-tartrate and the chloride give a soluble dextrorotatory tartrate $[Ni3R]C_4H_4O_6,6H_2O$ which on double decomp. with NH_4Cl furnished an optically active tris-αα′-dipyridyl nickelous chloride. The fall in optical activity corresponded with that for a unimol. reaction; max. activity corresponded with [α] +550°. Analogous complex salts of $Mn^{\cdot\cdot}$ have also been obtained. Tripyridyl (R′) gives rise to well-defined compounds of the type $[M2R']X_2$ with $Fe^{\cdot\cdot}$ and Ni. L. S. Theobald.

Optical activity in terms of the theory of coupled surfaces. K. Scheringa (Chem. Weekblad, 1931, **28**, 363—365).—Theoretical. H. F. Gillbe.

Anomalous dispersion of active tartaric acid. K. Scheringa (Chem. Weekblad, 1931, **28**, 394—395).—A theoretical note. H. F. Gillbe.

Double refraction of thin layers of anisotropic liquids in a magnetic field, and the force orienting these layers. V. Fréedericksz and V. Zolina (Z. Krist., 1931, **79**, 255—267).—Previous results (cf. A., 1927, 505; 1929, 743) are extended to acetoxybenzaldazine and anisaldazine and the existence of a layer in contact with the wall unaffected by the magnetic field is confirmed. C. A. Silberrad.

Optics of mesophases. H. Zocher (Z. Krist., 1931, **79**, 122—133).—A non-mathematical account of the phenomena observed. C. A. Silberrad.

Magneto-optical dispersion of organic liquids. III. Active *iso*amyl alcohol and *n*-propyl formate. E. Thomas and E. J. Evans (Phil. Mag., 1931, [vii], **11**, 1220—1232; cf. this vol., 411).—Data are recorded and expressions found for the magneto-optical and natural dispersion for various wave-lengths in the visible and ultra-violet. N. M. Bligh.

Molecular and atomic volumes. XXXI. Low-temperature densities of certain elements. A. Sapper and W. Biltz [with (Frl.) Wünnenberg]. **XXXII. Zero volumes of the elements.** W. Biltz and K. Meisel (Z. anorg. Chem., 1931, **198**, 184—190, 191—203).—XXXI. Data are given for the halogens, Ca, Hg, S, and P (white). The extrapolated zero vols. of the halogens are in extremely close agreement with the calc. val. of Hertz, but for the other elements the discrepancies are considerable.

XXXII. Existing data for the densities, zero vol., at. vol., and expansion coeff. of the elements are summarised, and the regularities observed when the zero vol. are classified according to the periodic system are discussed. Calculation of the packing densities demonstrates the close packing of the metals compared with the definitely non-metallic elements, the inert gases and H being the sole exceptions. H. F. Gillbe.

Problems in the theory of anisotropic liquids. C. W. Oseen (Z. Krist., 1931, **79**, 173—185).—A mathematical treatment of the effects of temp. on anisotropic liquids. C. A. Silberrad.

Para- and ortho-hydrogen. A. Bijl and J. van Heiningen (Chem. Weekblad, 1931, **28**, 359—363).—A survey. H. F. Gillbe.

Pseudopolar reaction between atoms of hydrogen. E. Maiorana (Atti R. Accad. Lincei, 1931, [vi], **13**, 58—61).—Mathematical. O. J. Walker.

Paramagnetism of bivalent silver. G. T. Morgan and S. Sugden (Nature, 1931, **128**, 31).—The magnetic susceptibility of $[Ag3R](ClO_3)_2$ (R= dipyridyl) at 20° gives χ $1{\cdot}93 \times 10^{-6}$ and χ_M 1434×10^{-6}; the Weiss magneton no. is 9·1. L. S. Theobald.

Magnetic susceptibility [of mesomorphic substances]. W. Kast (Z. Krist., 1931, **79**, 161—172).—A crit. summary of recent work.

C. A. Silberrad.

Influence of chemical combination on the absorption spectrum of the Röntgen series. R. Swinne (Wiss. Veröff. Siemens-Konz., 1931, **10**, [2], 89—94).—From London's theory of non-polar valency linkings it follows that in the case of non-polar compounds of certain elements peripheral electronic arrangements and Röntgen terms would be expected which do not occur in polar compounds or with free neutral atoms. This conclusion is held to explain qualitatively the nature of the absorption observed by Meyer in the K series of elements with a higher at. no. than Fe. The special effect of rhombic S in causing displacement of the Röntgen absorption edges of elements and compounds is attributed to its powerful association action. A. R. Powell.

Two modifications of liquid carbon disulphide. M. Wolfke and J. Mazur (Nature, 1931, **127**, 926—927).—The heating curve of CS_2 shows a break at $-90·03°$. The two modifications of CS_2 become visible on cooling. The heat of transformation is approx. 0·04 g.-cal./g. L. S. Theobald.

Viscosity, surface tension, and parachors of some cyclic hydrocarbons. M. Godchot and (Mlle.) G. Cauquil (Compt. rend., 1931, **192**, 1560—1562).—These consts. have been determined for 12 cyclanes and 11 cyclenes (C_5 to C_8). The cyclanes have higher viscosities than the cyclenes, both very much higher than the corresponding paraffins. Surface tension increases with no. of C atoms in the ring, and is always much higher than in the corresponding paraffin. The parachors agree with the calc. values within 1%; the values for closure of a C_7 and a C_8 ring are respectively 4·6 and 2·37.

C. A. Silberrad.

Surface tension of saturated vapours and the equation of Eötvös. J. L. Shereshefsky (J. Physical Chem. 1931, **35**, 1712—1720).—Theoretical. An expression connecting surface tension of saturated vapours with temp. is deduced and compared with experimental values for C_6H_6, PhCl, Et_2O, CCl_4, $H·CO_2Me$, and AcOEt. A new modification of Eötvös' law is developed and tested against observed data for the same compounds in the liquid state.

L. S. Theobald.

Methods and apparatus employed at the Bureau of Physico-Chemical Standards. IV. Surface tension of a number of organic compounds. (Mme.) H. Roland and Lek (Bull. Soc. chim. Belg., 1931, **40**, 177—188).—An apparatus is described for the measurement of surface tension by the capillary-flow method; the results are accurate to within about 0·2%. Data are given for a large number of org. liquids for the interval 15—30°; results for C_6H_6 are compared with recorded results.

H. F. Gillbe.

Calculation of van der Waals forces. H. Margenau (Physical Rev., 1931, [ii], **37**, 1425—1430).—Mathematical. N. M. Bligh.

Diffuse scattering of *X*-rays by solids. G. E. M. Jauncey (Physical Rev., 1931, [ii], **37**, 1193—1202).—Theoretical. From the classical theory of *X*-ray scattering applied to that by the electrons in the atoms of one kind in a solid an expression is deduced for the scattered intensity per electron. N. M. Bligh.

Diffuse scattering of *X*-rays by simple cubic crystals. G. E. M. Jauncey and G. G. Harvey (Physical Rev., 1931, [ii], **37**, 1203—1209).—The expression previously obtained (cf. preceding abstract) is modified for a cubic crystal of atoms of one kind.

N. M. Bligh.

Principles determining the arrangement of atoms and ions in crystals. M. L. Huggins (J. Physical Chem., 1931, **35**, 1270—1280).—A review of fundamental principles. L. S. Theobald.

Electrical figures on photographic plates in liquids. K. Przibram (Physikal. Z., 1931, **32**, 481—482).—The method of obtaining the figures is described.

A. J. Mee.

Causes of the broadening of the lines in *X*-ray powder and rotating-crystal diagrams. U. Dehlinger (Z. Metallk., 1931, **23**, 147—149).—From a review of recent work on the effect of cold work on the broadening of the lines in röntgenograms of various metals it is concluded that this effect can be due only to the non-homogeneous distortion or bending of the grains remaining after slip has occurred, which is produced by pressure perpendicular to the direction of deformation by rolls or by dies in cold-working.

A. R. Powell.

***X*-Rays for the determination of small changes in the lattice constants of α-iron.** A. E. van Arkel and W. G. Burgers (Z. Metallk., 1931, **23**, 149—151).—Accurate results are obtained for the lattice consts. of α-Fe by using Co-$K\alpha$ radiation with an angle of incidence of 80—81°. Pure Fe has *a* 2·8614; after annealing in H_2 for 8 days at 100 atm. no change occurs. A. R. Powell.

Crystal structure of the compound Fe_2B. G. Hägg (Z. physikal. Chem., 1931, **B**, **12**, 413—414).—Complete analogy exists between the structure of Fe_2B and that of $CuAl_2$. The space-group is most probably D_{4h}^{18}, and not V_d^{11} (cf. this vol., 151).

F. L. Usher.

Crystal structures of Cu_5Zn_8 and Cu_5Cd_8. A. J. Bradley and C. H. Gregory (Phil. Mag., 1931, [vii], **12**, 143—161).—The structures are of the γ type, with 52 atoms in the unit cell; in Cu_5Cd_8 there are 16 Cu atoms in groups of 8 and 8, and 4 Cu and 32 Cd atoms distributed at random amongst groups of 12 and 24. In Cu_5Zn_8, similarity of *X*-ray scattering powers prevents a distinction of the atoms, and deductions on analogy with Ag_5Zn_3 and Au_5Zn_8 appear incorrect. Data obtained from interat. distance values and ternary Cu–Zn–Al alloys indicate a structure differing from that of Cu_5Cd_8.

N. M. Bligh.

Crystal lattice of anhydrous sodium sulphite. W. H. Zachariasen and H. E. Buckley (Physical Rev., 1931, [ii], **37**, 1295—1305).—Four methods were employed. The hexagonal unit cell contains 2 mols., and has *a* 5·441, *c* 6·133 Å., requiring the assumption of twin crystals with the *c*-axis as twinning axis. The disposition of the atoms is described, and the presence of SO_3 groups shown. N. M. Bligh.

Crystal structure of potassium permanganate. R. C. L. MOONEY (Physical Rev., 1931, [ii], **37**, 1306—1310).—The unit cell is orthorhombic, contains 4 mols., and has *a* 9·09, *b* 5·72, *c* 7·41 Å. The observed intensity and calc. structure · amplitude agree satisfactorily. The grouping of the atoms is described. N. M. BLIGH.

Crystal structure of the tetrahalides of the lighter elements. Structure of silicon tetra-iodide. O. HASSEL and H. KRINGSTAD (Z. physikal. Chem., 1931, **B**, **13**, 1—12).—The structure is cubic, and the edge of the unit cell, which contains 8 mols., is 11·99 Å. in length. R. CUTHILL.

Crystal structure of molybdenum trioxide: a correction. N. WOOSTER (Nature, 1931, **128**, 35).—*c* should be 3·67 and *u* and *v* should be interchanged (this vol., 289). L. S. THEOBALD.

Structure of XO_3 groups in crystals. W. H. ZACHARIASEN (J. Amer. Chem. Soc., 1931, **53**, 2123—2130; cf. A., 1929, 1131).—The data indicate two classes of structure for the groups $(XO_3)^{-m}$, one coplanar and having 3×8 valency electrons and the other low pyramidal and having $3\times8+2$ valency electrons. The formation of asymmetrical groups is explained in terms of the polarisability of ions. The pyramidal groups consist of 3 O ions at 3 corners of a tetrahedron, the fourth corner being occupied by two displaced electrons and the centre by the core of the cation. Inter-atomic distances are tabulated. A rule relating the symmetry of the groups $(XY_2)^{-m}$ and $(XY_3)^{-m}$ with the number of valency electrons is given.

J. G. A. GRIFFITHS.

***X*-Ray investigation of orthotitanates.** S. HOLGERSSON and A. HERRLIN (Z. anorg. Chem., 1931, **198**, 69—78).—Orthotitanates of Mg, Co, Zn, and Mn, prepared synthetically, possess the spinel type of lattice. Mg_2TiO_4 has *a* 8·44, Co_2TiO_4 8·43, Zn_2TiO_4 8·44, and Mn_2TiO_4 8·67 Å. H. F. GILLBE.

Molecular symmetry of hexa-aminobenzene in the crystalline state and certain other properties of the substance. (MISS) I. E. KNAGGS (Proc. Roy. Soc., 1931, **A**, **131**, 612—620).—Powder photographs have been taken of hexa-aminobenzene The space-group is O_h^1 with a Γr lattice. There are 16 mols. in the unit cell (15·14 Å.), and they possess a threefold axis of symmetry. The coeff. of linear expansion between —183° and +15° is 0·000102. The *X*-ray evidence is in agreement with the view of Flürscheim and Holmes (A., 1929, 438) that the stability of hexa-aminobenzene is greater than has hitherto been supposed. A possible structure is suggested. L. L. BIRCUMSHAW.

***X*-Ray study of mannitol, dulcitol, and mannose.** (MISS) T. C. MARWICK (Proc. Roy. Soc., 1931, **A**, **131**, 621—633).—Mannitol has *a* 8·65, *b* 16·90, *c* 5·56 Å., space-group Q_4, 4 mols. per unit cell, *d* (flotation) 1·497. Dulcitol has *a* 8·61, *b* 11·60, *c* 9·05 Å., β 113° 45′, space-group C_{2h}^5, 4 mols. per unit cell, *d* 1·466. Mannose has *a* 7·62, *b* 18·18, *c* 5·67 Å., space-group Q_4, 4 mols. per unit cell, *d* 1·501. In each case the long dimension of the mol. corresponds with the *a*-axis. The alcohol mols. appear to have the long-chain configuration, the sugar mol. that of the mannopyranose ring. The relationship is traced between the structures of mannitol and dulcitol, and those of mannose and other saccharides. The area of cross-section of the alcohol end-group $CH_2\cdot OH$ is found to be 22·1 Å. from measurements on docosanol. This is in very fair agreement with the value 21·5 Å. obtained by Adam using a widely different method of measurement (*ibid.*, 1922, **A**, **101**, 452).

L. L. BIRCUMSHAW.

Interferometric determination of molecular form. II. H. MARK (Z. angew. Chem., 1931, **44**, 525—531; cf. this vol., 413).—A survey, with special reference to long-chain and simple aromatic compounds. H. F. GILLBE.

***X*-Ray examination of liquid-crystalline substances. II. Allyl phenetoleazoxybenzoate.** K. HERRMANN and A. H. KRUMMACHER (Z. Krist., **79**, 134—145; cf. this vol., 290).—*X*-Ray examination of the ester [solid $\longrightarrow$ fluid crystal I (smectic) 66° $\longrightarrow$ fluid crystal II (nematic) 77° $\longrightarrow$ amorphous liquid 95°] shows in the fluid crystal phases, with Cu-$K\alpha$ radiation, two rings, the inner due to white radiation (cf. A.,1930, 843), the outer corresponding with $d=$ 4·6 Å., a mean of the length 5·7 Å. and breadth 3·5 Å. of the mol. C. A. SILBERRAD.

***X*-Ray diffraction study of fractionated paraffin waxes.** G. L. CLARK and H. A. SMITH (Ind. Eng. Chem., 1931, **23**, 697—701).—Fractionated paraffin waxes were photographed (1) as very thin films, slowly cooled, by the oscillating method, (2) by the Laue method. The orders of diffraction due to oriented mols. varies directly with the m. p. of the fraction. From a consideration of the mol. refractions it is concluded that all the fractions contain both normal and *iso*-paraffins. In the 16 fractions studied 5 normal paraffin hydrocarbons were found that give an identity period diffraction. Two of these, $C_{38}H_{78}$ and $C_{42}H_{86}$, are new identifications. C. IRWIN.

Apparent crystallographic anomaly for choleic acid. R. O. HERZOG, O. KRATKY, and S. KURIYAMA (Naturwiss., 1931, **19**, 524—525).—The crystallographic investigation of choleic acid gives results which do not agree with the theory, so far as it requires the basic cell to be made up of a single mol., or a whole no. of mols. Reasons are put forward to explain the anomaly. A. J. MEE.

***X*-Ray studies of structure of hair, wool, and related fibres. I.** W. T. ASTBURY and A. STREET (Phil. Trans., 1931, **A**, **230**, 75—101).—All animal hairs give essentially the same *X*-ray diagram, the typical fibre diagram, presumably that of cryst. keratin. Only part of the hair substance is cryst. When the hair is stretched, this α-diagram is gradually replaced by another, the β-diagram. This transformation is reversible, and accounts quantitatively for various of the elastic properties of hair. It apparently depends on the elongation of an intramol. group of length 5·15 Å. to a group of length 6·64 Å. Hair in the β state is more readily attacked by Na_2S solution than it is in the α state, and it is likely that the β form is composed of mol. chains linked side to side by nuclei of cystine or cysteine. It is probable that unstretched fibrous keratin is built up of hexagonal ring systems linked along the fibre axis by bridge atoms. The lattice units seem to be of relatively low mol. wt., and the primary mol. grouping may be based on equimol. proportions of leucine, glutamic acid, cysteine, and arginine. Cystine has a hexagonal lattice with three mols. per cell, and a 9·40, c 9·42 Å. R. CUTHILL.

Changes in X-ray spectrum through swelling of cellulose in aqueous lithium thiocyanate solutions. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1931, **50**, 736—745).—The X-ray diffraction spectrum of cellulose is not changed by swelling in solutions of LiCNS containing less than 3·0 g. LiCNS per g. H_2O, but a new spectrum, due to a compound of cellulose and LiCNS, appears when cellulose swells in solutions containing more than 3·25 g. LiCNS per g. H_2O. E. S. HEDGES.

Lattice changes through swelling of cellulose acetate in aqueous lithium thiocyanate solutions. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1931, **50**, 746—752).—The X-ray diffraction spectrum of cellulose acetate is changed by swelling in conc. solutions of LiCNS, but not in dil. solutions. The change is due to an alteration in the lattice structure with formation of a compound, and not to the formation of an adsorption layer at the surface of the micelle. Unlike the results obtained with cellulose under similar conditions, no change occurs in the identity period in the direction of the fibre axis. E. S. HEDGES.

Magnetisation curve in strong fields. N. S. AKULOV (Z. Physik, 1931, **69**, 822—831).

Transverse effect of magnetostriction. A. ESAU (Physikal. Z., 1931, **32**, 483—485).—The transverse effect of magnetostriction can readily be calc. from the longitudinal and vol. effects. A. J. MEE.

Magnetic after-effect. H. KÜHLEWEIN (Physikal. Z., 1931, **32**, 472—480).—Two methods for determining the change of magnetisation with time are described. A. J. MEE.

Electrical resistance of nickel and iron wires as affected by longitudinal magnetic fields. O. STIERSTADT (Physical Rev., 1931, [ii], **37**, 1356—1366; cf. A., 1930, 984).—Available data are applied to a consideration of change of resistance in small fields and the early saturation of the magneto-resistance effect. N. M. BLIGH.

Magnesium and magnesium alloys. E. SCHIEBOLD, and G. SIEBEL (Z. Physik, 1931, **69**, 458—482).—X-Ray and micrographical study of the relative motion, during strain of a single Mg and Al–Zn–Mg crystal, of the crystal planes, and a study of the anisotropy of chemical attack; the basic crystal plane was most readily attacked. A. B. D. CASSIE.

Elastic anisotropy of iron. E. GOENS and E. SCHMID (Naturwiss., 1931, **19**, 520—524).—The elastic parameter of the Fe crystal is determined. Both the moduli of elasticity are greatly dependent on orientation of the crystal. A. J. MEE.

Impurities in metals. F. BITTER (Physical Rev., 1931, [ii], **37**, 1527—1547).—Mainly mathematical. The distorting effect of impurities in the crystal lattice is investigated; applications to ferromagnetic solutions are discussed. N. M. BLIGH.

Physical properties and classification of mesomorphic stases. G. FRIEDEL and E. FRIEDEL (Z. Krist., 1931, **79**, 1—60).—A proposed scheme of classification. C. A. SILBERRAD.

Chemistry of crystalline fluids. D. VORLÄNDER (Z. Krist., 1931, **79**, 61—89).—An account of the author's views on the connexion between the properties of cryst. fluids and mol. constitution. C. A. SILBERRAD.

Symmetry groups of the amorphous and mesomorphic phases. C. HERMAN (Z. Krist., 1931, **79**, 186—221).—The 18 structure types intermediate between those of a truly amorphous and of a truly cryst. substance are described. C. A. SILBERRAD.

Mesomorphic and colloid systems. WO. OSTWALD (Z. Krist., 1931, **79**, 222—254).—A discussion of the relations between these systems with reference to the varieties of mesomorphic systems, their forms, arrangements, and the size of the component elements, the effects of varying conditions, the degree of dispersion, viscosity, and electrophoresis. C. A. SILBERRAD.

Allotropy of phosphorus. V. N. IPATIEV, A. FROST, and A. V. VEDENSKI (Bull. Soc. chim., 1931, [iv], **49**, 670—680).—The ignition temp. and density of red P are independent of the pressure (1—200 atm.) at which the transition from the white form is effected. When white P is heated in N_2 at 330°/160 atm. a violet and a red modification are formed. The density of red P varies from 2·13 to 2·34 when the temp. of formation is raised from 210° to 590°. It is suggested that red P consists of extremely small particles of violet P (d 2·34) on which is adsorbed a more volatile and less dense variety; this view is supported by the increase of density observed when red P is heated at low temp. in vac. H. F. GILLBE.

Superheating of crystal nuclei. R. BLOCH, T. BRINGS, and W. KUHN (Z. physikal. Chem., 1931, **B**, **12**, 415—426).—Regarding fusion as a process of dissolution of a solid in its own liquid, it is shown from kinetic considerations that at const. temp. the linear dimensions of a crystal should decrease exponentially with time, so that extremely small crystals (nuclei) may have a comparatively long life. The duration of nuclei of salol at 23° above its m. p. is calc. to be 7 min., in approx. agreement with the observed time, 10 min. F. L. USHER.

Loss of recrystallising power by re-moulding. P. BECK and M. PÓLÁNYI (Naturwiss., 1931, **19**, 505—506).—The phenomena of recovery and recrystallisation are distinguished and discussed. A. J. MEE.

Refraction in hydrogen, oxygen, argon, and nitrogen. J. TAUSZ and H. GÖRLACHER (Z. tech. Physik, 1931, **12**, 19—24; Chem. Zentr., 1931, i, 1571—1572).—The following values of x (where $n=1+x\times10^{-8}$) are recorded for 6564, 5876, 5461, and 4358 Å., respectively: H_2 13869, 13963, 14018, 14188; O_2 27008, 27151, 27227, 27627; A 28110, 28237, 28314, 28611; N_2 29729, 29842, 29914, 30226. A. A. ELDRIDGE.

B. p. of water as a function of pressure. A. Bonhoure and A. Zmaczyński (Rocz. Chem., 1931, **11**, 354—361).—The b. p. of water determined by means of Swientoslawski's ebullioscope, and resistance thermometers, at 683—832 mm. Hg is $\theta=57\cdot2587+79\cdot3722\times10^{-3}p-35\cdot5273\times10^{-6}p^2+6\cdot695\times10^{-9}p^3$, where p is the pressure in mm. Hg.
R. Truszkowski.

F. p. of naphthalene for standardisation of mercury thermometers. P. de Beule (Bull. Soc. chim. Belg., 1931, **40**, 195—200).—$C_{10}H_8$, purified by recrystallisation from Et_2O, has m. p. 80·21—80·23°; considerable irregularities occur among the individual measurements, as a result of slow solidification and other factors. $C_{10}H_8$ is unsuitable as a thermometric standard. H. F. Gillbe.

Calculation of heats of dissociation from electrolytic conductivity. J. Zirkler (Z. Physik, 1931, **69**, 515—525).—Using Nernst's method of calculating heats of dissociation from the chemical const., heats of dissociation can be deduced from the temp. coeff. of the conductivity of electrolytes. The conductivities of KI, KBr, KCl, KNO_3, $AgNO_3$, $TlNO_3$, $CuSO_4$, $ZnSO_4$, and $MgSO_4$ were accurately determined between 0° and 26° and for concentrations between $0\cdot1N$ and $0\cdot001N$, and from them were determined heats of dissociation and of dilution; the results show a general deviation, but no sp. error, due to the Debye effect. A. B. D. Cassie.

Variation of the specific heats (C_p) of oxygen, nitrogen, and hydrogen with pressure. E. J. Workman (Physical Rev., 1931, [ii], **37**, 1345—1355; cf. A., 1930, 1508).—Data are recorded and plotted for the pressure range 10—130 kg. per sq. cm.
N. M. Bligh.

M. p. and heats of crystallisation of the normal long-chain hydrocarbons. W. E. Garner, (Miss) K. Van Bibber, and (Miss) A. M. King (J.C.S., 1931, 1533—1541; cf. A., 1929, 1225).—Heats of crystallisation, Q, of the α and β forms of the following hydrocarbons are, respectively, $C_{22}H_{46}$, 11·7, 18·6; $C_{26}H_{54}$, 14·04, 22·41; $C_{30}H_{62}$, 16·45, 25·17; $C_{34}H_{70}$, 19·11, 30·59; $C_{35}H_{72}$, 20·65, 30·47 kg.-cal. per mol. Q and Q/T are linear functions of the no. of C atoms. An empirical expression is found for the f. p. of the hydrocarbons, giving good agreement with observed values between C_{20} and C_{70}; the convergence temp. is 135°. The increment of Q for the Me group is 0·608 for the α- and 1·0 kg.-cal. for the β-forms. The heat of transition (α—β) is 6—11 kg.-cal., and varies with chain length.
N. M. Bligh.

Thermal energy of hydrogen-charged palladium, iron, and palladium–silver alloys. R. Nübel (Ann. Physik, 1931, [v], **9**, 826—838).—The thermal energy depends on the amount of H_2 adsorbed and on the nature of the electrolytes. With Pd and Pd–Ag alloys the thermal energy increases with the concentration of the electrolyte and has its peak value at N-H_2SO_4. W. R. Angus.

Change of density of nitrobenzene with temperature. J. Mazur (Nature, 1931, **127**, 893—894; cf. this vol., 148).—$PhNO_2$ has d^{20} 1·1916, rising to $d^{9\cdot8}$ [?$d^{9\cdot5}$] 1·2134; a sharp change then occurs in the slope of the density–temp. curve. At the f. p., 5·5°, d is 1·2569. L. S. Theobald.

Thermodynamical studies. A. Press (Z. Physik, 1931, **69**, 483—494).—Theoretical. A new general equation of state is deduced from classical considerations, and from this equation is deduced a more general entropy expression for the Willard Gibbs transformation for the (p,v) plane.
A. B. D. Cassie.

Densities of *iso*propyl and *n*-butyl alcohols at low temperature. T. Tonomura and K. Uehara (Bull. Chem. Soc. Japan, 1931, **6**, 118—124).—Data are given for $Pr^{\beta}OH$ and BuOH for the temp. intervals 0° to −106° and 0° to −80°, respectively, together with interpolation formulæ. H. F. Gillbe.

Lithium hydride. H. Bode (Z. physikal. Chem., 1931, **B**, **13**, 99—104).—The values of $0\cdot70_5\pm0\cdot02$ and 1·615 have been obtained for d and n_D, respectively. The value of 4·21 Å. is deduced for the lattice const. R. Cuthill.

Coefficient of expansion of gallium and the value of αT_s for the elements. W. Klemm (Z. anorg. Chem., 1931, **198**, 178—183).—Specimens of Ga and Bi, after being maintained at a low temp. (−78°) for several months, underwent no vol. change, and therefore no transition. The temp. coeff. of expansion of Ga, α, is $5\cdot3(\pm0\cdot5)\times10^{-5}$ for the interval 18° to −78·3°. The relationship between the m. p. (abs.) and values of α for the elements is discussed.
H. F. Gillbe.

Compressibilities of the permanent gases. W. Wild (Phil. Mag., 1931, [vii], **12**, 41—49).—Data for the coeff. p_0v_0/p_1v_1, required in determining at. wt. by the limiting density method, obtained from high- and low-pressure experiments on H_2, N_2, O_2, He, and A are compared. N. M. Bligh.

Explicit formulæ for slip and fluidity. M. Mooney (J. Rheology, 1931, **2**, 210—222).

Law of elasticity for isotropic and quasi-isotropic substances by finite deformations. H. Hencky (J. Rheology, 1931, **2**, 169—174).

Inner friction and the liquid state. N. Gerasimov (Physikal. Z., 1931, **32**, 444—450).—Theoretical. A. J. Mee.

Calculation of critical viscosity and applicability of Stokes' law [with Tausz ball viscosimeter]. A. Rabl and F. Geiger (Petroleum, 1931, **27**, 439—442).—A new formula indicates the extreme limit of Stokes' law. It is analogous to Reynolds' data for concentric cylinder and capillary systems.
E. Doctor.

Viscosities of *iso*propyl and *n*-butyl alcohols at low temperatures. T. Tonomura (Bull. Chem. Soc. Japan, 1931, **6**, 124—126).—Data obtained by the modified Ostwald viscosimeter are given for the temp. interval 0° to −60°. For $Pr^{\beta}OH$, $\log\eta=5\cdot4727+1127\cdot09t$ and for BuOH $\log\eta=5\cdot0562+1051(t-5\cdot2)$. H. F. Gillbe.

Diffusion problem for a solid in contact with a stirred liquid. T. E. W. Schumann (Physical Rev., 1931, [ii], **37**, 1508—1515).—Mathematical.
N. M. Bligh.

Specific heat of binary liquid mixtures. K. M. Stachorski (Ukrain. Chem. J., 1930, **5**, [Sci.], 317—331).—The association factor of alcohols in C_6H_6 solution, as deduced from sp. heat measurements, varies from 1·24 in 3·52% to 3 in 100% MeOH, and from 1·37 in 3·62% to 2·5 in 100% EtOH. The association factor of H_2O in $CaCl_2$ solutions is similarly calc. to be 3. R. Truszkowski.

Method of calculating [the partial vapour pressures of liquid mixtures] by means of distillation experiments. G. Bozza (Atti R. Accad. Lincei, 1930, [vi], **12**, 675—681).—Mathematical (cf. A., 1914, ii, 766). O. J. Walker.

Dielectric constants of binary mixtures. XII. Dipole moment data for (A) naphthalene and its derivatives, (B) α- and β-benzene hexachlorides. J. W. Williams and J. M. Fogelberg (J. Amer. Chem. Soc., 1931, **53**, 2096—2104).—Dielectric const. and density data at 25° for C_6H_6 solutions are tabulated, and the following electric moments are recorded: $C_{10}H_8$ and 2 : 6-dichloronaphthalene 0 (cf. A., 1928, 229); α-$C_6H_6Cl_6$ $2{\cdot}15\times10^{-18}$; β-$C_6H_6Cl_6$ $0{\cdot}7\times10^{-18}$ e.s.u. The results indicate an extended rather than a folded arrangement of the C_6H_6 rings in the $C_{10}H_8$ derivatives, and further that in the hexachlorides there is a strong interaction between the Cl atoms accounting for the unpredicted moment of β-$C_6H_6Cl_6$ (cf. this vol., 24). J. G. A. Griffiths.

Diamagnetism of liquid mixtures. S. P. Ranganadham (Nature, 1931, **127**, 975).—Mixtures of C_6H_6 and CCl_4 show no deviation from the additive law, and those of $COMe_2$ and $CHCl_3$ only a slight deviation at the concentration for which density deviation is greatest (cf. this vol., 676). L. S. Theobald.

Interatomic forces in binary liquid alloys. Determination from thermodynamic data. N. W. Taylor (J. Amer. Chem. Soc., 1931, **53**, 2421—2423; cf. A., 1929, 398, 1374).—Existing data for Zn–Cd, Cd–Pb, Cd–Sn, and Tl–Sn liquid alloys support Langmuir's theory. The discrepancies in the Zn–Sn system are attributed to factors inhibiting random orientation of the mols. (A., 1924, ii, 89). J. G. A. Griffiths.

Periodic phenomenon for alcoholic, aqueous, and other mixtures. J. Plotnikov and S. Nishigishi (Physikal. Z., 1931, **32**, 434—444).—The Plotnikov light-scattering effect affords a very sensitive method of showing the variation in complexity of large mol. complexes. By using this method periodic phenomena connected with mol. complexity were observed for aq. solutions of MeOH, EtOH, PrOH, $COMe_2$, glycerol, CH_2O, H_2O_2, sucrose, and various salt and acid solutions. The amplitude and wave period of the periods are functions of temp. and concentration. For pure H_2O, the higher the temp. the smaller is the amplitude, whilst there is a characteristic change in the type of scattering in the range 28—44°. The importance of these periodic phenomena in biological processes is discussed. A. J. Mee.

Equilibrium diagram of copper–tin alloys. M. Hamasumi and S. Nishigori (J. Study Met., 1930, **7**, 535—551).—The change in electrical resistance on heating and the thermal dilatation have been measured, and the quenched bars subjected to thermal and microscopical examination. The compounds Cu_3Sn_8 (δ) and Cu_3Sn (η) exist; at 675° η affords the solid solution γ. There are 3 eutectoid transformations at 510° ($\alpha+\delta\rightleftharpoons\beta$), 570° ($\delta+\eta\rightleftharpoons\varepsilon$), and 630° ($\beta+\eta\rightleftharpoons\gamma$), and 2 peritectic transformations at 580° ($\delta\rightleftharpoons\beta+\varepsilon$) and 625° ($\varepsilon\rightleftharpoons\beta+\eta$). The existence of the new phase ε is proved microscopically. Chemical Abstracts.

Structure analogies of intermetallic phases. A. Westgren and W. Ekman (Arkiv Kemi, Min., Geol., 1931, **10**, *B*, No. 11, 6 pp.).—Recent research has shown that many binary intermetallic compounds have structures analogous to those of β- and γ-brass; in all these alloys one of the constituents is always a metal of the transition group or Cu, Ag, or Au, and the atoms of these metals do not appear to contribute any of their electrons to those common to the lattice, but act as if they had a valency of zero. Phases having the β-brass structure are NiAl and CoAl. Further investigation of the phase previously formulated as Fe_3Zn_{10} shows that it has the γ-structure and should therefore be more correctly formulated as Fe_5Zn_{21}. Phases of the same structure and composition have been prepared by heating Zn or Cd with the transition elements in sealed quartz tubes at 1000°; Co_5Zn_{21}, Ni_5Zn_{21}, Rh_5Zn_{21}, and Pd_5Zn_{21} have a body-centred cubic lattice, Ni_5Cd_{21} has a simple cubic lattice, and Pt_5Zn_{21} a face-centred cubic lattice with a parameter double that of the others. A. R. Powell.

Equilibrium diagram of calcium–sodium alloys. E. Rinck (Compt. rend., 1931, **192**, 1378—1381).—Using Ca distilled in vac. (m. p. 848°), the data obtained in an atm. of A afford no evidence of compound formation. The liquidus is horizontal at 710° from 7 to 86% Ca, Ca being sol. in Na to the extent of 7% and Na in Ca to 15%. Complete miscibility occurs at 1185° (cf. A., 1930, 1252). Caβ changes to Caα at 450° (cf. this vol., 416). C. A. Silberrad.

Change in the elastic modulus of Au–Cu alloys with transition to single crystal form. H. Röhl (Z. Physik, 1931, **69**, 309—312).—Young's modulus for the Au–Cu alloy diminishes as the atoms assume a regular structure. A. B. D. Cassie.

Lead alloys. B. Garre and A. Müller (Z. anorg. Chem., 1931, **198**, 297—309).—Alloys of Pb, Cd, and Sb harden considerably on quenching from about 200°, and the hardening continues at room temp. The effect, which is independent of cold-working, is a max. in alloys containing 2·5% CdSb, and increases with rise of the quenching temp. With alloys of certain composition hardening occurs even on slow cooling. The corrosion-resistance of the alloys towards H_2SO_4 is scarcely altered by hardening, but the electrical resistance of the quenched alloys diminishes with time. The presence of Sn tends to prevent hardening of Pb alloys. Cold-working causes Pb–Sn alloys to become softer, the max. hardness being at 8% Sn and the max. softening effect at the eutectic point (64% Sn), whereas the hardness of the cast alloys is a max. when the composition is that of the eutectic. The brittleness which appears in commercial Pb on heating to just below the m. p. is the result of the melting of the Pb–Sb eutectic, but pure, coarsely crystalline Pb also exhibits brittleness under certain conditions. H. F. Gillbe.

Crystal structures of electrodeposited alloys. Silver–cadmium. C. W. Stillwell (J. Amer. Chem. Soc., 1931, 53, 2416—2417).—In contrast to results with thermal alloys (A., 1928, 1175), the X-ray structure of electrodeposited alloys, containing 20—96% Cd, shows that with 40% Cd the α, β', and γ phases, and possibly β, are present, whilst with 46—75% of Cd, only ε (apparently metastable between 46 and 66% of Cd) is deposited. With 89—96% Cd, ε and η are deposited. J. G. A. Griffiths.

Ternary eutectic in aluminium–silicon–beryllium alloys. W. Kroll and E. Jess (Wiss. Veröff. Siemens-Konz., 1931, 10, [2], 25—28).—The eutectic composition, determined by micrographical examination of specimens annealed for long periods at 500—520°, is 13·4% Si and 0·75% Be. A. R. Powell.

Crystalline form in the formation of solid solutions. VII. Thermal analysis of the anhydrous systems $SrCl_2$–$FeCl_2$, $SrCl_2$–$CoCl_2$, $ZnCl_2$–$FeCl_2$, and $ZnCl_2$–$CoCl_2$. A. Ferrari and A. Inganni (Atti R. Accad. Lincei, 1930, [vi], 12, 668—675; cf. A., 1930, 285).—The first two systems show no miscibility in the solid state; eutectics occur at 541° (50 mol.-% $FeCl_2$) and 564° (40·5 mol.-% $CoCl_2$), respectively. In the $ZnCl_2$ systems there is also no miscibility, and the eutectic temp. is the same as the m. p. of $ZnCl_2$ (300°). Complete miscibility would be expected if $ZnCl_2$ had a rhombohedral structure of the $MgCl_2$ type. O. J. Walker.

Crystalline form in the formation of solid solutions. VIII. Thermal and X-ray analysis of the anhydrous system Li_2Br_2–$MgBr_2$. A. Ferrari and C. Colla (Atti R. Accad. Lincei, 1931, [vi], 13, 78—80).—Two series of mixed crystals are formed, one having the $MgBr_2$ structure (up to 35 mol.-% $MgBr_2$), the other of the Li_2Br_2 type (up to 60 mol.-% $MgBr_2$) with a small region of incomplete miscibility between the two. O. J. Walker.

Mixed crystal formation in molecular lattices by irregular exchange of molecules. L. Vegard (Naturwiss., 1931, 19, 443).—Substances with analogous mol. lattices form mixed crystals by the interchange of mol. groups. A. J. Mee.

F. p. and b. p. of the ternary system ethyl alcohol–methyl alcohol–water. E. W. Aldrich and D. W. Querfeld (Ind. Eng. Chem., 1931, 23, 708—711).—Mixtures of MeOH and EtOH in various proportions were diluted with H_2O and the f. p. and b. p. of solutions of different concentrations determined. Each of these for a given aq. solution falls uniformly as the EtOH is gradually replaced by the MeOH. As a rule the b. p. differences are only small. C. Irwin.

Electrical energy of dipole molecules in solution, and the solubilities of ammonia, hydrogen chloride, and hydrogen sulphide in various solvents. R. P. Bell (J.C.S., 1931, 1371—1382).—Existing data for the solubility of Hg halides in various solvents support the hypothesis that the energy of transference of a dipole mol. from one continuous medium to another is equal to the change of energy of the electrical field of the dipole. The solubilities of HCl, H_2S, and NH_3 in hydrocarbons and halogenated hydrocarbons tend to increase with increase of the dielectric const. of the solvent, but the measurements indicate that the media cannot be regarded as homogeneous, probably because of displacement of the solvent mols. by those of the solute and not because of deformation of the latter. Nevertheless, even for solvents of low dielectric const., the energy of the dipoles may influence the solubility considerably. H. F. Gillbe.

Water content of benzene. A. W. C. Menzies (J. Physical Chem., 1931, 35, 1655—1659).—The H_2O content of C_6H_6 at its b. p. has been determined by the author's apparatus for measuring the v.-p. lowering of a solvent and by determining the v. p. corresponding with the equilibrium $ZnSO_4,(NH_4)_2SO_4,6H_2O \rightleftharpoons ZnSO_4,(NH_4)_2SO_4,2H_2O+4H_2O$. When one fourth of a sample of ordinary, undried C_6H_6 is distilled at 1 atm. the residue contains less H_2O than that which changes the b. p. by 0·1°. C_6H_6 dried by Na contains less H_2O than that which alters the b. p. by 0·01°. The bearing of the results on work with intensively dried C_6H_6 is discussed. L. S. Theobald.

Solubility of barium sulphate in sulphuric acid. N. R. Trenner and H. A. Taylor (J. Physical Chem., 1931, 35, 1336—1344).—The system $BaSO_4$–H_2SO_4–H_2O, investigated at 25° for 83—100% H_2SO_4, has only two solid phases, $BaSO_4$ and probably $BaSO_4,H_2SO_4$, with a transition at approx. 85% of acid. The solubility in abs. H_2SO_4 is 15·89 wt.-%. Compound formation has been distinguished from solid solution and adsorption by a conductance method. κ for abs. H_2SO_4 is 1045×10^{-6} ohm^{-1} (cf. A., 1909, ii, 38). L. S. Theobald.

Solubility of picric acid and naphthalene picrate. L. Piatti (Z. angew. Chem., 1931, 44, 519—520).—The solubilities of picric acid and naphthalene picrate in C_6H_6 and tetrahydronaphthalene have been measured at different temps. The solubility rises steeply with rise of temp. The results are discussed in connexion with the determination of picric acid. E. S. Hedges.

Solubility of naphthalene in some derivatives of furfuraldehyde. A. S. Sunier (J. Physical Chem., 1931, 35, 1756—1761).—Solubility data obtained by the synthetic method for temp. between 20° and 75° are recorded in furfuryl alcohol, the acetate, and in Me, Et, Pr, and Bu furoates. Certain regularities are discussed. L. S. Theobald.

Solubilities of the soluble electrolytes. V. Estimation of the radii of ions in saturated solutions. A. F. Scott (J. Physical Chem., 1931, 35, 1410—1417; cf. A., 1930, 1362).—The empirical relationship $V^{2/3}=\alpha N+\beta$ between the vol., V, of a saturated solution and the solubility, N, of the saturating salt is discussed, and the radii of individual ions for the limiting state when no H_2O is present are calc. The apparent radii thus found are, for certain alkali salts, generally larger than the corresponding radii in the cryst. state and smaller than in dil. solution. In the saturated state, the effective vol. of the anions may be the same as in dil. solutions, whilst those of the cations may be approx. the same as in the cryst. state. L. S. THEOBALD.

Crystals of lower refractive index than the mother-liquor. E. GILTAY (Chem. Weekblad, 1931, 28, 395).—The coloration observed when Na_2SiF_6 is precipitated from aq. solution is ascribed to the lower refractive index of the crystals compared with that of the solution. H. F. GILLBE.

Cyclic separation of two salts. A. V. RAKOVSKI (Trans. Inst. Pure Chem. Reag., 1931, 11, 62—113).—From an examination of the theory of the separation by crystallisation from solution of two salts which do not form double salts a cyclic process giving any required degree of purification has been devised. Methods of washing are also considered.
R. CUTHILL.

Influence of traces of water on solution equilibria. S. MIYAKE (Mem. Coll. Eng. Kyushu, 1931, 6, 1—114).—The solubility of a number of org. compounds in a variety of completely anhyd. org. solvents has been determined. Traces of H_2O cause in general a marked increase of the solubility, and the results are therefore lower than those in the lit. The percentage increase rises at first with increasing dielectric const. and internal pressure of the solvent, and, after passing through a max., diminishes. It is suggested that the H_2O added, on account of its highly polar nature, causes deformation of the dipoles of the other components, and consequently an increase of the dipole moment; as a result the solvation, and therefore the solubility, of the solute is increased. If the solute mols. are associated when in solution, and addition of H_2O diminishes the degree of association, the decreased size of the solute mols. causes an increase of the forces of attraction between the solvent and solute, and the solubility again tends to increase. This view is confirmed by measurements of the mol. wt. by the f.-p. method for certain systems in which the increase of solubility is especially pronounced; addition of H_2O causes an increase of the number of smaller mols. Hildebrand's theory of solution is supported by the measurements. The influence of miscibility of the solvents on the distribution coeff. of various solutes between H_2O and C_6H_6 or CCl_4 has been studied. A method for the determination of traces of H_2O in org. solvents by measurement of the increase of solubility of a given solute is described. Results for H_2O and C_6H_6 yield for the heat of dissolution at 23° 8·016 kg.-cal. per mol. H. F. GILLBE.

Distribution of ammonia between chloroform and water at 25°. V. J. OCCLESHAW (J.C.S., 1931, 1436—1438).—The distribution coeff. K of NH_3 between $CHCl_3$ and H_2O at 25° for aq. solutions from 0·1388 to 1·022M is given by K=24·10—28·45c, where c is the concentration in the $CHCl_3$ layer. A const. is not obtained if correction is made for the equilibrium $NH_3+H_2O \rightleftharpoons NH_4^{\cdot}+OH'$, but K still decreases with rise of the NH_3 concentration.
H. F. GILLBE.

Determination of sorption isothermals on charcoal by the retentivity technique. Experiments with carbon tetrachloride and water. A. J. ALLMAND and L. J. BURRAGE (J. Physical Chem., 1931, 35, 1692—1703).—Details of the results previously reported (A., 1930, 1513) are given and the discontinuous nature of the isotherms is discussed.
L. S. THEOBALD.

Rate of sorption of ammonia on meerschaum. M. G. EVANS (Trans. Faraday Soc., 1931, 27, 333—340).—The form of the curves representing the progress of the sorption of NH_3 by meerschaum varies with the temp. at which the latter is initially outgassed, and is possibly a consequence of the presence of both a cryst. and a gel constituent. The Freundlich isotherm is applicable, except at the higher pressures, and the total amount of NH_3 sorbed decreases as the amount of H_2O present diminishes.
R. CUTHILL.

Sorption of ammonia on chabazite. M. G. EVANS (J.C.S., 1931, 1556—1564).—The H_2O in chabazite is probably loosely held and not present in chemical combination, since the hydration and dehydration curves are smooth, and the processes are reversible and without hysteresis. The rate of sorption of NH_3 is greater for dehydrated than for hydrated chabazite. The sorption-pressure curves conform to the Langmuir isotherm, and the heat of sorption is a linear function of the sorption.
H. F. GILLBE.

Adsorption of iodine on thin layers of sublimed calcium fluoride. J. H. DE BOER [with J. BROOS] (Z. physikal. Chem., 1931, B, 13, 134—154).—The adsorption of I on CaF_2 sublimed in vac. may be represented by the isotherm previously deduced (A., 1929, 875). Adsorption apparently occurs on the F ions. R. CUTHILL.

Molecular and activated adsorption of hydrogen on manganous oxide surfaces. H. S. TAYLOR and A. T. WILLIAMSON (J. Amer. Chem. Soc., 1931, 53, 2168—2180; cf. this vol., 421).—Data for the adsorption and rate of adsorption of H_2 by MnO and MnO–Cr_2O_3 surfaces between —78·5° and 450° are recorded. At the lower temps., the H_2 is reversibly and rapidly adsorbed by MnO–Cr_2O_3 with negligible energy of activation and a heat of adsorption of about 1900 g.-cal. per mol. (" molecular " adsorption). The second type of adsorption (" activated ") becomes prominent above 0° and the energy of activation increases from 6000 to 10,000 as successive portions of the MnO–Cr_2O_3 surface are covered. At about 300°, the heat of adsorption is of the order 20,000. Thus, at const. pressure and with rise of temp. the adsorption passes through a min. at about 0° and then increases to a max. between 200° and 300°, finally decreasing again at still higher temp.

Both types of adsorption are exhibited by CO on MnO–Cr_2O_3 surfaces between —78·5° and 450°.
J. G. A. GRIFFITHS.

Adsorption of hydrogen by nickel poisoned with carbon monoxide. T. A. WHITE and A. F. BENTON (J. Physical Chem., 1931, 35, 1784—1789).—At 0°, small amounts of CO increase the quantity of H_2 adsorbed by Ni at all pressures up to 1 atm.;

larger amounts only decrease the rate of adsorption. At −183°, the H_2 adsorbed at pressures up to 1 atm. is decreased by an amount approx. equal to the amount of CO used. The poisoning action of CO in hydrogenations using Ni is discussed.

L. S. Theobald.

Effect of the ignition loss on the adsorptive power of decolorising clays. O. Eckart (Z. angew. Chem., 1931, **44**, 326—327).—Tests on numerous types of decolorising clays show that there is no relation between their decolorising power and the loss on ignition. This loss is due entirely to H_2O of constitution and not to adsorbed H_2O; prolonged cleaning of the clay with dil. acids or the use of too highly conc. acids results in partial decomp. of the hydrated silicates in the clay and a corresponding decrease in the decolorising power. A. R. Powell.

Condition of the surface of platinised charcoal in the simultaneous presence of hydrogen and oxygen, and the mode of action of active centres. A. Frumkin, S. Levina, and O. Zarubina (Z. physikal. Chem., 1931, **155**, 41—50).—The alteration in the potential of platinised charcoal in an atm. of H_2 from positive to negative with increasing Pt content (A., 1929, 640) raises the question as to whether, in the intermediate neutral state, the surface (i) possesses an equal number of positive and negative centres, or (ii) is at the same potential throughout. Since positive charcoal adsorbs the anion and negative charcoal the cation from neutral salts, neutral charcoal will adsorb (i) both or (ii) neither. Experiments on the adsorption of 0·01*N*-NaCl solution by charcoals with different Pt contents show (ii) to be correct, as do experiments in which the composition of the charcoal (0·5% Pt) and solution (0·01*N*-NaCl) are fixed and the composition of the atm., H_2+O_2, is varied. In the former series the neutral charcoal contained 0·002—0·003% Pt, which corresponds with a covering of only about 0·002% of the charcoal surface by the Pt even if the Pt is in a unimol. layer, which from *X*-ray photographs of more highly platinised charcoals seems doubtful. The ability of such a small covering of Pt to promote a uniform potential is discussed, and it is suggested that the results are of significance in the theory of heterogeneous catalysis.

N. H. Hartshorne.

Determination of the energy level of adsorbed hydrogen and oxygen by the method of electron bombardment. N. I. Kobosev and V. L. Anochin (Z. physikal. Chem., 1931, B, **13**, 18—62).—The desorption of H_2 and O_2 from Pt as a result of ionisation caused by bombardment with electrons has been studied. The curve representing the relation between the energy of the electrons and their desorbing power towards H_2 shows three well-defined maxima. These represent the ionising potentials of H_2 adsorbed on the faces, edges, and corners of crystals; the adsorbed H_2 is apparently in the at. state. Adsorbed O_2 also exhibits definite ionisation potentials, but is in both the at. and mol. states. With both O_2 and H_2 the firmness with which the gas as a whole is held increases as the amount of adsorbed gas diminishes, and also, with O_2, as the roughness of the metal surface increases. At saturation with either H_2 or O_2, 12—15% of the surface is filled, the three types of adsorption occurring to approx. equal extents. This is of the same order as the value for the active surface calc. from kinetic data. With Pt the adsorption complex seems to be PtH_2. The rate of desorption of H_2 follows the unimol. law at the start, but ultimately becomes const. owing to the loss by desorption being compensated by diffusion from the interior of the metal. O_2 diffuses much less rapidly than H_2. H_2 is adsorbed more tenaciously than O_2 and readily displaces O_2. Nevertheless, adsorbed O_2 and H_2 can be present simultaneously. In this case, the H_2 is largely in the interior of the metal, whilst the O_2 is on the surface, and prevents the diffusion of the H_2 from the interior. The desorption of H_2 from Pd is essentially similar to that from Pt. The order of the desorption potentials of H_2 from a series of metals is exactly opposite to that of the H_2 overvoltages of the same metals, which confirms the theory of overvoltage previously advanced (A., 1930, 1254). R. Cuthill.

Translational motion of molecules in the adsorbed phase on solids. D. H. Bangham and N. Fakhoury (J.C.S., 1931, 1324—1333).—Comparisons of Schofield and Rideal's equation of state for two-dimensional adsorbed films with the equation relating the quantity adsorbed *S* with the linear expansion *x* of the adsorbent suggest that films of H_2O, CO_2, NH_3, and SO_2 behave as two-dimensional gases. The curves of $Mx/S-x$ resemble the $PV-P$ curves of imperfect gases, but those for C_6H_6 and pyridine are of a different form; in all cases they become linear at high surface concentrations. The hypothesis is supported by the agreement of the observed *S*–pressure curves with the curves derived by combining Gibbs' equation with the two-dimensional equation of state. The Langmuir isotherm cannot apply to a mobile phase, as it ignores the finite area of the min. space necessary for the condensation of a mol. H. F. Gillbe.

Influence of neutral salts on properties of solutions of non-electrolytes. I. Adsorption of phenol and benzoic acid by charcoal. P. P. Kozakievitsch and N. A. Izmailov. **II. Capillary activity of organic solutes.** P. P. Kozakievitsch and N. S. Kozakievitsch (J. Gen. Chem. Russ., 1931, 1, 105—120, 121—132).—I. The adsorption by charcoal of PhOH from aq. solution and of BzOH from alcoholic solutions is increased by addition of alkali halides; in H_2O and MeOH solutions the activity of ions diminishes in the order $Cl>Br$ and $Na>Li>K$, whilst in EtOH $Br>Cl$. The action of salts is a function of their solvation.

II. The surface activity of PhOH, *o*-cresol, thymol, and menthol is augmented by ions in the order $Cl>Br>I$, and in the case of menthol $Na>Li$. Schofield and Rideal's (A., 1925, ii, 960) formula, $FA/RT-BF/RT=x$, is applicable to the surface layer of PhOH, *o*-cresol, and thymol, but not of menthol solutions. The relation between FA/RT and F, where F is the depression of surface tension and A the area occupied by 1 mol. of the surface-active substance on the surface of the solution, is unaffected by the presence of salts if the activity and not the concentration of the non-electrolyte is considered. The above formula is applicable to the calculation of the activity of non-electrolytes in salt solutions.

R. Truszkowski.

Adsorption in binary systems of electrolytes. (Mlle.) L. S. Lévy (Ann. Chim., 1931, [x], **15**, 85—200).—The adsorption of an electrolyte by MnO_2, in presence of a second electrolyte at various concentrations, can be represented by the Freundlich equation. The consts. depend on the nature of the second component and vary in a simple manner with its concentration, and since the isotherms intersect those obtained for the electrolyte when present alone, the second substance is able to depress or increase the adsorption according to its relative concentration. Hydrolysis plays an important rôle in the mechanism of the process, since if the hydroxide of the second component tends to enhance the stability of the colloidal hydroxide of the adsorbed salt the adsorption is increased, and *vice versa*. The influence of aq. NH_3 on the adsorption by $Fe(OH)_3$ of $Cu^{\cdot\cdot}$ and $Ni^{\cdot\cdot}$, present separately or simultaneously, is due partly to its influence on the p_H of the solution and partly to the formation of complexes, and at higher concentrations, to the stabilisation of such complexes. Measurements of the adsorption of $Mn^{\cdot\cdot}$ by MnO_2 demonstrate the existence of an adsorption equilibrium, and data for the replacement of the $Mn^{\cdot\cdot}$ by other metal ions indicate the existence of a displacement equilibrium.

H. F. Gillbe.

Adsorption equilibria on precipitated manganese dioxide. (Mlle.) L. S. Levy (Compt. rend., 1931, **192**, 1376—1378; cf. B., 1927, 205; A., 1927, 407).—In the adsorption of $Mn^{\cdot\cdot}$ from a solution of a $Mn^{\cdot\cdot}$ salt (0·001N) by MnO_2, equilibrium is reached in 1 hr., and remains const. for at least 50 hr. From a solution of p_H 1·4 it is about 2·4 times that from one of p_H 0·6. On addition of a $Cu^{\cdot\cdot}$ salt the ratio of $Mn^{\cdot\cdot}$ displaced to $Cu^{\cdot\cdot}$ adsorbed is a function of the initial concentration of $Mn^{\cdot}$, and for small additions is const. It is independent of the p_H.

C. A. Silberrad.

Relation between gas content and adsorption of electrolytes by activated charcoal. VI. B. Bruns and A. Pilojan (Z. physikal. Chem., 1931, **155**, 77—83; cf. this vol., 34).—The adsorption of H_2SO_4 in dil. solution by activated charcoal in an atm. of O_2 is accompanied by adsorption of O_2 (cf. A., 1930, 684). Activated charcoal is oxidised by O_2 even at room temp., but this effect was satisfactorily controlled and allowed for by working at 0° and by previously determining the rate of disappearance of O_2 due to oxidation. More equivs. of electrolyte than of gas are adsorbed, as in the case of alkali and H_2, but the difference is here much greater. This is attributed to the supply of chemically bound or ionised O on the charcoal surface being greater than that of H_2, and also, possibly, to mol. adsorption of the H_2SO_4.

On addition of NaOH to activated charcoal carrying H_2SO_4 adsorbed as above, evolution of O_2 does not occur, owing not to the formation of CO_2 by the O_2, but to the formation of alkali-adsorbing oxides similar to those obtained when charcoal is heated to 300—400° in presence of O_2 (cf. A., 1929, 261).

N. H. Hartshorne.

Adsorption of solutes by crystals in relation to compatibility of space lattice. C. A. Sloat and A. W. C. Menzies (J. Physical Chem., 1931, **35**, 2022—2025).—The amounts of the bromides of Li, Na, K, Rb, Cs, and NH_4 adsorbed by PbS at 25° depend mainly on the solubility of the bromide in H_2O. Adsorption does not appear to be related to lattice dimension or to orientation of the deposited salt on the substrate.

L. S. Theobald.

Solubility as a complicating factor in adsorption measurements at gas-solid interfaces. E. W. R. Steacie (J. Physical Chem., 1931, **35**, 2112—2117).—Evidence supporting the hypothesis of an activation energy for adsorption processes (this vol., 421) is re-examined. It is concluded that the hypothesis is not of general applicability and that irreversible adsorption and slow effects accompanying adsorption processes can be explained by existing data for the solubility of gases in solids.

L. S. Theobald.

Heat of adsorption of hydrogen and carbon monoxide on zinc and chromium oxide catalysts. W. E. Garner and F. E. T. Kingman (Trans. Faraday Soc., 1931, **27**, 322—333).—The heat of adsorption of H_2 and CO on ZnO and Cr_2O_3 and ZnO–Cr_2O_3 catalysts is a max. in the initial stage of the process. Since the heat of adsorption of CO on a mixed catalyst is the same as that on ZnO, the promoter action of the Cr_2O_3 must be attributed to its increasing the internal surface of the catalyst; Cr_2O_3 has, however, considerable adsorptive power for CO. The mixed catalyst adsorbs H_2 more strongly than either oxide singly. At low temps. H_2 and CO are largely adsorbed without dissociation of the mols., and the adsorption is partly reversible, whereas at 100° or above adsorption is irreversible, and the gas is then released only at high temp. in the form of H_2O or CO_2.

R. Cuthill.

Reflexion of vapour molecules at a liquid surface. T. Alty (Proc. Roy. Soc., 1931, **A**, **131**, 554—564).—The rate of evaporation from a water surface is measured as a function of the b. p. above the surface and the actual temp. of the surface. Extrapolation to zero pressure enables the rate of evaporation into a vac. to be deduced, and this result is compared with the formula derived from the kinetic theory for the no. of vapour mols. striking a water surface per sec. from the saturated vapour. Extensive reflexion of water vapour mols. must occur, since only about 1% of the mols. incident on the surface enter the liquid.

L. L. Bircumshaw.

Specific properties of surface molecular fields. V. V. Iljin and J. P. Simanov (J. Gen. Chem. Russ., 1931, **1**, 85—90).—The X-ray spectrum of charcoal activated by heating at 1000° in CO_2 is of the same type as that activated at 850° in air; these charcoals adsorb homologous hydrocarbons in the order of increasing and decreasing at. wt. respectively. The sp. properties of adsorbent charcoals are not connected with their crystal structure.

R. Truszkowski.

Spreading of some saponins [on aqueous surfaces]. F. Grendel (Pharm. Weekblad, 1931, **68**, 610—615).—From surface tension measurements, the film thicknesses of various saponins on water are found to be between 12·8 and 42×10^{-8} cm.; the films are thus of unimol. thickness. S. I. LEVY.

Investigation of specific surface of pulverised substances by optical methods. G. I. POKROVSKI (Kolloid-Z., 1931, **55**, 321—323).—Theoretical.
E. S. HEDGES.

Capillary systems. X. Electro-osmotic behaviour of collodion membranes of graded porosity. E. MANEGOLD and K. SOLF (Kolloid-Z., 1931, **55**, 273—310).—A mathematical investigation is made of the application of Helmholtz' equation to capillary systems and of the relation between velocity of dialysis, ohmic resistance, and capillary structure, and the electro-osmotic transport of H_2O through capillary systems. Observations have also been made on the ohmic resistance of collodion membranes impregnated with various liquids, the electro-osmotic permeability of the membranes for pure H_2O, and the maximal osmotic flow. The quotient of the conductivity of the impregnated membrane and that of the impregnating liquid is greater than 1 for pure H_2O, and with increasing electrolyte concentration approaches a const. value, which is less than 1, the constancy being reached at the concentration 0·03*N*. The electrical conductivity of the capillary-bound H_2O is 10—12 times that of the free H_2O. The electro-osmotic permeability for H_2O increases with the size of the pores, but in electrolyte solutions more conc. than 0·03*N* the value is independent of the porosity. For equal current densities the max. electro-osmotic flow is independent of the porosity of the capillary system, a result which must be due to the variation of conductivity with the porosity. E. S. HEDGES.

Osmotic pressure of dilute benzene solutions by the porous disc method. W. C. EICHELBERGER (J. Amer. Chem. Soc., 1931, **53**, 2025—2036; cf. this vol., 423).—The author's apparatus has been modified for the measurement of the osmotic pressure of non-aq. solutions. With the temp. controlled to within 0·0005°, the osmotic pressures of solutions of 0·02—0·004*M*-tetraphenylethylene in C_6H_6 have been determined with an accuracy of 1%.
J. G. A. GRIFFITHS.

Cellulose acetate solutions [viscosity]. H. BARTHÉLEMY (Chim. et Ind., 1931, **25**, 819—831).—The viscosities of 6% solutions of cellulose acetate in $COMe_2$–H_2O mixtures have been determined, and are discussed in relation to the composition of the solvent. Pure $COMe_2$ solutions containing up to 30% of cellulose acetate have also been examined. 99% MeOH depresses the viscosity of $COMe_2$ solutions of cellulose acetate more than H_2O or abs. EtOH. The high viscosities of cellulose acetate in methylene chloride, $CHCl_3$, dichloroethylene, and tetrachloroethane are greatly reduced by MeOH, the min. in 6% solutions being attained when 20 vol.-% is present. The viscosities of conc. solutions in $COMe_2$, *e.g.*, 25%, can be determined by the rate of fall of steel balls. The difference between the true and apparent viscosity of such a solution is a measure of its rigidity. A. RENFREW.

Apparent molar volumes of dissolved electrolytes. I. W. GEFFCKEN (Z. physikal. Chem., 1931, **155**, 1—28).—Priority for the equation $\phi_c=\phi_0+Kc^{\frac{1}{2}}$ (this vol., 680) is now accorded to Masson (A., 1930, 31). The values of ϕ_c for solutions of all the alkali halides except the fluorides of Li, Na, Rb, and Cs, and for solutions of HCl and $BaCl_2$ at different temp. are tabulated, using the best data available. The equation holds over wide ranges of temp. and concentration. Redlich's equation (this vol., 560) $\overline{V}=\overline{V}_0+K_2c^{\frac{1}{2}}$, where $\overline{V}$ and $\overline{V}_0$ are the partial molar vol. of a dissolved electrolyte at the molar concentrations *c* and infinite dilution respectively, is shown to be related to Masson's equation by the approximation $K_2=1\cdot5/K$. Masson's equation affords a convenient means of calculating the densities of solutions of given concentration with great accuracy, and is suggested as an aid to the crit. examination of published tables.
N. H. HARTSHORNE.

Partial molar volume of dissolved electrolytes. I. O. REDLICH and P. ROSENFELD (Z. physikal. Chem., 1931, **155**, 65—74).—Theoretical. On the basis of the Debye–Hückel theory, the dependence of the partial molar vol. of an electrolyte on its concentration is derived for high dilutions.
N. H. HARTSHORNE.

Absorption spectra of the rare earths. Y UZUMASA and H. OKUNO (Bull. Chem. Soc. Japan, 1931, **6**, 147—152).—The absorption spectrum of $Nd(NO_3)_3$ in H_2O, glycerol, MeOH, EtOH, and $COMe_2$ is shifted toward the red in passing from H_2O to $COMe_2$. The same effect is observed with solutions of $Pr(NO_3)_3$. The addition of $Mg(NO_3)_2$ also produces the same displacement. The phenomenon is attributed to the deformation of the metallic ion.
F. J. WILKINS.

Electrochemical and spectral investigations of nickel chloride solutions. II. M. PAVLÍK (Coll. Czech. Chem. Comm., 1931, **3**, 302—313).—Addition of org. dehydrating agents such as glycerol or EtOH or of an excess of inorg. chlorides to $NiCl_2$ solutions causes an increase of absorption in the blue and a decrease in the red part of the spectrum; rise of temp. produces the same effect. The change of the absorption spectrum in the shorter wave-length region occurs with solutions of the same composition as those in which the polarographic current–voltage curves show reversible deposition at the dropping Hg cathode, and both phenomena are attributed to the formation of complexes of the type $[NiCl_n]^{(n-2)'}$ by replacement of the hydration H_2O mols. by the easily deformed Cl ions. H. F. GILLBE.

Varying magnetic state of the nickel ion in solutions of the chloride. G. FOEX and (MLLE.) B. KESSLER (Compt. rend., 1931, **192**, 1638—1640; cf. A., 1928, 454; 1930, 1095).—Ni^{++} (in $NiCl_2$ solution) when not heated above 90° has a magnetic moment of 17 Weiss magnetons with $\theta=-16°$ to $-29°$. When heated above 100° the moment diminishes and θ approaches zero, and after heating at 120° the respective values are 17 magnetons and $-3°$. C. A. SILBERRAD.

General limiting law of internal friction of strong electrolytes. H. FALKENHAGEN (Z. physikal. Chem., 1931, **B**, **13**, 93—98).—The relation previously deduced (A., 1929, 1389; 1930, 155) between the viscosity and concentration of a solution of a uni-univalent electrolyte with ions of equal mobility has been generalised to include electrolytes of any type. The results are in satisfactory agreement with the experimental data. R. Cuthill.

Constitution of nitric acid in aqueous solution. R. Brunetti and Z. Ollano (Atti R. Accad. Lincei, 1931, [vi], **13**, 52—57).—A study of the Raman spectra of solutions of nitrates, nitrites, and HNO_3 of various concentrations. The results indicate that conc. aq. solutions of HNO_3, down to about 7·0*M*, contain the species $O_2N{\cdot}OH$ and also a hydrated form $O_2N{\cdot}OH,H_2O$. O. J. Walker.

Preparation of gold sols by reduction with hydrogen. Influence of visible light on sol formation. A. Schmidt (Kolloid-Z., 1931, **55**, 333—341).—In order to prepare reproducible Au sols it is necessary to keep light intensity, temp., and alkali content const. Highly disperse Au sols can be prepared by reducing a dil. $AuCl_3$ solution, to which excess of NaOH has been added, irradiated with visible light. The light does not appear to be capable of promoting the formation of nuclei. $HAuCl_4$ has a coagulating effect on these Au sols. E. S. Hedges.

Standardisation of gold sols for the Lange gold sol reaction. G. Ettisch and O. Einstein (Naturwiss., 1931, **19**, 506—510).—The prep. of a standard Au sol is described, and a method of standardisation based on coagulation is given. The mechanism of Lange's Au sol reaction with cerebrospinal fluid is discussed. A. J. Mee.

Colour of colloidal solutions of arsenic trisulphide. S. S. Bhatnagar (J. Physical Chem., 1931, **35**, 1803—1804).—The view that the colour of colloidal solutions of As_2S_3 is due only to variations in the physical character of the precipitated substance is contested (cf. A., 1930, 721). L. S. Theobald.

Tyndall beam intensity of turbid coloured solutions. L. Sattler and F. W. Zerban (Science, 1931, **73**, 641).—The turbidity in coloured raw sugar solutions can be measured with the Pulfrich photometer. Wells' formula (Chem. Reviews, **3**, 331) holds when certain adjustments are made.

L. S. Theobald.

Method for determination of mol. wt. of colloids from the dielectric constant. N. Marinesco (J. Chim. phys., 1931, **50**, 233—235).—A theoretical exposition. The method gives the value 11,300 for gelatin. E. S. Hedges.

Viscosity and rigidity in suspensions of fine particles. II. Non-aqueous suspensions. C. M. McDowell and F. L. Usher (Proc. Roy. Soc., 1931, **A**, **131**, 564—576; cf. this vol., 681).—Measurements were made of the viscosity of starch suspended in amyl acetate and tetrachloroethane, the mixed liquids containing 0·05% of rubber and a 6% suspension of starch protected with 0·05% of rubber. Only the unprotected suspension showed an increase of viscosity at low rates of shear; in the others the viscosity was approx. const. Similarly a solution of 0·5% of cellulose nitrate in amyl acetate and a 0·13% gas black suspension protected with cellulose nitrate gave a const. viscosity, but a 0·13% gas black suspension unprotected in the liquid mixture gave rapidly increasing viscosity at low rates of shear. Microscopical examination related the latter phenomenon with the appearance of aggregates in the suspension. The extreme shear gradients were 114,000 : 1. Rigidity was detected in starch suspension >8%. A suspension of this content was perfectly elastic for small strains (0·005). Neither the starch nor the gas black showed cataphoresis, from which it is inferred that the particles are unchanged. The results are discussed from the viewpoint of possible solvation.

L. L. Bircumshaw.

Action of immiscible organic liquids on colloidal gold. T. R. Bolam and J. Crowe (J. Physical Chem., 1931, **35**, 1448—1460).—Carefully purified CS_2, CCl_4, $CHCl_3$, Et_2O, C_6H_6, PhCHO, PhBr, *o*-, *m*-, and *p*-chlorotoluene, PhMe, PhEt, *m*-xylene, salicylaldehyde, and paraffin have no action on either Nordenson or Zsigmondy sols. Miscible alcohols are also without effect, but immiscible alcohols exert a sp. influence by causing the Au to collect at the liquid–liquid interface. The formation of red interfacial films under certain conditions shows, however, that coagulation is not essential for the transference of Au to the interface. With amyl alcohol film formation is generally promoted by the addition of electrolytes. The action of an immiscible alcohol may be due to its strong tendency to be adsorbed at the surface of the sol particle. L. S. Theobald.

Effect of aldehydes on solutions of molybdenum-blue. S. L. Malowan (Kolloid-Z., 1931, **55**, 342—343).—Aldehydes containing a double linking in the α-position (citral, cinnamaldehyde, and α-amylcinnamaldehyde) decolorise Mo-blue, a green reduction product being formed in the aldehyde layer. Other aldehydes and ketones examined had no effect on Mo-blue. The reaction is favoured by a high degree of dispersion of the Mo-blue sol.

E. S. Hedges.

Dispersoid chemical acceleration of vaporisation. R. Stumper (Kolloid-Z., 1931, **55**, 310—321).—Measurements of the rate of vaporisation of H_2O at the boiling temp. under the influence of various additions show that molecularly or ionically dispersed substances produce little effect, although substances of high mol. wt. (sucrose) or those which give colloidal hydrolysis products ($FeCl_3$) accelerate the rate of distillation. Colloids accelerate the rate of vaporisation, the effect increasing in the order dextrin, gelatin, tannin, soap. No relation was found between the diminution of surface tension and the acceleration of vaporisation. Coarsely disperse substances (C, $BaSO_4$, $CaCO_3$, MgO, etc.) have a much greater accelerating effect than colloids, the effect depending on particle size and adsorbent power.

E. S. Hedges.

Difform systems. I. Stereometry and classification of difform systems. Wo. Ostwald (Kolloid-Z., 1931, **55**, 257—272).—The concepts of continuity and discontinuity, homogeneity and heterogeneity are discussed. Discontinuous systems may be made by dispersion or by "difformation" (an unsymmetrical alteration of form involving the relatively great reduction of 1 or 2 dimensions). The forms produced from cubes or spheres are thus lamellæ or threads, which are regarded as simple difform systems, whilst multiple or disperse laminated or fibrillar systems, such as graphite and asbestos, constitute complex difform systems. Intermediate forms between disperse and difform systems are classified as reticular, spongoid, and porodin. Calculations are made of the increase of discontinuity resulting from the formation of various types of difform systems. E. S. Hedges.

Triangular co-ordinates in colloid chemistry. II. Fehling's solution. A. Dumanski and A. A. Dikanova (J. Gen. Chem. Russ., 1931, **1**, 163—171).—The system $CuSO_4$–K Na tartrate–NaOH may contain both negatively- and positively-charged colloidal particles. Cryst. or amorphous black or blue ppts. may form. $Cu(OH)_2$ is peptised by both NaOH and Na tartrate. R. Truszkowski.

Mechanism of the coagulation of sols by electrolytes. II. Hydrous alumina sols. H. B. Wieser (J. Physical Chem., 1931, **35**, 1368—1396).—The changes in chloride-ion concentration and p_H values accompanying the stepwise addition of various electrolytes to Al_2O_3 sols prepared by two different methods have been followed as with Fe_2O_3 sols (this vol., 425) and similar results have been obtained. Curves showing the displacement of chloride from the micelles when K_2SO_4, $K_2C_2O_4$, KNO_3, potassium citrate, and $AcONH_4$ are added to the sols are given. The chloride displacement curve is S-shaped with electrolytes containing multivalent precipitating ions which cause rapid coagulation above a crit. concentration, the amount of chloride displaced for a given increment in precipitating ion being proportionally greater as the point of rapid coagulation is approached. Above this point chloride is displaced by exchange adsorption and the curve follows the usual course of the adsorption isotherm. Univalent precipitating ions which do not cause rapid coagulation in a crit. zone give displacement curves resembling the adsorption isotherm, and this is attributed to exchange adsorption and gradual agglomeration. The chloride-displacing power and the coagulating power follow the order citrate$>SO_4''>C_2O_4''>OAc'>NO_3'$, and the order in which the salts increase p_H on addition to the sols is citrate$>C_2O_4''>OAc'>NO_3'>SO_4''$; at the precipitation value this order is modified. An adsorption mechanism explaining the effect of electrolytes on the chloride displacement, the lowering of the charge, and the change in p_H is advanced. The prep. of Al_2O_3 sols with any required chloride content from $Al(OH)_3$ formed by the action of H_2O on Al–Hg is described. L. S. Theobald.

Influence of light on flocculation of colloidal sols in a fluorescent medium. Effect of coloured inhibitors and of viscosity. A. Boutaric and J. Bouchard (Compt. rend., 1931, **193**, 45—46).—The photo-sensitising effect of a fluorescent substance, *e.g.*, fluorescein (cf. this vol., 425), is diminished in presence of an electrolyte by the addition to the sol (*e.g.*, of As_2S_3) of a dye with absorption bands similar to those of the fluorescent substance, *e.g.*, eosin or erythrosin, although either alone increases the photo-sensitising power. The effect of rhodamine-*B* on the flocculating power of an electrolyte on a $Fe(OH)_3$ sol is also much diminished if the electrolyte is $KMnO_4$. Increased viscosity of a sol, by addition, *e.g.*, of glycerol or sucrose, has a similar effect (cf. A., 1930, 133). C. A. Silberrad.

Equivalent discharging and charging of lyophilic sols. H. G. B. de Jong and J. Lens (Biochem. Z., 1931, **235**, 174—184).—Electro-equiv. concentrations of electrolytes sometimes neutralise the charge of lyophilic sols the more strongly the higher is the valency, but in some cases the effect is independent of the valency of the oppositely-charged ions. The latter is designated "equivalent discharging." The appearance or non-appearance of equiv. discharging depends on the type of the disperse phase, of the discharging ions, and of the medium. Often a mass equivalence is detected between the equiv. discharging ions and the colloidal substance. P. W. Clutterbuck.

Optical study of secondary Liesegang rings. L. Bull and (Mlle.) S. Veil (Compt. rend., 1931, **192**, 1314—1315; cf. this vol., 563).—The secondary rings occasionally exhibit a cryst. formation. C. A. Silberrad.

Periodic precipitation. F. E. Lloyd and V. Moravek (J. Physical Chem., 1931, **35**, 1512—1547; cf. A., 1929, 507).—Photographic and kinemaphotographic records are discussed. Every reaction may proceed periodically under the necessary conditions of space and concentration. Exceptions may occur when a reagent reacts with the medium or when the gel fails to act as a protective colloid for the ppt. The medium may act chemically or mechanically, but its nature is not of fundamental importance. Viscosity plays a minor rôle, but in higher concentrations of the medium there is more periodicity. Surface is of importance in capillary tubes, but not in larger tubes, and periodicity is often obtained in the former but not in the latter. The relative importance depends on the nature of the ppt. or on the degree of adsorption. Inhomogeneities such as occur in starch or agar affect the behaviour of the reagents and ppt. in any system. Periodicity is independent of the states in which the reaction product may occur and there may be at least two types of periodic precipitation in a single system. At high concentrations of internal reagent a plug tends to form near the mouth of the tube, and the entering reagent is more rapidly consumed, reducing the rate of diffusion throughout the tube. Effects produced by a rise of temp. are due to a change in the velocity of the reaction concerned. Exposure to light may induce periodicity or may disturb it if already established. The influence of foreign ions is described as well as experiments in U-tubes with $HgCl_2$ and KI. Diffusion, adsorption, recrystallisation, and polymorphic changes of the ppt. and the apparent and real absence of periodicity are discussed. A theory is elaborated in which backward diffusion of a complex formed between the reaction product and internal reagent plays an essential part. L. S. Theobald.

Desorption of electrolytes from colloidal particles on coagulation. II. S. A. Vosnessenski and L. P. Artemova (J. Gen. Chem. Russ., 1931, **1**, 173—177).—Conductivity measurements of Au sols or dialysed Ag sols, to which increasing quantities of HCl are added, indicate that the electrolyte is in small concentrations adsorbed by the particles, and that desorption takes place on coagulation.

R. Truszkowski.

Colloid chemistry of dyes. Aqueous solutions of benzopurpurin-4*B* and its isomeride prepared from *m*-tolidine. I. II. C. Robinson and H. A. T. Mills (Proc. Roy. Soc., 1931, A, 131, 576—595, 596—611).—I. Solutions of benzopurpurin-4*B* and the isomeride prepared from *m*-tolidine have been examined from a colloid viewpoint, and a method has been devised for purifying these and similar dyes. The phenomenon of ageing found by previous workers is not exhibited if the solutions are pure. The viscosity does not vary with the rate of shear, is the same for both dyes, and is of the order expected for a typical, unhydrated, lyophilic colloid. Flocculation experiments with NaCl, $CaCl_2$, $AlCl_3$, and NaOH show that the particle of the 4*B* dye is probably of colloidal dimensions (confirmed by ultra-filtration measurements), whilst that of the *m*-dye is more nearly in true solution. The latter is much more sol. than the former. On the addition of small quantities of electrolytes to the two dyes, non-spherical ultramicrons are obtained in the case of the 4*B* dye, but not in that of its isomeride. Similarly, the 4*B* dye showed streaming double refraction. Measurements over a wide range of concentrations showed the conductivities of the two dyes to be nearly the same; by subtracting the conductivity of the filtrate, that of the micelle is obtained.

II. The osmotic pressures of the two dyes are the same. It is shown how the errors arising from membrane equilibria can be reduced and the amount of alkali necessary to prevent membrane hydrolysis calc. The micelle of the *m*-dye consists of about 10 anions, whilst that of the 4*B* dye must contain considerably more. By the application of Donnan's membrane equilibrium theory attempts are made to measure the activity of the Na ions. It is concluded that both dyes exist in solution as completely dissociated colloidal electrolytes and that hydrolysis is negligible. L. L. Bircumshaw.

Refraction of protein colloids. N. F. Jermolenko (J. Gen. Chem. Russ., 1931, 1, 21—30).—Equiv. concentrations of various chlorides produce an equal change in the *n* of fish glutin, ovalbumin, and gelatin sols which is proportional to the concentration of the protein. The *n* of gelatin sols is const. during 33 hr. after preparation, and is probably unaffected by time. On keeping gelatin or glutin sols for varying periods at 0—90°, and allowing them slowly to attain 25°, the final value of *n* is the same in all cases. Min. refraction of gelatin is found at the isoelectric point.

R. Truszkowksi.

Relations between colloids and constitutive changes of some proteins. I. W. Pauli and R. Weiss (Biochem. Z., 1931, 233, 381—443).—A detailed record of observations on the coagulation of egg-albumin, serum-albumin, and pseudoglobulin produced by acids, neutral salts, and alcohols, and by heating. Considerable attention has been paid to the reversibility of the processes and to changes in the optical rotation of the sols under the influence of various addition agents. E. S. Hedges.

Colloid-chemical behaviour of typical hydrophilic phosphatide sols. H. G. B. de Jong and R. F. Westerkamp (Biochem. Z., 1931, 234, 347—366).—Both hydrophobic and hydrophilic sols of lecithin can be prepared from commercial lecithins by mixing the alcoholic solution with H_2O. Hydrophilic sols are favoured by high temp., low concentration of the original lecithin solution, and the use of higher alcohols (*e.g.*, $Pr^{\beta}OH$) as solvents. Hydrophilic sols prepared from egg- or soya-bean-lecithin are not flocculated by NaCl, $BaCl_2$, or HCl. Sols containing 5% of resorcinol behave as dehydrated sols and are coagulated by neutral salts, the effect increasing with the valency of the cation, whilst the anion is of little account. Sols containing 50% of EtOH behave similarly, except that the effects of ter- and sexa-valent cations are practically identical. In the presence of a sufficient quantity of neutral salt (the concentration decreasing with increasing valency of the cation) lecithin can be extracted from the hydrophilic sols by shaking with Et_2O. The hydrophilic sols are negatively charged; egg-lecithin sols have an isoelectric point at about p_H 2·7. The electroviscous effect is shown with small concentrations of neutral salts, but at high concentrations viscosity anomalies occur. E. S. Hedges.

Complex coacervation. VI. Lecithin as a complex component. H. G. B. de Jong and R. F. Westerkamp (Biochem. Z., 1931, 234, 367—400).—Lecithin sols form complex coacervates with gelatin, ichthyocoll, casein, egg-albumin, and clupein. The formation of gelatin–egg-lecithin coacervates is confined to the p_H region between the isoelectric points of the components (4·8—2·7). In the neighbourhood of the isoelectric point of gelatin the complex coacervate is obtained in the form of liquid drops; in the middle part of the effective p_H region a flocculent ppt. of droplets is obtained, uniting with difficulty, but more readily in the presence of neutral salts. Higher concentrations of neutral salts destroy the coacervate. The droplets show the Büchner effect in the electric field. The resistance to neutral salts is zero at both isoelectric points, and passes through a max. in the intermediate p_H region. Measurements of viscosity and light absorption and observations of the morphological characters of the coacervate have established that a neutral salt is more effective the greater the difference between the valencies of the cation and the anion. The sp. effect of the cation is less important, but is in the following order: $Li > Na > K > Ca > Mg > Sr > Ba$. The resistance towards neutral salts depends on both of the components of the complex coacervate; complexes with clupein are more resistant than those with gelatin, and complexes of soya-bean-lecithin are more resistant than those of egg-lecithin. At $p_H < 2·7$ egg-lecithin can act as a positive component and give complex coacervates with negatively-charged thymus-nucleic acid and gum arabic.

E. S. Hedges.

Complex coacervation. VII. Autocomplex coacervation. H. G. B. de Jong and J. Lens

(Biochem. Z., 1931, **235**, 185—204).—The coacervate of gum arabic sol with $[Co\{(OH)_2Co\ en_2\}_3](NO_3)_6$ shows towards neutral salts and also in an electric field the characteristics of a complex coacervate, although only colloidal substances are concerned. The opposite charges are taken up by particles of the same type or even on the surface of one and the same particle. The type is designated "autocomplex coacervation." An explanation of the phenomenon is discussed and further examples are given. P. W. CLUTTERBUCK.

Swelling minimum and isoelectric point of fibrin. H. J. VONK (Z. physiol. Chem., 1931, **198**, 201—218).—The swelling min. of fibrin, which must correspond with its isoelectric point, depends both on p_H and on the presence of other ions. If the p_H is attained by the use of HCl and NaOH the min. lies at about 7·1; if by the use of buffer mixtures it may be displaced as far as 3·7. J. H. BIRKINSHAW.

Distribution of hydrochloric acid in gelatin gels. L. HALPERN (J. Gen. Physiol., 1931, **14**, 575—581).—No evidence of a permanent ionic concentration gradient, such as that reported by Bigwood (this vol., 306) when NaOH solution diffuses into gelatin gel, is obtained when dil. aq. HCl is allowed to diffuse, when the concentration of the aq. liquid is unchanged; $d/\sqrt{t}$ is const. When an artificial gradient of protein concentration is set up the $[Cl']$ at equilibrium varies in the same direction as protein concentration, whilst the $[H^{\cdot}]$ varies in the opposite direction. These facts are in accordance with Donnan's theory. R. K. CALLOW.

Flocculation of gelatin at the isoelectric point. D. STRAUP (J. Gen. Physiol., 1931, **14**, 643—660).—Isoelectric gelatin solutions, after purification by electrodialysis, flocculate when cooled below 30°. The following observations have been made with stock solutions sterilised at 80° for 10 min., a treatment which does not affect flocculation properties. Solutions heated at 100° show a decrease in the rate and amount of flocculation. An equilibrium point with the same concentration in the liquid phase is reached by allowing a solution to flocculate at 25° or by redispersing a solution previously flocculated at a lower temp. The concentration of the liquid phase at equilibrium decreases with fall of temp., and the rate of attaining equilibrium is greater. At const. temp. the equilibrium concentration in the liquid phase is proportional to the initial concentration. Ppts. redissolved in H_2O give solutions which flocculate more rapidly and completely than the original solutions. When flocculation at low temp. is followed by warming, an opalescent solution is formed temporarily by disruption of the floccules and reflocculation then occurs. If the liquid phase is removed from the ppt. and concentrated, this may be flocculated, but only at a lower temp. The fraction of gelatin from the liquid phase is less readily salted out by $(NH_4)_2SO_4$ than that from the ppt. phase. Solutions of the liquid fractions have the same n as those of the ppt. fractions, but the viscosity is lower. It is concluded that gelatin is a mixture of mol. aggregates of widely differing degrees of association.

R. K. CALLOW.

Structure of silica gel. *X*-Ray study. L. KREJCI and E. OTT (J. Physical Chem., 1931, **35**, 2061—2064).—After heating at 1150° for 5 hr. precipitated SiO_2 gives the same X-ray pattern as cristobalite. Cryst. centres of colloidal dimensions have also been detected by means of X-rays in precipitated SiO_2 which has never been heated above 100°; the crystals appear to be cristobalite.

L. S. THEOBALD.

Cobalt sulphide bands in solid silica gel. E. R. RIEGEL (J. Physical Chem., 1931, **35**, 1674—1683).—Rhythmic bands of CoS are formed when SiO_2 gel containing Na_2S is placed on a solid SiO_2 gel containing $Co(NO_3)_2$; Na_2S solution forms similar bands, but produces collapse of the SiO_2 gel. The greater the concentration of Na_2S and the less that of $Co(NO_3)_2$ the more rapid is the advance of the rings, and generally, but not invariably, advance is slower the more conc. are the gels. The behaviour of air bubbles in a gel in which bands are being formed is described. Bands of CoS formed on a microscope slide have also been studied and a mechanism for both cases is discussed. L. S. THEOBALD.

Reduction reactions in silica gels. D. S. DEDRICK (J. Physical Chem., 1931, **35**, 1777—1783).—NH_2OH,HCl reduces $Cu^{\cdot\cdot}$ to $Cu^{\cdot}$ and Cu in SiO_2 gels made from Na_2SiO_3 and $CuSO_4$ in dil. H_2SO_4; a 1% aq. solution gives well-defined crystals in banded rings, but a 2% solution gives no banded structure. Gels made from Na_2SiO_3 of d 1·06 are more satisfactory than those made from Na_2SiO_3 of d 1·10. Variations in the concentration of $Cu^{\cdot\cdot}$ or the H_2SO_4 used in making the gel have little effect. A M-aq. solution of SO_2 diffuses rapidly into the alkaline gels, forming a ppt. of yellow, metastable Cu_2O which dissolves as more H_2SO_3 diffuses through the gel. In acid solution the oxide is reprecipitated as well-defined crystals of red Cu_2O. During the first 20 hr. the rate of diffusion of SO_2 solution in the more conc. gel (d 1·10) is greater than that in the more dil. gel (d 1·06). After this the rates become equal, indicating that at first the gels are structurally different. Variations of factors other than concentration have no effect. Diffusion of a 5% dextrose solution into the dil. but not into the conc. gel produces yellow Cu_2O. The mols. of dextrose are larger than the interstices of the conc. gel, but smaller than those of the dil. gel.

L. S. THEOBALD.

Alkali peptisation of stannic acid gels. R. WINTGEN and W. KEILHOLZ (Kolloid-Z., 1931, **55**, 323—330).—Experiments on the peptisation of precipitated SnO_2 by NaOH indicate that in sols prepared at 18° the average particles contain 40,000 mols. of SnO_2, 2,600,000 mols. of H_2O, and 900 atoms of Na in the kernel. In addition, there are 530 elementary charges, which are balanced by 530 $Na^{\cdot}$ ions. The radius of such a particle is 26 mμ. The size of particle increases with rise in the temp. of peptisation, the ratio SnO_2/H_2O also increasing. E. S. HEDGES.

Radiochemical equilibrium in ammonia synthesis. S. C. LIND (J. Amer. Chem. Soc., 1931, **53**, 2423—2424).—The observed low equilibrium concentration of NH_3 (this vol., 580), as compared with that calc., indicates that the intermediate steps of the opposed reactions are not independent. The results are explained if an exchange of ionisation from H_2^+ (16 volts) or N_2^+ (17 volts) to give NH_3^+ (11 volts) occurs, assuming that H_2^+ and N_2^+ in some way cause synthesis and NH_3^+ decomp. J. G. A. Griffiths.

Maximum concentration of endothermic compounds at elevated temperatures. Ozone and nitric oxide. E. Briner and B. Susz (J. Chim. phys., 1931, **50**, 206—227).—Although the formation of endothermic compounds from the constituent elements is favoured by rise of temp., the elementary mols. tend to dissociate into atoms, resulting in a max. yield of the endothermic compound at a particular temp. The max. concentration is evaluated for O_3 and NO on the basis of the law of mass action and the Nernst theorem, using the known heats of dissociation of N_2 and O_2. The max. concentration of O_3 produced from O_2 at 1 atm. is 0·0000276% at 3750°, whilst the max. concentration of NO produced from air at 1 atm. is 10·9% at 4000°. The extremely small value of the concentration of O_3 shows that its production in electrical discharges is not a thermal effect. E. S. Hedges.

Cryoscopic study of paraldehyde in solutions of lithium and magnesium chlorides. F. Bourion and E. Rouyer (Compt. rend., 1931, **192**, 1724—1726; cf. this vol., 430).—The values of the cryoscopic consts. indicate the stability of paraldehyde in these solutions. C. A. Silberrad.

Ionisation constant of acetic acid [at 25°]. D. A. MacInnes and T. Shedlovsky (J. Amer. Chem. Soc., 1931, **53**, 2419—2420).—From conductance measurements, the thermodynamic ionisation const., *K*, of AcOH in $0·03—10\times10^{-3}N$ solution is computed to be $1·746\times10^{-5}$. At higher concentrations, *K* decreases. J. G. A. Griffiths.

Universal buffer solutions and the dissociation constant of veronal. H. T. S. Britton and R. A. Robinson (J.C.S., 1931, 1456—1462).—The dissociation const. of diethylbarbituric acid is $1·1\times10^{-8}$ at 18°. A universal buffer solution, containing citric acid, Na diethylbarbiturate, H_3BO_3, HCl, and KH_2PO_4, exhibits a strictly linear change of p_H in relation to the quantity of strong acid or alkali added over the greater part of the range p_H 2—12. Below 16% neutralisation the deviation is slight, but above 64% a pronounced inflexion of the curve occurs as a result of the transition from the neutralisation of H_3BO_3 to that of the third stage of H_3PO_4. For the range p_H 3·85—12·0 the HCl may be omitted. The Prideaux–Ward buffer mixture has been further investigated (cf. this vol., 585). H. F. Gillbe.

Electrochemical method for approximate determination of the constitution of complexes in solution. Application to some complex ions of copper and nickel. F. K. V. Koch (J.C.S., 1931, 1418—1421).—The method (A., 1930, 1372) has been extended to electrodes which do not give const. and reproducible potentials, and applied to $CuSO_4$ and $NiSO_4$ solutions containing NH_3 or pyridine. The results are in accordance with those obtained by the distribution coeff. method, and indicate the formation of $Cu(NH_3)_4^{\cdot\cdot}$, $Cu(C_5H_5N)_4^{\cdot\cdot}$, and $Ni(NH_3)_2^{\cdot\cdot}$. H. F. Gillbe.

Determination of hydrolysis of zinc sulphate solutions with quinhydrone electrode. P. Dupont (Compt. rend., 1931, **192**, 1643—1645).—The p_H–log concentration curve obtained with $ZnSO_4$, using the quinhydrone electrode, agrees with Kolthoff and Kameda's results (cf. this vol., 565). To obtain an accurate result pure N_2 was passed through the solution for 30 min., atm. CO_2 otherwise causing a diminution in the p_H. $ZnSO_4$ calcined at a red heat or agitated with ZnO probably contains some basic sulphate. C. A. Silberrad.

Measurement of the hydrolysis of zinc and cadmium sulphates by means of the hydrogen and quinhydrone electrodes. V. Čupr and O. Viktorin (Publ. Fac. Sci. Univ. Masaryk, 1931, No. 134, 18 pp.).—Measurements of the hydrolysis of Zn salts with the aid of the H electrode yield unsatisfactory results; the deviations depend more on the p_H of the solution than on its concentration. Since colloidal Pt does not reduce the p_H of the solution, and in absence of H_2 the solution becomes acid in presence of Pt-black, the reaction suggested by Denham and Marris, viz., $Zn^{\cdot\cdot}+H=Zn^{\cdot}+H^{\cdot}$, does not occur; the change of p_H is attributed to a replacement of H ions by Zn ions on the Pt surface. Measurements with the quinhydrone electrode indicate that the degree of hydrolysis in $1·0-0·1M$-$ZnSO_4$ is about 0·0023—0·0046%, and in $1·0—0·1M$-$CdSO_4$ 0·0006—0·0016%. H. F. Gillbe.

Hydrolysis of salts of beryllium and aluminium with strong acids. II. V. Čupr (Publ. Fac. Sci. Univ. Masaryk, 1931, No. 133, 3—50).—The salt error of simple quinhydrone electrodes increases for anions in the series $Cl<Br<NO_3<ClO_3<ClO_4$ and for cations $K<Na<Li$. The degree of hydrolysis of solutions of $BeCl_2$, $BeBr_2$, $BeSO_4$, $MgCl_2$, $MgSO_4$, $AlCl_3$, $AlBr_3$, and $Al_2(SO_4)_3$ is independent of the age of the solution. The apparent increase in the acidity of more conc. solutions of Be salts is due to their influence on the activity of $H^{\cdot}$. The influence of neutral salts on the hydrolysis of $BeCl_2$ and $BeBr_2$ is ascribed to hydration. R. Truszkowski.

Hydrolysis of salts. V. Čupr (Z. anorg. Chem., 1931, **198**, 310—328).—Partly an account of work published elsewhere (see preceding abstracts). Slow hydrolysis does not occur with Be and Al salts. Deviations occur at high concentrations from the logarithmic law connecting the p_H of the solution with the concentration of the Be or Al ion, and these are ascribed to the change of activity of the H ion in presence of other ions; the min. in the concentration-degree of hydrolysis curve is due to the same cause. H. F. Gillbe.

Potentiometric measurement of the acidity of acids, and its alteration by solvents. A. Hantzsch (Helv. Chim. Acta, 1931, **14**, 665—669).—Polemical against Schwarzenbach (A., 1930, 1526). It is not possible to compare the acidity of acids in different solvents by means of the H electrode. In such solutions the complicated equilibria between free acids, solvates, and oxonium salts must be studied by as many different physical methods as possible, bearing in mind the purely chemical facts.

[With K. Berger.] The sp. conductivity of practically anhyd. $HClO_4$ is $10{\cdot}7\times10^{-4}$ mho at 0°. This is of the same order as the sp. conductivities of abs. HNO_3 and H_2SO_4, and about 10^3 that of the common hydracids. Dissociation of a polymerised mol. into the ions $[(H_2O)_2ClO_2]^{\cdot}$ and $[ClO_4]'$ is suggested as the explanation, and the behaviour is thus similar to that of HNO_3 and H_2SO_4.

[With D. Karvé.] The heats of dissolution of 1 mol. of H_2SO_4 in 1, 2, 5, 10, 25, and 50 mols. of H_2O are 6200, 9000, 13,500, 15,200, 16,400, 16,800 g.-cal., respectively, whilst for $CCl_3{\cdot}CO_2H$ the heat of dissolution in 50 mols. of H_2O is only 800 g.-cal. Such results are difficult to reconcile with Schwarzenbach's conclusion that in 2*N*-ethereal solution $CCl_3{\cdot}CO_2H$ is as strong an acid as H_2SO_4. N. H. Hartshorne.

Existence of undissociated salt molecules in aqueous solutions of strong electrolytes. L. Dede (Helv. Chim. Acta, 1931, **14**, 743—751).—The dilution–equiv. conductivity curves for conc. solutions of strong electrolytes show frequently a min. This can be correlated with Debye's view that the electrolyte acquires a dipole character as the concentration is increased, the dipoles being either ion-associations or undissociated mols. The curve for HBr shows no min., whilst that for KBr is very marked. This points to the existence of undissociated mols. of HBr which, owing to the small size of the H nucleus, should have a very weak dipole moment as compared with $OH_3^{\cdot}Br'$; the latter, from a comparison of the size of the $OH_3^{\cdot}$ and $K^{\cdot}$ ions, should have a greater dipole moment than $K^{\cdot}Br'$. This conclusion is borne out by the viscosity of HBr solutions, which is greater than that of water at all concentrations, whereas the viscosities of solutions of the halides of the heavier alkali metals are lower than that of H_2O except at low concentrations. This points to the presence of a weak dipole in the case of HBr, and of a strong dipole in the alkali halide solutions. N. H. Hartshorne.

Composition of acid boric acid–diol compounds. J. Böeseken and N. Vermaas (J. Physical Chem., 1931, **35**, 1477—1489).—Bancroft and Davis' conclusions (this vol., 163) are criticised.
L. S. Theobald.

System metal–acid–reducible compound. H. J. Prins (Chem. Weekblad, 1931, **28**, 390—393).—A lecture. The assumption that nascent H forms complexes with the metal and reducible compound is rejected. H. F. Gillbe.

Physico-chemical studies of complex acids. VI. Precipitation of molybdates. H. T. S. Britton and W. L. German (J.C.S., 1931, 1429—1435).—The ppts. resulting from the interaction of Na molybdate, paramolybdate, or metamolybdate with salts of Zr, Th, Al, Cu, Cr, Be, Ni, and Mg consist of either normal molybdate, sometimes contaminated with basic molybdate, basic molybdate, or the normal or basic salt accompanied by MoO_3. The precipitation is controlled largely by the relation between the resultant p_H, determined by the degree of neutralisation of H_2MoO_4, and that necessary to cause precipitation of the hydroxide.
H. F. Gillbe.

Aqueous salt solutions in equilibrium with solid secondary calcium phosphate at 40°. J. W. H. Lugg (Trans. Faraday Soc., 1931, **27**, 297—309).—The form of $CaHPO_4$ which is stable in contact with aq. solutions of NaCl at 40° is brushite, the solubility product, *s*, of which in aq. solutions of NaCl, KCl, Na_2SO_4, $CaCl_2$, and $MgSO_4$ at 40° has been determined. From p_H data at 23·5° for solutions of these salts containing primary and secondary alkali phosphates values for the second dissociation const., K_2, of H_3PO_4 have been obtained. Equations connecting the concentration of foreign salt with *s* and with K_2 have been derived by means of the Debye–Hückel theory. R. Cuthill.

Molecular combination of aliphatic iodides. J. C. Smith (Nature, 1931, **127**, 928).—The system hexadecyl iodide–octadecyl iodide has a eutectic at 19·3° and a non-congruent m. p. at 22·3°, showing the existence of an equimol. *compound.*
L. S. Theobald.

Theory of Löwig's process. V. I. Sokolov (J. Chem. Ind. Russ., 1931, **8**, 248—252).—The ferrite obtained by the combination of Na_2O with Fe_2O_3 in Löwig's process has the composition Na_2O,Fe_2O_3. The decomp. of ferrite by H_2O is endothermic (−55·14 g.-cal.) and the heat of formation of ferrite is +58 g.-cal. R. Truszkowski.

Melting diagram of the system Al_2O_3–Cr_2O_3–MgO. K. J. A. Bonthron and R. Durrer (Z. anorg. Chem., 1931, **198**, 141—156).—The system has been studied at 1900—2550°, but owing principally to evaporation losses and decomp. of the Cr_2O_3 the results involve large errors. Cr_2O_3 and Al_2O_3 form a eutectic at 30 mol.-% Cr_2O_3, and possibly another, resulting from the formation of a compound, at 90 mol.-% Cr_2O_3. The ternary system contains at least two ternary eutectics, but there is no evidence of the formation of ternary compounds.
H. F. Gillbe.

Use of rhodium vessels for investigation of oxide systems. G. Trömel and F. Wever (Naturwiss., 1931, **19**, 519—520).—The use of Rh vessels for the investigation of equilibria at high temps. is recommended. A. J. Mee.

System P_2O_5–CaO–H_2O and the recrystallisation of calcium dihydrogen phosphate. N. A. Clark (J. Physical Chem., 1931, **35**, 1232—1238; cf. A., 1908, ii, 675).—The equilibrium relations have been examined and methods for the recrystallisation of $CaHPO_4$ are given. L. S. Theobald.

Equilibrium in the system potassium sulphate–sulphuric acid–water. A. V. Babaeva (Trans. Inst. Pure Chem. Reag., 1931, **11**, 114—128).—The equilibrium data for 30°, 50°, and 75° indicate the formation of the *salts* $K_2SO_4,3KHSO_4$ and $K_2SO_4,6KHSO_4$. R. Cuthill.

Equilibrium in the system sodium sulphate–sodium dichromate–water. A. V. Rakovski and E. A. Nikitina (Trans. Inst. Pure Chem. Reag., 1931, **11**, 5—14).—The isotherms for 0°, 15°, 25°, 40°, 60°, 80°, and 98° have been examined, the results showing that in practice pure $Na_2Cr_2O_7$ cannot be obtained by recrystallisation. The solid phases separating from the system $Na_2Cr_2O_7$–$NaHSO_4$–H_2O at 20° are

$Na_2Cr_2O_7,2H_2O$, Na_2SO_4, $Na_3H(SO_4)_2,H_2O$, and $Na_3H(SO_4)_2$. R. Cuthill.

Equilibrium in the system potassium dichromate–potassium sulphate–water. A. V. Rakovski and A. V. Babaeva (Trans. Inst. Pure Chem. Reag., 1931, **11**, 15—19).—The isotherms for the above system at 0°, 20°, 40°, 60°, 80°, and 98° have been derived. R. Cuthill.

Equilibrium in ternary systems of nitrites, nitrates, and chlorides of sodium and potassium. A. V. Rakovski and D. S. Slavina (Trans. Inst. Pure Chem. Reag., 1931, **11**, 20—33).—The isotherms for $NaNO_2$–$NaNO_3$–H_2O at 15° and for KNO_2–KNO_3–H_2O, $NaNO_2$–NaCl–H_2O, and KNO_2–KCl–H_2O at 0°, 20°, 40°, 60°, 80°, and 98° have been derived. R. Cuthill.

Equilibrium in the quaternary system sodium dichromate–ammonium chloride–water. J. Gerasimov (Trans. Inst. Pure Chem. Reag., 1931, **11**, 34—61).—The isotherms for the above quaternary system and for the ternary systems $(NH_4)_2Cr_2O_7$–NH_4Cl–H_2O, $(NH_4)_2Cr_2O_7$–$Na_2Cr_2O_7$–H_2O, $Na_2Cr_2O_7$–NaCl–H_2O, and NH_4Cl–NaCl–H_2O have been obtained at 0°, 20°, 50°, and 75°. $(NH_4)_2Cr_2O_7$ and $Na_2Cr_2O_7$ exhibit slight miscibility in the solid state. R. Cuthill.

Relationship of m.-p. energy to absolute temperature. Z. Herrmann (Z. anorg. Chem., 1931, **198**, 204—205).—The "m.-p. energy" of an element, *i.e.*, the total heat content of the liquid phase at the m. p., bears a linear relation to the abs. temp. H. F. Gillbe.

Free energy of formation in fused salts. IV. Alkaline-earth halides. G. Devoto and G. Jeny (Gazzetta, 1931, **61**, 305—311; cf. A., 1928, 135).—Further measurements of the decomp. potentials of the fused halides of Mg and of the alkaline-earth metals are in approx. agreement with the thermodynamically calc. values. The temp. coeff. of the free energy of formation of the halides of Ba, Sr, and Ca is higher than the theoretical value, and the anomaly is ascribed to the formation of sub-salts. O. J. Walker.

Hydrogen exponent of water. A. Kling and A. Lassieur (Ann. Chim., 1931, [x], **15**, 201—227).—A more detailed account of work already noted (A., 1930, 1520).

Activity coefficients and heats of transfer of cadmium sulphate from electromotive force measurements at 25° and 0°. Application of the extended theory of Debye and Hückel. V. K. La Mer and W. G. Parks (J. Amer. Chem. Soc., 1931, **53**, 2040—2061; cf. A., 1928, 241).—The activity coeff. and partial molal free energies of transfer of $CdSO_4$ have been calc. from the e.m.f. of the cell Pb–Hg (2 phase)|$CdSO_4(0{\cdot}000458-3{\cdot}7M)$|$PbSO_4(s)$|Pb–Hg(2 phase). The e.m.f. of the cell, E_0, when the ion activities of the $CdSO_4$ are hypothetically M, is 0·00142 volt at 25° and 0·0162 volt at 0°. The Gronwall, LaMer, and Sandved extension of the Debye–Hückel theory affords const. values of $a=3{\cdot}6$ Å. in solutions between 0·0006 and 0·01M, whereas the Debye–Hückel approximation affords variable negative values for the distance of closest approach of the ions (a). $\partial a/\partial T$ is very small, and indicates that the hydration of ions is not involved in a. The mean heat of the cell reaction Cd (s, sat. with Hg)+$PbSO_4(s)=CdSO_4(m)$+Pb (s, sat. with Hg) at 12·5° is 8375 g.-cal. J. G. A. Griffiths.

Heat of dissociation of fluorine. M. S. Desai (Nature, 1931, **128**, 34).—The heat of dissociation of F_2 calc. from the absorption spectrum data for NaF and KF is 76±2 kg.-cal. L. S. Theobald.

Thermochemistry of fluorine; heat of formation of hydrogen fluoride, chloride fluoride, and fluorine oxide. O. Ruff and W. Menzel (Z. anorg. Chem., 1931, **198**, 375—382).—Recalculation of existing data and correction for polymerisation yields for the heat of formation of HF 64·0 kg.-cal. per mol.; that of ClF then becomes 27·4 kg.-cal. per mol. Crit. comparison of various data relating to F_2O point to a value of -7 ± 2 kg.-cal. per mol. H. F. Gillbe.

Heat capacity and free energy of formation of ethane gas. V. R. Thayer and G. Stegeman (J. Physical Chem., 1931, **35**, 1505—1511).—The sp. heat of C_2H_6 between 2·20° and 64·40° has been measured using a const.-flow calorimeter; $C_p=5{\cdot}981+0{\cdot}2193T$. The free energy of C_2H_6 gas has been recalc.; $\Delta F=-18{,}789+16{\cdot}17T\log T-0{\cdot}006T^2-63{\cdot}9T$. L. S. Theobald.

Heat of ionisation of water. F. D. Rossini (Bur. Stand. J. Res., 1931, **6**, 847—856).—From existing data for heats of dilution and heats of neutralisation the heat of the reaction $H_2O=H^{\cdot}+OH'$ at infinite dilution and over the temp. range 10—35° is calc. to be $\Delta H=13{,}721-57{\cdot}9(t-18)+0{\cdot}15(t-18)^2$ g.-cal. per g.-mol., where t is the temp. and the uncertainty is ±16 g.-cal. per g.-mol. This gives 57,370 abs. joules per g.-mol. for ΔH at 18°. R. Cuthill.

Calorimetric determinations of thermal properties of methyl alcohol, ethyl alcohol, and benzene. E. F. Fiock, D. C. Ginnings, and W. B. Holton (Bur. Stand. J. Res., 1931, **6**, 881—900).—The heat contents of the liquids and saturated vapours referred to the values for the liquids at 0°, and also the latent heats of evaporation, have been determined from 40° to 110°. R. Cuthill.

Heat of dissolution of benzoic acid in toluene. G. Chapas (Compt. rend., 1931, **192**, 1446—1448).—The sp. heat of a solution of BzOH in PhMe is identical with that of PhMe. The heat of dissolution varies but slightly with the concentration of the solution, *viz.*, from −2880 to −3040 at 18°, and from −3160 to −3220 at 25°. Such solutions are not ideal. C. A. Silberrad.

Heat of dissolution of some potash minerals. L. T. Richardson and R. C. Wells (J. Washington Acad. Sci., 1931, **21**, 243—248).—Preliminary measurements of the heats of dissolution of polyhalite, langbeinite, kainite, carnallite, and anhydrite have been made. C. W. Gibby.

Heat content values for aqueous solutions of the chlorides, nitrates, and hydroxides of hydrogen, lithium, sodium, and potassium at 18°. F. D. Rossini (Bur. Stand. J. Res., 1931, **6**, 791—806).—Published data for the heats of dilution of the above compounds have been used to calculate the relative apparent molal heat content of the solute, the relative partial molal heat content of the solute, and the relative partial molal heat content of the H_2O at 18° from infinite dilution to a concentration of about 2 molal. R. CUTHILL.

Viscosity isotherms and differential heats of dilution in aqueous solutions. Z. V. VOLKOVA and V. S. TITOV (Z. physikal. Chem., 1931, **155**, 51—58).—The differential heats of dilution, U, of a number of solutions have been compared with their $1/\eta-V$ isotherms (η being the coeff. of viscosity, and V the sp. vol.), the data being drawn from a variety of sources. For solutions of, *e.g.*, N-$KI+HgI_2$, $AgNO_3$, NH_4NO_3, CsCl, and carbamide $U<0$, and the isotherms are convex to the $1/\eta$ axis. For solutions of $ZnCl_2$, $AlCl_3$, $MgCl_2$, and sucrose $U>0$, and the isotherms are convex to the V axis and may also have a straight portion. In the latter series the relation U/η=const., previously found for glycerol–water mixtures (A., 1930, 679), holds within the probable limits of accuracy imposed by errors in the determination of U. N. H. HARTSHORNE.

Thermal expansion and the Debye–Hückel heat of dilution. G. SCATCHARD (J. Amer. Chem. Soc., 1931, **53**, 2037—2039).—Heats of dilution calc. from the Debye–Hückel theory by differentiation at const. vol. are incorrect. A complete equation is derived for one case, and it is shown that neglect of thermal expansion leads to errors in the limiting law. J. G. A. GRIFFITHS.

Thermochemistry of the system ammonia–sulphuric acid. W. A. ROTH and H. ZEUMER (Z. angew. Chem., 1931, **44**, 559—565).—The heat of formation of cryst. $(NH_4)_2SO_4$ from NH_3 (gas) and 100% H_2SO_4 at 20° is 65·44 kg.-cal. per mol. and from the 96·6% acid is 63·89 kg.-cal. per mol. The values obtained for the heat of dissolution of $(NH_4)_2SO_4$ differ considerably from those of Thomsen. The heat of formation of the salt from the saturated solution containing 10% of free H_2SO_4 and NH_3 diluted with air is not altered if H_2O vapour or CO_2 be present separately in the gas phase, but if both are present it is depressed. Thus although NH_4OH or NH_4 carbamate is not present in the vapour phase, $(NH_4)_2CO_3$ or NH_4HCO_3 is formed therein. When moist NH_3 containing the same quantity of CO_2 as is present in the technical gas is used the heat of formation is 58—59 kg.-cal. per mol. H. F. GILLBE.

Thermal properties of cellulose and its derivatives. E. HEISENBERG (Cellulosechem., 1931, **12**, 159—162).—The heat of formation of a cellulose ester, calc. from its heat of combustion, increases with the no. of C atoms in the esterifying acid (triacetate, -600 ± 1000; 2·9-hexoate, $20{,}000\pm1000$; and 2·73-laurate, $26{,}500\pm4000$ g.-cal. per mol. of acid). Cellulose monoacetate is formed exothermically (heat of formation of 0·43-acetate, $21{,}000\pm6000$ g.-cal.), but further esterification is endothermic. The energy contents of viscose and acetate silks, measured by their heats of combustion, increase with the spinning tension. A. RENFREW.

Galvanometric method of measuring an electrolytic resistance. J. A. C. TEEGAN (Phil. Mag., 1931, [vii], **11**, 1250—1252; cf. A., 1930, 1375).—Results obtained by the telephone and galvanometric methods are compared. N. M. BLIGH.

Calculation of the equivalent conductivity of strong electrolytes at infinite dilution. A. FERGUSON and A. I. VOGEL (Trans. Faraday Soc., 1931, **27**, 285—294; cf. A., 1925, ii, 1163).—Arguments are put forward to justify the method of calculation previously adopted. J. W. SMITH.

Conductivity of aluminium bromide in non-aqueous solution. E. WERTYPOROCH (Ber., 1931, **64**, [*B*], 1369—1380).—The molar conductivity of $AlBr_3$ in ethereal solution is const. for concentrations between 0·5 and 0·4M, but diminishes to 0·1 of this value between 0·4 and 0·1M, subsequently remaining const. Addition of substances containing O or N (MeCN, PhCHO, phenylthiocarbimide, BzOEt, allyl alcohol, anisole), or of amylene, CS_2, or C_6H_6 usually increases the conductivity of ethereal solutions of $AlBr_3$; marked exaltation of K is not caused, however, by amounts equiv. to the dissolved $AlBr_3$, but by such as cause a greater or less displacement of the solvent into the solvates. In EtBr the conductivity of $AlBr_3$ increases with the concentration up to about 20%. At room temp., the final value for the conductivity is not immediately reached, particularly in dil. solution. Addition of C_6H_6 to a solution of $AlBr_3$ in EtBr causes very marked increase in the conductivity, the max. value being observed after 5—6 hr. The solution becomes golden-yellow and finally reddish-brown; HBr is rapidly evolved, but its presence is not the cause of the increased conductivity. With trimethylethylene the considerable increase in conductivity is partly masked by polymerisation of the hydrocarbon. Increase is observed also with tetramethylethylene and $C_{10}H_8$. Dimethylpyrone and $AlBr_3$ in EtBr yield a *ppt.*, $5C_7H_8O_2,HAlBr_4,2H_2O$, m.p. 205°; similar ppts. are obtained with NH_2Ph, *p*- and *m*-nitroaniline, NHPhMe, $NPhMe_2$, $NHPh_2$, cineole, and quinoline. Electrolysis of solutions of $AlBr_3$ in EtBr causes accumulation of Al at the anode, indicating the presence of a salt $Al[AlBr_4]_3$, the existence of which is confirmed by observations in solutions in hexaethylbenzene. The conductivity of C_6H_6 is not increased by dissolution of $AlBr_3$ (up to 20%). Addition of C_6H_6, $C_{10}H_8$, or diphenyl to $AlBr_3$ in Et_2O diminishes the conductivity. The occurrence of a primary compound, *e.g.*, $(PhAlCl_3)^-H^+$, appears excluded. The existence of a compound $\begin{matrix}\text{CH:CH·C}\cdots\\ \text{CH:CH·C}\cdots\end{matrix}\text{ClAlCl}_2$ is improbable, since solutions of $AlBr_3$ in C_6H_6 do not appreciably absorb Br, do not add H in presence of spongy Pt more rapidly than in the absence of Al halide, and do not react with HNO_2. Complex formation between C_6H_6 and Al salts appears actually to restrict the reaction, which progresses only so far as the Al complex is transformed into the ternary compound by partial displacement of C_6H_6 by the compound containing halogen or O. The conductivity per mol. of $AlBr_3$ is increased by the addition of hydrocarbons to such an extent that the solutions have an equiv. conductivity of the same order as that of normal salts (measurements of NEt_4Br and ethyltriamylammonium bromide in EtBr are recorded). Migration experiments show that the Al atoms wander to anode and cathode in the approx. ratio 3 : 1, and that formed or added hexaethylbenzene becomes about five times as highly conc. at the cathode as at the anode, thus indicating a complex $[Al(EtBr)_n(C_{18}H_{30})_4][AlBr_4]_3$. In $COMe_2$ the conductivity of $AlBr_3$ immediately attains its final value, and is diminished by C_6H_6 or EtBr. Solutions of $AlBr_3$ in ethylene bromide do not conduct; addition of C_6H_6 causes slight conductivity. BF_3, BCl_3, and $TiCl_4$ in benzotrichloride are inactive.

H. Wren.

Conductivity of fused sodium tungstates. V. Spitzin and A. Tscherepnev (Z. anorg. Chem., 1931, **198**, 276—286).—The conductivity of Na_2O–WO_3 melts has been determined at temp. from 750° to 900° as a function of the composition; it falls as the ratio $WO_3 : Na_2O$ is increased from 1 to 4·5, and thereafter becomes const., and for a given mixture increases linearly with rise of temp. The curves demonstrate the existence of di- and quadri-tungstates, and the non-formation of $Na_2W_8O_{25}$; the existence of $Na_2W_5O_{16}$ is doubtful.

H. F. Gillbe.

Electro-endosmosis. V. Electro-endosmosis and surface conductivity against a glass surface of solutions of hydrogen chloride in benzene and other solvents. F. Fairbrother and M. Balkin (J.C.S., 1931, 1564—1578).—Solutions of dry HCl in C_6H_6 exhibit marked electro-endosmosis through a sintered glass membrane, which increases with increase of the HCl concentration. In *cyclo*hexene the electro-endosmosis is very small, and in CCl_4 and *cyclo*hexane it is not measurable. In contact with glass powder all the solutions exhibit surface conductivity; this effect is not a result of the electro-endosmosis, but may be due to ionisation caused by extreme deformation of the HCl mols. at the polar glass surface or by a surface film of adsorbed H_2O. The solubility of HCl in the 4 solvents has been determined; the sp. conductivity of the solutions is less than 7×10^{-13} mho.

H. F. Gillbe.

Null point of the charge of silver. M. Proskurnin and A. Frumkin (Z. physikal. Chem., 1931, **155**, 29—40).—Measurements of the adsorption on an etched Ag surface in contact with dil. solutions of Ag ions have been made by two methods. From the concentration at which no adsorption occurs the null point of the charge of the Ag surface is calc. to correspond with $\varepsilon_h = +0{\cdot}51$ volt, the charge being defined as the quantity of electricity which the surface must send into the solution in order to keep const. the concentration of the Ag ions, when the surface is increased by 1 sq. cm. This value agrees well with those obtained from electrokinetic measurements by Billitzer and Bennewitz.

N. H. Hartshorne.

Quinhydrone electrode. III. [Effect of electrode materials.] J. L. R. Morgan and O. M. Lammert (J. Amer. Chem. Soc., 1931, **53**, 2154—2168; cf. this vol., 456).—Au electrodes, from whatever source, afford erratic results when the area is less than 1 sq. cm. Sufficiently large electrodes of Pt, Au, and lead-pencil graphite, but not lamp-carbons, produce equal p.d. in $0{\cdot}1N$-HCl, but the current capacity of the half-cell with Pt is greater than with a Au electrode of equal area. Au-plated and Pt-alloy electrodes give different p.d., but these differences are eliminated by stirring with N_2. The reproducibility of Pt, Pt–Rh and Pt–Ir alloy, but not of Au and graphite electrodes, is improved by stirring with N_2.

J. G. A. Griffiths.

Problem of the Haber glass electrode. J. Zirkler (Z. physikal. Chem., 1931, **155**, 75—76).—When the same solution of HCl is placed inside and outside the bulb of a glass electrode a potential drop is set up across the glass which is independent of the HCl concentration within the range N to $0{\cdot}001N$, but varies with the kind of glass, being about 30—60 mv. with "Violax," and about 90—110 mv. with "Jena Normalglas 16'''." The phenomenon is not shown by quartz bulbs. It is not influenced by the addition of small quantities of surface-active substances, nor by the replacement of HCl by H_2SO_4, nor by the use of bulbs blown with O_2 or CO_2 instead of with air.

N. H. Hartshorne.

Polarographic studies with the dropping mercury cathode. XIX. Effect of some organic dyes on the current maxima due to absorption of oxygen. B. Rayman (Coll. Czech. Chem. Comm., 1931, 3, 314—327).—The suppressive effect produced by org. dyes on the current max. caused by the electro-reduction of dissolved O_2 is due to preferential adsorption of the dye and consequent removal of O_2 from the electrode–solution interface. The dilutions of the dyes at which the max. in $0{\cdot}001N$-KCl is reduced to one half may be regarded as a measure of the extent to which each dye is adsorbed; data are given for a number of substances. The less readily adsorbed acid dyes suppress the max. at cathode potentials which are more positive than the electrocapillary zero, and cause a discontinuity on the curve; this effect is ascribed to adsorption of anions at the interface and preferential adsorption of O_2 mols. in the neighbourhood of the electrocapillary zero.

H. F. Gillbe.

Electrochemical behaviour of platinum in hydrochloric acid solution. G. Grube and H. Reinhardt (Z. Elektrochem., 1931, **37**, 307—320; cf. A., 1929, 1403).—From experiments on the dissolution of Pt in HCl solutions of H_2PtCl_6 the position of the equilibrium $2H_2PtCl_4 \rightleftharpoons H_2PtCl_6 + Pt + 2HCl$ has been approx. determined at 60°. The following values of ${}_0E_h$ at 60° have been obtained: $PtCl_4''|PtCl_6''$, $+0{\cdot}745 \pm 0{\cdot}01$; $Pt|PtCl_6''$, $+0{\cdot}765 \pm 0{\cdot}01$; $Pt|PtCl_4''$, $+0{\cdot}785 \pm 0{\cdot}01$ volt. Compact and fine-grained grey deposits of Pt are obtained by electrolysis at 60° of a $0{\cdot}1M$ solution of H_2PtCl_6 in $5N$-HCl with a current density of 0·01—0·02 amp. per sq. cm.; the current yield of Pt is 60—70%.

R. Cuthill.

Electrolytic reduction of chloroplatinic acid in hydrochloric acid solution. I. O. Stelling (Z. Elektrochem., 1931, **37**, 321—328).—The potential of a Pt electrode in a HCl solution of H_2PtCl_6 which has been partly reduced by electrolysis is, for a given HCl concentration, represented by the equation $E = E' + RT/2F \,.\, \log \text{(platinic)}/\text{(platinous)}\ (Cl)^2$, where (platinic) and (platinous) are calculated from the initial composition of the solution and the amount of current passed. At 50° the value of $_0E_h$ is $+0{\cdot}74$ volt. The cathodic current density–potential curves of a $0{\cdot}1M$ solution of H_2PtCl_6 in HCl show discontinuities, corresponding with the processes $Pt^{\cdot\cdot\cdot\cdot}+2\ominus=Pt^{\cdot\cdot}$, $Pt^{\cdot\cdot}+2\ominus=Pt$, $Pt^{\cdot\cdot\cdot\cdot}+4\ominus=Pt$, and $2H^{\cdot}+2\ominus=H_2$, but these are apparently complicated by the presence of a film on the electrode. R. CUTHILL.

Electrochemical and chemical behaviour of polonium in tartaric acid solution. M. HAÏSSINSKY (Compt rend., 1931, **192**, 1448—1451).—Using Joliot's method (cf. A., 1927, 633) and a solution of Po of concentration $2\times10^{9}N$ in N-tartaric acid the velocity of deposition is only about one fourth that in AcOH under similar conditions. There are two crit. potentials, 0·38 and 0·03 volt (cf. A., 1930, 713). A similar solution, but with a Po concentration of $7{\cdot}6\times10^{-9}N$, lost no Po when centrifuged; after the addition of aq. NH_3 to raise p_H to 7—8 the solution was found, however, to lose 42% Po in an hour. It is inferred that Po forms a sol. complex with tartaric acid similar to Bi (cf. A., 1914, ii, 148), the Po being present in two forms of different valencies. C. A. SILBERRAD.

Measurement of the electricity liberated during the downgrade reactions of organic compounds. J. H. WOLFENDEN (Nature, 1931, **128**, 69).—No systematic effect due to the fermentation of sucrose by yeast could be observed in the cell C|15% sucrose|15% sucrose+yeast|C. No evidence of a continuous supply of electrical energy from a chemical reaction proceeding irreversibly has been obtained (cf. this vol., 703). L. S. THEOBALD.

Passivity of chromium. W. J. MÜLLER (Z. Elektrochem., 1931, **37**, 328—330).—The observations and theory of E. Müller and Essin (this vol., 173) are essentially in agreement with the author's theory. The influence of the acid anion on the temp. at which passive Cr becomes active in an acid solution is, however, ascribed to variation in the solubility of the protective film, the solubility being maximal in HCl. Activation by cathodic liberation of H_2 is attributed to mechanical loosening of the oxide film. R. CUTHILL.

Becquerel effect of the second order. G. E. MUCHIN and M. I. SILBERFARB (Ukrain. Chem. J., 1930, **5**, [Sci.], 323—347).—The Becquerel effect of the second order is measured by $B=(E_1-E_0)100/E_0t$, where E_1 is the max. p. d. observed during illumination with a C arc of a Pt electrode in H_2SO_4 solution, as measured against a Hg_2Cl_2 electrode, E_0 is the p. d. in the dark, and t is the time of illumination in min. The difference in potential is partly due to heating of the solution, and this part is given by $W=(E_W-E_0)100/E_0 30$, where E_W is the p. d. found by illuminating vessels covered with black paper during 30 min. W is in all cases negative. The value of $B-W$ increases from $-0{\cdot}121$ in $0{\cdot}05M$-H_2SO_4 to $+0{\cdot}453$ in $0{\cdot}49M$-acid, and at higher concentrations of acid it falls to $-0{\cdot}033$ in $1{\cdot}24M$-H_2SO_4. R. TRUSZKOWSKI.

Velocity and affinity of chemical processes. J. V. MEDVEDEV (Bull. Acad. Sci. U.S.S.R., 1931, 393—400).—A theoretical discussion, based principally on Nernst's work. T. H. POPE.

Thermal decomposition of chlorine monoxide. J. J. BEAVER and G. STIEGER (Z. physikal. Chem., 1931, **B**, **12**, 93—108).—The thermal decomp. of Cl_2O at 100—140° in a quartz vessel appears to be a complex chain reaction, normally ending in explosion, and not, as Hinshelwood supposed (A., 1924, ii, 749), a simple bimol. reaction. After the period of induction, the velocity at 100—130° may be represented by $-d[Cl_2O]/dt=k[Cl_2O]$, and that at 140° by $-d[Cl_2O]/dt=k[Cl_2O]^{0{\cdot}75}$; in both equations the velocity coeff., k, is approx. proportional to the initial pressure of Cl_2O. Judged by the effect of variations in the ratio of surface area to vol. of the containing vessel the reaction as a whole is homogeneous in either a quartz or a glass vessel. Some intermediate product, comparatively stable at 0°, is formed during the period of induction and sets up reaction chains with the monoxide, and then when the concentration of the latter has become small reacts with itself explosively. Probably after the period of induction the concentration of this intermediate product remains appreciably const. until very near the end of the reaction, its reaction with the monoxide thus becoming kinetically unimol. The intermediate product may be the oxide ClO, and it is very probable that ClO_2 also plays an important part. The reaction is not affected by Cl_2, O_2, N_2, air, or CO. R. CUTHILL.

Thermal decomposition of nitryl chloride. A homogeneous gas reaction of the first order. H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1931, **B**, **12**, 115—131).—The thermal decomp. of nitryl chloride (cf. A., 1929, 1395) at 100—150° is a homogeneous unimol. reaction, the heat of activation calc. from the temp. coeff. being about 20·5 kg.-cal. The collision number is, however, exceptionally small under moderate pressures, and, probably in consequence of this, the velocity coeff. increases with increasing pressure, and has not reached a steady value even at 10 atm. H_2, O_2, Cl_2, CO_2, N_2, and CO all accelerate the reaction to approx. the same extent; NO_2 has an accelerating effect which is about 20% greater, and a mixture of NO_2 and Cl_2 in the stoicheiometric ratio has the same effect as undecomp. nitryl chloride. R. CUTHILL.

Possibility of bimolecular association reactions. L. S. KASSEL (J. Amer. Chem. Soc., 1931, **53**, 2143—2147).—The bimol. association reaction is regarded as the reverse of the unimol. decomp., and is shown, theoretically, to be possible in the case of complex mols. at a considerable fraction of all collisions. The polymerisation of C_2H_4 (this vol., 436) is probably of this type. J. G. A. GRIFFITHS.

Thermal decomposition of methane. II. Homogeneous reaction. G. C. HOLLIDAY and W. J. GOODERHAM (J.C.S., 1931, 1594—1604; cf. A., 1929, 773).—The decomp. of CH_4 in SiO_2 bulbs is mainly a homogeneous reaction. Above 900° the reaction proceeds in two stages: in the first, 2 mols. of CH_4 react to form C_2H_2, which, in the second stage decomp. to H and C. F. J. WILKINS.

Thermal decomposition of carbon tetrabromide. H. A. TAYLOR (J. Physical Chem., 1931, **35**, 1795—1799).—The thermal decomp. of CBr_4, investigated colorimetrically, is a heterogeneous reaction apparently of the first order between 300° and 330°. The average energy of activation, calc. by means of Arrhenius' equation, is 57,200 g.-cal.

L. S. Theobald.

Thermal decomposition of diazomethane. E. W. R. Steacie (J. Physical Chem., 1931, 35, 1493—1495).—The slow decomp. of diazomethane in quartz between 140° and 220° (products N_2 and C_2H_4) is apparently bimol.; calc. heat of activation 36×10^3 g.-cal. per mol. Traces of org. matter cause serious explosions. L. S. Theobald.

Thermal decomposition of dimethyltriazene. Homogeneous unimolecular reaction. H. C. Ramsperger and J. A. Leermakers (J. Amer. Chem. Soc., 1931, 53, 2061—2071).—The rate of decomp. at 200—230° of 0·019—8 cm. of dimethyltriazene has been measured by the increase of pressure (factor, 2·175). The reaction is homogeneous and of the first order; the velocity coeff., $4{\cdot}05\times10^{11}e^{-33,800/RT}$, falls with initial pressures less than 1 cm. The data are in agreement with the theories of Rice and Ramsperger (A., 1927, 833). J. G. A. Griffiths.

Influence of hydrogen on chemical changes in silica vessels. M. W. Travers, L. E. Hockin, and T. J. P. Pearce (Nature, 1931, 128, 66).—In the condensation of C_2H_6 at 600° reproducible results can be obtained only in thick-walled SiO_2 vessels or in thin-walled vessels surrounded by an atm. of H_2. This suggests that in SiO_2 there exists a complex equilibrium which consists of solid phase : glass–gas interface : gas–glass interface : gas phase. The H_2 in the solid phase may be more highly dissociated than in the gaseous phase and the life of the H atoms passing from glass–gas to gas–glass interface may be long enough to bring about processes commonly attributed to at. H in the adsorbed layer on the SiO_2.

L. S. Theobald.

Explosive reactions. W. P. Jorissen (Natuurwetensch. Tijds., 1931, 13, 189—202).—Previous work on the explosion limits of various three-component gaseous mixtures is summarised. Three principal types of mixture are recognised, according to the type of diagram obtained, but there are at least eight less common types, which are described and discussed. The diagrams obtained with solid explosive mixtures are described and the similarity with those obtained with gases is indicated.

H. F. Gillbe.

Photographic flame studies in the petrol engine. L. Withrow and T. A. Boyd.—See B., 1931, 618.

Reaction between arsenious acid and iodine. H. A. Liebhafsky (J. Physical Chem., 1931, 35, 1648—1654).—The kinetics of the reaction $H_3AsO_3+I_3^-+H_2O=H_3AsO_4+2H^++3I^-$ are discussed (cf. A., 1906, ii, 76). L. S. Theobald.

Carbon dioxide absorption by solutions of sodium and potassium hydroxide. K. Masaki (J. Biochem. Japan, 1931, 13, 211—217).—Aq. *N*-NaOH absorbs CO_2 more rapidly (1 : 0·93) than *N*-KOH at 11°, whilst at 18° and 25° the KOH solution more rapidly absorbs the gas, the ratios being 1 : 1·17 and 1 : 1·29 respectively. F. O. Howitt.

Reactions involving hydrogen peroxide, iodine, and iodate ion. IV. Oxidation of iodine to iodate ion by hydrogen peroxide. H. A. Liebhafsky (J. Amer. Chem. Soc., 1931, 53, 2074—2090; cf. this vol., 324, 573).—The velocity of the reaction $I_2+5H_2O_2=2IO_3'+2H^{\cdot}+5H_2O$ has been investigated at 0° over a wide range of initial concentration of IO_3', H_2O_2, $HClO_4$, and I_2. The oxidation of I to IO_3' does not proceed appreciably by the direct oxidation of I, I', or HIO by H_2O_2. The induction period, which occurs at certain concentration, is prolonged by low $[IO_3']$ and $[H^{\cdot}]$ and high $[H_2O_2]$, and is attributed to the building up of the intermediate HIO_2. The following mechanism is in accord with the observations : (*a*) $I_2+H_2O \rightleftharpoons H^{\cdot}+I'+HIO$ (rate determining step), (*b*) $IO_3'+I'+2H^{\cdot}=H_2I_2O_3$, (*c*) $H_2I_2O_3+H_2O_2=2HIO_2+H_2O$, (*d*) $HIO_2+HIO=H_2I_2O_3$ (cf. A., 1930, 1378), (*e*) $HIO_2+H_2O_2=IO_3'+H^{\cdot}+H_2O$. I is reduced to I' by H_2O_2 when $[H^{\cdot}]$ is less than $4\times10^{-3}N$, since the I' formed by the reaction $HIO+H_2O_2=H^{\cdot}+I'+H_2O+O_2$ cannot be as effectively removed as at higher $[H^{\cdot}]$ at which reaction (*b*) is favoured, and hence the H_2O_2 is decomp. catalytically by the I_2–I' couple. The results do not establish the sp. rate of the hydrolysis of I_2 (reaction *a*), but indicate that the coeff. is probably greater than 0·06 at 0° and 0·6 at 25°.

J. G. A. Griffiths.

Interaction between nitrogen trichloride and nitric oxide at −150°. III. Interaction of nitric oxide and chlorine at −80° and −150°. W. A. Noyes (J. Amer. Chem. Soc., 1931, 53, 2137—2143).—In the presence of CCl_4, NO and Cl_2 combine much more slowly at − 150° than at −80°. The reaction is very slow at − 180°. Further support is obtained for the mechanisms proposed for the reactions between NO and NCl_3 (this vol., 52). The structure of N_2O is discussed. J. G. A. Griffiths.

Velocity and heat of saponification of amides. E. Calvet (Compt. rend., 1931, 192, 1569—1572).—The velocity of saponification by NaOH of aliphatic amides at 17° has been measured by determining the NH_3 evolved. The reaction is bimol. and decreases rapidly as shown by the values of *k*: formamide, 4·45; acetamide, 0·0692; propionamide, 0·0669; butyramide, 0·0237; valeramide, 0·0239; and hexamide, 0·0237. The corresponding heats of saponification in g.-cal. are respectively : 6·73, 6·55, 6·6, 5·8, 5·65, 5·6 (all $\times10^{-3}$). F. R. Shaw.

Kinetic theory of the velocity of biochemical processes. I. J. V. Medvedev (Bull. Acad. Sci. U.S.S.R., 1931, 277—313).—Mainly a theoretical paper, with a few data concerning the inversion of sucrose by invertase. The interaction of a particle of an enzyme with a mol. of the substrate undergoing chemical change, resulting in an enormous increase in the velocity of this change, is regarded as consisting in the transference to the mol. of substrate of a quantum of energy, which is the true agent of the acceleration of the reaction. The association of the enzyme particle with the mol. of substrate accompanying the transference of the energy quantum differs from that of chemical compounds and is regarded as an impact of the second type. On this basis it is possible to calculate the order of the abs. magnitude of the chemical reaction with the help of the equations of static mechanics. The results obtained in this way for the inversion of sucrose by invertase agree with the experimental data within the limits of accuracy of these. T. H. Pope.

Kinetics of transitions in polymorphic solids. A. F. Benton and R. D. Cool (J. Physical Chem., 1931, **35**, 1762—1769).—The rates of transition of HgI_2 and of TlI have been measured by means of a dilatometer in which vol. changes are transmitted by an inert gas instead of a liquid. Both transitions are autocatalytic in each direction. The rate of reaction increases with increasing temp. intervals above and below the transition temp.; in the latter case this rate increases to a max. with a fall in temp. and then decreases to values which are very small at liquid air temp. The rate is sensitive to the thermal history of the sample. With TlI the rate of conversion is the same in air, CO_2, or N_2. The transition temp. for TlI lies between 150° and 174° and probably between the narrower limits 160° and 170°, and for HgI_2 at 1 atm. it is between 123° and 129·5°. The vol. changes are 0·0028 and 0·003 c.c. per g., respectively, the red variety being denser in each case. L. S. Theobald.

Thermal decomposition of potassium chlorate. J. B. M. Coppock, J. Colvin, and J. Hume (Trans. Faraday Soc., 1931, **27**, 283—284).—The decomp. of $KClO_3$ at 223° is interfacial and proceeds from nuclei on the surface. Crystals of $KClO_3$ in light contact with particles of MnO_2 or rubbed with MnO_2 failed to show any increase in the rate of decomp. J. W. Smith.

Rate of calcination of limestone. C. C. Furnas. —See B., 1931, 629.

Kinetics of reactions between colloids. I. Formation of uranium–vanadium complexes. V. A. Kargin (Z. anorg. Chem., 1931, **198**, 79—87).—The reaction between UO_3 and V_2O_5 sols has been studied spectrophotometrically and by potentiometric titration. The change of the extinction coeff. *E* with time indicates the formation of the colloidal compounds $UO_3,2V_2O_5$,aq., and UO_3,V_2O_5,aq. The reaction is of zero order and exhibits a marked induction period; it takes place between the particles which are in true solution, and not between the colloidal particles. The addition of an abnormally high quantity of uranyl salts is necessary to cause coagulation of sols containing the complexes, owing to the production of a compound $3UO_3(UO_3,2V_2O_5)$,aq., of which the naturally occurring uranovanadates are probably derivatives. The induction period, and the total period of the reaction, diminish on dilution of the mixed sols, the former being determined by the time required for the production of nuclei of the complex acids; addition of a sol in which the final reaction product is present reduces the induction period less than does addition of a sol in which the induction period has just terminated, owing to the protective action of the double layer and hydrate envelope which are subsequently formed. H. F. Gillbe.

Reaction between magnesium and salt solutions. II. I. Iitaka (J. Iron Steel Inst. Japan, 1930, **16**, 1056—1063).—The velocity of reaction of Mg with dil. HCl ($[Cl']$ kept at $10^{-2}N$; $[H^{\cdot}]$ 0—10^{-13}) diminishes with decrease in $[H^{\cdot}]$, but does not vanish when $[H^{\cdot}]=0$; it is const. for $[H^{\cdot}]$ 10^{-4} to 10^{-11}. The stirring effect is attributed to autocatalysis, a compound of Mg, H_2O, and Cl′ being formed. Chemical Abstracts.

Influence of stress on corrosion. D. J. McAdam, jun. (Amer. Inst. Min. Met. Eng., Tech. Pub., 1931, No. 417, 39 pp.).—The behaviour of various metals under similar conditions of corrosion is illustrated. The rate of net damage (lowering of the fatigue limit) varies as the 3rd to the 5th power of the corrosion stress. The conditions favouring intercryst. corrosion are discussed. Chemical Abstracts.

Initial corrosion rates of metals. R. H. Brown, B. E. Roetheli, and H. O. Forrest.—See B., 1931, 681.

Method of testing the local-element theory of corrosion. W. Guertler and B. Blumenthal.—See B., 1931, 681.

Catalysis by heavy metal ions in aqueous solution, and autoxidation of sulphite solutions. J. Franck and F. Haber (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1931, **13**, 250—256).—Homogeneous catalysis in aq. solution by heavy metal ions is attributed to their reacting with constituents of the solution to give radicals or atoms, which in turn react with other constituents of the solution, *e.g.*, with dissolved O_2 in autoxidation, the heat of activation in this instance being small or even zero. If a new atom or radical is produced in the second reaction, a reaction chain is established, and ends only when the atoms or radicals combine to form saturated mols. In absence of O_2, $H_2S_2O_6$ is formed in alkali sulphite solutions containing the $Cu^{\cdot\cdot}$ ion, the intermediate product being the anion of monothionic acid, SO_3', which acts as a free radical: $2SO_3''+2Cu^{\cdot\cdot}=2SO_3'+2Cu^{\cdot}$, $2SO_3'=S_2O_6''$. If, however, O_2 is present, the SO_4'' ion and free OH result: $SO_3H+O_2+SO_3''+H_2O=2SO_4''+OH+2H^{\cdot}$, or possibly $HSO_3+O_2=HSO_5$, $HSO_5+SO_3''+H_2O=2SO_4''+OH+2H$. The chain is propagated by the reactions $SO_3''+OH=SO_3'+OH'$, and $SO_3'+H^{\cdot}=SO_3H$, which explains why autoxidation does not occur in strongly alkaline solutions. In the photo-reaction, the primary process is probably $SO_3'',H_2O+h\nu=SO_3'+H+OH'$. R. Cuthill.

Action of ferrous iron in induced reactions. D. Richter (Ber., 1931, **64**, [*B*], 1240—1243).—The possibility that the induced oxidation of H_3PO_2 by O in presence of $Fe^{\cdot\cdot}$ is a chain reaction is strengthened by the observation that it is restricted by typical negative catalysts, *e.g.*, quinol, I, and $NHPh_2$. Similar observations are recorded for the effect of benzyl and *iso*propyl alcohol on the induced oxidation of Na_2SO_3. H. Wren.

Reduction of silver halides by sodium sulphite and nitrite in the presence of inductors and a cheap developer in photography. R. B. L. Verma and N. R. Dhar (J. Physical Chem., 1931, **35**, 1770—1776).—AgCl, AgBr, AgI, and AgCNS are reduced by developers in the following, decreasing order: metol, pyrogallol, quinol, hydrazine sulphate, NH_2OH,HCl, and $FeSO_4$. Na_2SO_3 or $NaNO_2$ alone does not reduce

Ag salts but increases reduction by the developers, the order remaining unchanged. Reduction in the Ag salts is in the order AgCl>AgBr>AgCNS>AgI. The efficiency of ordinary developers can be maintained by increasing the Na_2SO_3 and diminishing the metol or quinol present. L. S. Theobald.

Comparative catalytic dehydration [of alcohols] by sulphuric acid and alkali hydrogen sulphates. J. B. Senderens (Compt. rend., 1931, **192**, 1422—1425).—To test the hypothesis that the differences in catalytic activity as regards dehydration of alcohols (cf. A., 1929, 695; 1930, 889) of H_2SO_4, $NaHSO_4$, and $KHSO_4$ are due to their differing avidity for water, the amounts of water absorbed from saturated air in equal times are shown to be in the order of this activity; the amounts absorbed in 110 days by $H_2SO_4+2H_2O$, $NaHSO_4$, and $KHSO_4$ are in the ratios 33·2, 21·6, and 16·0. C. A. Silberrad.

Catalytic effect of solvents. Decomposition of malonic acids. R. E. Burk and W. Daus (J. Physical Chem., 1931, **35**, 1461—1473).—The rate of decomp. of malonic acids, especially the benzyl derivative, has been determined in different solvents. Oleic and palmitic acids, *o*-, *m*-, and *p*-chloronitrobenzene show no catalytic effect, but dimethylaniline has a marked effect, accompanied by a lowering of the temp. coeff., which, however, is not due to salt formation. Mechanisms for activation by the catalyst are discussed. L. S. Theobald.

Catalytic action of manganese on oxidation of quinol. E. A. Sym (Annalen, 1931, **487**, 174—196).—In buffered solutions the catalytic effect of Mn on the oxidation of quinol to benzoquinone is most marked at p_H about 7·0, and, unlike the autoxidation, is depressed by addition of quinone. It decreases with time, and increases with increasing concentrations of quinol, Mn, and O_2. In non-buffered solutions dissolved $Mn(OH)_2$ exerts a greater effect less dependent on quinol concentration. Evidence for the formation of a catalytically active Mn–quinol complex is obtained both by a kinetic study of the reaction and by determinations of the solubility of $Mn(OH)_2$ in aq. quinol, but very different results are obtained for the dissociation coeff. of the supposed complex by the two methods. During the air-oxidation of quinol in presence of an excess of an aq. suspension of $Mn(OH)_2$ the quinhydrone formed carries down with it much of the Mn, and it is to this behaviour that the suppression of catalysis by quinone is attributed. H_2O_2 is formed during the autoxidation of quinol, but the method employed to detect it [oxidation of $Ce(OH)_3$] could not be used in presence of Mn. Neither $Fe^{\cdot\cdot}$ nor $Fe^{\cdot\cdot\cdot}$ salts catalyse the air-oxidation of quinol under the conditions employed with Mn, and the activity of Mn is unaffected by glycine, Na K tartrate, or $Na_4P_2O_7$. H. A. Piggott.

Effect of neutral salts on the rate of hydrolysis of cellulose acetate in acetic acid solutions. J. F. Fuess and C. J. Staud (J. Amer. Chem. Soc., 1931, **53**, 1934—1941).—The rate of hydrolysis of cellulose acetate dispersed in AcOH containing small amounts of H_2O, H_2SO_4, H_3PO_4, and $NaHSO_4$ is retarded by the addition of $NaNO_3$, KNO_3, Na_2SO_4, K_2SO_4, or NaCl; NaCl has the least effect. Addition of the salts after partial hydrolysis also causes a retardation. All hydrolyses were carried out at 53±1°. H. Burton.

Velocity of crystallisation of chrome alums. S. I. Orlova and N. N. Petin (J. Gen. Chem. Russ., 1931, **1**, 65—69).—The velocity of crystallisation of chrome alums is unaffected by light, and is greater for K than for Na salts. The accelerating action of various substances is in the order: $H_2SO_4>HNO_3>Na_2SO_3>K_2SO_4>NaNO_3>KNO_3>Na_2SO_4$. R. Truszkowski.

Absolute rates of heterogeneous gas reactions. B. Topley (Nature, 1931, **128**, 115—116).—An expression for a decomp. reaction catalysed by a surface in which the catalysis depends on adsorption, thermal activation, and break-up into new mol. species is applied to various gas reactions on heated wire catalysts. L. S. Theobald.

Quantum mechanics of adsorption catalysis. M. Born and V. Weisskopf (Z. physikal. Chem., 1931, **B**, **12**, 478).—A correction (cf. this vol., 576). F. L. Usher.

Intermediate compound theory of heterogeneous catalysis. An attempt at a quantitative investigation of the range of validity of this theory for the reaction $2H_2+O_2\longrightarrow 2H_2O$ on a copper catalyst. F. J. Wilkins and S. H. Bastow (J.C.S., 1931, 1525—1532).—A quant. method has been devised to test the validity of the intermediate compound theory of heterogeneous catalysis for the reaction $2H_2+O_2\longrightarrow 2H_2O$ on an activated Cu catalyst. When Cu is heated in an atm. of H_2 and O_2 at 10^{-2} mm. more reaction takes place than that calc. on the assumption that only the oxidation of Cu and the reduction of the oxide are occurring in the system. This excess reaction is attributed to the formation of H_2O in an activation catalysis at the Cu_2O surface. At 142°, the activation catalysis preponderates, but as the temp. is raised it becomes of decreasing importance, and at 250° the intermediate compound catalysis appears to account for practically the entire reaction. F. J. Wilkins.

Temperature coefficient of the thermal decomposition of ammonia on platinum. J. K. Dixon (J. Amer. Chem. Soc., 1931, **53**, 2071—2074; cf. this vol., 803).—The rate of decomp. at 1 atm. of NH_3 on a Pt gauze catalyst has been determined dynamically, with and without the addition of N_2 and H_2, at 772°, 826°, and 858°. The rate is proportional to the pressure of NH_3 and inversely proportional to that of H_2; as the pressure of H_2 is increased, the inhibiting effect approaches a const. value. The heat of activation is 40,000 g.-cal. per mol. (cf. A., 1929, 890). J. G. A. Griffiths.

Limitations in capacity of a platinum catalyst for ammonia oxidation. H. W. Webb.—See B., 1931, 674.

Decomposition of nitrous oxide at low pressures on a platinum catalyst. G. van Praagh and B. Topley (Trans. Faraday Soc., 1931, **27**, 312—322).—The activity of the Pt wire used as catalyst increases during use, and ultimately reaches a max. When the catalyst in this state is brought in contact with N_2O no reaction occurs until the temp. lies within the range 490—720°. Reaction starts slowly and either dies away when only partial decomp. has been effected, or, if the temp. is high enough, rapidly increases in speed and then abruptly slows down before reaction is complete. It is suggested that the primary reaction is $N_2O+Pt=N_2+Pt(O)_{adsorbed}$, followed by $Pt(O)_{adsorbed}+N_2O=Pt+N_2+O_2$. The peculiar behaviour of the catalyst in the state of max. activity is ascribed to the existence at the active centres of energy chains, during the existence of which the mean kinetic energy associated with each group of active Pt atoms corresponds with a temp. much higher than that of the system as a whole. R. CUTHILL.

Topochemistry of contact catalysis. V. Hydrogenating activity, magnitude, and structure of nickel surfaces. G. M. SCHWAB and L. RUDOLPH (Z. physikal. Chem., 1931, B, **12**, 427—448; cf. A., 1929, 1150).—The hydrogenating activity and the surface area of Ni decrease with a rise in temp., or with the duration of reduction; for a given sample activity increases more rapidly than surface. The surface area was calc. from the initial rate of dissolution of the powder in acid as compared with that of polished sheet. Hydrogenation of Et cinnamate, the reaction chosen for reference, proceeds linearly with time, and the velocity is proportional to the quantity of Ni after allowing for a fraction of the metal which is poisoned by a substance of undetermined nature. From the relation between the activity and the surface area it is inferred that active centres occur chiefly in the edges and angles of the micro-crystals of the metal.
F. L. USHER.

Preparation and testing of nickel catalysts for hydrogenation. H. ADKINS and L. W. COVERT (J. Physical Chem., 1931, **35**, 1684—1691).—Improved methods for the prep. of Ni catalysts are described and the relative merits of Na_2CO_3, $NaHCO_3$, and KOH as precipitants for depositing Ni on kieselguhr have been measured for the hydrogenation of PhMe, $COMe_2$, $CH_2Ph{\cdot}OH$, and resorcinol. Comparisons of 8 different Ni catalysts are made from (i) the time required for the middle 60% hydrogenation, (ii) the temp. at which max. pressure of H_2 is reached, (iii) the time required for absorption of all the H_2, and (iv) the ratios of *cyclo*hexylcarbinol/toluene and *cyclo*hexane-1 : 3-diol/*cyclo*hexanol in the case of $CH_2Ph{\cdot}OH$ and resorcinol, respectively. The question of a basis of comparison for Ni catalysts is discussed. So many variables are involved, however, that a satisfactory basis is practically impossible. With Ni catalysts there is no necessary relationship between rate of hydrogenation and the relative rates of competitive reactions. L. S. THEOBALD.

Relation between the activity of catalysts for the synthesis of methyl alcohol and their chemical and crystalline structure. II. Absorption measurements of the gaseous reactants. G. NATTA and E. CASAZZA (Giorn. Chim. Ind. Appl., 1931, **13**, 205—212; cf. A., 1930, 552).—The coeffs. of absorption of CO_2, CO, and H_2, respectively, by various metallic oxide catalysts used in the synthesis of MeOH have been measured. Catalysts which show a strong absorption for H_2 are not suitable, since they bring about further hydrogenation and formation of CH_4. The most active catalysts are those which show a high absorption for CO and for CO_2; *e.g.*, those prepared by decomp. of the precipitated basic carbonates are more active than those obtained from the hydroxides, and the catalysts obtained from certain varieties of neutral $ZnCO_3$ have an even greater activity and absorbing power for CO_2.
O. J. WALKER.

Competitive hydrogenations. II. F. F. DIWOKY and H. ADKINS (J. Amer. Chem. Soc., 1931, **53**, 1868—1875).—The rate of hydrogenation of the following substances over a nickel catalyst at 125—175°/125—200 atm. decreases in the order quoted: quinoline, C_6H_6, PhMe, PhOH, benzyl alcohol, pyridine, $NHPh_2$, acetanilide, NH_2Ph. Hydrogenation of mixtures of any two of the above compounds with H_2 sufficient to reduce completely one of the components, and determination of the products formed, show that preferential reduction occurs in the following order: quinoline, pyridine, NH_2Ph, benzyl alcohol, PhOH, $NHPh_2$, C_6H_6, acetanilide, PhMe. NH_2Ph has practically no effect on the hydrogenation of quinoline or pyridine, but all these bases inhibit the reduction of C_6H_6 or PhMe. The hydrogenation of $NHPh_2$ is accelerated by C_6H_6 or PhMe. There is no relationship between the relative rates of hydrogenation of the above compounds singly and in mixtures. H. BURTON.

Explosion during catalytic reduction of nitroanisole in the liquid phase. T. S. CARSWELL (J. Amer. Chem. Soc., 1931, **53**, 2417—2418).—400 g. of nitroanisole in an autoclave at 250° containing a Ni catalyst rapidly absorbed hydrogen at 500 lb. per sq. in., but exploded violently after 20 min. (cf. A., 1928, 600). J. G. A. GRIFFITHS.

Protection of iron in aërated saline solutions: an Evans pile. E. HERZOG and G. CHAUDRON.—See B., 1931, 682.

Electrodeposition of chromium from ammonium chromioxalate. A. MAZZUCCHELLI.—See B., 1931, 682.

Chemical action in the glow discharge. VI. Oxidation of carbon monoxide. VII. Dissociation and oxidation of methane. A. K. BREWER and P. D. KUECK (J. Physical Chem., 1931, **35**, 1281—1292, 1293—1302; cf. A., 1930, 1533).—VI. In a $2CO : O_2$ mixture at liquid air temp. an electric discharge gives CO_2, but with an excess of CO or neutral gases carbon suboxide is deposited with the CO_2 on the tube walls. CO alone dissociates into CO_2 and the suboxide. In the negative glow the rate of oxidation of CO is practically independent of pressure, but it is proportional to the current. It is accelerated by excess of CO when the total $CO \ngtr 80\%$ and retarded by that of O_2 almost in proportion to the amounts added. In the positive column the rate is proportional to current and independent of pressure below 10 mm. Above this pressure it is slightly less than proportional to the current, whilst at higher pressures the rate increases rapidly to the ignition point. Ignition is apparently confined to the positive column. The CO_2 formed in the negative glow reaches the walls as positive ions, but in the positive column is deposited mainly as neutral mols. In the spectrum of the negative glow bands of the first negative group for CO appear with approx. equal intensity from 0·5 to 10 mm. pressure. The data indicate a simple ion cluster mechanism in the negative glow and an ion chain mechanism in the positive column. The $CO^{\cdot}$ ions appear to be more effective than $O_2^{\cdot}$ ions in initiating the reaction. In the negative glow the ratio M/N, *i.e.*, the no. of mols. synthesised per positive ion, is 2.

VII. CH_4 is quantitatively converted into C_2H_4 and H_2 in the glow discharge at the temp. of liquid air, one mol. of C_2H_4 being formed per $CH_4^{\cdot}$ ion. (At room temp. a large amount of a greyish-yellow deposit is formed on the walls of the tube.) In a CH_4–$2O_2$ mixture CO_2 and H_2O are the sole products of reaction; no H_2O_2 is formed as is the case with $2H_2$–O_2 mixtures. The rate of oxidation is accelerated to a max. at the 1 : 1 mixture by excess of CH_4. O_2 retards the reaction even more than does A, whilst He at first has an accelerating effect even in relatively large amounts and then retards reaction. The reaction between CH_4 and O_2 is initiated primarily by $CH_4^{\cdot}$ ions; it is most pronounced in the negative glow, is negligible in the dark spaces, and is approx. const. in the positive column. $M/N_{\text{obs.}}$ is approx. 7, but a val. of 6 is more probably correct. The efficiency of the positive column in terms of electron volts per mol. rapidly increases with pressure above 5·5 mm., indicating the presence of ionic chain reactions.

L. S. THEOBALD.

Reactions of ionised gases : synthesis of nitric acid. M. LAPORTE (Compt. rend., 1931, **192**, 1555—1558).—To effect more completely the union of ionised O and N a current of air and N_2, in controllable proportions together with steam, is passed between the armatures (of Hg at 140°) of a condenser similar to Berthelot's ozoniser; the products are cooled and the gases passed into aq. NaOH. The frequency of the oscillating discharge used is about 500,000. The presence of steam in the ozoniser greatly facilitates the reaction. Only O_3 is produced if the temp. of the electrodes is below 100°, but none at 140°. The best proportion of air to N_2 is such that O_2 forms 3% of the whole. The efficiency of the process is about 2%.

C. A. SILBERRAD.

Decomposition of sodium azide by controlled electron bombardment. R. H. MÜLLER and G. C. BROUS (J. Amer. Chem. Soc., 1931, **53**, 2428).—With potentials at or less than 11·5 volts, no effect was observed, but with higher potentials N_2 was evolved. Thermal decomp. was absent. J. G. A. GRIFFITHS.

Applicability of Einstein's law of photochemical equivalence. B. K. MUKERJI and N. R. DHAR (J. Physical Chem., 1931, **35**, 1790—1794).—Determinations of the quantum efficiency at different temps. and with different wave-lengths show that this law fails in most of the following reactions : $(CO_2K)_2$ and I, $H{\cdot}CO_2Na$ and $HgCl_2$, quinine sulphate and H_2CrO_4, $H{\cdot}CO_2Na$ and I, $KMnO_4$ and $(CO_2H)_2$, $FeSO_4$ and I, $NaNO_2$ and I, H_2CrO_4 and $(CO_2H)_2$, sodium potassium tartrate and Br, sodium citrate and I, sodium malate and iodine, $(CO_2NH_4)_2$ and $HgCl_2$ in the presence of eosin, the photo-oxidation of CHI_3 in amyl alcohol or C_6H_6, and the bleaching of dicyanine. Quantum efficiency increases with a rise in temp. and with an increase in frequency. The reactions which show the most marked deviations are strongly exothermal. L. S. THEOBALD.

Correlation of certain photochemical reactions and wave-length of light. II. F. C. HYMAS (J.S.C.I., 1931, **50**, 193—195T).—When exposed to light from a vac. Hg vapour arc, the $COMe_2$–methylene-blue reaction responds almost exclusively to radiation between 250 and 400 mμ, whilst the KNO_3–KNO_2 reduction covers the region 220—400 (max. 255) mμ. The KI–starch reaction is suitable for the range 220—320 (max. 255) mμ, and the oxalic acid–uranyl sulphate reaction for the range 220—500 mμ (max. 325 and 260, min. 280 mμ). In general, when corrected on the basis of equal energy distribution, the photochemical effects increase with decrease of wave-length, the exception being the $COMe_2$–methylene-blue reaction.

Quantum yield in photolysis of silver chloride. P. FELDMANN (Z. physikal. Chem., 1931, **B**, **12**, 449—466; cf. A., 1928, 815).—AgCl was exposed to radiation of wave-length 365 mμ under $NaNO_2$ solution, and the liberated Cl, which was present exclusively as chloride, was determined potentiometrically. The quantum yield approached 1 for short exposures, but decreased on prolonged illumination owing to recombination of Ag and Cl. Irregularities exceeding the experimental error were encountered.

F. L. USHER.

Photolysis of silver chloride. P. FELDMANN and A. STERN (Z. physikal. Chem., 1931, **B**, **12**, 467—477).—Irregularities in the results obtained in determining the quantum yield (cf. preceding abstract) were traced to a delay of several min. in the attainment of a const. potential after interrupting the illumination. When this error is eliminated the mean quantum yield is 0·99 if the chloride is under $NaNO_2$ solution. Under water, the quantum yield is only 0·5, the discrepancy probably being due to recombination rather than to formation of HOCl, which could not be detected. F. L. USHER.

Action of low-speed electrons on photographic emulsions. R. E. BURROUGHS (Rev. Sci. Instr., 1931, [ii], **2**, 321—328).—The image produced is due to radiations excited by the electrons in the residual gas covering the emulsion, and not appreciably by direct energy transfer. The lowest energy electron recorded is not primarily characteristic of the emulsion, but is related to the crit. potential of the residual gas. The sensitivity of emulsions to electrons is proportional to their sensitivity to blue and ultraviolet light. J. LEWKOWITSCH.

Photosynthesis in tropical sunlight. I. II. Photosynthesis of formaldehyde and carbohydrates from alkali hydrogen carbonates in the presence of coloured insoluble substances. G. G. RAO and N. R. DHAR (J. Physical Chem., 1931, **35**, 1418—1423, 1424—1432).—I. CH_2O is formed when CO_2 and H_2O are exposed to sunlight in the presence of chlorophyll, methylene-blue, malachite-green, methyl-orange, colloidal $Fe(OH)_3$, uranyl nitrate,

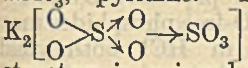
$Cr_2(SO_4)_3$, and $CuSO_4$ (cf. A., 1925, ii, 884). CO_2 issuing from a suspension of chlorophyll exposed to the light of a W-filament lamp contained traces of CO. Burk's experiments (A., 1927, 1040) are criticised.

II. Exposure to sunlight of a 2% solution of $NaHCO_3$ containing $CoCO_3$ gives small amounts of CH_2O, whilst solutions containing $NiCO_3$ give larger amounts and carbohydrate in addition. Small quantities of reducing sugar were also obtained by exposing to sunlight aq. solutions of CH_2O containing ZnO, $FeCl_3$, or methyl-orange. A suggested mechanism is discussed.

L. S. Theobald.

Action of sunlight on allylthiocarbimide. D. Ganassini (Arch. Ist. Biochim. Ital., 1931, **3**, 1—10).—Allylthiocarbimide kept in sunlight in bottles (*a*) dry, containing air, and (*b*) containing water and air, turned yellow and deposited a ppt., showing, respectively, 15% and 5% decomp. after one month. The products detected indicate that the following photochemical reactions occur: $3C_3H_5{\cdot}NCS+3H_2O=C_3H_5{\cdot}NH_2+(C_3H_5)_2O+2HCNS+H_2S+CO_2$ and $9HCNS=2(CNS)_3+3HCN+3H_2S$, and that H_2SO_4 and NH_3 are formed by secondary reactions. A slight yellow colour developed in a completely filled bottle, and control samples remained unchanged.

R. K. Callow.

Reaction of potassium pyrosulphate with ammonia and amines and of pyrosulphuric acid and monohydrate with pyridine. P. Baumgarten (Ber., 1931, **64**, [*B*], 1502—1506).—In cold aq. solution $K_2S_2O_7$ reacts with NH_3 and its derivatives or *tert.* amines thus: $K_2[SO_4(SO_3)]+2NH_3=K_2SO_4=NH_2{\cdot}SO_3NH_4$ and $K_2[SO_4(SO_3)]+R_3N=K_2SO_4+R_3\overset{+}{N}{\cdot}SO_2{\cdot}\overset{-}{O}$. Examples cited are NH_3, NH_2Ph, NMe_3, pyridine. For $K_2S_2O_7$ the constitution  is suggested. An analogous structure is assigned to $H_2S_2O_7$ mainly on account of the immediate production from it and pyridine of *N*-pyridiniumsulphonic acid. Since anhyd. H_2SO_4 and pyridine also yield *N*-pyridiniumsulphonic acid it probably contains the compound $H_2\overset{+}{O}{\cdot}SO_2{\cdot}\overset{-}{O}$ in equilibrium with the dihydroxyl form or its association products.

H. Wren.

Preparation of chemically pure potassium and sodium nitrites. D. S. Slavina (Trans. Inst. Pure Chem. Reag., 1931, **10**, 21—35).—Commercial $NaNO_2$ can be freed from NaCl and $NaNO_3$ by recrystallisation. Commercial KNO_2 cannot be freed from KCl and KNO_3 by recrystallisation and the method of decomp. with $AgNO_2$ is recommended.

E. S. Hedges.

Action of anhydrides on metals. M. Lemarchands and H. L. Roman (Compt. rend., 1931, **192**, 1381—1383).—CO_2 passed over K mixed with sand gives a max. yield (17%) of $K_2C_2O_4$ at 230—240°; Na one of 1·5% at 350°, the predominant reaction in this case being $CO_2+4Na=C+2Na_2O$. These results are in conformity with thermochemical data.

C. A. Silberrad.

Stability constants of complexes in aqueous solution. W. Knobloch (Lotos, 1930, 78, 110—111; Chem. Zentr., 1931, i, 1869).—Addition of excess of NH_3, NH_2Me, $NHMe_2$, pyridine, Na aminoacetate, K Na tartrate, and Na citrate, but not of formamide, glycerol, acetonitrile, thiocarbamide, carbamide, hexamethylenetetramine, NH_2Ph, or *o*-toluidine, gave stable complexes with $Cu^{\cdot\cdot}$; with $Cd^{\cdot\cdot}$, KI, KBr, KCl, and K tartrate gave positive, whilst urethane, thiocarbamide, pyrocatechol, resorcinol, quinol, nitroguanidine, and alkali thiocyanate gave negative results. Substitution of H in NH_3 by alkyl diminishes the stability; complex formation increases in the order Cl, Br, I, CN.

A. A. Eldridge.

Cæsium tetrabromide. N. Rae (J.C.S., 1931, 1578—1581).—The only solid polybromides of Cs are the tri- and tetra-bromides. The "pentabromide" described by Wells is a tetrabromide.

F. J. Wilkins.

Cæsium tetraiodide. N. Rae (J. Physical Chem., 1931, **35**, 1800—1802).—The volatilisation curve for a fused mass of Cs+I (excess) shows a break corresponding with CsI_4, the v. p. of which is much lower than that of I (cf. A., 1930, 1374).

L. S. Theobald.

Preparation and characterisation of di- and tri-calcium silicate and calcium aluminate. I. Weyer (Zement, 1931, **20**, 48—51; Chem. Zentr., 1931, i, 1423).—2CaO and $1SiO_2$ were heated 5 times for $\frac{3}{4}$ hr. at 1400°; at first only the γ-form of $2CaO,SiO_2$ was obtained, the amount of β-form then increasing to 85%. Crystallographic and *X*-ray measurements are recorded for both forms. The compounds $3CaO,SiO_2$ and $3CaO,Al_2O_3$ were also obtained and similarly examined.

A. A. Eldridge.

Hydrosol of silicic acid. III. Stability and influence of electrolytes. K. Inaba (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 277—287).—When NaOH is added to silicic acid sols containing 0·0001*N*-NaOH, the charge on the particles and the viscosity are increased and the stability is decreased. In solutions containing more than 0·01*N*-NaOH, however, the viscosity decreases and the stability increases, a mol. solution of Na_2SiO_3 being formed. No coagulation is observed when KCl or $BaCl_2$ is added to sols containing less than 0·01*N*-NaOH, but above this concentration $BaCl_2$ gives a ppt., due to the formation of insol. $BaSiO_3$.

E. S. Hedges.

Preparation and properties of refractory carbides, nitrides, and borides. C. Agte and K. Moers [with Heyne and K. Becker] (Z. anorg. Chem., 1931, **198**, 233—275).—Pure TiC, ZrC, HfC, NbC, and TaC have been prepared by heating the metals or their oxides with C at 1700—2100° in a graphite tube and sintering the product in A at a high temp., whereby impurities are volatilised. TiC has m. p. 3410°±90°. TiN, ZrN, and TaN, prepared by heating the metals in N_2 at 1100—1200° in a Mo tube and purified by sintering in N_2, have m. p. (±50°) 3220°, 3255°, and 3360°, respectively. The solidus curves for the mixtures TaN–TaC and TiN–TiC have been determined; the mixed crystals produced in the former system at high temp. are not stable at room temp., whereas those formed in the latter system are stable. The carbides, nitrides, and borides of Ti, Zr, Hf, V, and Ta have been prepared by passing the vapour of a halide of the metal, mixed with H_2 and a hydrocarbon vapour, N_2, or BBr_3 vapour, over a heated W filament. ZrB and HfB have m. p. 3265° and 3335°, respectively. SiC has been prepared by the same reaction on a W or ZrC filament; it forms yellow transparent crystals which have no measurable conductivity either at room temp. or at very high temp. The prep. of single crystals of these compounds is described. The sp. resistances have been determined over a wide range of temp. The borides have the highest conductivity, which is greater than that of the respective metal, and the carbides the lowest; TiC alone has a negative temp. coeff. At very high temp. (3500—4000°) the sp. resistances all tend to the same limiting value, viz., $2—2{\cdot}5\times10^{-4}$.

H. F. Gillbe.

Anhydrous lower bromides of zirconium. R. C. Young (J. Amer. Chem. Soc., 1931, **53**, 2148—2153).—$ZrBr_3$ is prepared by reducing $ZrBr_4$ with Al in an atm. of H_2 at 450° in the hot–cold tube. $ZrBr_3$ is a bluish-black powder which turns brown on partial hydrolysis and affords H_2 and a rapidly fading yellow acid solution with H_2O. $Zr^{\cdot\cdot\cdot}$ reduces CrO_4'' to $Cr^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$ to $Fe^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$ to Bi, $Cu^{\cdot\cdot}$ to $Cu^{\cdot}$, $TiO^{\cdot\cdot}$ to $Ti^{\cdot\cdot}$; $SnCl_2$ and $ZnSO_4$ are not reduced.

$ZrBr_2$ is prepared at 350° by the reaction $2ZrBr_3 \longrightarrow ZrBr_4+ZrBr_2$; it is a black powder which ignites spontaneously in air, and reacts violently with H_2O, H_2 being liberated. The reaction $2ZrBr_2 \longrightarrow ZrBr_4+Zr$ is fairly rapid above 400°. J. G. A. Griffiths.

Interaction between nitric oxide and hydrogen sulphide in the presence of water. H. B. Dunnicliff, S. Mohammad, and J. Kishen (J. Physical Chem., 1931, **35**, 1721—1734).—NO reacts with H_2S in aq. solution to form $(NH_4)_2S_2O_3$, NH_4NO_2, S, N_2O, and N_2. H_2SO_4 accelerates the reaction in its early stages, apparently increases the proportion of N_2O formed, and practically prevents the formation of NH_3 in the solution. NO in an atm. of H_2 has no action on aq. solutions of NH_4NO_2 or of NH_3 (dil.). It forms NH_4 polysulphides and small quantities of $(NH_4)_2S_2O_3$ when passed into NH_4 sulphide solution; N_2O and N_2 are evolved. Excess of NO increases the yield of N_2O, but with an excess of NH_4 sulphide pure N_2 is formed. A saturated solution of H_2S reduces N_2O completely to N_2 and NH_3, with the formation of S. Dil. solutions of $(NH_4)_2S_2O_3$ are converted into sulphate by NO. Small quantities of N_2 are evolved when solutions of NH_4NO_2 are kept in contact with H_2S for several days (cf. A., 1928, 1342). Possible reactions accounting for the observed products are outlined. L. S. Theobald.

Reactions and properties of nitric oxide and its compounds. I. Action of nitric oxide on sodium hyposulphite. H. Gehlen (Ber., 1931, **64**, [*B*], 1267—1276).—The action between NO and alkaline $Na_2S_2O_4$ proceeds mainly thus: $Na_2S_2O_4+6NO+2NaOH=Na_2SO_3,N_2O_2+Na_2SO_4+2N_2O+H_2O$, and to a minor extent: $Na_2S_2O_4+6NO+2NaOH=2Na_2SO_3,N_2O_2+N_2O+H_2O$. A simplified method for the prep. of 98·5% $Na_2S_2O_4$ free from NaCl is given. The analogous isolation of $K_2SO_3.N_2O_2$ is recorded.

H. Wren.

Reduction of nitric oxide. M. L. Nichols and C. W. Morse (J. Physical Chem., 1931, **35**, 1239—1252).—The effect of temp., acidity, and concentration of the reducing agent ($SnCl_2$ and $TiCl_3$) on the reduction products of NO has been determined. With $SnCl_2$ the amount of NO reduced in 30 min. decreases almost linearly with a rise in temp., but with $TiCl_3$ a max. occurs at 25°. Above 0° the rate of reduction of NO by $SnCl_2$ depends on the rate of formation of nitrohydroxylaminic acid ($H_2N_2O_3$). Below 25° the rate of reduction by $TiCl_3$ depends on the speed of the reduction reaction, but above 25° the formation of $H_2N_2O_3$ is the limiting factor. Reduction is decreased with an increase in acidity, slightly with $SnCl_2$, and markedly with $TiCl_3$; an increase in concentration of the reducing agent also decreases reduction. The reduction of $H_2N_2O_3$ can be represented by $H_2N_2O_3 \longrightarrow H_2N_2O_2 \longrightarrow H_4N_2O_2 \longrightarrow NH_2OH \longrightarrow NH_3$. The relative proportion of N_2O and N_2 in the final product depends on the relation of the speed of the decomp. reaction to the speed of the reduction reaction. NH_2OH is the apparent end-product with $SnCl_2$ because of its very slow rate of reduction to NH_3 by this reagent. The addition of platinised Pt to the $SnCl_2$ and of $FeCl_2$ to the $TiCl_3$ increases reduction by increasing the rate of dissolution of NO.

L. S. Theobald.

Heavy metal phosphides. I. Action of hypophosphite on nickel and cobalt salts. R. Scholder and H. Heckel (Z. anorg. Chem., 1931, **198**, 329—351).—With alkaline solutions of Ni and Co salts hypophosphites yield a mixture of metal and phosphides, and with acid solutions a mixture of various phosphides, which on drying at room temp. retain much H_2O and O. By treatment with aq. HCl and with AcOH fairly pure Ni_2P and Ni_5P_2 respectively have been isolated, but the O content is increased owing to decomp. of the H_2O present. By using alcoholic HCl or anhyd. AcOH, O-free phosphides may be prepared. On dissolution in HCl both yield H_2, H_3PO_3, and $NiCl_2$, PH_3 probably being formed as an intermediate product. The phosphides are regarded not as salts of PH_3, but as compounds of an intermetallic type. Phosphides are not produced by the action of H_3PO_2 on Ni and Co complex cyanides.

H. F. Gillbe.

Phosphoric acid. IV. Oxonium salts of orthophosphoric acid with certain organic compounds. G. B. King and J. H. Walton (J. Physical Chem., 1931, **35**, 1745—1755).—F.-p. data for H_3PO_4 with different org. substances show the existence of the following: $AcOH,H_3PO_4$, m. p. 33·8°; $AcCO_2H,H_3PO_4$, m. p. 36·4°; $PhCHO,H_3PO_4$, m. p. 43·0°; $MeO{\cdot}C_6H_4{\cdot}CHO.H_3PO_4$, m. p. 83·6°; $PhCOMe,H_3PO_4$, m. p. 87·9°; $COPh_2,H_3PO_4$, m. p. 71·3°; (coumarin) $C_9H_6O_2,H_3PO_4$, m. p. 113·4°. Propionic, *n*-butyric, *n*-hexoic, and phenylacetic acids, $CH_2Cl{\cdot}CO_2H$, and BzOH form no compounds. Oxalic, succinic, cinnamic, and malic acids decompose when heated with H_3PO_4. The additive compounds are probably true oxonium salts. Kendall's acidity rule holds, and H_3PO_4 forms additive compounds with org. compounds less readily than does H_2SO_4.

L. S. Theobald.

Co-ordination compounds of phosphorus and antimony pentachlorides. J. C. Hutton and H. W. Webb (J.C.S., 1931, 1518—1525).—By the action of

PCl_5 on dry pyridine a *compound*, $H,PCl_6,2C_5H_5N$, is obtained in which the covalency of P is at least six. In $CHCl_3$ solution $SbCl_5$ and pyridine give two *products*, $SbCl_5,C_5H_5N$ and $2SbCl_5,3C_5H_5N$, the former when $SbCl_5$ is in excess and the latter when pyridine is in excess. With no diluent and at higher temp. a third *derivative*, $H,SbCl_6,C_5H_5N$, is obtainable. Its structure is probably similar to that of the above P compound. By the action of EtOH on $2SbCl_5,3C_5H_5N$ the *compound* $2SbCl_5,2HCl,3C_5H_5N$ is formed. The possible existence of singlet linkings in these pentachlorides is discussed. It is further suggested that the hypothesis that chemical reaction is preceded by the formation of co-ordination compounds may be extended to chlorination.

F. J. WILKINS.

Reactions of the dioxides of selenium and tellurium with the halogen acids. T. W. PARKER and P. L. ROBINSON (J.C.S., 1931, 1314—1324).—Direct union of SeO_2 and HCl to $SeO_2,2HCl$ takes place at 107°. HBr and SeO_2 give the corresponding compound at 30°: at higher temp. liquids are formed which deposit H_2SeO_3 on cooling, whilst below 30° solids are produced. Temp.–composition curves indicate a region of stability between 2° and 8° corresponding with $SeO_2,4{\cdot}5HBr$. The solubilities of TeO_2 in aq. HCl and HBr have been determined.

F. J. WILKINS.

Constitution of the sulphates of molybdenum. F. H. NICHOLLS, H. SAENGER, and W. WARDLAW (J.C.S., 1931, 1443—1446).—Mo^{V} and Mo^{III} sulphates have been investigated. The following complex *oxysulphates* of Mo have been isolated:

$(NH_4)_2SO_4,(MoO_2)_2SO_4,2H_2O$ and
$4R_2SO_4,5(MoO_2)_2SO_4,aq.$ ($R{=}C_5H_6N$);

$R_2SO_4,2Mo_2O(SO_4)_2,6H_2O$ ($R{=}NH_4$, K, Rb). The constitution of these compounds is discussed. The existence of the substance $Mo_2O_3(SO_4)_2$ was not confirmed.

F. J. WILKINS.

Oxy-salts of molybdenum and ammonium. V. CAGLIOTI (Gazzetta, 1931, **61**, 257—264).—The interaction of solutions of H_2O_2 and of ordinary $(NH_4)_2MoO_4$ gives only the two oxy-salts $5(NH_4)_2O,12MoO_4,18H_2O$ and $5(NH_4)_2O,9MoO_3,3MoO_4,10H_2O$. Ammonium trimolybdate gives no oxy-salts with H_2O_2, but the latter reacts with solutions of $(NH_4)_2MoO_4$ to give the compound $5(NH_4)_2O,6MoO_3,6MoO_4,13H_2O$ with evolution of NH_3. *X*-Ray examination shows that the introduction of up to 2·26% of active O into the $(NH_4)_2MoO_4$ mol. does not materially alter its structure.

O. J. WALKER.

Compounds of sexavalent molybdenum with hydroxylamine. W. F. JAKÓB and B. JEŻOWSKA (Rocz. Chem., 1931, **11**, 229—253).—NH_2OH first forms double so-called polyhydroxylamine compounds with molybdic acid, and these compounds decompose spontaneously, to yield N_2 and N oxides as products of oxidation of NH_2OH, Mo being transiently reduced to the Mo^{IV} form. This, however, is almost immediately oxidised back to Mo^{IV} by NH_2OH, part of which is thereby reduced to NH_3, whilst the remainder combines with Mo^{VI} to yield salts of Heide and Hofmann's series of hydroxylaminomolybdic acids (A., 1896, ii, 605). These have the general formula $[(Mo_2NOH)(MoO_4)_9]M_4H_4$ and contain exclusively Mo^{VI}; their reducing properties are due to NH_2OH. On dissolution in $KHCO_3$ solution these salts are converted into $[(Mo_2NOH)(CO_3)_3O_6]K_5H_3$, precipitated by EtOH from aq. solution. The polyhydroxylamine compound $[Mo(NOH)_2(MoO_4)_2](NH_4)_2H_2$, is prepared and described, whilst the composition of compounds containing more NH_2OH, such as those described by Canneri (A., 1928, 260), must be regarded as doubtful, owing to the instability of the compounds and to the impossibility of obtaining reproducible results in their synthesis. The above results are discussed from the viewpoint of polar theories of at. structure.

R. TRUSZKOWSKI.

Complex acid tungstates. R. H. VALLANCE (J.C.S., 1931, 1421—1428).—Formic acid and aq. Na tungstate in slightly acid solution give Na paratungstate, $5Na_2O,12WO_3,28H_2O$. The corresponding K and Ba salts, obtained by precipitation, crystallise with 11 and 27 mols. H_2O, respectively. No evidence of the existence of $4Na_2O,10WO_3,23H_2O$ has been obtained. The solubility of Na paratungstate in H_2O has been determined over the temp. range 0—102°.

F. J. WILKINS.

Preparation of standard uranium oxide and determination of its saturation current. A. N. PILKOV (J. Gen. Chem. Russ., 1931, **1**, 133—142).—Fergansk urano-vanadate ore is dissolved in HCl, and $BaCl_2$ and H_2SO_4 are added to the filtrate, thereby removing Ra, meso- and radio-Th, U, and Io. $Bi(NO_3)_3$ and $Pb(NO_2)_2$ are added to the filtrate from $BaSO_4$, and H_2S is passed, Ra-*D*, Ra-*F*, and Ra-*G* being adsorbed on the ppt. of sulphides. The filtrate is freed of excess of H_2S, excess of Br is added, and the solution is kept 10 days, with occasional shaking. Heavy metals are then precipitated as hydroxides by CO_2-free aq. NH_3, and $Ca(OH)_2$ and $Mg(OH)_2$ are removed from the ppt. by CO_2-free H_2O. The ppt. is then treated with $(NH_4)_2CO_3$, yielding a solution of $UO_2CO_3,2(NH_4)_2CO_3$ and NH_4VO_3, which on boiling with HNO_3 deposits $(NH_4)_2U_2O_7$ and V_2O_5; these are converted into nitrates and the dry mixture is extracted with Et_2O, from which uranyl nitrate is separated by shaking with H_2O. $UO_2(NO_3)_2$ thus prepared is again purified by fractional adsorption as above, and the final product on ignition yields chemically and radiologically pure U_3O_8.

R. TRUSZKOWSKI.

Gaseous compound of polonium. (MME.) I. CURIE and M. LECOIN (Compt. rend., 1931, **192**, 1453—1454).—On heating to a red heat Ni on which Po has been deposited (cf. A., 1928, 810), in a current of N_2 in a quartz tube dipping into an acid solution, practically all the Po condenses on a cool part of the tube. If, however, the gas used is $CO+CO_2$, only a portion can be so recovered, and that distributed all along the tube; the rest, which may amount to half, is found in the acid, indicating the formation of a gaseous compound of Po, possibly a carbonyl.

C. A. SILBERRAD.

Preparation of sources of polonium of high activity. (MME.) I. CURIE and F. JOLIOT (J. Chim. phys., 1931, **28**, 201—205).—Deposits of Po of high activity can be obtained by rotating polished Ni or Ag in a solution of a salt of Po containing 0·2N-HNO_3 and 0·1N-HCl. Deposits may be formed on other metals by volatilisation in a current of gas. E. S. HEDGES.

Liesegang rings. O. F. TOWER and E. E. CHAPMAN (J. Physical Chem., 1931, **35**, 1474—1476; cf. A., 1929, 643).—The method of Hedges and Henley (A., 1928, 1323) does not apply to rings of CdS and ZnS. Liesegang's rings of MnS are formed from 0·1—2N-$MnCl_2$ placed on gelatin containing NH_4 sulphide or on agar containing NH_4 or Na sulphide. Rings of NiS or CoS are formed from 0·7—2N-$NiCl_2$ or $CoCl_2$ on 0·4—0·6N-Na_2S in agar. L. S. THEOBALD.

Sulphides and selenides of rhenium. H. V. A. BRISCOE, P. L. ROBINSON, and E. M. STODDART (J.C.S., 1931, 1439—1443).—Either H_2S or $Na_2S_2O_3$ precipitates *rhenium heptasulphide* from K per-rhenate solutions: in the second case the precipitation is quant. When heated, the heptasulphide gives the disulphide. The corresponding *selenides* have been prepared. F. J. WILKINS.

Sulphur [thio-]derivatives of per-rhenic acid. W. FEIT (Z. angew. Chem., 1931, **44**, 65—66).—By passing excess of H_2S through saturated aq. K per-rhenate, a yellow solution was obtained which became dark brown (A) after 2—3 days and was not precipitated by salts of Fe, Ni, Co, or Zn; dark ppts. were formed with Ag, Pb, Cu, $Hg^{\cdot\cdot}$ and $Tl^{\cdot}$ salts. On concentrating the solution A brown crystals of K per-rhenate, containing a small amount of an isomorphous thio-derivative, were formed; on complete evaporation a H_2O-soluble dark brown mass (14—15% S), probably a mixture of partly substituted thio-rhenates, was obtained. On treating solution A with Tl_2SO_4 a dark brown ppt., probably consisting of $TlReS_4$, was obtained; further addition of Tl_2SO_4 to the yellow filtrate yielded *thallous monothioper-rhenate*, $TlReO_3S$, golden needles. The solution of the salt gradually deposited sulphide after acidification. E. LEWKOWITSCH.

Change in properties of oxides of iron, aluminium, and chromium in relation to the ignition temperature. P. P. BUDNIKOV and K. E. KRAUSE (Kolloid-Z., 1931, **55**, 330—333).—Fe_2O_3 is completely dehydrated by ignition at 650°, Al_2O_3 at 750°, and Cr_2O_3 at 850°. With rising temp. of ignition the solubility of all these oxides in HCl falls. The solubility is in the order $Fe_2O_3 > Al_2O_3 > Cr_2O_3$. Cr_2O_3 has an optimum solubility when ignited at 300°. The density of all these oxides increases with rising temp. of ignition. The particle size of the ignited oxides varies between 0·003 and 0·0005 mm. E. S. HEDGES.

Nickelous oxide. M. PRASAD and M. G. TENDULKAR (J.C.S., 1931, 1403—1407).—The density and electrical resistance of NiO increase, whilst its solubility in H_2SO_4 and its catalytic activity decrease, as its temp. of prep. is raised. This effect is particularly marked at temp. about 800°. NiO probably exists in two forms, a black variety prepared at 400° and another, which is greenish-yellow, obtained at 1000°. F. J. WILKINS.

Action of sulphuric acid on nickel-copper matte. M. PRASAD and M. G. TENDULKAR (J.C.S., 1931, 1407—1411).—The slight solubility of Ni from a Ni–Cu matte in H_2SO_4 is due probably to the formation of a little Ni_2O_3. The incomplete removal of Cu is attributed to the formation of CuO,4NiO. F. J. WILKINS.

Optically active tetrammines of bivalent platinum and palladium. H. REIHLEN and W. HÜHN (Naturwiss., 1931, **19**, 442).—Many αβ-diamines have been prepared by the catalytic hydrogenation of N-acetyl-α-amino-acid nitriles. These form di- and tetra-ammine complex salts with bivalent Pt and Pd. Since these mols. are optically active, there is no plane of symmetry. A. J. MEE.

Examples of titration in Wood's light. A. G. NASINI and P. DE CORI (Atti III Cong. Naz. Chim., 1929, 668—678; Chem. Zentr., 1931, i, 2088).—A discussion. A. A. ELDRIDGE.

Increase of accuracy in quantitative emission spectral analysis. G. SCHEIBE, C. F. LINSTRÖM, and O. SCHOETTLER (Z. angew. Chem., 1931, **44**, 145—151).—By means of a method based on studies of the relation between the density of a photographic image and wave-length and the quant. relations between the intensity of spectral lines and their term analyses, impurities in a given compound may be determined with an accuracy of ±3%. For the evaluation of such results a graphical method utilises only three measurements of the galvanometer displacements in a thermo-electric photometer. F. G. TRYHORN.

Spectrum analysis of alloys. G. GUZZONI (Atti III Cong. Naz. Chim., 1929, 636—637; Chem. Zentr., 1931, i, 2087—2088).—The comparison method affords the most accurate results, but a complete series must be prepared for each binary alloy. Schweitzer's method, although less accurate, is convenient. The relation between the concentration of an element and the intensity of its lines is hyperbolic; hence only a portion is suitable for quant. work. The intensity change caused by the presence of a third substance introduces difficulties, but the method can be applied to ternary alloys. A. A. ELDRIDGE.

Qualitative micro-electrolysis with small electrodes. H. J. BRENNEIS (Mikrochem., 1931, **9**, 385—394).—The electrodes consist of two fine Pt wires sealed through a glass tube; the upper ends of the wires are connected to fixed terminals in a small base-board which themselves are connected to the terminals of the accumulator, and a drop of the solution to be tested is placed between the lower ends of the wires, which are then placed in a closed chamber in which the air is kept saturated with moisture to avoid evaporation of the drop. Any deposit on the cathode is tested by microchemical methods for the identification of the metal; an anode deposit is tested for MnO_2 and PbO_2. A. R. POWELL.

"Isopyknoscopic" volumetric determination of the concentration of solutions of pure compounds. A. DEL CAMPO, C. NOGAREDA, and M. G. DE CELIS (Anal. Fís. Quím., 1931, **29**, 386—391).—The end of a burette is drawn out to a capillary and bent at 90°. The solution of unknown concentration, containing a dye, is allowed to flow through the capillary into a solution of known concentration of the same substance, at a point below the surface. The unknown concentration is determined by adjusting that of the second solution until the thread of coloured liquid neither rises nor falls.

H. F. Gillbe.

Colorimetric determination of p_H in sea-water. O. G. Ibáñez (J. Marine Biol. Assoc., 1931, **17**, 483—488).—The p_H of sea-water is unaffected by the preservation of samples in glass tubes if a minimal air space is left and if a little $HgCl_2$ is added.

C. W. Gibby.

Hydrogen electrode. V. Čupr and O. Viktorin (Z. anorg. Chem., 1931, **198**, 363—374; cf. this vol., 910).—The anomalies encountered in determinations of hydrolysis in solutions of Zn, Mg, and Cd sulphate are due to the use of the H electrode. Denham's results are ascribed to the use of Pt-black; an exchange of H ions with other cations probably occurs on the surface of the electrode, and this causes irregularities in measurements with feebly acid or feebly buffered solutions. H. F. Gillbe.

Microchemical detection of hydrogen peroxide and vanillin. C. Griebel (Mikrochem., 1931, 9, 313—315).—A 1% solution of vanillin in 25% HCl containing 10% of EtOH yields bluish- to violet-black aggregates of hair-like needles with H_2O_2. Perborates give a similar result with vanillin, but ClO', ClO_2', NO_2', and NH_2Cl are without action.

A. R. Powell.

Use of bromate in volumetric analysis. V. Internal indicators suitable for use in direct titrations. G. F. Smith and H. H. Bliss (J. Amer. Chem. Soc., 1931, **53**, 2091—2096; cf. A., 1924, ii, 614).—16 org. dyes of different colours have been selected as suitable internal indicators in volumetric bromate reactions. In many cases, back titration of excess of bromate is rendered unnecessary, and titrations are possible in the cold and at lower acidities than permissible heretofore. All of the indicators are applicable in the determination of As^{III}.

J. G. A. Griffiths.

Volumetric determination of iodides. P. Fleury and J. Courtois.—See B., 1931, 630.

Volumetric determination of fluorine by means of cerous nitrate. G. Batchelder and V. W. Meloche (J. Amer. Chem. Soc., 1931, **53**, 2131—2136).—Excess of $Ce(NO_3)_3$ is added to the neutral fluoride solution, and the excess is determined at 80° by titration with $KMnO_4$ in the presence of ZnO. The ppt. is filtered just before the end-point. A better, and direct titration of 0·15 g. of NaF in 10 c.c. with $Ce(NO_3)_3$ is effected at room temp. in the presence of 0·02 g. per litre of ampho-magenta (diazotised *p*-aminoethylacetanilide coupled with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid; colour change deep blue to purple). SO_4'', PO_4''', and C_2O_4'' interfere. The anomalies observed in the method involving methyl-orange were not confirmed (A., 1930, 1542). J. G. A. Griffiths.

Reaction of fluorides. C. Pertusi (Atti III Cong. Naz. Chim., 1929, 573—575; Chem. Zentr., 1931, i, 2089—2090).—Addition of a solution of benzidine acetate to one of a fluoride in presence of $Hg(OAc)_2$ affords in the cold and in absence of much $H^{\cdot}$ or OH' a yellow ppt., stable at 105—110°, $[(\cdot C_6H_4\cdot NH_2,HF)_2]_2,HgF_2$. A. A. Eldridge.

Determination of potassium and sodium fluorides. A. V. Frost (Trans. Inst. Pure Chem. Reag., 1931, **10**, 53—61).—An investigation of the accuracy of different methods of determining F shows that the CaF_2, PbClF, and gravimetric ThO_2 methods give accurate results; the $NaHF_2$ and volumetric CaF_2 methods give an error of 0·2—0·4%. The determination of SO_4'' after precipitation of F as CaF_2 is inaccurate. E. S. Hedges.

Determination of bound sulphuric acid in presence of chromium salts. E. A. Nikitina and A. V. Babajeva (Trans. Inst. Pure Chem. Reag., 1931, **10**, 20).—The determination of SO_4 in mixtures of $CrCl_3$ and alkali sulphates is satisfactory, using a cold 1% solution of $BaCl_2$. In the presence of chromates or dichromates a preliminary reduction is essential; precipitation with 1% $BaCl_2$ in the cold or with 1% $Ba(OAc)_2$ and warming is recommended.

E. S. Hedges.

Colorimetric determination of ammonia. K. G. Makris (Z. anal. Chem., 1931, **84**, 241—242).—The test for NH_3 previously described (A., 1930, 1263) is made the basis of the colorimetric determination.

R. Cuthill.

Oxidation and determination of hydrazine and of semicarbazide by means of potassium iodate. V. Hovorka (Coll. Czech. Chem. Comm., 1931, 3, 285—301).—The liberation of I from the excess of the reagent and the KI produced during the oxidation of N_2H_4 by KIO_3 may be suppressed by adding $Hg(ClO_4)_2$, since non-ionised HgI_2 is formed; any I which is produced is converted into HgI_2 and $Hg(IO_4)_2$. In presence of H_2SO_4 the oxidation is slow, and in presence of HCl rapid, but the quantity of HCl added must be insufficient to convert all the Hg present into $HgCl_2$. Under the conditions described the reaction is complete within 30—35 min., and an excess of KI may then be added and the liberated I titrated with $Na_2S_2O_3$ solution. Semicarbazide may be determined in acid solution by the same method. Oxidation of the N_2H_4 by hypobromite in alkaline solution yields low results, owing to the occurrence of secondary reactions resulting in the formation of NH_3. H. F. Gillbe.

Titration of phosphoric acid. P. Villard (Compt. rend., 1931, **192**, 1332—1334).—A criticism of Sanfourche's results (cf. this vol., 812), based on those of the author (cf. Compt. rend., 1930, **191**, 1101).

C. A. Silberrad.

Detection of acids. S. I. Dijatschkovski and T. I. Isaenko (J. Gen. Chem. Russ., 1931, **1**, 81—84).—The powder examined is placed near a cathode on a sheet of wet filter-paper, a crystal of $AgNO_3$ is placed near an anode, and a current is passed, when AsO_4''' produces a reddish-brown stain around the crystal, and PO_4''' a yellow stain. CNS' is detected similarly by the appearance of a red stain around a crystal of $Fe(NO_3)_3$, which becomes surrounded by a blue ring in the presence of $Fe(CN)_6'''$ and $Fe(CN)_6''''$. A starch paper placed beneath the anode turns blue in the presence of I', whilst a paper dipped in Schiff's reagent and fixed above the anode becomes coloured in the presence of Br'. Cl' is detected by the coloration given by a starch–iodide paper at the anode, and CN' by suspending a paper soaked in NH_4 polysulphide over the anode, and then washing it with a few drops of HCl, and adding $FeCl_3$, when a red colour due to CNS' appears. R. Truszkowski.

Titanous chloride in the determination of arsenic, antimony, and bismuth. A. Oliverio (Annali Chim. Appl., 1931, **21**, 211—216).—The necessary apparatus for the potentiometric titration of As, Sb, and Bi (cf. Zintl and Wattenberg, B., 1923, 295; Zintl and Rauch, B., 1925, 430, 787) is not everywhere available, but the reaction $As^{\cdot\cdot\cdot}+3Ti^{\cdot\cdot\cdot}\rightarrow As+3Ti^{\cdot\cdot\cdot\cdot}$ proceeds practically to completion and may be used for the determination of As and Sb; details of the procedure are given. This method is not applicable to Bi, for which, however, an indirect method is described. T. H. Pope.

Nitro-perchloric acid for determination of silica in vegetable substances. L. Lematte, G. Boinot, E. Kahane, and (Mme.) M. Kahane (Compt. rend., 1931, **192**, 1459—1462).—The org. matter is totally removed and the SiO_2 left pure and insol. by heating the material with about 10 times its vol. of a mixture (40 : 60) of fuming HNO_3 and $HClO_4$ (*d* 1·61). Accurate results are obtained with as much as 12 g. of material (*e.g.*, bran). C. A. Silberrad.

Determination of carbon monoxide by means of silver oxide. W. Manchot and G. Lehmann (Ber., 1931, **64**, [*B*], 1261—1266; cf. A., 1927, 331).—The important factors in the reaction are intense agitation and the use of about 3 times the necessary amount of Ag reagent. Lower temp. can be compensated by increased time of agitation. Alternatively, a measured volume of Ag solution is treated with a slight excess of Cl-free NaOH and shaken with the gas; the mixture is acidified with AcOH and the unconsumed Ag in the filtrate is titrated with NaCNS. The presence of H_2, CH_4, or C_2H_4 is without influence. Accurate results are obtained for CO in coal gas, possibly without the necessity of pre-treatment with fuming H_2SO_4. With the usual apparatus a CO content of about 2% can be determined and with a larger absorption vessel the concentration of the gas may be as low as 1—0·25%. In the ordinary ammoniacal Ag reagent, the essential component is AgOH, the function of NH_3 being to discriminate between Ag and AgOH (also achieved by AcOH). Excess of NH_3 diminishes the sensitiveness of the reagent. AgOH held in solution by pyridine is more sensitive towards CO than that dissolved by NH_3 and apparently more sensitive than AgOH precipitated by NaOH. H. Wren.

Determination of carbon monoxide by burning with oxygen, using a new double catalyst. A. Schmidt (Z. angew. Chem., 1931, **44**, 152—155).—CO, in presence of air, is not quantitatively converted into CO_2 when passed over heated CuO (wire); the conversion becomes quant., and much higher streaming velocities are permissible, when a double catalyst consisting of fine quartz particles (1—2 mm.) and a trace of CuO (0·008—60 g. of quartz) is used. F. G. Tryhorn.

Determination of sodium plus potassium as benzidine sulphate. H. B. Brown and A. T. Shohl (J. Biol. Chem., 1931, **91**, 745—749).—Na+K in small quantities of fæces, milk, or urine are rapidly determined (±2%) by the benzidine method (Stadie and Ross, A., 1926, 100) if Ca and Mg are first removed (in one precipitation) as CaC_2O_4 and $MgNH_4PO_4$, and phosphate and Fe are then precipitated together as $FePO_4$ and $Fe(OH)_3$. J. W. Baker.

Microchemical detection of sodium with uranyl acetate. A. Martini (Mikrochem., 1931, **9**, 422—423).—The reagent is prepared by dissolving 1 part of $UO_2(NO_3)_2,6H_2O$ in 4 parts of glacial AcOH, allowing the solution to cool, and pouring the supernatant liquor from the crystals. One drop of this solution is added to 1 drop of the solution to be tested for Na, to which a little powdered $(NH_4)_2CO_3$ has been added. When effervescence ceases a drop of pyridine is added; in the presence of Na tetrahedral crystals of Na UO_2 acetate separate round the edges of the liquid. Ba, Mg, Cd, Cu, Co, Ni, K, NH_4, Rb, and Cs salts do not interfere. A. R. Powell.

Colorimetric determination of sodium. R. A. McCance and H. L. Shipp (Biochem. J., 1931, **25**, 449—456).—The Na is precipitated as $NaZn(UO_2)_3(OAc)_6$ and the U is determined colorimetrically with $K_3Fe(CN)_6$. The method is applicable to neutral or acid solutions. Ca, Mg, and Fe do not interfere; phosphates, which can be removed with $Zn(OAc)_2$, do so. Na may be determined directly in the presence of 30 times its wt. of K. The limits of the method are 0·02—0·8 mg. Na; in the absence of phosphates the range is 0·01—0·4 g. Na. S. S. Zilva.

Determination of small quantities of alkalis in acids insoluble in water [*e.g.*, tungstic acid]. G. Heyne (Z. angew. Chem., 1931, **44**, 328—329).—The alkalis are removed by electrodialysis in an apparatus comprising a central horizontal drum closed at each end with membrane filter discs communicating with vertical tubes containing distilled H_2O in which the electrodes are immersed against the outer sides of the filters. On passing a current at 220—440 volts through the drum the H_2O from the anode compartment passes to the cathode compartment, thereby washing out the adsorbed salts in the H_2WO_4 suspension contained in the drum. The solution in the cathode compartment is evaporated to dryness and the alkalis are determined as usual. A. R. Powell.

Use of volumetric methods for determining the basic constituents in quicklime and slaked lime. F. Mach and R. Herrmann.—See B., 1931, 675.

Separation of lead from barium, calcium, and strontium with ammonium acetate. F. Feigl and L. Weidenfeld (Z. anal. Chem., 1931, **84**, 220—224).—Comments on Majdel's paper (this vol., 453). It is probable that when $PbSO_4$ and $BaSO_4$ are precipitated together an adsorption complex is formed. R. Cuthill.

Mechanism of precipitation processes. V. Some types of precipitation reaction. Z. Karao-

GLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1931, **198**, 352—362).—The amount of Cl contained in $BaSO_4$ precipitated by adding H_2SO_4 to $BaCl_2$ solutions is independent of the period of contact between the ppt. and the solution. In presence of HCl the Cl content of the ppt. is not markedly altered, but it diminishes as the rate of precipitation is reduced. CaC_2O_4, precipitated from a solution of $CaCl_2$, is free from Cl. The Cl content of $PbSO_4$ precipitated rapidly by adding a $PbCl_2$ solution to aq. H_2SO_4 diminishes with the period of contact, whereas if the precipitation is slow the Cl content increases with the period of contact; reverse precipitation yields a product containing much less Cl. Analogous experiments have been carried out on the precipitation of $PbCrO_4$; the results when $PbCl_2$ and $PbBr_2$ are used resemble those obtained for the precipitation of $PbSO_4$ from the corresponding halide. Three types of precipitation processes are recognised: (1) those in which no secondary reactions occur; (2) those in which a secondary reaction, independent of time, takes place; and (3) those in which the quantity of secondary product varies with time. The secondary reaction becomes increasingly pronounced as the solubility of the halide used decreases. H. F. GILLBE.

Gravimetric microanalysis of beryllium silicate rocks. Separation and determination of phosphoric acid and aluminium. H. THURNWALD and A. A. BENEDETTI-PICHLER (Mikrochem., 1931, **9**, 324—332; cf. A., 1930, 1544).—The rock is decomposed with HF and H_2SO_4, the P_2O_5 precipitated as phosphomolybdate, and finally determined as $MgNH_4PO_4$, and the Al_2O_3 in the filtrate is determined with 8-hydroxyquinoline after removal of excess of Mo with H_2S. A. R. POWELL.

Micro-determination of copper with salicylaldoxime. W. REIF (Mikrochem., 1931, **9**, 424—429).—The Cu solution is treated with dil. aq. NH_3 until blue, then with feebly acid $AcONH_4$ until the blue colour disappears, and finally with a 5% solution of salicylaldoxime in EtOH. The ppt. is collected in a Pregl filter tube, washed alternately with cold H_2O and EtOH, dried at 105°, and weighed; it contains 18·95% Cu. If Ni and $Fe^{\cdot\cdot\cdot}$ are present the former is precipitated with dimethylglyoxime in neutral tartrate solution and the Cu precipitated in the filtrate with the aldoxime, the $Fe^{\cdot\cdot\cdot}$ being retained in solution by the tartrate. A. R. POWELL.

Microchemical reaction of salts of copper and other heavy metals. I. M. KORENMAN (J. Chem. Ind. Russ., 1931, **8**, 276).—Characteristic cryst. salts are obtained by the addition of a solution of 2 parts of saturated aq. picric acid and 1 part of 10% aq. NH_3 to solutions containing the following min. quantities of heavy metal: Cu 0·00005 mg., Ag 0·02 mg., Co 0·0003 mg., Ni 0·0001 mg., Cd 0·001 mg., Hg 0·00015 mg., Au 0·0002 mg. R. TRUSZKOWSKI.

Drop method for [detecting] copper. K. M. FILIMONOVITSCH (Ukrain. Chem. J., 1930, **5**, [Sci.], 383—386).—Cu (0·0635 mg.) may be detected by adding $MnCl_2$, NaOH, and NaOBr solutions to the solution under examination and to 0·001*M*-$CuSO_4$, and heating to boiling, when a red coloration appears simultaneously in both tubes. Cr gives a yellow colour under these conditions, whilst other ions do not interfere. R. TRUSZKOWSKI.

Separation and determination of gallium. III. Separation of gallium from bivalent elements and those of the rare earths, and determination of all these elements. S. ATO (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1931, **15**, 289—301).—Ga can be separated quantitatively from Zn, Cd, Pb, Mn, Ni, Co, Mg, Ca, Sr, and Ba and from rare-earth elements, such as La, Ce, Pr, and Nd, in AcOH solution by precipitation with camphoric acid or Na camphorate solution, and can be determined by igniting the ppt. and weighing as Ga_2O_3. The elements remaining in the filtrates from the ppt. of Ga can be determined as usual. Bivalent elements of the H_2S group (Pb, Cd, etc.) can be separated quantitatively from Ga by precipitation with H_2S in HCl solutions. The adhesion of the Ga ppt. with camphoric acid to the wall of the vessel can be avoided by adding about 2% of NH_4NO_3 before the camphoric acid.

E. S. HEDGES.

Precipitation of manganese by water-soluble carbonates. A. JÍLEK and J. LUKAS (Chem. Listy, 1931, **25**, 225—230, 249—254).—Mn is precipitated quantitatively by $(NH_4)_2CO_3$ only under special conditions. Na_2CO_3 and K_2CO_3 ppt. about 99·8% of the Mn present, guanidine carbonate 98—100%, Li_2CO_3 and Tl_2CO_3 give high values (101%), owing to adsorption of Li or Tl on the precipitate of mixed hydroxide and carbonate, and Rb_2CO_3 and Cs_2CO_3 give practically quant. precipitation. R. TRUSZKOWSKI.

Permanganometric investigations. I. J. H. VAN DER MEULEN (Chem. Weekblad, 1931, **28**, 377—381).—Mn salts are oxidised to $KMnO_4$ at 55—60° by $K_2S_2O_8$ in presence of $AgNO_3$ or Ag_2SO_4 as catalyst and HF or H_3PO_4, or, preferably, a mixture of both acids. The excess of $K_2S_2O_8$ is decomp. by heating the liquid to the b. p., and, after cooling, the $KMnO_4$ is determined by addition of KI and titration of the liberated I with $Na_2S_2O_3$. Fe^{III} salts do not interfere, as they are converted into inactive complexes.

H. F. GILLBE.

Molybdenum-blue in analysis. S. L. MALOWAN (Z. anal. Chem., 1931, **84**, 209—217).—A review of the literature. R. CUTHILL.

Stable colorimetric comparison substance for cœruleo-molybdimetry. G. DENIGÈS (Bull. Soc. Pharm., Bordeaux, 1930, **68**, 1—3; Chem. Zentr., 1931, i, 2088).—A solution containing either $Cu(OAc)_2$ (3 g.), $CuSO_4$ (1·80 g.), and AcOH (2 c.c. in 50 c.c.) or $Co(NO_3)_2$ (5%, 36 c.c.), AcOH (2 c.c.), and $Cu(OAc)_2$ (3 g.) is equiv. in colour to that obtained by treating 5 c.c. of a solution containing 12 mg. P_2O_5 per litre with the Mo reagent. The test and comparison solutions must be compared in equal layer depths.

A. A. ELDRIDGE.

Electrometric titration of uranium with ceric sulphate. D. T. EWING and (MRS.) M. WILSON (J. Amer. Chem. Soc., 1931, **53**, 2105—2110).—A hot solution of U sulphate in 2% H_2SO_4 is reduced in a Zn reductor and titrated electrometrically with $Ce(SO_4)_2$ in an atm. of CO_2 or N_2. The reagent added between the two end-points is a measure of the U present.

The two end-points obtained when U acetate in 2—4*M*-HCl is treated similarly are less sharp. When $Fe^{\cdot\cdot}$ is also present, the first end-point occurs when all tervalent U is oxidised to quadrivalent U, the second, when all quadrivalent U is oxidised to sexavalent U, and the third when all $Fe^{\cdot\cdot}$ is oxidised to $Fe^{\cdot\cdot\cdot}$.
J. G. A. GRIFFITHS.

Iodometric determination of small quantities of tin. R. HÖLTJE (Z. anorg. Chem., 1931, **198**, 287—296).—The correct end-point of $Na_2S_2O_3$–I titrations, using starch as indicator, is obtained when the solution contains 0·2—1% HCl and 0·1—0·5% KI. I, KIO_3, and $KBrO_3$, but not $K_2Cr_2O_7$, are suitable for standardisation of $Na_2S_2O_3$ solutions for use in micro-analysis. Sn^{II}, in quantities of less than 1 mg., may be determined by addition of a slight excess of I solution and titration of the excess with $Na_2S_2O_3$ in absence of air; the mean error is 5 microg. KIO_3, but not $KBrO_3$, may be used in place of I. Sn^{IV} may be reduced with Fe or Al; Fe (powder) is the more satisfactory and its action is accelerated and rendered complete by addition of a small quantity of KI. Reduction by Zn yields low results, and with Mg the reduction is incomplete and $Sn(OH)_4$ separates. Details are given of the determination, to within 5 microg., of 1 mg. or less of Sn. H. F. GILLBE.

Specific detection of zirconium. F. FEIGL, P. KRUMHOLZ, and E. RAJMANN (Mikrochem., 1931, **9**, 395—400).—$ZrOCl_2$ in HCl solution gives a characteristic brown ppt. with a solution of *p*-dimethylaminoazophenylarsinic acid in 5% alcoholic HCl. Ti, Mo, and W give similar ppts., but addition of H_2O_2 inhibits the reaction in these cases. Sn gives a brown ppt. in dil. HCl solution, but not in 2*N*-HCl. To detect traces of Zr a drop of the solution is placed on a filter-paper which has been impregnated with a solution of 0·1 g. of the reagent in a mixture of 5 c.c. of conc. HCl and 100 c.c. of EtOH. The paper is then immersed for a short time in 2*N*-HCl at 50—60° to dissolve the excess of reagent from the paper; a brown spot insol. in the acid indicates Zr (sensitivity 1 : 500,000).
A. R. POWELL.

Micro-determination of m. p. H. LINSER (Mikrochem., 1931, **9**, 253—268).—The apparatus described by Klein (A., 1929, 1261) is useful for the identification of org. compounds by determining their m. p. if certain precautions are taken and the apparatus is standardised on a series of known substances.
A. R. POWELL.

Application of resistance thermometers to ebullioscopy and tonometry. I. Comparison of resistance with standard mercury thermometers. A. ZMACZYŃSKI (Rocz. Chem., 1931, **11**, 327—353).—Swientosławski's ebullioscope is adapted to the standardisation of thermometers. Pt resistance thermometers are more sensitive and permit more accurate reading than do Hg thermometers. The temp. of 0·007° obtained using Michels' apparatus is reproducible with an accuracy of 0·0005°. R. TRUSZKOWSKI.

High-temperature electric furnace and a micro-adaptation. R. C. EMMONS (Science, 1931, **73**, 499—500).—Furnaces electrically heated by nichrome or Pt wire, and a small C resistance furnace are described. L. S. THEOBALD.

Ebullioscope for testing purity of liquids. W. SWIENTOSŁAWSKI (Compt. rend., 1931, **192**, 1457—1459; cf. A., 1927, 642).—A more elaborate apparatus, with two separate condensing columns, for determining with greater accuracy the difference between boiling and condensing temp. is described.
C. A. SILBERRAD.

Vacuum sublimation under the microscope. L. KOFLER and W. DERNBACH (Mikrochem., 1931, **9**, 345—349).—The apparatus comprises a square glass plate covered with a vac. bell, the upper, circular glass cover of which is a plane parallel to the glass plate. The tube for attachment to the pump is fused into one side of the bell. By means of the apparatus the actual formation of the sublimate on the underside of the cover can be observed under the microscope at magnifications up to 135 diameters.
A. R. POWELL.

Fluorescence microscope. M. HAITINGER (Mikrochem., 1931, **9**, 430—440).—The illuminating system comprises an arc lamp with cored Fe electrodes provided with brass cooling channels, quartz lenses, and Cr-plated Fe mirrors. The object under examination is illuminated by means of a quartz dark field condenser and the light is filtered through $CuSO_4$ solution. The iron arc provides a powerful source of light of wave-length 3000—4000 Å.
A. R. POWELL.

Quantitative determination of the colour and intensity of fluorescence phenomena. M. HAITINGER (Mikrochem., 1931, **9**, 441—450).—The intensity of the fluorescence of a substance is measured by comparing the light passing through red, green, and blue filters photometrically with that reflected from a standard substance under the same conditions; the results are then plotted in the triangular diagram of König as percentages of the total light emitted and the position of the point is calc. on a rectangular pair of axes, one of which coincides with the base of the triangle. The rectangular co-ordinates of this point are a measure of the colour tone of the fluorescence.
A. R. POWELL.

Refractometer for reactive liquids. W. C. DAVIES and W. J. JONES (J. Physical Chem., 1931, **35**, 1490—1492).—An instrument based on the principle of the spectrometer with a prism filled with liquid is described. AcCl has n_F^{20} 1·39335, n_D^{20} 1·38708, and n_C^{20} 1·38548. L. S. THEOBALD.

***X*-Ray fibre photography.** S. ZEIDENFELD (Nature, 1931, **128**, 70).—The arrangement used for obtaining an *X*-ray photograph of wool, artificial silk, and ramie fibre is described. L. S. THEOBALD.

Improved null instrument for glass electrode or other high-resistance circuits. S. E. HILL (Science, 1931, **73**, 529—530).—The incorporation of a special vac. tube in the circuit permits the use of thick glass membranes of small area or of thick-walled glass bulbs. L. S. THEOBALD.

Micro-hydrogen electrode. F. SAUNDERS (J. Amer. Chem. Soc., 1931, **53**, 2180).—The electrode is made by modifying a Pt hypodermic needle, insulating the outside with bakelite paint, and platinising the inside. J. G. A. GRIFFITHS.

Use of quinhydrone electrode. G. M. Moir (Analyst, 1931, **56**, 445—448).—The use of the quinhydrone electrode is described. Test-tubes with U-tubes filled with 5% agar in 3·5N-KCl, as bridges, are preferred to the usual type of electrode vessel.
T. McLachlan.

Simple, inexpensive quinhydrone cell for rapid work. J. G. Davis (Analyst, 1931, **56**, 449—450; cf. preceding abstract).—In a modification of Moir's vessel the test-tube is drawn out at the bottom to form a U-tube, omitting the agar bridge. The $[H^{\cdot}]$ of solids may be determined by making a cell containing a mixture of finely-powdered quinhydrone and the substance to be tested. T. McLachlan.

Reduced circular bridge with additional resistances. J. Biczyk (Rocz. Chem., 1931, **11**, 376—378).—A new type of Wheatstone bridge is described. R. Truszkowski.

Lampbank rheostat. C. C. Coffin (J. Amer. Chem. Soc., 1931, **53**, 2180—2181).—To one terminal of each lamp is soldered a hook perpendicular to the axis. By this means, the lamps are pivoted about a brass rod below which is a brass strip against which the other terminals of the lamps, when lowered, press.
J. G. A. Griffiths.

New cell for electrodialysis. H. N. Holmes and A. L. Elder (J. Physical Chem., 1931, **35**, 1351—1354).—With the cell described $Na^{\cdot}$ and Cl' were removed from 0·01N-NaCl after 10 hr. dialysis at 155 volts at 165—170°. Satisfactory removal of salts from gelatin and of HCl from silica gel was also obtained. L. S. Theobald.

Extraction-dialyser. H. Raab (Chem.-Ztg., 1931, **55**, 395).—The extraction-dialyser is suitable for use at atm. or reduced pressure. W. J. Boyd.

Leakage of helium through pyrex glass at room temperature. II. G. P. Baxter and H. W. Starkweather (Science, 1931, **73**, 618).—A continuous regular loss of He corresponding with that previously observed (A., 1929, 903) has been maintained. In 3·5 years the total loss of He amounts to approx. 3·5% (35 c.c.). L. S. Theobald.

Simple device for humidity regulation. G. E. R. Hervey and J. G. Horsfall (Science, 1931, **73**, 617—618).—An apparatus for controlling R.H. to ±2% is described. L. S. Theobald.

Modification of Krogh's differential manometer. D. E. Fink (Science, 1931, **73**, 592—593).
L. S. Theobald.

Apparatus to circulate liquid under constant pressure in a closed system. Anon. (Science, 1931, **73**, 566). L. S. Theobald.

Tilting stopcock. P. L. du Noüy (Science, 1931, **73**, 530).—Hg in a small glass vessel is utilised for cutting off low-pressure supplies of gas.
L. S. Theobald.

Levelling vessel for producing a constant receiving pressure in gas analysis. W. Herbert and W. Wahlig (Chem.-Ztg., 1931, **55**, 474).—The liquid displaced from the burette by the gas evolution passes through a side limb into a reservoir of special design so that the liquid in the burette is not in direct contact with that in the reservoir. The pressure of the gas, being governed by the difference in levels of the burette and the side limb, remains const. while the reservoir is stationary. H. J. Dowden.

Transference of small quantities of liquids. G. Owen (J.S.C.I., 1931, **50**, 189—190T).—The manipulation of small quantities of liquids is facilitated by the use of a bent narrow glass tube of capillary bore. Transfer of the liquid is effected by siphoning, which commences automatically.

Automatically controlled slow cooling or heating. G. Owen (J.S.C.I., 1931, **50**, 190T).—Details are given of a device for inserting a hydrostatic resistance into the flow of gas used for heating; the value of this resistance increases or decreases at any desired rate.

Modified form of Kundt's tube. R. C. Colwell (Science, 1931, **73**, 480).—An apparatus suitable for lecture demonstration is described.
L. S. Theobald.

Recrystallisation apparatus. H. Ulich (Chem. Fabr., 1931, 278—279).—Two flasks (one inverted) with side tubes are connected by a wide glass tube containing a Schott filter plate and surrounded by an electrical heating spiral. By inverting the apparatus and employing the side connexions a salt can be dissolved, the solution filtered and crystallised, and the crystals washed with absence of air, under pressure, in vac. etc. C. Irwin.

Alchemical apparatus. J. R. Partington (Nature, 1931, **128**, 118).—The alchemical "waterbath" (bain-marie) may actually represent a small charcoal brazier. L. S. Theobald.

Arabic source of Zadith's "Tabula Chemica." H. E. Stapleton and M. H. Husain (Nature, 1931, **127**, 926).—Historical. L. S. Theobald.

Democritus. H. Kopp (Riv. Chim. scient. ind., 1930, **1**, 211—213; Chem. Zentr., 1931, i, 2014).

Geochemistry.

Origin of subterranean water. F. Diénert (Compt. rend., 1931, **192**, 1402—1404).—An experiment is described demonstrating that rain-water passes down through surface soils to the underground water level. The view that subterranean water supplies largely depend on condensation of water vapour from the air in the soil, which in the author's opinion is possible only from air actually circulating in the soil, is opposed. C. A. Silberrad.

Relative radioactivity of deep-well waters in Manila and vicinity. R. H. Aguilar (Philippine J. Sci., 1931, **45**, 183—197).—Measurements show no wide variations and the average results compare very

favourably with those obtained in other parts of the world. The Ra emanation content is far below the min. necessary to produce any therapeutic effect, and there is thus no support for the belief that the radioactivity confers a special medicinal value.
N. H. Hartshorne.

Variation due to rain in salinity of tidal pools. R. Lami (Compt. rend., 1931, **192**, 1579—1580).—The surface water of three tidal pools 3 hr. after isolation from the sea, about 1 mm. rain having fallen, had fallen to 30·81, 31·78, and 24·40, and that of the last at 4 cm. depth to 31·46. At 10 cm. in all cases the salinity was practically that of the sea, about 34.
C. A. Silberrad.

Dissolved phosphorus and inorganic nitrogen in the water of the Mississippi River. A. H. Wiebe (Science, 1931, 73, 652).—Analytical data for sol. P, nitrate-N, and NH_3-N for 1929—1930 are recorded. Inorg. N is apparently not a limiting factor in plankton production, but sol. P may become one at certain periods. L. S. Theobald.

Possible rôle of micro-organisms in the precipitation of calcium carbonate in tropical seas. W. Bavendamm (Science, 1931, 73, 597—598).—Carbamide bacteria, which occur in many sea muds, can ppt. $CaCO_3$ under certain conditions. Other observations support the view that the formation of $CaCO_3$ sediments is primarily a microbiological process.
L. S. Theobald.

Soils of the bed of Lake Albert, S. Australia. J. K. Taylor and H. G. Poole (J. Counc. Sci. Ind. Res. Austral., 1931, 4, 83—95).—Chemical and physical examination of the soils is described. The lack of uniformity and high salinity of the soils are unfavourable to reclamation. A. G. Pollard.

Muds of the Clyde sea area. III. Chemical and physical conditions; rate and nature of sedimentation; and fauna. H. B. Moore (J. Marine Biol. Assoc., 1931, 17, 325—358; cf. A., 1930, 448).—The PO_4''' content, O_2 adsorption, p_H, H_2O content, *d*, and rate of sedimentation have been determined.
C. W. Gibby.

Russian eruptive and metamorphic rocks. Z. Némova and F. Loewinson-Lessing (Mem. Com. Geol., Moscow, 1930, [ii], No. 186, 361).—Analyses (1676) are recorded. Chemical Abstracts.

Minerals in nephelinic syenite of Kassa Is. (Los Archipelago, French Guinea). Pneumatolytic phases of these syenites. A. Lacroix (Compt. rend., 1931, **192**, 1322—1326).—The nephelinic syenite contains, besides greyish soda-orthoclase and nepheline, acmite and arfvedsonite, with a little pyrochlore, lavenite, and fluorite. In a pegmatitic facies occur astrophyllite, eucolite with inclusions of catapleiite and accompanied by cancrinite, intensely fluorescent blue sodalite, and wine-red villiaumite. Other geodes yield serandite (cf. this vol., 332), natrolite, rhodochrosite, and pyrophanite. Elsewhere occur nodules of natrolite containing fine crystals of analcite, *d* 2·243—2·248, coloured rose by Mn, and accompanied by scales of stilpomelane. The bulk of the above minerals are ascribed to the author's "constructive" phase of pneumatolysis, secondary zeolites and pyrite following in the "destructive" phase. Apophyllite does not occur (cf. A., 1890, 1077). C. A. Silberrad.

Action of heat on braunite. S. Pavlovitch (Compt. rend., 1931, **192**, 1400—1402).—Braunite crystals, *d* 4·81, containing 8·92% SiO_2 and perfectly homogeneous, when heated in N_2, were transformed at 1190° into many minute crystals of the same; at 1400° in 4 hr. 3·8 wt.-% of O_2 was evolved, with formation of tephroite, $MnSiO_4$, and a partly fused eutectoid of tephroite and hausmannite, Mn_3O_4. Analysis showed 30% tephroite and 70% hausmannite. Braunite is therefore $(MnSi)_2O_3$. When heated in air at 1400° only 2·78% O_2 was evolved (cf. A., 1894, 99).
C. A. Silberrad.

Clays as minerals and as colloids. C. E. Marshall (Trans. Ceram. Soc., 1931, 30, 81—96).—A table is given in which clays are classified as minerals on the basis of existing knowledge. The problem of base exchange is discussed from the colloidal and the mineralogical points of view. Recent *X*-ray work on the structure of clays is reviewed. Clays are considered as polydisperse colloidal systems, and a centrifugal method of carrying out mechanical analysis down to 0·2 μ is described. The distribution of particle size in 4 types of clay is tabulated. A brief account is given of the different types of coagulation. F. Salt.

Melilite. F. Machatschki (Zentr. Min. Geol., 1931, A, 28—30; Chem. Zentr., 1931, i, 1895).—A discussion of the formula. A. A. Eldridge.

Composition and age of thucholite. A. Faessler (Zentr. Min. Geol., 1931, A, 10—18; Chem. Zentr., 1931, i, 1895).—The following elements were detected spectroscopically: U, Th, Pb, Lu, Yb, Er, Ho, Dy, Tb, Gd, Sm, Nd, Pr, Ce, La, Ru (?), Zr, Y, Sr, As, Zn, Fe, V, Ca; spectroscopic determinations indicated: ThO_2 14·3, U_3O_8 1·65, Y 8, Sr, 1·3, Zr 0·6—0·7, Fe and Ca 2—3%. Other proportions are estimated. The age is estimated at 250×10^6 years.
A. A. Eldridge.

Composition of eucrite. R. Brauns (Zentr. Min. Geol., 1931, A, 18—23; Chem. Zentr., 1931, i, 1895).—The felspar is closely related to anorthite (80—87%). The CaO content of the pyroxenes is insufficient for the ratio CaO : (Fe,Mg)O=1 : 1. Hence in the diopside pyroxenes a solid solution of $(Mg,Fe)SiO_3$ is postulated. A. A. Eldridge.

Radium in rocks. III. Radium content of Hawaiian lavas. C. S. Piggot (Amer. J. Sci., 1931, [v], 22, 1—8; cf. this vol., 332).—The average Ra content of 16 samples of Hawaiian lavas is $0·96\times10^{-12}$ g. per g. All samples from the Kilauea crater, of whatever age, had the same content (cf. A., 1909, ii, 848). C. W. Gibby.

The system of monticellite. D. Beliankin and B. Ivanov (Amer. J. Sci., 1931, [v], 22, 72—80).—Ural monticellite contained: SiO_2 32·88, TiO_2 0·25, Al_2O_3 3·76, FeO 8·20, MnO 10·45, MgO 13·03, CaO 28·62, Na_2O 1·57, K_2O 0·54, P_2O_5 0·18, CaS 0·23, total 99·71%. C. W. Gibby.

Alkaline rocks of the Highwood type in S.E. Idaho. A. L. Anderson and V. R. D. Kirkham (Amer. J. Sci., 1931, [v], 22, 51—68).—A petrographic description is given. C. W. Gibby.

Age of flint. M. Burton (Nature, 1931, **128**, 32—33).—A discussion. A criterion for the age of flint is suggested. L. S. Theobald.

Unique iron meteorite from Mexico. H. H. Nininger (Amer. J. Sci., 1931, [v], **22**, 69—71).—An analysis and description are given. C. W. Gibby.

Origin of the salt domes of the gulf coastal plain of the United States. E. de Golyer (J. Inst. Petroleum Tech., 1931, **17**, 331—333).—A discussion. N. H. Hartshorne.

Moot points in salt dome theory. L. Owen (J. Inst. Petroleum Tech., 1931, **17**, 334—337).—The areal distribution of salt domes, the derivation of the "cap rock," and the shape of the salt mass are discussed. The calcite in the cap rock may have been originally incorporated with the anhydrite, collected by the anhydrite in its upward movement, or introduced by surface waters. The shape of the salt mass is probably an inverted cone, and if this is so the search for oil in the flank wells of the dome should not end with the striking of salt. N. H. Hartshorne.

Salt dome geochemistry. M. Stuart (J. Inst. Petroleum Tech., 1931, **17**, 338—345).—A genetic relation between salt domes and the oil sometimes associated with them can, if it exists, be due only to the occurrence of animal and vegetable life in the original salt lake from the dried deposit of which the dome was extruded. The existence of $CaSO_4$ in the cap rock is due to the action of calcareous waters either on sulphate layers in the deposit corresponding with the kieserite and polyhalite zones in the Stassfurt beds, or Fe sulphide as found in the Indian deposits. The presence of anhydrite as well as gypsum in the cap is a possible result of pressure and the dehydrating action of dissolved salts. The occasional association of dolomite with the gypsum is attributed to an abundance of $MgSO_4$ in the upper layers of the salt deposit forming the dome. The absence of cap rock in the Roumanian domes is thought to be due to their having been extruded to such an extent that only the "anhydrite zone" remains to form a cap; this contains practically no soluble sulphates. The effect of pressure on the "flow" of different zones of a salt deposit becomes less marked with increasing depth, and may possibly be connected with the accompanying decrease in the combined H_2O. N. H. Hartshorne.

Base exchange and the formation of coal. W. H. A. Penseler (N.Z. J. Sci. Tech., 1931, **12**, 284—295).—Claystone samples from the Waikato coal seams were generally of an acid character, and the predominant exchangeable bases were Ca and Mg. Contrary to Taylor's views, the formation of the bituminous coal examined does not appear to have been controlled by base exchange and hydrolysis in the roofing clay. A. G. Pollard.

Origin of coal. E. Berl, A. Schmidt, and H. Koch (Z. angew. Chem., 1931, **44**, 329—330). W. Fuchs and O. Horn (*ibid.*, 330).—Polemical (cf. B., 1931, 456). A. R. Powell.

Lignin theory [of the origin of coal]. R. Lieske and K. Winzer (Brennstoff-Chem., 1931, **12**, 205—211; cf. A., 1930, 570, 571, 1017).—The occurrence of whole leaves which have been converted into coal is not inconsistent with the lignin theory of coal formation; contrary to general belief, not only the veins, but the whole of the leaf contains relatively large amounts of lignin. The lower *d* of some fossil woods compared with fresh wood corresponds with the determined loss in cellulose content; the higher *d* of other fossil woods is due to deposition therein of material from the surrounding medium. The decomp. of cellulose in the lower layers of the peat bog is attributed mainly to hydrolysis by the peat acids, the sugars thereby formed being further decomposed by micro-organisms. The question as to whether sp. cellulose-decomp. bacteria or fungi are present or not is therefore immaterial. A. B. Manning.

Classification and development of carbonaceous minerals. H. Briggs.—See B., 1931, 659.

Microscopic structure and origin of coking and bituminous coals. A. Duparque (Compt. rend., 1931, **192**, 1472—1474).—The great majority of coking coals are produced from deposits rich in lignin and free from spores, cuticle, and resinous material; a small number from such as contained much cutin, or from mixed deposits of ligneous tissue, spores, and cuticle. The three classes of bituminous coal—forge, gas, and long-flame—are due to different processes acting on deposits rich in cutin, and consisting largely of spores and cuticle. The anthracites formed by metamorphosis of such coals (cf. this vol., 818) differ greatly from other anthracites. This duality of origin explains the difference between two coals showing the same content of volatile matter. C. A. Silberrad.

Composition of the mother substance of the coals of the Kuzneck basin. M. D. Zaleski and E. F. Tschirkova (Bull. Acad. Sci. U.S.S.R., 1931, 269—275).—Many coal strata of the Koltschuginski region of the Kuzneck basin contain mineralised $CaCO_3$, which includes well-preserved vegetable residues. T. H. Pope.

Palæobotany of coal from Wemyss Colliery, East Wemyss, Fife. D. J. W. Kreulen (Fuel, 1931, **10**, 270—273).—The durain of this coal is rich in spores. Photomicrographs are reproduced. A. B. Manning.

Organic Chemistry.

Configurational relationship of hydrocarbons. II. Optical rotations of hydrocarbons of the normal series. P. A. Levene and R. E. Marker (J. Biol. Chem., 1931, **91**, 761—772).—l-β-*Methyl*-n-*butan*-α-*ol*, b. p. 127°/760 mm., $[\alpha]_D^{23}$ −2·41° (*brucine phthalate*, $[\alpha]_D^{23}$ +1·15° in EtOH), is converted by PBr_3 into *d*-α-bromo-β-methyl-*n*-butane, b. p. 119°/760 mm., $[\alpha]_D^{22}$ +2·16°, converted through its Grignard compound by CO_2 into d-β-*methyl*-n-*valeric acid*, b. p. 110°/30 mm., $[\alpha]_D^{25}$ +3·66°, and by MeCHO into d-γ-*methyl*-n-

hexan-ε-ol, b. p. 146—147°/760 mm., $[\alpha]_D^{23}$ +4·24°. Reduction of the corresponding iodide with Zn+HCl affords d-*γ-methyl*-n-*hexane*, b. p. 91—92°/760 mm., $[\alpha]_D^{23}$ +3·67° (+9·87°). Similarly using higher homologues of the aldehyde are obtained d-*γ-methyl*-n-*heptan-ε-ol*, b. p. 72°/22 mm., $[\alpha]_D^{23}$ +2·98°, the *bromide*, b. p. 63°/16 mm., $[\alpha]_D^{23}$ +4·82°, of which is converted by hydrolysis of its Grignard compound into d-*γ-methyl*-n-*heptane*, b. p. 116—118°/760 mm., $[\alpha]_D^{22}$ +4·45° (+11·97°); d-*γ-methyl*-n-*octan-ε-ol*, b. p. 89°/15 mm., $[\alpha]_D^{23}$ +3·67° (*bromide*, b. p. 94°/20 mm., $[\alpha]_D^{23}$ +5·63°); d-*γ-methyl*-n-*octane*, b. p. 143—144°/760 mm., $[\alpha]_D^{23}$ +5·27° (+14·18°). In the *l*-series are similarly prepared: l-*ε-methyl*-n-*octan-β-ol*, b. p. 92°/15 mm., $[\alpha]_D^{25}$ −0·32°; l-*ε-methyl*-n-*octane*, b. p. 53°/25 mm., $[\alpha]_D^{22}$ −0·46°; l-*ζ-methyl*-n-*nonan-γ-ol*, b. p. 105°/15 mm., $[\alpha]_D^{24}$ −0·65°; l-*ζ-methyl*-n-*nonane*, b. p. 72°/25 mm., $[\alpha]_D^{22}$ −0·59°; l-*ζ-methyl*-n-*decan-γ-ol*, b. p. 117°/22 mm., $[\alpha]_D^{24}$ −0·33°; and l-*ζ-methyl*-n-*decane*, b. p. 94°/30 mm., $[\alpha]_D^{24}$ −0·39°. Levene and Marker's rule (this vol., 598) concerning the direction of rotation of secondary carbinols is also applicable to the active hydrocarbons. The max. rotation values calc. indirectly are included in parentheses.

J. W. BAKER.

Preparation of hydrocarbons and alcohols by reduction of fats under high pressure. W. SCHRAUTH, O. SCHENCK, and K. STICKDORN (Ber., 1931, 64, [*B*], 1314—1318).—Hydrocarbons are produced by the hydrogenation of fats at temp. exceeding 350° and pressures up to 200 atm. in presence of Ni, whereas alcohols corresponding with the fatty acids are formed in presence of Cu at temps. not greatly exceeding 320°/200 atm. Mixed catalysts can be employed under conditions which vary according to the catalyst and the nature of the fat. Reaction is applicable to any fatty acid or ester and to fatty-aromatic carboxylic acids. The following examples are cited: dodecane from Me laurate; hydrocarbons from coconut oil and hydrogenated sperm oil; dodecane and octadecane from lauric and stearic acids respectively; dodecyl alcohol from Me laurate; decyl alcohol from Me decoate; fatty alcohols from coconut oil; octyl and octadecyl alcohols from octoic and stearic acids respectively.

H. WREN.

Catalytic oxidation of non-benzenoid hydrocarbons and mineral oils in their vapour phase. R. SHIMOSE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 251—276).—Maleic acid, with CO_2 and CH_2O, is the main product of the catalytic oxidation of the following vapours with air: *n*-pentane, *n*-heptane, *n*-octane, β-amylene, β-*iso*amylene, di*iso*amyl, and *cyclo*hexane. Decahydronaphthalene gives phthalic acid in addition to the products mentioned. Maleic acid is obtained as a main product from gasoline, and both maleic and phthalic acids from kerosene, kerosene treated with 98% H_2SO_4, spindle oil treated with 98% H_2SO_4, liquid and solid paraffin; CO_2 and CH_2O are also among the products in each case. The catalysts used were oxides or salts of V, Mo, U, Cr, and Mn. Mineral oils are considered to contain polynaphthenes.

E. S. HEDGES.

Hydrogenation of unsaturated hydrocarbons under the electric discharge. Y. VOLMAR and G. HIRTZ (Bull. Soc. chim., 1931, [iv], 49, 684—702).—When a slow stream of H_2 and C_2H_4 is submitted to the silent electric discharge at 20 mm., the % hydrogenation, reaction velocity, and yield of saturated hydrocarbons increase with the proportion of H_2 in the mixture. The C deposited similarly decreases from 19% with excess of C_2H_4 to 2·6—5·5%. CH_4 and C_3H_8 as well as C_2H_6 are among the reaction products. Since under similar conditions a mixture of C_2H_6 and H_2 yields polymerisation but not scission products, the saturated mol. is stable, and it is suggested that the primary reaction is scission of the C_2H_4 mol. at the double linking. The free CH_2 radical thus formed reacts with excess of H_2 giving CH_4, or with a second mol. of C_2H_4 to yield, after hydrogenation, C_3H_8, or decomposes yielding C and H. Since the yield of saturated hydrocarbons and of CH_4 from a mixture of 1 mol. of C_2H_4 and 1 mol. of H_2 increases as the pressure decreases, the proportion of higher homologues decreasing, either active H or a compound activated by the H is considered the hydrogenating agent. In hydrogenation of C_2H_4 at low pressures in the silent discharge CH_4 and not C_2H_6 is the stable and chief product.

Under similar conditions C_2H_2 yields a mixture containing (initial ratio, C_2H_2, 1 part; H_2 4 parts) acetylenic hydrocarbons up to C_{10} and saturated hydrocarbons up to C_8. It is impossible to assert that the olefines also formed represent an intermediate stage, and the presence of CH_4 in the reaction products indicates the possibility of scission at the triple linking as a primary reaction. The percentage of polymerised products increases with the duration of the exposure to the electric discharge and with the pressure. At very low pressures polymerisation products practically disappear, and with a rapid flow hydrogenation to CH_4 should be practically quant. Active H is probably the hydrogenating agent. The proportion of olefinic and saturated hydrocarbons increases as the percentage of H in the initial mixture decreases. It is possible that the C_2H_4 and C_2H_2 may themselves be activated under these conditions.

R. BRIGHTMAN.

Dichloroacetylene (II) and the influence of rate of reaction on the stereochemical course of halogen addition at the acetylenic linking. E. OTT and K. PACKENDORFF (Ber., 1931, 64, [*B*], 1324—1329; cf. A., 1930, 1402).—The preparation of dichloroacetylene from trichloroethylene by means of pure KOH is effected without danger only when a rapid current of gas is used. Addition of a small amount of water-glass to KOH before granulation ensures a non-dangerous catalyst which becomes inactive if excess of water-glass is used. Reaction proceeds safely with pure KOH if 5% of Et_2O is admixed with the trichloroethylene. Distillation of a solution of dichloroacetylene in Et_2O gives a product, b. p. 32·5°/743 mm., apparently an unstable mol. *compound* insensitive to O. It can be preserved unchanged in the dark, but when exposed to light is converted into a number of *compounds*, one of which, Et_2O,C_2Cl_2, has b. p. 47·5°/18 mm., d_4^{20} 1·1753, and does not contain an unsaturated linking; a second *substance* (?)$[Et_2O,C_2Cl_2]_2$, b. p. 110°/18 mm., is described. Rapid addition of I to dichloroacetylene in CCl_4 yields

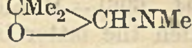
10% of liquid dichlorodi-iodoethylene, b. p. 72°/0·06 mm., m. p. 5—7°, d_4^{20} 2·9437, and 90% of the solid isomeride, m. p. 70°, whereas the slower addition in Et_2O leads to only traces of the liquid isomeride. Similarly, the slow addition of Br to acetylenedicarboxylic acid in the dark yields exclusively dibromofumaric acid, whereas the more rapid addition in sunlight leads to a product containing up to about 25% of dibromomaleic acid.

Slow autoxidation of dichloroacetylene yields in addition to $COCl_2$, CO, and CO_2 an oil with an odour resembling that of an acid chloride and transformed by NH_2Ph into an anilide, m. p. 186°. H. Wren.

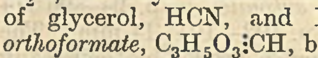
Catalytic dehydration of aliphatic alcohols in the gaseous phase in presence of pumice moistened with sulphuric or phosphoric acid. J. B. Senderens (Compt. rend., 1931, **192**, 1335—1337).—Passage of the vapours of $Pr^{\alpha}OH$, $Pr^{\beta}OH$, and $Bu^{\beta}OH$ over pumice moistened with $H_2SO_4,3H_2O$ gives the same results as with $NaHSO_4$ (cf. A., 1930, 889). With EtOH at 135° pure Et_2O is formed in quant. yield, and there is no evidence of deterioration of the catalyst; at 140° a little C_2H_4 is also formed. MeOH is dehydrated above 140°, best at 145—155°, to Me_2O. Use of syrupy H_3PO_4 in place of H_2SO_4 gives with EtOH no Et_2O, and only a comparatively feeble generation of C_2H_4 at 180—185°. H. A. Piggott.

Conversion of polyhydric alcohols into mono- and poly-chlorohydrins with thionyl chloride. P. Carré and P. Mauclère (Compt. rend., 1931, **192**, 1567—1569).—Glycerol is converted by $SOCl_2$ in presence of piperidine successively into mono-, di-, and tri-chlorohydrins. Mannitol gives a complex mixture, but mannide forms a mono-, b. p. 128—130°/17 mm. (*phenylurethane*, m. p. 163°), and a di-chlorohydrin, m. p. 67°. Hydrobenzoin affords a mixture with 1 mol. of $SOCl_2$ but with 2 mols. dichlorostilbene, m. p. 190°, is obtained. Excess of $SOCl_2$ with cotton cellulose causes only 1 atom of Cl to combine for each $C_6H_{10}O_5$ unit, and with reprecipitated cellulose decomp. takes place. F. R. Shaw.

Ethylene chlorohydrin. II. G. Bozza and G. Gallarati (Giorn. Chim. Ind. Appl., 1931, **13**, 163—173; cf. A., 1930, 1269).—The value of n_D^{20} is 1·4421 and the values for aq. solutions are virtually linear in relation to the composition by wt. Aq. solutions show the min. b. p. 97·8°/760 mm., or 80·55°/400 mm.; at 400 mm. the azeotropic mixture contains 45% (0·132 mol.) of the chlorohydrin, this proportion changing little with the pressure. Solutions in saturated NaCl have the min. b. p. 101·4°/760 mm. or 85·4°/400 mm. (57·8% or 0·234 mol. of chlorohydrin). Chlorohydrin solutions must be distilled rapidly at low temp., as the hydrolysis velocity coeff. is about 0·006 at 100°, so that 10% decomposes during about 8 hr. boiling. The vapours generally differ greatly from the liquids in equilibrium with them, so that separation of mixtures into pure components and azeotrope is easy. The displacement of the azeotrope by NaCl renders possible concentration by alternate distillations of aq. and NaCl solutions. Diagrams are given showing the course of the distillation of any aq. solution of the chlorohydrin. T. H. Pope.

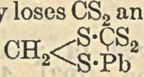
Action of organic bases on dichloro-tertiary alcohols, $CRR(OH)\cdot CHCl_2$. A. Avy (Bull. Soc. chim., 1931, [iv], **49**, 514—522).—The products obtained by the action of org. bases on dichloro-*tert.* alcohols in anhyd. media differ widely according to the nature of the base. With 5*N*-alcoholic NH_3, dimethyldichloromethylcarbinol yields 2 : 2 : 5 : 5-tetramethyldihydropyrazine, m. p. 83—84° (*chloroplatinate*, m. p. 194—195°); with 7*N*-alcoholic NH_2Me at 100° for 4 hr. it furnishes a complex *substance*, $H\cdot[NMe\cdot C(CMe_2)]_3\cdot NHMe$(?), sublimes and melts at 85—90°/3 mm., and with 7*N*-$NHMe_2$ in C_6H_6 at 100° for 4 hr. the ethylene oxide,  $\begin{smallmatrix}CMe_2\\ |\\ O\end{smallmatrix}\!\!>CH\cdot NMe_2$, b. p. 28—30°/13 mm. [*methiodide*, m. p. 245° (decomp.)]. Dichloromethyldiethylcarbinol similarly yields *tetraethyldihydropyrazine*, b. p. 89°/3 mm. (*chloroplatinate*), a complex *compound*, $C_{22}H_{44}N_4$, b. p. 101—102°/2·5 mm., and with a 33% solution of $NHMe_2$ in C_6H_6 at 130° for 5 hr., an *ethylene oxide*, b. p. 65°/12 mm. NMe_3 does not react with these dichloro-*tert.*-alcohols at 130° and NHPhMe and $NHPh_2$ do not react at 140°. R. Brightman.

Derivatives of pentane-αδε-triol. R. Paul (Compt. rend., 1931, **192**, 1574—1576).—Et allylacetate is reduced by Na and EtOH to Δ^{δ}-pentenol [*phenylurethane*, b. p. 184—185°/16 mm.; *allophanate*, m. p. 147—148° (decomp.)], which adds Br to give *δε-dibromopentanol* (I), b. p. 132—133°/16 mm., which, when distilled, loses HBr to form 1-*bromomethyltetrahydrofuran*, b. p. 66—67°/20 mm., and αβε-tribromopentane. KOAc and Ac_2O transform I into *αβε-triacetylpentane*, b. p. 170°/16 mm., converted by $ZnCl_2$ into *δ-bromo-Δ^{δ}-pentenyl acetate*, b. p. 103—105°/18 mm., hydrolysed by $Ba(OH)_2$ to *pentane-αδε-triol*, b. p. 190—191°/13 mm. (*triphenylurethane*, m. p. 92°). F. R. Shaw.

Preparation of acetals. F. Pauer (Monatsh., 1931, **58**, 1—11).—Improved methods for the prep. of acetals by Claisen's method (A., 1896, i, 463) using formimido-ethers (A., 1883, 731) obtained from alcohols and anhyd. HCN (preparation in 95% yield described) are detailed. From PhCHO and glycerol is obtained benzylideneglycerol, b. p. 152—154°/12 mm. (94% yield), together with *hydroxymethyleneglycerol*,  $OH\cdot CH_2\cdot CH\!<\!\begin{smallmatrix}O\text{---}CH\cdot OH\\ CH_2\cdot O\end{smallmatrix}$, decomp. by H_2O into CO_2, H_2O, and allyl alcohol. From equimol. proportions of glycerol, HCN, and HCl is obtained *glyceryl orthoformate*, $C_3H_5O_3{:}CH$, b. p. 126°/12 mm., together with a little of the *diglyceryl* ester $C_3H_6O_3{:}CH\cdot O_3C_3H_7$, b. p. 150—160°/12 mm. J. W. Baker.

Hexosemonophosphate (Robison), natural and synthetic. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1931, **91**, 751—760).—The structure of the dextrose-6-phosphate (this vol., 63) synthesised from *iso*propylideneglucose and its identity with Robison's ester (A., 1923, i, 86; osazone, m. p. 154—154·5°, and not 139° as previously recorded) are established by the following data. Dextrose-6-phosphate is converted through its *brucine* salt, $[\alpha]_D^{25}$ −16·6° in H_2O, into its *barium* salt, $[\alpha]_D^{25}$ +16·6° in H_2O, oxidised by $Ba(IO)_2$ to the aldonic acid (*tribrucine*, $[\alpha]_D^{25}$ −29·9° in H_2O, and *trisodium*, $[\alpha]_D^{25}$ +1·9° in H_2O, salts), the lactone formation of which was followed polarimetrically at 25°. The rotation–time curve is identical with that of the aldonic acid similarly prepared from the Robison ester. Dextrose-3-phosphate (*loc. cit.*; brucine salt, $[\alpha]_D^{25}$ $-14{\cdot}5°$ in aq. pyridine) is similarly oxidised to the aldonic acid (*dibrucine*, $[\alpha]_D^{25}$ $-24{\cdot}5°$ in H_2O, and *trisodium*, $[\alpha]_D^{25}$ $+1{\cdot}3°$, salts). Thus both hexosemonophosphates have free OH groups in the 4- and 5-positions.

J. W. Baker.

Reduction of carbon disulphide. J. A. Mitchell, E. Ott, and E. E. Reid (Ind. Eng. Chem., 1931, 23, 694—696).—Dithiolmethane distils over with CS_2 when the latter is reduced with Zn dust and boiling AcOH, practically no H_2S being produced. Addition of $Pb(OAc)_2$ in 50% EtOH solution to the distillate gives a yellow ppt. of the methylenebistrithiocarbonate, $CH_2(S{\cdot}CS_2)_2Pb$, formed by interaction of the CS_2 with the Pb dimercaptide. Corresponding Ag, Cu, Ni, Hg¨, Fe‴, Co, and Na salts are described. The free methylenebistrithiocarbonic acid, precipitated as a heavy brown oil on adding conc. HCl to an aq. solution of the Na salt, readily loses CS_2 and the residue gives a Pb salt which may be  $CH_2{<}\begin{matrix}S{\cdot}CS_2\\S{\cdot}Pb\end{matrix}$ or a mixture of dimercaptide and bistrithiocarbonate.

C. Hollins.

Xanthates and nitrosoxanthates. L. Cambi and L. Szegö [with A. Cagnosso] (Atti R. Accad. Lincei, 1931, [vi], 13, 93—99).—The compound, $Fe(NO)_2(S{\cdot}CS{\cdot}OEt)_2$, regarded by Manchot and Davidson (A., 1929, 526) as a Fe¨ compound, may be obtained readily by the action of NO on Fe‴ xanthate in EtOH and appears to be Fe‴ nitrosoxanthate, one of the NO groups exerting the functions of a halogen. This interpretation is in agreement with the magnetic susceptibility and reactions of the compound.

T. H. Pope.

Ethyl chlorosulphinate and mixed alkyl sulphites. P. Carré and P. Mauclère (Compt. rend., 1931, 192, 1738—1740).—Et_2SO_3 and PCl_5 yield $POCl_3$, SO_2, $SOCl_2$, and EtCl. EtOH (1 mol.), pyridine (1 mol.), and $SOCl_2$ (1 mol.) at 0° give *Et chlorosulphinate*, $Cl{\cdot}SO_2Et$, decomp. about 18°, the presence of which is shown by its reaction with alcohols to yield mixed alkyl sulphites. The following were prepared: Me Et sulphite, b. p. 52—53°/14 mm., 140—142° (decomp.)/760 mm.; *Me Bu sulphite*, b. p. 86—88°/14 mm.; *Et Bu sulphite*, b. p. 94—96°/14 mm.; *Pr^a Bu sulphite*, b. p. 102—104°/14 mm. The constitution of these products is proved by their ready hydrolysis to Na_2SO_3 and the respective alcohols.

R. S. Cahn.

Esterification with mixed anhydrides and mixtures of anhydrides. I. A. Rollett [with F. Pavlovitsch and F. Scholz] (Monatsh., 1931, 58, 47—58).—The relative proportions of BzOEt and AcOEt formed by interaction of EtOH with an equimol. mixture of BzCl and NaOAc at 190° can be determined by titration of the total acids formed, distillation of the AcOEt, and quant. ester hydrolysis. When the ratio mixed anhydride/EtOH=1/1, only 30 mol.-% of the total esters formed is BzOEt. Addition of an extra mol. of NaOAc has only a slight effect, decreasing the BzOEt to 27·7 mol.-%, whilst similar addition of 1 mol. of NaOBz increases the amount of BzOEt to 45 mol.-%. When the ratio is 1/2, 40 mol.-% of BzOEt is formed, this value being largely diminished (to 20·8 mol.-%) by addition of another mol. of NaOAc, but only slightly increased (to 49 mol.-%) by similar addition of 1 mol. of NaOBz. Sources of error in the measurements are investigated and in anhyd. medium no appreciable esterification of the acids formed in the reaction $R{\cdot}CO{\cdot}O{\cdot}COR'+R''OH \longrightarrow R{\cdot}CO_2R''+R'{\cdot}CO_2H$ or $\longrightarrow R'{\cdot}CO_2R''+R{\cdot}CO_2H$, could be detected.

J. W. Baker.

Three-carbon system. XXVI. Some substituted acrylic acids. G. A. R. Kon, E. Leton, R. P. Linstead, and L. G. B. Parsons (J.C.S., 1931, 1411—1418; cf. A., 1930, 1582).—The introduction of a Me group into the α-position retards the mobility and shifts the equilibrium towards the αβ-form in the system β-ethyl-Δ^{α}-pentenoic acid $\longleftrightarrow$ β-ethyl-Δ^{β}-pentenoic acid, and an Et group has a similar effect in the system β-methyl-Δ^{α}-hexenoic acid $\longleftrightarrow$ β-methyl-Δ^{β}-hexenoic acid. The αβ- and βγ-acids are prepared from the β-OH-esters by known methods, and are purified by partial esterification. The following are recorded: *Et* β-*hydroxy*-β-*methylhexoate*, b. p. 98°/13 mm. (*Ag* salt); *Et* β-*hydroxy*-α-*methyl*-β-*ethylvalerate*, b. p. 105—108°/17 mm.; β-ethyl-Δ^{α}-pentenoic acid (21%, 0·64); α-methyl-β-ethyl-Δ^{α}-pentenoic acid (50%, 0·0058), b. p. 122°/12 mm. (*Ag* salt); α-methyl-β-ethyl-Δ^{β}-pentenoic acid, b. p. 116—117°/14 mm.; β-methyl-Δ^{α}-hexenoic acid (33%, 0·39) (exists in a stereoisomeric *form*, m. p. 40°); β-*methyl*-Δ^{β}-*hexenoic acid*, b. p. 113°/10 mm.; β-*methyl*-α-*ethyl*-Δ^{α}-*hexenoic acid* (57%, 0·0030), b. p. 127°/12 mm. (*Ag* salt); and β-methyl-α-ethyl-Δ^{β}-hexenoic acid, b. p. 130°/13 mm. The percentages and figures given above refer respectively to the proportions of αβ-acids at equilibrium and to the mobility.

D. A. Fairweather.

Differentiation of *cis*- and *trans*-ethylenic compounds by catalytic hydrogenation. III. β-Chlorocrotonic acid and β-chloro*iso*crotonic acid. C. Paal, H. Schiedewitz, and K. Rauscher (Ber., 1931, 64, [*B*], 1521—1530; cf. A., 1930, 740).—Catalytic hydrogenation of the two β-chlorocrotonic acids and their Na salts proceeds unusually rapidly with quant. production of butyric acid and HCl or NaCl. Since β-chlorobutyric acid and its Ca salt are not attacked by H in presence of small amounts of Pd, it follows that the Cl atom must be first removed with intermediate production of crotonic and *iso*crotonic acid, which suffer further reduction. β-Chloro*iso*crotonic acid is hydrogenated more rapidly than β-chlorocrotonic acid. Semi-hydrogenation of the β-chlorocrotonic acids proceeds essentially but not quantitatively according to the scheme:

$$CMeCl{:}CH{\cdot}CO_2H+H_2=CHMe{:}CH_2{\cdot}CO_2H+HCl.$$

With β-chloro*iso*crotonic acid or its Na salt semi-hydrogenation proceeds approx. twice as rapidly as with β-chlorocrotonic acid and its Na salt. The ready replaceability of Cl in the chlorocrotonic acids in contrast with its stability in β-chlorobutyric acid under like conditions is attributed to the negativing influence of the ethylenic linking. Hydrogenation of the β-chlorocrotonic acids proceeds more rapidly than that of the crotonic acids, although requiring twice the quantity of H. The evidence thus obtained confirms the conclusion that β-chloro*iso*crotonic acid and β-chlorocrotonic acid are *cis*- and *trans*-forms respectively. H. Wren.

Rapid determination of solid saturated fatty acids. T. P. Hilditch and J. Priestman (Analyst, 1931, 56, 354—367).—Bertram's method is modified by oxidising either the soap with alkaline $KMnO_4$ at 35—50°, or the free fats in $COMe_2$ with anhyd. $KMnO_4$. For rapid work it is advisable to carry out a parallel determination by an improved form of the Twitchell process, which, by itself, however, may give misleading results. T. McLachlan.

Determination of solid unsaturated fatty acids. L. V. Cocks, B. C. Christian, and G. Harding (Analyst, 1931, 56, 368—380).—The Pb salts of the mixed acids are prepared in 92—93% (by wt.) EtOH, left over-night at 15—20°, washed with light petroleum, b. p. 40—60°, and then crystallised from 92—93 wt.-% EtOH at 15—20° for 3 hr., after which the free solid acids are liberated and weighed. The I val. of these acids is determined and, after allowing a mean of 90 for the unsaturated acids unless interfering acids such as erucic acid are present, the proportion of saturated and unsaturated acids may be found. T. McLachlan.

Distribution of saturated and unsaturated higher fatty acids in mixed synthetic glycol esters. R. Bhattacharya and T. P. Hilditch (J.C.S., 1931, 901—907).—By oxidising the products of interaction of glycol, a saturated acid (lauric, palmitic, or stearic acid), and a mixture of oleic and linoleic acids, the proportion of fully saturated ester is determined, the proportions of saturated and unsaturated esters being estimated from the I absorption. It is found that the molar percentage of disaturated or diunsaturated esters obtained is proportional to the square of the molar percentage of saturated or unsaturated acids in the total acids present, compared with the cube of the molar percentage when glycerol is the alcohol present (this vol., 63), *i.e.*, the fatty acids are combined indiscriminately, two or three at a time, with the alcohol according to their relative concentrations. The significance of some regular variations from the y–x^2 curve is discussed. G. Discombe.

Ether-soluble lead salt of lumbang oil. D. M. Birosel (Philippine J. Sci., 1931, 45, 251—261).—3·79% of heptadecoic (probably identical with daturic) acid, m. p. 57·5°, has been isolated from lumbang oil. Cryst. salts of Pb, Li, Sr, and U are described; Rb, Na, and K give cryst. hydrogen salts, as well as normal salts, the alcoholic solutions of which gelatinise on cooling. E. Lewkowitsch.

Micro-analytical determination of certain hydroxy-acids by means of the photo-electric cell. A. S. Williams, R. H. Müller, and J. B. Niederl (Mikrochem., 1931, 9, 269—287).—The method is based on the colour produced by the reaction of the acids with a feebly acid solution of $FeCl_3$, the light intensity of the resulting coloured solution being measured by means of the photo-electric colorimeter. Good results are obtained with solutions containing more than 0·1—0·3 mg. of lactic, citric, tartaric, or salicylic acid. A. R. Powell.

Reagent concentration in the Walden inversion. W. D. Bancroft and H. L. Davis (J. Physical Chem., 1931, 35, 1253—1269).—Mainly a discussion. The rate of conversion of *l*-chlorosuccinic acid into malic acid is proportional to the [OH′], the final products being mixtures of *d*- and *l*-malic acids; alkaline solutions favour the preponderance of *d*-acid to an extent approx. proportional to the alkalinity. Good yields of this acid can be prepared by keeping a warm solution of chlorosuccinic acid alkaline to phenolphthalein. In the hydrolysis of *l*-bromosuccinic acid less than 2·7 equivs. of Ag_2O per mol. of acid give a product containing excess of *l*-malic acid, whilst larger proportions give more than 50% of *d*-acid. A mechanism is outlined whereby acid hydrolysis of the lactone gives a malic acid of the same rotation and configuration as the original chlorosuccinic acid and alkaline hydrolysis results in a Walden inversion. L. S. Theobald.

Determination of mixtures of isomeric unsaturated compounds. III. Review of the iodometric method and a new bromometric method. R. P. Linstead and J. T. W. Mann (J.C.S., 1931, 723—725).—The iodometric method (A., 1927, 1167) is inapplicable to itaconic and mesaconic acids owing to slowness of addition. The Br addition of these acids, obtained by using a 0·05*N*-Br solution in 40% aq. KBr, proceeds at a measurable rate, the Br remaining after 10 min. being determined by treatment with KI and titration with $Na_2S_2O_3$. G. Discombe.

Olefinic acids. IV. Two types of tautomerism of itaconic acids. Connexion between configurational and tautomeric changes in alkali. R. P. Linstead and J. T. W. Mann (J.C.S., 1931, 726—740).—Citraconic, mesaconic, and itaconic acids on heating with alkali at 105° yield the equilibrium mixture containing 15% of citraconic (*cis*-αβ-), 69% of mesaconic (*trans*-αβ-), and 16% of itaconic (βγ-) acid, the configurational change proceeding through the βγ-isomeride. The γ-methyl-γ-ethyl-itaconic and -aticonic acids can be interconverted slowly by boiling with 25—33% alkali, the equilibrium mixture containing 28·4% of itaconic acid. The slow equilibration of the itaconic–aticonic system is attributed to steric hindrance. G. Discombe.

Olefinic acids. V. Influence of bases on the condensation of aldehydes and malonic acid; Knoevenagel reaction. S. E. Boxer and R. P. Linstead (J.C.S., 1931, 740—751).—The reaction product from *n*-butaldehyde and malonic acid in presence of organic bases at room temp. and then at 100° depends on the base used (cf. A., 1926, 1245; 1928, 1214; 1929, 1271, 1275). Δ^{α}-*n*-Hexenoic acid is obtained when pyridine is used in mol. proportion, whilst triethanolamine in small quantity gives nearly pure Δ^{β}-acid, m. p. 12°, b. p. 109°/15 mm., d_4^{17} 0·9600, n_D^{17} 1·4402, other bases giving a mixture of the two, the Δ^{β}-acid also being obtained by the hydrolysis of *Et butylidenemalonate*, b. p. 144°/25 mm., $d_4^{19·5}$ 1·0029, from Et malonate, *n*-butaldehyde, and Ac_2O. From propaldehyde impure Δ^{β}-*n*-pentenoic acid, and from *iso*valeraldehyde Δ^{β}-*iso*heptenoic acid, is obtained by the use of triethanolamine. The condensation of *cyclo*pentanone with Et cyanoacetate in presence of triethanolamine proceeds less rapidly than when piperidine is used. G. DISCOMBE.

Chloride and other derivatives of dichloromaleic acid. "Kauder's tetrachloride." L. LEDER (J. pr. Chem., 1931, [ii], 130, 255—288).—Chlorination of succinyl chloride in presence of Fe powder at 145° gives a little dichloromaleic anhydride and 81% of dichloromaleyl chloride (I). Refractometric data indicate that preps. of I exist mainly in (*a*) *sym.*- or (*b*) *asym.*-forms, which with NH_2Ph in C_6H_6 give colourless, m. p. 193°, and yellow, m. p. 170°, *dianilides*, respectively; *b* is converted into *a* by treatment with $AlCl_3$. The yellow dianilide is hydrolysed more readily by dil. alkali than the colourless form. Both forms of I react almost quantitatively with NH_2Ph, but only one (probably *a*) with MeOH, in C_6H_6. Dichloromaleic anhydride and NH_2Ph in $CHCl_3$ afford *dichloromale*-N-*phenylimide* (or the corresponding *anil*), m. p. 148° (decomp.), whilst an *isomeride*, m. p. 202°, is obtained from I and the yellow dianilide (not from the colourless form) at 140°. MgMeBr and I give mainly a *substance* (probably the lactone of αβ-dichloro-γ-hydroxy-γ-methyl-Δ^{α}-pentenoic acid), m. p. 81° (not affected by O_3), and a small amount of a liquid *isomeride*. *Dyes* are prepared from I and 1-amino-, 1-amino-4-methyl-, and 1-amino-4-methoxy-anthraquinones; the shades on cotton are recorded.

Treatment of I with PCl_5 at 230° gives unchanged material and hexachloroethane. No tetrachloride of dichloromaleic acid is formed, nor could any be obtained by Kauder's procedure (A., 1885, 651). The m. p. (41·5°) of Kauder's tetrachloride may be the transition point (45°) of rhombic hexachloroethane.

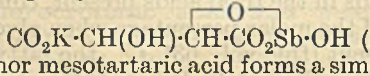
Succinic anhydride is obtained in 92% yield when $COCl_2$ is passed through the acid at 210°.

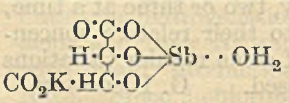
H. BURTON.

Decarboxylation of dihydroxymaleic acid. W. FRANKE and G. BRATHUHN (Annalen, 1931, 487, 1—52).—The spontaneous decomp. of dihydroxymaleic acid, $[CO_2H{\cdot}C(OH){:}]_2 \longrightarrow OH{\cdot}CH_2{\cdot}CHO+2CO_2$, is more rapid in buffered than in non-buffered aq. solution, but its velocity bears the same relation to p_H in both cases, being greatest at p_H 2·7, corresponding with the mono-H salt This suggestion that the univalent ion $(C_4H_3O_6)'$ is the actively decomp. constituent is confirmed by measurements of the relation between the velocity coeff. of decarboxylation and the degree of dissociation of the free acid, its Li H salt, and Li salt solutions of varying p_H; these show a proportionality between the velocity coeff. of decarboxylation and concentration of the primary ion, and also indicate decomp. of the free acid itself at 1/40 the velocity for the ion. The ratio of the two ionisation coeffs. of the acid is that of a *trans*-acid of this series.

H_3BO_3 exerts a stabilising action proportional both to its own concentration and that of the dihydroxy-acid. A kinetic investigation similar to the above indicates the formation of an equimol. complex for which a structure is suggested. Minute traces of Fe are without appreciable influence on decarboxylation, but larger amounts catalyse the decomp. The effect is a max. at p_H 4—5, and is not directly proportional to the Fe concentration. The autocatalytic stage is suppressed, due, it is suggested, to the effect of Fe on the keto-enol equilibrium. The catalytic effect is also shown by other metals of the Fe group, Cu, Zn, and Al, but only slightly by noble metals in colloidal form; in the case of Cu the activity increases continuously with p_H.

The velocity of decomp. is generally less in org. solvents due to depression of formation of the active ion, and the inverse proportionality of $-\log k$ (for decarboxylation) to the dissociation const. of the solvent is established for H_2O, MeCN, MeOH, EtOH, and $COMe_2$. The catalytic action of weak bases in aq. solution does not appear to be related to the strength of the base. There is a marked decrease in activity in the series $NH_2Ph > NHMePh > NMe_2Ph$. In all cases an ill-defined max. occurs at the mono-H salt, further additions of base leading to a suppression of the decomp. The effect is more marked in non-aq. solvents in which the active salt might be expected to be more stable. H. A. PIGGOTT.

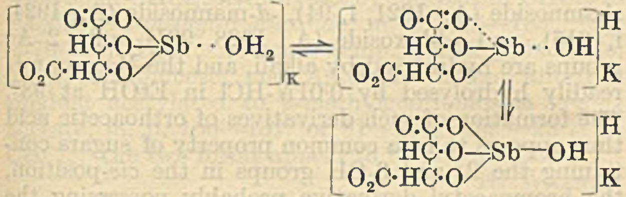
Constitution of tartar emetic. H. REIHLEN and E. HEZEL (Annalen, 1931, 487, 213—224).—F.-p. determinations show that Na antimonyl tartrate, and, by analogy, tartar emetic (too insoluble for measurement), are not associated in H_2O. α-*Phenylethylammonium* and p-*nitro*-α-*phenylethylammonium antimonyl tartrate* prepared from the Ba salt (+$2H_2O$) (both non-resolvable) crystallise without H_2O of crystallisation. The H_2O in other salts is, therefore, not constitutive. Tartar emetic contains one CO_2H group, but not the other, bound to Sb, because it is only weakly acidic, but is very easily esterified. The formula $CO_2K{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO_2SbO$ is incorrect (because the OH groups must be involved in the complex), as also is  $CO_2K{\cdot}CH(OH){\cdot}\overset{\ulcorner\!-\!-O-\!-\!\urcorner}{CH{\cdot}CO_2Sb}{\cdot}OH$ (because neither malic nor mesotartaric acid forms a similar compound).



(I.)

Formula I, shown to be unstrained by models, is supported by the replacement of the H_2O by pyridine in Ba antimonyl tartrate, which probably exists as acidic $[C_5H_5N\cdot\cdot SbC_4H_2O_6]H$ in the solid state, and as the salt $[H_2O\cdot\cdot SbC_4H_2O_6]H,C_5H_5N$ in solution (because the rotation increases rapidly with dilution to that of tartar emetic). The existence of the auxiliary valency in I is supported by the loss of H_2O from the Na salt in vac. at room temp., but from the K salt only at 120°, owing to the larger ionic vol. of the cation, and the free acid exists only in the anhyd. form. I is further supported by the fact that 0·1*M*-K mesotartrate can dissolve only 0·7 atom of Sb at room temp., that no antimonyl compound can be isolated from this solution, and that $M[\alpha]_D$ for 0·1*N*-tartar emetic solution is 7·5—8·7 times that of 0·2*N*-Na K tartrate solution. Unlike the corresponding B and As compounds, tartar emetic is only slightly hydrolysed to $HK[C_4O_6H_4]+Sb(OH)_3$, but its acid reaction (a

0·2N solution has p_H 4·2 at 16°) is due to "intramolecular hydrolysis":



dl-Acetyl-α-phenylethylamine, m. p. 75° (not 57°, A., 1894, i, 579), b. p. 176°/15 mm., gives the p-*nitro*-derivative, m. p. 122° (oxidised by $KMnO_4$ to p-$NO_2·C_6H_4·CO_2H$), which is slowly hydrolysed to dl-p-*nitro-α-phenylethylamine*, m. p. 27°, b. p. 162°/14 mm. [*hydrochloride*; *sulphate* (+$2H_2O$ cryst.)], non-resolvable as hydrogen tartrate or malate.

R. S. CAHN.

Methylose series. I. E. VOTOČEK and S. MALACHTA (Coll. Czech. Chem. Comm., 1931, 3, 265—275).—The product of the action of aq. HCN solution on Ba δ-ketorhamnonate consists of two salts differing in solubility in H_2O. The less sol. one (56%) affords the *dilactone* of *α-methyltetrahydroxyadipic acid* (I), m. p. 196° (decomp.), $[\alpha]_D$ −182° to −107·6°, (*diphenylhydrazide*, m. p. 187—188°). The more sol. salt (21·6%) gives a *dilactone* isomeric with I, +$\frac{1}{2}H_2O$, m. p. 166—167°, $[\alpha]_D$ −154°·1 to −75·7°; anhyd. *form*, m. p. 172°, $[\alpha]_D$ −162·8° to −75·6° (*bisphenylhydrazone*, m. p. 236—237°). Crystallographic measurements of the forms of the dilactones and of δ-ketorhamnonolactone have been made.

F. R. SHAW.

Use of 2 : 4-dinitrophenylhydrazine as reagent for carbonyl compounds. O. L. BRADY (J.C.S., 1931, 756—759; cf. A., 1926, 394).—The alcoholic solution of the carbonyl compound is added to the mixture of 1 g. of reagent in 2 c.c. of conc. H_2SO_4, and 15 c.c. of EtOH are added. The dinitrophenylhydrazones of cyclo*heptanone*, m. p. 148°, cyclo*octanone*, m. p. 163°, cyclo*pentadecanone*, m. p. 105°, *crotonaldehyde*, m. p. 190°, *glyoxylic acid*, m. p. 190° (decomp.), *anisaldehyde*, m. p. 250°, m-*hydroxybenzaldehyde*, m. p. 241°, *cuminaldehyde*, m. p. 241°, *piperonal*, m. p. 265° (decomp.), p-*nitrobenzaldehyde*, m. p. 320°, *phenylacetaldehyde*, m. p. 110°, *cinnamaldehyde*, m. p. 248°, *camphor*, m. p. 175°, *fenchone*, m. p. 140° after sintering at 125°, *pulegone*, m. p. 142°, *ionone*, m. p. 125—128°, and 1-(2′ : 4′-*dinitrophenyl*)-3 : 5-*dimethylpyrazole*, m. p. 122°, from acetylacetone, and 1-(2′ : 4′-*dinitrophenyl*)-3(or 5)-*phenyl*-5(or 3)-*methylpyrazole*, m. p. 151°, from benzoylacetone are described.

G. DISCOMBE.

Formaldehyde condensation by J. Blanc's method. Intermediate stage of formation of bakelite from phenol and formaldehyde. N. N. VOROSCHCOV and E. N. IURUIGINA (J. Gen. Chem. Russ., 1931, 1, 49—64).—The action of H·CHO on HCl at low temp. gives an optimum yield of dichlorodimethyl ether. Addition of $ZnCl_2$ and C_6H_6 and heating to 60° under various conditions gives CH_2PhCl, p-xylylene dichloride, phenylchlorotolylmethane, and dichloroditolylmethane. Pyridine and 1-nitronaphthalene in place of C_6H_6 do not react. Formation of pp'-dihydroxydiphenylmethane is the intermediate stage in "bakelite" formation using PhOH in place of C_6H_6. Other acids may also be used, H ions having a catalytic action.

E. B. UVAROV.

Course of organic chemical reactions. II. Intermolecular and intramolecular reactivity of hydrazonium compounds. A. WOHL [with A. PRANSCHKE] (Ber., 1931, 64, [*B*], 1381—1389).—β-Chloropropaldehyde diethylacetal, N_2H_4,H_2O, NaI, and EtOH at 100° yield β-*hydrazinopropaldehyde diethylacetal*, b. p. 73°/0·4 mm. (*H oxalate*, m. p. 122°), and NN-*di-γγ-diethoxy*-n-*propylhydrazine*, b. p. 125°/0·7 mm. (*H oxalate*). Treatment of the hydrazinoacetal with Me_2SO_4 and aq. KOH affords β-N^{α}-*methylhydrazinopropaldehyde diethylacetal*, $NH_2·NMe·CH_2·CH_2·CH(OEt)_2$, b. p. 55—56°/0·1 mm. (*H oxalate*), transformed by MeI and KOH into the corresponding *methiodide*, m. p. 91°, which yields NH_3 when reduced with Na and EtOH. Methylation is preferably effected with MeI in Et_2O. Treatment of the methiodide with AgCl yields the corresponding, very hygroscopic *methochloride*, analysed as the *chloroplatinate* $C_9H_{24}O_2N_2Cl_6Pt$. The methochloride is hydrolysed by HCl in H_2O to the very hygroscopic β-*methylhydrazinopropaldehyde methochloride*, identified as the corresponding *chloroplatinate*, m. p. 197—198°, which passes in acid solution into the *chloroplatinate*, $C_{10}H_{24}N_4Cl_6Pt$, m. p. 191—195° (decomp.). β-*Dimethylhydrazinopropaldehyde diethylacetal hydrogen oxalate*, m. p. 102°, from the iodide, Ag oxalate, and oxalic acid, passes in oxalic acid solution into (?) the *H oxalate* of the *semiacetal*, m. p. 82—86°. If the acidity of the solution is diminished by gradual addition of $CaCO_3$, *dimethylpyrazoline H oxalate*, m. p. 146°, is formed. Pyrazoline is methylated with MeI and the dimethylpyrazoline is identified as the H oxalate, m. p. 146—147° (*v.s.*), *picrate*, m. p. 154—155°, *chloroplatinate*, m. p. 76—78°, and *chloroaurate*, m. p. 152—153°. The H oxalate of the quaternary acetalised base, in presence of $CaCO_3$, does not give a hydrazone with PhCHO or p-nitrobenzaldehyde. The trimethylhydrazino-oxalate behaves similarly.

H. WREN.

Preparation of keten. E. OTT, R. SCHRÖTER, and K. PACKENDORFF (J. pr. Chem., 1931, [ii], 130, 177—179).—An apparatus for the prep. of keten in yields of about 50% is described; $COMe_2$ vapour is passed over a hot W filament.

H. BURTON.

Action of chloroacetone on dimagnesium dibromoacetylene. S. A. ZABOEV (J. Gen. Chem. Russ., 1931, 1, 143—149).—The product of the reaction is an *oil*, d_4^0 1·277, having the structure $[:C·CMe(OH)·CH_2Cl]_2$. Prolonged action of aq. Ag_2O gives the corresponding *hydroxy*-derivative, m. p. 115—118°.

E. B. UVAROV.

Oximes. J. V. DUBSKÝ, F. BRYCHTA, and M. KURAŠ (Publ. Fac. Sci. Univ. Masaryk, 1930, No. 129, 3—26).—The Cu salts of acetonedicarboxylic acid, oximinoacetone, dioximinoacetone, trinitrosopropane, and aminoacetoxime are green, that of diaminoacetoxime is black, and of phenylmethylpyrazolone brown. Dioximinoacetone gives a blue colour with the smallest traces of $Fe^{\cdot\cdot}$; its Ni salt is brownish-black. Trinitrosopropane has a black $Fe^{\cdot\cdot\cdot}$ salt, and brown Ni and Co salts. The oxime of acetonedicarboxylic acid gives a green Co salt and an orange Pb salt. Phenylmethylnitrosopyrazolone forms a greenish-blue Fe$^{\cdot\cdot}$ salt. R. Truszkowski.

Reasons for the difference in the behaviour of analogous compounds of bivalent cobalt, nickel, and copper containing diacetyldioxime. E. Thilo and H. Heilborn (Ber., 1931, 64, [*B*], 1441—1455).—The action of dimethylglyoxime on ignited $CoCl_2$ in anhyd. $COMe_2$ yields a red salt which gradually, particularly in presence of a little H_2O, passes into Feigl's green salt. Since the red compound vigorously evolves HCl with conc. H_2SO_4, whereas the green compound does not, the constitutions $[DH_2CoH_2D]Cl_2$ and $[(DH_2)_2CoCl_2]$ are respectively ascribed to them [DH_2=OH·N:CMe·CMe:N·OH]. In $COMe_2$ the equilibria exist $CoCl_2+2DH_2 \rightleftharpoons$ red salt $\longrightarrow$ green salt. The precipitation of unchanged green halide from solution by conc. H_2SO_4 and the displacement of the Br atoms of Feigl's bromide into the outer sphere by ethylenediamine are regarded as criteria of the *trans*-structure of the salt. Attempts to prepare the base corresponding with Feigl's salts were only partly successful.

The tendency of the addition of acids to $Ni(DH)_2$ [DH=OH·N:CMe·CMe:N·O$^-$] according to the scheme $Ni(DH)_2+2HX \longrightarrow [Ni(DH_2)_2]X_2$ diminishes with decreasing strength of acid. Similar addition occurs only when the dissociation const. of the acid is equal to or greater than 5×10^{-2}. The differing behaviour of Ni and Co appears to lie in the ability of the former to give a stable $Ni(DH)_2$, since it is co-ordinatively quadrivalent even in the salt-like derivatives of this compound, whereas Co is co-ordinatively sexavalent in all stable compounds with DH_2, and hence does not yield a stable cobalt diacetyldioxime in which it must be co-ordinatively quadrivalent. In $COMe_2$, $Cu(DH)_2$ yields only the two green *salts* DH_2CuSO_4 and $DH_2Cu(PO_4H_2)_2,0{\cdot}5H_2O$; other acids do not react or yield the corresponding salts free from DH_2. Only those salt-like DH_2 compounds of Cu are stable which contain 1 mol. of org. component; the tenacity of DH_2 is less towards Cu than towards Ni. Gaseous HCl converts Ni chloromethylglyoxime into $C_3H_5O_2N_2ClNiCl_2$ and chloromethylglyoxime. The following *salts* are described: $C_8H_{18}O_4N_4Ni(SO_4)_2$; $C_4H_8O_2N_2NiSO_4,2H_2O$ and the anhyd. compound; $C_4H_8O_2N_2NiC_2O_4$ and the dihydrate; $C_4H_{12}O_2N_2Ni(PO_4)_2$. All the Ni compounds are very sensitive to H_2O, moist air, EtOH, NH_2Ph, etc., giving red Ni dimethylglyoxime. They react immediately with gaseous NH_3 giving NH_4 salts and $Ni(DH)_2$ or $DNi(NH_3)_2$. H. Wren.

Historical résumé of the chemistry of oses particularly since the time of Emil Fischer. G. Bertrand (Bull. Soc. chim., 1931, [iv], 49, 627—650).

Acetyl monoses. VII. Isomeric triacetylmethyl-*d*-ribosides. P. A. Levene and R. S. Tipson (J. Biol. Chem., 1931, 92, 109—115).—Ribose is converted by Ac_2O and pyridine at 0° into *tetra-acetylribose*, m. p. 110°, $[\alpha]_D^{24}$ −52·0° in $CHCl_3$, converted by HBr in AcOH into *triacetylribosidyl bromide*, m. p. 96°, $[\alpha]_D^{25}$ −209·3° in $CHCl_3$. This is converted by MeOH in the presence of Ag_2CO_3 into *γ-triacetylmethyl*-d-*riboside*, m. p. 77—78°, $[\alpha]_D^{24}$ +2·4° in $CHCl_3$, in which, as in the corresponding γ-triacetylmethyl-*l*-rhamnoside (A., 1921, i, 94), -*d*-mannoside (A., 1924, i, 615), and -*d*-lyxoside (A., 1928, 991), only 2 Ac groups are hydrolysed by alkali, and the Me group is readily hydrolysed by 0·01*N*-HCl in EtOH at 98°. The formation of such derivatives of orthoacetic acid thus appears to be a common property of sugars containing the 2- and 3-OH groups in the *cis*-position, the bromoacetyl derivative probably possessing the α-configuration. Methylriboside with Ac_2O and pyridine affords the normal Ac_3 derivative, b. p. 120°/0·05 mm., $[\alpha]_D^{26}$ −17·4° in $CHCl_3$, stable under the above conditions of HCl hydrolysis. J. W. Baker.

Rotatory powers of some sugar-hydrazones in relation to the stereochemical structure of the α-carbon atom. E. Votoček, F. Valentin, and O. Leminger (Coll. Czech. Chem. Comm., 1931, 3, 250—264).—The rotations of the following phenylbenzylhydrazones in MeOH are in agreement with the Hudson rule: d-*arabinose*, m. p. 173°, *l*-arabinose, *d*-xylose, *d*-lyxose, *l*-rhamnose, rhodeose, fucose, *d*-mannose, l-α-*rhamnohexose*, m. p. 183—184°, and *d*-α-glucoheptose. On the other hand, ethyl-, butyl-, and di-phenylhydrazones of different sugars show no regularity in the rotations. *Phenyl*-p-*chlorobenzylhydrazine*, m. p. 44° (*hydrochloride*), affords the following *hydrazones* (the figures in parentheses are the final values of $[\alpha]_D$ in MeOH and are in agreement with the Hudson rule): *p*-chlorobenzaldehyde, m. p. 109°; $COMe_2$, m. p. 68°; furfuraldehyde, m. p. 101—102°; PhCHO, m. p. 99°; *l*-arabinose, m. p. 172° (−6·4°); *d*-arabinose (+2·8°); *d*-xylose, $0{\cdot}5H_2O$, m. p. about 80° (−21·1°); *d*-lyxose, m. p. 134—135° (+29·2°); *d*-ribose, m. p. 144—145° (−17·2°); *l*-rhamnose, m. p. 118—119°; *d*-fucose, m. p. 153° (+11·8°); *d*-glucose, m. p. 155—156° (−13·2°); *d*-mannose, m. p. 167—168° (+12·9°); *d*-galactose, $0{\cdot}5H_2O$, m. p. 161° (−9·8°); *l*-α-rhamnohexose, m. p. 172° (+10·0°); and *d*-α-glucoheptose, m. p. 158—159° (−13·5°). The rotations of the following *dibenzylhydrazones* in MeOH also agree with the rule: *l*-arabinose, m. p. 135° (−1·3°); *d*-arabinose, m. p. 133—135° (+1·0°); *d*-ribose, m. p. 101—103° (−15·2°); *d*-xylose, m. p. 130° (−8·6°); *d*-lyxose, m. p. 115—118° (+27·7°); *l*-rhamnose, m. p. 121—123° (−10·3°); rhodeose, m. p. 162·5° (0°); fucose, m. p. 162·5° (0°); *d*-glucose, m. p. 99—101° (−1·0°); *d*-mannose, m. p. 156—157° (+12·9°); *d*-galactose, m. p. 151—152° (−4·3°); *l*-α-rhamnohexose, m. p. 164° (+2·4°); and *d*-α-glucoheptose, m. p. 140—141° (−15·6°). The conclusion is reached that the benzyl group enhances the rotation so that the configuration of the rest of the sugar chain has no influence on the sign of the rotation of the hydrazone.

F. R. Shaw.

Solubility of carbohydrates in dioxan and applicability of the solutions. B. Helferich and H. Masamune (Ber., 1931, 64, [*B*], 1257—1260).—The solubilities of α- and β-glucose, lævulose, galactose, α- and β-methylglucoside, mannitol, sucrose, and β-phenylglucoside in dioxan at b. p., 20°, and 12—16° are recorded. Acetobromoglucose, β-methylglucoside, and Ag_2O in dioxan at 100° followed by treatment of the product with Ac_2O in pyridine yield *ethylidene*-β-*methyl*-d-*glucoside diacetate*, m. p. 175—177°, $[\alpha]_D^{20}$ −65·8° in $CHCl_3$, hydrolysed by MeONa in $CHCl_3$ to *ethylidene*-β-*methyl*-d-*glucoside*, m. p. 182—183°, $[\alpha]_D^{20}$ −79·3° in H_2O. At room temp. β-methylglucoside, acetobromoglucose, and Ag_2O in dioxan afford a product acetylated to β-methylgentiobioside hepta-acetate, m. p. 150—151° or 81—83°, $[\alpha]_D^{18}$ −23·7° in $CHCl_3$; the two forms appear to be polymorphic.

H. WREN.

Dextrose. H. HIBBERT (Science, 1931, 73, 500—501).—The structures which follow from the assumption that the normal C·O·C valency angle is 32° are worked out. L. S. THEOBALD.

Microchemical determination of dextrose in sugar solutions and in urine. C. CIMERMAN and P. WENGER (Mikrochem., 1931, 9, 295—299).—The sugar solution is added to a known amount of a boiling alkaline solution of Cu tartrate which is then centrifuged and a drop of the clear solution tested for the presence of Cu with filter-paper impregnated with guaiacum and a drop of 0·5% KCN solution. More of the sugar solution is added and boiling and centrifuging are repeated until no Cu test is obtained on the paper.

A. R. POWELL.

Action of alkali molybdates on dextrose. E. DARMOIS and J. MARTIN (J. Chim. phys., 1931, 28, 149—162).—Dextrose combines with molybdates of the type $NaHMoO_4$, giving compounds of the type $(2C_6H_{12}O_6,MoO_3)Na$. Polarimetric investigations of the kinetics of the reaction indicate that it is unimol. with respect to dextrose. Both $H^{\cdot}$ and MoO_4'' catalyse the mutarotation of dextrose. Mutarotation experiments at 0° suggest the presence of a small proportion of a labile form of dextrose in equilibrium with the stable forms. The labile form probably combines with molybdates. E. S. HEDGES.

Derivatives of 6-methoxy-*d*-glucose. B. HELFERICH and E. GÜNTHER (Ber., 1931, 64, [*B*], 1276—1280).—Fresh investigations result in the isolation of 6-methoxy-*d*-glucosazone, m. p. 184—187° (corr., decomp.), $[\alpha]_D^{16}$ −69° in EtOH, which is certainly not identical with 3-methoxyglucosazone (cf. A., 1929, 1044). 6-Methoxy-*d*-glucose is transformed by NaOAc and Ac_2O into β-6-*methoxy*-d-*glucose tetra-acetate*, m. p. 91—98° (corr.), $[\alpha]_D^{21}$ +20·9° in $CHCl_3$ (depresses the f. p. of the corresponding 3-OMe-compound), and α-6-*methoxy*-d-*glucose tetra-acetate*, m. p. 119—120° (corr.), $[\alpha]_D^{21}$ +111·8° in $CHCl_3$. The β-compound is transformed through the acetobromo-derivative into 6-methoxy-β-methylglucoside triacetate, m. p. 107—108°, $[\alpha]_D^{18}$ −12·4° in $CHCl_3$, and thence into 6-methoxy-β-methylglucoside, $[\alpha]_D^{19}$ −26·4° in H_2O.

H. WREN.

Unsaturated reduction products of sugars. XVI. Products of the dismutation of sugars. M. BERGMANN and L. ZERVAS (Ber., 1931, 64, [*B*], 1434—1438).—Hydroxyglucal tetra-acetate and phenylhydrazine in 50% AcOH give an *acetylated phenylosazone*, $C_{20}H_{22}O_3N_4$, decomp. 205° (corr.), $[\alpha]_D^{21}$ −98·6° in pyridine, also obtained from hydroxygalactal tetra-acetate and hydrolysed by NaOMe in $CHCl_3$ to the *phenylosazone* $C_{18}H_{22}O_2N_4$, decomp. 183° (corr.), $[\alpha]_D^{17}$ −159·8° in pyridine. Hydroxyglucal tetra-acetate is converted by NH_3 in MeOH and subsequently by phenylhydrazine into a *phenylosazone*, $C_{18}H_{22}O_3N_4$ or $C_{18}H_{20}O_3N_4$, decomp. 187° (corr.) (also derived after hydrolysis with NaOH), which differs from the osazone derived similarly from hydroxygalactal tetra-acetate. Hydroxycellobial acetate affords an *osazone*, decomp. 173°. Hydrolactal acetate yields a similar product. Other osazones are obtained if hydrolysis precedes treatment with phenylhydrazine. H. WREN.

Thiosugars and their derivatives. XVI. Walden inversion during fission of α-alkylglucothiosides by mercuric chloride. W. SCHNEIDER and W. SPECHT (Ber., 1931, 64, [*B*], 1319—1320; cf. this vol., 73).—Observation of the sp. rotation of α-methyl-, α-ethyl-, and α-propyl-glucothioside during fission under the influence of $HgCl_2$ shows that a min. value is passed through, after which a gradual rise to approx. the value of the equilibrium dextrose mixture is noted. Fission is therefore accompanied by a Walden inversion at the 1-C atom of the sugar with formation of β-glucose. H. WREN.

Thiosugars and their derivatives. XVII. Properties of β-glucothiose tetra-acetate. W. SCHNEIDER and A. BANSA (Ber., 1931, 64, [*B*], 1321—1324; cf. this vol., 73).—Octa-acetyl-ββ-diglucosyl disulphide, m. p. 144°, $[\alpha]_D^{20}$ −185° in $PhNO_2$, when treated with Al–Hg by a modification of Wrede's method gives glucothiose tetra-acetate, $C_6H_7O_5Ac_4{\cdot}SH$, m. p. 113—114° (lit. 75°), $[\alpha]_D^{20}$ −2·14° in *s*-tetrachloroethane; mutarotation is observed in 90% EtOH, pyridine, and dioxan. Oxidation with I transforms it smoothly into octa-acetyl-ββ-diglucosyl disulphide, whilst Ac_2O in pyridine and diazomethane afford β-glucothiose penta-acetate, m. p. 121°, and β-methylglucothioside tetra-acetate, m. p. 94—95°. The *compound*, $C_6H_7O_5Ac_4{\cdot}S{\cdot}HgCl$, m. p. 155°, $[\alpha]_D^{20}$ −64·81° in *s*-tetrachloroethane, and β-2 : 3 : 4 : 6-*tetra-acetyl*-1-*benzoylglucothiose*, m. p. 126°, $[\alpha]_D^{20}$ −12·44° in *s*-tetrachloroethane, are described.

H. WREN.

Structure of carbohydrates and their optical rotatory power. VI. 4-Glucosidomannose and its methylated derivatives. W. N. HAWORTH, E. L. HIRST, and H. R. L. STREIGHT (J.C.S., 1931, 1349—1354).—Structural rigidity of derivatives of 4-glucosidomannose on methylation is demonstrated. Complete methylation of 4-β-glucosidomannonic acid yields *methyl octamethyl*-4-β-*glucosidomannonate*, m. p. 118°, $[\alpha]_D^{21}$ −19·5° in $CHCl_3$, −3° in C_6H_6, which on hydrolysis yields 2 : 3 : 5 : 6-tetramethyl-γ-mannonolactone and 2 : 3 : 4 : 6-tetramethylglucopyranose. Similarly methylation of 4-β-glucosido-α-methylmannoside gives *heptamethyl*-4-β-*glucosido-α-methylmannoside*, b. p. 177—180°/0·01 mm. (bath temp.), $[\alpha]_D^{21}$ +28° in H_2O, +74° in $COMe_2$, hydrolysed to 2 : 3 : 4 : 6-tetramethylglucopyranose and 2 : 3 : 6-trimethylmannose (*anilide*, m. p. 127—128°). The results provide further evidence of absence of isomeric change during the methylation of α-methylmannoside.

D. A. FAIRWEATHER.

Structure of carbohydrates and their optical rotatory power. VII. 4-Galactosidomannose and its methylated derivatives. W. N. HAWORTH,

E. L. Hirst, and M. M. T. Plant (J.C.S., 1931, 1354—1358).—Evidence complementary to that in the preceding abstract is furnished on the behaviour of 4-galactosidomannose. Methylation of 4-β-galactosido-α-methylmannoside gives *heptamethyl-4-β-galactosido-α-methylmannoside*, b. p. about 170°/0·02 mm., $[\alpha]^{20}_{D}$ +41° in C_6H_6, +63° in Et_2O, hydrolysed to 2 : 3 : 4 : 6-tetramethylgalactopyranose and 2 : 3 : 6-trimethylmannose. *Methyl octamethylgalactosidomannonate*, prepared from 4-β-*galactosidomannonic acid* (*Ca* salt), gives on hydrolysis 2 : 3 : 4 : 6-tetramethylgalactose and tetramethyl-γ-mannonolactone. The behaviour of 4-galactosidomannose is therefore exactly analogous with that of its epimeride lactose.

D. A. Fairweather.

Sugars of human milk: gynolactose and allolactose. M. Polonovski and A. Lespagnol (Compt. rend., 1931, 192, 1319—1320).—*Gynolactose*, m. p. 205°, $[\alpha]_D$ −27° in water, and *allolactose*, m. p. 165° (*phenylosazone*, m. p. 172°), are present in human milk-serum, and are separated by repeated fractional crystallisation from H_2O. The former is feebly reducing, does not show mutarotation, and does not form an osazone in absence of free acid. The latter is similar to lactose in reducing properties, and shows rapid mutarotation. Both are hydrolysed by dil. acids, the former more readily, to dextrose and galactose.

H. A. Piggott.

Phloridzin. R. Weidenhagen (Z. Ver. deut. Zucker-Ind., 1931, 81, 125—129).—The sugar component of phloridzin is β-dextrose. Phloridzin and phlorin are hydrolysed by the β-glucosidase of emulsin, but not by the β-*h*-fructosidase of yeast (cf. A., 1930, 1316). Cryst. dextrose was obtained after hydrolysis of phloridzin with HCl.

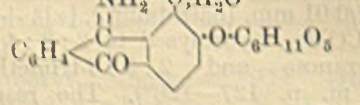
J. H. Lane.

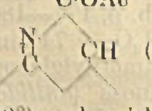
Preparation of the cyanidin from quercetin. Y. Asahina and M. Inubuse (Ber., 1931, 64, [*B*], 1256—1257).—When treated with Na–Hg in alkaline solution, quercetin affords only a trace of the carbinol base of the cyanidin. Its rhamnoglucoside, rutin (from *Sophora japonica*), is transformed by reduction and treatment of the product with HCl into the *cyanidin chloride*, $C_{15}H_{11}O_6Cl,H_2O$ (*compound* $C_{15}H_{11}O_6Cl,FeCl_3$).

H. Wren.

Structure of nitrogenous derivatives of hydroxyanthraquinone glucosides. A. Müller (Ber., 1931, 64, [*B*], 1410—1431).—Alizarin or its diacetate is converted by NH_3 in MeOH into the *salt* $C_{14}H_7O_4(NH_4)$, decomp. by org. acids. Alizaringlucoside tetra-acetate is transformed into the *imonium* salt of 1-hydroxy-2-glucosoxyanthraquinone-9-imine (I), m. p. 199° (also *sesquihydrate*, m. p. 198—199°, and *dihydrate*, m. p. 197—198°), sol. without change in AcOH. It is converted by Ac_2O and NaOAc at 100° into (?)O-*acetyl-2-acetoglucosoxyanthrapyridone* (II), m. p. 292° (decomp.), transformed by H_2SO_4–AcOH into 1 : 9 : 9-*triacetoxy-2-acetoglucosoxyanthrone*, m. p. 153—154° after softening at 150°, whereas treatment with Ac_2O in anhyd. pyridine affords the *imonium* salt of 1-*acetoxy-2-acetoglucosoxyanthraquinone-9-imine*, m. p. 218°, stable to cold formic acid, but converted by the boiling acid into acetylacetoglucosylalizarin, m. p. 195—196°, and by NaOH in EtOH into alizaringlucoside. With Ac_2O and NaOAc at 100° or with Ac_2O and pyridine, the imonium salt yields the corresponding N-*acetyl* derivative $C_{32}H_{31}O_{14}N$, m. p. 218°, hydrolysed by boiling formic acid or NaOH to acetylacetoglucosylalizarin or the free glucoside respectively.

(I.)





(II.)

Acetoglucosylalizarin and NH_2Me in EtOH afford the *methylammonium* salt $C_{21}H_{23}O_9N$, m. p. 220° (indef.) after becoming discoloured above 207°, immediately decomp. by AcOH to the alizaringlucoside and converted by Ac_2O and AcONa at 100° or Ac_2O and pyridine at room temp. into the completely acetylated alizaringlucoside. The *dimethylammonium* salt, m. p. 235° after becoming discoloured, behaves similarly. The *imonium* salt of 1-*hydroxy*-2-*cellobioxyanthraquinone*-9-*imine*, m. p. 230°, and its *sesquihydrate*, m. p. 230° after softening at 218°, are described. Hydroxy-2-acetoglucosylanthrarufin, MeOH, and NH_3 yield the *imonium* salt $C_{20}H_{19}O_9N,0{\cdot}5H_2O$, m. p. 237° after softening at 170°. The behaviour of 1-hydroxy-2 : 7-diacetoglucosoxyanthraquinone with NH_3 is described. 2 : 6-Diacetoglucosylrufiopin affords the *imonium* salt $C_{26}H_{27}O_{15}N$, m. p. 213° (also *monohydrate*), whilst acetoglucosylquinalizarin gives the *compound* $C_{20}H_{19}O_{10}N$, acetylated to $C_{34}H_{32}O_{17}N$, m. p. 223° (decomp.); acetocellobiosylquinalizarin yields the *substance* $C_{26}H_{29}O_{15}N,H_2O,1{\cdot}5H_2O$, m. p. 224°. Acetoglucosylchrysazin affords the *imonium* salt $C_{20}H_{19}O_8N,0{\cdot}5H_2O$, decomp. about 200° (also $+0{\cdot}5H_2O$ and $3{\cdot}5H_2O$), converted by dil. HCl into chrysazinglucoside. 1-Hydroxy-8-glucosoxyanthraquinone-9-imonium is converted by Ac_2O in cold pyridine into 1-*hydroxy*-8-*acetoglucosoxyanthraquinone*-9-*imonium*, $C_{28}H_{27}O_{12}N$, m. p. 165—166°, transformed by HCl in EtOH into acetoglucosylchrysazin and by Ac_2O and NaOAc at 100° into *compounds* $C_{32}H_{29}O_{13}N$, decomp. about 270°, and $C_{32}H_{30}O_{15}$ or $C_{34}H_{32}O_{16}$, m. p. 212°. The *imonium* salt of 1 : 4(or 1 : 5)-*dihydroxy*-8-*glucosoxyanthraquinone*-9-*imine*, $C_{20}H_{19}O_9N,H_2O$, decomp. 200°, is described. The hydrolysis of the following completely glucosylated hydroxyanthraquinones by NH_3 in MeOH is described: acetoglucosylerythro-oxyanthraquinone to 1-*glucosoxyanthraquinone*, m. p. 225—230° after softening at 220°; anthrarufin acetoglucoside to 1 : 5-*diglucosoxyanthraquinone* ($+0{\cdot}5H_2O$), m. p. 226—227°; diacetoglucosylhystazarin to 2 : 3-*diglucosoxyanthraquinone* ($+H_2O$), m. p. 232·5—233° after softening at 228°. 1-*Amino*-2-*acetoglucosoxyanthraquinone*, m. p. 153°, is obtained from acetoglucosyl bromide, 1-amino-2-hydroxyanthraquinone and Ag_2O in quinoline.

H. Wren.

Synthetic nucleosides. III. Theophylline-*d*-glucodesoside. P. A. Levene and F. Cortese (J. Biol. Chem., 1931, 92, 53—57).—Condensation of 1-bromo-3 : 4 : 6-tribenzoyl-*d*-glucodesose (A., 1923, i, 653) with the Ag salt of theophylline affords the *tribenzoate*, m. p. (indef.) 150—193°, $[\alpha]^{20}_{D}$ +14·2° in $CHCl_2{\cdot}CHCl_2$, hydrolysed by $Ba(OH)_2$ in MeOH to *theophylline*-d-*glucodesoside*, m. p. 258°, $[\alpha]_D^{21}$ −26·9° in H_2O. J. W. BAKER.

Polysaccharides. VIII. Evidence of continuous chains of α-glucopyranose units in starch and glycogen. W. N. HAWORTH and E. G. V. PERCIVAL (J.C.S., 1931, 1342—1349).—Trimethylamylose and trimethylglycogen have been degraded to tetramethylglucopyranose and 2 : 3 : 5 : 6-tetramethyl-γ-gluconolactone. The results are interpreted as evidence of the presence of α-glucopyranose units in each of these polysaccharides. D. A. FAIRWEATHER.

Plant colloids. XXVII. Differentiation of amylo- and erthyro-substances in starch. M. SAMEC [with E. PEHANI and J. STOJKOVIĆ] (Kolloidchem. Beih., 1931, 33, 103—130).—The amylo- and erythro-substances in sols of potato-starch, made by boiling with H_2O under pressure, may be differentiated by adsorption on cotton, the amylo-substance being more strongly adsorbed. The viscosity of aq. amylo-sols increases rapidly with rise of temp., but that of erythro-sols remains unaltered. In EtOH–H_2O mixtures the amylo-sols have a higher relative viscosity than in H_2O, whilst EtOH has little effect on the viscosity of erythro-sols. Whilst the sp. viscosity of amylo-sols is markedly influenced by the addition of neutral salts, that of the erythro-sols is scarcely affected. These observations lead to the conclusion that the amylo-substance is relatively more highly associated, hydrated, and electrically charged than the erythro-substance. The erythro-compounds are more rapidly hydrolysed by acids and by H_2O_2 than the amylo-compounds. The amylopectin fractions obtained by fractional dissolution of starch contain fatty acids. E. S. HEDGES.

Plant colloids. XXVI. Relations between phosphorus and nitrogen in potato- and wheat-starch. M. SAMEC [with W. BENDGER] (Kolloidchem. Beih., 1931, 33, 95—102).—Determinations of the P and N in potato- and wheat-starch after treatment with dil. acids and alkalis support the view that a substance (phytovitellin), containing both P and N, is combined with the polysaccharide by means of a radical containing P. The linking is looser in wheat- than in potato-starch, and the main portion of both P and N can be extracted. By careful treatment of wheat-starch with alkalis the N-containing substance can be removed preferentially and the P left in the starch becomes electrochemically active, the wheat-starch then becoming similar in properties to potato-starch. Treatment of the residue with hot H_2O causes a substance containing P to be split off, and the starch reverts to the wheat type. Heating the starch with H_2O under pressure at 120° removes substances containing P, the ratio N/P falling to 0·7, whilst the electrical conductivity and active [H˙] decrease. The N content is not altered by this treatment. E. S. HEDGES.

Inulin. XI. H. PRINGSHEIM and W. G. HENSEL (Ber., 1931, **64**, [*B*], 1431—1434).—Sufficiently active inulinase could not be obtained from dahlia, but is derived from *Aspergillus niger*; this converts inulin into a new *difructose anhydride acetate*, m. p. 121·5—122°, $[\alpha]_D^{20}$ +25·0° in $CHCl_3$. H. WREN.

[**Inulin. II. Supposed depolymerisation of inulin.**] E. BERNER (Ber., 1931, **64**, [*B*], 1531; cf. this vol., 716).—The values 3700 and 4900 are recorded for the mol. wt. of inulin in freezing formamide. H. WREN.

Polysaccharides. VI. Trimethylcellulose. VII. Isolation of octamethylcellobiose, hendecamethylcellotriose, and a methylated cellodextrin (cellotetrose ?) as crystalline products of the acetolysis of cellulose derivatives. W. N. HAWORTH, E. L. HIRST, and H. A. THOMAS (J.C.S., 1931, 821—824, 824—829).—$COMe_2$-sol. cellulose acetate can be completely methylated by treatment with Me_2SO_4 and 30% aq. NaOH in $COMe_2$ at 55°. Cellulose pulp and finely-ground cellulose on similar methylation in two stages yielded trimethylcellulose, m. p. 215—216°, $[\alpha]_D$ −10·0° in $CHCl_3$, mol. wt. 2500 in camphor, different samples varying only in the viscosity of their solutions. Acetolysis of trimethylcellulose at 15°, followed by simultaneous deacetylation and methylation, yields tetramethylmethylglucoside (15%), heptamethyl-β-methylcellobioside (18%), and *decamethyl*-β-*methylcellotrioside*, b. p. 208—220°/0·02 mm., m. p. 117—118°, $[\alpha]_D$ −14·5° in MeOH, mol. wt. 620 in camphor, hydrolysed to a mixture of tetramethylglucopyranose and 2 : 3 : 6-trimethylglucopyranose. From the residue is obtained a methylated cellodextrin, m. p. 151—152°, $[\alpha]_D$ −10° in H_2O, mol. wt. 855 in camphor, not methylated by Ag_2O and MeI, yielding on acetolysis and methylation tetramethylmethylglucopyranoside (30%) and heptamethyl-β-methylcellobioside (25%). G. DISCOMBE.

Formation of alkali-celluloses. G. CHAMPETIER (Compt. rend., 1931, **192**, 1593—1595).—The absorption curve of NaOH from aq. solutions by cellulose shows, by the titration method, the formation of the compounds $(C_6H_{10}O_5)_2,NaOH$, $(C_6H_{10}O_5)_3,2NaOH$, $(C_6H_{10}O_5)_4,3NaOH$, and $C_6H_{10}O_5,NaOH$, in solutions containing from 10 to 60% of NaOH. C. N. VASS.

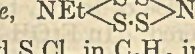
Isolation of *n*-propylguaiacol as a degradation product of lignin. M. PHILLIPS (Science, 1931, 73, 568—570).—The phenolic portion of the oil obtained by distilling lignin with Zn dust yields, in addition to guaiacol, *n*-propylguaiacol (confirmed through the 3 : 5-dinitrobenzoyl derivative). These two substances thus appear to be the fundamental units in the structure of lignin. L. S. THEOBALD.

Lignin. II. E. WEDEKIND, O. ENGEL, K. STORCH, and L. TAUBER (Cellulosechem., 1931, **12**, 163—173).—Contrary to Hillmer (B., 1926, 46) there appears to be a free OH group in phenol-lignin, since it gives readily an alkali-insol. *Ac* derivative, m. p. 175—180° after colouring at 150° and sintering (*Me* derivative, decomp. 175°). Phenol-lignin, for which the formula $[(C_8H_7O_2)(OMe)(OH)(C_6H_4{\cdot}OH)]_x$ is proposed, and acetylphenol-lignin yield colloidal solutions in $COMe_2$ and $CHCl_3$. In transport experiments in EtOH phenol-lignin wanders to the cathode. The possibility of a CO group condensation between phenol and lignin is discussed. Phenol-lignin and lignin behave in the same way towards oxidising agents. *Resorcinol-lignin* (*Ac* derivative, m. p. 160—170° after darkening at 145—150° and sintering), *guaiacol-lignin* [the phenol-lignin acids of the oak and pine (A., 1923, i, 1183), and phenol-metalignin (A., 1927, 597)], all of which give *Ac* derivatives, resemble phenol-lignin in their properties. A. RENFREW.

Lignin. III. R. O. HERZOG and A. HILLMAR (Ber., 1931, **64**, [*B*], 1288—1306; cf. A., 1929, 915).—The ultra-violet absorption spectrum of lignin preps. and of various benzenoid derivatives has been examined according to Henri's method, using the H line as source of light. A standard alkali lignin is prepared by treating rye straw with 2% methyl-alcoholic NaOH at room temp. in absence of O_2 and light of short wave-length and purification of the product by electrodialysis. Therewith are compared ligninsulphonic acid from pine, rye, and larch, alkali lignin from rye, jute, and larch, alkali methyl-lignin from rye, primary ethyl-lignin from beech, glycol-lignin from pine, and pectin lignin from flax. The connexion between botanical origin of the lignin and position of the chief max. in the region of long wave-length and between the chemical nature of the prep. and the intensity of absorption is very marked. Among benzenoid derivatives, substitution in the C_6H_6 nucleus leads to increased absorption and extension of the region of absorption towards longer wave-lengths. Only when a single, saturated substituent is introduced is the character of the C_6H_6 spectrum preserved and merely a displacement is observed (cf. PhMe, PhEt, PhPr, allylbenzene, β-phenylethyl alcohol). A double linking or a OH group in a side-chain is without effect if two or more C atoms are interspersed between it and the C_6H_6 nucleus. If the double linking is in conjugation with the ring or the OH group is proximate to the nucleus, three bands are observed (as with PhCHO) in contrast to the two bands of C_6H_6. The presence of OH attached to the nucleus does not essentially alter the C_6H_6 character, but the intensity of the C_6H_6 bands of longer wave-length is increased about 10-fold, and displacement towards the red increases in the sequence pyrogallol, phenol, pyrocatechol. The picture is reproduced by derivatives of the phenols. Coniferaldehyde gives a spectrum differing greatly from that of coniferyl alcohol. The continued conjugation of the C:C double linking and of the C:O group in the side-chain with the nucleus causes a very marked increase of the absorption coeffs. and a simultaneous displacement of the whole region of absorption towards greater wave-lengths.

It is considered that the well-defined band at $\lambda=276$ mμ in lignin is characteristic of a C_6H_6 derivative, since the presence of a series of double linkings, carbonyl or optically similar groups in conjugated position in lignin is excluded by the chemical evidence. This conception is in harmony with the presence of a second stronger band in the extreme ultra-violet which is very prominent in ligninsulphonic acid at λ 233 mμ. Spectroscopic and chemical evidence indicates in lignin the presence of a substance composed fundamentally of di- or tri-hydric phenols which are partly methylated. Double linkings in conjugation with the C_6H_6 nucleus or similar ketonic or aldehydic groups in free form do not appear to be present. Glycols, oxides, or ether-like linkings are not excluded. H. WREN.

Thermal decomposition of αζ-diamino-*n*-hexane hydrochloride. A. MÜLLER and E. FELD (Monatsh., 1931, **58**, 12—21).—K phthalimide converts αζ-dibromo-*n*-hexane into *αζ-phthalimido-*n*-hexane*, dimorphous, m. p. 181° and 170° on remelting, hydrolysed by HCl (*d* 1·19) at 180—190° to αζ-diamino-*n*-hexane dihydrochloride. The hexamethyleneimine obtained (A., 1922, i, 761) by thermal decomp. of this is proved by direct comparison to be 2-ethylpyrrolidine (p-*toluenesulphonyl* derivative, m. p. 76·5—77°; *phenylthiourethane*, m. p. 88°), the *Bz* derivative, b. p. 185°/11 mm., of which is oxidised by $KMnO_4$ to γ-benzamido-*n*-hexoic acid identical with a synthetic specimen (cf. this vol., 943). J. W. BAKER.

Reactions of primary amines with sulphur chloride and with sulphur and lead oxide at ordinary temperatures. T. G. LEVI (Gazzetta, 1931, **61**, 294—300).—NH_2Et (3 mols.) and S_2Cl_2 (1 mol.) in Et_2O yield 1 : 4-*diethyl*-2 : 3 : 5 : 6-*tetrathiodiazine*,  $NEt{<}\begin{smallmatrix}S\cdot S\\S\cdot S\end{smallmatrix}{>}NEt$, m. p. 35°. Benzylamine and S_2Cl_2 in C_6H_6 in presence of PbO give *bisthiobenzothioamide*, m. p. 100°. The following compounds prepared from secondary amines are also described: *bisdipropylamino-disulphide*, which does not solidify at −75°; *bisdi*iso*butylamino-disulphide*, m. p. 31°; *bisdibenzylamino-disulphide*, m. p. 79°. E. E. J. MARLER.

Polythioamines higher than the dithio-compounds. T. G. LEVI (Gazzetta, 1931, **61**, 286—293; cf. this vol., 474).—By the action of S in presence of PbO on the corresponding secondary bases the following trisulphides have been prepared: *bisdimethylamino-*, m. p. −28° to −31°; *bisdiethylamino-*, which does not solidify at −80°; *bispiperidino-*, m. p. 74°; also *bispiperidino-tetrasulphide*, m. p. 78°. E. E. J. MARLER.

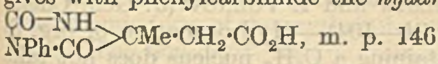
Separation and isolation of organic bases by electrodialysis. E. GEBAUER-FÜLNEGG and A. I. KENDALL (Ber., 1931, **64**, [*B*], 1067—1072).—The process has been applied to the separation of histidine from histamine or choline, of an artificial mixture of protein or gelatin from histamine or choline, and of the base from histamine dipicrate or chloroplatinate. It is suitable for the separation of relatively strong, crystalloidal bases from mixtures with amphoteric or more weakly basic substances or from colloids. It can be advantageously employed in purification of bases by separation from their picrates, chloroplatinates, or compounds with the salts of heavy metals. H. WREN.

Higher amino-alcohols. I. Action of the Grignard reagent on ethyl γ-dimethylaminobutyrate. C. PRELOG and V. HANOUSEK (Coll. Czech. Chem. Comm., 1931, **3**, 276—280).—Ethyl γ-dimethylaminobutyrate reacts with MgEtBr to give a mixture of *ζ-dimethylaminohexan-γ-one*, b. p. 70—75°/13 mm. (*picrate*, m. p. 111·5°; *picrolonate*, m. p. 135·5°; *semicarbazone hydrochloride*, m. p. 190—191°), and *ζ-dimethylamino-γ-ethylhexan-γ-ol*, b. p. 100—105°/13 mm. [*hydrochloride*, m. p. 173—174°; *picrate*, m. p. 104—105°; *methiodide*, m. p. 133—134° (*chloroaurate*, m. p. 88°; *chloroplatinate*, m. p. 220° (decomp.); *picrate*, m. p. 104°)]. The same mixture is obtained independently of the proportions of the reacting substances. F. R. Shaw.

Co-ordination compounds of the chloroplatinates of choline and its esters. H. W. Dudley (J.C.S., 1931, 763—769).—The stability of choline-acylcholine chloroplatinates is determined by the acyl group (A., 1929, 1479), decreasing with increasing size of acyl group. *Propionylcholine* [*chloroaurate*, m. p. 131—133°; *chloroplatinate*, m. p. 244° (decomp.)], *cholinepropionylcholine chloroplatinate*, m. p. 262° (decomp.), n-*butyrylcholine chloroplatinate*, m. p. 244° (decomp.), *choline*-n-*butyrylcholine chloroplatinate*, m. p. 254° (decomp.), n-*valerylcholine chloroplatinate*, m. p. 237° (decomp.), n-*hexoylcholine chloroplatinate*, m. p. 236—238° (decomp.), *dibutylacetyl*(*decoyl*)*choline chloroplatinate*, m. p. 236° (decomp.), *cholinepyruvylcholine chloroplatinate*, m. p. 248° (decomp.), *cholineglycollylcholine chloroplatinate*, m. p. 244° (decomp.), *acetylglycollylcholine chloraurate*, m. p. 158—160°, and *chloroplatinate*, m. p. 232° (decomp.), are described. The m. p. of mixtures of choline and choline ester chloroplatinates which form co-ordination compounds are above those of either of the components.

G. Discombe.

Synthetic preparation and isolation of some of the simpler amino-acids. W. Cocker and A. Lapworth (J.C.S., 1931, 1391—1403).—Improved general methods of isolation are given for a number of the more soluble amino-carboxylic acids. In the preparation of α-amino-nitriles from open-chain aldehydes and ketones by means of NH_3 and HCN, heating is not necessary and the nitriles are readily hydrolysed by 40% H_2SO_4 at atm. pressure. *dl*-α-Amino-*iso*butyric acid gives a *phenylcarbamido*-derivative of m. p. 187—188° (decomp.); *dl*-methylaspartic acid gives with phenylcarbimide the *hydantoin*



$\left.\begin{matrix}\text{CO—NH}\\ \text{NPh·CO}\end{matrix}\right>\text{CMe·CH}_2\text{·CO}_2\text{H}$, m. p. 146° (decomp.).

D. A. Fairweather.

Nitrate formation from amino-acids. B. Sjollema (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 468—470).—When aq. solutions of aliphatic amino-acids are treated with $KMnO_4$ at room temp. a rise in temp. occurs and a brown ppt. is formed. If after 1 hr. the excess of $KMnO_4$ is reduced with H_2O_2 a colourless liquid remains which contains appreciable quantities of nitrate. Possible mechanisms are discussed. J. W. Smith.

Method of assigning optically active α-amino-acids to the *d*- or *l*-series. II. O. Lutz and B. Jirgensons (Ber., 1931, 64, [*B*], 1221—1232).—Application of the method already described (A., 1930, 460) to lysine, arginine, α-amino-β-3 : 4-dihydroxyphenylpropionic acid, ornithine, histidine, tryptophan, proline, and oxyproline shows that these natural amino-acids, like natural aspartic acid, belong to the *l*-series. The varying optical activity of the amino-acids in neutral, acid, or alkaline solution is attributed to their existence mainly as internal salts in aq. solution. In the presence of increasing amounts of HCl the dissociation of the basic portion greatly increases, whereas increase of NaOH facilitates dissociation of the CO_2H. H. Wren.

Compounds of dextrose with ethyl aminoacetate and glycylglycine ester. H. von Euler and K. Zeile (Annalen, 1931, 487, 163—174).—The isolation of cryst. Et α-cyanoethylaminoacetate hydrochloride, m. p. 100° (corr.), is described (cf. A., 1926 942). By interaction of the $NaHSO_3$ derivative of Et pyruvate with Et aminoacetate and aq. KCN, *Et α-cyano-α-carbethoxymethylaminopropionate*, liquid, is obtained; it is converted by NaOEt (1 mol.) and NaOH (2 mols.) in EtOH into the yellow, hygroscopic *salt* $CO_2Na\cdot CMe{:}N\cdot CH_2\cdot CO_2Na$, reduction of which with Na–Hg is accompanied by hydrolysis to glycine. The interaction of dextrose with Et aminoacetate in presence of Al–Hg to remove the H_2O produced gives a cryst. *glucoside*, m. p. 112° (corr.), converted by dry NH_3–EtOH into the corresponding *amide*, m. p. 140° (corr.), and hydrolysed, slowly in aq. solution, and rapidly in presence of acids, into its constituents. It is fermentable at a velocity approx. the same as that of dextrose. Diketopiperazine and indefinite products were obtained from dextrose and glycylglycine ester, but the latter combines when melted with acetobromoglucose or tetra-acetylglucose with formation of the *tetra-acetylglucoside*, m. p. 140° (corr.), convertible as before into the *amide* (?), m. p. 90°.

H. A. Piggott.

Synthesis of γ-amino-*n*-hexoic acid and of 5-keto-2-ethylpyrrolidine. A. Müller and E. Feld (Monatsh., 1931, 58, 22—28).—The Et ester of succinic acid monochloride (obtained from the acid and di-ester by Fourneau and Sabetay's method, A., 1928, 1115) reacts with ZnEtI to give, after hydrolysis, γ-keto-*n*-hexoic acid, the *phenylhydrazone*, m. p. 73°, of which is reduced by Al amalgam to *γ-amino*-n-*hexoic acid*, m. p. 180—181° [*hydrochloride*, m. p. 120—121°; *chloroplatinate*, m. p. 190—191° (decomp.)], benzoylated to *γ-benzamido*-n-*hexoic acid*, m. p. 146·5—147° (*Me* ester, m. p. 87·5°). Distillation of the γ-amino-acid affords *5-keto-2-ethylpyrrolidine*, b. p. 130°/8 mm., m. p. 22° [*hydrochloride*; *chloroplatinate*, m. p. 125—127° (decomp.)]. All m. p. are corr. J. W. Baker.

Formation of sodium derivatives of compounds containing a reactive methylene group. K. G. Naik and L. D. Shah (J. Indian Chem. Soc., 1931, 8, 45—49).—*N*-Alkyl and *N*-aryl substituted cyanoacetamides react with Na in C_6H_6 or Et_2O at the b. p. of the solvent, the Na derivatives formed being insol. in C_6H_6. The reactivity of the arylated amides is much less than that of the alkyl compounds. The prep. of *sodiocyanoacet-methylamide*, m. p. 225° (decomp.), -*butylamide*, m. p. 200° (decomp.), -*heptylamide*, m. p. 195° (decomp.), -o-*toluidide* (decomp. above 220°), -m-*toluidide* (decomp. above 230°), -p-*toluidide* (decomp. above 245°), -*benzylamide* (decomp. 205°); -α-*naphthylamide* (discolours above 170°), and -β-*naphthylamide* (darkens above 205°) is described. G. Discombe.

Mercury acetamide as mercurating agent. K. G. Naik and L. D. Shah (J. Indian Chem. Soc., 1931, 8, 29—35).—In place of HgO and $Hg(OAc)_2$ (A., 1899, i, 54, 428; 1902, i, 656, 849; 1898, i, 635; 1909, i, 218), mercury acetamide is used as a mercurating agent (A., 1909, i, 464). The OH·Hg group replaces H in the CH_2 group of various *N*-alkylated cyanoacetamides, yielding hydroxymercuricyanoacetamides, decomp. by H_2S, $(NH_4)_2S$, and Na_2S, KI, phenylhydrazine, and N_2H_4,H_2O, and by hot 0·25*N*-HCl.

Hydroxymercuricyanoacet-methylamide, m. p. 300° (discolours at 287°), *-ethylamide*, m. p. 300° (discolours at 285°), -n-*propylamide*, m. p. 280° (decomp. after darkening at 265°), -n-*butylamide*, m. p. above 300°, -iso*butylamide*, m. p. 300° (darkens above 280°), -n-*amylamide*, m. p. 285° (decomp.); -iso*hexylamide*, m. p. 273° (decomp.), and -n-*heptylamide*, m. p. 284° after darkening at 270°, are described. *Cyanoacet*-n-*butylamide*, m. p. 73°, -iso*butylamide*, m. p. 45°, -n-*amylamide*, m. p. 47°, -iso*hexylamide*, m. p. 42°, and -n-*heptylamide*, m. p. 67°, are also described. The *hydroxymercuri*-derivatives of ethyl cyanoacetate, cyanoacetamide, cyanoacet-anilide, *-m*-toluidide, *-o*-toluidide, *-p*-toluidide, -1 : 3 : 4-xylidide, and -1 : 4 : 5-xylidide all have m. p. above 300°; those of cyanoacetbenzylamide, m. p. 293°, -α-naphthylamide, m. p. 272° (after darkening at 253°), and -β-naphthylamide, m. p. 283° (decomp.), are also described.

G. Discombe.

Arylamides of lævulic acid. Conversion of 5-keto-2-hydroxy-1-phenyl-2-methyltetrahydropyrrole into lævulanilide. R. Lukeš and V. Prelog (Chem. Listy, 1931, 25, 76—79).—Lævulanilide condenses with *p*-toluidine to yield γ-p-*tolyliminovaleranilide*, m. p. 153°, giving lævulanilide and acet-*p*-toluidide on hydrolysis, and γ-p-*tolylaminovaleric acid*, m. p. 82·5°, on hydrogenation. γ-*Phenyliminovaleri*-p-*toluidide*, m. p. 142—143°, is prepared as above, and yields on hydrolysis lævul-*p*-toluidide and acetanilide. The product of hydrogenation of γ-phenyliminovaleranilide is γ-anilinovaleric acid, which on dehydration yields 1-phenyl-2-methylpyrrolid-5-one. The above reactions indicate that lævulanilide has the structure $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh$.

R. Truszkowski.

Structure of carbamide in aqueous solution. G. Devoto (Ber., 1931, 64, [*B*], 1329—1332).—In reply to Ebert (this vol., 609), reasons are adduced in favour of the view that the polar formula for carbamide in aq. solution is the most probable. H. Wren.

Cyanogen, thiocyanogen, and methylamine. H. Emde and T. Hornemann (Arch. Pharm., 1931, 269, 336—340).—The possibility that HCN in plants may arise from the oxidation of NH_2Me, or other amines, is discussed. NH_2Me in excess gives 10% yield of HCN with CrO_3 in H_2SO_4. Aq. NH_2Me when saturated with H_2S and heated at 200° with S or $Na_2S_2O_3$ gives some thiocyanic acid. A. A. Levi.

Hexacyanocobaltic acid and methyl alcohol. F. Hölzl [with A. Sallmann] (Monatsh., 1931, 58, 29—46).—Hexacyanocobaltic acid dissolves in abs. MeOH between −10° and +65° to form the *oxonium* salt $H[CO(CN)_6](H{\cdot}OHMe)_2$. Tensimetric measurements show that with diminishing pressure this is converted first into $H_2[CO(CN)_6](H{\cdot}OHMe)$ and finally into the free complex acid. Under no conditions could a *tert.*-oxonium salt be obtained. Within the above temp. limits the solubility in MeOH (data given) increases rapidly with rise of temp. The alkali titre of a solution of $H_3[Co(CN)_6]$ in MeOH decreases on keeping (at 65° or 98°), due to esterification of the co-ordinated HCN, which is accelerated by the presence of small amounts of H_2O or by rise of temp. Methylcarbimide is formed and a reddish-violet ppt., which consists of a mixture of the *compounds* $[(CN)_3(H_2O)_2{\cdot}Co{\cdot}CN{\cdot}Co(CN)_3(CNMe)(H_2O)_2]$ (I) and $[(CN)_3(H_2O)_2{\cdot}Co\{{\cdot}(CN){\cdot}Co(CN)_2(H_2O)_2\}_2{\cdot}CN{\cdot}Co(CN)_2(CNMe)(H_2O)_2]$ (II), containing hexacovalent Co and a μ-cyano-bridge, I (rose) being converted into II (violet) by H_2O. When I is heated to 100°/vac. only some of the CN linkings are split ($-2H_2O$) giving the *compound* $[(MeNC)(CN)(H_2O)Co\vdots(CN)_3\vdots Co(CN)_2(H_2O)]$, whilst II ($-6H_2O$) similarly affords the compound $[(CN)_2(H_2O)Co\vdots(CN)_3\vdots\{Co\vdots(CN)_3\vdots\}_2Co(CN)(CNMe)(OH_2)]$. These cyano-aquo-complexes possess acidic character and their formation under such mild conditions suggests that the CN linkings in hexacyanocobaltic acid are derived from the *iso*-form, HNC, the C atom being bound to the central Co atom. J. W. Baker.

Properties of the β-chlorovinylarsines and their interaction with benzene in presence of aluminium chloride. Production of 9 : 10-dimethylanthracene. C. S. Gibson and J. D. A. Johnson (J.C.S., 1931, 753—756).—β-Chlorovinyldichloroarsine, ββ′-dichlorodivinylarsine, and ββ′β″-trichlorotrivinylarsine all yield with C_6H_6 in presence of $AlCl_3$ 9 : 10-dimethylanthracene, produced also from ββ′-dichlorodivinylchloroarsine in the same way (A., 1926, 1030; 1929, 1434), thus confirming the view that 9 : 10-dimethyl-9 : 10-dihydroanthracene (A., 1887, 753; 1914, i, 156) is actually 9 : 10-dimethylanthracene. G. Discombe.

Silico-organic compounds. II. Hydrogenation and rearrangement of silicomethane derivatives. B. Dolgov and I. Volnov (J. Gen. Chem. Russ., 1931, 1, 91—104).—Hydrogenation of org. Si compounds containing a C_6H_6 nucleus does not take place due to the anticatalytic action of the Si. There is no resemblance between the behaviour of *tert.*-alcohols and the corresponding Si compounds, which do not undergo hydrogenation in the substituent C_6H_6 rings, do not condense with PhOH, or react with phenylcarbimide. Compounds of the type $RSiR'_3$ when heated with H_2 under pressure undergo the rearrangement $2RH+Si_2R'_6 \xleftarrow{+H_2} 2RSiR'_3 \longrightarrow R_2SiR'_2+SiR_4$, where R, R′ are Et, Me, Pr, Ph. In the case of *iso*butyl- and *iso*amyl-triethylsilicomethane a more complex rearrangement and condensation takes place. E. B. Uvarov.

Hydrogenation and decomposition of organic silicon compounds at high temperatures and pressures. I. V. N. Ipatiev and B. N. Dolgov (J. Gen. Chem. Russ., 1931, 1, 5—12).—$SiEt_4$ at 350—360°/30—80 atm. is transformed by H into disilicon hexaethyl and C_2H_6. Under the same conditions $SiPhEt_3$ eliminates C_6H_6, forming Si_2Et_6, and by an interchange of radicals gives $SiPh_2Et_2$ and $SiEt_4$, and a condensation product. $SiPh_4$ is transformed above 490° into an inert condensation product. Unsymmetrical silico-org. compounds tend to assume a symmetrical structure under these conditions.

E. B. Uvarov.

1-Methyl-2-ethyl*cyclo*propane. LESPIEAU and R. L. WAKEMAN (Compt. rend., 1931, **192**, 1395—1397).—Hexane-βδ-diol, d_4^{21} 0·9516, is converted by PBr_3 and a little pyridine into βδ-*dibromo*-n-*hexane*, b. p. 81·5—83°/10 mm., d_4^{22} 1·5756, which with Zn and 95% EtOH at the b. p. gives 1-*methyl*-2-*ethyl*cyclo-*propane*, b. p. 63·9—64·9°, d_4^{21} 0·6961. The Raman spectrum points to the absence of the isomeric ethylenic hydrocarbon; nevertheless the substance decolorises aq. $KMnO_4$, and shows an optical exaltation which is considered to be due to the *cyclo*propane ring.

H. A. PIGGOTT.

Preparation of trimethylene hydrocarbons; 1-methyl-2-propyl*cyclo*propane. LESPIEAU and R. L. WAKEMAN (Compt. rend., 1931, **192**, 1572—1573).—The action of Mg in Et_2O on β-bromopropaldehyde (prepared from crotonaldehyde and HBr at low temp.) affords β-*bromoheptan-γ-ol*, b. p. 99—101°/10 mm., which reacts with PBr_3 to give βδ-*dibromoheptane*, b. p. 99—100°/12 mm., debrominated with Zn to 1-*methyl*-2-*propyl*cyclo*propane*, b. p. 92—93°/ 747 mm.

F. R. SHAW.

Oxidation of *cyclo*hexadiene with permanganate, perbenzoic acid, and free oxygen. N. D. ZELINSKI and A. N. TITOVA (Ber., 1931, **64**, [*B*], 1399—1406).—Distillation of *cis*-*cyclo*hexane-1 : 4-diol with 2 mols. of $KHSO_4$ gives a mixture of *cyclo*hexadiene (40% yield) and Δ^3-*cyclo*hexenol, b. p. 164—164·5°/763 mm., d_4^{23} 0·9845; a similar mixture is obtained when anhyd. $MgSO_4$ is employed, except that the more volatile $\Delta^{1:3}$-*cyclo*hexadiene predominates in the hydrocarbon mixture. If half the above quantities of $KHSO_4$ or $MgSO_4$ are used, the main product is Δ^3-*cyclo*hexenol. Oxidation of $\Delta^{1:4}$-*cyclo*hexadiene with $KMnO_4$ yields *tetrahydroxy*cyclo*hexane*, m. p. 241—242° after darkening at 216° (dihydrate), possibly the racemic form of the erythritol obtained from sugar beet. The non-cryst. residue from the above experiment is transformed by Ac_2O into 1 : 2 : 4 : 5-*tetra-acetoxy*cyclo*hexane*, m. p. 52—54° and 168°, and a *tetra-acetyl* derivative, m. p. 101°. Oxidation of Δ^3-*cyclo*hexenol by $KMnO_4$ or perbenzoic acid yields cyclo*hexanetriol*, m. p. 122° after softening at 104°. $\Delta^{1:4}$-*cyclo*Hexadiene in $CHCl_3$ is oxidised by perbenzoic acid to the corresponding 1 : 2 : 4 : 5-*dioxide*, m. p. 110° (converted by H_2O at 100° into cyclo*hexane*-1 : 2 : 4 : 5-*tetraol monohydrate*, m. p. 195° (slight decomp.), and a fraction, b. p. 85—86°/25 mm., with the approx. composition of the dioxide. The autoxidation of $\Delta^{1:3}$-*cyclo*hexadiene is fully discussed.

H. WREN.

Determination of bromine in highly brominated hydrocarbons. F. SCHULZ (Coll. Czech. Chem. Comm., 1931, **3**, 281—284).—The Stepanoff method (A., 1907, ii, 50) for determination of halogen in hexabromobenzene, m. p. 327°, pentabromotoluene, m. p. 288°, and hexabromonaphthalene, m. p. 317° (m. p. determined in a special apparatus), is successful if EtOH be replaced by BuOH.

F. R. SHAW.

Aromatic compounds of fluorine. VIII. Reactions with *p*-bromofluorobenzene. G. SCHIEMANN and R. PILLARSKY (Ber., 1931, **64**, [*B*], 1340—1345).—Since F is much more firmly attached than Br to the C_6H_6 nucleus it is possible so to treat *p*-bromofluorobenzene that only the Br atom is removed and the fluorophenyl residue is introduced. *p*-Bromofluorobenzene, b. p. 155°/767 mm., m. p. —8° to —7·5°, d_4^{25} 1·7267, is prepared in 80% yield by addition of Br to fluorobenzene in presence of Fe filings [2 : 4(or 3 : 4)-*dibromofluorobenzene*, m. p. 69°, is obtained as by-product] or from *p*-bromoaniline through the corresponding *diazonium fluoborate*, decomp. 133°. 4-Fluorodiphenyl is monobrominated to 4′-*bromo*-4-*fluorodiphenyl*, m. p. 98° (corr.), oxidised by CrO_3 in AcOH to *p*-bromobenzoic acid. The main product of the action of Na and EtBr on *p*-fluorobromobenzene in Et_2O is 4 : 4′-difluorodiphenyl, m. p. 88—89°, *p*-fluoroethylbenzene, b. p. 142—143°/755 mm., being obtained in smaller amount. With PrBr the yield of p-*fluoropropylbenzene*, b. p. 164—165°/759 mm., obtained is only 5%, whilst with *iso*amyl bromide no trace of *p*-fluoro*iso*amylbenzene is produced. Mg *p*-fluorophenyl bromide, readily obtained in Et_2O solution, is transformed by PhCHO into *p*-fluorobenzhydrol, m. p. 48°, in 47% yield and by acetonitrile into p-*fluoroacetophenone*, b. p. 77—78°/10 mm., m. p. —4·5°, in 7% yield.

H. WREN.

Position of the nitroso-group among substituents capable of activating suitably placed halogens etc. in aromatic nuclei. R. J. W. LE FÈVRE (J.C.S., 1931, 810—813).—Nitrosobenzene can be mono-*p*-brominated in C_6H_6 at 6—8°. The Br atom is removed, very slowly, by the action of an AcOH solution of $AgNO_3$ at room temp., whilst picryl bromide reacts less rapidly. *p*-Nitrosodimethylaniline and 2 : 4 : 6-trinitrodimethylaniline are readily hydrolysed by *N*-NaOH, whilst 2 : 4-dinitrodimethylaniline is scarcely attacked. These observations are explained by Robinson's formulation of nitrosobenzene as a crotonoid or crotenoid system (A., 1918, i, 548; 1925, i, 800; 1930, 1566).

G. DISCOMBE.

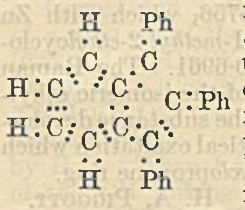
Polymerisation processes. II. Two dimerides of α-methylstyrene. E. BERGMANN, H. TAUBADEL, and H. WEISS (Ber., 1931, **64**, [*B*], 1493—1501; cf. A., 1930, 901).—The similarity of the unsaturated dimeride of α-methylstyrene and of the corresponding derivative of *as*-diphenylethylene suggests that the former substance is βδ-*diphenyl*-δ-*methyl*-Δ^β-*pentene*; the hypothesis is confirmed as follows. Addition of Na to α-methylstyrene or the unsaturated dimeride and alcoholysis of the product affords a mixture of isomeric βε-*diphenyl*-γδ-*diphenyl*-iso*propylhexanes*, b. p. 290—310°/22 mm. The Na derivative and CO_2 afford the dicarboxylic *acid* $C_{38}H_{42}O_4$, m. p. 268—269° (decomp.). Ozonisation of the dimeride followed by reductive fission gives acetophenone and phenyl*iso*butaldehyde in small amount. Mesityl oxide, $AlCl_3$, and C_6H_6 give β-phenyl-β-methylpentan-δ-one, b. p. 121°/12 mm., transformed by MgPhBr and subsequent distillation into βδ-diphenyl-δ-methyl-Δ^β-pentene, b. p. 170—171°/17 mm., identical with the unsaturated dimeride. The analogous suggestion that the saturated dimeride is 3-*phenyl*-1 : 1 : 3-*trimethylhydrindene* is verified as follows. Whilst most simply obtained from α-methylstyrene and $SnCl_4$, it is also prepared from βδ-diphenyl-δ-methyl-Δ^β-pentene and $SnCl_4$ or $AlCl_3$ and C_6H_6. Dimethylacrylic acid is transformed by $AlCl_3$ and C_6H_6

into β-*phenyl*isovaleric *acid*, b. p. 165—166°/20 mm., and β-*phenyl*-βδδ-*trimethylpentane*-3 : 5-*dicarboxylic acid*, m. p. 200°. β-*Phenyl*isovaleryl *chloride*, b. p. 125—126°/16 mm., and $AlCl_3$ in boiling CS_2 afford 1 : 1-*diphenylhydrind*-3-*one*, b. p. 119°/13 mm., converted by MgPhBr into 3-*phenyl*-1 : 1-*dimethylhydrinden*-3-*ol*, m. p. 88—89°, which could not be etherified; treatment of it with K and MeI in boiling xylene gave 3-*phenyl*-1 : 1-*dimethylindene*, m. p. 50—51°. β-Methylcinnamic acid is transformed by $AlCl_3$ and C_6H_6 into ββ-*diphenylbutyric acid*, m. p. 102—103°. *Me* ββ-*diphenylbutyrate*, b. p. 182—183°/13 mm., is converted by MgMeI into δδ-*diphenyl*-β-*methylpentan*-β-*ol*, b. p. 185—187°/13 mm., transformed by HCl and $SnCl_4$ in C_6H_6 into 3-phenyl-1 : 1 : 3-trimethylhydrindene, m. p. 53°, identical with the saturated dimeride. H. Wren.

***o*- and *m*-Divinyl- and -diacetylenyl-benzenes.** M. Deluchat (Compt. rend., 1931, **192**, 1387—1389; cf. A., 1930, 588).—*o*-Di-(α-hydroxyethyl)benzene (A., 1930, 471) is converted by PBr_3 in $CHCl_3$ into its *dibromohydrin*, m. p. 91°, which crystallises in optically active hemihedral forms, and when distilled with excess of quinoline at 3 mm. gives o-*divinylbenzene*, b. p. 78·5°/11 mm., d^{21} 0·934. This differs from its position isomerides in that it does not polymerise at room temp.; its *tetrabromide*, m. p. 71—74°, gives $C_{10}H_8$ and other products with excess of KOH in EtOH, but on careful treatment with NaOEt gives αα′-*dibromo*-o-*divinylbenzene*, b. p. 125—126°/2 mm., d^{23} 1·714, o-(α-*bromovinyl*)*acetylenylbenzene*, b. p. 127°/11 mm., $d^{21.5}$ 1·4105 (*Ag* salt), and o-*diacetylenylbenzene*, b. p. 82°/14 mm., m. p. −20°, $d^{17.5}$ 0·9788 (*Ag* salt). The *dibromohydrin* of *m*-di(hydroxyethyl)-benzene, an unstable liquid, is decomposed by distillation at 2 mm. into m-*divinylbenzene*, b. p. 52°/3 mm., d^{22} 0·926, and m-α-*bromoethylvinylbenzene*, b. p. 88·5°/3 mm., d^{20} 1·319, when distilled with quinoline; the former is the main product. The *tetrabromide*, m. p. 64°, of *m*-divinylbenzene is converted by KOH in EtOH into m-*diacetylenylbenzene*, b. p. 78°/15 mm., m. p. −2·5°, d^{18} 0·9669 (*Ag* salt, sinters 280°). All three acetylenic derivatives give yellow ppts. with ammoniacal CuCl. H. A. Piggott.

Electron affinity of free radicals. II. Diphenyl-α-naphthylmethyl, diphenyldiphenylyl- and phenyldiphenylyl-α-naphthyl-methyl. H. E. Bent (J. Amer. Chem. Soc., 1931, **53**, 1786—1794; cf. A., 1930, 699).—The free energy changes, ΔF, of the reaction $Na(s)+R$ (in Et_2O)$=Na^++R^-$ are −17·9, −18·6, −19·1, and −19·5 kg.-cal., where $R=Ph_3C$, $Ph_2C(\alpha\text{-}C_{10}H_7)$, $Ph_2C\cdot C_6H_4Ph$, and $PhC(\alpha\text{-}C_{10}H_7)\cdot C_6H_4Ph$, respectively. The electron affinities of the four radicals in the gaseous state are computed to be approx. 60 kg.-cal. Since the larger radicals, as compared with the smaller, have slightly greater electron affinities and smaller tendencies to form ethane derivatives, it is suggested that owing to steric hindrance the C atoms cannot approach so closely, and hence the energy liberated is smaller. The solvent has essentially equal effects on the four equilibria. J. G. A. Griffiths.

Polycentricity as cause of resistance to association of free radicals. A. Löwenbein (Annalen, 1931, **487**, 97—104).—Mainly theoretical. On the electronic theory "polycentric" free radicals, *e.g.*, pentaphenylethyl, pentaphenyl*cyclo*pentadienyl, etc., have symmetrical structures with an intra-at. linking of the free valency electrons as the cause of their slight tendency to association. In the case of triphenylindenyl (annexed formula), among others, this implies that monosubstitution in a Ph nucleus cannot lead to isomerism. It is reported that the action of HBr on 1 : 2-diphenyl-3-*p*-tolyl- and 2 : 3-diphenyl-1-*p*-tolyl-1-indenols gives the same *bromide*, m. p. 112°. H. A. Piggott.



Effect of nitrates on dinuclear benzene derivatives. G. Bacharach and J. E. Brolles, jun. (Rec. trav. chim., 1931, **50**, 732—735).—Diphenyl and dibenzyl are not nitrated by $LiNO_3$ according to Menke's method (A., 1925, i, 386, 655), but with $Cu(NO_3)_2$ the former yields *p*-nitrodiphenyl and *pp*′-dinitrodiphenyl, and the latter *pp*′-dinitrodibenzyl. Whereas benzoin is oxidised to benzil by this method, benzil and stilbene are unaffected by both nitrates. J. D. A. Johnson.

Orientation effects in the diphenyl series. IX. Nitration of 4-chloro-4′-fluoro- and 4-bromo-4′-fluoro-diphenyl. (Miss) E. E. J. Marler and E. E. Turner (J.C.S., 1931, 1359—1363).—4-Nitro-4′-aminodiphenyl is converted into 4-*fluoro*-4′-*nitrodiphenyl*, m. p. 120—121°, which is reduced to 4-*fluoro*-4′-*aminodiphenyl*, m. p. 121°, and this gives 4-*chloro*-4′-*fluorodiphenyl*, m. p. 87—88°. This is dinitrated, and the proportions of 4-*chloro*-4′-*fluoro*-2-*nitrodiphenyl* (72%) and of 4-*chloro*-4′-*fluoro*-2′-*nitrodiphenyl* (28%) present as intermediates are determined by analysis of the dinitrated mixture. Similarly 4-bromo-4′-nitrodiphenyl is reduced and converted into 4-*bromo*-4′-*fluorodiphenyl*, m. p. 99—100°, which passes during dinitration through 4-*bromo*-4′-*fluoro*-2-*nitrodiphenyl* (86%) and 4-*bromo*-4′-*fluoro*-2′-*nitrodiphenyl* (14%). The mononitro-derivatives cannot be isolated. D. A. Fairweather.

Diphenyl and its derivatives. VII. New 3 : 3′-disubstituted diphenyls. L. Mascarelli and D. Gatti (Gazzetta, 1931, **61**, 320—325; cf. A., 1930, 205, 464).—Diazotisation of 3-nitro-3′-aminodiphenyl followed by the Sandmeyer reaction gives 3-*bromo*-3′-*nitro*-, m. p. 92°, 3-*iodo*-3′-*nitro*-, m. p. 96—97°, 3-*chloro*-3′-*nitro*-, m. p. 101°, and 3-*hydroxy*-3′-*nitro-diphenyl*, m. p. 114—116°.

E. E. J. Marler.

Aromatic compounds of fluorine. VII. 4 : 4′-Difluoro-2-nitrodiphenyl and reactions of fluoro-compounds of diphenyl. G. Schiemann and W. Roselius (Ber., 1931, **64**, [*B*], 1332—1340).—4 : 4′-Difluoro-2-nitrodiphenyl, m. p. 94—94·5°, obtained from 2-nitrobenzidine is identical with the product of the nitration of 4 : 4′-difluorodiphenyl, previously regarded as the 3-nitro-compound. The derivatives must therefore be considered to be 4 : 4′-difluoro-2-aminodiphenyl, 2 : 4 : 4′-trifluoro-, 2 : 4 : 4′-trifluoro-5-nitro-, 2 : 4 : 4′-trifluoro-5-amino-, and 2 : 4 : 4′ : 5-tetrafluoro-diphenyl. 4 : 4′-Difluoro-2-

nitrodiphenyl is converted by 2 mols. of KOH in boiling MeOH into 4-*fluoro-2-nitro-4-methoxydiphenyl*, m. p. 79—80°, and by a large excess of the reagent into *dinitro*-4 : 4′-*dimethoxybenzerythrene*, $[\cdot C_6H_4\cdot C_6H_3(OMe)\cdot NO_2]_2$, m. p. 202—203° (corr.). 2 : 4 : 4′-Trifluoro-5-nitrodiphenyl and 2 mols. of KOH in MeOH afford 5 : 5′-*dinitro*-2 : 2′ : 4 : 4′-*tetramethoxydiphenyl*, m. p. 182—183°. 4′-*Fluoro-2-nitro-4-piperidinodiphenyl*, m. p. 74—74·5°, is derived from 4 : 4′-difluoro-2-nitrodiphenyl and piperidine at 165—172°. Drastic nitration of 4 : 4′-difluorodiphenyl or 4 : 4′-difluoro-2-nitrodiphenyl yields a non-homogeneous product from which 4 : 4′-*difluoro*-2 : 3′-*diaminodiphenyl*, m. p. 86·6°, is prepared.

o-Tolidine is transformed along the usual lines into 4 : 4′-*difluoro*-3 : 3′-*ditolyl*, m. p. 59°, b. p. 137—138°/21 mm., converted by HNO_3 (*d* 1·5) in AcOH into 4 : 4′-*difluoro-6-nitro*-3′ : 3′-*ditolyl*, m. p. 89·5°, obtained also from 6-nitro-*o*-tolidine through the corresponding *bisdiazonium borofluoride*, decomp. 97·5—98·5°.

H. WREN.

Modes of reaction of phosphorus pentachloride. II. E. BERGMANN and A. BONDI (Ber., 1931, 64, [*B*], 1455—1480; cf. A., 1930, 1050).—Unlike *as*-diphenylethylene, αα-diphenyl-Δ^{α}-propene, αα-diphenyl-Δ^{α}-butene, ααγ-triphenyl-Δ^{α}-propene, αα-diphenyl-β-methyl-Δ^{α}-propene, αγ-diphenyl-Δ^{α}-propene, and γ-phenyl-Δ^{γ}-pentene do not react with PCl_5 or Na, although they readily add halogen. Allylbenzene is inactive, whereas triphenylethylene affords chlorotriphenylethylene, m. p. 117°, and stilbene in $CHCl_3$ reacts with 4 mols. of PCl_5 giving a product transformed by ice into stilbene dichloride, m. p. 193°, obtained also from *iso*stilbene. Addition is not restricted by halogen in the *p*-position. Thus, p-*chlorodiphenylethylene*, $ClC_6H_4\cdot CPh\colon CH_2$, b. p. 164°/16 mm., from *p*-chlorobenzophenone and MgMeI followed by distillation with steam, yields p-*chlorodiphenylvinylphosphinic acid*, $ClC_6H_4\cdot CPh\colon CH\cdot PO_3H_2$, m. p. 181° (*Pb*, $Hg^{\cdot\cdot}$, *Cu*, $Fe^{\cdot\cdot\cdot}$, *Al*, *Zn*, *Ba*, *Ca* salts), oxidised by CrO_3 to *p*-chlorobenzophenone. Similarly, as-*di*-p-*chlorodiphenylethylene*, m. p. 91°, obtained from *pp*′-dichlorobenzophenone and MgMeI (αα-*di*-p-*chlorophenylethyl alcohol*, m. p. 167—168°) affords pp′-*dichlorodiphenylvinylphosphinic acid*, m. p. 158—159° (*Ag*, *Pb*, $Hg^{\cdot\cdot}$, *Cu*, $Sn^{\cdot\cdot}$, *Co*, *Mn*, $Fe^{\cdot\cdot\cdot}$, *Al*, *Zn*, *Ba*, *Ca* salts), oxidised to *pp*′-dichlorobenzophenone. The *p*-OMe group is more restrictive. Thus, *as*-di-*p*-methoxydiphenylethylene does not react, whereas *p*-methoxydiphenylethylene, m. p. 75°, yields p-*methoxydiphenylvinylphosphinic acid*, m. p. 145° (*Ag*, *Pb*, *Zn*, *Al*, $Hg^{\cdot\cdot}$, *Cu*, *Co*, $Fe^{\cdot\cdot}$, *Ba*, and *Ca* salts), converted in boiling PrOH or AcOH into *p*-methoxydiphenylethylene and H_3PO_3 and hydrogenated in presence of $Pd–BaSO_4$ to β-phenyl-β-*p*-methoxyphenylethane-α-phosphinic acid, m. p. 102—103°. *p*-Chlorobenzoyl chloride and anisole in presence of CS_2 and $AlCl_3$ give p-*chloro*-p-*methoxybenzophenone*, m. p. 127°, transformed by MgMeI and subsequent acid treatment into as-p-*chlorophenyl*-p′-*methoxyphenylethylene*, m. p. 77°, which yields p-*chloro*-p′-*methoxydiphenylvinylphosphinic acid*, m. p. 132—133° (*Ag*, *Pb*, *Cu*, *Ba*, $Hg^{\cdot\cdot}$, $Sn^{\cdot\cdot}$, *Co*, *Fe*, *Al*, *Zn*, and *Ca* salts), decomposed by boiling AcOH, oxidised to *p*-chloro-*p*′-methoxybenzophenone, and hydrogenated to β-p-*chlorophenyl*-β-p-*methoxyphenylethane-α-phosphinic acid*, m. p. 126—127°. AcOEt is grignarded with Mg and *o*-bromoanisole to αα-*di*-o-*anisylethyl alcohol*, m. p. 125°, converted by acid into as-*di*-o-*methoxydiphenylethylene*, m. p. 90°, unaffected by PCl_5. as-*Phenyl*-o-*bromophenylethylene*, b. p. 155—156°/12 mm., and as-*phenyl*-o-*chlorophenylethylene*, b. p. 162—163°/18 mm., do not add PCl_5; the effect appears attributable to the size of the halogen atom, since as-*phenyl*-o-*fluorophenylethylene*, b. p. 137°/11 mm., affords o-*fluorodiphenylvinylphosphinic acid*, m. p. 180° (*Ag*, *Pb*, *Cu*, $Hg^{\cdot\cdot}$, *Co*, $Fe^{\cdot\cdot\cdot}$, *Zn*, *Ba*, and *Ca* salts), oxidised to *o*-fluorobenzophenone. [Methyl anthranilate is transformed into the *diazonium fluoroborate*, $C_8H_7O_2N_2F_4B$, decomp. 102°, whence successively *Me* o-*fluorobenzoate*, b. p. 89—90°/14 mm., *o*-fluorobenzoic acid, o-*fluorobenzoyl chloride*, b. p. 85°/14 mm., and o-*fluorobenzophenone*, b. p. 150°/16 mm. (dimorphous *oxime*, m. p. 126°), are obtained; the ketone is converted by MgMeI into *as*-phenyl-*o*-fluorophenylethylene or α-*phenyl*-α-*fluorophenylethyl alcohol*, m. p. 45°.] Whereas *p*-phenyldiphenylethylene gives p-*phenyldiphenylvinylphosphinic acid*, m. p. 201°, oxidised to *p*-phenylbenzophenone and hydrogenated to p-*phenyl*-ββ-*diphenylethane*-α-*phosphinic acid*, m. p. 236° (decomp.), and as-p-*tolyl*-p-*diphenylylethane*, m. p. 102—103°, yields a non-cryst. phosphinic acid, o-*phenyldiphenylethylene*, m. p. 55—56°, appears to yield an isomeric *hydrocarbon*, m. p. 86°, in place of the phosphinic acid; the substance is not identical with 9-*phenyl*-9-*methylfluorene*, m. p. 84—85°, prepared by treating 9-methoxy-9-phenylfluorene with Na and subsequently with MeI. as-*Phenyl*-m-*methoxyphenylethylene*, b. p. 168°/14 mm., does not afford a phosphinic acid probably by reason of the formation of an insol., yellow compound of the hydrocarbon and PCl_5. as-*Phenyl*-m-*chlorophenylethylene*, b. p. 152—153°/14 mm., from m-*chlorobenzophenone*, m. p. 82°, is transformed into m-*chlorodiphenylvinylphosphinic acid*, m. p. 168° (*Ag*, *Pb*, *Cu*, *Sn*, *Al*, *Zn*, *Co*, $Hg^{\cdot\cdot}$, *Ba*, and *Ca* salts), oxidised to *m*-chlorobenzophenone. *iso*Safrole and *iso*eugenol methyl ether yield compounds with PCl_5, hydrolysed to their components. p-*Di*-α-*phenylvinylbenzene*, m. p. 138—139°, from *p*-dibenzoylbenzene and MgMeI followed by "acid treatment" yields the *phosphinic acid* $C_6H_4(CPh\colon CH\cdot PO_3H_2)_2$, m. p. 210°. α-Phenyl-$\Delta^{\alpha\gamma}$-butadiene gives a product considered to be 8-*phenyl*-$\Delta^{\alpha\gamma}$-*butadienephosphinic acid*, m. p. 192° (decomp.) [*Ag*, *Pb*, $Fe^{\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, *Cu*, *Al*, *Zn*, *Ba*, and *Ca* salts], since it is hydrogenated to 8-*phenylbutanephosphinic acid*, m. p. 95°, not resolvable by brucine or quinine (*brucine* salt, m. p. 95°, [α] −69·89° in $CHCl_3$; *quinine* salt, m. p. 99—100°, [α] −100° in $CHCl_3$). α-Phenyl-$\Delta^{\alpha\gamma}$-pentadiene and αδ-diphenylbutadiene do not add PCl_5.

1-Benzylidene- and 1-piperonylidene-indenyl-2-phosphinic acid are converted by Zn dust and aq. NaOH into indenyl-2-phosphinic acid, m. p. 184°. Indene and PBr_5 in C_6H_6 afford 1 : 2-dibromohydrindene, b. p. 140°/12 mm.

The close analogy in the behaviour of Na and PCl_5 justifies the belief that addition of the latter is a reaction of at. residues differing from that of halogen mols. In the P pentahalides, one halogen atom is united differently from the remaining four. The structure of the PCl_5 mol. is considered in detail.

H. Wren.

Action of lithium on tolane. E. Bergmann and O. Zwecker (Annalen, 1931, **487**, 155—163).—The constitution of 1 : 2 : 3-triphenylnaphthalene (cf. A., 1928, 1034) is confirmed by its oxidation by CrO_3 in AcOH to *o*-benzoylbenzoic acid, its reduction by Na and amyl alcohol to a *tetrahydro*-derivative, m. p. 136—137°, and its conversion by addition of Na followed by hydrolysis into the 1 : 4(?)-*dihydro*-derivative, m. p. 165°. The last-named is dehydrogenated in contact with Pd–$BaSO_4$. The crude Li derivative of 1 : 2 : 3-triphenylnaphthalene gives on alcoholysis 9-phenyl-1 : 2 : 3 : 4-dibenz-9 : 10-dihydroanthracene (*loc. cit.*), with CO_2 gives 2 : 3 : 4-triphenyl-α-naphthoic acid, and with I or Hg gives triphenylnaphthalene and 9-*phenyl*-1 : 2 : 3 : 4-*dibenzanthracene*, m. p. 227° [the constitution of which follows from the hydrolysis of its Na additive product to the 9 : 10-dihydro-derivative (above)], by disproportionation of the primarily formed 1 : 2 : 3-triphenylnaphthyl. The constitution of 9-phenyl-1 : 2 : 3 : 4-dibenz-9 : 10-dihydroanthracene is confirmed by its oxidation with CrO_3 to *o*-benzoylbenzoic acid and phenanthraquinone. In contrast to its behaviour with Hg, the product of interaction of Li and tolane in Et_2O is converted by I into 4-*iodo*-1 : 2 : 3-*triphenylnaphthalene*, m. p. 225°, reduced by Zn and KOH in MeOH to 1 : 2 : 3-triphenylnaphthalene, and by Na and amyl alcohol to an *isomeride* (geometrical ?), m. p. 151°, of 1 : 2 : 3-triphenyltetrahydronaphthalene; it reacts with Li with formation of 4-lithio-1 : 2 : 3-triphenylnaphthalene.

H. A. Piggott.

Allylisomerism in hydrocarbons. E. Bergmann and H. Weiss (Ber., 1931, **64**, [*B*], 1485—1493).—*Phenyl benzhydryl ketone*, m. p. 135—136°, prepared by the action of boiling aq. H_2SO_4 on phenylhydrobenzoin or, together with *phenyldibenzhydrylcarbinol*, m. p. 229—231°, from Na diphenylmethyl and BzCl, is converted by $MgCH_2PhCl$ into *ααβγ-tetraphenylpropan-β-ol*, m. p. 136—137°, dehydrated by H_2SO_4 and AcOH at 100° to *ααβγ-tetraphenyl-*Δ^{α}*-propene*, m. p. 142°, *ααβγ-tetraphenyl-*Δ^{β}*-propene*, m. p. 131°, and a *hydrocarbon* $C_{27}H_{22}$, m. p. 109—110°; under somewhat different conditions, *ααβγ-tetraphenyl-β-propyl acetate*, m. p. 151—153°, is also produced. The structure of ααβγ-tetraphenyl-Δ^{α}-propene is established by its production (with *ααβεζζ-hexaphenyl-*$\Delta^{\alpha\epsilon}$*-hexadiene*, m. p. 222°) from ααβ-triphenyl-β-bromomethylethylene and MgPhBr. It adds Br with great difficulty, ultimately giving the nuclear-substituted *compound* $C_{27}H_{20}Br_2$, m. p. 114°, whereas the isomeride, m. p. 131°, readily adds Br and loses HBr to give (?) *γ-bromo-ααβγ-tetraphenyl-*Δ^{β}*-propene*, m. p. 151°. The hydrocarbon, m. p. 131°, is readily oxidised by CrO_3 in AcOH to BzOH and *o*-dibenzoylbenzene, presumably with intermediate formation of 1 : 2 : 3-triphenylhydrindene; ααβγ-tetraphenyl-Δ^{α}-propene is much more slowly converted into *o*-dibenzoylbenzene, isomerisation to the Δ^{β}-propene regulating the rate of the change. ααβγ-Tetraphenyl-Δ^{α}-propene and Na give a red *Na* compound, hydrolysed to ααβγ-tetraphenylpropane, m. p. 87—89°, and converted by Hg into the original substance. The Δ^{β}-propene is slowly transformed by Na into a brown product sparingly sol. in Et_2O and yielding when treated with Hg a resin from which ααβγ-tetraphenyl-Δ^{α}-propene and *ααβγδεζζ-octaphenyl-*$\Delta^{\alpha\epsilon}$*-hexadiene*, m. p. 255°, are extracted; the only definite product of hydrolysis is ααβγ-tetraphenylpropane in minimal amount.

Et β-phenylpropionate and Mg α-naphthyl bromide afford *α-naphthyl β-phenylethyl ketone*, m. p. 53—54°. *Et methylbenzylacetoacetate*, b. p. 117—118°/12 mm., and MgPhBr give *αα-diphenyl-β-benzyl-*Δ^{α}*-propene*, m. p. 70—71°.

H. Wren.

Synthesis of alkyl naphthalenes. III. 2 : 3 : 5-Trimethylnaphthalene. D. G. Wilkinson (J.C.S., 1931, 1333—1336).—*o*-Xylyl bromide condenses with ethyl sodiomethylacetoacetate to give *Et* o-*xylylmethylacetoacetate*, b. p. 177—179°/20 mm., which on hydrolysis with 10% NaOH affords β-o-*tolyl*iso*propyl methyl ketone*, b. p. 132—133°/20 mm. (*semicarbazone*, m. p. 152—153°). This is reduced by Na and EtOH to δ-o-*tolyl-γ-methyl*-sec.-*butyl alcohol*, b. p. 152—153°/20 mm., which is converted by way of its bromide and cyanide into γ-*o*-tolyl-αβ-dimethylbutyric acid (amide, m. p. 73°), the *acid chloride* of which (b. p. 140—145°/15 mm.) with $AlCl_3$ gives 1-*keto*-2 : 3 : 5-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 87°. Reduction of the ketone by Clemmensen's method furnishes 2 : 3 : 5-*trimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, dehydrogenated with Se to 2 : 3 : 5-*trimethylnaphthalene* (*picrate*, m. p. 122°; *styphnate*, m. p. 148—149°).

D. A. Fairweather.

Fluorine derivatives of naphthalene. G. Schiemann, W. Gueffroy, and W. Winkelmüller (Annalen, 1931, **487**, 270—287; cf. A., 1930, 201).—The hydrofluoroboric acid method gives usually good yields of fluoronaphthalene compounds. 1-Fluoro- but not 2-fluoro-naphthalene gives homogeneous substitution products. 1-Fluoronaphthalene (I) (*picrate*, m. p. 113°) has m. p. −9° to −8°, b. p. 212°/760 mm. (slight decomp.), 89°/17 mm. 2-Fluoronaphthalene (II) (*picrate*, m. p. 101°) has m. p. 61°, b. p. 211·5°/737 mm., 90°/16 mm. I and $ClSO_3H$ at 0—5° give 1-fluoronaphthalene-4-sulphonyl chloride (also obtained from diazotised naphthionic acid and HF), which when heated with H_2O at 130—150° for 15 hr. yields 1-*fluoronaphthalene*-4-*sulphonic acid* ($2+H_2O$), m. p. 100° (*Na*, *Pb*, and *Ag* salts; *amide*, m. p. 206°; *anilide*, m. p. 144°), also obtained from I and oleum (15% SO_3). II and $ClSO_3H$ in CCl_4 give 2-*fluoronaphthalene*-6(?)-*sulphonyl chloride*, m. p. 97°, b. p. 144°/0·05 mm., hydrolysed to the corresponding *acid* ($+1H_2O$), hygroscopic, m. p. 105° (*Na* and *Pb* salts; *amide*, m. p. 133°; *anilide*, m. p. 129°), which was also obtained in poor yield from II and oleum (15% SO_3). Diazotised β-naphthylamine-1-sulphonic acid and HF gave 2-*fluoronaphthalene*-1-*sulphonyl chloride*, m. p. 59·5° [*anilide*, m. p. 142·5° (decomp.)]. Nitration of I gives 1-*fluoro*-4-*nitronaphthalene* (III), m. p. 80° (transformed by KOH in EtOH into 4-nitro-1-ethoxynaphthalene, and thereafter by conc. HCl into 4-nitro-α-naphthol). Nitration of II gives a mixture of mono- and di-nitro-compounds (from which by hydrolysis 1-nitro-2-methoxy- and 1-nitro-2-ethoxy-naphthalene were obtained), a mixture of dinitro-compounds, or 2-*fluoro-?-trinitronaphthalene*, m. p. 192—193°, according to the experimental conditions. III with Zn and HCl yields 4-*fluoro-α-naphthylamine*, m. p. 48°, b. p. 162°/16 mm. [*hydrochloride*, m. p. 280° (decomp., sealed tube); *sulphate*, m. p. 230°; *Bz* derivative, m. p. 197°], which by the hydrofluoroboric acid method gives 4-*fluoronaphthyl*-1-*diazonium fluoroborate*, decomp. 163°, and 1 : 4-*difluoronaphthalene*, m. p. 31·5°, b. p. 97—98°/21 mm. 1 : 5-Diaminonaphthalene affords *naphthalene*-1 : 5-*bisdiazonium fluoroborate*, decomp. 180° (commencing at 150°), and 1 : 5-*difluoronaphthalene*, m. p. 70·5°. 4-*Bromo*-1-*fluoronaphthalene*, m. p. 37°, was obtained (*a*) from I by bromination in CCl_4, and (*b*) from 4-bromo-α-naphthylamine by the hydrofluoroboric acid method, and was oxidised by CrO_3 in AcOH in the presence of V_2O_5 to *o*-phthalic acid and 3-*bromo*-6-*fluorophthalic acid* (?), m. p. 155° after sintering at 150°. 4-*Bromonaphthalene*-1-*diazonium fluoroborate* decomposes at 151·5°. R. S. Cahn.

Monosulphonic acids of 1-methylnaphthalene. V. Veselý and F. Štursa (Coll. Czech. Chem. Comm., 1931, 3, 328—332).—The isomeride obtained in the prep. of the 4-sulphonic acid by cold sulphonation of 1-methylnaphthalene (A., 1930, 593) is the 5-*sulphonic acid*, m. p. 115° (*amide*, m. p. 176—178°), converted by KOH into 5-methyl-α-naphthol. Sulphonation at 110—120° with H_2SO_4 (*d* 1·84) gives the 3-*sulphonic acid* (*chloride*, m. p. 124—125°; *amide*, m. p. 143—144°), isolated as *Ba* salt, an isomeride being also formed. Fusion of the Na salt of the 3-sulphonic acid with KOH gives 4-methyl-β-naphthol.

A. A. Levi.

2-Ethylnaphthalene and its hydrogenation products. G. Lévy (Compt. rend., 1931, 192, 1397—1399).—2-Ethylnaphthalene (A., 1908, i, 411), purified by means of its picrate, m. p. 76—77°, has m. p. —7·5°, b. p. 252°/760 mm., d_4^{15} 0·9958. Reduction with Na and EtOH gives a *dihydro*-derivative, b. p. 241°/760 mm., d_0^0 0·9772. With Ni (reduced at 280°) and H_2 at 200°, a *tetrahydro*-derivative, probably 2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 114—115°/16 mm., 237°/760 mm. (corr.), d_4^{15} 0·9447, is formed; on further hydrogenation at 160° over Ni (reduced at 250°) it is converted into the *decahydro*-derivative, b. p. 221°/760 mm. (corr.), 92°/13 mm., $d_4^{13\cdot2}$ 0·8763. H. A. Piggott.

[**Action of halogens on fulvenes.**] E. Bergmann (Ber., 1931, 64, [*B*], 1481—1485).—The constitution of 2 : 3 : 6-tribromoindone is established synthetically (cf. A., 1930, 1569). The action of Mg and *p*-dibromobenzene in Et_2O on Et orthoformate leads to p-*bromobenzaldehyde diethylacetal*, b. p. 140°/16 mm., hydrolysed to *p*-bromobenzaldehyde, converted by malonic acid and NH_3 into *p*-bromocinnamic acid. Addition of Br to Me *p*-bromocinnamate affords *Me* αβ-*dibromo*-β-p-*bromophenylpropionate*, m. p. 111°, converted by KOH in aq. EtOH into p-*bromophenylpropiolic acid*, m. p. 201° (decomp.), which by successive treatment with Br and P_2O_5 gives 2 : 3 : 6-tribromoindone, m. p. 145—146°. 2 : 6-*Dibromo*-3-*phenylindoneoxime*, m. p. 160°, is described. The red substance $C_{22}H_{14}O_2$ obtained by oxidation of monobromodiphenylbenzofulvene (*loc. cit.*) is an *o*-diketone, since it affords a *monoxime*, $C_{22}H_{15}O_2N$, m. p. 245° (decomp.) after darkening at 220°, and a *quinoxaline*, $C_{28}H_{18}N_2$, m. p. 215°. H. Wren.

Stability of organic molecular compounds. T. S. Moore, F. Shepherd, and E. Goodall (J.C.S., 1931, 1447—1456).—The partition curves of picric acid and NH_2Ph between H_2O and $CHCl_3$ were determined. The following are equilibrium consts., determined by the partition method, for the reaction: picric acid+hydrocarbon (or derivative) in $CHCl_3 \rightleftharpoons$ additive compound: C_6H_6 0·08 (0·09); PhMe 0·09 (0·12); *o*-, *m*-, and *p*-xylenes 0·12 (0·16), 0·10 (0·14), 0·12 (0·16); mesitylene 0·12 (0·18); $C_{10}H_8$ 2·17; 1- and 2-$C_{10}H_7Me$ 2·76, 3·44; tetrahydronaphthalene 0·20 (0·26); $PhNO_2$ 0·56; *m*-dinitrobenzene 1·03; *o*- and *p*-nitrotoluenes 0·41, 0·57; 2 : 4-dinitrotoluene 0·67; 2 : 4 : 6-trinitrotoluene 1·02; 1-$C_{10}H_7{\cdot}NO_2$ 1·02; PhBr 0·06 (0·09); *o*- and *p*-dichlorobenzenes 0·07 (0·10), 0·00 (0·03); 1-$C_{10}H_7Br$ 0·17 (0·23). The following are equilibrium consts. for the reaction NH_2Ph+NO_2-compound $\rightleftharpoons$ additive compound: 2 : 4 : 6-trinitrotoluene 0·56; 1 : 5-$C_{10}H_6(NO_2)_2$ 0·57; *p*- and *m*-dinitrobenzenes 0·18, 0·17; 2 : 4-dinitrotoluene 0·10 (0·15); *m*-bromonitrobenzene 0·02 (0·06); *p*-chloronitrobenzene 0·01 (0·03); 1-$C_{10}H_7{\cdot}NO_2$ (0·02); $PhNO_2$ (0·01). Figures in parentheses are corrected for the mol.-vol. effect. The assumptions that (*a*) the compounds are formed from 1 mol. of each constituent, (*b*) that association of picric acid and NH_2Ph in $CHCl_3$ is negligible, and (*c*) that combination of picric acid or $NHPh_2$ with $CHCl_3$ does not alter the relative order of consts. are justified. The effect (apart from compound formation) of a number of substances on the partition curves obscures only the lower consts. The results are discussed and it is concluded (*a*) that introduction of a NO_2-group into a hydrocarbon changes the mode of its reaction with picric acid, and (*b*) that the reaction of $NHPh_2$ with mononitro-compounds may be purely physical, becoming chemical with di- and tri-nitro-compounds. The compound $C_{10}H_7{\cdot}NO_2(1),C_6H_2(NO_2)_3{\cdot}OH$ has m. p. 71°. R. S. Cahn.

Interaction of anilides and hypochlorous acid. D. R. Pryde and F. G. Soper (J.C.S., 1931, 1510—1514).—Velocity coeffs. are recorded for the formation of *N*-Cl derivatives in buffered solutions from pure HOCl and acetanilide, *o*-, *m*-, and *p*-acetamidobenzoic acids, *o*-, *m*-, and *p*-chloroacetanilides. These are proportional to the [OH′] over the range $p_{\rm H}$ 5·7—6·2 examined. The implications of this relation and the possibility of the reaction proceeding between the *aci*-form of the anilide and OCl′ are discussed.

R. S. Cahn.

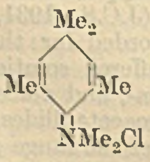
Direct interchange of chlorine in the interaction of *p*-toluenesulphonamide and *N*-chloroacetanilide. D. R. Pryde and F. G. Soper (J.C.S., 1931, 1514—1518).—The times for 50% hydrolysis of *N*-chloroacetanilide (I) and *p*-toluenesulphonchloroamide (II) in neutral solution at 25° are 7 days and 7 min., respectively. The former estimate is confirmed by the stability of aq. solutions of I in the presence of phenols. A neutral aq. solution of I reacts with *p*-toluenesulphonamide to form II and acetanilide, the bimol. velocity coeff. being 0·47 at

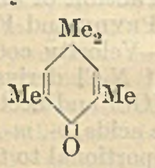
25°. This reaction must proceed by direct interchange of Cl, because it is several hundred times as fast as the production of HOCl from I. The velocity is approx. the same in 0·1*N*-HCl, and since II is more unstable than I towards HCl, the rate of production of Cl_2 from I in this medium is increased by the addition of *p*-toluenesulphonamide. R. S. CAHN.

Use of polychlorobenzenes in the synthesis of dyes. II. Preparation of chloronitroanilines from *o*- and *p*-dichlorobenzenes. A. I. KIPRIANOV and M. M. DASCHEVSKI (Ukrain. Chem. J., 1930, 5, [Tech.], 241—248).—Heating a dichloronitrobenzene with conc. aq. NH_3 in an autoclave gives the corresponding chloronitroaniline. The effects of concentration and quantity of NH_3 are discussed. The use of bronze autoclaves is not recommended owing to the injurious effect of Cu on the reaction. E. B. UVAROV.

Action of nitrous acid on 3-nitro- and 4-nitrodimethylaniline and the so-called β-3 : 4-dinitrodimethylaniline. H. H. HODGSON and E. W. SMITH (J.C.S., 1931, 1508—1510).—The α-form of 3 : 4-dinitrodimethylaniline (I) (J.C.S., 1920, **117**, 1) has the structure assigned to it, but the β-form is a mixture of I and 2 : 4 : 5-trinitrodimethylaniline (II). When the prep. is carried out at 30°, 2 : 4 : 5-trinitromonomethylaniline replaces II. I is also prepared from 3-nitrodimethylaniline and HNO_2. HNO_2 with 3-nitro- and 4-nitroso-dimethylaniline yields *N*-nitroso-3-nitro- and *N*-nitroso-4-nitro-monomethylaniline, respectively, hydrolysed by boiling conc. HCl to 3-nitro- and 4-nitro-methylaniline, respectively. R. S. CAHN.

Nuclear alkylation of aromatic bases. I. Action of methyl alcohol on the hydrochlorides of *o*- and *p*-toluidine, mesidine, and dimethylmesidine. D. H. HEY (J.C.S., 1931, 1581—1594).—Contrary to the usual view, methylation may occur in the *m*-position in the Hofmann–Martius reaction after the *p*- and *o*-positions have been substituted. Phenols, hydrocarbons, and acridine derivatives are by-products. *m*-Methylation is considered to occur by action of MeCl on, *e.g.*, *N*-dimethylmesidine to yield

(I.) 

 (II.)

I, which either by loss of HCl and migration of a Me group yields *N*-dimethyl*iso*duridine, or is hydrolysed to II, which by rearrangement yields *iso*durenol. Alkylation was carried out in electrically-heated steel autoclaves, temp. being the most important factor in determining the extent of the reaction. Fe had no effect on the yield of phenols obtained. MeOH and *o*-toluidine hydrochloride, heated at 260—280° for 10 hr., yielded mesitol (III), *iso*durenol (*bromo*-derivative, m. p. 135°; *phenylurethane*, m. p. 178—179°; *benzoate*, m. p. 71—72°; *bromoisodurenyl acetate*, m. p. 98°), mesidine (>50%) (IV) (p-*toluenesulphonyl* derivative, m. p. 167°; *picrate*, m. p. 189—191°), *iso*duridine (V), m. p. 217·5°, b. p. 258—260° (*picrate*, m. p. 199—200°), 1 : 3 : 7 : 9-tetramethylacridine (VI), and another acridine derivative, m. p. 73—74° (possibly 1 : 3-dimethylacridine). MeOH and *p*-toluidine hydrochloride, heated at 250—275° for 12 hr., gave III, IV, V, and VI. Mesidine hydrochloride and MeOH, heated at 240—270° for 12 hr., gave III, hexamethylbenzene, IV, V, and an acridine derivative. Methylation of mesidine (cf. A., 1907, i, 122) yielded *N*-methylmesidine, b. p. 220—221° (*picrate*, m. p. 179°; p-*toluenesulphonyl* derivative, m. p. 145—146°), or *N*-dimethylmesidine [*picrate*, m. p. 182° (decomp.)], according to the conditions. Dimethylmesidine, MeOH, and conc. HCl, heated at 230—250° for 12 hr., gave III, pentamethylphenol (*phenylurethane*, m. p. 215°; *Bz* derivative, m. p. 127°), methylamines, IV, and V. R. S. CAHN.

Catalytic hydrogenation of nitriles under reduced pressure: a correction. V. GRIGNARD, R. ESCOURROU, and A. FARGIER (Bull. Soc. chim., 1931, [iv], 49, 522—527).—Hydrogenation of phenylacetonitrile in presence of PtO_2 on pumice at 150°/80 mm. yields, not the imine, but a mixture (mol. compound) in approx. equimol. proportions of phenylacetonitrile and β-phenylethylamine which distils at 215°, together with a little β-phenylethylamine carbonate, m. p. 83—84°. Similarly, PhCN in presence of Ni at 175°/13 mm. yields an equimol. mixture, b. p. 80—82°/15 mm., of PhCN and benzylamine, together with dibenzylamine and a little benzylamine carbonate, m. p. 89—90°. Hydrogenation of phenylacetonitrile in presence of an equal wt. of Ac_2O at 175—180°/18—20 mm. (Pt-black catalyst) affords β-phenylethylacetamide, indicating that the imine formed in the first stage of the hydrogenation is acetylated more rapidly than it condenses, but that the acetylated imine is too readily hydrogenated to be isolated. R. BRIGHTMAN.

Nitration of derivatives of α- and β-naphthylamines. I. Nitration of methyl and ethyl α-naphthylcarbamates and of *N*-α-naphthyl-*N'*-ethylcarbamide. C. GROENEVELD (Rec. trav. chim., 1931, 50, 681—707).—An investigation of the protection afforded in nitration, by conversion of an NH_2 group into the corresponding ethylcarbamide or Me (Et) carbamates. Me (I) and Et (II) α-naphthylcarbamates give with HNO_3 (*d* 1·45), *Me* (III), m. p. 205—207° (decomp.), and *Et* (IV), m. p. 183—185°, 2:4-*dinitro-α-naphthylcarbamates*, hydrolysed to 2 : 4-dinitro-α-naphthylamine. The latter is also formed by nitration of *N*-α-naphthyl-*N'*-ethylcarbamide. I and II with 100% HNO_3 give 2 : 4 : 5-trinitro-α-naphthylamine (V), formed also by nitrating III and IV, and a little *Me* (VI), m. p. 230°, and *Et*, m. p. 196—198°, 2 : 4 : 5-*trinitro-α-naphthylcarbamates* (?) (VII). *N*-α-Naphthyl-*N'*-ethylcarbamide with 100% HNO_3 gives V and *N*-(2 : 4 : 5-trinitro-α-naphthyl)-*N'*-nitro-*N'*-ethylcarbamide, the presence of the latter being inferred from the formation of VI and VII when the nitration product is treated with the appropriate alcohol. The nitration of α-naphthylamine derivatives is discussed. J. D. A. JOHNSON.

Preparation of benzidinesulphone. C. COURTOT and R. EVAIN (Bull. Soc. chim., 1931, [iv], 49, 527—530).—Benzidinesulphone, m. p. 327—328° (Ac_2, m. p. 382—383°; Bz_2 derivative, m. p. 384—385°), is obtained (yield 70%) by sulphonation of benzidine (finely-powdered) with 1600 parts per mol. of 21% oleum at 70—80° for 5 hr. The sulphate of the sulphone is precipitated on dilution with ice and decomposed with 20% NaOH. More dil. or small amounts of oleum give lower yields and more conc. oleum affords no proportionate increase. Benzidine sulphate as starting material is unnecessary (cf. A., 1890, 57). Although benzidinesulphone is not readily tetrazotised in presence of HCl, the finely-divided sulphate obtained by pouring a H_2SO_4 solution on to ice is readily tetrazotised. R. BRIGHTMAN.

Action of *p*-nitrobenzeneazo-β-naphthol on sodium hydrogen sulphite. IV. Hydrogen sulphite compounds of azo-dyes. N. N. VOROSCHCOV and P. A. BELOV (J. Gen. Chem. Russ., 1931, **1**, 39—47).—*p*-Nitrobenzeneazo-β-naphthol forms a hydrogen sulphite compound in EtOH or $CHCl_3$ solution, which is decomposed by alkali, giving unchanged para-red, showing that the NO_2 group is not affected. The hydrogen sulphite compound forms Ca, Ba, Ni, Cu, Pb, Ag *salts*. Dissociation of the Na salt increases with dilution in aq. solution and with addition of OH ions. Increase of H ions slightly increases the stability up to a limit. E. B. UVAROV.

Constitution of *o*-hydroxyazo-compounds. K. VON AUWERS and E. WOLTER (Annalen, 1931, **487**, 79—97).—Refractometric data are determined for a number of derivatives of *o*-hydroxyazo-compounds and quinonephenylhydrazones, but cannot be used to distinguish between the azo- and hydrazone formulæ for benzeneazo-α- and -β-naphthols; the similarity of their behaviour, however, indicates that they have similar structures, and both are therefore azo-compounds (cf. A., 1930, 214).

Interaction of benzeneazo-*p*-cresol with $Cl\cdot CO_2Et$ gives the O-*carbethoxyl ether*, m. p. 46—47°, b. p. 236°/14 mm., the constitution of which is determined by reduction to the *hydrazo*-derivative (I), m. p. 69° [*Bz* derivative $C_7H_6(O\cdot CO_2Et)\cdot NH\cdot NBzPh$ (II), m. p. 143°], with Zn and AcOH in cold EtOH; further reduction in boiling EtOH proceeds in the two directions: $C_7H_6(OH)\cdot NH\cdot CO_2Et+NH_2Ph \longleftarrow C_7H_6(O\cdot CO_2Et)\cdot NH\cdot NHPh$ (I) $\longrightarrow C_7H_6(OH)\cdot NH_2 +NHPh\cdot CO_2Et$. Reduction of II gives 3-hydroxy-*p*-tolylurethane and benzanilide; the absence of rearrangement of an *N*- into an *O*-acyl derivative under these conditions is confirmed by the reductive fission of benzoquinone- and benzaldehyde-acetyl- and -benzoyl-phenylhydrazones and 3-phenylhydrazino-*p*-cresol. The O-*carbethoxyl* derivatives, m. p. 86—87° and 67—68°, respectively, of β-benzeneazo-α- and α-benzeneazo-β-naphthols were not successfully reduced to stable hydrazo-derivatives; in both cases NH_2Ph was formed, but no other product was isolated in a pure condition. A quant. study of the reductive fission of the Bz derivatives of the benzeneazonaphthols gave similar results in the two cases, favouring the *O*-Bz structure. A similar study of the Bz derivative of 5-chloro-2 : 6-dihydroxy-1-benzeneazonaphthalene indicates that fission occurs (about 90%) to the aminonaphthol and benzanilide, and (10%) to the benzamidonaphthol and NH_2Ph.
H. A. PIGGOTT.

Addition of phenylthiocarbimide to alkylhydrazines. M. BUSCH and R. SCHMIDT (J. pr. Chem., 1931, [ii], **130**, 342—346).—Fischer's phenylethylthiosemicarbazide from ethylhydrazine and phenylthiocarbimide combines with PhCHO to give *benzylidene-4-phenyl-2-ethylthiosemicarbazone*, m. p. 104°, and reacts with HNO_2 to form phenylethylthiocarbamide; it must therefore be the 4-phenyl-2-ethylthiosemicarbazide, $NH_2\cdot NEt\cdot CS\cdot NHPh$. Ethylhydrazine hydrochloride, however, reacts with phenylthiocarbimide (2 mols.) in EtOH to give the *hydrochloride* (decomp. 291°) of 3-*anilino*-1-*ethylthiodiazolone*-5-*anil*, m. p. 147°. Benzylhydrazine hydrochloride similarly affords with phenylthiocarbimide the *hydrochloride*, decomp. 295°, of *anilinobenzylthiodiazoloneanil*, m. p. 128°, but phenylhydrazine gives 1 : 4-diphenylthiosemicarbazide. F. R. SHAW.

Diazo-compounds. A. QUILICO (Gazzetta, 1931, **61**, 326—332).—The oxidising properties of normal diazo-hydrates are discussed, and evidence is adduced in favour of the formula $R\cdot NO\colon NH$ suggested by Angeli (A., 1926, 947; 1929, 1290). E. E. J. MARLER.

1-Diazo-β-naphthol-4-sulphonic acid. M. BATTEGAY, H. SILBERMANN, and P. KIENZLE (Bull. Soc. chim., 1931, [iv], **49**, 716—723).—Nitration of 1-diazo-β-naphthol-4-sulphonic acid yields an extremely stable nitrodiazo-compound, decomp. 203°, converted by elimination of the N_2 group, reduction, and elimination of the SO_3H group with Na–Hg into 2 : 6-aminonaphthol (Ac_2, m. p. 220°, and Bz_2 derivative, m. p. 234°). Further evidence that the NO_2 group enters the 6-position is obtained by conversion of the aminonaphthol into 2 : 6-dihydroxynaphthalene (diacetate, m. p. 175°) (cf. A., 1930, 205), also obtained from 6-amino-β-naphthol-4-sulphonic acid. The 6-chloro-β-naphthol-4-sulphonic acid obtained from the aminonaphtholsulphonic acid by the Sandmeyer reaction is converted by excess of PCl_5 at 170—180° into 2 : 6 : 8(or 1 : 3 : 7)-trichloronaphthalene, m. p. 113°, phosphoric esters of chloronaphthol being also formed, and some 1 : 4 : 6-*trichloro*-β-*naphthol*, m. p. 136—137° (*benzoate*, m. p. 175—176°). Chlorination of 1-diazo-β-naphthol-4-sulphonic acid in H_2SO_4 (100%) at 65—70° yields 6-*chloro*-1-*diazo*-β-*naphthol*-4-*sulphonic acid*, decomp. 180—182°, converted by successive elimination of the N_2 and SO_3H groups into 6-chloro-β-naphthol, m. p. 115° (benzoate, m. p. 124—125°). 6-*Bromo*-1-*diazo*-β-*naphthol*-4-*sulphonic acid* and 6-*bromo*-β-*naphthol*-4-*sulphonic acid* are similarly obtained, but with Na–Hg the latter affords β-naphthol. Elimination of the SO_3H group with HCl (20% and 37%) at 130° and at 180° yielded tars, but oxidation with $KMnO_4$ yields 4-bromophthalic acid, m. p. 170—171°. Sulphonation of 1-diazo-β-naphthol-4-sulphonic acid with 20% and 30% oleum at 50° and 70—75° for 30 hr. yielded no definite product, but a product containing Cl was obtained with $ClSO_3H$ at 70—75°. R. BRIGHTMAN.

Transformation of diazoaminobenzene into aminoazobenzene. E. ROSENHAUER (Ber., 1931, **64**, [*B*], 1438—1439).—Contrary to Earl, benzenediazoaminoazobenzene is not an intermediate product of the transformation but a secondary product of the aminoazobenzene. Its isolation establishes the intermediate formation of diazonium salt. H. Wren.

Action of αγ-dichloropropylene on sodium derivatives of phenols. L. Bert (Compt. rend., 1931, **192**, 1565—1567).—The α-Cl atom in αγ-dichloropropylene is the more reactive and the compound reacts with the Na derivatives of phenols to form β-*chloroallyl ethers* of the following (all b. p. at 20 mm.): phenol, b. p. 120—121°; *o*-cresol, b. p. 132—133°; *m*-cresol, b. p. 137—138°; *p*-cresol, b. p. 137—138°; cumenol, b. p. 156°; carvacrol, b. p. 156—157°; thymol, b. p. 157·5°; guaiacol, b. p. 153—154°; eugenol, b. p. 185°; *iso*eugenol, b. p. 189°; salicylaldehyde, b. p. 179°; Me salicylate, b. p. 188°; β-naphthol, b. p. 195°, m. p. 60°; quinol, b. p. 213—214°, m. p. 69°. The products from α-naphthol, pyrocatechol, and resorcinol decompose when distilled at 20 mm. F. R. Shaw.

Nitrosation of phenols. XI. Constitution of 3-chloro-4-nitrosophenol. H. H. Hodgson (J.C.S., 1931, 1494—1499; cf. A., 1930, 1281).—As previously suggested (A., 1929, 1062), direct nitrosation of *m*-chlorophenol yields 3-chloro-4-nitrosophenol (I), m. p. 135°, and not 3-chlorobenzoquinone-4-oxime (II), since the product (*a*) is reduced by sodium hyposulphite and Na_2CO_3 to 3-chloro-4-aminophenol, (*b*) reacts more readily than II with NH_2OH, and (*c*) forms a picrate. I in MeOH gives a deep green colour with a drop of conc. H_2SO_4 or oleum, and a deep red with more oleum. I with HCl in Et_2O yields II, and with CH_2N_2 the Me ether of II. I with $AgNO_3$ and (but not without) NH_3, and I and II with AgOAc and NaOAc give the *Ag* salt, brick-red, of II, which with MeI gives the Me ether of II. I and II give the p-*nitrophenylhydrazone* of II, m. p. indef. (blue in aq. or alcoholic NaOH or NH_3, owing to isomerisation to a double indamine structure). With NH_2OH,HCl in MeOH or EtOH I gives *m*-chlorophenol, whereas II gives only a trace. Addition of β-naphthylamine to I and NH_2OH,HCl in MeOH gives 3-*chloro*-1-*hydroxybenzene*-4-*azo*-β-*naphthylamine*, m. p. 210—212°. Addition of β-naphthol and NaOAc gives similarly an azo-compound with I, but not with II. The *picrate* of I has m. p. 151° (decomp.), and 3-*chloro*-4-*nitroanisole picrate*, m. p. 174·5° (decomp.). I in dry Et_2O or C_6H_6 with $AlCl_3$ yields II. R. S. Cahn.

Indicators. II. 2 : 6-Dinitrophenol. I. V. Kulikov and S. V. Panova (Trans. Inst. Pure Chem. Reag., 1931, **10**, 36—45).—The greatest yield of 2 : 6-dinitrophenol in the nitration of *o*-nitrophenol is obtained in the presence of definite proportions of AcOH and H_2SO_4. It is possible to isolate 30—35% of 2 : 6- and 40% of 2 : 4-dinitrophenol in the pure state. E. S. Hedges.

Explosion during catalytic reduction of nitroanisole in the liquid phase. T. S. Carswell.—See this vol., 919.

Use of polychlorobenzenes in the synthesis of dyes. I. Preparation of chloronitrophenols, chloroaminophenols, and chloroaminophenolsulphonic acids from *o*- and *p*-dichlorobenzene. A. I. Kiprianov and P. P. Michailenko (Ukrain. Chem. J., 1930, **5**, [Tech.], 225—239).—Hydrolysis of 2 : 5- and 3 : 4-dichloronitrobenzenes gives 4 : 2 : 1- and 2 : 4 : 1-chloronitrophenols, giving rise to green dyes with Na polysulphide. Reduction of 4-chloro-2-nitrophenol with Na_2SO_3 gives the corresponding *chloroaminophenol*, m. p. 138°. Methods for the prep. of two chloroaminophenolsulphonic acids are described. Analogous attempts to prepare corresponding derivatives of 2 : 3-dichloronitrobenzene were unsuccessful. An explanation of the failure is put forward. E. B. Uvarov.

Phenacetin hydrochloride. I. H. Sanborn (J. Physical Chem., 1931, **35**, 1345—1350).—Phenacetin combines with HCl mol. for mol. to form the hydrochloride, m. p. 154°/741 mm., stable in an atm. of HCl, but decomposing under room conditions, and in H_2O, into its components. L. S. Theobald.

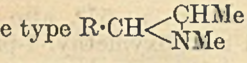
β-Phenylethylamines. II. Synthesis of tyramine. K. H. Slotta and W. Altner (Ber., 1931, **64**, [*B*], 1510—1520; cf. this vol., 213).—β-Phenylethyl alcohol is converted into β-phenylethyl bromide by distillation with 48% aq. HBr or, preferably, by repeated saturation with gaseous HBr and heating of the mixture at 100°. Treatment of the bromide with HNO_3 (d 1·51) at 0—10° affords in 48% yield β-*p*-nitrophenylethyl bromide, m. p. 69°, which yields with hexamethylenetetramine in $CHCl_3$ the additive *compound*, $C_{14}H_{20}O_2N_5Br$, m. p. 181—182° according to the rate of heating (best isolated by keeping the mixture at room temp. and periodic removal of the precipitated adduct). Treatment of the additive compound with 95% EtOH and conc. HCl affords β-*p*-nitrophenylethylamine hydrochloride, m. p. 214°, in 85% yield, reduced by $SnCl_2$ and conc. HCl to the *Sn* compound, $C_{16}H_{28}N_4Cl_{12}Sn_2$, converted by successive diazotisation, heating in aq. solution, treatment with Na_2CO_3, and extraction with anisole into β-*p*-hydroxyphenylethylamine (tyramine), m. p. 165—166° after softening at 155°, in 64% yield. β-*p*-Nitrophenylethyl bromide, phthalimide, and anhyd. K_2CO_3 at 150° afford β-p-*nitrophenylethylphthalimide*, m. p. (indef.) 223—224° after softening at 190°, reduced by $SnCl_2$ and HCl through a $Sn^{\cdot\cdot\cdot\cdot}$ double salt to β-p-*aminophenylethylphthalimide hydrochloride*, m. p. 231—232°. β-*p*-Aminophenylethylamine is obtained by fission of the $Sn^{\cdot\cdot\cdot\cdot}$ salt described above with K_2CO_3 and NaOH, reduction of β-*p*-nitrophenylethylamine hydrochloride with Zn–Hg, or reductive fission of β-*p*-nitrophenylethylphthalimide with Na_2S.

β-Phenylethyl bromide and hexamethylenetetramine yield the *product* $C_{14}H_{21}N_4Br$, m. p. 177—178°, converted by 96% EtOH and conc. HCl into β-phenylethylamine hydrochloride in 82·5% yield. H. Wren.

2-Nitro-*m*-cresol. A. Corbellini and C. Ravazzoni (Atti R. Accad. Lincei, 1931, [vi], **13**, 132—137; cf. this vol., 956).—Repetition of the series of reactions employed by Gibson (J.C.S., 1923, **123**, 1270) to establish the constitution of the nitro-*m*-cresol, m. p. 41°, shows that this compound is 6-(not 2-)nitro-*m*-cresol. The values of the m. p. given by Jacobsen (A., 1883, 1124) for 3-methoxyphthalic acid and its anhydride are actually those for 4-methoxyphthalic acid and anhydride, and if Gibson obtained this acid from the nitro-*m*-cresol, transference of the substituent from the 2- to the 6-position must be assumed. The methoxytoluic acid obtained according to Gibson's scheme has m. p. 138—139° (not 114°) and is identical with the 3-methoxy-*o*-toluic acid formed on oxidation of β-*m*-homosalicylaldehyde methyl ether (Chuit and Bolsing, A., 1906, i, 283). Oxidation of 3-methoxy-*o*-toluic acid by means of alkaline $KMnO_4$ gives 3-methoxyphthalic acid, m. p. 173—174° (anhydride, m. p. 159—160°); a mixture of this anhydride with that prepared from 3-nitrophthalic acid (Corbellini and Rossi, *loc. cit.*) has the same m. p. T. H. Pope.

Phosphoric esters of 2 : 4-diphenyl-α-naphthol. A new case of dimorphism. A. Franssen (Bull. Soc. chim., 1931, [iv], **49**, 550—556).—When 2 : 4-diphenyl-α-naphthol (I) is heated for 7—8 hr. with PCl_5 in CCl_4, *tri*-2 : 4-*diphenyl-α-naphthyl phosphate* is obtained, m. p. 198—199° (from CCl_4) and m. p. 130° (from C_6H_6), together with a residue sol. in EtOH containing acid phosphoric esters, and, probably, unchanged I, but only traces of 1-chloro-2 : 4-diphenylnaphthalene and di-2 : 4-diphenyl-α-naphthyl ether. The form m. p. 130° is converted into the form m. p. 198—199° by suspension in boiling EtOH; the reverse transformation is effected at about 200°. On hydrolysis tri-2 : 4-diphenyl-α-naphthyl phosphate affords I and a little di-2 : 4-diphenyl-α-naphthyl phosphate, m. p. 220—221°. R. Brightman.

Synthesis of 4-ethylguaiacol (4-hydroxy-3-methoxyethylbenzene). K. Brand and G. Westerburg (Arch. Pharm., 1931, **269**, 326—335).—Condensation of vanillin and malonic acid in pyridine with a little piperidine at 100° gives ferulic acid (4-hydroxy-3-methoxycinnamic acid). A higher temp. gives an oil [(?) 4-hydroxy-3-methoxystyrene] which easily resinifies. Hydroferulic acid (from the reduction of ferulic acid with Pd–$CaCO_3$ catalyst) when distilled with soda-lime gives a small yield of 4-ethylguaiacol. Apocynin benzoate (from apocynol benzoate, the prep. of which is improved; cf. J.C.S., 1908, **93**, 1520) is reduced by Clemmensen's method to 4-ethylguaiacol benzoate. This substance, and its NO_2 derivative, are identical with similar products obtained from beech-wood creosote. Hydrolysis gives 4-ethylguaiacol. A. A. Levi.

Bases derived from substituted propenylbenzenes. Preparation of pure methylamine. T. M. Sharp and W. Solomon (J.C.S., 1931, 1468—1478).—α-Acetoxy-β-bromopropylbenzenes, containing an AcO group in the *p*-position to the side-chain, yield αβ-di(methylamino)-compounds on treatment with NH_2Me; when, however, the substituent is in the *m*-position or when the *p*-OH group is methylated, methylamino-alcohols are formed. *iso*Myristicin acetoxybromide gives the α-NHMe-β-OH-derivative. Acetyl*iso*chavibetol acetoxybromide gives two bases; one of these probably has the NHMe group in the α-position, but the structure of the other is uncertain, as both yield an α-OH-β-NHMe-compound on methylation. The position of the substituents is determined by comparison with bases derived from the corresponding methoxybromides. Migration of the NHMe group is assumed to take place through compounds of the type  $R\cdot CH<\begin{smallmatrix}CHMe\\ \vert\\ NMe\end{smallmatrix}$ (cf. A., 1914, i, 667, 828).

Acetyl*iso*eugenol dibromide in AcOH with AgOAc gives the *acetoxybromide*, crystals, which with NH_2Me in EtOH at 110° yields αβ-*di*(*methylamino*)-α-4-*hydroxy*-3-*methoxyphenylpropane* (*sulphate*, m. p. 254°). *iso*Myristicin dibromide similarly yields the *acetoxybromide*, m. p. 62—64°, and α-*methylamino*-β-*hydroxy*-α-3-*methoxy*-4 : 5-*methylenedioxyphenylpropane*, an oil [*hydrochloride*, m. p. 233—235° (decomp.) after sintering at 231°; *hydrobromide*, m. p. 239° (decomp.); *oxalate*, m. p. 251° (decomp.); *picrate*, m. p. 179—182°]. This, when boiled with Ac_2O and AcCl and subsequently hydrolysed by alcoholic KOH, is partly transformed into its diastereoisomeride (*hydrochloride*, m. p. 212—216°). *Acetyl*iso*chavibetol dibromide*, m. p. 109—111° (prep. from *acetyl*iso*chavibetol*, m. p. 101°, in Et_2O), similarly gives the *acetoxybromide*, a syrup; *base* A, $C_{11}H_{17}O_3N$, m. p. 143—146° [*oxalate* $+1\cdot5H_2O$, m. p. 222·5° (decomp.)], and *base* B, $C_{11}H_{17}O_3N$, m. p. 166—167° [*oxalate*, m. p. 222·5° (decomp.)]. Base *A* with CH_2N_2 yields α-methylamino-β-hydroxy-α-3 : 4-dimethoxyphenylpropane, m. p. 60—62° [hydrochloride, m. p. 206—207°; *oxalate*, m. p. 147° (decomp.)] (cf. A., 1910, i, 411). Base *B* similarly yields a *Me ether*, m. p. 95—97° [*hydrochloride*, m. p. 204—205°; *oxalate*, m. p. 147° (decomp.)]. *iso*Myristicin dibromide and NaOMe gives β-*bromo*-α-*methoxy*-α-3-*methoxy*-4 : 5-*methylenedioxyphenylpropane*, a varnish, which with $NHMe_2$ in EtOH at 130° gives 3-methoxy-4 : 5-methylenedioxyphenyl ethyl ketone (A., 1912, i, 196), and β-*methylamino*-α-*methoxy*-α-3-*methoxy*-4 : 5-*methylenedioxyphenylpropane*, an oil [*hydrochloride*, m. p. 252° (decomp.)], which with cold HCl yields β-*methylamino*-α-*hydroxy*-α-3-*methoxy*-4 : 5-*methylenedioxyphenylpropane*, m. p. 122—124° (*hydrochloride*, m. p. 194—198°). Methyl*iso*eugenol dibromide similarly yields the *methoxybromide*, a syrup, β-*methylamino*-α-*methoxy*-α-3 : 4-*dimethoxyphenylpropane*, an oil (*hydrochloride*, m. p. 167° to a cloudy liquid clear at 190°), and β-*methylamino*-α-*hydroxy*-α-3 : 4-*dimethoxyphenylpropane*, m. p. 130—131° [*oxalate*, m. p. 217—218° (decomp.)]. This last base, together with neutral material, was also obtained when the Me ether of base *A* or *B* was treated with PCl_5 in $CHCl_3$, followed by boiling with alcoholic KOH. *p*-Hydroxyphenylethylcarbinol (A., 1908, i, 260) on acetylation followed by treatment with Br yields p-*acetoxypropenylbenzene dibromide*, m. p. 125—129°, which with AgOAc and AcOH gives β-*bromo*-α-p-*diacetoxy*-α-*phenylpropane*, oil. This with NH_2Me in EtOH at 110° gives neutral material and αβ-*di*(*methylamino*)-α-p-*hydroxyphenylpropane* (*sulphate*, $+1\cdot5H_2O$, m. p. 211—213°). All m. p. are corrected.

A method is given for preparing NH_2Me,HCl containing less than 0·5% of NH_4Cl from material containing 5% of the latter. R. S. Cahn.

Decomposition products of safrole with methyl alcohol and alkali. T. Hiraidzumi (J. Soc. Chem. Ind. Japan, 1931, **34**, 208—212B).—Benzoylation of the mixture of methoxymethyl-4-propenylpyrocatechols obtained by the action of MeOH and KOH on safrole gives benzoylmethoxy*iso*eugenol and *benz*-

*oylmethoxyiso*chavibetol, m. p. 55°, also obtained as follows: the mixed methoxymethyl-4-propenylpyrocatechols give diacetyl-4-propenylpyrocatechol, hydrolysed by NH_3 in Et_2O to 4-propenylpyrocatechol, new m. p. 105·5°, and b. p. 152°/7 mm. (cf. A., 1908, i, 260) (*Et_2 ether*, m. p. 54·5°; *Bz_2* derivative, m. p. 100°). The 2-Ac derivative of this when condensed with Na and chlorodimethyl ether gives acetylmethoxy*iso*chavibetol, hydrolysed and benzoylated to benzoylmethoxy*iso*chavibetol. Physical properties are recorded for pure methoxy*iso*eugenol, b. p. 144°/10 mm., and methoxy*iso*chavibetol, b. p. 154°/10 mm. (decomp. when kept), recovered from the Bz derivatives.

A. A. Levi.

Separation of methoxy*iso*chavibetol from methoxy*iso*eugenol. T. Kuwata (J. Soc. Chem. Ind. Japan, 1931, **34**, 212—214b).—Separation is effected by fractionation of the Ac derivatives.

A. A. Levi.

Primary additive products in indirect substitution in the benzene nucleus. III. Additive products of 4 : 4′-dialkoxydiphenyls with nitric acid. J. van Alphen (Rec. trav. chim., 1931, **50**, 657—668; cf. this vol., 723).—The stability of additive compounds of dialkoxydiphenyls and HNO_3 is shown to be related to the basicity of the former. 4 : 4′-*Dimethoxy*-3 : 3′-*dimethyldiphenyl* (I), m. p. 154·5°, gives with 2 mols. of HNO_3 in CCl_4 a blue additive compound which rapidly decomposes and when crystallised gives 5(?)-*nitro*-4 : 4′-*dimethoxy*-3 : 3′-*dimethyldiphenyl*, m. p. 137°. Methylation of *pp*′-diphenol gives 4′-*hydroxy*-4-*methoxydiphenyl* (II), m. p. 183·5°, which behaves like I, giving 3′-*nitro*-4′-*hydroxy*-4-*methoxydiphenyl* (III), m. p. 117°. The *Ac* derivative (m. p. 101°) of II similarly gives 3-*nitro*-4′-*acetoxy*-4-*methoxydiphenyl*, m. p. 152·5°, hydrolysed to 3-*nitro*-4′-*hydroxy*-4-*methoxydiphenyl*, m. p. 127°. Methylation of the last gives 3-*nitro*-4 : 4′-*dimethoxydiphenyl*, m. p. 121° (also prepared from III), nitrated to 3 : 3′-dinitro-4 : 4′-dimethoxydiphenyl. From II, 3 : 3′ : 5′(?)-*trinitro*-4′-*hydroxy*-4-*methoxydiphenyl*, m. p. 219° (*Ac* derivative, m. p. 218°), has also been prepared. 4-*Methoxy*-, m. p. 158°, and 4-*ethoxy*-4′-*benzoyloxydiphenyl*, m. p. 175·5°, form no additive compound with HNO_3. 4-*Methoxy*-4′-*ethoxydiphenyl*, m. p. 152°, from II by ethylation or by methylation of 4-*ethoxy*-4′-*hydroxydiphenyl*, m. p. 168°, gives a relatively stable additive *compound* with 2 mols. of HNO_3.

J. D. A. Johnson.

Dissociable organic oxides: a dimethoxyrubrene. C. Dufraisse and R. Buret (Compt. rend., 1931, **192**, 1389—1391).—The prep. from *p*-methoxyphenylacetylene of the *carbinol* $OMe{\cdot}C_6H_4{\cdot}C{\vdots}C{\cdot}CPh_2{\cdot}OH$, m. p. 67—68° (*Me ether*, m. p. 119—210°; *Et ether*, m. p. 104—105°), its *chloride*, m. p. 137—138°, a *dimethoxyrubrene*, m. p. 244—245° ($+0{\cdot}5C_6H_6$, m. p. 238—239°), and α-*anisoyl*-ββ-*diphenylethylene*, m. p. 104—105°, is reported. The dimethoxyrubrene has the characteristic properties and absorption spectrum of the rubrenes, and when insolated in solution in presence of O_2 forms an *oxide*, which, however, yields only 52% of its oxidic O in the gaseous form on dissociation.

H. A. Piggott.

Structure of di*iso*eugenol. R. D. Haworth and C. R. Mavin (J.C.S., 1931, 1363—1366).—Di*iso*eugenol has the annexed structure, since its Me_2 ether is oxidised to 2 : 3 : 6 : 7-*tetramethoxyanthraquinone* (I), which has been synthesised. Dimethyl*iso*eugenol is stable to $KMnO_4$ in $COMe_2$, but with CrO_3 in AcOH gives 2 : 3 : 6 : 7-*tetramethoxy*-9-*ethylanthranol* (?), red, m. p. 193°, or using more CrO_3 I, yellow, m. p. 344°. *m*-Hemipinic acid, veratrole, and $AlCl_3$ in CS_2 give 4 : 5 : 3′ : 4′-*tetramethoxy*-2-*benzoylbenzoic acid*, m. p. 222—223°, which when heated with 80% H_2SO_4 gives I.

R. S. Cahn.

Dehydration of *cis*- and *trans*-secondary cyclanols. G. Vavon and M. Barbier (Bull. Soc. chim., 1931, [iv], **49**, 567—582).—The rate of dehydration of secondary alcohols of the *cyclo*pentane, *cyclo*hexane, terpene, and aliphatic series by 3% of H_2SO_4 in Bu_2O at 120°, 140°, and 160° has been determined. The dehydration is normally autocatalytic, the rate finally decreasing progressively, whether H_3PO_4, I, or H_2SO_4 is used as catalyst. H_3PO_4 only dissolves slowly in Bu_2O and is less satisfactory than H_2SO_4. The gradual disappearance of I during the reaction leads to erratic results. Comparing the time required for 25% dehydration, *cyclo*pentanol and its homologues are dehydrated more readily than the corresponding *cyclo*hexanols; *e.g.*, at 140° in 45 min. with *cyclo*pentanol, and in 155 min. with *cyclo*hexanol. For the *trans*-*cyclo*pentanols at 120° the following are the comparative times: 1-propyl-, 72; 1-*iso*propyl-, 64; dipropyl-*cis*-*cis*-, 35; for *cis*-isomeride of dipropyl-*cis*-*cis*-*cyclo*pentanol, 25% dehydration is attained only in 75 min. at 120°. In all other cases examined the *cis*-isomeride is dehydrated much more rapidly than the *trans*. The 2-substituted *cyclo*hexanols are dehydrated more rapidly than the corresponding 4-derivatives; with the *trans*-1 : 2-*cyclo*hexanols the rate of dehydration increases with the substituent group in the order: Me, Et, Pr^a, Pr^β, Bu. With the *cis*-isomerides the rate of dehydration varies irregularly with the substituent alkyl group. Similarly, for the 1 : 4-*cyclo*hexanols the rate of dehydration increases in the order: Pr^β, Bu, *tert*.-Bu, for the *cis*- and *trans*-isomerides. These results are in contradiction with the assumption that the isomeride which dehydrates most readily is that in which the *tert*. OH group and the H atom eliminated are spatially closest together (*trans*-isomeride). Since the structures established from steric hindrance principles are based on various reactions yielding consistent results, and other evidence is available to show that the *cis*-structure favours the elimination of halogen or hydracid to give olefines, the assumption of *trans*-dehydration is rejected. The order of 25% dehydration at 160° of dibutylcarbinol (36 min.), *n*-butyl-*sec*.-butylcarbinol (12 min.), and di-*tert*.-butylcarbinol (3 min.) supports the same view, the last, which is the most readily dehydrated, alone containing no H atom in close relation to the OH group. The times of 25% dehydration of neomenthol (10 min. at 140°), menthol (30 min. at 160°), *iso*borneol (5 min. at 77°), and borneol (37 min. at 160°) are in agreement with results of other workers. R. BRIGHTMAN.

Heteropolarity. XIV. Constitution and colour. W. DILTHEY (Ber., 1931, 64, [*B*], 1280—1285).—The blue colour produced when triphenylmethyl chloride reacts with *p*-dianilinobenzene in CS_2 is due to the *salt* $C_6H_4(NHPh)_2,C_6H_4({:}NPh)_2,HCl$, m. p. 182—183°, which yields the *base* $C_{36}H_{30}N_4$, m. p. 132—135°. Presumably the colour obtained with the perchlorates of anisylcarbinols etc. depends on a similar cause (cf. A., 1928, 627; this vol., 487). H. WREN.

[Supposed *meri*quinonoid compounds from diphenyl-*p*-phenylenediamine and triarylcarbonium salts.] I. LIFSCHITZ (Ber., 1931, 64, [*B*], 1439—1440).—A reply to Schwechten (this vol., 835). H. WREN.

Intermediate products in the synthesis of greater di- and tri-arylmethane dyes. I. TOMIOKA (J. Soc. Chem. Ind., Japan, 1931, 34, 176—178B).—Dimethylaminobenzhydrol is formed as an intermediate product during the condensation of PhCHO and $NPhMe_2$ to give the leuco-base of malachite-green. Of the general methods for the formation of diarylmethane derivatives, the initial condensation occurs most easily in the reaction in which CH_2O is used, to give the diphenylmethane; the use of PhCHO giving the benzhydrol form and of BzCl to give the benzophenone derivative are reactions having a slower initial condensation. $NPhMe_2$ condenses with $PhCCl_3$ to give dichloro-*p*-dimethylaminodiphenylmethane much more easily than it condenses with BzCl, but not as easily as it does with PhCHO to give the benzhydrol. E. H. SHARPLES.

Monomethyl and monoethyl ethers of *p*-xylylene glycol. R. QUELET (Compt. rend., 1931, 192, 1391—1393).—Treatment of a *p*-xylylene glycol dialkyl ether (1·5 mols.) with AcCl (1 mol.) and a trace of $ZnCl_2$ replaces a single alkoxyl group by Cl, giving the corresponding *p*-alkoxymethylbenzyl chloride in almost quant. yield; this is either hydrolysed directly with dil. aq. NaOH at 150°, or converted into the acetate by heating with NaOAc and this hydrolysed with aq.-alcoholic NaOH. The following are described: p-*xylylene glycol monomethyl ether*, b. p. 152°/16 mm., d_4^{17} 1·076 (*phenylcarbamido*-derivative, m. p. 62°; *acetate*, b. p. 150°/16 mm., d_4^{20} 1·08; *chloride*, b. p. 125°/17 mm., d_4^{20} 1·095), and p-*xylylene glycol monoethyl ether*, b. p. 154°/16 mm., d_4^{17} 1·047. Small amounts of the monoalkyl ethers are also formed by action of KOH in 95% EtOH on ωω′-dichloro-*p*-xylene (the yield is not increased by use of more dil. EtOH), and during etherification, *e.g.*, by action of EtBr on the Na derivative of the glycol. H. A. PIGGOTT.

Dehydration by heat of *d*-α-phenyl-ββ-dibenzylethylene glycol (αγ-diphenyl-β-benzylpropane-αβ-diol). A. MCKENZIE and E. R. L. GOW (Bull. Soc. chim., 1931, [iv], 49, 709—715).—When dehydrated by slow distillation at 350—400 mm., *d*-α-phenyl-ββ-dibenzylethylene glycol yields *r*-αγ-diphenyl-α-benzylacetone; in presence of pumice 1-phenyl-2-benzylindene is also formed, and in presence of porous brick some dibenzyl ketone. In the latter case an oil, α_D +0·33°, not racemised by alcoholic KOH, and probably the *d*-glycol are also obtained. Since, however, *d*-αγ-diphenyl-α-benzylacetone is partly racemised by distillation, the semipinacolic dehydration of the glycol is not excluded. It is suggested that the *d*-ketone is formed first by semipinacolin dehydration: *d*-$C(CH_2Ph)_2(OH)\cdot CHPh\cdot OH \longrightarrow C(CH_2Ph)_2(\dot{O})\cdot\dot{C}HPh \longrightarrow$ *d*-$CH_2Ph\cdot CO\cdot CHPh\cdot CH_2Ph$, and subsequently racemised, the PhCHO formed in the distillation resulting from decomp. of the dibenzyl ketone. R. BRIGHTMAN.

Phenylsulphopropionic acids. I. C. H. K. MULDER and (MME.) M. A. VAN DAM-VEENHOVEN (Rec. trav. chim., 1931, 50, 719—724).—The action of K_2SO_3 on atropic acid, and treatment of the product with AcOH, gives *K H* β-*sulpho*-α-*phenylpropionate* (+H_2O), [*Ba* salt (+0·5H_2O)], converted into the *strychnine* (+3H_2O) and *brucine* (+6H_2O) salts. The strychnine salt (+2H_2O) of the pure *d*-acid is obtained after 10 crystallisations, the corresponding Ba salt having $[M]_D^{20}$+ 185°. The brucine salt after eight crystallisations leads to the Ba salt of the *l*-acid (not quite pure), $[M]_D^{20}$ −178°. The *d*-acid (not isolated) has $[M]_D^{20}$ +194°, not changed by conversion into the Na or Na H salt. Addition of K_2SO_3 to cinnamic acid leads to K H β-sulpho-β-phenylpropionate, from which the *quinine* (A,2B+5½H_2O), *strychnine* (A,2B +3½H_2O), and *brucine* (A,2B+6H_2O) salts are prepared. Fractional crystallisation of the quinine salt leads to the *l*-Ba salt, $[M]_D$ −14·8° (acid, not isolated, has $[M]_D$ +3·2°). Neutralisation of the latter with NaOH causes the rotation to rise slightly for the first mol. of NaOH and then to fall to −14° for the second mol. J. D. A. JOHNSON.

Preparation in a pure state and reactions of crystalline enolates. W. SCHLENK, H. HILLEMANN, and I. RODLOFF (Annalen, 1931, 487, 135—154).—Colourless, cryst. *Na enolates* of Me diphenylacetate (+0·5Et_2O), diphenylacetaldehyde (+Et_2O), and Me fluorene-9-carboxylate (A., 1928, 1037; not analysed) are obtained by interaction of the carbonyl compounds with CPh_3Na in Et_2O. They react with acyl chlorides etc. to form *C*-acyl derivatives, *e.g.*, $CPh_2{:}CH\cdot ONa+R\cdot COCl \longrightarrow CPh_2(COR)\cdot CHO+NaCl$, of which the following are described: (from diphenylacetaldehyde) *benzoyl-*, m. p. 98—99°; *acetyl-*, m. p. 59°; *benzyl-*, m. p. 85—87° (converted by MgPhBr into αββγ-tetraphenylpropyl alcohol), and *benzhydryl-diphenylacetaldehyde*, m. p. 159—160° ($CHPh_2Br$); *ethyl diphenylmalonaldehydate*, m. p. 65—66° ($Cl\cdot CO_2Et$); ββδδ-*tetraphenylpentan*-γ-*one*-αε-*dial*, m. p. 118—119° ($COCl_2$); ααββ-*pentaphenylpropaldehyde* (CPh_3Cl), m. p. 115—120° (with dissociation; also dissociated, yielding CPh_3-, in $Ph\cdot CO_2Et$); (from Me diphenylacetate) *Me benzoyl-*, m. p. 118° (also obtained in pyridine; gives with N_2H_4,H_2O a *substance*, m. p. 210°); *acetyl-*, m. p. 57° (N_2H_4,H_2O derivative, m. p. 90°); *benzyl-*, m. p. 125—127°; *carboxymethyl-*, m. p. 96°, and *benzhydryl-*, m. p. 110° (sinters 105°), *-diphenylacetates*; *Me* αα βββ-*pentaphenylpropionate*, (CPh_3Cl), m. p. 163° (from Me fluorene-9-carboxylate): *Me 9-benzoylfluorene-9-carboxylate*, m. p. 121°, and *Me fluorene*-9 : 9-*dicarboxylate* ($Cl\cdot CO_2Me$), m. p. 167°, hydrolysed by KOH in MeOH to fluorene-9-carboxylic acid. Benzoyldiphenylacetaldehyde and PhOH result from interaction of the enolate with $Ph{\cdot}CO_2Ph$, but no reaction occurs with PhCHO or $Et_2C_2O_4$; the Bz derivative gives with N_2H_4,H_2O 3 : 4 : 4-*triphenyl*iso*pyrazole* (?), m. p. 168—170° (decomp.; sinters 157°). The enolate of diphenylacetaldehyde gives with I an unstable *iodine* derivative which decomposes spontaneously into *tetraphenylsuccindialdehyde,* m. p. 127—128° (cyclic *azine,* $C_{28}H_{22}N_2$, m. p. 173—174°). The dialdehyde is reversibly dissociated into yellow radicals in $Ph{\cdot}CO_2Et$ or $C_{10}H_8$. The unstable I derivative of Me diphenylacetate decomposes into a *peroxide,* $C_{30}H_{26}O_6$, m. p. 151—153° (decomp.), of Me tetraphenylsuccinate, also obtained by action of Cu-bronze on Me diphenylchloroacetate in C_6H_6.

The action of Ph·NCO or Ph·NCS is analogous to that of acyl chlorides, *C*-phenyl-carbamido- or -thiocarbamido-derivatives being obtained, *e.g., formyldiphenylacetanilide,* m. p. 115—117°, and *Me phenylthiocarbamidodiphenylacetate,* m. p. 113—114°; the last-named is hydrolysed by MeOH–KOH to diphenylthioacetanilide. An impure specimen of *Me H diphenylmalonate,* m. p. 123° (decomp.), was obtained by action of CO_2 on the enolate of diphenylacetic acid; CS_2 gives carbomethoxydithioacetic acid [isolated as *Ag* salt $CPh_2(CO_2Me){\cdot}CS{\cdot}SAg$; *Bz* derivative, blue, m. p. 138°; *disulphide,* m. p. 173°].

ββββ′β′-*Pentaphenyl*iso*propyl alcohol,* m. p. 208—209° (*Ac* derivative, m. p. 211—213°), is obtained as a by-product in the reaction between $CHPh_2{\cdot}CHO$ and CPh_3Na; $CHPh_2{\cdot}CO_2Me$ and $CHPh_2Na$ similarly give $CHPh_2{\cdot}CO{\cdot}CHPh_2$. The *acetate* of benzpinacolin alcohol has m. p. 165°. The interaction of *Me* βββ-*triphenylpropionate,* m. p. 125°, with MgPhBr gives *Me* αβββ-*tetraphenylpropionate,* m. p. 240°; the *Et* ester, m. p. 219—220°, is similarly prepared.

H. A. Piggott.

Physical properties of optical antipodes. G. Kortüm (Ber., 1931, 64, [*B*], 1506—1510).—Contrary to Campbell and Garrow (A., 1930, 1289), measurable differences in the sp. rotation and solubility in H_2O are not observed with *d*- and *l*-mandelic acids if the preps. are sufficiently purified. H. Wren.

3-Methoxyphthalic acid. A. Corbellini and E. Rossi (Gazzetta, 1931, **61**, 281—285).—3-Nitrophthalic acid (A., 1925, 1066) on replacement of the NO_2-group by OH and treatment with CH_2N_2 gives 3-methoxyphthalic acid, m. p. 173—174° (anhydride, m. p. 160°). This confirms the work of Bentley and co-workers (J.C.S., 1907, **91**, 107), who describe 3-methoxyphthalic acid, m. p. 173—174° (anhydride, m. p. 160—161°), prepared by oxidation of 5-methoxy-α-naphthol, but disagrees with that of Jacobsen (A., 1883, 1124). E. E. J. Marler.

Unsaturated acids of the succinic series. P. Cordier (Ann. Chim., 1931, [x], **15**, 228—308; cf. this vol., 483).—Prolonged action of Ac_2O on αβ-di(aralkyl) derivatives of succinic acid containing one double linking gives derivatives of α-hydroxysuccinic anhydride by addition of AcOH and subsequent hydrolysis. The OH group so formed has acidic properties. Diphenylmaleic anhydride is unchanged by prolonged boiling with Ac_2O. α-Methoxybenzylidene-β-phenylethylsuccinic acid (A., 1929, 1273) is reduced to α-*methoxybenzyl*-β-*phenylethylsuccinic acid,* m. p. 98°, also obtained by reduction and hydrolysis of α-hydroxy-α-methoxybenzyl-β-phenylethylsuccinic anhydride (*loc. cit.*), the Me ether of which, when hydrolysed with KOH in EtOH, gives the same hydroxy-anhydride and α-methoxybenzylidene-β-phenylethylsuccinic acid. Hydrolysis of α-methoxy-αβ-dibenzylsuccinic anhydride (A., 1930, 915) with KOH in EtOH gives the corresponding hydroxy-anhydride (corr. m. p. 65°; cf. *loc. cit.*), and, by prolonged action, *dibenzylmaleic acid,* m. p. 80° (decomp.) (*anhydride,* m. p. 92°), reduced to *i*-dibenzylsuccinic acid. Dibenzylmaleic anhydride by prolonged action of Ac_2O gives α-hydroxy-αβ-dibenzylsuccinic anhydride. Condensation of anisaldehyde with benzylsuccinic acid gives α-*anisylidene*-β-*benzylsuccinic acid,* m. p. 154° (rapid heating) (*anhydride,* m. p. 124°), reduced to α-methoxybenzyl-β-benzylsuccinic acid, m. p. 160—161°. Prolonged treatment of the above anhydride with Ac_2O gives α-*hydroxy*-α-p-*methoxybenzyl*-β-*benzylsuccinic anhydride* (*Me ether,* m. p. 57°). A. A. Levi.

Colour changes of sulphonephthaleins, benzeins, and phthaleins. I. M. Kolthoff (J. Physical Chem., 1931, **35**, 1433—1447).—Mainly a discussion. The concentration of the lactone form in an aq. solution of phenolphthalein is approx. 10^4 times that of the carboxylic acid configuration. The colour change of the sulphonephthaleins in their alkaline range is quant. controlled by the equilibrium between the quinone and the quinone phenolate forms. α-Naphtholphthalein in aq. solution is present mainly as the quinonoid form. The colour change of the sulphonephthaleins, benzeins, and phthaleins in acid solution is attributed to the weak basic character of the quinone group. Moderately sol. benzeins can replace the corresponding sulphonephthaleins with advantage as indicators. L. S. Theobald.

Constitution of bile acids. XVI. Halogenated dehydrocholic acids and dehydrodeoxycholic acids. W. Borsche and K. Diacont (Z. physiol. Chem., 1931, **198**, 115—126; cf. this vol., 841).—ICl in AcOH with dehydrocholic acid (I) yields *di-iododehydrocholic acid,* m. p. 187—188° (decomp.) (*Me* ester, m. p. 220° (decomp.)], and (in small amount) *iododehydrocholic acid,* m. p. 158° (decomp.). Bromination in AcOH gives 2-bromodehydrocholic acid (II) [*Me* ester, m. p. 204° (decomp.), obtained by means of CH_2N_2 or by bromination of the ester of I]. Bromination of I in $CHCl_3$ yields a *product,* $C_{50}H_{67}O_{10}Br_3$, m. p. 175° (decomp.). II is oxidised by $KMnO_4$ to bilianic acid. Bromination of I in AcOH furnishes *tetrabromodehydrocholic acid,* m. p. 168—170°. Bromination of dehydrodeoxycholic acid (III) in AcOH gives a *product,* $C_{50}H_{69}O_7Br_3$, m. p. 125—126°. Bromination of the Me ester of III with 1 mol. of Br gives *Me dibromodehydrodeoxycholate,* m. p. 186°, and with 4 mols. of Br, *Me tribromodehydrodeoxycholate,* m. p. 168—169°.

J. H. Birkinshaw.

Constitution of bile acids. XVII. Action of phosphorus pentachloride on some keto-acids of the bile acid group. A new way into the lithocholic acid series. W. Borsche and A. L.

MORRISON (Z. physiol. Chem., 1931, **198**, 165—180; cf. preceding abstract).—Lassar-Cohn's "*iso*dehydrocholal" (A., 1892, i, 741) proves to be 3-*chloro*-7 : 13-*diketocholenic acid*, m. p. 252° (*Me* ester, m. p. 193°; *dioxime* of Me ester, m. p. 257°). Decomp. of the reduction product from dehydrocholic acid and PCl_5 with MeOH instead of alkali gave a mixture of Me chlorodiketocholanate and *Me dichlorodiketocholanate*, m. p. 148° (*dioxime*, m. p. 264—265°). The latter separated on keeping the mixture. The acid mixture obtained by hydrolysis when heated above its m. p. until no more HCl was evolved gave chlorodiketocholenic acid. The latter with H_2SO_4 gave dehydrocholic acid, and by Clemmensen reduction, *chloro*-3-*cholenic acid*, m. p. 174—175° (*Me* ester, m. p. 120°; *disemicarbazone*, unchanged at 300°). Chlorocholenic acid with H_2SO_4 yielded *dehydrolithocholic acid*, m. p. 140—141° (*Me* ester, m. p. 116—117°; *oxime* of Me ester, m. p. 148°), which with HNO_3 gave lithobilianic acid, m. p. 276°.

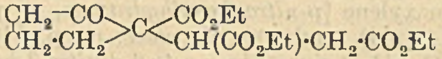
From dehydrodeoxycholic acid by the method outlined, *chloro*-3-*keto*-7-*cholenic acid*, m. p. 195—199° (*Me* ester, m. p. 131—135°), was obtained. Diketo-7 : 13-cholanic, bilianic, *iso*bilianic, and deoxybilianic acids by similar treatment gave corresponding acid chlorides, which were converted by MeOH into the esters. J. H. BIRKINSHAW.

Constitution of bile acids. XXXVI. *apo*-Cholic acid. H. WIELAND and V. DEULOFEU (Z. physiol. Chem., 1931, **198**, 127—134; cf. this vol., 841).—Thermal decomp. of *apo*cholic acid (I) at about 340° yields a β-*cholatrienic acid*, m. p. 131—133°, in which only two double linkings are saturated by hydrogenation, giving β-*cholenic acid*, m. p. 142—143°, but a small amount of cholanic acid is also formed as by-product. Oxidation of I with perbenzoic acid gives dihydroxycholadienic acid, which on reduction forms β-*apo*cholic acid (cf. A., 1922, i, 1027).

J. H. BIRKINSHAW.

Ursodeoxycholic acid. IV. K. KAZIRO (Z. physiol. Chem., 1931, **197**, 206—212; cf. A., 1930, 89).—Thermal decomp. of ursodeoxybilianic acid (I) yields a *pyro-acid* (II), m. p., 182° (*Me* ester, m. p. 129—131°), a cyclic ketone, by loss of CO_2 and H_2O. The acid ester of I (m. p. 150—152°) gives the same pyro-acid (II). The *Me*$_3$ ester of I, m. p. 94°, on distillation furnishes an *isomeride*, m. p. 69—70°. The open ring of I is a six-C ring. J. H. BIRKINSHAW.

Synthesis of substances analogous to bile acid degradation products. I. Methods of attachment of carboxylated side-chains to the *cyclo*pentane nucleus. J. W. BAKER (J.C.S., 1931, 1546—1556).—Attempts to synthesise substances possessing the structures considered probable for the acids $C_{13}H_{20}O_6$ and $C_{16}H_{24}O_8$ (A., 1928, 1007; 1930, 1435) obtained from cholesterol etc. were unsuccessful, but several substances similar to, or possibly derivable from, them were prepared. Modified directions are given for the prep. of Et β-methylbutane-αβδ-tricarboxylate, which with "mol." Na in C_6H_6 gave *Et* 3-*methyl*cyclo*pentanone*-2 : 3-*dicarboxylate* (I), b. p. 130—134°/2—2·5 mm. (gives no semicarbazone) (cf. A., 1918, i, 22). The structure of I is proved by oxidation with alkaline $KMnO_4$ to α-methylglutaric acid, α-hydroxy-α-methylglutaric acid (*Ag* salt), and a little succinic acid. I is only partly ethylated by alcoholic NaOEt and EtI or Et_2SO_4, but with $NaNH_2$ and EtI yields *Et* 3-*methyl*-2-*ethyl*cyclo*pentanone*-2 : 3-*dicarboxylate* (II), b. p. 135°/3 mm. (*hydrazone dihydrazide*, m. p. 163°), the constitution of which is proved by hydrolysis to γ-*methyl*-n-*hexane*-αγδ-*tricarboxylic acid*, m. p. 155° (*Ag* salt). II does not condense with Zn and Et α-bromopropionate in C_6H_6. Et dimethylacetoacetate, Et α-bromopropionate, and Zn in C_6H_6 yield *Et* β-*hydroxy*-ααα'β-*tetramethylglutarate*, b. p. 125—127°/6 mm., which on reduction by Clemmensen's method or on treatment with PCl_5 followed by alcoholic KOH affords ααα'β-*tetramethylglutaconic acid*, m. p. 128° (*Ag* salt). This on reduction in AcOH with H_2 and Pt-black gives ααα'β-*tetramethylglutaric acid*, m. p. 121°. The sodio-derivative of II with Et fumarate in EtOH gives a *substance*, b. p. 124—126°/8 mm. (hydrolysed to adipic acid), but with Et bromosuccinate gives *Et* 2-*carbethoxy*-1-*keto*cyclo*pentyl*-2-*succinate* (III), b. p. 211—215°/10 mm., which with boiling conc. HCl gives 1-*keto*cyclo*pentyl*-2-*succinic acid*, m. p. 138—139° (*anhydride*, m. p. 116°).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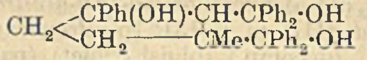

(IV.)

II with excess of MgPhBr gave a substance, m. p. 231°, possibly IV. Et γ-bromo-*n*-valerate does not condense with the 5-sodio-derivative of Et 2-methyl*cyclo*pentanone-2-carboxylate. R. S. CAHN.

Properties of benzaldehyde. J. R. POUND (J. Physical Chem., 1931, **35**, 1496—1497).—Values of d^{30}, n^{20}, and η^{30} for PhCHO containing up to 14·01 wt.-% BzOH are given; probable values for pure PhCHO are d_4^{30} 1·0365, d_4^{14} 1·0567, η^{30} 0·01296, and n_D^{20} 1·5460. L. S. THEOBALD.

Basic properties of hydrazones. R. CIUSA and G. OTTOLINO (Gazzetta, 1931, **61**, 189—190; cf. A., 1922, i, 474).—On passing gaseous HCl into hot solutions of aromatic arylhydrazones or by boiling these compounds with conc. HCl, green, resinous substances separate. By treating an equimol. mixture of benzaldehydephenylhydrazone and PhCHO or PhCHO (2 mols.) and phenylhydrazine (1 mol.) with $ZnCl_2$ (Giacalone's method) a green product with a golden lustre is obtained. The substance obtained by crystallisation from glacial AcOH is a *zincichloride* of the *compound* $C_{33}H_{26}N_4$, which is regarded as the base of a triphenylmethane dye,

$CHPh{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}N{\cdot}N{:}CHPh$.

O. F. LUBATTI.

Condensation of aldehydes with hydrazones. IV. Condensation of benzaldehyde with salicylaldehydephenylhydrazone. A. GIACALONE (Gazzetta, 1931, **61**, 301—305; cf. A., 1930, 213; this vol., 222).—In presence of $ZnCl_2$, PhCHO (1 mol.) condenses with salicylaldehydephenylhydrazone (2 mols.), giving the *bisphenylhydrazone* (I), m. p. 210° (*Bz*$_4$ derivative, m. p. 125—126°), of 4 : 4'-*dihydroxytriphenylmethane*-3 : 3'-*dialdehyde*,

$CHPh[C_6H_3(OH){\cdot}CHO]_2$, m. p. 55°, obtained by condensing PhCHO with salicylaldehyde in presence of H_2SO_4. Condensation of salicylaldehyde with

dihydrazinotriphenylmethane in AcOH gives 4 : 4′-bis-*o*-hydroxybenzylidenedihydrazinotriphenylmethane, $CHPh(C_6H_4\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OH)_2$, m. p. 115—116° ($Bz_4$ derivative, m. p. 205—206°), isomeric with I.
E. E. J. Marler.

Nitration of brominated 3-hydroxybenzaldehydes and bromination of nitrated 3-hydroxybenzaldehydes, with cases of group migration. H. H. Hodgson and E. W. Smith (J.C.S., 1931, 1500—1508).—The following nitrations are by HNO_3 (*d* 1·42), unless otherwise stated. Colours given in parentheses are produced (1) by KOH on the solution in EtOH, and (2) by conc. H_2SO_4 on the solid. Mercuriacetato-3-hydroxybenzaldehyde with Br in Ac_2O gives 2-bromo-3-hydroxybenzaldehyde, m. p. 148° (not 141—142°, A., 1925, i, 674) (I), which yields 2-*bromo*-4-*nitro*-3-*hydroxybenzaldehyde*, yellow, m. p. 176° [p-*nitrophenylhydrazone*, m. p. 265° (bluish-violet) (orange)], and 2-*bromo*-6-*nitro*-3-*hydroxybenzaldehyde*, buff, m. p. 174° [p-*nitrophenylhydrazone*, m. p. 230° (pale red) (no colour)], both of which with Br in EtOH give 2 : 4-*dibromo*-6-*nitro*-3-*hydroxybenzaldehyde* (II), m. p. 148° and m. p. 152·5° after long boiling in xylene [p-*nitrophenylhydrazone*, m. p. 249° (decomp.) (red) (amber); *Me ether*, m. p. 119°]. I with HNO_3 (*d* 1·5) gives 2-*bromo*-4 : 6-*dinitro*-3-*hydroxybenzaldehyde* (III), m. p. 131° [p-*nitrophenylhydrazone*, m. p. 242° (decomp.) (bluish-violet) (pale yellow)]. 4-Bromo-3-hydroxybenzaldehyde with HNO_3 and H_2O (7 : 3) gives 4-*bromo*-2-*nitro*-3-*hydroxybenzaldehyde* (IV), m. p. 167° [p-*nitrophenylhydrazone*, m. p. 205°, (purple) (yellowish-brown)], and 4-*bromo*-6-*nitro*-3-*hydroxybenzaldehyde* (V), m. p. 72° [p-*nitrophenylhydrazone*, m. p. 271° (purple) (amber)], and with HNO_3 (*d* 1·42) 4-*bromo*-2 : 6-*dinitro*-3-*hydroxybenzaldehyde* (VI) [p-*nitrophenylhydrazone*, m. p. 226° (decomp.) (violet) (amber)]. 6-Bromo-3-hydroxybenzaldehyde gives 6-*bromo*-4-*nitro*-3-*hydroxybenzaldehyde* (VII), m. p. 118° [p-*nitrophenylhydrazone*, m. p. 236° (blue) (red)], and with HNO_3 (*d* 1·5) 6-*bromo*-2 : 4-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 129° [p-*nitrophenylhydrazone*, m. p. 256° (greenish-blue) (red)]. VII with hot dil. HNO_3 yields III. 4 : 6-Dibromo- and 2 : 4 : 6-tribromo-3-hydroxybenzaldehyde give II. 2-Nitro-3-hydroxybenzaldehyde with Br in $CHCl_3$ gives IV, and in EtOH 4 : 6-*dibromo*-2-*nitro*-3-*hydroxybenzaldehyde*, m. p. 140° (decomp.) [p-*nitrophenylhydrazone*, m. p. 218° (decomp.) (purple) (amber)], which yields VI. 4-Nitro-3-hydroxybenzaldehyde cannot be monobrominated, but in suspension in H_2O gives 2 : 6-*dibromo*-4-*nitro*-3-*hydroxybenzaldehyde* (VIII), m. p. 95° [p-*nitrophenylhydrazone*, m. p. 242° (brownish-purple) (yellowish-brown)], also obtained by bromination of VII in EtOH, and transformed by HNO_3 into III. 6-Nitro-3-hydroxybenzaldehyde with Br in EtOH gives II. VI and III are obtained on bromination of 2 : 6- and 4 : 6-dinitro-3-hydroxybenzaldehydes, respectively; 2 : 6-dinitro-3-hydroxybenzaldehyde has m. p. 106°, previously assigned (A., 1927, 1075) to the 4 : 6-isomeride. A modified method of nitrating 6-nitro-3-hydroxybenzaldehyde is given. 4-Nitro-3-hydroxybenzaldehyde with HNO_3 (98%) gives 4 : 6-dinitro-3-hydroxybenzaldehyde, m. p. 104°, previously designated (*loc. cit.*) the 2 : 6-dinitro-compound. The group migrations are discussed on the basis of electronic theories. II exists in three isomeric forms, which are accounted for by co-ordination, or lack of it, between the bromo-hydroxy- and nitro-aldehydo-groups.
R. S. Cahn.

α-Amylcinnamaldehyde. A. A. Rosenthal (Deut. Parfümerieztg., 1931, **17**, 3—5; Chem. Zentr., 1931, i, 2047).—Condensation of PhCHO with heptaldehyde affords α-amylcinnamaldehyde (α-benzylideneheptaldehyde), b. p. 140°/5 mm., α-amylnonenaldehyde, b. p. 130°/5 mm., and products of condensation of these substances with heptaldehyde. When kept in contact with air PhCHO is oxidised five times, and α-amylnonenaldehyde twice, as rapidly as α-amylcinnamaldehyde, for which a specification is proposed.
A. A. Eldridge.

Manufacture of odoriferous substances [cyclic acetals]. I. G. Farbenind. A.-G.—See B., 1931, 710.

Manufacture of aromatic *N*-dialkylaminoalkylaminoaldehydes and derivatives. I. G. Farbenind. A.-G.—See B., 1931, 622.

1-4-*iso*Propyl-Δ^2-*cyclo*hexen-1-one. R. S. Cahn, A. R. Penfold, and J. L. Simonsen (J.C.S., 1931, 1366—1369).—The oil from *Eucalyptus cneorifolia* contains 1-4-iso*propyl*-Δ^2-cyclo*hexen*-1-*one* (I), b. p. 98—100°/10 mm., α_D −59·3° to −66·4° (*semicarbazone*, decomp. 185°; p-*nitrophenylhydrazone*, m. p. 168—169°), the constitution of which is proved by its giving a H_2S compound, decomp. 82°, and on reduction electrolytically and catalytically in the presence of Pd-charcoal 4-*iso*propyl*cyclo*hexanone (A., 1908, i, 424) (*semicarbazone*, m. p. 188—189°; p-*nitrophenylhydrazone*, m. p. 123—124°), oxidised by CrO_3 to β-*iso*propyladipic acid. Electrolytic reduction gave also a little 4-*iso*propyl*cyclo*hexanol (A., 1906, i, 194) (*phenylurethane*, m. p. 75—77°). There is no means of separating I from cryptal (J.C.S., 1922, **121**, 266), which has been isolated only from *E. hemiphloia*. The oil of *E. polybractea* contains (I). I may be derived from β-phellandrene or cryptal.
R. S. Cahn.

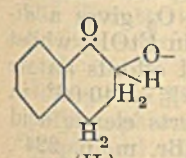
***cyclo*Hexane-*spiro*-*cyclo*butanone.** G. A. R. Kon (J.C.S., 1931, 1604).—The statements of Vogel this vol., 727) regarding the prep. of *cyclo*hexane-*spiro*-*cyclo*butane and the corresponding *cyclo*heptane derivative are incorrect (cf. J.C.S., 1922, **121**, 513).
R. S. Cahn.

Preparation of hydrobenzoin, and the system benzoin–hydrobenzoin. P. Carré and P. Mauclère (Compt. rend., 1931, **192**, 1393—1395).—Benzoin is not reduced by $SnCl_2$ and HCl in EtOH at 100° (cf. A., 1904, i, 510), and is converted by Sn and aq. HCl into deoxybenzoin. It is readily reduced to hydrobenzoin in good yield by Ni (formed by reduction at 280°) and H in EtOH at 125—160°/150 atm. if carefully freed from cyanide, which poisons the catalyst. Data are given for the m. p.–composition relationship of benzoin and hydrobenzoin. During the reduction of PhCHO to hydrobenzoin by Zn and HCl (cf. A., 1928, 64) a *substance*, $C_{14}H_{12}O$, m. p. 85°, which differs from both of the known stereoisomeric forms of diphenylethylene oxide, is formed.
H. A. Piggott.

Formation of mixed benzoins. Influence of the nature of the cyclic radicals. Tiffeneau and (Mlle.) J. Levy (Bull. Soc. chim., 1931, [iv], 49, 725—740).—Of seven pairs of aldehydes only the two pairs, PhCHO–*m*-methoxybenzaldehyde and anisaldehyde–piperonal, in which the aryl radicals are equal or similar in their affinity capacity, yield a mixture of two isomeric benzoins. Except the pair PhCHO–*o*-anisaldehyde, the other pairs yield a single mixed benzoin in which the radical with the higher affinity capacity is linked to the CO group, and this is regarded as the general rule when the aryl radicals differ considerably in affinity capacity. In the simple benzoin condensation aromatic aldehydes in which the aryl radical has a high affinity capacity give low yields of the benzoin.

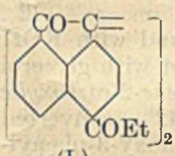
PhCHO and *o*-methoxybenzaldehyde with alcoholic KCN yield benzoyl-*o*-methoxyphenylcarbinol (semicarbazone, m. p. 175—176°) and very small quantities of benzoin, the former with alcoholic KOH yielding BzOH and on hydrogenation *o*-methoxyphenylacetophenone. PhCHO and *m*-methoxybenzaldehyde similarly afford a mixture of two isomeric benzoins, m. p. 184°, semicarbazones, m. p. 99—102° and 80°, which could not be separated, and with alcoholic KOH yield a mixture of BzOH and *m*-methoxybenzoic acids. PhCHO and anisaldehyde yield anisobenzoin, m. p. 105·5—106·5° (semicarbazone, m. p. 185—186°; oxime, m. p. 136—138°); PhCHO and piperonal, piperobenzoin, m. p. 120—121° (semicarbazone, m. p. 181—182°; oxime, m. p. 156°), converted into *benzyl piperonyl ketone* (*semicarbazone*, m. p. 171°) on hydrogenation, together with a little benzoin. PhCHO and furfuraldehyde yield furobenzoin (furoylphenylcarbinol), m. p. 135° (*semicarbazone*, m. p. 192—193°; *oxime*, m. p. 165—166°), and a little benzoin, and anisaldehyde and *o*-methoxybenzaldehyde give 70% of p-*anisoyl*-o-*methoxyphenylcarbinol*, m. p. 101—102° (*semicarbazone*, m. p. 204°; *oxime*, m. p. 138—139°), also obtained from Mg anisyl bromide and *o*-methoxybenzaldehydecyanohydrin. Anisaldehyde and piperonal yield a little piperoanisoin, anisopiperoin, m. p. 110—111°, and a substance, m. p. 75°, probably a mixture of the anisopiperoin and piperoanisoin. R. Brightman.

Oxidation processes. V. Autoxidation of 2-hydroxy-1-ketotetrahydronaphthalene. A. Weissberger and W. Schwarze (Annalen, 1931, 487, 53—61).—The autoxidation of 2-hydroxy-1-ketotetrahydronaphthalene (I) in alkaline solution is a unimol. reaction similar in velocity, and in the linear relationship of velocity to alkali concentration, to that of other α-hydroxyketones (cf. A., 1930, 475), and therefore most probably proceeds in the stages: (1) formation of the ion (II), (2) rearrangement into the ion of 1 : 2-dihydroxy-3 : 4-dihydronaphthalene (III), (3) oxidation of this to 1 : 2-diketotetrahydronaphthalene (IV), (4) enolisation to 1 : 2-dihydroxynaphthalene (V), and (5) oxidation to 2-hydroxy-1 : 4-naphthoquinone (VI). The final velocity is determined by stage 1. The presence of excess of O_2 is necessary for the final stage, which proceeds at 5—7 times the velocity of the overall reaction and is dependent on alkali concentration. The indigo-blue coloration observed in aq. Na_2CO_3 but not in aq. NaOH and destroyed by shaking with air is probably due to quinhydrone formation from III and IV, its non-appearance in NaOH being the result of rapid enolisation of III. The formation of dinaphthyl derivatives in presence of insufficient O_2 for complete oxidation (cf. A., 1925, 1155) is due to the oxidation of V to 1 : 2 : 1′ : 2′-tetrahydroxy-4 : 4′-dinaphthyl (VII) by the H_2O_2 produced in the second stage; in presence of excess of O_2 oxidation to VI occurs without intermediate formation of VII on account of the greater rapidity of this reaction. The autoxidation of V to VII also produces H_2O_2, and to explain the yield of VII in relation to the O_2 used the activation of mol. O_2 is suggested (cf. this vol., 604). H. A. Piggott.



(II.)

Syntheses and transformations of 3-propionyl- and 3:4-dipropionyl-acenaphthene. K. Dziewoński and J. Moszew (Rocz. Chem., 1931, 11, 415—425).—3-*Propionylacenaphthene*, m. p. 69·5—70° (*picrate*, m. p. 109°: 4-*nitro*-derivative, m. p. 164—165°), is prepared from EtCOCl and acenaphthene in the presence of $AlCl_3$. 3-*Propionamidoacenaphthene*, m. p. 150—151°, and 3-*aminoacenaphthene*, m. p. 108—109°, are prepared from its *oxime*, m. p. 185—186°; on oxidation it yields 3 : 3′-*dipropionylbisacenaphthenedione* (I), m. p. 286°, and 4-*propionylnaphthalic acid*, m. p. 152—153° (*imide*, m. p. 221—222°; *diphenylhydrazone*, m. p. 192—193°). 2-*Acenaphthyl*-3-*methylindole*, m. p. 179° (*dipicrate*, m. p. 148°), is prepared from the *phenylhydrazone* of 3-propionylacenaphthene, m. p. 107°. 3 : 4-*Dipropionylacenaphthene*, m. p. 122—123° (*picrate*, m. p. 129°), formed together with the monopropionyl derivative, yields a *dioxime*, m. p. 143°, from which 3 : 4-*dipropionyldiaminoacenaphthene*, m. p. 181—182°, is obtained by the Beckmann change. R. Truszkowski.



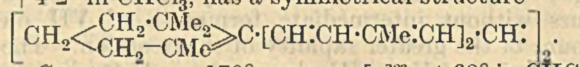
(I.)

Manufacture of [1 : 4 : 5 : 8-tetra-amino-] derivatives of anthraquinone. Soc. Chem. Ind. in Basle.—See B., 1931, 623.

Vitamin of growth. I. Separation of carotene into its components. R. Kuhn and E. Lederer (Ber., 1931, 64, [B], 1349—1357; cf. this vol., 733).—Optically active carotene preparations are obtained from *Daucus carota*, *Sorbus aucuparia*, and *Aesculus hippocastanum*. Almost inactive preparations are derived from fresh-winter spinach and preserved stinging nettle. Fractional precipitation of carotene with I removes a large proportion of the inactive material as the iodide; the residual hydrocarbon is purified by adsorption with Al_2O_3. Inactive carotene (β-carotene) is isolated by adsorption of feebly active initial materials or, less readily, from the di-iodide. α-Carotene has m. p. 174—175°, $[\alpha]_{Cd}^{20}$ +380°, whilst β-carotene has m. p. 181—182°, $[\alpha]_{Cd}^{20}$ +0°; the absorption bands in CS_2 are respectively 511 and 478 mμ and 521 and 485·5 mμ. Crystallographic data are given. Karrer's formula in which two β-ionone residues are placed at the ends of a dehydrogenated chain of isoprene residues may be applicable to β-carotene. In α-carotene the ends of the polyene chain are probably attached to α-ionone rings, the asymmetric C atoms of which are responsible for the optical activity of the hydrocarbon.

H. Wren.

Carotene isomerides. P. Karrer, H. von Euler, and H. Hellström (Arkiv Kemi, Min., Geol., 1931, **10**, B, No. 15, 6 pp.; cf. this vol., 846).—Carotene from carrots is a mixture of two isomerides distinguishable by solubility, optical activity, and m. p. β-*Carotene*, m. p. 181—182° (uncorr.), $[\alpha]^{22}_{6080}$ $+4\cdot2°$ in $CHCl_3$, has a symmetrical structure



$$\left[CH_2\Big<\begin{matrix}CH_2\cdot CMe_2\\ CH_2-CMe\end{matrix}\Big>C\cdot[CH{:}CH\cdot CMe{:}CH]_2\cdot CH{:}\right]_2.$$

α-*Carotene*, m. p. 170° approx., $[\alpha]^{23}_{6080}$ $+68°$ in $CHCl_3$, is asymmetric. The $SbCl_3$ reagent with the two isomerides gives solutions with the same absorption spectrum directly after mixing, but after 1 hr. there is a considerable difference. The spectrum of the β-isomeride is nearer to the red end than that of the α-isomeride both in true (CS_2) and colloidal solution.

F. O. Howitt.

Constitution of hydrangenol and phyllodulcin. IV. Synthesis of phyllodulcin dimethyl ether. Y. Asahina and J. Asano (Ber., 1931, **64**, [*B*], 1252—1256; cf. A., 1930, 1442).—Homoveratric acid is converted by 3-methoxyphthalic anhydride and NaOAc at 180—190° into 7 : 3′ : 4′-*trimethoxybenzylidenephthalide*, m. p. 184°, reduced by Na and aq. EtOH to 7 : 3′ : 4′-*trimethoxybenzylphthalide*, m. p. 142°. Hydrolysis of the last-named compound with KOH in MeOH and treatment of the product with glycerol at 180° affords 3 : 3′ : 4′-*trimethoxystilbene*-2-*carboxylic acid*, m. p. 172° (*Me* ester, m. p. 142°), converted by conc. H_2SO_4 into 8 : 3 : 4′-trimethoxy-3-phenyl-3 : 4-dihydro*iso*coumarin, m. p. (unstable form) 105°, (stable variety) 125°, identical with *dl*-phyllodulcin dimethyl ether. *dl*-Phyllodulcin is transformed by KOH in glycerol at 180—200° into 6-*hydroxy*-2 : 3′-*hydroxy*-4′-*methoxystyrylbenzoic acid*, m. p. about 165° after softening at 130°, converted by diazomethane into *Me* 3 : 3′ : 4′-*trimethoxystilbene*-2-*carboxylate*, m. p. 142°, hydrolysed to 3 : 3′ : 4′-trimethoxystilbene-2-carboxylic acid, m. p. 172°. Optically active phyllodulcin is racemised by hot aq. or alcoholic HCl. Only *d*- and *dl*-phyllodulcin occur in *Amatscha* leaves; the name *iso*phyllodulcin should be deleted from the literature.

H. Wren.

Shellac. VI. Separation of aleuritic and shellolic acids. W. Nagel (Wiss. Veröff. Siemens-Konz., 1931, **10**, [2], 108—118; cf. B., 1928, 376).—The finely-divided resin is kept mixed with NaOH for 2 days. The resulting solution is diluted, saturated with CO_2, and evaporated. The residue is extracted with 96% EtOH, the solvent distilled off, and steam blown through the residual liquid, which is then diluted and treated several times with a 5% solution of $Ba(OH)_2$ followed by a current of CO_2 and filtration of the $BaCO_3$ etc. The resulting solution of Na salts is evaporated and the acids are liberated by addition of H_2SO_4; the pasty mass is extracted with Et_2O, which removes all the decomp. products of the shellac with the exception of aleuritic acid. The residue is therefore purified by recrystallisation and the shellolic acid recovered from the Et_2O solution is purified by direct esterification of the ether-moist acid. The following derivatives of aleuritic acid are described: *triacetylmethyl* ester, b. p. 232—234° (0·2 mm.), *hydrazide*, m. p. 139—140°, *azide*, decomp. 50°, NN′-*bistrihydroxypentadecylcarbamide*, m. p. 122—123°, *trihydroxypentadecylurethane*, m. p. 73—74°, *trihydroxydecylamine*, m. p. 110—120° (not sharp). The *Zn*, *Ba*, and K salts of aleuritic and shellolic acid have also been prepared.

A. R. Powell.

Theelin. Physical and chemical properties. S. A. Thayer, L. Levin, and E. A. Doisy (J. Biol. Chem., 1931, **91**, 791—801).—In agreement with Butenandt (A., 1930, 1480), the follicular hormone, theelin, highest m. p. 254—257°, I val. 95·1 (*ibid.*, 1069) (*monomethyl ether*, m. p. 165°), is a ketomonohydric alcohol $C_{18}H_{21}O(OH)$ containing one double linking. The Ac derivative, m. p. 125·3°, and oxime, m. p. 229° (decomp.), are described.

J. W. Baker.

Resin of *Garcinia mangostana*. II. O. Dragendorff (Annalen, 1931, **487**, 62—79).—The freshly extracted sap of the stem and unripe fruits of *G. mangostana* do not contain β-mangostin (cf. A., 1930, 1578); that from the latter is also free from the sterol and essential oil. Analyses of the *tetrabromide*, $C_{21}H_{25}O_5Br_4$, decomp. 200°, p-*nitrobenzoate*, m. p. 147°, and *nitrohexahydromethylmangostin*, m. p. 127° (prepared with HNO_3 of *d* 1·1), agree better with the formula $C_{21}H_{24}O_5$ than that already proposed (*loc. cit.*). The Ac derivative previously described is actually the Ac_3 derivative, m. p. 133—134°, and is converted by H_2 and PtO in AcOH into a *hexahydro*-derivative, m. p. 123—124°; as Zerevitinov's method indicates only two active H in mangostin, and one in methylmangostin, the introduction of the third Ac group must be due to enolisation. The action of perbenzoic acid on mangostin indicates three double linkings, in accordance with the above formula. Oxidation of hexahydromethylmangostin with CrO_3 in AcOH gives *iso*hexoic acid and neutral substances, and of mangostin or methylmangostin with cold alkaline $KMnO_4$ α-hydroxy*iso*butyric acid. Methylmangostin is converted by O_3 in CCl_4 into a cryst. *ozonide* and acetone peroxide; the former on hydrolysis gives a *substance*, $C_{15}H_{14}O_6$, m. p. 199° (*oxime*, m. p. 207°), unaffected by CH_2N_2 or Br, but oxidised by alkaline $KMnO_4$.

H. A. Piggott.

Elemic acid from Manila elemi resin. II. H. Lieb, M. Mladenović, and (in part) F. Gstirner and M. Sobotka (Monatsh., 1931, **58**, 59—68).—Reduction of elemic acid, m. p. 221°, with H_2 and Pd in AcOH at 960 mm. gives dihydroelemic acid, $C_{30}H_{50}O_3$, m. p. 238°, $[\alpha]^{19}_{D}$ $-12\cdot36°$ in $CHCl_3$ (not $C_{27}H_{44}O_3$; cf. A., 1928, 412). Other derivatives also confirm the C_{30} constitution. Thus O_3 gives a *diozonide*, decomp. 199°, $[\alpha]^{19}_{D}$ $-30\cdot17°$ in EtOH, whilst with Ac_2O and pyridine, elemic acid affords an *Ac* derivative $C_{32}H_{50}O_4$, m. p. 225° $[\alpha]^{20}_{D}$ $-40\cdot06°$ in $CHCl_3$. Anhyd. HBr in Et_2O converts elemic acid into *bromohydroelemic acid*, $C_{30}H_{49}O_3Br$, m. p. 224°, whilst Br in Et_2O affords *dibromoelemic acid*, m. p. 207°, $[\alpha]^{20}_{D}$ $-17\cdot14°$ in $CHCl_3$, converted by KOH in

MeOH into *bromoelemic acid*, $C_{30}H_{47}O_3Br$, m. p. 285°. Since analysis of elemic acid itself even after repeated crystallisation corresponds with the C_{27} formula, it must be contaminated with another acid of lower C content which can be removed only by conversion into derivatives (cf. following abstract).

J. W. Baker.

New resin acid from Manila elemi resin. I. M. Mladenović and H. Lieb (Monatsh., 1931, **58**, 69—72).—Fractional crystallisation of elemic acid from EtOH affords the less sol. *γ-elemic acid*, $C_{30}H_{50}O_3$, m. p. 281°, $[\alpha]_D^{20}$ +68·76° in MeOH (*K* salt $+2H_2O$; *Ac* derivative, m. p. 180°, $[\alpha]_D^{20}$ +59·17° in EtOH), which contains one OH and one CO_2H group, does not add Br, and is differentiated from the α-acid by its ready solubility in most org. solvents except MeOH and EtOH.

J. W. Baker.

Reactions of *g*- and *k*-strophanthin. L. Ekkert (Pharm. Zentr., 1931, **72**, 388—389).—The addition of a few drops of aq. Cl, aq. Br, an acid solution of NH_2Cl, or a solution of neomagnol to an alkaline solution of *g*- or *k*-strophanthin in presence of β-naphthol produces successively a wine-red, a ruby-red, and in 15 sec. a yellow colour. At the junction of an alcoholic solution of α-naphthol and conc. H_2SO_4 *g*-strophanthin produces an intense reddish-violet ring; after mixing, the liquid is carmine, whereas *k*-strophanthin gives a garnet-red ring, and after mixing a violet-red liquid.

C. C. N. Vass.

Microchemistry of artemisin and santonin sublimates. C. van Zijp (Pharm. Weekblad, 1931, **68**, 526—535, 615—616).—Reactions and methods of differentiation of artemisin and santonin are discussed. If the sublimate is liquid, gently breathing upon it causes the appearance of quadratic crystals only if artemisin is present, whilst if a drop of water is added to the sublimate santonin crystallises much more readily than does artemisin. The product of the reaction between HI containing I and santonin is sparingly sol. in H_2O, whilst that derived from artemisin is readily sol. Finally, cryst. artemisin, but not santonin, when treated with 10% KI + I solution, yields dichroic brown–dark brown prismatic crystals.

H. F. Gillbe.

Isoprene and caoutchouc. XXXIII. Terminal groups in caoutchouc. H. Staudinger (Ber., 1931, **64**, [*B*], 1407—1408).—The determination of mol. wt. by the behaviour of terminal groups is not possible in the case of caoutchouc in which they form only an insignificant part of the mol.

H. Wren.

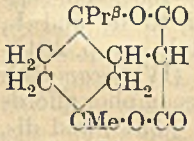
Polymorphism of guttapercha hydrocarbons. H. Mark and G. von Susich (Naturwiss., 1931, **19**, 399—400).—For the α- and β-modifications of the isoprene complex occurring in guttapercha and balata, the "röntgenographic m. p.," *i.e.*, temp. at which crystal interference patterns disappear, are 64—66° and 55—57°, respectively. The phase diagram, determined röntgenographically, indicates that the polymorphism of guttapercha hydrocarbons is monotropic and that under suitable conditions of heating and cooling both changes, $\alpha \rightleftharpoons \beta$, can be realised.

F. O. Howitt.

Optical activity and the polarity of substituent groups. XIX. *l*-Menthyl esters of benzenesulphonic acids, and of benzoic acids with sulphur-containing *o*-substituents. H. G. Rule and G. Smith (J.C.S., 1931, 1482—1490).—l-*Menthyl* o-*nitrobenzenesulphonate*, m. p. 66°, has a low rotation and anomalous dispersion, whilst l-*menthyl toluene*-p-*sulphonate*, m. p. 91—92°, *toluene*-o-*sulphonate*, m. p. 78°, m-*nitrobenzenesulphonate*, m. p. 80°, and p-*nitrobenzenesulphonate*, m. p. 70·5°, resemble the corresponding benzoic esters, and differ little from the unsubstituted compound. In the series, l-*menthyl* o-*thiolbenzoate*, b. p. 202—205°/0·2 mm., and o-*methylthiolbenzoate*, b. p. 210°/0·3 mm., l-*menthyl* ester of o-*carboxyphenylmethylsulphone*, b. p. 190—193°/0·2 mm. (o-*carboxyphenylmethylsulphone monohydrate*, m. p. 73°), *K* salt of *l*-menthyl *o*-sulphobenzoate, and *Me* o-*carbomenthoxybenzenesulphonate*, the influence of substitution is given by $SMe > SH > H > SO_2Me > SO_2{\cdot}OMe > SO_2{\cdot}OH$. Ionisation of the SH or SO_3H group depresses the rotatory power, and the characteristic effect of the *o*-substituents is in every case more pronounced in C_6H_6 than in EtOH.

F. R. Shaw.

Constitution of citrylidenemalonic acid. R. Kuhn and M. Hoffer (Ber., 1931, **64**, [*B*], 1243—1252).—Whereas Et citrylidenemalonate absorbs 3 mols. of H_2 in accordance with the structure $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}C(CO_2Et)_2$ the acid is indifferent towards H, and does not add Br. The acid is shown to be *menthane*-3-*malono*-1 : 4-*dilactone* (I).



(I.)

It is converted by aq. NaOH (1 mol.) into *menthan*-1-*ol*-3-*aceto*-4-*lactone*, m. p. 123—123·5° (corr.), and by an excess of boiling, aq. KOH into *menthan*-4-*ol*-3-*aceto*-1-*lactone*, m. p. 118—119°, also derived by similar treatment of the first-named lactone. The OH group of both lactones is esterified with difficulty, but easily replaced by Cl, yielding respectively 1-*chloromenthan*-3-*aceto*-4-*lactone*, m. p. 89—90°, and 4-*chloromenthan*-3-*aceto*-1-*lactone*, m. p. 59·3—60·5°. Either lactone is transformed by HCl in MeOH into *Me* 1 : 4-*dichloromenthane*-3-*acetate*, m. p. 123·5—124° (decomp.), converted by KOH in EtOH into an acidic oil containing Cl. When heated at 290°, 1-chloromenthan-3-aceto-4-lactone loses HCl and yields *menthene*-3-*aceto*-4-*lactone*, b. p. 160—162°/11 mm., d_4^{19} 1·041, hydrogenated to *menthane*-3-*aceto*-4-*lactone*, b. p. 156—158°/11 mm., d_4^{20} 1·015. For purposes of comparison, "synthetic menthol," $[\alpha]_D^{20}$ −14·7° in EtOH, is oxidised to menthone, which is condensed with Me bromoacetate to *Me menthol-acetate*, b. p. 138—139°/12 mm. Treatment of the last-named compound with $KHSO_4$ at 150—160° affords menthane-3-aceto-4-lactone, b. p. 154—159°/11 mm., d_4^{20} 1·015, isomerised by P and HI in AcOH to the cryst. lactone, m. p. 93·5—95°, identical with that derived from citrylidenemalonic acid.

H. Wren.

Hydration of turpentine terpenes to terpin hydrate by mineral acids. A. Paris (Acta Comm. Univ. Tartu. [Dorpat], 1930, **16**, No. 1, 3—28; Chem. Zentr., 1931, i, 1607).—Pinene fractions of different age and history show small indefinite differences on hydration. Terpin hydrate was employed as homogeniser for the turpentine–aq. acid mixtures, since it forms a hydrophobic layer on the droplets of the aq. phase. Hydration in presence of H_2SO_4, HCl, or HNO_3 (0·5—6 mol.) proceeds relatively rapidly at first, then ceases (presumably owing to the formation of a film of solid terpin hydrate around the drops of the aq. phase) or appears retrogressive. At higher temp. and acid concentration dehydration, and with HCl addition of HCl, also occur. The reaction system is regarded as a macro-emulsion; the interfaces are relatively small and saturated with pinene. The reaction velocity is proportional to the square of the acid concentration or, at 25°, to the square of the activity of the acid. The temp. coeff. is 3·4—3·8 per 10°. A. A. ELDRIDGE.

Dependence of optical rotatory power on chemical constitution. XI. Rotatory dispersion of stereoisomeric trans-*oo′*-stilbene and *oo′*-dibenzyl derivatives of bisimino-, bisamino-, and bisaminomethylene-camphors. B. K. SINGH and B. BHADURI (J. Indian Chem. Soc., 1931, **8**, 181—198; cf. A., 1930, 1441).—Condensation of the appropriate camphorquinone with *trans-oo′*-diaminostilbene and *s*-di-*o*-aminophenylethane affords d- and l-, m. p. 231—232°, $M[\alpha]^{35}_{5461}$ ±456°, and dl-, m. p. 238—239°, -oo′-*stilbene-bisimino-* (I), reduced by Zn dust and 12% KOH to d- and l-, decomp. 220°, m. p. 240—241°, $M[\alpha]^{35}_{5461}$ ±45·6°, and dl-, m. p. 210—212°, -oo′-*stilbenebisamino-* (II), d- and l-, m. p. 187—188°, $M[\alpha]^{35}_{5461}$ ±684°, and dl-, m. p. 194—195°, -oo′-s-*diphenylethanebisimino-* (III), reduced to d- and l-, m. p. 214—216°, $M[\alpha]^{31}_{5461}$ ±157°, and dl-, m. p. 204—205°, oo′-s-*diphenylethanebisamino-* (IV) *-camphor.* Similar condensation of oxymethylenecamphor affords d- and l-, m. p. 295—296°, $M[\alpha]^{35}_{5461}$ ±394°, and dl-, m. p. 295—296°, -oo′-*stilbenebisaminoethylene-* (V), d- and l-, m. p. 266—268°, $M[\alpha]^{35}_{5461}$ ±392°, and dl-, m. p. 272—273°, oo′-s-*diphenylethanebisaminoethylene-* (VI) *-camphor.* All rotations are in $CHCl_3$, but they are also recorded in various other solvents. Whilst destruction of conjugation at a distance from the asymmetric centre causes only a small depression in rotatory power (*e.g.*, I ⟶ V; III ⟶ VI), breaking it near that centre results in a large depression (*e.g.*, I ⟶ II; III ⟶ IV). Apparent anomalies to this conclusion in certain solvents are probably explained by the existence of the compound in the completely conjugated *o*-quinonoid–enol form. With the exception of IV in pyridine and C_6H_6, all these derivatives exhibit simple rotatory dispersion. In pyridine, V exhibits mutarotation $M[\alpha]^{35}_{5461}$ 435·4° ⟶ 413·3° in 15 hr. J. W. BAKER.

Essential oil of Taiwania cedar. K. KAFUKU and R. KATO. **Essential oil of leaves of *Chamæcypyrasis obtusa*, Sieb. et zucc., f. *Formosana*, Hayata, or Arisan "Hinoki." II.** K. KAFUKU and T. NOZOE.—See B., 1931, 698.

Synthesis of *dl*-pilopic acid. K. N. WELCH (J.C.S., 1931, 1370).—The successive action of CH_2O and HCl on Et butane-ααβ-tricarboxylate gives 2-keto-3-ethyltetrahydrofuran-4-carboxylic acid, m. p. 86—87°, which appears to be identical with that obtained by Tschitschibabin and Preobraschenski (A., 1930, 452). F. R. SHAW.

Relation between odour and chemical behaviour. A. ANGELI and A. POLVERINI (Gazzetta, 1931, **61**, 276—280).—Determination of the oxidisability of the double linking $\cdot\overset{4}{CH_2}\!:\!\overset{3}{CH}\cdot\overset{2}{CO}\cdot$ in coumarin and its alkyl derivatives shows parallelism between this property and strength of odour, coumarin itself and its 7- and 3-Me derivatives, which have a strong odour, being readily oxidised, whilst the practically odourless 4-Me derivatives resist oxidation. E. E. J. MARLER.

Synthesis of coumarins from phenols and β-ketonic esters using phosphorus pentoxide. I. Coumarins from resorcinol and ethyl acetoacetates. D. CHAKRAVARTI (J. Indian Chem. Soc., 1931, **8**, 129—136).—Contrary to Simonis and Remmert (A., 1914, i, 980), the product obtained by condensation of Et methylacetoacetate and resorcinol in the presence of P_2O_5 or NaOEt is not 7-hydroxy-2 : 3-dimethylchromone (A., 1901, i, 735), but is 7-hydroxy-3 : 4-dimethylcoumarin, m. p. 256° (not m. p. 262°, as given by Simonis and Remmert) (cf. A., 1884, 66) (*Ac* derivative, m. p. 165°; *Me*, m. p. 140°, and *Et*, m. p. 121°, *ethers*). This explains the failure of Heilbron and others (J.C.S., 1923, **123**, 2569) to condense the Et ether with MeCHO, their suggestion that failure was due to the presence of the 7-OH group being incorrect, since 7-methoxy-2 : 3-dimethylchromone readily condenses with PhCHO to give 7-*methoxy*-2-*styryl*-3-*methylchromone*, m. p. 152°, whilst 7-methoxy-2-methyl*iso*flavone (Baker and Robinson, A., 1925, i, 1299) and PhCHO afford 7-methoxy-2-styryl-3-phenylchromone identical with a specimen differently prepared by these authors. Thus the formation of coumarins, rather than chromones, by condensation of resorcinol with substituted acetoacetic esters is a general reaction. Contrary to Jacobson and Ghosh (J.C.S., 1915, **107**, 1053), resorcinol and Et benzylacetoacetate afford only 7-hydroxy-3-benzyl-4-methylcoumarin, m. p. 224°, the other product, m. p. 186°, obtained by these authors being an impure specimen. Similarly are prepared 7-*hydroxy*-3-*ethyl*-, m. p. 194—198° (*Ac* derivative, m. p. 110°; *Me ether*, m. p. 93°); -3-n-, m. p. 169—171° (*acetyl* derivative, m. p. 119°), and -3-*iso*-, m. p. 224° (*Ac* derivative, m. p. 124°), *-propyl-*; -3-iso*butyl*-, m. p. 153° (*Ac* derivative, m. p. 109°); -3-*phenyl*- (Me ether, m. p. 104°; lit. m. p. 87°), and -3-chloro- (A., 1901, i, 210) -4-*methylcoumarin.* J. W. BAKER.

Hydroxy-carbonyl compounds. III. Preparation of coumarins and 1 : 4-benzopyrones from phloroglucinol and resorcinol. F. W. CANTER, F. H. CURD, and A. ROBERTSON (J.C.S., 1931, 1255—1265).—Phloroglucinol and resorcinol condense with Et acylacetates in presence of P_2O_5 forming coumarins instead of the expected 1 : 4-pyrones (cf. A., 1913, i, 890; 1914, i, 424, 980). The following are prepared: (*a*) from phloroglucinol: 5 : 7-dihydroxy-4-methyl- [*Me₂ ether*, m. p. 171°, also formed when phloroglucinol Me_2 ether is condensed with $CH_2Ac\cdot CO_2Et$ in presence of P_2O_5 (not with conc. H_2SO_4)]; 5 : 7-*dihydroxy*-3 : 4-*dimethyl*-, m. p. 291—292° (*diacetate*,

m. p. 130°; *Me_2 ether*, m. p. 157—158°, also obtained from phloroglucinol dimethyl ether and $CHMeAc \cdot CO_2Et$ as above); 5 : 7-*dihydroxy*-4-*methyl*-3-*ethyl*-, m. p. 217° (*diacetate*, m. p. 124°; *Me_2 ether*, m. p. 112°), and 5 : 7-dihydroxy-4-phenylcoumarin (also prepared from 2 : 4 : 6-trihydroxybenzophenone, Ac_2O, and NaOAc at 170—180°); (*b*) from resorcinol: 7-hydroxy-4-methyl-; 7-hydroxy-3 : 4-dimethyl-, m. p. 258° (*Ac* derivative, m. p. 164°; *Me*, m. p. 142·5°, and Et ethers, m. p. 120°) [the 7-hydroxy-2 : 3-dimethylbenzo-1 : 4-pyrone of Simonis and Remmert (A., 1914, i, 980) is this coumarin], and 7-*hydroxy*-4-*methyl*-3-*ethyl-coumarin*, m. p. 198° (*Ac* derivative, m. p. 107°; *Me ether*, m. p. 93°). All the above coumarins were prepared also using conc. H_2SO_4 as the condensing agent.

Treatment of phlor-propiophenone and -butyrophenone with Ac_2O and NaOAc at 170—180° gives 5 : 7-*dihydroxy*-2 : 3-*dimethyl*-, m. p. 215° (*diacetate*, m. p. 141—142°), and 5 : 7-*dihydroxy*-2-*methyl*-3-*ethyl*-1 : 4-*benzopyrone*, m. p. 206—207° (*diacetate*, m. p. 124°), respectively. Similar acetylation of phloroacetophenone affords nuclear acetylated *compounds*, m. p. 127° and 131° (hydrolysed to *substances*, m. p. 226° and 274° after sintering at 269°, respectively), whilst respropiophenone and resbutyrophenone afford 7-hydroxy-2 : 3-dimethyl- and 7-*hydroxy*-2-*methyl*-3-*ethyl*-1 : 4-*benzopyrones*, m. p. 238°, respectively. 5 : 7-*Dihydroxy*-3-*methyl*-, m. p. 262° (*diacetate*, m. p. 132°), 5 : 7-*dihydroxy*-3-*ethyl*-, m. p. 243°, and 7-*hydroxy*-3-*methyl-flavones*, m. p. 278° (*acetate*, m. p. 137°), are prepared by the action of Bz_2O and NaOBz at 180—190° on phlorpropiophenone, phlorbutyrophenone, and respropiophenone, respectively.

H. Burton.

Condensation of α-formylphenylacetonitriles with phenols. I. I. C. Badhwar, W. Baker, B. K. Menon, and K. Venkataraman (J.C.S., 1931, 1541—1546).—Condensation of α-formylphenylacetonitrile (I), its *O*-Bz and some other derivatives on the one hand with resorcinol and other phenols and their derivatives on the other under the conditions of the Hoesch reaction produces 3-phenylcoumarins in poor yields and not, as usually, 3-phenylchromones. Unless otherwise stated, the following condensations were performed by saturating a solution of the components in dry Et_2O with HCl at 0° in the presence of $ZnCl_2$. Resorcinol and I gave 7-hydroxy-3-phenylcoumarin (II) (cf. A., 1928, 70) and an amorphous *substance*, m. p. about 245—255° (amorphous *Ac* derivative, m. p. 150—156°). Resorcinol Me ether and I gave 7-methoxy-3-phenylcoumarin (replaced in one experiment by 7-methoxy*iso*flavone) and an amorphous substance. Phloroglucinol and I gave 5 : 7-dihydroxy-3-phenylcoumarin. *p*-Methoxyphenylacetonitrile, Na, abs. EtOH, and $H \cdot CO_2Et$ gave p-*methoxyphenylacetonitrile* (III), m. p. 120—121°. 3 : 4 : 5-Trimethoxyphenylacetonitrile similarly gave α-*formyl*-3 : 4 : 5-*trimethoxyphenylacetonitrile* (IV), dimorphous, m. p. 83—85° and then 114—115°. Phloroglucinol Me_2 ether and III gave 5 : 7 : 4′-trimethoxy-3-phenylcoumarin. 3 : 4 : 5-Trimethoxyphenol and IV gave 5 : 6 : 7 : 3′ : 4′ : 5′-*hexamethoxy*-3-*phenylcoumarin*, m. p. 157°. Phenylacetonitrile, $H \cdot CO_2Et$, Na, and dry Et_2O, followed by BzCl and aq. NaOH gave benzoyloxymethylenephenylacetonitrile (V), which with resorcinol yielded II and a non-phenolic *substance*, m. p. 145—146°. V gave with pyrogallol 7 : 8-dihydroxy-3-phenylcoumarin, and with orcinol 7-hydroxy-3-phenyl-5-methylcoumarin (previously described as the chromone, J.C.S., 1916, **109**, 117). V with resorcinol diacetate, $ZnCl_2$, and HCl in AcOH gave 4 : 6-diacetylresorcinol and a little II, and with resorcinol Me ether yielded 7-methoxy-3-phenylcoumarin. No reaction occurred with V and quinol, pyrocatechol, or phenol under the conditions stated, nor in conc. H_2SO_4.

R. S. Cahn.

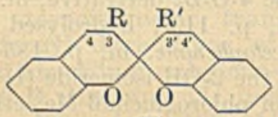
Hydroxy-carbonyl compounds. II. Benzoylation of ketones derived from phloroglucinol. F. W. Canter, F. H. Curd, and A. Robertson (J.C.S., 1931, 1245—1255).—Treatment of 2 : 4 : 6-trihydroxyacetophenone (*tribenzoate*, m. p. 117—118°) with BzCl in cold dil. KOH gives some 2-O-*Bz* derivative, m. p. 168°, but mainly the 4-O-*Bz* derivative, m. p. 210—211° [*Me_2 ether*, m. p. 119°, hydrolysed to 4-*hydroxy*-2 : 6-*dimethoxyacetophenone*, m. p. 185·5°, also formed together with the 2-OH-isomeride (I) by the Hoesch condensation of phloroglucinol Me_2 ether and MeCN]. 5 : 7-*Dimethoxy*-3-*acetyl*-2-*methyl*-1 : 4-*benzopyrone*, m. p. 169°, is obtained from I, Ac_2O, and NaOAc at 180°. Hoesch condensation of phloroglucinol and EtCN affords 2 : 4 : 6-*trihydroxypropiophenone* ($+H_2O$), m. p. 174—175°, benzoylated to the 2-O-*Bz*, m. p. 191—192° after sintering at 187—188°, and 4-O-*Bz* derivatives, m. p. 193° after sintering at 188° (main product) [*Me_2 ether*, m. p. 103°, hydrolysed to 4-*hydroxy*-2 : 6-*dimethoxypropiophenone*, m. p. 180° (*acetate*, m. p. 76°), also formed with 2-*hydroxy*-4 : 6-*dimethoxypropiophenone* (II), m. p. 111°, from phloroglucinol Me_2 ether and EtCN by the Hoesch reaction]. 5 : 7-*Dimethoxy*-2 : 3-*dimethyl*-1 : 4-*benzopyrone*, m. p. 189—190°, and 5 : 7-*dimethoxy*-3-*methylflavone*, m. p. 178—179°, are prepared from II and Ac_2O and Bz_2O, respectively. 2 : 4 : 6-Trihydroxybutyrophenone, m. p. 183° (lit. 179—180°), is benzoylated to the 4-O-*Bz* derivative, m. p. 164° (*Me_2 ether*, m. p. 86°, hydrolysed to 4-*hydroxy*-2 : 6-*dimethoxybutyrophenone*, m. p. 107°, which is formed with 2-*hydroxy*-4 : 6-*dimethoxybutyrophenone*, m. p. 70°, by a Hoesch condensation). 5 : 7-*Dimethoxy*-2-*methyl*-3-*ethyl*-1 : 4-*benzopyrone* has m. p. 118°. 2 : 4 : 6-Trihydroxybenzophenone (*tribenzoate*, m. p. 125—126°) affords the 4-O-*Bz* derivative, m. p. 186° (*Me_2 ether*, m. p. 170—171°).

H. Burton.

Chromone group. II. 1 : 4-α-Naphthapyrones. A. S. Bhullar and K. Venkataraman (J.C.S., 1931, 1165—1170).—2-Acetyl-α-naphthol (I) [benzoate, m. p. 128° (lit. 96·5°)] reacts more readily with acid anhydrides than any of the ketones previously used (A., 1926, 1149; 1929, 325, 1459); mixtures of 1 : 4-α-naphthapyrones and their 3-acyl or -aroyl derivatives are produced. The following are prepared: 2-methyl-1 : 4-α-naphthapyrone (3-acetyl derivative), from I and Ac_2O; α-naphthaflavone (3-*Bz* derivative, m. p. 218°), from I and Bz_2O; 4′-methoxy-α-naphthaflavone (3-*anisoyl* derivative, m. p. 211—212°). 1-*Acetoxy*-2-*naphthyl* αβ-*dibromo*-β-3 : 4-*dimethoxyphenylethyl ketone*, m. p. 161°, is converted by aq.-alcoholic KOH into 3′ : 4′-*dimethoxynaphthaflavone*,

m. p. 192° after sintering at 184°, demethylated to 3′ : 4′-*dihydroxynaphthaflavone*, m. p. 317—319° (*di-acetate*, m. p. 204°). H. Burton.

Styrylpyrylium salts. XIII. Reactivity of methyl β-phenylethyl and γ-phenylpropyl ketones. I. M. Heilbron, R. N. Heslop, F. Irving, and J. S. Wilson (J.C.S., 1931, 1336—1342; cf. A., 1929, 822).—Condensation of methyl β-phenylethyl ketone (I) (from ethyl α-benzylacetoacetate) with salicylaldehyde in the presence of piperidine or NaOH gave 2-*hydroxystyryl* β-*phenylethyl ketone*, m. p. 128—129°, which with β-naphthol-1-aldehyde and HCl yielded non-ionising 3′-*benzylbenzo*-β-*naphtha*spiro*pyran* (II; R=H, R′=CH_2Ph), m. p. 129—130°, colourless in boiling xylene, rapidly giving a wine-red colour in AcOH (contrast benzyl methyl ketone, *loc. cit.*). Condensation in the presence of HCl gave the pyrylium salt (III) (hydrolysed to 3-benzyldibenzo-*spiro*pyran), which on condensation with β-naphthol-1-aldehyde and hydrolysis yielded 3-*benzylbenzo*-β-*naphtha*spiro*pyran* (II; R=CH_2Ph, R′=H), m. p. 157° to a purple liquid, colourless in cold xylene, reddish-purple when boiling, and slowly giving a blue colour in AcOH. Methyl γ-phenylpropyl ketone (IV) [from Et α-(β-phenylethyl)acetoacetate] gave similarly 2-*hydroxystyryl γ-phenylpropyl ketone*, m. p. 114°; 3′-β-*phenylethylbenzo*-β-*naphtha*spiro*pyran*, m. p. 180°, colourless in boiling xylene or veratrole, wine-red in AcOH; 3-β-*phenylethylbenzo*-β-*naphtha*spiro*pyran*, m. p. 140—141° to a deep purple liquid, colourless in cold xylene, deep purple when heated, and slowly giving a blue colour in AcOH. I and IV with β-naphthol-1-aldehyde and HCl gave the pyrylium salts, from which 3-benzyldi-β-naphtha*spiro*pyran and 3-β-*phenylethyldi*-β-*naphtha*spiro*pyran*, m. p. 219—220° (bluish-purple in boiling xylene), respectively, were obtained. I with PhCHO yielded either styryl β-phenylethyl ketone, m. p. 53—54° (cf. this vol., 92; A., 1904, i, 427) (*semicarbazone*, m. p. 135°) [the structure of which is proved by its prep. from *benzylidene-α-benzylacetoacetic acid*, m. p. 157° (decomp.) (from PhCHO and ethyl benzylacetoacetate)], or *di*(*styryl* β-*phenylethyl ketone*), m. p. 184°, according to the experimental conditions. IV gave similarly *styryl γ-phenylpropyl ketone*, m. p. 51°, and *di*(*styryl γ-phenylpropyl ketone*), m. p. 138° (contrast benzyl methyl ketone, A., 1899, i, 140). R. S. Cahn.



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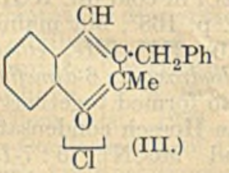


(III.)

Formation of phlobaphens. M. Bergmann and G. Pojarlieff (Collegium, 1931, 244—247).—Phlobaphens were formed by boiling tetramethylcatechin with alcoholic HCl, from which it is inferred that phenolic OH groups are not essential to phlobaphen formation, but that probably unsaturated linkings in close proximity with OH groups, as in pyran rings, cause a tendency to acid condensation. This view is supported by the behaviour of glucal. Pyrocatechol tannins are therefore related structurally to the sugars. D. Woodroffe.

Organic compounds of sulphur. XIX. Novel intramolecular atomic displacement (migration of a chlorine atom from carbon to sulphur). Tautomerism and desmotropy of thiocarbonic esters. A. Schönberg and L. von Vargha (Ber., 1931, 64, [*B*], 1390—1399; cf. A., 1930, 1574).—Diphenyldiazomethane and Ph chlorothionformate in Et_2O afford β-*chloro*-β-*phenoxy*-αα-*diphenylethylene sulphide*, m. p. 78°, which passes at 100—130° into 2-*phenoxy*-3-*phenylthionaphthen*, m. p. 116°, stable to heat, acids, and alkali, but decomposed by molten KOH with production of PhOH. Similarly, diphenyldiazomethane and Ph chlorodithioformate give β-*chloro*-β-*phenylthiol*-αα-*diphenylethylene sulphide*, m. p. 99—100° (decomp.) when rapidly heated, converted by LiPh into ββ-diphenylthiol-αα-diphenylethylene, m. p. 112° (Ph_2S, b. p. 156°/16 mm., is obtained in the same manner from LiPh and chlorothiolbenzene), and passing at 95—100° into 2-*phenylthiol*-3-*phenylthionaphthen*, m. p. 123°. Di-*p*-tolyldiazomethane and Ph chlorothionformate give a noncryst. product which is transformed at 110—120° into 2-*phenoxy*-3-p-*tolyl*-6-*methylthionaphthen*, m. p. 102°. *Me* β-*phenoxy*-αα-*diphenylvinylsulphenate*, $CPh_2{:}C(OPh){\cdot}S{\cdot}OMe$, m. p. 117°, is obtained by the action of boiling MeOH on β-chloro-β-phenoxy-αα diphenylethylene sulphide; the corresponding *Et* ester has m. p. 105—106°. *Me* β-*phenylthiol*-αα-*diphenylvinylsulphenate*, m. p. 127°, is prepared analogously from β-chloro-β-phenylthiol-αα-diphenylethylene sulphide, but the main product is 2-phenylthiol-3-phenylthionaphthene when boiling EtOH is used. Reduction of β-chloro-β-phenoxy-αα-diphenylethylene sulphide with Al–Hg in moist Et_2O affords *Ph diphenylthionacetate*, $CHPh_2{\cdot}CS{\cdot}OPh$, m. p. 67°, hydrolysed by H_2SO_4 to diphenylacetic acid. β-Chloro-β-phenylthiol-αα-diphenylethylene sulphide is converted by similar means into β-*thiol*-β-*phenylthiol*-αα-*diphenylethylene*, m. p. 112°, hydrolysed to diphenylacetic acid and PhSH. H. Wren.

Reactivity of conjugated systems. III. Condensation of αβ-unsaturated esters with cyanoacetamide. C. Barat (J. Indian Chem. Soc., 1931, 8, 37—44).—αβ-Unsaturated esters and amides react with cyanoacetamide in presence of NaOEt to form 4-alkyl-2 : 6-diketo-3-cyanopiperidines, which on acid hydrolysis form β-alkylglutaric acids. The reactivity decreases from αβ-unsaturated ketones, through the acids to amides (A., 1930, 925). Et acrylate, crotonate, cinnamate, and *p*-nitrocinnamate give respectively 2 : 6-*diketo*-3-*cyanopiperidine*, m. p. 206—207°, 2 : 6-*diketo*-3-*cyano*-4-*methylpiperidine*, m. p. 140—142°, 2 : 6-*diketo*-3-*cyano*-4-*phenylpiperidine*, m. p. 224—225°, and 2 : 6-*diketo*-3-*cyano*-4-p-*nitrophenylpiperidine*, m. p. 279—280°, the amides giving the same products in better yield. G. Discombe.

Condensation of an amine and formaldehyde with quinaldine and picoline. T. Héou-Féo (Compt. rend., 1931, 192, 1242—1244).—Condensation of $NHEt_2$,HCl, CH_2O, and quinaldine in aq. solution affords 2-β-*diethylaminoethylquinoline*, b. p. 181°/12 mm. (*monopicrate*, m. p. 122°; *dipicrate*, m. p. 153°; *chloroplatinate*, decomp. 185°; *chlorozincate*, m. p. 230°; *hydrochloride*), and a little bisdiethylaminomethane. Similar condensation with NH_2Et,HCl affords a product, b. p. 160—180°/0·2 mm., converted by BzCl into 2-(β-*benzethylamidoethyl*)*quinoline*, $C_9H_7N{\cdot}[CH_2]_2{\cdot}NBzEt$, m. p. 130°, whilst α-picoline, $NHEt_2$, and CH_2O give 2-(β-*diethylaminoethyl*)*pyridine*, b. p. 153°/16 mm. (*picrate*, m. p. 164°; *methiodide*, m. p. 183°; *chloroplatinate*, decomp. 205°; *cadmichloride*, m. p. 186°; *hydrochloride*).

J. W. Baker.

Quinoline derivatives. XIX. β-Diethylaminoethyl 2-phenylquinoline-4-carboxylate and β-diethylaminoethyl 6-methoxy-2-phenylquinoline-4-carboxylate. XX. Derivatives of 2-phenylquinoline-4-carboxylic acid and 6-methoxy-2-phenylquinoline-4-carboxylic acid. XXI. 4-Amino-6-hydroxy-2-phenylquinoline. XXII. Decomposition of 6-methoxy-2-phenylquinoline-4-carboxylic acid. XXIII. 4-Halogeno-6-methoxy-2-phenylquinolines. XXIV. 6-Ethoxy-2-phenylquinoline-4-carboxylic acid and 4-amino-6-ethoxy-2-phenylquinoline. H. John [with H. Lukas] (J. pr. Chem., 1931, [ii], 130, 289—292, 293—304, 304—313; 314—327, 328—331, 332—341).—XIX. β-*Chloroethyl 2-phenylquinoline-4-carboxylate*, m. p. 72° (from the acid chloride) gives with $NHEt_2$ the corresponding β-*diethylaminoethyl* ester (*dihydrochloride*, m. p. 160°). β-*Chloroethyl*, m. p. 98°, and β-*diethylaminoethyl 6-methoxy-2-phenylquinoline-4-carboxylate*, m. p. 78°, are similarly prepared.

XX. 2-Phenylquinoline-4-carboxyl chloride condenses to give with (*a*) 0·5 mol. of carbamide, 2-*phenyl-4-quinoloylcarbamide*, m. p. 232°; (*b*) 1 mol. of carbamide, NN′-*bis*-(2-*phenyl-4-quinoloyl*)*carbamide*, m. p. 215°; (*c*) β-aminoethyl alcohol, β-2-*phenyl-4-quinoloylamidoethyl alcohol*, m.p. 165°; and (*d*) ethylenediamine, NN′-*bis*-(2-*phenyl-4-quinoloyl*)*ethylenediamine*, m. p. above 300°. 6-*Methoxy-2-phenyl-4-quinoloylcarbamide*, m. p. 245°, NN′-*bis*-(6-*methoxy-2-phenyl-4-quinoloyl*)-*carbamide*, m. p. 181°, β-6-*methoxy-2-phenyl-4-quinolyl-amidoethyl alcohol*, m. p. 243°, -*ethylenediamine*, m. p. 105°, and -*diethylamide*, m. p. 163° (*picrate*, m. p. 141°), NN′-*bis*-(6-*methoxy-2-phenyl-4-quinoloyl*)*ethylenediamine*, m. p. above 300°, 6-*methoxy-2-phenyl-4-quinoloyl*)-p-*phenetidine*, m. p. 230°, and (6′-*methoxy-2′-phenyl-4-quinoloyl*)-4-*aminoantipyrine*, m. p. 280° (decomp.) (*picrate*), m. p. 126°, are similarly prepared.

XXI. 6-Hydroxy-2-phenylquinoline-4-carboxylic acid, m. p. above 300°, prepared from benzylidene-*p*-aminophenol and pyruvic acid or from the corresponding OMe-compound, affords the following derivatives: *Me* ester, m. p. 183°; *Et* ester, m. p. 176°; *hydrazide*, m. p. 242°; iso*propylidenehydrazide*, m. p. 218°; *benzylidenehydrazide*, m. p. 287°; *azide*, decomp. at 100°. *Et* 6-*hydroxy-2-phenyl-4-quinolylaminoformate* has m. p. 208°; NN′-*bis*-(2-*phenyl-6-hydroxy-4-quinoloyl*)*carbamide*, m. p. 166°; 4-*amino-6-hydroxy-2-phenylquinoline*, m. p. 153° (*hydrochloride*, m. p. 215°, from the urethane).

XXII.—6-*Methoxy-2-phenylquinoline-4-carboxylic acid*, m. p. 237° (*salts* described), obtained from benzylidene-*p*-anisidine and pyruvic acid, affords the *chloride*, m. p. 237°; *amide*, m. p. 246°; *Et* ester, m. p. 106°; *Pr* ester, m. p. 85°; Pr^{β} ester, m. p. 80°; *hydrazide*, m. p. 200°; *benzylidenehydrazide*, m. p. 223°; *methylbenzylidenehydrazide*, m. p. 218°; *azide*. *Et* 6-*methoxy-2-phenyl-4-quinolylaminoformate* has m. p. 164°; NN′-*bis*-(6-*methoxy-2-phenyl-4-quinolyl*)*carbamide*, m. p. 273° (decomp.); 6-*methoxy-2-phenyl-4-quinolylcarbimide*, m. p. 221°, which is converted by alcoholic KOH into 6-*methoxy-2-phenyl-4-aminoquinoline*, m. p. 143° (*hydrochloride*, m. p. 258°, from the urethane); and 4-*diacetamido-6-methoxy-2-phenylquinoline*, m. p. 100°.

XXIII. 4-*Chloro-6-methoxy-2-phenyl*-, m. p. 109°, 4-*bromo*-, m. p. 157°, and 4-*iodo-quinoline*, m. p. 178°, are prepared from the corresponding amine.

XXIV. 6-*Ethoxy-2-phenylquinoline-4-carboxylic acid*, m. p. 203°, obtained from benzylidene-*p*-phenetidine and pyruvic acid, affords a *Me* ester, m. p. 118°; *Et* ester, m. p. 114°; *hydrazide*, m. p. 195°; iso*propylidenehydrazide*, m. p. 183°; *benzylidenehydrazide*, m. p. 218°; *azide*, decomp. 108°. *Et* 6-*ethoxy-2-phenylquinolylaminoformate* has m. p. 135°; 6-*ethoxy-2-phenylquinolylcarbimide*, m. p. 213°, reacts with alcoholic KOH to give 4-*amino-6-ethoxy-2-phenylquinoline*, m. p. 187° [Ac_2 derivative, m. p. 108°; *hydrochloride*, m. p. 292° (also obtained from the urethane)]; N : N′-*bis*-(6-*ethoxy-2-phenyl-4-quinolyl*)-*carbamide*, m. p. 275°.

F. R. Shaw.

Optical activity and the polarity of substituent groups. XVIII. *l*-Menthyl and *d*-β-octyl esters of picolinic, quinaldinic, nicotinic, and cinchoninic acids. H. G. Rule, J. B. Miles, G. Smith, and (Miss) M. M. Barnett (J.C.S., 1931, 1478—1482).—The rotatory powers of l-*menthyl quinaldinate*, m. p. 141—142°, and *picolinate*, b. p. 170°/1 mm., d-β-*octyl quinaldinate*, b. p. 168°/0·6 mm., *picolinate*, b. p. 170—173°/12 mm., *nicotinate*, b. p. 142—145°/0·02 mm., and *cinchoninate*, b. p. 154—156°/0·3 mm., in EtOH and in EtOH and HCl are discussed with reference to the polar changes involved on conversion into their salts.

F. R. Shaw.

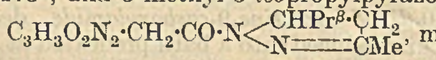
Acridine. VI. *ms*-Acridine derivatives. II. K. Lehmstedt (Ber., 1931, 64, [*B*], 1232—1239; cf. A., 1930, 926).—Acridine-9-carboxylamide is converted by Br and NaOMe (2 mols.) into 9 : 10-*dihydroxy-9 : 10-dihydroacridine-9-carboxylamide*, decomp. 169° when introduced into a bath preheated at 167°; under similar conditions acridine affords acridone. With 1 mol. of Br and 3 mols. of NaOMe in MeOH the amide yields *Me* 9-*acridylcarbamate*, m. p. 203·5° (slight decomp.) [*hydrochloride*]; the corresponding *Et*, m. p. 193°, Bu^{α}, m. p. 148—150°, and CH_2Ph, m. p. 193—194°, esters are described. 4-Nitroacridine-9-carboxylamide yields the corresponding red $(OH)_2$ derivative and *Me* 4-*nitro-9-acridylcarbamate*, m. p. 218° (slight decomp.). 9-Cyanoacridine is converted by H_2SO_4 and HNO_3 into 4-*nitro-9-cyanoacridine*, m. p. 216° (decomp.), hydrolysed by 90% H_2SO_4 to 4-*nitroacridine-9-carboxylamide*, decomp. 280° [*sulphate*, m. p. 275° (decomp.)], which with H_2SO_4 and $NaNO_2$ yields 4-*nitroacridine-9-carboxylic acid*, decomp. 203°, decarboxylated to 4-nitroacridine. Me 9-acridylcarbamate and $Ca(OH)_2$ at 220° give 9-*aminoacridine*, m. p. 234°; with conc. H_2SO_4 at 110—120° the carbamate yields a dehydrated 9-*aminoacridine*-

disulphonic acid, m. p. above 350° (*K* salt). 9-Phenylacridine with Br and KOH in MeOH affords *dibromo-9-phenylacridine*, m. p. 267—269° (*hydrochloride*). 9-*Cyanoacridine* is prepared from 9-chloroacridine, KCN, CuCN, and MeOH at 160—170°.

H. Wren.

Chloride, esters, and amides of hydantoin-3-acetic acid, and their use in the identification of alcohols and amines. R. Locquin, V. Cerchez, and (in part) A. A. Policard (Bull. Soc. chim., 1931, [iv], 49, 595—600, 600—602, 602—607, 607—612).—When hydantoin-3-acetyl chloride (I) in tetrachloroethane is treated with alcohols, preferably in presence of pyridine, quant. yields of the corresponding well-cryst. acetates are obtained. Since I is readily obtained from the acid and $SOCl_2$ and these esters are readily hydrolysed by dil. HCl they have advantages for identifying primary and secondary alcohols and certain phenols. They cannot be used for identifying *tert.* or terpene alcohols; the extreme solubility of the geranyl and citronellyl esters makes purification difficult. The esters may in many cases also be obtained quantitatively by normal esterification of hydantoin-3-acetic acid. I with dry NH_3 in tetrachloroethane yields hydantoin-3-acetamide. With amines and other NH_2-compounds *N*-substituted hydantoin-3-acetamides are similarly obtained, and are suitable for the identification of the parent compounds, especially of pyrazolines.

The following esters of hydantoin-3-acetic acid are described: *Pr*, m. p. 116°, *Bu*, m. p. 95°; Bu^{β}, m. p. 124°; sec.-*Bu*, m. p. 142°; iso*amyl*, m. p. 104°; sec.-*octyl*, m. p. 84°; *benzyl*, m. p. 142°, and cyclo*hexyl*, m. p. 184° (all obtained by esterification); *Me*, m. p. 91° (from hydantoin-3-acetic acid and diazomethane, and not from I); *Ph*, m. p. 205—206°; *cholesteryl*, m. p. 304—305° (together with substances, m. p. 131° and 185—186°).

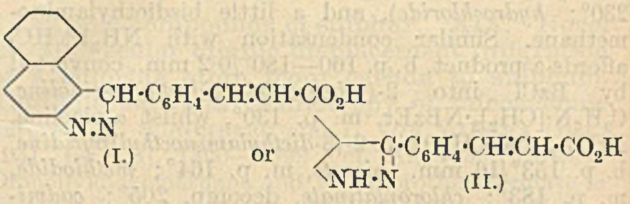
The following are described: *hydantoin-3-acetanilide*, m. p. 215°; N-*benzyl-*, m. p. 209—210°; N-*piperidyl-*, m. p. 160°; N-*methyl-*, m. p. 223° (together with a substance, m. p. 173°); and N-m-*xylyl-hydantoin-3-acetamide*, m. p. 242°. Et aminoacetate yields an *amide*, m. p. 168°, Et aminomalonate an *amide*, m. p. 172—173°, and 3-methyl-5-*iso*propylpyrazoline a *derivative*,  $C_3H_3O_2N_2\cdot CH_2\cdot CO\cdot N<\begin{matrix}CHPr^{\beta}\cdot CH_2\\ N{=\!=\!=}CMe\end{matrix}$, m. p. 185°.

R. Brightman.

Diagnosis of "veronalides" [derivatives of malonylcarbamide] by micro-crystalloscopy. G. Denigès (Mikrochem., 1931, 9, 316—323).—The substance is dissolved in a drop of aq. NH_3 on the microscope slide and a drop of 10% H_2SO_4 is placed at the side of the first drop and allowed to diffuse into it, when characteristic crystals of the derivative are formed. Illustrations and descriptions of the following are included: veronal, soneryl, rutonal, luminal, dial, allonal, and allyl*iso*propylmalonylcarbamide.

A. R. Powell.

Anomalous decomposition of the tetrazo-derivative of 2 : 2′-diamino-1 : 1′-dinaphthyl. A. Corbellini and L. Barbaro (Atti R. Accad. Lincei, 1930, [vi], 12, 445—451).—Purification of the acid substance, m. p. 250—252° (A., 1929, 1172), yields [4 : 5-(*naphtho*-1′ : 2′)-*pyrazole*(3)]-o-*cinnamic acid*, m. p. 269·5° (decomp.), which forms a *Me*, m. p. 158°,



and an *Et* ester, m. p. 143—143·5°; the latter yields an unstable *dibromide*, m. p. about 205° (crude). On sublimation, the acid gives [4 : 5-(*naphtho*-1′ : 2′)-*pyrazole*(3)]-o-*styrene* ($:CH_2$ for $:CH\cdot CO_2H$ in II), m. p. 154°, which forms an unstable *dibromide*, m. p. about 255—258° (crude). Oxidation of the acid by alkaline $KMnO_4$ yields [4 : 5-(*naphtho*-1′ : 2′)-*pyrazole*(3)]-o-*benzaldehyde*, m. p. 230° (p-*nitrophenylhydrazone*, m. p. 258°), an *acid*, m. p. about 287°, and another acid not obtained pure.

T. H. Pope.

Existence of true semiquinones. L. Michaelis (Naturwiss., 1931, 19, 461).—Although reduction of pyocyanin (I), α-hydroxyphenazine (II), and rosinduline-GG (III) with Pd and H_2 proceeds normally in alkaline solution, in acid solution true semiquinones are formed intermediately, since determination of the oxidation–reduction potential of the completely reduced dye gives two values of this potential for each value of p_H below certain limits (I, p_H 5; III, p_H 1—2), the region between the fork of the curve being that in which the semiquinone is in equilibrium with the other form of the dye.

J. W. Baker.

Reduction products of certain cyclic methylene-amines. J. Graymore (J.C.S., 1931, 1490—1494).—Reduction of hexamethylenetetramine with Zn dust in acid solution gives chiefly NH_3 and trimethylamine. The action of CH_2O on *hexamethylenetetramine picrate*, m. p. 179° (decomp.), yields *dimethylpentamethylenetetramine picrate*, m. p. 196° (decomp.). Reduction of trimethyltrimethylenetetramine affords mainly $NHMe_2$ and some NH_2Me, and of triethyltrimethylenetetramine, NHMeEt (*picrate*, m. p. 196°) and some NH_2Me. Tripropyltrimethylenetetramine (*urate*; *di-iodide*, m. p. 85°; *dibromide*) is reduced to NHMePr only (*picrate*, m. p. 43°; *oxalate*, m. p. 155°; *hydrochloride*, m. p. 140°). The mechanism of the reaction is discussed.

F. R. Shaw.

Phyllobombycin: the biological degradation of chlorophyll. H. Fischer and A. Hendschel (Z. physiol. Chem., 1931, 198, 33—42).—A new chlorophyll derivative, $C_{34}H_{36}O_6N_4$, named *phyllobombycin*, can be isolated from silk-worm fæces and detected in the fæces of the death's-head caterpillar. It is free from Mg, phytol, and OMe groups, forms a *Mg* salt and an *Et* ester, m. p. 209°, gives with NaOEt choline (spectroscopically identified) and with HBr–AcOH (cf. this vol., 496) phylloerythrin (spectroscopically identified). Reduction with HI–AcOH gives a *porphyrin*, spectroscopically identical with phæoporphyrin a_5, the ester of which does not depress the m. p. of phæoporphyrin a_5 ester. With HBr–AcOH a mixture of porphyrins, spectroscopically identical with chloroporphyrin e_6 and chloroporphyrin e_4, respectively, is obtained. Chlorophyll is converted by the intestinal cells of the worm into a red *dye*, which can be detected microscopically.

Penicillium glaucum and *Aspergillus oryzæ* have no action on coproporphyrin I, hæmin, or phæophorbid *a*, but act on chlorin *e* giving a porphyrin spectroscopically identical with phylloerythyrin (the cryst. form of the ester supports the identity) and on rhodin *g* giving an unknown *porphyrin*, which is the first biologically prepared derivative of chlorophyll b_1. A *compound* spectroscopically identical with choline can be extracted from human fæces. A. Renfrew.

Synthesis of deuteroætioporphyrin, deuterorhodin, and two tetramethylmonoethyldicarboxyethylporphins: synthesis of hæmoporphyrin. H. Fischer and A. Kirstahler (Z. physiol. Chem., 1931, **198**, 43—81).—Hæmoporphyrin is a mixture of mesoporphyrin, deuteroporphyrin, and porphyrins *A* and *B* (see below).

4 : 5 : 3′ : 5′-*Tetramethyl*-4′-*ethylpyrromethene hydrobromide* (methene I), m. p. 214° (*perbromide*, m. p. 138°, which when crystallised from AcOH gives a *dibromomethene hydrobromide*, m. p. above 300°), condenses (succinic acid method) with methene II (A., 1926, 1256) to give 1 : 3 : 5 : 8-*tetramethyl*-4-*ethyl*-6 : 7-*dicarboxyethylporphin* (porphyrin *A*) {Me_2 ester, m. p. 213° [*Fe* salt, m. p. 259° (corr.); *Cu* salt, m. p. 220° (corr.)], which depresses the m. p. of mesoporphyrin IX dimethyl ester by 23°; *hæmin*; *Cu* salt}. Bromination of porphyrin *A* and its Me_2 ester gives amorphous *perbromides*, converted into the *monobromo*-derivatives by aq. $COMe_2$. The *bromodimethyl* ester, m. p. 270° (corr.) [*Cu* salt, m. p. 230° (corr.)], can also be prepared by the succinic acid method. Acetylation of the Me_2 ester Fe salt is accompanied by much decomp. Removal of the Fe gives, with difficulty, 1 : 3 : 5 : 8-*tetramethyl*-4-*ethyl*-2-*acetyl*-6 : 7-*dicarboxyethylporphin* {Me_2 ester, m. p. 261° (corr.) [*Fe* salt, m. p. 260° (corr.); *Cu* salt, m. p. 227° (corr.)]}. The entry of the Ac group displaces the first spectrum band towards the red. The Ac group can be replaced by both the $OH\cdot C_2H_4$ and vinyl groups.

Condensation (succinic–pyrotartaric acid method) of 4′-*bromo*-4 : 3′ : 5′-*trimethyl*-3-*ethyl*-5-*bromoethylpyrromethene hydrobromide*, m. p. 315° (decomp.) (prepared by brominating 4 : 5 : 3′ : 5′-tetramethyl-3-ethylpyrromethene hydrobromide), and 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-dicarboxyethylpyrromethene hydrobromide yields 1 : 3 : 5 : 8-*tetramethyl*-2-*ethyl*-6 : 7-*dicarboxyethylporphin* (porphyrin *B*) {Me_2 ester, m. p. 214° [*Fe* salt, m. p. 220° (corr.); *Cu* salt, m. p. 230° (corr.)]}, which depresses the m. p. of both the Me_2 ester of the isomeric porphyrin, m. p. 213°, and the Me_2 ester of mesoporphyrin; *Fe* salt; *Cu* salt; cryst. *perbromide*, giving on partial debromination 4-*bromo*-1 : 3 : 5 : 8-*tetramethyl*-2-*ethyl*-6 : 7-*dicarboxyethylporphin* [*Cu* salt; Me_2 ester, m. p. 259° (corr.) (*Cu* salt, m. p. 276°)].

Porphyrins *A* and *B* are spectroscopically identical and give the same HCl no. Projection of the ether spectrum of one on that of the other gives a spectrum identical with that of hæmoporphyrin (A., 1913, i, 1251). The HCl nos. of mesoporphyrin (0·5), porphyrins *A* and *B* (0·4), and deuteroporphyrin (0·3) depend on the no. of free methine groups in the porphin nucleus. A modification of Willstätter's method for determining HCl nos. is described. Mixed m. p. of various combinations of the Me_2 esters of the above four porphyrins show that hæmoporphyrin ester is a mixture of these esters.

2 : 3-Dimethylpyrrole and 5-formyl-3-carbethoxy-2 : 4-dimethylpyrrole give, with HBr, 4′-*carbethoxy*-4 : 5 : 3′ : 5′-*tetramethylpyrromethene hydrobromide* (methene IV), m. p. 216° (corr.), giving, on bromination, 3-*bromo*-4′-*carbethoxy*-4 : 5 : 3′ : 5′-*tetramethylpyrromethene hydrobromide*, m. p. above 300°, which condenses (succinic acid method) with 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-dicarboxyethylpyrromethene hydrobromide to give 4-*carbomethoxy*-1 : 3 : 5 : 8-*tetramethyl*-6 : 7-*dicarboxyethylporphin* (Me_2 ester, m. p. 205°), spectroscopically identical with rhodoporphyrin. Another porphyrin, probably deuteroporphyrin, since the Me ester, m. p. 212°, does not depress the m. p. of deuteroporphyrin Me ester and gives a bromo-derivative, m. p. 274°, which does not depress the m. p. of dibromodeuteroporphyrin Me ester, is formed in small amounts.

[With O. Günther.] At least three porphyrins (*tetramethylmonocarboxylic acid porphin*; *tetramethyldicarboxylic acid porphin*, m. p. 275—280°; and *tetramethylporphin*) can be synthesised by heating 3 : 5-dicarbethoxy-4-methyl-2-bromoethylpyrrole with AcOH–HBr mixture in a sealed, Ag-lined tube. 3 : 4′ : 5-Tribromo-4 : 3′ : 5′-trimethylpyrromethene hydrobromide (methene VI) gives when similarly treated 1 : 3 : 5 : 7-*tetramethylporphin* (*Cu* salt). The same compound is formed, also in poor yield, from 3 : 4′ : 5-tribromo-4 : 3′ : 5′-trimethylpyrromethene hydrobromide (succinic acid method).

3 : 4 : 5-*Tribromo*-3′ : 4′ : 5′-*trimethylpyrromethene hydrobromide* (formed by brominating 3′ : 4′ : 5′-*trimethylpyrromethene hydrobromide*, which results from the action of HBr on a mixture of pyrrole-2-aldehyde and trimethylpyrrole) gives either by the succinic acid method or by heating with HBr–AcOH mixture under pressure very small amounts of a porphyrin $C_{24}H_{21}N_4Br$ (*Cu* salt).

3 : 4′-Dibromo-4 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide (A., 1926, 621) yields a free *base*, m. p. 182° (corr.), giving, on oxidation, bromocitraconimide, m. p. 176° (corr.), Et_2 ester, m. p. 204°, which does not depress the m. p. of *deuteroporphyrin* Et_2 ester, m. p. 204°, obtained by the resorcinol fusion of hæmin. The corresponding deuterorhodin gives a *Me* ester, m. p. 245° (corr.).

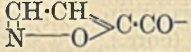
Deuteroætioporphyrin, m. p. 282° (corr.) [*Cu* salt, m. p. 280° (corr.); *monobromo*-derivative; *dibromo*-derivative, m. p. 368°; *hæmin*], is formed by condensing (succinic acid method) 3 : 4′-dibromo-4 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide with 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-diethylpyrromethene hydrobromide. A. Renfrew.

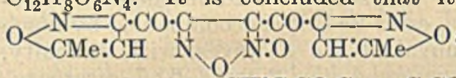
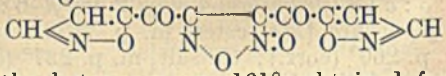
Bile pigments. V. Syntheses of bilirubic and xanthobilirubic acids and their isomerides, also of tripyrrans and bilirubinoid pigments. H. Fischer and E. Adler (Z. physiol. Chem., 1931, **197**, 237—280; cf. this vol., 853).—5-Bromo-4 : 3′ : 5′-trimethyl-3-ethyl-4′-carboxyethylpyrromethene hydrobromide (I) when heated with AgOAc or KOAc in AcOH gives xanthobilirubic acid (II), reduced by Na–Hg or HI to bilirubic acid (III). II may also be obtained from I by means of NaOMe. The Br of I may be replaced by OMe to form an *ether*, m. p. 145—146° (*Me* ester, m. p. 62°), hydrolysable by NaOMe or resorcinol fusion. 5-Bromo-3 : 3′ : 5′-trimethyl - 4 - ethyl - 4′- carboxyethylpyrromethene hydrobromide (IV) heated with AgOAc gives a xanthobilirubic acid *isomeride* (V), m. p. 289—290° (*Me* ester, m. p. 197°), yielding a bilirubic acid *isomeride* (VI), m. p. 207°. Hæmopyrrolecarboxylic acid and 2-formyl-4-methyl-3-ethylpyrrole-5-carboxylic acid give 5-carboxy-4 : 4′ : 5′-trimethyl-3-ethyl-3′-carboxyethylpyrromethene hydrobromide, which, by way of the 5-*bromo*-derivative, m. p. 214°, gives another xanthobilirubic acid *isomeride* (VII), m. p. 289—290° (*Me* ester, m. p. 205°; corresponding bilirubic acid *isomeride*, m. p. 174°). 5-Bromo-3 : 4′ : 5′-trimethyl - 4 - ethyl - 3′- carboxyethylpyrromethene hydrobromide gives another xanthobilirubic acid *isomeride* (VIII), m. p. 265° (*Me* ester, m. p. 173°; corresponding bilirubic acid *isomeride*, m. p. 171°).

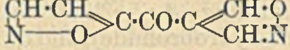
5-Carbethoxy-4-methyl-2-bromomethylpyrrole-3-propionic acid gives a 2-*ethoxy*-derivative (IX), m. p. 151° (2-*methoxy*-, m. p. 75°). 5-Carbethoxy-4-methyl-2-bromomethyl-3-ethylpyrrole gives a 2-*methoxy*-, m. p. 73°, and a 2-*ethoxy*-derivative (X), m. p. 54°. 5-Carbethoxy-2-ethoxymethyl-4-ethylpyrrole and methyl cryptopyrrolecarboxylate form 5-*carbethoxy*-4 : 3 : 5′-*trimethyl*-3-*ethyl* - 4′-*carbethoxyethylpyrromethane*, m. p. 96—97°. IX with opsopyrrole yields 1 : 8-*dicarbethoxy*-2 : 4 : 7-*trimethyl*-5-*ethyl*-3 : 6-*dicarboxyethyltripyrran*, m. p. 217°, giving a tetracarboxylic acid on hydrolysis. Opsopyrrole and X give 1 : 8-*dicarbethoxy*-2 : 4 : 7-*trimethyl*-3 : 5 : 6-*triethyltripyrran*, m. p. 195°. 5-Hydroxy-3-carbethoxy-2:4-dimethylpyrrole with 1 mol. of SO_2Cl_2 yields 5-*hydroxy*-3-*carbethoxy*-4-*methyl*-2-*chloromethylpyrrole* (XI), m. p. 186°, with 3 mols. 5-*hydroxy*-3-*carbethoxy*-4-*methyl*-2-*trichloromethylpyrrole* (XII), m. p. 117°. Et α-methyl-ββ-diacetylpropionate with NH_3 affords 5-*hydroxy*-3-*acetyl*-2 : 4-*dimethylpyrrole*, m. p. 143° (XIII) (*isomerides*, m. p. 196° and 173°; 5-*acetoxy*-derivative, m. p. 202—203°). XIII with 3 mols. of SO_2Cl_2 furnishes 5-*hydroxy*-3-*acetyl*-4-*methyl*-2-*trichloromethylpyrrole* (XIV), m. p. 152° (5-*acetoxy*-derivative, m. p. 151—152°); XII with aq. NaOH loses HCl and gives a product, m. p. 185°; XIV with aq. NaOH loses HCl and gives a *product*, m. p. 141°. XI with aniline yields a *substance* (probably Schiff's base), m. p. 241°, XII a *substance*, m. p. 227°.

5-Hydroxy-3-carbethoxy-2 : 4-dimethylpyrrole with Br gives 5-*hydroxy*-3-*carbethoxy*-4-*methyl*-2-*bromomethylpyrrole* (XV), decomp. 169° (excess of Br gives a *dibromo*-compound, m. p. 146°), which was used to prepare the following methenes: (5-*hydroxy*-3-*carbethoxy*-4-*methylpyrryl*)-(3-*carbethoxy*-2 : 4-*dimethylpyrryl*)*methene*, m. p. 266°; (5-*hydroxy*-3-*carbethoxy*-4-*methylpyrryl*) - (2 : 4 - *dimethyl* - 3 - *ethylpyrryl*)*methene*, m. p. 250° (3-*carboxy*-derivative, m. p. 296°); 5-*hydroxy* - 3 - *carbethoxy* - 4 - *methylpyrryl*) - (2 : 4 - *dimethylpyrryl*)*methene*, m. p. 264°; (5-*hydroxy*-3-*carbethoxy*-4-*methylpyrryl*) - (3-*acetyl*-2 : 4-*dimethylpyrryl*)*methene*, m. p. 286°; 5-*hydroxy*-3-*carbethoxy*-4-*methylpyrryl*)-(2 : 4-*dimethylpyrryl*-3-*carboxyethyl*)*methene* (XVI), m. p. 286° [*Ac* derivative, m. p. 241°; 3-*carboxy*-derivative, m. p. 294° (decomp.)]. XI and opsopyrrolecarboxylic acid give 5-*hydroxy*-3-*carbethoxy*-4 : 3′ - *dimethyl* - 4′ - *carbomethoxyethylpyrromethene* (XVII), m. p. 198° [corresponding 4′-*ethylpropionate* (XVIII), m. p. 159°]. XVIII condenses with CH_2O to the *di*-(XVIII)-*methane*, m. p. 244°, with PhCHO to *di*-(XVIII)-*phenylmethane*, m. p. 184°.

Chloromethyl ether reacts with substituted pyrroles to give methenes (cryptopyrrolemethene, 2 : 4-dimethylpyrrolemethene); with opsopyrrole, ætioporphyrin; with opsopyrrolecarboxylic acid, coproporphyrin. J. H. Birkinshaw.

Structure of products of reaction of nitric acid on acetonylacetone. IV. Action of nitric acid on acetylene. A. Quilico (Gazzetta, 1931, 61, 265—276; cf. A., 1930, 622).—The action of HNO_3 on C_2H_2 containing $COMe_2$ vapour gives, besides 4 : 5′-di*iso*oxazolyl ketone (I), small amounts of a *ketone*, $C_5H_2O_3N_2$, m. p. 161° (decomp.), which dissolves in alkali with evolution of heat, evolving CO_2 and HCN on acidification and giving on extraction with Et_2O *iso*oxazole-5-carboxylic acid, identical with that obtained by the action of alkali on I, showing that the group  is present.

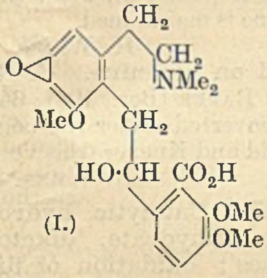
The action of HNO_3 on acetonylacetone (A., 1891, 890) gives a ketone $C_6H_4O_3N_2$, m. p. 128—129° (decomp.), which behaves with alkali like the C_5 ketone, of which it is probably the Me homologue, giving 3-methyl*iso*oxazole-5-carboxylic acid (A., 1901, i, 499). The mol. wt. of the C_6 ketone shows it to be $C_{12}H_8O_6N_4$. It is concluded that its structure is  and by analogy the structure  is assigned to the ketone, m. p. 161°, obtained from C_2H_2. E. E. J. Marler.

4 : 5′-Di*iso*oxazolyl ketone. M. Freri (Gazzetta, 1931, 61, 312—320).—The behaviour of this substance with various reagents has been found to confirm the structure,  (I) (this vol., 622). With $SnCl_2$ in HCl solution it gives 4 : 5′-*di*iso-*oxazolylcarbinol*, m. p. 88°, with EtMgBr 4 : 5′-*di*iso-*oxazolylethylcarbinol*, m. p. 68—69°, and with cold alcoholic NH_3 in a sealed tube a *compound* which very readily loses NH_3, re-forming I. Analysis of a freshly prepared specimen gives the formula $C_7H_7O_3N_3$, and the structure $\gg$C·C(OH)(NH_2)·C$\ll$ is suggested. Prolongation of treatment with NH_3 for two months gives 4 : 5′-*diisooxazolylketimine*, m. p. 88—89°. Heating I in a sealed tube with alcoholic NH_3 causes scission, giving a small amount of the *amide*, m. p. 142°, of *iso*oxazole-5-carboxylic acid. On boiling I with NH_2Ph (4 mols.) and excess of EtOH, the Schiff's base, $\gg$C·C(NPh)·C$\ll$, m. p. 99°, is obtained. Use of excess of NH_2Ph with a small amount of EtOH gives a *compound*, m. p. 125°, regarded as a stereoisomeride of the Schiff's base, into which it is converted by prolonged heating in an inert solvent. The *anilide,* m. p. 142°, of *iso*oxazole-5-carboxylic acid is described. E. E. J. MARLER.

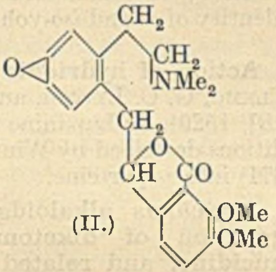
Unsaturation and tautomeric mobility of heterocyclic compounds of the thiazole type in relation to modern electronic conceptions. G. M. DYSON, R. F. HUNTER, J. W. T. JONES, and E. R. STYLES (J. Indian Chem. Soc., 1931, **8**, 147—180).—An attempt to summarise and explain the authors' published results on the lines indicated in the title. The following compounds appear to be new. s-p-*Tolylethylthiocarbamide,* m. p. 97° (from *p*-tolylthiocarbimide and NH_2Et), with Br affords the *hydrotetrabromide,* m. p. 78° (decomp.), of 1-*ethylamino-5-methylbenzthiazole,* m. p. 129° [3-*bromo*-derivative, m. p. 150° (*hydrotribromide,* m. p. 147°)]. Similarly are obtained s-p-*tolyl*-n-*propyl*-, m. p. 70°, -iso*butyl*-, m. p. 87°; s-p-*chlorophenyl-ethyl*-, m. p. 119°, -n-*propyl*-, m. p. 110°, -iso*butyl*-, m. p. 122°; s-o-*tolyl-ethyl*-, m. p. 90°, -n-, m. p. 53°, and -iso-, m. p. 68°, -*butyl*-, -n-, m. p. 74°, and -iso-, m. p. 57°, -*amyl*-, -n-*hexyl*-, m. p. 76°; p-*fluorophenyl*-, m. p. 164° (*thiocarbimide,* b. p. 228°/760 mm.); s-p-*fluorophenylmethyl*-, m. p. 70°; s-p-*iodophenylmethyl*-, m. p. 169°, -*thiocarbamide* : 1-n-*propylamino*-, m. p. 116° [*hydrotetrabromide,* m. p. 61°; 3-*bromo*-derivative, m. p. 116° (*hydrotribromide,* m. p. 130°)], 1-iso*butylamino*-, m. p. 132° {*hydrotribromide,* m. p. 89° (decomp.); 3-*bromo*-derivative, m. p. 95° [*hydrotribromide,* m. p. 126° (decomp.)]}, -5-*methylbenzthiazole* : 5-chloro-1-aminobenzthiazole [*hydrodibromide,* m. p. 230—235° (decomp.), previously described (A., 1927, 680) as a *dibromide,* m. p. 82—83°] is converted by Br in $CHCl_3$ into its 3-*bromo*-derivative, m. p. 245° (*dibromide*), and similarly are obtained 5-*chloro*-3-*bromo*-1-*methylamino*-, m. p. 180° [*hydrotribromide,* m. p. 270° (decomp.); *dibromide,* decomp. 250°], -1-*ethylamino*-, m. p. 155° [*dibromide,* m. p. 190°; *hydrotribromide,* m. p. 181—183° (decomp.)] [from 5-*chloro*-1-*ethylamino*-, m. p. 159° (*hydrotetrabromide,* m. p. 64—66°)], -1-n-*propylamino*-, m. p. 190° (*dibromide,* m. p. 173°; *hydrotribromide,* m. p. 191°) [from 5-*chloro*-1-n-*propylamino*-, m. p. 129° (*hydrotetrabromide,* m. p. 87°)], -1-iso*butylamino*-, m. p. 93° (*dibromide,* m. p. 265°) [from 5-*chloro*-1-iso*propylamino*-, m. p. 138° (*hydrotribromide,* m. p. 101°)], -*benzthiazole* ; 1-*ethylamino*-, m. p. 114° (*hydrotetrabromide,* m. p. 78°), 1-n-*butylamino*-, m. p. 50° (*hydrohexabromide,* m. p. 61°), 1-iso*butylamino*-, m. p. 58° (*hydrohexabromide,* m. p. 70—72°), 1-n-*amylamino*-, m. p. 48° (*hydrohexabromide,* m. p. 61°), 1-iso*amyl*-, m. p. 59° (*hydrohexabromide,* m. p. 57°), and 1-n-*hexylamino*-, m. p. 46° (*hydrohexabromide,* m. p. 58°); 5-*fluoro*-1-*amino*-, m. p. 182° (*Ac* derivative, m. p. 221°), -1-*methylamino*-, m. p. 174° (*Ac* derivative, m. p. 156°); 5-*fluoro*-1-*acetimino-2-methyl*-1 : 2-*dihydro*-, m. p. 197°; and 5-*iodo*-1-*amino*-, m. p. 210°, -1-*methylamino*-, m. p. 219° (*Ac* derivative, m. p. 185°; *picrate,* m. p. 245°), and -1-*imino-2-methyl*-1 : 2-*dihydro*- (*picrate,* m. p. 222°) -*benzthiazole.* Bromination of 2 : 4-dimethylthiazole [(*chloroplatinate,* m. p. 230—232° (decomp.)] gives the 5-*bromo*-derivative, b. p. 188—190°/745 mm. (*hydropentabromide,* m. p. 93—95°), and similarly are obtained 2-p-*toluidino*-, m. p. 127—128° {5-*bromo*-derivative, m. p. 142—143° [*hydrotribromide,* m. p. 128—129° (decomp.)]}, 2-o-*bromo*-p-*toluidino*-, m. p. 84—85°, and 2-p-*tolylmethylamino*-, m. p. 60°, -4-*methylthiazole*; and 2-p-*tolylimino*-3 : 4-*dimethyl*-2 : 3-*dihydrothiazole,* m. p. 107—108° (*hydriodide,* m. p. 224—226°). J. W. BAKER.

Quinoline derivatives. VIII. Photochemical oxidation of conchinine. H. JOHN and E. ANDRASCHKO (Ber., 1931, **64**, [*B*], 1286—1287; cf. A., 1926, 525).—When conchinine dissolved in 10% H_2SO_4 is irradiated in presence of anthraquinone-2-sulphonic acid, quinic acid is obtained in 56% yield together with about 2·6% of a dark resin, insol. in dil. mineral acids, whilst 36% of the base and 90·9% of the sulphonic acid can be recovered. H. WREN.

Some derivatives of narcotine. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1931, [iv], **49**, 542—550).—Reduction of narceine in aq. solution (Na–Hg) gives the secondary alcohol, *hydronarceine* (I), m. p. 154—155°, similarly obtained from narcotimethine and narcotine methiodide, which are intermediately converted into narceine. Reduction (Zn and HCl) of narceine and narcotimethine gives *hydronarcotimethine* (II) (*hydrochloride,* m. p. 200—210°; *nitrate,* m. p. 196°; *tartrate,* m. p. 140°; *chloroplatinate,* m. p. 192°; *methiodide,* m. p. 233—234°; *anil*). With narcotine methiodide the insol. $ZnCl_2$ compound of narcotine methiodide, m. p. 248°, is formed.



(I.)

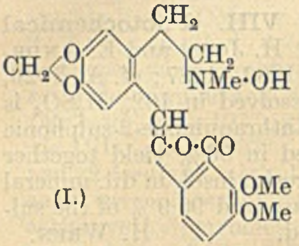


(II.)

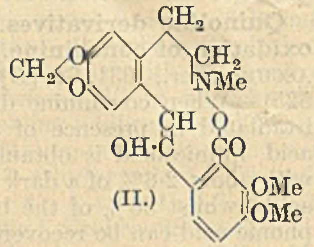
30% H_2O_2 in $COMe_2$ converts hydronarcotimethine into its N-*oxide,* m. p. 153°. On esterification in presence of HCl hydronarcotimethine and hydronarceine yield the same *Me,* m. p. 197°, and *Et,* m. p. 199—200°, esters of chlorohydronarceine. Nornarceine and excess of Ac_2O give *acetylnornarccmethine,* m. p. 120°, hydrolysed by alkali to acetylnornarceine, m. p. 130°. Reduction (Na–Hg and H_2O) of nornarceine yields *hydronornarceine,* m. p. 172°, which with HCl gives *hydronornarcotimethine,* m. p. 176°.

R. BRIGHTMAN.

Amine oxides of alkaloids. VIII. Transformation of hydrastine *N*-oxide into dialkylhydroxylamine; *N*-hydroxynorhydrastimethine and *N*-hydroxyhydrasteine. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1931, [iv], **49**, 533—543; cf. A., 1930, 935).—Hydrastine *N*-oxide slowly in the cold or rapidly in boiling $CHCl_3$ loses H_2O, basicity, and optical activity, giving anhydro-*N*-hydroxynorhydrastimethine (I), m. p. 189° (*hydrochloride,* m. p. 196°). In HCl with SO_2 I yields a mixture of a *sulphamino*-derivative, $C_{21}H_{20}O_6N{\cdot}SO_3H$, m. p. 229° (*Ba* salt), and a *sulphone,* $C_{21}H_{20}O_6N{\cdot}SO_2$, m. p. 218°, which on alkaline hydrolysis both yield the same *Na₂* salt of hydrasteinesulphamic acid, $C_{21}H_{21}O_5(CO_2Na)(SO_3Na)$; when kept for several months I becomes insol. in HCl and is converted into *anhydro*-N-*hydroxyhydrasteine* (II), m. p. 192°. It therefore represents an intermediate stage in the conversion of hydrastine-*N*-oxide into the disubstituted hydroxylamine.



(I.)



(II.)

N-Hydroxynorhydrastimethine dissolves in warm aq. $Ba(OH)_2$, yielding on acidification and extraction with $CHCl_3$ 70% of N-*hydroxyhydrasteine*, m. p. 205° [*Et ether*, m. p. 125° (*hydrochloride*, m. p. 132°; *sulphanic acid*, m. p. 177°), from either *N*-hydroxynorhydrastimethine or *N*-hydroxyhydrasteine], which on reduction with alkaline $FeSO_4$ yields a small amount of a secondary base, m. p. 175°, probably hydrasteine, together with a secondary alcohol. R. Brightman.

Yohimbine and quebrachine. Identity of α-yohimbine and *iso*yohimbine. K. Warnat (Ber., 1931, 64, [*B*], 1408—1410; cf. this vol., 243).—Contrary to Hahn and Schuch (this vol., 243), the identity of α- and *iso*-yohimbine is maintained. H. Wren.

Action of hydriodic acid on lupanine. G. R. Clemo, G. C. Leitch, and R. Raper (Ber., 1931, 64, [*B*], 1520).—*r*-Lupanine is converted under the conditions described by Winterfeld and Kneuer (this vol., 371) into *r*-sparteine. H. Wren.

***Strychnos* alkaloids. LX. Catalytic hydrogenation of diketonucine dihydrate, diketonucidine, and related bases; oxidation of dihydrobrucidine and a second degradation of diketonucidine to hydroxy*apo*nucidine.** H. Leuchs and F. Krohnke (Ber., 1931, 64, [*B*], 1307—1314).—Catalytic reduction of the pentahydrated Wieland acid in presence of PtO_2 or of 2-keto-3-hydroxynucine hydrate affords the acid $C_{17}H_{24}O_5N_2$, m. p. 224—225° (decomp.) (*perchlorate*). 2-*Keto*-3-*hydroxydihydronucidine* (*mono*- and *semi-hydrate*), m. p. (vac.) 257—259° after softening at 246°, $[\alpha]_D^{18}$ +67·7°/*d* in H_2O, is similarly derived from diketonucidine or 2-keto-3-hydroxynucidine; the *hydroperchlorate*, $[\alpha]_D^{18}$ +61·7°/*d* in H_2O, *hydrochloride*, $[\alpha]_D^{20}$ +68·4°/*d*, and *Ac* derivative, m. p. 143°, are described. 3-*Bromo-2-ketodihydronucidine* has m. p. 292° (decomp.). Dihydrobrucidine is oxidised by CrO_3 and H_2SO_4 at 75—80° to 2 : 3-*diketodihydronucidine*, $C_{17}H_{22}O_3N_2$, m. p. 252—252·5°, $[\alpha]_D^{15}$ +184·°/*d* in H_2O [*perchlorate*, $[\alpha]_D^{15}$ +136°/*d*; *semicarbazone*, m. p. (vac.) 252—254°], reduced (Clemmensen) to 2-keto-3-hydroxydihydronucidine. Catalytic reduction of the amino-acid $C_{16}H_{22}O_3N_2,4H_2O$ in presence of PtO_2 leads to *carboxydihydro*apo*nucidine*, $C_{16}H_{24}O_3N_2$, m. p. 289—291° (decomp.), $[\alpha]_D^{18}$ −32·1°/*d* (*perchlorate*), decarboxylated by distillation at 280—340°/15 mm. to dihydro*apo*nucidine, also obtained by hydrogenation of *apo*nucidine and isolated as the *dipicrate* $C_{27}H_{30}O_{15}N_8$, m. p. 187—189°, decomp. 190°. Oxidation of 2 : 3-diketonucidine by H_2O in presence of aq. NH_3 and subsequent addition of $HClO_4$ gives a *perchlorate*, $C_{17}H_{20}O_4N_2,HClO_4,H_2O$, $[\alpha]_D^{12}$ +35°/*d* to +8·9°/*d* or 9·9°/*d*; the corresponding base is transformed by aq. $Ba(OH)_2$ into oxalic acid and *hydroxy*apo*nucidine*, m. p. 216—218°, $[\alpha]_D^{12}$ −123°/*d* (*diperchlorate*). H. Wren.

Sinomenine and disinomenine. XXVI. Decomposition of sinomenine with methyl sulphate. K. Goto and K. Takubo (Bull. Chem. Soc. Japan, 1931, 6, 126—132; cf. this vol., 635).—Sinomenine with Me_2SO_4 in aq. suspension gives *sinomenine methyl methosulphate*, m. p. 265° (decomp.), whilst with Me_2SO_4 and 33% NaOH added alternately in small portions at room temp. it gives *methylsinomenine methyl methosulphate*, m. p. 245°. At 45° and with more alkali and Me_2SO_4 the same reaction gives *methylsinomenine violeomethine methyl methosulphate*, m. p. 204°, $[\alpha]_D^{13}$ +478° in H_2O, $[\alpha]_D^{20}$ +581·6° in $CHCl_3$, also obtained by methylating at 0° the sinomenine violeomethine which results from the action of cold 10% alkali on the crude achromethine. The mother-liquors from this last methylation when boiled yield *tetramethylbis*-5 : 5′-*sinomenol*, m. p. 288°, also obtained when sinomenine is kept for 3 weeks with Me_2SO_4 and NaOH, some dimethylsinomenol being also formed. The mother-liquors from this prep. are oxidised by $KMnO_4$ to dimethylsinomenolquinone (A., 1929, 1187). Sinomenine with Me_2SO_4 and NaOH, and subsequent boiling of the neutralised solution with Na_2CO_3, gives *methylsinomenine roseomethine methyl methosulphate*, m. p. 178°. The above methylsinomenine violeomethine methyl methosulphate when boiled with 2% NaOH gives 4 : 4′-*dimethylbis*-5 : 5′-*sinomenol*, m. p. 310° (*Ac_2* derivative, m. p. 230°) (yield 20%), and NMe_3. A. A. Levi.

Preparation of 3-carbamido-4-hydroxyphenylarsinic acid. W. G. Christiansen and A. E. Jurist (J. Amer. Pharm. Assoc., 1931, 20, 544—545).—The compound is prepared by Ehrlich and Bertheim's method. It is about twice as toxic as stovarsol. E. H. Sharples.

"Tryparsamide." G. Gilta (Bull. Soc. chim. Belg., 1931, 40, 189—194).—Spontaneous evaporation of an aq. solution of sodium anilinoacetamide-4-arsinate ("tryparsamide") affords a trihydrate (crystallographic data given). This loses, and the anhyd. salt absorbs, H_2O in the air. Precipitation of aq. solutions by EtOH gives a mixture of the trihydrate and anhyd. form. H. Burton.

Quinoline compounds. III. A. N. Brahmachari and T. Bhattacharjee (J. Indian Chem. Soc., 1931, 8, 7—10).—As derivatives of quinoline cannot be obtained by Bart's reaction or by the $Hg(OAc)_2$ method. Chloroacetyl-*p*-arsanilic acid reacts with aminoquinolines in alkaline aq. EtOH solution to form quinolineaminoacetyl-*p*-arsanilic acids. *Quinoline*-8-, m. p. 171° (decomp.) [*nitroso*-derivative, m. p. 182° (decomp.)], 6-*methoxyquinoline*-5-, *quinoline*-6-, and 2-*methylquinoline*-6-*aminoacetyl*-p-*arsanilic acid*, and their *nitroso*-derivatives (all m. p. above 240°) are described. 8- and 6-Aminoquinoline *p*-arsanilates are prepared from the amine and atoxyl, and melt above 240°. G. Discombe.

Resolution of *trans*-tetrahydroselenophen-2 : 5-dicarboxylic acid. A. Fredga (J. pr. Chem., 1931, [ii], **130**, 180—184).—*trans*-Tetrahydroselenophen-2 : 5-dicarboxylic acid (*quinine* salt $+2H_2O$) (A., 1930, 1196) is resolved by brucine and quinine into the l-, m. p. 173°, $[M]_D^{25}$ $-649°$ in 0·4N-HCl (*brucine* and *brucine hydrogen* salts), and d-*forms*, m. p. 173°, $[M]_D^{25}$ $+650·5°$ in 0·4N-HCl (*quinine hydrogen* salt $+1·5H_2O$). H. Burton.

Preparation of some new organo-thallium halides. F. Challenger and (Miss) B. Parker (J.C.S., 1931, 1462—1467).—$TlCl_3$ reacts immediately in hot aq. solution with phenylboric acid to give, according to the proportions of the reactants, *phenylthallium dichloride*, m. p. 235° (decomp.), and *diphenylthallium chloride*, m. p. above 310°. Similarly, $TlBr_3$ affords *phenylthallium dibromide*, m. p. 152° (decomp.). The dihalides are decomposed with H_2O and also give an immediate yellow ppt. with KI, which turns black, eliminating PhI. The black ppt. is $5TlI,TlI_3$. The presence of phenylthallium dihalides has also been detected in the product of the interaction of MgPhBr and ethereal $TlCl_3$. p-Tolylboric acid is converted by $TlBr_3$ into p-*tolylthallium dibromide*, m. p. 160—165° (decomp.), with some p-bromotoluene. The constitution of these compounds is discussed. F. R. Shaw.

Polymorphism of substances of high mol. wt. I. Amorphous and crystalline gelatin and the nature of the gelatinisation process in gelatin. J. R. Katz, J. C. Derksen, and W. F. Bon (Rec. trav. chim., 1931, **50**, 725—731).—Gelatin exists in a cryst. (β) form consisting of micelles, and in an amorphous (α) form. The reversible transformation of the two forms has been followed by X-ray examination. Ordinary air-dried gelatin (containing 18% H_2O) consists almost completely of the β-form, which is converted into the α-form by heating at 100° in a sealed tube. Stabilisation of the α-form is effected by cooling rapidly in liquid air. At room temp. and in the air the α-form is stable, but if it is allowed to swell in water and is then air-dried at 20°, it reverts to the β-form. It is concluded that the gelatinisation of gelatin sols consists in the transformation $\alpha \longrightarrow \beta$. J. D. A. Johnson.

Action of alkalis on the absorption spectrum of proteins. Dakin's theory of racemisation and enolisation of proteins. J. Gróh and M. Weltner (Z. physiol. Chem., 1931, **198**, 267—275; cf. A., 1930, 1460).—With egg-albumin and caseinogen in N-NaOH there was no change in the absorption spectrum at 25°; serum-globulin showed an increase in the extinction coeff. at the absorption max. in 0·1N-NaOH. At 100°, all the proteins examined showed considerable changes in absorption. The change, which is not reversible on acidification, is related to Dakin's enolisation theory of racemisation. In the large group of easily racemised proteins the enolisation is regarded as relatively slow and the re-formation of the inactive keto-compound as rapid, hence the enol form is not detected spectrophotometrically. When enolisation is still more difficult (second group), the enol form is probably more stable and hence detectable. J. H. Birkinshaw.

Micro-determination of carbon by wet combustion. H. Lieb and H. G. Kraineck (Mikrochem., 1931, **9**, 367—384).—The substance containing 1—3 mg. of C is heated at 130—135° with 3—4 c.c. of a solution of 20 g. of $Ag_2Cr_2O_7$ and 10 g. of $K_2Cr_2O_7$ in 200 c.c. of conc. H_2SO_4 in a current of O_2. The gases from the combustion vessel are passed through a tube containing platinised asbestos, Pt gauze, and Ag wool heated to dull redness, and then through a capillary tube into 0·1N-$Ba(OH)_2$ containing 1% $BaCl_2$ and sufficient phenolphthalein to give a pink solution. After 1 hr. the substance is completely decomposed and without stopping the O_2 current the $Ba(OH)_2$ solution is titrated with 0·05N-HCl containing 3% $BaCl_2$; filtration of the $BaCO_3$ ppt. is unnecessary. A. R. Powell.

Organic ultra-micro-analysis. Determinations of carbon and hydrogen on fractions of a milligram of a substance. J. B. Niederl and J. R. Meadow (Mikrochem., 1931, **9**, 350—359).—The substance is burnt in O_2 in a Pregl tube; the H_2O is absorbed in a $CaCl_2$ tube and the CO_2 in 1 c.c. of saturated $Ba(OH)_2$ solution containing 0·1 c.c. of EtOH. The $Ba(OH)_2$ solution is contained in a tube protected from ingress of air by soda-lime tubes and so constructed that the $BaCO_3$ formed can be collected, washed, dried, and weighed in the tube without coming into contact with the air. A. R. Powell.

Microchemical determination of nitrogen by Pregl's method (micro-Dumas). F. Govaert (Mikrochem., 1931, **9**, 338—344).—The method of Pregl is modified in that the CO_2 is generated by heating magnesite in a hard glass tube connected to the combustion apparatus by means of a T-piece provided with glass stopcocks and a Hg valve. A. R. Powell.

Micro-Dumas method. O. R. Trautz (Mikrochem., 1931, **9**, 300—312).—Possible sources of error in the determination of N by the micro-Dumas method are discussed. A. R. Powell.

Detection of organic compounds. L. Rosenthaler (Pharm. Ztg., 1931, **76**, 775—776).—p-Toluenesulphonic acid is suggested as condensing agent for the detection of alcohols by the odour of their esters. The odour of the ester can easily be detected when 1 c.c. of 1% EtOH is heated for 5 min. at 100° with a little BzOH and 1 g. of p-toluenesulphonic acid. It may advantageously replace H_2SO_4 in the " flower odour " reaction of atropine. $Pr^{\beta}OH$ can be recognised in presence of EtOH by its reaction with aromatic aldehydes; if to a mixture of 5 c.c. of a 5% solution of protocatechualdehyde in EtOH and 2 c.c. of 2% $Pr^{\beta}OH$ in EtOH be added 10 c.c. of H_2SO_4, the liquid turns brown and on dilution with H_2O blue. Fusel oil behaves similarly. $COMe_2$ produces the sequence red and purple to green after addition of H_2O. The formation of CHI_3 occurs more readily with $Pr^{\beta}OH$ than with EtOH and the rate of formation under standard conditions from the sample and pure EtOH by the action of alkaline hypoiodite can be followed nephelometrically. Terpin hydrate forms a lilac colour when its mixture with H_2SO_4 is poured into vanillin–HCl mixture. Menthol with similar treatment gives a raspberry-red colour.

Microchemical reactions of atroscine are described. They show no difference from those of *r*-scopolamine.
E. H. Sharples.

Colour reactions of phenols in common use. M. François and (Mlle.) L. Seguin (Bull. Soc. chim., 1931, [iv], **49**, 680—684).—The characteristic colour reactions of phenol, α- and β-naphthol, thymol, pyrocatechol, guaiacol, resorcinol, orcinol, quinol, pyrogallol, phloroglucinol, gallic acid, and salicylic acid with phthalic anhydride and H_2SO_4, H_2SO_4 alone, and with $CHCl_3$ in presence of KOH in the cold are described. The slight colour and fluorescence formed by H_2SO_4 in absence of added phthalic acid are attributed to the formation of phthaleins, due to phthalic acid formed by oxidation of the phenol. The coloration produced with $CHCl_3$ is better marked in alcoholic solution, the colouring matters formed being mostly insol. in $CHCl_3$ but sol. in EtOH. Whilst the three reactions can be used for the characterisation of the commonest phenols, the colorations obtained must be reviewed with those tabulated to avoid errors in interpretation.
R. Brightman.

Colour reactions in the system phenol–aldehyde–acid. V. E. Levine (J. Amer. Pharm. Assoc., 1931, **20**, 537—543).—The use of this system for detecting phenols of all types, aldehydes, substances which easily form aldehydes such as alcohols, many carboxylic acids, carbohydrates, and alkaloids, and inorg. acids is illustrated by an exhaustive list of examples.
E. H. Sharples.

Determination of citronellol and rhodinol in presence of geraniol and nerol. L. S. Glichitch and Y. R. Naves (Parfums de France, 1930, **8**, 326—333; Chem. Zentr., 1931, i, 1842).—The oil (1 vol.) is refluxed with 90% formic acid (2 vols.) and is frequently shaken during 1 hr. on the water-bath; after cooling it is washed with NaCl solution (50 c.c., repeatedly), 2% $NaHCO_3$ solution, and H_2O and dried with Na_2SO_4. The product (2 g.) is hydrolysed during 45 min. with 30 (or 20) c.c. of 0·5*N*-KOH. Tiemann and Schmidt's method employing PCl_3 gives low results.
A. A. Eldridge.

Colour reaction for quinones. R. Craven (J.C.S., 1931, 1605—1606).—*p*-Benzoquinone, *p*-benzoquinone dichloride, *o*-toluquinone, chloranil, α-naphthaquinone, and thymoquinone yield a bluish-violet colour, changing to blue, green, and finally red-dish-brown, on addition of 2—3 drops of $CN{\cdot}CH_2{\cdot}CO_2Et$ and excess of alcoholic NH_3. The reaction, which is intense with 0·1 mg. per c.c., and recognisable with 0·01 mg. per c.c., is not given by β-naphthaquinone, anthraquinone, chloranilamide, or phenanthraquinone.
R. S. Cahn.

Determination of morphine. L. Dávid (Pharm. Ztg., 1931, **76**, 706—708).—Morphine, heroine, and physostigmine react with diazotised anæsthesin, forming orange-red colours which can be extracted from the reaction mixture with $CHCl_3$. Many morphine derivatives react similarly, but the colours are not extracted. The reaction has been adapted to the determination of morphine in its preps. Physostigmine can be distinguished separately and the method will detect 0·00002 g. of morphine.
E. H. Sharples.

Determination and buffer action of polypeptides. J. Enselme (Bull. Soc. chim., 1931, [iv], **49**, 723—725).—The quantity of 0·001*N*-NaOH necessary to produce a given p_H val. in a buffer solution to which glycylglycine or Witte's peptone has been added is, within certain limits, directly proportional to the quantity of polypeptide added.
H. F. Gillbe.

Triketohydrindene hydrate as a reagent for albumin, peptone, and amino-acids. H. Gardner (Lancet, 1930, ii, 525—526).—Triketohydrindene hydrate is not a trustworthy reagent for the products of protein hydrolysis. The colour reaction is due to traces of free NH_3, or NH_3^+ ions, and is masked by NH_4OH or excess of alkali. H_2O containing 0·00865% NH_3 gives the characteristic blue colour.
L. S. Theobald.

Biochemistry.

Carbon dioxide compounds in hæmoglobin solutions. O. M. Henriques (J. Biol. Chem., 1931, **92**, 1—11).—Polemical. The author supports the formation of a mol. complex of hæmoglobin and CO_2 (cf. A., 1928, 1389) and refutes the view of Van Slyke and Hawkins (A., 1930, 1053) that catalytic acceleration of the reaction $HCO_3'+H^+ \rightleftharpoons H_2CO_3$ occurs.
F. O. Howitt.

Action of aluminium hydroxide sol on blood. H. Kühl (Z. ges. Getreidew., 1931, **18**, 22—24; Chem. Zentr., 1931, i, 1936).—A hæmoglobin solution may be almost completely decolorised by addition of a suspension of $Al_2(OH)_6$. The toxic action of alum in flour depends therefore on the coagulation of serum-albumin and the precipitation of the colouring matter of the hæmoglobin.
A. A. Eldridge.

Protein coagulation and its reversal. (*a*) Identity of normal hæmoglobin with hæmoglobin prepared by reversal of coagulation, as determined by solubility tests. (*b*) Globin. M. L. Anson and A. E. Mirsky (J. Gen. Physiol., 1931, **14**, 597—604, 605—609; cf. this vol., 426).—(*a*) The solubilities in aq. $(NH_4)_2SO_4$ of amorphous methæmoglobin, whether (i) normal, (ii) prepared by reversal of coagulation, or (iii) prepared from hæmin and globin prepared by reversal of coagulation of globin, are the same within 2%.

(*b*) Globin prepared from hæmoglobin by the acid $COMe_2$ method (Hill and Holden, A., 1927, 67, 689) is denatured globin, but the denaturation is readily reversible, for sol globin can be obtained from denatured globin after precipitation with trichloroacetic acid or heating to 100°.
R. K. Callow.

Differences between the gas analysis and colorimetric hæmoglobin determinations on splenectomised dogs. F. Haurowitz and M.

Reiss (Z. physiol. Chem., 1931, **198**, 191—195).—The differences between the figures obtained by the two methods are ascribed to a lipæmia induced by splenectomy, since strongly lipæmic blood gives erroneous results by the colorimetric method.

J. H. Birkinshaw.

Relationship between sedimentation rate of red corpuscles and the protein spectrum. W. M. Bendien and I. Snapper (Biochem. Z., 1931, **235**, 14—34).—The sedimentation rate and cell vol. of erythrocytes, the protein spectrum of the plasma, and in many cases the sedimentation rate of the defibrinated blood of 119 patients are compared. The sedimentation rate is always proportional to the fibrinogen content of the plasma. In most cases showing high sedimentation rate, the fibrinogen content is increased much more than the globulin content. In a few cases (cirrhosis of the liver) fibrinogen is present in normal or decreased amount, but the sedimentation rate is increased, due to the presence of greatly increased amounts of globulin. In a few cases both the fibrinogen and globulin contents are increased and the sedimentation rate is extremely high (100 mm. per 30 min.). In defibrinated blood, increased sedimentation rate runs parallel with increased globulin content. An empirical formula gives sedimentation rate as a function of the albumin and fibrinogen contents and the cell vol.

P. W. Clutterbuck.

Effect of sunlight on human blood-cells. W. W. Lepeschkin (Science, 1931, **73**, 568).—Exposure to direct sunlight gradually disintegrates and hæmolyses red corpuscles. Diffuse sunlight increases susceptibility only to subsequent hæmolysis by direct sunlight. Resistance to poisons and hypotony is diminished by the visible rays, but this effect is counteracted by short exposures to ultra-violet light. Ultra-violet light (Hg) destroys the red corpuscles.

L. S. Theobald.

Importance of the medium in the study of catalase. II. Action of alkali on blood-catalase. U. Sammartino and G. Lucchetti (Arch. Farm. sperim., 1931, **52**, 149—180).—When the p_H of rabbits' blood is raised by injection of $NaHCO_3$ the catalase activity increases slightly when the increase of p_H is large, but otherwise shows no significant variation. The variation of catalase activity in pathological conditions is, therefore, not merely an effect of the alteration of p_H.

R. K. Callow.

Analysis of whole blood. I. Precipitation of the proteins. II. Determination of sugar and non-fermenting copper-reducing substances. S. R. Benedict. **III. Determination and distribution of uric acid.** S. R. Benedict and J. A. Behre (J. Biol. Chem., 1931, **92**, 135—139, 141—159, 161—169).—I. Blood is diluted with 7 vols. of H_2O, and 1 vol. of Na tungstomolybdate reagent (A., 1929, 1189) is added followed by 1 vol. of $0{\cdot}62N$-H_2SO_4. Any one or all of the non-protein constituents of the blood may be accurately determined by the use of a filtrate so prepared. The use of laked blood for analysis is upheld.

II. The use of a new Cu reagent (a solution of Na_2CO_3, $CuSO_4$, Na R tartrate, and alanine) to which is added a small amount of $NaHSO_3$ is described. By use of tungstomolybdate filtrates satisfactory vals. are obtained for the total and (after fermentation) the non-fermentable Cu-reducing sugars (for which the term "saccharoids" is advocated). Zn filtrates contain non-fermentable reducing substances (cf. A., 1930, 801) the distribution and nature of which are discussed. By the use of the reagent without addition of $NaHSO_3$ the true sugar content is ascertained. Human blood (10 samples) contains 0·012—0·031% of non-fermentable Cu-reducing substances. The application of the method to 0·1 c.c. of blood is described.

III. The tungstomolybdate filtrate is mixed with a HCl–LiCl reagent followed by $AgNO_3$ solution and centrifuged. The supernatant fluid (free from thioneine) is treated with NaCN solution and arsenotungstate reagent (A., 1922, ii, 405) and the colour compared with appropriate standards. Corpuscular uric acid averages 72% of the plasma content. A micro-technique is also given.

F. O. Howitt.

Ionic equilibria in the serum in relation to the critical temperature. P. L. Du Noüy (Science, 1931, **73**, 595—597).—The precipitation by H_2O of the globulins in horse-serum has been followed optically. The instability of the serum reaches a max. at 0·33% of salts. Heating above 55° increases the instability of the system, but at 60° no sedimentation of the globulins occurs.

L. S. Theobald.

Lactic acid determination in blood. O. Jervell (Biochem. Z., 1931, **235**, 101—103).—The $K_2Cr_2O_7$ method of Hansen (A., 1926, 444) for determination of lactic acid in pure solutions is somewhat modified and applied to its determination in blood-filtrates.

P. W. Clutterbuck.

Influence of diet and avitaminosis on blood-glycolysis. I. Cholesterol and lecithin. Y. Kawashima and J. Chiwaki (J. Biochem., Japan, 1931, **13**, 107—132).—Cholesterol-feeding in rabbits results in an increase of blood-cholesterol, especially of the plasma, and, at a later period, in a decrease in glycolytic activity both of the serum and corpuscles. The fasting blood-sugar level is generally increased. Lecithin exhibits no such phenomena, but when administered to rabbits soon after discontinuance of cholesterol-feeding it induces a more rapid return of the glycolytic activity and blood-sugar to normal levels.

F. O. Howitt.

Calcium. IV. Blood-calcium changes following administration of calcium gluconate given subcutaneously to normal and parathyroidectomised dogs and *per os* to human beings. A. L. Lieberman (J. Pharm. Exp. Ther., 1931, **42**, 245—252).—In dogs subcutaneous administration of 10% solutions of Ca gluconate (25 mg. per kg. body-wt.) causes a rise in blood-Ca, max. in about 1 hr., followed by a fall which is steeper in parathyroidectomised than in normal animals. In man oral administration of Ca gluconate (10 g. in 250—375 c.c. H_2O) brings about a rise in blood-Ca (max. after 4 hr.) provided that it does not produce diarrhœa. Food may favour adsorption by decreasing peristaltic action.

W. O. Kermack.

Determination of iron in blood. F. Reis and H. H. Chakmakjian (J. Biol. Chem., 1931, 92, 59—63).—Blood (0·2 c.c.) is oxidised by H_2SO_4 and $KClO_4$ and then treated with $K_4Fe(CN)_6$ in gum-ghatti solution. The colour due to the dispersed Prussian-blue is compared with suitable standards.
F. O. Howitt.

Determination of phosphorus in small quantities of serum. G. Popoviciu (Bull. Soc. Chim. biol., 1931, **13**, 548—551).—The serum (0·12 c.c.) is deproteinised by trichloroacetic acid and treated with an $(NH_4)_2MoO_4$ reagent containing strychnine nitrate. The ppt. is washed with H_2O, dissolved in NaOH, $K_4Fe(CN)_6$ and HCl are added, and the solution is compared colorimetrically with appropriate standards. F. O. Howitt.

Bromide distribution in blood. I. Bromide and chloride distributions *in vitro*. A. B. Hastings and H. B. van Dyke. **II. Bromide and chloride distributions following oral administration of sodium bromide.** H. B. van Dyke and A. B. Hastings (J. Biol. Chem., 1931, 92, 13—25, 27—32).—An electrometric method for the determination of Br′ and Cl′ in presence of each other is described. Addition of NaBr to dog's blood *in vitro* results in a distribution ratio of Br′ between corpuscles and serum 10% higher than the corresponding ratio for chloride. Br ions are freely diffusible between corpuscles and serum. Change in reaction or degree of oxygenation produces a change of distribution in agreement with the Donnan equilibrium theory.

II. The abnormally high (up to 2·0) Br′ distribution ratios between corpuscles and serum following oral administration of 40 g. of NaBr to dogs and the concomitant low vals. for the corresponding Cl′ ratios indicate that corpuscular Cl′ is present partly in non-ionic form which can be displaced by Br, a conclusion supported by the extent of diffusion of Br′ occurring when normal serum is mixed with Br-containing cells and *vice versa*. F. O. Howitt.

Action of acids on blood coagulation. Neutralisation of acid character. R. Douris, C. Mondain, and M. Plessis (Compt. rend. Soc. Biol., 1930, **104**, 278—280; Chem. Zentr., 1931, i, 1936).—When H_2SO_4 (1 c.c.) is added to coagulated blood (10 c.c.) the titratable acidity diminishes rapidly, reaching a practically constant val. (76%) after 45 min. With HNO_3 the fall continues for 5 hrs., but a rise is observed on the fourth and fifth days. With HCl, H_3PO_4, AcOH, and oxalic acid the effect continues for 4—5 hr. A. A. Eldridge.

Action of anticoagulants on serum-enzymes and -complement. K. Yanagisawa (J. Biochem., Japan, 1931, 13, 11—42).—Heparin exerts no influence on the action of the blood-enzymes except glycerophosphatase and lecithinase, the actions of which are slightly enhanced. The action of proteinogenic, but not of lipinogenic, hæmolysins is inhibited by heparin, whilst novirubin inhibits the action of both types. Hence the hæmolysis due to the complex hæmolysin system produced by injection of goat blood into rabbits is inhibited by novirubin but not by heparin. The mixtures of the globulin and albumin fractions separated from guinea-pig serum by normal methods retain their complement action for proteinogenic but not for lipinogenic hæmolysis.
F. O. Howitt.

Chemical significance of immunohæmolysis. L. Jarno and L. Suranyi (Z. Immunität., 1930, 69, 298—304; Chem. Zentr., 1931, i, 1780).—Various amino-acids behave differently towards the normal amboceptors of various animals. Immunohæmolysis is increased by amino-acids, and particularly by glycine. The participation of cholate in hæmolysis is supported. A. A. Eldridge.

Enzymic phosphatide fission and immune hæmolysis. E. Brunius (Arkiv Kemi, Min., Geol., 1931, **10**, **A**, No. 8, 13 pp.).—Kidney- but not pancreatic lipase or guinea-pig serum splits off phosphoric acid from lecithin. Goat-blood erythrocytes treated with complement and amboceptor undergo hæmolysis with concomitant formation of free phosphate. Equal phosphate formation occurs with saponin in place of amboceptor, the results being in agreement with those on fat-splitting in immune hæmolysis (cf. A., 1924, i, 784). The theory of complement action being of a lipolytic nature is not upheld.
F. O. Howitt.

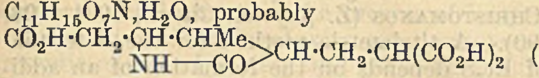
Saponin hæmolysis. E. Gorter, F. Grendel, and W. A. Seeder (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 471—473).—Complete hæmolysis occurs when there is sufficient saponin available to cover the surface of the cells with a layer 1 mol. thick. J. W. Smith.

Nature and specificity of antigens. P. Carneiro and W. Kopaczewski (Compt. rend., 1931, **192**, 1595—1598).—Guinea-pigs can be sensitised to colloids, more particularly to positively-charged colloids. After sensitisation to horse serum positively-charged colloids induce anaphylactic shock. C. C. N. Vass.

Diminution in chloride measurement after drying blood and tissues. F. W. Sunderman and P. Williams (J. Biol. Chem., 1931, **92**, 99—107).—The Cl content of dried blood and tissues as determined by normal analytical methods is up to 31% less than that given by the moist samples. Soaking of the dry samples in water for some hrs. results in a recovery equal to that for the original wet samples. This retention of Cl is due to fats or fatty acids.
F. O. Howitt.

Iodometric titration of glutathione. E. J. King and C. C. Lucas (Biochem. Z., 1931, **235**, 66—69).—Accurate vals. for the glutathione content of any solution by this method can be obtained only when the I titration is carried out in acid solution and at temp. below 25°. P. W. Clutterbuck.

Tribasic acid present in liver, convertible into pyrrole derivatives. H. D. Dakin and R. West (J. Biol. Chem., 1931, **92**, 117—133).—An aq. solution of liver extract powder is precipitated by basic Pb acetate, the filtrate, freed from Pb, is treated with picric acid and extracted with $BuOH-Et_2O$ mixture. The aq. layer is precipitated by phosphotungstic acid and the ppt. is treated according to the technique previously described (A., 1930, 1309). This yields a water-sol., EtOH-insol., *Ba* salt of a tribasic acid, $C_{11}H_{15}O_7N,H_2O$, probably



$$\begin{matrix}CO_2H\cdot CH_2\cdot CH\cdot CHMe \\ \qquad NH—CO\end{matrix}\!>\!CH\cdot CH_2\cdot CH(CO_2H)_2$$

(*quinine* salt, $C_{11}H_{15}O_7N,H_2O,1\cdot5C_{20}H_{24}O_2N_2$, m. p. 149—150°, $[\alpha]_D^{20}$ $-147°$). Intravenous administration of the acid in a single dose of 0·25—0·75 g. results in a distinct rise in reticulocytes, which, however, is not considered identical with that produced by liver extract. Heating the acid in a sealed tube with excess of $Ba(OH)_2$ at 120—130° yields an Et_2O-sol. pyrrolecarboxylic acid, whilst at 155—165° hæmopyrrole is produced. The possibility of the acid being a precursor of hæmoglobin is discussed. F. O. HOWITT.

Preparation of egg-yolk lecithin. Y. SUEYOSHI (J. Biochem., Japan, 1931, **13**, 145—154).—The ethereal extract of egg-yolk is evaporated in vac. and the residue repeatedly extracted with cold $COMe_2$. The wax-like, colourless residue is treated with 5—6 vols. of EtOH and the extract cooled to −14°, when cephalins are precipitated. The fluid portion is evaporated in a vac. and precipitated by $COMe_2$. Digestion with $COMe_2$ at 55° removes fats, yielding a product containing 3·84% P and 1·74% N. The Cd compound contained 11·13% Cd. F. O. HOWITT.

Fatty acids of egg-yolk lecithin. I. Saturated acids. II. Unsaturated acids. Y. SUEYOSHI and T. FURUKUBO (J. Biochem., Japan, 1931, **13**, 155—175, 177—183).—I. Small amounts of stearic and palmitic acids are present. The main constituent is *iso*palmitic acid, m. p. 56—57°.

II. The unsaturated acids include oleic acid (73·2%), clupanodonic acid (5·1%), and linoleic acid (2·1%). F. O. HOWITT.

Fatty acids and unsaponifiable substances in tissue. T. FURUKUBO (J. Biochem., Japan, 1931, **13**, 185—209).—An increase of the muscle-fatty acids is produced in rabbits by administration of vitamin-*A* in excess, of adrenaline and of insulin in small amounts, whereas starvation, injection of insulin in large doses, and thyroid-feeding cause a decrease. The unsaponifiable fraction is increased by starvation and decreased by hunger, by injection of insulin in large doses, and by thyroid-feeding. Thus insulin in small amounts brings about a change of sugar to fat, whilst large doses have the opposite effect. The relation of the unsaponifiable fraction to the carbohydrate metabolism is discussed. F. O. HOWITT.

Cholesterol of protoplasm. VIII. Ox spinal chord. G. PFEIFFER (Biochem. Z., 1931, **235**, 97—100).—The percentage oxy- and esterified- of the total cholesterol of ox spinal chord is greater than with brain. The esters are exclusively formed from oleic acid and oxycholesterol. P. W. CLUTTERBUCK.

Insect wax. III. Wax of the wool louse (*Pemphigus xylostei*). F. N. SCHULZ and M. BECKER (Biochem. Z., 1931, **235**, 233—239).—Wax of *Pemphigus xylostei*, $C_{68}H_{136}O_4$, m. p. 108—109°, on hydrolysis gives a dialcohol, $C_{34}H_{70}O_2$, m. p. 100—105°, and a hydroxy-acid, $C_{33}H_{67}(OH)\cdot CO_2H$, m. p. 101—102° (cf. this vol., 642). P. W. CLUTTERBUCK.

Phosphatase activity of transplants of the epithelium of the urinary bladder to the abdominal wall producing heterotopic ossification. C. B. HUGGINS (Biochem. J., 1931, **25**, 728—732).—In heterotopic osteogenesis with transplants of the urinary bladder epithelium to the abdominal fibrous tissue in the dog, the ratio of phosphatase activity to dry wt. was very high, at least 2·5 to 8 times the max. and 10—20 times the mean vals. of the control tissues without bone. S. S. ZILVA.

Soluble enzymes in the spleen. E. LABORDE and H. WYLER (Bull. Soc. Chim. biol., 1931, **13**, 552—554).—The presence of the following enzymes in extracts of spleen was demonstrated: amylase, glycogenase, invertase, inulase(?), lipase, lecithase, pepsin, trypsin, erepsin, urease, hippuricase, salicylase, peroxidase, and catalase. Lactase, glycolase, nuclease, deamidase, oxidases, tyrosinase, and phosphatase could not be detected. F. O. HOWITT.

Modification of Mallory's triple stain. B. KRICHESKY (Stain Tech., 1931, **6**, 97—98).—An improvement in detail of the technique of staining connective tissue is described. H. W. DUDLEY.

***iso*Hæmatein as a biological stain.** E. C. COLE (Stain Tech., 1931, **6**, 93—96).—*iso*Hæmatein has a staining power greater than that of hæmatoxylin, but is not so selective for nuclei. The dye may be useful as a differential stain for nerve-cell bodies. H. W. DUDLEY.

Rapid methods for tissue diagnosis. A. M. HJORT and C. H. MOULTON (Stain Tech., 1931, **6**, 83—91).—Two new methods for staining fixed and fresh frozen tissue sections are presented. H. W. DUDLEY.

Vapour pressures of aqueous solutions with special reference to the problem of the state of water in biological fluids. A. GROLLMAN (J. Gen. Physiol., 1931, **14**, 661—683).—Using Hill's method (A., 1930, 689, 1211) data for the depression of v. p. have been obtained for aq. solutions of NaCl (0·03—0·1*M*), KCl (0·03—0·1*M*), carbamide (0·05—0·5*M*), sucrose (0·05—0·1*M*), lactic and succinic acids, creatine, $CaCl_2$ (0·05*M*), and mixtures of these substances with one another and with certain other solutions, *e.g.*, gelatin, gum-acacia, sea-water, and LiCl. The relation of the depression of v. p. of a mixed solution to that of solutions of the individual constituents was investigated in order to see how far such methods could be applied to the determination of the degree of hydration or the state of water ("free" or "bound") in solutions. Org. substances showed anomalous results, unpredictable in mixed solutions, and in the case of LiCl and $CaCl_2$ the principle of the additive nature of colligative properties is only approx. true, and the determination of degree of hydration is possible only with certain limitations.

Using NaCl or KCl, hydration in gelatin is relatively small at p_H 7, and undetectable in gum-acacia solutions. The supposed high degree of hydration of hydrophilic colloids is, therefore, not substantiated. The change from sol to gel in gelatin or blood is not accompanied by appreciable change in the degree of hydration. R. K. CALLOW.

Cerebrospinal equilibrium of hydrogen carbonates. P. CRISTOL (Compt. rend., 1931, **192**, 1672—

1674).—If hydrogen carbonates obey Derrien's law, the ratio of the concentration of CO_2 in cerebrospinal fluid to that in blood is 1. In keto-acidosis the ratio is less than 1, the more so as acetoacetic acid accumulates in the blood. A decreased ratio is also given if the cerebrospinal fluid contains organisms which induce glycolysis. C. C. N. Vass.

***Post-mortem* changes in cerebrospinal fluid.** I. Sümegi and L. Findeisen (Magyar orvosi Arch., 1930, **31**, 464—467; Chem. Zentr., 1931, i, 1938).—Colloid reactions were normal for 9 hr., later changes being connected with the increase in total and non-protein-N, the change in the albumin : globulin ratio, and the shift of p_H towards the acid side.
A. A. Eldridge.

Uric acid and allantoin in gastric juice. Y. Inatsugu (J. Biochem., Japan, 1931, **13**, 1—9).—Uric acid and allantoin are normal components of the gastric fluid of man and dog. Intravenous administration of uric acid in the dog results in a marked increase in the allantoin content of the juice. No relation exists between the quantity of either substance and the gastric acidity. F. O. Howitt.

Polarimetric determination of bile acids in body-fluids and organs. F. Rosenthal (Arch. exp. Path. Pharm., 1931, **160**, 460).—Polemical against Jenke (this vol., 509; cf. *ibid.*, 251).
W. O. Kermack.

Influence of bile acids on the inorganic salts of the bile. Y. Kawada (J. Biochem., Japan, 1931, **13**, 133—144).—Oral administration of Na cholate to dogs increases the relative and abs. contents of H_3PO_4 and Ca in the bile due to an increased nuclein catabolism. F. O. Howitt.

Nature of the "ether reaction" of urine. W. J. Boyd (Biochem. J., 1931, **25**, 812—817).—Two substances responsible for the reaction have been isolated from the urine of asthmatic and normal subjects. One is an irreversibly coagulable protein possibly identical with serum-albumin and the other a mucoid containing 12·5% of N, possibly derived from the urinary passages. S. S. Zilva.

New clinical method for determination of protein in urine. P. M. T. Kerridge (Lancet, 1931, i, 21—22).—Urine is mixed with a suspension of C, and C and protein are precipitated by $CCl_3{\cdot}CO_2H$. With a const. amount of C, the grey colour depends on the amount of protein. The error is 0·025—0·05 g. protein-N% and the accuracy is unaffected by artificial light. L. S. Theobald.

Micro-determination of allantoin. Application to human urine. R. Fosse, A. Brunel, and P. E. Thomas (Compt. rend., 1931, **192**, 1615—1619).—The absorption density of glyoxylic acid phenylhydrazone is proportional to its concentration. Allantoin in human urine is hydrolysed for 24 hr. in presence of KCN by allantoinase. After removal of the proteins, phenylhydrazine and HCl are added and the absorption spectrum is examined before and after hydrolysis. In 7 individuals the concentration of allantoin varied from 18 to 35 mg. per litre.
C. C. N. Vass.

Occurrence of ethyl sulphide in dog's urine. A. A. Christomanos (Z. physiol. Chem., 1931, **198**, 185—190).—A titrimetric method for the determination of Et_2S depends on the formation of an additive compound with I. Dogs excrete 4—7 mg. of Et_2S daily. With a diet rich in carbohydrate the Et_2S is higher than with a diet rich in protein.
J. H. Birkinshaw.

Determination of sugar in urine by means of "glucophot." J. J. Hofman and J. de Keuning (Pharm. Weekblad, 1931, **68**, 584—589).—The method and apparatus are satisfactory for rapid approximations. S. I. Levy.

Excretion of uric acid. V. B. Wigglesworth (Nature, 1931, **128**, 116).—Evidence is given for the view that in *Rhodnius prolixus* the upper parts of the 4 Malpighian tubes secrete a solution of acid urates from the blood into the lumen and in the lower parts H_2O and base are re-absorbed and insol. uric acid is precipitated. A continuous circulation of H_2O and base results. L. S. Theobald.

Determination of uric acid. J. L. St. John and O. Johnson (J. Biol. Chem., 1931, **92**, 41—45).—Uric acid in avian excrement is determined by extraction with piperidine solution and formation of NH_4 urate which is converted into uric acid and weighed as such. The error does not exceed 0·22%.
F. O. Howitt.

Intraperitoneal iron. C. G. Grulee and H. N. Sanford (Amer. J. Dis. Children, 1931, **41**, 53—61).—Fe injected intraperitoneally into rabbits is deposited in the liver rather than the spleen; the hæmoglobin and erythrocyte contents of the blood are unchanged. Injection of colloidal $Fe(OH)_3$ into children with secondary anæmia increases the blood-hæmoglobin and -erythrocytes. Chemical Abstracts.

Value of determinations of iron content of whole blood. W. P. Murphy, R. Lynch, and I. M. Howard (Arch. Int. Med., 1931, **47**, 883—892).—The "iron index" (ratio of mg. of Fe per 100 c.c. of whole blood to millions of red cells per cu.mm.) is nearly const. for normal persons, and averages 8·46. In pernicious anæmia the index is above 10, and is generally below normal in secondary anæmia.
A. Cohen.

Inhibitory effect of monoiodoacetic acid on lactic acid production by cancer tissue. S. T. Harrison and E. Mellanby (Biochem. J., 1931, **25**, 770—772).—The aërobic production of lactic acid by tumour slices is inhibited by iodoacetic acid. A single injection of a sublethal dose in mice did not produce an inhibition of lactic acid production.
S. S. Zilva.

Mineral metabolism in multiple inoculation-sarcoma in rats. F. Eichholtz (Biochem. Z., 1931, **235**, 170—173).—The Ca content of this tissue for different animals is 70—350 mg. per 100 g. dry substance. The val. does not vary by more than 1—2% in different slices from the same animal. The Mg content of the tumour cells is also const. in the same animal (differences 5—10%).
P. W. Clutterbuck.

Tumour immunity. T. Lumsden (Amer. J. Cancer, 1931, **15**, 563—640).—The euglobulin fraction of an anti-malignant-cell serum contains the anti-malignant-cell bodies; in the process of its precipitation most of the heterotoxins are destroyed. The cytolytic effects of the eu- and pseudo-globulin fractions on mouse and human cancer cells are described. The results demonstrate that antibodies which are specifically lethal to malignant cells exist; they are toxic to malignant cells of all varieties, which may therefore have a common constituent capable of acting as an antigen. CHEMICAL ABSTRACTS.

Malignant conditions. J. H. ROE and H. M. DYER (Amer. J. Cancer, 1931, **15**, 725—731).—Fowls bearing Rous sarcoma No. 1 have a reduced carbohydrate tolerance. The glycogenolytic activity of the blood is normal, but the glycolytic activity is double the normal. The glycolytic activity of the blood is of no clinical diagnostic value.

CHEMICAL ABSTRACTS.

Effect of ergotamine on the blood-sugar in normal and diabetic conditions and in disease of the liver. G. CORBINI (Policlinico, 1930, 11 pp.; Chem. Zentr., 1931, i, 2078).—In diabetes hyperglycæmia is produced; the other cases are unaffected.

A. A. ELDRIDGE.

Diabetes insipidus. F. MAINZER (Arch. exp. Path. Pharm., 1931, **160**, 461—478).—The ability to concentrate the body-fluids in diabetes insipidus is quant. similar for chlorides and hydrogen carbonates, although the basic equiv. is of greater significance than the actual concentration of Cl′. Previous findings with regard to the protein content of the serum in diabetes insipidus (Arch. klin. Med., 1930, **169**, 1) are confirmed. P. G. MARSHALL.

Creatinine metabolism in diabetes insipidus. L. D'ANTONA (Arch. Ist. Biochim. Ital., 1931, **3**, 187—204).—Contrary to Pakodzy (Z. klin. Med., 1930, **112**), excretion of creatinine in the urine is not necessarily augmented in diabetes insipidus. Records are given of the excretion of urine and creatinine of four patients, and of the effects of administering pituitary extract or mercurials (*e.g.*, "salyrgan"), which sometimes have a notable antidiuretic effect accompanied by retention of creatinine.

R. K. CALLOW.

Carbamide content of cerebrospinal fluid in status epilepticus. O. R. BINYON and J. T. FOX (Lancet, 1930, ii, 1233—1234).—Carbamide and dextrose contents are high. L. S. THEOBALD.

Guanidine-like substances in the blood in experimental yellow fever. G. M. FINDLAY and E. HINDLE (Lancet, 1930, ii, 678—679).—In experimental yellow fever in monkeys the guanidine-like substances in the blood are increased. Ca lactate reduces this increase, tends to prevent hæmorrhages, but does not prevent death. L. S. THEOBALD.

Gallstone formation. I. Determination of streaming potential and applicability of Schultze–Hardy rule; relation between ζ-potential and coagulation. II. Lyotropic series and influence of acids and alkalis; relation between ζ-potential and adsorption. III. Influence of anions and halogen group. N. FURUTANI, T. KUROKOCHI, and Y. ASODA (Japan. J. Gastroenterol., 1930, **2**, 148—157, 158—161, 162—165).—I. The e.m.f. was proportional to the pressure but independent of the diameter and length of the glass capillary. The potential decreases in the order (equiv. mol. conc.) KCl, $BaCl_2$, $AlCl_3$, $Th(NO_3)_4$. Lyophobic sols are coagulated by a solution of an electrolyte when the streaming potential of the latter becomes sufficiently low. Crystal-violet behaves like quadrivalent electrolytes.

II. The streaming potential decreases in the order (*a*) Li, Na, K, Rb, NH_4, Cs, (*b*) Mg, Ca, Ba, as chlorides. The max. potential of NaOH is much greater than that of HCl.

III. The streaming potential decreases in the order (*a*) $0{\cdot}25K_4Fe(CN)_6$, $0{\cdot}33K_3Fe(CN)_6$, $0{\cdot}5K_2SO_4$, KCl, (*b*) I, Br, Cl. CHEMICAL ABSTRACTS.

Ultra-violet light and goitre. T. VON FELLENBERG (Biochem. Z., 1931, **235**, 205—213).—The I contents of the thyroid glands of white rats kept in the dark and in bright light (Davos) did not show differences parallel with the histological changes obtained under similar conditions by Bergfeld (Strahlenther., 1930, **39**, 245). The I contents of the air, drinking water, milk, etc. of Davos and that of the urine of a few inhabitants are tabulated. The incidence of goitre is what would be expected from the I content of the environment, and no evidence could be obtained that ultra-violet irradiation decreased the incidence of goitre. P. W. CLUTTERBUCK.

Differential stain favourable to the diagnosis of Neisserian infection. S. A. SCUDDER (Stain Tech., 1931, **6**, 99—105).—Air-dried films are stained for 3—5 min. in 1% crystal-violet solution in 10 parts of phosphate buffer of p_H 6·6—7·0 and 90 parts of H_2O. They are then flushed with 2% I in 0·1*N*-NaOH, after which they are decolorised in $COMe_2$ for 10 sec. After air-drying they are counterstained for 1·5—2 min. in a mixture of 2 parts of 2% aq. Me-green and 1 part of 0·3% aq. pyronin-yellowish. They are then washed and air-dried. Bergamot oil is preferable to xylene as a clearing agent. H. W. DUDLEY.

Congestive heart failure. VIII. Effect of administration of dibasic potassium phosphate on the potassium content of certain tissues. J. A. CALHOUN, G. E. CULLEN, G. CLARKE, and T. R. HARRISON (J. Clin. Invest., 1931, **9**, 693—703).—The tissue-K was subnormal in heart failure; administration of K increases the tissue-K, the difference being most marked in skeletal muscle and least in heart muscle. CHEMICAL ABSTRACTS.

Hypoglycæmia. Clinical syndrome, etiology, and treatment: a case due to hyperinsulinism. G. D. GAMMON and W. C. TENERY (Arch. Int. Med., 1931, **47**, 829—854).—A clinical review. A. COHEN.

Analyses of the blood of idiots. S. S. NEGUS (Science, 1931, **73**, 449—450).—Abnormal amounts of inorg. phosphate were not found.

L. S. THEOBALD.

Biochemistry in relation to intelligence. H. D. POWERS (Science, 1931, **73**, 316).—In idiots, blood-Ca is normal but blood-P is high. L. S. THEOBALD.

[Nature of] two types of bilirubin diazo-reaction in serum. Hypothesis on nature of bilirubin in serum from hæmolytic jaundice.

G. Hunter (Brit. J. Exp. Path., 1930, **11**, 415—419).—The "direct" reaction is probably due to Na H bilirubinate, and the "delayed" reaction to free bilirubin in an undetermined solvent. The bilirubin may be combined with its solvent (lipin or sterol) or some other serum constituent so that it resists salt formation and oxidation. Chemical Abstracts.

Manganese in foodstuffs. Possible relation to cirrhosis of the liver. A. E. Boycott and G. R. Cameron (Lancet, 1930, ii, 959).—The Mn contents of various foodstuffs are recorded. Cloves, tea, spice, pepper, scallops, winkles, and ginger contain most Mn. No relation to cirrhosis is evident.
L. S. Theobald.

Chemotherapeutic treatment by colloidal magnesium hydroxide of liver and kidney lesions produced experimentally by poisons. E. Přibyl (Arch. exp. Path. Pharm., 1931, **160**, 255—268).—Colloidal $Mg(OH)_2$ administered intravenously to rabbits suffering from kidney and liver lesions produced experimentally by As_2O_3, P, and $UO_2(NO_3)_2$ exerts a distinct beneficial effect on the animals. The action is probably due partly to the basic nature of the reagent and partly to the sp. action of $Mg^{\cdot\cdot}$. W. O. Kermack.

Plasma-protein loss with œdema but without proteinuria, and its bearing on the concept of nephrosis. T. I. Bennett, E. C. Dodds, and J. D. Robertson (Lancet, 1930, ii, 1006—1008).—Considerable protein loss may occur from blood by routes other than the kidney and œdema follows such loss.
L. S. Theobald.

Rôle of the lipins and proteins of blood on water exchange in the organism. A. Machebœuf (Compt. rend., 1931, **192**, 1413—1415).—Serum-albumin from the blood of patients suffering from lipoid nephrosis has a greater combining capacity than normal serum-albumin on the basic but not on the acid side of the isoelectric point. It also exerts a greater osmotic pressure per g. in solution and, further, the lipins associated with it are more readily extracted with Et_2O than in the case of normal serum-albumin. An albumin fraction was obtained from horse serum of high lipin content showing abnormally high combining power on the alkaline side of the isoelectric point. W. O. Kermack.

Lipin nephrosis. I. Lipins carried down with serum-globulin and -albumin precipitates. M. A. Machebœuf and R. Wahl. **II. Lipins and lipin fractions of blood-serum.** M. A. Machebœuf, R. Wahl, and G. Sandor. **III. Fractionation of serum-albumin and the accompanying lipins.** M. A. Machebœuf and R. Wahl (Bull. Soc. Chim. biol., 1931, **13**, 486—503, 504—510, 511—515; cf. this vol., 759).—I. In lipin nephrosis, for which the globulin–albumin ratio is not characteristic, there occurs a diminution of protein in the serum. The increase in globulin-lipins is not so marked as with the albumin-lipins.

II. In lipin nephrosis there is an increase in total unsaponifiable matter, cholesterol, and phospholipins of the serum, whilst the cholesterol : phospholipin ratio is decreased and the free cholesterol : cholesteryl ester ratio unchanged. The division of the various lipins between the globulin and albumin fractions is given.

III. Lecithin–sterol–protein complexes were prepared by repeated precipitation of the albumin–lipin fraction at p_H 3·7—3·8 in presence of moderate concentrations of $(NH_4)_2SO_4$. For normal sera they contain approx. 60% of protein and 40% of lipins. Little unsaponifiable material is found in the complex from horse serum, whilst human serum has a higher content. The complexes are sol. at alkaline reactions. No marked variation in the amount or type of complex occurs in lipin nephrosis. F. O. Howitt.

Physical properties of blood-serum in lipin nephrosis. C. Achard and A. Boutaric (Compt. rend., 1931, **192**, 1611—1615).—The ratio of the total vol. of particles comprising 1 g. of dry matter to the mean vol. of these particles is fairly const. in normal sera. If the serum is warmed for 1 hr. at rising temp. the luminous absorption increases, but the ratio remains const. until gelation sets in at 64°. In lipin nephrosis the ratio is 1·25 instead of 6; warming induces clarification, and the ratio increases. At 64° after 5 hr. the luminous absorption and the viscosity were increased, and the ratio became equal to that of normal sera. Coupled with other pathological conditions the physical data obtained were not markedly different from those obtained in normal sera.
C. C. N. Vass.

Case of animal ochronosis and experimental porphyria. G. Fink (Z. physiol. Chem., 1931, **197**, 193—205).—The colouring matter extracted from the bones of an ox with marked ochronosis coincided spectroscopically with uroporphyrin. The ultraviolet fluorescence of the teeth and bones of animals receiving daily injections (1 mg. dose) of various porphyrins varied widely with the nature of the porphyrin. *iso*Uroporphyrin was the most readily absorbed; deuteroporphyrin had no effect.
J. H. Birkinshaw.

Physiology of the parathyroid glands. II. Relation of serum-calcium to serum-phosphorus at different levels of parathyroid activity. F. Albright, W. Bauer, J. R. Cockrill, and R. Ellsworth (J. Clin. Invest., 1931, **9**, 659—677).—The product Ca×inorg. P is approx. const. In parathyroid dysfunction the body-fluids exhibit normal Ca phosphate but abnormal Ca : phosphate. At high Ca levels the fluids contain a large amount of Ca phosphate. Chemical Abstracts.

Blood constituents in acute rheumatism before and after salicylate treatment. E. M. Hickmans and S. H. Edgar (Arch. Dis. Childhood, 1930, **5**, 387—396).—The blood-urea, -non-protein-N, and -uric acid are high in acute rheumatism, and remain high during treatment with salicylate. The urea tends to become increased.
Chemical Abstracts.

Effect of phosphorus in rickets. I. Röntgenological changes in rickets following administration of phosphorus. II. Chemical changes. E. L. Compere (Amer. J. Dis. Children, 1930, **40**, 941—967, 1177—1192).—The effect of cod-liver oil is enhanced by a small amount of P; the serum-Ca and -P are markedly increased. The administration of P alone neither cures severe rickets nor affects the serum-Ca or -P. The healing of rickets is not associated with changes in the p_H of the blood-serum.

Chemical Abstracts.

Causes and origin of "incurable" forms of rickets and the amount of inorganic phosphorus in the serum of the afflicted animals. A. van Harreveld (Arch. Néerland. physiol., 1931, 16, 234—250).—Rats fed on a diet deficient in vitamin-*D* and also in other respects, viz., in P, vitamin-*B*, and in protein, develop severe rickets which is not cured by the administration of large doses of vitamin-*D*, even although the serum-P rises to a level equal to or exceeding the normal. When only one of the three defects is corrected, response to the administration of vitamin-*D* still fails to occur, but when two of the three defects are corrected, improvement is brought about by vitamin-*D* administration. When all three defects are corrected, marked healing occurs after administration of vitamin-*D*. Rat diets used in testing for vitamin-*D* should therefore not be deficient in any factor except vitamin-*D*. The conclusion of Hess *et al.* (A., 1930, 949) that rickets not curable by administration of vitamin-*D* is specifically produced by a diet deficient in P with a high Ca : P ratio is not supported. W. O. Kermack.

Metabolism studies in tetany. S. Morris, A. M. Watson, and N. Morris (Biochem. J., 1931, 25, 786—798).—The following metabolic changes occur after parathyroidectomy or injection of guanidine. There is a marked retention of Cl in the tissues. In the late tetany stage there is an increase of volatile Cl in both the blood and tissues, whilst in the active period there is almost complete absence of volatile Cl. The urinary output of N, amino-acids, and purine-N rises, whilst that of creatinine and NH_3 falls. The percentage retention of Ca decreases as a result of relative excess in the urinary excretion. There is a correlation between the excess of Ca and amino-acid excreted. The retention of P is either slightly diminished or unchanged. S. S. Zilva.

Adsorption in relation to some physiological phenomena. I. The physical problem. II. Meaning of the potentials determined at the surface of a tissue and at the surface of a wound by means of reversible electrodes. J. W. Langelaan (Arch. Néerland. physiol., 1931, 16, 145—159, 160—167).—I. A discussion of the relation between adsorption, electrokinetic potential, and thermodynamic potential with special reference to the theory of Stern (Z. Elektrochem., 1924, 30, 508) according to which the double layer in a liquid in the neighbourhood of a solid surface is partly unimol. and partly diffuse.

II. The general theory is applied to the interpretation of potential measurements made on the system muscle–tendon–lymphatic fluid.

W. O. Kermack.

Metabolism of tissues growing *in vitro*. IV. Effect of lævulose, galactose, and xylose on ammonia and urea production of embryo kidney tissue. E. Watchorn and B. E. Holmes (Biochem. J., 1931, 25, 843—848).—The addition of lævulose, galactose, and xylose tends to increase the growth of embryo kidney tissue, but whilst the first inhibits the production of NH_3 and urea (A., 1927, 479) by the growing cells, galactose does so only irregularly and xylose not at all. The added sugars were utilised by the tissue, the non-growing using less than the growing tissue. S. S. Zilva.

Factors limiting the growth of tissue cultures *in vitro*. B. Ephrussi (Compt. rend., 1931, 192, 1763—1765).—In fibroblastic tissues grown in a nutrient medium but washed free from stimulating substances, small initial cultures grow faster to attain the same development as larger initial cultures, which suggests that the arrest of growth is not due to metabolites but rather to the exhaustion of certain substances in the initial culture. The glutathione reaction is positive during growth, but diminishes as the rate of growth decreases and is absent at cessation of growth. Elimination of substances which can yield SH radicals is the cause of arrest of growth, whilst addition of such substances, *e.g.*, embryonic extract, to a culture in which growth has ceased can induce growth. C. C. N. Vass.

Fat metabolism in muscular work. C. P. Stewart, R. Gaddie, and D. M. Dunlop (Biochem. J., 1931, 25, 733—748).—In normal men performing muscular work the blood-fat usually rose after about 8000 kg. of work. With greater rates of work the rise appeared earlier. After recovery it appeared more easily on the performance of a second period of work. A high fasting blood-fat in normal or diabetic subjects led on the other hand to a preliminary fall when work was performed. An abnormally low blood-fat was increased by relatively small amounts of work. This alteration in the blood-fat was confined to the glyceride fraction. Continuance of work led to a return of the blood-fat towards normal and later to a second rise. The CO_2-combining power of the blood was roughly the reciprocal of the blood-fat, but these changes preceded those in the blood-fat. The R.Q. for exercise and recovery was unity for amounts of work up to about 6000 kg. and thereafter fell steadily with increasing amounts of work. Protein was not used for work. Carbohydrate continued to be used throughout, although in decreasing amounts. Fat was used in increasing amounts. There was no relationship between the utilisation of fat and the changes in the blood-fat concentration. There was no diminution in efficiency at the lower R.Q. and no conversion of fat into carbohydrate. Diabetic subjects showed no less efficiency and no wastage of O. S. S. Zilva.

Metabolic rate and respiratory quotients of rats following the ingestion of dextrin and during fasting. L. G. Wesson (J. Nutrition, 1931, 3, 503—518).—With rats a low basal rate of 718 kg.-cal. per sq. in. per 24 hr. was reached 13 hr. after feeding dextrin. R.Q. values are recorded.

Chemical Abstracts.

Passage of carbohydrate through the animal organism. II. F. Holtz (Biochem. Z., 1931, 235, 104—161).—The factors which vary and condition the blood-sugar curve are investigated (cf. A., 1930, 1312). The changes of sugar content of serum and corpuscles in man, dog, swan, goose, and goat do not always run parallel, but may be antagonistic. The serum-sugar content of 325 dogs in the morning of the third day of fasting was between 60 and 130 mg. per 100 c.c., and showed considerable variation for the same dog under the same conditions of life and food. The typical alimentary serum-sugar curve rises, falls below the initial val., and then slowly rises again to normal. A large number of curves show the influence of diet, acidosis, and alkalosis on the course of the blood-sugar vals. Carbohydrate causes increased secretion not only of insulin, but also of an antagonistic secretion designated glycæmin—possibly adrenaline. P. W. Clutterbuck.

Cyclic changes in the glycogen content of the liver and the muscles of rats and mice. Their bearing on the sensitivity of the animals to insulin and their influence on the urinary output of nitrogen. G. Ågren, O. Wilander, and E. Jorpes (Biochem. J., 1931, **25**, 777—785).—Glycogen accumulates in the liver of the rabbit, rat, and mouse during the night and disappears again to some extent during the next morning. This change is to a large extent independent of the intake of food. It occurs even in fasting animals. In the muscles the change is less marked. Mice show an increased resistance to insulin in the afternoon and particularly during the night. In rabbits the urinary N output is increased during the night. In fasting rabbits the excess of N thus eliminated is about 20% of the amount excreted during the day. S. S. Zilva.

Dietary deficiencies of milk. J. E. Becker and E. V. McCollum (Amer. J. Hyg., 1930, **12**, 503—510).—The best supplements (reproduction records) are ox liver, yeast, and a mixture of Fe^{III} citrate and $CuSO_4$. Chemical Abstracts.

Kidney metabolism. P. György and W. Keller (Biochem. Z., 1931, **235**, 86—96).—The phosphatase content of the cortex of pig's kidney measured in terms of hydrolysis of hexose-mono- and -di-phosphoric acids is many times as great as that of the medullary tissue. Whereas with the cortical tissue, the liberation of phosphate is about the same for both hexose-mono- and -di-phosphates, with the medullary tissue phosphate liberation is about twice as great with the di- as with the mono-phosphate. NH_3 formation is greater with the cortical than with the medullary tissue and is increased by addition of adenosinephosphoric acid, the increase, however, being greater with the medullary tissue. P. W. Clutterbuck.

Conjugation of benzoic acid in man. A. J. Quick (J. Biol. Chem., 1931, **92**, 65—85).—Ingestion of prunes is followed by fairly prolonged excretion of hippuric acid (cf. A., 1924, i, 121) due to presence of quinic acid. Benzoic acid appears to be the stimulus for the synthesis of glycine, a max. (0·55—0·70 g. per hr.) of which is formed when 15 g. of BzOH are ingested. Addition of glycine increases the rate of hippuric acid excretion until the kidney leak max. (1·42—1·82 g. per hr.) is reached. Administration of BzOH produces a decrease in uric acid excretion which returns to normal levels on glycine feeding. With large doses of BzOH a part (10—12%) is excreted conjugated with glycuronic acid. F. O. Howitt.

Legal's reaction and the excretion of conjugated glycuronic acid. A. Meyer and J. Jeannin (Bull. Soc. Chim. biol., 1931, **13**, 542—547).—The transitory red colour formed on addition of Na nitroprusside to urine at alkaline reactions is due to conjugated glycuronic acid. A positive response is obtained following administration of asparagus (which results in excretion of MeSH), camphor and its derivatives, menthol, salicylic acid, antipyrine, aspirin, hexatone, etc. F. O. Howitt.

Simple methods for metabolic balance studies and their interpretation. E. Donelson, B. Nims, H. A. Hunscher, C. F. Shukers, and I. G. Macy (J. Home Econ., 1931, **23**, 267—272).—The mean difference between the computed and experimental compositions of a diet was 2—5% (variations, N 0·7—38, Ca 0—22, P 0—38%). Chemical Abstracts.

Condition of water in a marine aquarium. W. R. G. Atkins (J. Marine Biol. Assoc., 1931, **17**, 479—481).—The use of CaO is preferable to that of $NaHCO_3$ for the control of the p_H of water in marine aquaria. The conclusions of Breder and Howley (Zoologica, 1930, **9**, 403—442) in this connexion are disputed. C. W. Gibby.

Physiological significance of some inorganic elements. E. V. McCollum and E. Orent (J. Maryland Acad. Sci., 1931, **2**, 33—36).—Mn is an indispensable nutrient element for mammals. Chemical Abstracts.

Biological function of zinc. D. Ganassini (Arch. Ist. Biochim. Ital., 1931, **3**, 131—138).—Basic Zn salts, or the hydroxide, act as catalysts in certain oxidation reactions *in vitro*. The evidence that Zn is an essential constituent of org. tissues and fluids is reviewed, and it is suggested that one of its functions is that of catalyst in oxidations. R. K. Callow.

Suffocation point in the horned lizard, *Phrynosoma cornutum*. G. E. Potter (Science, 1931, **73**, 314—315).—When confined in closed vessels these lizards survive until the O_2 content reaches 4—5·5% and that of CO_2 12—15%. When the CO_2 is continuously removed, they survive until the O_2 content reaches 4 or even 3·21%. L. S. Theobald.

Ether narcosis. [Determination of ether and regulation of dose.] G. Kärber (Arch. exp. Path. Pharm., 1931, **160**, 428—439).—Et_2O is determined by a modified CrO_3 oxidation method, the error being $\pm 3\%$ with 0·2—4·5 mg. Et_2O in 2 c.c. of blood or 20 c.c. of air. An apparatus is also described for supplying Et_2O–air mixtures of required concentrations. W. O. Kermack.

Action of ether on respiration. G. Kärber and L. Lendle (Arch. exp. Path. Pharm., 1931, **160**, 440—459).—The breathing by rabbits of Et_2O–air mixtures of const. concentration results first in a stimulation of the respiration, but when the concentration is such as to bring about the disappearance of the corneal reflex respirations cease almost simultaneously. No concentration of Et_2O could be found which would cause the breathing to continue steadily at a diminished rate. The paralysing effect of Et_2O on respiration is irreversible, and is probably due to secondary toxic effects. W. O. Kermack.

Elimination of ethyl iodide after inhalation and its relation to therapeutic administration.

H. L. Blumgart, D. R. Gilligan, and J. H. Swartz (J. Clin. Invest., 1931, 9, 635—650).—On inhalation of 1—3 c.c. EtI in air, 45% is exhaled immediately, 9% during the following 2 hr., and 31% by the kidneys as iodide. The percentage of EtI retained in the body is independent of the size of the dose.
Chemical Abstracts.

Occurrence of succinic acid in corpses and the detection of narcotics of the barbituric acid series in presence of succinic acid in toxicological cases. F. Weiss (Pharm. Zentr., 1931, 72, 433—436).—A discussion of published work on the occurrence of succinic acid in human remains. Barbituric acid derivatives may be separated from aq. solution which also contains succinic acid by neutralisation to Me-red with Na_2CO_3 followed by Et_2O extraction. The extract is evaporated, redissolved in H_2O, decolorised, and the barbituric acid extracted with Et_2O.
E. H. Sharples.

Biological assay of ergot preparations. II. Use of the paralysis of the renal vasomotors as an assay method. G. A. Wulp and E. E. Nelson (J. Pharm. Exp. Ther., 1931, 42, 143—154).—The method of Raymond-Hamet (Compt. rend., 1926, 182, 1045) is not recommended.
W. O. Kermack.

Increase of calcium content of blood-serum during strychnine poisoning. A. von Beznák (Arch. exp. Path. Pharm., 1931, 160, 397—400).—The rise in blood-Ca which occurs during the convulsions of strychnine poisoning is not diminished in dogs by parathyroidectomy or by cholecystectomy; the effect therefore is not due to stimulation of the parathyroids or of increased resorption of Ca from the gall-bladder. Intravenous administration of lactic acid to dogs produces no increase in blood-Ca, and thus the high blood-lactic acid resulting from the convulsions is not the cause of the increased blood-Ca. The additional Ca therefore probably comes from the muscles.
W. O. Kermack.

Effect of atropine on blood-sugar in man. D. Danielopolu, S. Stoicescu, and Cimino-Bérenger (Klin. Woch., 1931, 10, 311—313; Chem. Zentr., 1931, i, 2078).—Stimulant doses increase, whilst paralytic doses diminish, the blood-sugar.
A. A. Eldridge.

Effect of nicotine and the components of tobacco smoke on the blood-sugar. A. S. Salischtschev (Z. ges. exp. Med., 1930, 74, 14—19; Chem. Zentr., 1931, i, 2077).—Intravenous injection of nicotine (0·5 mg.) into rabbits caused hypoglycæmia (1·5—49·6%); with 1·0 mg. hyperglycæmia (7·7—51%) was followed by hypoglycæmia (2·5—10·9%). Tobacco smoke in toxic quantities leads in man to hypoglycæmia (18·3—61·7%). The changes are attributed to the action of nicotine on the sympathetic nervous system, whereby the production of adrenaline is increased.
A. A. Eldridge.

Adsorption. I. Adsorption of physiologically active substances by activated charcoal. F. Saunders, J. E. Lackner, and S. S. Schochet (J. Pharm. Exp. Ther., 1931, 42, 169—177).—Strychnine, brucine, adrenaline, histamine, and tyramine are quant. adsorbed or inactivated when aq. solutions of their salts are treated with activated charcoal for 20 min. In the case of acetylcholine and ephedrine inactivation is almost complete.
W. O. Kermack.

Contractile poisons and different types of frog's muscle. F. Petermann (Arch. exp. Path. Pharm., 1931, 160, 543—550).—The rectus abdominis muscle is the most sensitive to all poisons, followed by the gastrocnemius and the sartorius. The ratio of sensitivities to nicotine is 1,000,000 : 10,000 : 1 and for coniine 200 : 100 : 1. Caffeine and Nile-blue in small doses produce reversible histological changes in the muscle fibres. The sensitivity of *R. esculenta* to acetylcholine is greater than that of *R. temporaria*, although the sartorius muscle does not react in either even to high concentrations. *m*-Nitroaniline also produces a differential effect on the three types of muscle.
P. G. Marshall.

Effect of ephedrine on the blood-sugar and -lactic acid and on the plasma-fat. H. E. Himwich, H. Henstell, and J. Fazikas (Proc. Soc. Exp. Biol. Med., 1930, 28, 333—334; Chem. Zentr., 1931, i, 1779).—In the dog, injection of ephedrine (10 animals) caused a rise of blood-sugar in all cases, of -lactic acid in 5 cases, and of plasma-fat in 7 cases.
A. A. Eldridge.

Urinary phosphate following bile acid administration. K. Fuziwara (J. Biochem., Japan, 1931, 13, 43—56).—Subcutaneous injection of Na cholate into dogs increases the excretion of the secondary, and lowers that of the primary, phosphate, the net result being an increased phosphate excretion and a rise in p_H.
F. O. Howitt.

Behaviour of "germanin" *in vivo*. K. Lang (Arch. exp. Path. Pharm., 1931, 160, 560—568).—"Germanin" on acid hydrolysis, yields *m*-aminobenzoic acid, 3-amino-4-methylbenzoic acid, and α-naphthylamine-4 : 6 : 8-trisulphonic acid. The NH_2 compounds liberated by heating the serum with HCl are diazotised and coupled with α-naphthol and the resulting colour is compared with that obtained from the amines liberated from pure "germanin." The max. error of the method for serum is +7·5%. Shaking with kaolin does not affect the result. Germanin is not hydrolysed in the animal body and is only slowly excreted by the kidneys. It is not absorbed by the liver, whilst its concentration in the blood is affected by the mode of injection.
P. G. Marshall.

Toxicity of salvarsan. W. Milbradt (Arch. exp. Path. Pharm., 1931, 160, 489—526).—The toxicity of salvarsan is raised by alkaloids which paralyse the sympathetic, by bile salts and alkalis in high concentrations, by histamine-like substances, and by insulin and acetylcholine. In small doses salvarsan stimulates the sympathetic, whilst in larger doses it counteracts the rise of blood-sugar which follows the administration of a narcotic. The body itself detoxicates salvarsan, chemically by means of its Ca and dextrose metabolism, and mechanically by storage in the reticulo-endothelial system and elimination by the kidneys. Salvarsan poisoning can be cured by means of liver extract; its toxicity is increased where liver injury (phloridzin poisoning etc.) occurs.
P. G. Marshall.

Can the biological standardisation of arsenobenzene derivatives be replaced by a chemical method ? H. Bauer and M. Rothermundt (Z. Immunität., 1930, **69**, 213—220; Chem. Zentr., 1931, i, 1649).—Kielbasinski's "toxicity val." (*ibid.*, 1930, **69**, 346; A., 1930, 370) agrees with the results of biological (mouse) tests. When kept in contact with air, neosalvarsan solutions become more toxic.
A. A. Eldridge.

Influence of boron compounds on tissue respiration. B. Kisch (Biochem. Z., 1931, **235**, 35—44).—The respiration of isolated mammalian tissues (kidney, heart, liver of cat, rabbit, and guinea-pig) is inhibited by H_3BO_3 in concentrations of 10^{-5} (about $2 \times 10^{-4}M$) and is increased at concentrations of 10^{-7} to 10^{-9} (2×10^{-5} to $2 \times 10^{-7}M$). $Na_2B_4O_7$ has a similar but smaller action. The respiratory power of old tissues is better maintained in presence of traces of H_3BO_3. P. W. Clutterbuck.

Influence of aluminium salts on the respiration of isolated kidney tissue. B. Kisch and J. Leibowitsch (Biochem. Z., 1931, **235**, 45—50).—$AlCl_3$ and $Al_2(SO_4)_3$ added to normal Ringer's solution in concentrations of 10^{-5} ($10^{-4}M$) inhibit and of 10^{-7} to 10^{-9} (10^{-6} to $10^{-8}M$) increase respiration of isolated mammalian kidney tissue. The accelerating effect is obtained better in neutral and faintly acid than in alkaline solution. P. W. Clutterbuck.

Tissue respiration in calcium-free medium. B. Kisch (Biochem. Z., 1931, **235**, 51—65).—The action of $CaCl_2$ in increasing respiration is confirmed for old and fresh tissue, and a similar effect is obtained with certain tervalent cations ($AlCl_3$) and with H_3BO_3. $TlNO_3$ is inactive. High concentrations of $AlCl_3$ and H_3BO_3 which in normal Ringer's solution would inhibit respiration do not inhibit in Ca-free solution. Maximal increase of respiration is obtained with higher concentrations of these substances with Ca-containing than with Ca-free medium. "Omega" (the oxidation product of adrenaline) causes increased respiration in Ca-free Ringer's solution, but the action is not less than with normal Ringer's solution. Increased respiration is obtained in Ca-free solution with H_3BO_3 and $AlCl_3$ in concentrations of 1 in 10^{12}.
P. W. Clutterbuck.

Human absorption of magnesium with and without aspirin and other adjuvants. J. E. Winter and C. H. Richey (J. Pharm. Exp. Ther., 1931, **42**, 179—183).—The more efficient absorption of Mg from the alimentary tract brought about by the administration of aspirin, ginger, or alcohol together with MgO or $MgCl_2$ is probably to be correlated with the irritant action of these substances on the mucosa, resulting in an increased blood supply and also in the maintenance of an approx. normal level of gastric acidity. W. O. Kermack.

Effect of sodium thiosulphate on mercury poisoning. A. G. Young and F. H. L. Taylor (J. Pharm. Exp. Ther., 1931, **42**, 185—195).—In rabbits poisoned by $HgCl_2$, Hg succinimide, or Hg salicylate no beneficial results were produced by the administration of large and repeated doses of $Na_2S_2O_3$. In rabbits poisoned with K mercuri-tetraiodide a slight beneficial effect was noted. W. O. Kermack.

Calcification due to bismuth. C. Levaditi, A. Vaisman, R. Schoen, and Y. Manin (Compt. rend., 1931, **192**, 1768—1769).—Administration of toxic doses of fat- or H_2O-sol. Bi to the rabbit causes calcification of the kidney, and of the musculature at the site of injection. C. C. N. Vass.

Influence of orally administered iron on the animal organism. H. Mattis and E. Mandrysch (Arch. Pharm., 1931, **5**, 289—291).—Colloidal Fe on a substrate of liver protein, administered orally to rabbits during 12 weeks, causes an increase in the number of blood corpuscles, whilst Fe is deposited in the liver and kidneys; excess over the normal is found in the spleen, but none is present in the spinal cord.
A. A. Levi.

Toxicity of colloidal iodine. W. Nyiri and L. Dubois (J. Amer. Pharm. Assoc., 1931, **20**, 546—550).—Colloidal I (prepared by acidification at 0° of Na iodohypoiodite containing gum-acacia) has the same fatal dose as the U.S.P. tincture when administered intravenously, but the local corrosive action on the mucous membrane of the stomach is only about $\frac{1}{6}$—$\frac{1}{4}$ of that of the tincture. E. H. Sharples.

Iodine retention and distribution in rabbits. W. A. Peabody (J. Amer. Pharm. Assoc., 1931, **20**, 551—555).—Continued doses of KI or iodised fatty acid ester fed to rabbits showed greater retention after the org. form and a marked increase of I in most tissues and organs, but the latter effect bore no relationship to the form of administration.
E. H. Sharples.

Osmium tetroxide poisoning. F. R. Brunot (Analyst, 1931, **56**, 451).—Inhalation of fumes of OsO_4 in high concentration results in pneumonia and consequent death in animals. T. McLachlan.

Accumulation of strong electrolytes in living cells. S. C. Brooks (Science, 1931, **73**, 589—590).—Osterhout's hypothesis concerning the mechanism of selective accumulation of ions by living cells is criticised. L. S. Theobald.

Hæmatopoietic power of carotene. L. Binet and M. V. Strumze (Compt. rend., 1931, **192**, 1758—1760).—Oral administration of carotene to anæmic dogs markedly facilitates the production of hæmoglobin. C. C. N. Vass.

Effect of high altitudes on cholesterol, lecithin, and fatty acids in plasma of healthy men. G. L. Muller and J. H. Talbott (Arch. Int. Med. 1931, **47**, 855—860).—No significant changes were observed in the cholesterol, lecithin-P, fatty acids, and O_2 capacity of the blood of 4 healthy subjects at 10,000 and 14,000 ft. above sea-level. A. Cohen.

Comparative kinetics of the liquefaction and saccharification of starch. I. Soya-bean amylase. C. Artom and G. Orestano (Bull. Soc. Chim. biol., 1931, **13**, 516—541).—During the course of hydrolysis of 70% of the substrate the viscosity decreases in proportion to the square root of the reaction time, the relation between liquefaction and concentration of enzyme following the Schütz–Borissow law. The saccharification is a unimol. reaction, and is inversely and the liquefaction directly proportional to the concentration of substrate, the two reactions being expressed by $k_s=(c/Et)\log 75/(75-x)$ and $k_l=x/c\sqrt{Et}$, respectively, where x is the amount of substrate transformed at time t, E the quantity of enzyme, and c the concentration of substrate. F. O. Howitt.

Structure and enzyme reactions. IX. The systems amylase–starch–gelatin and urease–urea–gelatin. S. Freiberger (Biochem. J., 1931, 25, 705—712).—The velocity of reaction in the system amylase–0·6% starch–gelatin sol is unaffected below 9% gelatin, and appears to be little dependent on the viscosity of the medium. With 0·3% starch there is no retardation of reaction below 5% gelatin, whilst at higher concentrations of gelatin increasingly great retardation of reaction takes place. The velocity of the reaction between urease and urea is the same in the presence or absence of gelatin. The rate of diffusion of starch and amylase in gelatin jellies is considerably smaller than in similar sols. The velocity of reaction between amylase and starch in gelatin solution is little greater than in gelatin only.
S. S. Zilva.

Disaccharide fission by α-glucosidase. K. Myrbäck (Z. physiol. Chem., 1931, 198, 196—200).—The autolysis products of a strain of *B. coli* hydrolyse maltose strongly, but have no action on sucrose (cf. this vol., 654). This contradicts Weidenhagen's hypothesis (A., 1930, 499) and observation (this vol., 873). J. H. Birkinshaw.

Determination of enzymic processes by dilatometer. I. P. Rona and N. Neuenschwander-Lemmer (Biochem. Z., 1931, 235, 214—226).—During hydrolysis of sucrose both by enzymes and by acid, the decrease of vol. followed dilatometrically proceeds parallel with the polarimetrically determined decrease of sucrose. The vol. decrease in the enzymic hydrolysis of maltose is about half that of sucrose.
P. W. Clutterbuck.

Emulsin. L. Rosenthaler (Biochem. Z., 1931, 235, 227—232).—Racemisation of *d*-mandelonitrile proceeds slowly in 50% EtOH, more quickly in presence of emulsin. It occurs at the same rate with heated as with unheated emulsin, and the reaction is not enzymic. The conversion of *r*- into *l*-mandelonitrile by emulsin is an enzymic process.
P. W. Clutterbuck.

Effect of narcotics on some dehydrogenases. K. C. Sen (Biochem. J., 1931, 25, 849—857).—Ethylurethane, phenylurethane, diethyl- and phenylcarbamide, propionitrile, valeronitrile, and vanillin had no effect on xanthine oxidase or Schardinger enzyme in ordinary concentrations both as regards O_2 absorption and anaërobic reduction of methylene-blue. In the case of succinic dehydrogenase there was an inhibiting effect which increased with higher homologues of the same series. The degrees of inhibition of O_2 uptake and methylene-blue reduction agreed with each other in the majority of cases. Nitriles have no effect on methylene-blue reduction, although they inhibit O_2 uptake strongly. There is a competitive inhibition of hypoxanthine oxidation in presence of vanillin and piperonal. S. S. Zilva.

Kinetics of peroxidase action. P. J. G. Mann (Biochem. J., 1931, 918—930).—The temp. coeff. of peroxidase reaction is just below 2 at all H_2O_2 concentrations. The effect of variation of the concentrations of H_2O_2 and the reducing substrate (leucomalachite-green and guaiacol) on the velocity of peroxidase action suggests that both H_2O_2 and reducing substrate must be combined at the enzyme before catalysis can take place. S. S. Zilva.

Nature of tyrosinase. D. Narayanamurti and C. V. Ramaswami (Biochem. J., 1931, 25, 749—751).—*Dolichos* tyrosinase purified by ultrafiltration is more active than the dialysed preparation. The addition of cathode or anode cell liquid to the middle cell liquid of tyrosinase subjected to electro-osmosis and of ultrafiltrate to the enzyme causes slight inhibition. Tyrosinase does not lose its activity on repeated precipitation. S. S. Zilva.

Action of tannase on gallotannin. W. N. Nicholson, M. Nierenstein, J. C. Pool, and N. V. Price (Biochem. J., 1931, 25, 752—755).—*Aspergillus niger* produces in addition to tannase an enzyme (pyrogallase) which destroys gallic acid.
S. S. Zilva.

Synthesis of a hydrocarbon chain with help of enzymes. III. Distribution of carboligase in plants. A. Stepanov and A. Kusin (Ber., 1931, 64, [*B*], 1345—1349).—An enzyme is present in the green leaves of *Lactuca sativa*, which causes the formation of acetoin from pyruvic acid. The carboligase remains active in the rapidly dried leaves, whereas maceration affords only a feebly acidic extract. The absence of the enzyme from the internal leaves free from chlorophyll has led to the examination of plants of higher chlorophyll content. The leaves of *Urtica dioica* and *U. ureus* are appreciably more active, but dry preps. are difficult to secure by reason of the basic nature of the juice. The leaves of *Beta vulgaris* are extraordinarily active, and the activity persists after desiccation. Maceration of the dry leaves and subsequent addition of EtOH cooled to −20° to the extract yields a very active H_2O-sol. powder. The carboligase from yeast extract cannot be precipitated in a similar manner. Carboligase is also present in the leaves of *Rumex acetosa*, *Petroselinum sativum*, *Allium cepa*, *Prunus padus*, and in apples. H. Wren.

Action of dyes on enzymes. II. Fumarase. J. H. Quastel (Biochem. J., 1931, 25, 898—913).—Many acid and basic dyes are toxic to cell-free fumarase. There is a marked specificity in action and toxicity which is not associated with any simple grouping, but depends on the arrangement of the mol. as a whole. Methylene-blue and toluidine-blue which have little toxic action on brain-fumarase inhibit fumarase prepared from *B. coli* and *M. lysodeikticus*. The addition of dyes has no inhibiting action on the activity of the enzyme from blood. This is due to the presence of protein, which protects fumarase by combining with the dyes. A mixture of acid and of basic dyes forms a compound which is inert towards fumarase. A mixture of two acid or two basic dyes, on the other hand, is not less toxic than the more active of the two dyes present. Fumarate protects the enzyme from Congo-red or methyl-violet. The actual inhibition decreases as the amount of enzyme increases when a const. amount of dye is present. The combination of enzyme and dye is not easily reversible. Phosphates exert some protective action on the enzyme against toxic dyes.

S. S. ZILVA.

Enzymic hydrolysis of paired bile-acids. W. GRASSMANN and K. P. BASU (Z. physiol. Chem., 1931, **198**, 247—250).—Pancreatic, intestinal, and liver enzymes fail to hydrolyse tauro- and glyco-cholic acids, but kidney extract is active particularly with the latter acid, the optimum p_H being 8. *Aspergillus niger* extract and putrefactive organisms also attack glycocholic acid. J. H. BIRKINSHAW.

Influence of sodium taurocholate and copper sulphate on lipase. I. A. PARFENTJEV, W. C. DEVRIENT, and B. F. SOKOLOFF (J. Biol. Chem., 1931, **92**, 33—40).—The adrenal glands do not contain lipase. Neither Na taurocholate nor $CuSO_4$ has any influence on serum-lipase, whilst the former accelerates and the latter inhibits the actions of liver- and pancreas-lipase in concentrations as low as 1 : 500,000 of either substance. Some antagonism exists between the two salts in their action on liver- or pancreas-lipase. F. O. HOWITT.

Enzymic hydrolysis of lecithin. E. J. KING (Biochem. J., 1931, **25**, 799—811).—An enzyme "lecithinase" is described. The following is the relative activity of different tissues in decreasing order: kidney, small intestine, spleen, liver, testis, pancreas, large intestine, brain, ovary, bone, suprarenal, lung, blood vessels, cardiac muscle, skeletal muscle. The enzyme is fairly stable at neutral reaction, but is rapidly destroyed in acid or alkaline medium at 38°. Its optimal [H˙] is at about p_H 7·5, and it acts more rapidly at body temp. The addition of inorg. phosphate and choline and of glycerol to hydrolysing mixtures of lecithin and the enzyme does not affect appreciably either the rate or amount of hydrolysis. S. S. ZILVA.

Nitrogen distribution in the liver and serum of sensitised animals. H. HABS (Arch. exp. Path. Pharm., 1931, **160**, 527—534).—Subcutaneous injection of a foreign serum does not affect N-distribution in the liver. Sensitised guinea-pigs show no difference in protein-N content of the serum from that of normal animals, nor is there any difference between the non-protein-N of the serum of allergic and non-allergic individuals. P. G. MARSHALL.

Liver autolysis and treatment with serum of sensitised animals and allergic individuals. H. HABS (Arch. exp. Path. Pharm., 1931, **160**, 535—542).—The serum of sensitised guinea-pigs has no effect on the rate of autolysis of liver-pulp, whilst that of allergic individuals delays autolysis.

P. G. MARSHALL.

Northrop's crystalline pepsin. P. A. LEVENE and J. H. HELBERGER (Science, 1931, **73**, 494).—After 5 crystallisations, the material contains only 3·3% of total N as basic N. L. S. THEOBALD.

Specificity of animal proteases. XXIII. Zookinase. E. WALDSCHMIDT-LEITZ and A. PURR (Z. physiol. Chem., 1931, **198**, 260—266; cf. this vol., 520).—Zookinase is obtained in greater yield from partly autolysed organs. The isolation of the cryst. substance, which corresponds with reduced glutathione, is described. J. H. BIRKINSHAW.

Enzymic proteolysis. V. Structure of protamines. I. Protaminase and the products of its action on clupeine and salmine. E. WALDSCHMIDT-LEITZ, F. ZIEGLER, A. SCHÄFFNER, and L. WEIL (Z. physiol. Chem., 1931, **197**, 219—236; cf. A., 1928, 550).—Clupeine and salmine are purified by fractionation from conc. aq. solution. The oily ppt. has a N/NH_2 ratio of 104 (clupeine) and 340 (salmine), the smaller sol. fraction 35 and 32 respectively. A sp. protaminase from pancreas, which eliminates basic amino-acids from the carboxyl end of the substrate, removes $\frac{1}{5}$ of the total arginine from clupeine and $\frac{1}{4}$ from salmine. The residues, "clupean" and "salman," show the same high N/NH_2 ratios as the unchanged protamines, which therefore have no terminal NH_2 group, but a proline NH group.

J. H. BIRKINSHAW.

Polypeptide constitution and proteolytic enzymes. K. SUZUKI (J. Biochem., Japan, 1931, **13**, 57—80).—Erepsin but not papain, papain-HCN, pepsin, trypsin, or trypsin-kinase hydrolyses the tripeptides: glycylglycyl-*l*-asparagine (I), glycylglycyl-*l*-aspartic acid (II), glycyl-*dl*-asparagylglycine (III), and *dl*-asparagyldiglycine (IV), the peptides as given in this order exhibiting decreasing rates of hydrolysis. Thus lengthening of the chain of the glycylaspartic acid dipeptide does not result in a substrate acted on by trypsin. Balancing of the CO_2H group by an NH_2 group increases the rate of hydrolysis as shown by (I). *dl*-Asparagyldi-*l*-tyrosine is hydrolysed by trypsin-kinase, but not by pepsin, trypsin, papain, papain-HCN, or erepsin. This tripeptide has an optimum reaction for hydrolysis of approx. p_H 8·3. The proteinase and carboxypolypeptidase fractions of trypsin prepared by the Waldschmidt-Leitz adsorption method and activated by kinase effect a small hydrolysis in each case. The indispensability of kinase indicates, however, that the action is due to the proteinase and not to the carboxypolypeptidase. F. O. HOWITT.

Action of proteolytic enzymes on polypeptides. S. UTZINO (Z. physiol. Chem., 1931, **198**, 135—152).—The behaviour of various enzyme solutions was studied on the dipeptides *glycylsulphanilic acid* (I), darkens above 350° (from *chloroacetylsulphanilic acid*, blackens about 290°), glycyl-β-phenylalanine (II), *glycyl*-o-*aminobenzoic acid* (III), decomp. 235—236° (*chloroacetyl* derivative, m. p. 188—189°), -m-*aminobenzoic acid* (IV), decomp. 231—232° (*chloroacetyl* derivative, m. p. 230—231°), -*p*-aminobenzoic acid (V) and on the tripeptides diglycylanthranilic acid, *diglycylsulphanilic acid*, darkens above 300°, and *diglycyl*-o-*aminobenzoic acid*, m. p. 220—221° (decomp.) [*chloroacetylglycyl* derivative, m. p. 214—215° (decomp.)]. Glycylglycine and glycylphenylalanine were used as controls.

All the peptides were hydrolysed by kidney enzyme; intestinal and pancreatic enzyme were practically unable to hydrolyse II and III. Liver and spleen enzymes attacked II to a small extent, but not III. Enzymes of pig's liver and spleen, but not those of ox and dog's liver, hydrolysed I. Pig's, intestinal, and ox testes enzymes attacked only IV and V. III is attacked only by kidney enzyme, IV and V by all the enzymes employed. All the tripeptides were hydrolysed by all the enzyme solutions.

J. H. Birkinshaw.

Kinetic theory of the velocity of biochemical processes. J. V. Medvedev (Bull. Acad. Sci. U.S.S.R., 1931, 345—360).—A theoretical discussion of such points as Willstätter's results, indicating the possibility of the direct fermentation of polysaccharides without previous hydrolysis, and the disparity between the rates of fermentation by zymase and by living yeast.

T. H. Pope.

Fermentation and growth in dry yeast cells. III. C. Barthel, H. von Euler, and R. Nilsson (Z. physiol. Chem., 1931, **198**, 251—259; cf. A., 1929, 1199).—A prep. of dry yeast made by EtOH and Et_2O treatment from a sample showing no autofermentation (absence of reserve carbohydrate) contained no cells capable of reproduction, although the fermentative power was practically unchanged.

J. H. Birkinshaw.

Specific activators of enzymic carbohydrate fission. H. von Euler and R. Nilsson (Arkiv Kemi, Min., Geol., 1931, **10**, **B**, No. 14, 6 pp.).—Dried bottom yeast (washed with $0 \cdot 1N$-KH_2PO_4) in presence of dextrose, phosphate, Na hexosediphosphate, and co-enzyme ferments only on addition of 10^{-4} to $10^{-1}M$-$MgCl_2$. Such a yeast reduces methylene-blue, the reduction being accelerated on addition of Mg. The decrease in the amount of MeCHO disappearing and the simultaneous increase in CO_2-evolution when Mg is added to a yeast fermentation appear to be related to the antagonism of the metal to fluorides. Mg also stimulates phosphoric ester formation. The degradation of both hexose-mono- and -di-phosphoric acid is activated by muscle-adenylic acid, which, however, cannot replace the co-zymase with either dextrose or hexosediphosphate as substrate.

F. O. Howitt.

Co-zymase. XVIII. H. von Euler and K. Myrbäck (Z. physiol. Chem., 1931, **198**, 219—235; cf. A., 1930, 1318).—No separation of an adenylic acid fraction from highly active co-zymase was attainable with $Ba(OH)_2$. Uranyl acetate ppts. the whole of the active portion. The isolation from yeast of co-zymase of activity coeff. 100,000 in about 40% yield is described. The preps. have a composition closely related to those of the adenine nucleotides.

J. H. Birkinshaw.

Properties of highly purified co-zymase preparations. K. Myrbäck and H. von Euler (Z. physiol. Chem., 1931, **198**, 236—246).—The reaction consts. for elimination of H_3PO_4 in acid solution, inactivation at 100°, and elimination of adenine from co-zymase are 2, 120, and 50×10^{-3}, respectively. The co-enzyme thus falls in the inosic acid group: hence hydrolysis of the nucleotide or elimination of H_3PO_4 does not explain the inactivation. Changes in optical rotation were followed under various conditions.

J. H. Birkinshaw.

Reactivation of reductase in washed yeast preparations. A. Harden and M. G. Macfarlane (Biochem. J., 1931, **25**, 818—821).—The addition of lactate, succinate, or methylglyoxal restores the power of reducing methylene-blue to yeast preps. washed to a point at which no fermentation of hexosediphosphate occurs. Co-enzyme is probably not required for the action of the reductase in yeast preps.

S. S. Zilva.

Fermentation by yeast preparations. I. Effect of monoiodoacetate on the fermentation of hexosediphosphate. II. Action of arsenate on the induction period of zymin. M. G. Macfarlane (Biochem. J., 1931, **25**, 822—828).—The fermentation of hexosediphosphate by hexosephosphatase and arsenate (A., 1930, 1317) is inhibited by monoiodoacetate. The esterification of sugar by yeast-juice is inhibited by this compound in concentrations which only slightly inhibit that of glycogen. Arsenate does not accelerate the rate of fermentation by yeast-juice in presence of monoiodoacetate. The rate of liberation of inorg. phosphate during the induction period of zymin fermentation is not accelerated by arsenate.

S. S. Zilva.

Temperature-constant and -coefficient of the fermentation of press-juice and of maceration-juice. S. Kostytschev and G. Medvedev (Z. physiol. Chem., 1931, **197**, 213—218).—The temp. coeff. of fermentation by press-juice and maceration-juice increases rapidly as the temp. falls. This behaviour is similar to that of living yeast fermentation and is contrasted with the const. temp. coeff. shown by enzyme actions.

J. H. Birkinshaw.

Decomposition of malic acid by various *Saccharomyces* from fruit and grape wines. A. Osterwalder (Landw. Jahrb. Schweiz, 1930, **44**, 515—516; Chem. Zentr., 1931, i, 1983—1984).—Yeast reproduced after cessation of fermentation, with access of air and disappearance of alcohol, decomposes malic acid, but without formation of lactic acid.

A. A. Eldridge.

Enzyme formation in *Penicillium glaucum*. I.—III. S. Wada (Acta Schol. Med. Kioto, 1930, **13**, 128—144, 145—157, 158—161).—When the mould is grown on a protein- and carbohydrate-free medium (salts and glycerol) it contains deamidases, urease, a glucosamine-splitting enzyme, nuclease, pepsin- and trypsin-like enzymes, and erepsin. It does not show the relation between the nutrient medium and enzyme exhibited by bacteria. Lactase and glycolytic enzyme were absent. The culture liquid contains nuclease, pepsin, glycogenase, invertase, a glucosidase, a lipase, and a hippuric acid-splitting enzyme. When protein and carbohydrate are absent the pepsin, trypsin, and lipase content is greatly decreased.

Chemical Abstracts.

Production of gas and acid in the spontaneous fermentation of rye groats infusion. E. Beccard (Z. ges. Getreidew., 1930, **17**, 128—134, 150—153; Chem. Zentr., 1931, i, 2072).—H_2, N_2, CO_2, and volatile acids are formed in irregularly varying quantities.

A. A. Eldridge.

Bacterial chalk deposition in tropical seas. W. Bavendamm (Ber. deut. bot. Ges., 1931, **49**, 282—287).—In preference to the views that $CaCO_3$ is deposited by purely physico-chemical action, by the

action of bacterially produced CO_2 on CaC_2O_4 from higher plants, or by the interaction of bacterially produced $(NH_4)_2CO_3$ with $CaSO_4$, it is suggested that anaërobic bacteria reduce $CaSO_4$ to CaS, which reacts thus : $CaS+CO_2+H_2O=CaCO_3+H_2S$.
F. O. Howitt.

Nitrogen fixation and ammonia production by *Azotobacter*. S. Kostytschev and A. Scheloumov (Z. physiol. Chem., 1931, **198**, 105—114).—NH_3, the first detectable product of N fixation, is formed in presence of an excess of carbohydrate. *Azotobacter Winelandii* also produces NH_3 by dissimilation (probably deamination) of N compounds, but only in the absence of the N-free (*i.e.*, carbohydrate) material. Both types of NH_3 production are brought about only by living cultures. In an O_2-free atm. the *Azotobacter* cultures are not killed, but the N-fixation is strongly depressed.
J. H. Birkinshaw.

Respiration studies on *Azotobacter* under controlled conditions. J. M. Fife (Science, 1931, **73**, 533—534).—Measurements of the metabolic activity of *A. chroococcum* under different partial pressures of O_2 showed that the rate of respiration increased linearly to a const. value at 78% O_2 (cf. A., 1929, 473).
L. S. Theobald.

Nitrite formation by soil bacteria other than *Nitrosomonas*. D. W. Cutler and B. K. Mukerji (Proc. Roy. Soc., 1931, **B**, **108**, 384—394).—Four species of non-sporing soil bacteria differing widely from *Nitrosomonas* or *Nitrosococcus* were capable of oxidising NH_4 salts to nitrite, some being able to assimilate nitrites. Nitrite production was stimulated by aëration and by the presence of 0·1% of sucrose in the medium.
A. G. Pollard.

Occurrence of porphyrins in cultures of *C. diphtheriæ*. C. B. Coulter and F. M. Stone (J. Gen. Physiol., 1931, **14**, 583—596).—A new complex porphyrin with absorption max. at 574 and 537 mμ has been detected in liquid cultures of *C. diphtheriæ*. It contains Fe and Cu and coproporphyrin and shows an oxidation–reduction change. The amount present is proportional to the biological titre of the culture filtrate. It is suggested that both porphyrin and toxin are derived from the cytochrome of the bacilli.
R. K. Callow.

Immunological relationships among the pneumococci. VI. Anaphylaxis and precipitation between antigens and antisera of yeast and of type II pneumococci. J. Y. Sugg and J. M. Neill (J. Exp. Med., 1931, **53**, 527—534).
Chemical Abstracts.

Oxidation–reduction potentials of hæmolytic streptococci. II. Effect of catalase. L. F. Hewitt (Biochem. J., 1931, **25**, 858—862).—Catalase inhibits peroxide formation in cultures of hæmolytic streptococci. When catalase is added reducing conditions are maintained after the logarithmic phase of growth, and the high level corresponding with peroxide formation is not reached in aërated cultures. In cultures containing peroxide catalase causes an immediate and rapid fall in potential despite the resulting vigorous oxygenation of the culture.
S. S. Zilva.

Decomposition of hemicelluloses by *Bacillus gelaticus*, Gran. W. Bavendamm (Ber. deut. bot. Ges., 1931, **49**, 288—290).—The bacillus, isolated from marine mud-banks, hydrolyses starch and mannan, whilst agar is readily decomposed, serving as a source of energy in presence of nitrates.
F. O. Howitt.

Respiration of *B. coli communis*. R. P. Cook and J. B. S. Haldane (Biochem. J., 1931, **25**, 880—887 ; cf. this vol., 769).—The velocity of oxidition of dextrose, succinate, and lactate by *B. coli* at 16° does not reach a max. until more than 1 hr. has elapsed, owing to the gradual production of further metabolites. In the presence of formate the rate of O_2 uptake became const. after 30 min. as in the presence of PhMe. The effects of CO and HCN on these oxidations differ greatly.
S. S. Zilva.

Mechanism of the antiseptic action of lactic acid for *B. coli*. D. Bach (Compt. rend., 1931, **192**, 1680—1682).—Superimposed on the inhibitor factor due to p_H produced in the glucose–peptone medium there is the toxic factor due to the undissociated lactic acid mol.
C. C. N. Vass.

Action of acetone extracts of tubercle bacillus on pathogenic properties of the filtrate of the tubercle virus. L. Nègre and J. Valtis (Ann. Inst. Pasteur, 1931, **46**, 587—597).—Repeated subcutaneous injections of $COMe_2$ extracts of *B. tuberculosis* into guinea-pigs inoculated with a T. B. filtrate restore its virulence. Acetone extracts of *B. paratuberculosis* or olive oil are inactive. This technique has been successfully used for diagnostic purposes.
C. C. N. Vass.

Filtrates containing the filtrable element of the tubercle virus. C. Ninni (Ann. Inst. Pasteur, 1931, **46**, 598—603).—Young, rapidly grown cultures only yield filtrates of the ultravirus. The cultures are mixed with a min. quantity of saline and sterile sand, diluted with saline, and kept at 0° for 2 or 3 days before filtering first through paper and then through a candle.
C. C. N. Vass.

Action of pancreatic juice on tubercle bacilli. K. Vietorisz (Magyar Orvosi Arch., 1930, **31**, 546—560 ; Chem. Zentr., 1931, i, 1933—1934).—Destructive fermentation takes place.
A. A. Eldridge.

Detachment of bacteriophage from its carrier particles. D. M. Hetler and J. Bronfenbrenner (J. Gen. Physiol., 1931, **14**, 547—562).—Diffusion experiments show that phage in lytic broth filtrate is associated with particles of mean radius 4·4 mμ; particles of radius 0·6 to 11·5 mμ can be separated by ultrafiltration. Under certain conditions the active agent can be transformed from larger into smaller particles.
R. K. Callow.

Effects of ultra-violet light on *Paramecium*. L. B. Rentschler (Science, 1931, **73**, 480—481)—*Paramecium* gives a pale violet fluorescence when exposed to the light from a Hg-vapour lamp; the proteins of the cytoplasm are coagulated.
L. S. Theobald.

Electrosterilisation. I. II. Relative antibacterial effects of different electrodes. III. Single and multiple electrodes. L. I. Grossman and J. L. T. Appleton, jun. (Dental Cosmos, 1931, 73, 147—160, 250—253, 370—373).—Under the conditions tolerated, with oral bacteria, the antibacterial effect was greater at the anode; ZnI_2 was more efficient than KI. The effect depended on both the electrode and the electrolyte. The effect from a single electrode is greater than that of each member of a multiple electrode system. CHEMICAL ABSTRACTS.

Influence of soaps on the germicidal properties of certain mercurial compounds. B. HAMPIL (Amer. J. Hyg., 1931, **13**, 623—637).—The presence of Na oleate (1%) greatly increases the toxicity of $HgCl_2$ to virulent staphylococci at 37°; with other organisms different results were obtained. The toxicity of $Hg(CN)_2$ and *o*-chloromercuriphenol is increased by soap. A. A. ELDRIDGE.

Reality, nature, and localisation of "virtual" adrenaline. M. PAGET (J. Pharm. Chim., 1931, [viii], **13**, 617—626).—A modified colorimetric method (cf. A., 1929, 462) is described for determining adrenaline in suprarenal glands. The increase in adrenaline content observed when the glands are kept in a vac. over H_2SO_4 is confirmed by biological determinations. The nature of the "protoadrenaline" from which the "virtual" adrenaline is formed is undecided. Like the free adrenaline, it is concentrated in the medulla. R. K. CALLOW.

Preparation of adrenal extract. F. A. HARTMAN and K. A. BROWNELL (Science, 1931, **73**, 620).—Details are recorded. L. S. THEOBALD.

Cortico-adrenal hormone. S. W. BRITTON and H. SILVETTE (Science, 1931, **73**, 322—323).—Results obtained with cortico-adrenal extracts prepared by Swingle and Pfiffner's method and by Hartman's are discussed; they show that extracts prepared by the former method contain considerable amounts of the cortico-adrenal hormone, the presence of which is also indicated in some preps. made by the latter method. L. S. THEOBALD.

Influence of the adrenals on the residual nitrogen of the organism. G. WILL (Arch. exp. Path. Pharm., 1931, **160**, 317—328).—The residual N of the tissues of rabbits increases after adrenalectomy and after large doses of adrenaline, but this effect of adrenaline is exhibited only in presence of hormone produced by the adrenal cortex. Administration of uric acid causes a greater increase of residual N in adrenalectomised than in normal rabbits. W. O. KERMACK.

Blood-sugar response to intravenous insulin in normals and in diabetics. W. S. COLLENS and H. G. GRAYZEL (Proc. Soc. Exp. Biol. Med., 1931, **28**, 487—489).—Equiv. intravenous doses of insulin, on the basis of body-wt., produce a much greater fall in blood-sugar in diabetic than in normal man. CHEMICAL ABSTRACTS.

Distributions and concentrations of water and halides in the blood and urine during diuresis-inhibition by pituitary extract. A. R. MCINTYRE and H. B. VAN DYKE (J. Pharm. Exp. Ther., 1931, **42**, 155—168).—Administration of the extract of the posterior lobe of the pituitary to a dog so as to produce inhibition of diuresis causes a slight but definite increase in the water content of erythrocytes and serum and a slight fall in the concentration of halide, but has no effect on the distribution of Cl and Br between erythrocytes and serum. The extract produces no change on the serum-halide concentration of nephrectomised dogs. Posterior pituitary extract causes diuresis-inhibition in dogs probably solely through its direct action on the kidneys. W. O. KERMACK.

Inactivation by proteolytic enzymes of the anterior pituitary hormone from urine of pregnancy. M. REISS, A. SCHÄFFNER, and F. HAUROWITZ (Endokrinol., 1931, **8**, 22—24; Chem. Zentr., 1931, i, 2075).—The hormone is inactivated by activated trypsin, but not by pepsin at p_H 3—4, polypeptidase, or protamine-splitting enzymes. A. A. ELDRIDGE.

Diffusibility of female sex hormone into the spinal fluid and its relationship to the oxytocic activity of spinal fluid. R. W. WHITEHEAD and O. L. HUDDLESTON (J. Pharm. Exp. Ther., 1931, **42**, 197—211).—The intravenous injection of œstrus-producing preps. into dogs results in the appearance of the active principle in the cerebrospinal fluid. When certain preps. which had oxytocic activity were employed, the cerebrospinal fluid developed an oxytocic action, but this did not occur when highly purified preps., themselves devoid of oxytocic activity, were injected. W. O. KERMACK.

Antagonism between follicular and corpus luteum hormones. R. COURRIER (Compt. rend. Soc. Biol., 1930, **104**, 280—282; Chem. Zentr., 1931, i, 2075).—Large doses of folliculin repress the decidual reaction of the corpus luteum in guinea-pigs. A. A. ELDRIDGE.

Ovarian hormone. Biological assay. A. NOVELLI (Anal. Farm. Bioquím., Supl., 1931, **2**, 69—87).—A review. R. K. CALLOW.

Influence of vitamin-*D* and parathyroid hormone on calcium economy. F. HOFF and E. HOMANN (Z. ges. exp. Med., 1930, **74**, 258—273; Chem. Zentr., 1931, i, 1938).—After 50 injections of 50 units of parathyroid hormone the blood-Ca and -K increase, and the K : Ca quotient and the alkali reserve fall. Calcification of bone produced by vitamin-*D* is prevented by parathyroid hormone, but deposition of Ca in organs produced by excessive administration of vitamin-*D* is increased by simultaneous administration of parathyroid hormone. A. A. ELDRIDGE.

Effect of thyroxine on the blood-sodium chloride. E. COELHO and J. C. OLIVEIRO (Compt. rend. Soc. Biol., 1930, **105**, 801—802; Chem. Zentr., 1931, i, 2076).—The corpuscular, and sometimes the plasma-, Cl is diminished. A. A. ELDRIDGE.

Effect of injection of thyroxine on the urinary carbon and nitrogen. G. FONTÈS and L. THIVOLLE (Compt. rend. Soc. Biol., 1930, **105**, 558—559; Chem. Zentr., 1931, i, 1778).—Daily injection into dogs of 1 mg. of thyroxine increases the urinary C and N, but the ratio C : N remains unchanged. A. A. ELDRIDGE.

Effect of thyroidectomy and subsequent injection of thyroxine on the urinary carbon and nitrogen. G. FONTÈS and L. THIVOLLE (Compt. rend. Soc. Biol., 1930, **105**, 559—561; Chem. Zentr., 1931, i, 1778).—After thyroidectomy a transitory increase in both C and N is followed by an increase in N only; after injection of thyroxine (1—3 mg. daily) the excretion of C increases and the quotient C : N becomes normal, although the quantities excreted remain high. A. A. Eldridge.

[Carotene and] vitamin-*A*. P. Karrer, B. von Euler, H. von Euler, H. Hellström, and M. Rydbom (Arkiv Kemi, Min., Geol., 1931, **10**, **B**, No. 12, 6 pp.).—Ox-blood corpuscles are poor in carotene even when the serum is rich in the pigment. Human serum has a carotene content averaging 0·8 Lovibond unit per 10 c.c. following isolation and treatment with $SbCl_3$ in $CHCl_3$. The serum-carotene varies considerably in different animals; in herbivorous animals it is higher than in man or rat and it is higher in the summer than in the winter. Calves fed on milk poor in vitamin-*A* have a low serum-carotene value. Absorption spectra of serum indicate the presence only of carotene; the Lovibond units ($SbCl_3$ reaction), however, do not agree with direct colorimetric determination. Examination by spectrophotometry and by the $SbCl_3$ reaction shows that in fish oils a growth factor different from carotene is present. Carotene is provitamin-*A* and is considered to be reduced to the vitamin by a liver-carotenase. Carotene is absent from barley shoots, extracts of which and also of the sea-weed *Fucus vesiculosus* were investigated spectrophotometrically. F. O. Howitt.

Vitamin actions of carotene. H. von Euler and M. Rydbom (Arkiv Kemi, Min., Geol., 1931, **10**, **B**, No. 10, 6 pp.).—Carotene may be replaced by xanthophyll as a source of vitamin-*A* in chicks but not in rats owing to incomplete absorption by the latter. Injected intramuscularly, carotene dissolved in arachis oil results in less growth than when administered orally. Carotenoids occur in the eggs of the herring, perch, pike, cod, and to a smaller extent in pike spermatozoa where xanthophyll predominates. Fresh mature roe contains carotenoids equiv. to about 0·10 mg. of carotene per g. The gynæcium of the *Liliaceæ* and microspores of *Alnus glutinosa* are poor in carotenoids. F. O. Howitt.

Antimony trichloride colour test for vitamin-*A*. W. R. Brode and M. A. Magill (J. Biol. Chem., 1931, **92**, 87—98).—The normal $SbCl_3$ test (A., 1926, 870) for vitamin-*A* often produces a solution having two absorption bands, 578 mμ and 608 mμ, both of which fade and are replaced by bands at 472 and 532 mμ, there being a relation between the extinction coeff. of the two sets. By the use of a saturated (18·5%) $CHCl_3$ solution of $SbCl_3$ and of certain concentrations of cod-liver oil only the 608 mμ band is produced, the extinction coeff. of which is then proportional to the concentration of oil. F. O. Howitt.

Growth-promoting vitamin in liver-fat. P. Karrer, H. von Euler, and H. Hellström (Svensk Kem. Tidskr., 1931, **43**, 138).—An absorption band at 328 mμ occurs in the ultra-violet spectrum of shark oil in agreement with liver-oil (A., 1928, 1058; 1930, 380). Reduced forms of carotene, some of which possessed growth-promoting properties, previously exhibited no well-marked bands in the ultra-violet spectrum. Reduction of carotene by Al–Hg has now given a substance with characteristic lines at 315, 328—330, and 370 mμ, supporting the suggestion that the vitamin-*A* of animal oils is a hydrogenation product of carotene (cf. A., 1929, 1202). F. O. Howitt.

Vitamin-*A* in butter-fat. M. Lundborg (Biochem. Z., 1931, **235**, 1—13).—The colorimetric vals. ($SbCl_3$) for butter-fat give greater vals. for the carotene content than those obtained by direct colorimetric comparison with a solution of known carotene content. A known amount of added carotene can be determined in the hydrolysis residue by the colorimetric method, carotene being uninjured during hydrolysis of fat. During saponification a yellow colour is produced which makes it impossible to use direct colorimetric comparison except after addition of $SbCl_3$. P. W. Clutterbuck.

Occurrence of vitamin-*A* in cocoa and its extraction products. H. Labbé, H. de Balsac, and R. Lerat (Bull. Soc. Thér., 1930, 12 pp.; Chem. Zentr., 1931, i, 2079).—The results of tests with $AsCl_3$ and $SbCl_3$ are tabulated. Cacao butter contains a small quantity of vitamin-*A*. A. A. Eldridge.

Vitamin. XVIII. Biological assay of food materials for vitamin-*A* as influenced by yeast from various sources. H. E. Honeywell, R. A. Dutcher, and J. O. Ely (J. Nutrition, 1931, **3**, 491—498).—The vitamin-*A* response depends on the sample of yeast used as source of vitamin-*B*. Vitamin-*A* may consist of two factors, antiophthalmic and growth-stimulating. Chemical Abstracts.

Effect of vitamin-*B* deficiency on the vitamin-*A* reserves of the rat. W. J. Dann and T. Moore (Biochem. J., 1931, **25**, 914—917).—There is no material diminution in the vitamin-*A* reserves of the liver of albino rats, previously fed on diets containing large amounts of carotene, when severely emaciated as a result of a dietetic deficiency in the vitamin-*B* complex. S. S. Zilva.

Nutrition. X. Comparative vitamin-B_1 values of foodstuffs. Cereals. II. R. H. A. Plimmer, W. H. Raymond, and J. Lowndes (Biochem. J., 1931, **25**, 691—704).—The following are the comparative vitamin-*B* values obtained from the maintenance values for pigeons: dried yeast 100, marmite 67, wheat germ ("bemax") 62, middlings 40, baker's yeast 33, bran 20, buckwheat 20, millet 13, oatmeal 11, wheat 10, barley 10, malt 10, rye 10, dari 10, brown rice 10. S. S. Zilva.

Preparation and behaviour of vitamin-B_1 concentrates from yeast. B. C. Guha (Biochem. J., 1931, **25**, 931—944).—Preps. were obtained at the Pt stage (cf. A., 1929, 1496) which promoted good growth in rats in daily doses of 0·075—0·1 mg. The curative day dose for pigeons is about 0·047 mg. Vitamin-B_1 is not identical with co-zymase, secretin, or "bios," and the concentrates show no sp. absorption spectrum. Adenine, guanine, uracil, *dl*-thyroxine, histamine, and adrenaline cannot replace vitamin-B_1 in the diet of rats. S. S. Zilva.

Vitamin-B_2. I. Sources. II. Stability. III. Chemistry. B. C. Guha (Biochem. J., 1931, **25**, 945—959).—Milk powder, aq. extracts of brewer's yeast, baker's yeast, beef-muscle, Lilly's liver concentrate No. 343, and fresh ox-liver contain the vitamin. The last extract is the most potent. The stability of vitamin-B_2 depends on the source. An aq. extract of the liver concentrate autoclaved at p_H 9 for 30 min. at 124—125° is an excellent source of vitamin-B_2 free from vitamin-B_1. Picric acid, BzCl, phosphotungstic acid, and flavianic acid do not ppt. vitamin-B_2 from an aq. extract of liver. HNO_2 neither ppts. nor inactivates it. $Pb(OAc)_2$ and $AgNO_3$ ppt. it partly. Esterification inactivates it partly. It is not acted on by trypsin. Norite adsorbs it at p_H 4·6. It is not possible to elute it effectively by aq. EtOH, 30% PrOH, or saponin.

The vitamin is stable to SO_2, H_2O_2, and O_3. Rats not undergoing a drastic deprivation of vitamin-B_2 develop a form of depilation which is cured by the administration of the liver extract, but not by that of hæmin, hæmoglobin, or lactalbumin, which show no vitamin-B_2 activity. S. S. ZILVA.

Determination of vitamin-*C*. K. M. KEY and G. K. ELPHICK (Biochem. J., 1931, **25**, 888—897).—The method is based on the degree of protection afforded by the tested substance against the histological changes which take place in the teeth of young guinea-pigs subsisting on a scorbutic diet. The assessment is referred to a curve constructed from data obtained with different doses of orange-juice. S. S. ZILVA.

Fat-soluble vitamins. S. SCHMIDT-NIELSEN (Svensk Kem. Tidskr., 1931, **43**, 141—155; cf. A., 1930, 1222)—An examination of the following fishes: *Chimæra monstrosa*, *Somniosus microcephalus*, *Etmopterus spinax*, *Squalus acanthias*, *Cetorhinus maximus*, *Lamna cornubica*, *Raja fullonica*, *Raja oxyrhynchus*, *Gadus morrhua*, indicated that the vitamin-*D* content of the liver oils showed a relationship to the total Ca content of the fish. On the other hand, examination of the liver fat of various sea and land mammals (whales, oxen, pigs, etc.) showed no such corresponding relation, all these creatures having a very low content of vitamin-*D*. Liver oil from certain bony fish such as salmon, flounder, and tunny contains unusual amounts of vitamin-*D*; the last-named is especially rich in this constituent, and contains, in addition, the largest proportion of vitamin-*A* hitherto found. An explanation of the above irregular variations cannot as yet be given. H. F. HARWOOD.

Ultra-red absorption spectrum of ergosterol and of the antirachitic substance. W. HIRSCH and L. KELLNER (Biochem. Z., 1931, **235**, 162—169).—The ultra-red absorption spectrum of ergosterol has only one band at 3·71 μ, whilst that of irradiated ergosterol has two bands, one as above and a second, much fainter, at 0·976 μ. Irradiated ergosterol in this range has a greater absorption than ergosterol.

P. W. CLUTTERBUCK.

Toxicity of vitamin-*D*. J. B. DUGUID (Lancet, 1930, ii, 983—984).—A *résumé* of pathological effects in animals resulting from overdosage with vitamin-*D*.

L. S. THEOBALD.

Overdosage of vitamin-*D*. II. R. F. LIGHT, G. E. MILLER, and C. N. FREY (J. Biol. Chem., 1931, **92**, 47—51; cf. A., 1930, 119).—Moderate daily administration (40 units) of vitamin-*D* to rats has no influence on the calcification or ash content of the bones when continued through to the fourth generation. Such animals are, however, more susceptible to massive overdosage than normal animals. Overdosage (2500 units daily) just insufficient to produce toxic symptoms in the first and second generations produces pathological changes (decalcification of the bones, calcification of the kidneys, and certain pellagra-like symptoms) in the third and fourth generations.

F. O. HOWITT.

Increasing the vitamin-*D* potency of cow's milk by the daily feeding of irradiated yeast or irradiated ergosterol. B. H. THOMAS and F. L. MACLEOD (Science, 1931, **73**, 618—620).—Addition of irradiated yeast or irradiated ergosterol to the diet increased the vitamin-*D* potency of cow's milk up to 16 times. L. S. THEOBALD.

Rickets. IV. [Non-]formation of protective substance in germination of various seeds in the dark. P. GYÖRGY and H. SCHALL (Jahrb. Kinderheilk., 1929, **124**, 260—267; Chem. Zentr., 1931, i, 2079—2080).—Seeds germinated in the dark and ergosterol exposed to Gurwitsch radiation possessed no vitamin-*D* activity. A. A. ELDRIDGE.

Vitamin-*D* in whole maize. H. GOLDBLATT (Science, 1931, **73**, 494—495).—The unexpected non-production of rickets occurring with certain diets may be due to the settling out of $CaCO_3$ and a fall in ratio Ca : P below the necessary val. A method of avoiding this is described. L. S. THEOBALD.

Certain factors necessary for the normal nutrition of the rat. B. C. GUHA (Biochem. J., 1931, **25**, 960—971).—Yeast contains a factor other than vitamin-B_1 or -B_2, and milk contains a factor other than those present in yeast. The latter is not identical with vitamin-*A*, -*D*, -*C*, or -*E*. It is inactivated by autoclaving and is also present in egg-yolk, egg-white, spinach, grass, lucerne, and to a smaller extent in pig- and sheep-liver. It is not replaceable by carotene or chlorophyll. Milk and "light white casein" vary in their content of the factor. Male rats are more responsive than females. S. S. ZILVA.

Conditions of assimilation in tropical rain forests. O. STOCKER (Ber. deut. bot. Ges., 1931, **49**, 267—273).—A study of the respiration and assimilation of the leaves of 3 tropical trees (*Stelechocarpus burahol*, *Cassia fistula*, L., and *Calophyllum inophyllum*, L.) shows an extensive adaptation for high temps. There is a fall in the optimum of assimilation but no abs. increase in the amount of assimilation. The CO_2 content of the air in rain forests is slightly less than in temperate forests. F. O. HOWITT.

Glutathione, growth, and cancer of plants. L. BINET and J. MAGROU (Compt. rend., 1931, **192**, 1415—1416).—The growing tumour of a plant (*Pelargonium zonale*) inoculated with *B. tumefaciens* contains more glutathione than does the green stem, the flower bud, or the open flower. A still higher content is, however, found in the rapidly growing terminal bud, whilst that in the tumour disappears after necrosis, and consequently it is considered that the glutathione content is a function of the rapidity of growth. H. A. PIGGOTT.

Effects of X-rays on the growth of wheat seedlings. W. Cattell (Science, 1931, 73, 531—533).—Average results for hundreds of measurements are summarised graphically. The order of increasing effect is coleoptiles, leaves, primary roots, and lateral roots. Vitamin-B in the embryo is destroyed by excessive exposure to X-rays. L. S. Theobald.

Protein studies. X. Glutenin in different forms of wheat. XI. Gliadin in different forms of wheat. K. Kondo and T. Hayashi. **XII. Globulins of polished rice.** K. Kondo and T. Ito (Mem. Coll. Agric. Kyoto, 1931, No. 11, 1—19, 21—29, 31—35).—X. Glutenin from various sources was freed from globulin by stirring with $0 \cdot 5N$-NaCl solution (yields, 3·04—7·67 g. per kg. of flour; 17·30—17·66% N). The isoelectric points of different samples were identical in AcOH–acetate buffer (p_H 5·19—5·58) and in citric acid–phosphate buffer, although invariably more acid in the latter medium (p_H 4·57—4·98). Admixture of 10% of gliadin does not alter the isoelectric point.

XI. Gliadin was extracted from crude gluten by means of 70% EtOH. The amounts obtained from different sources were 5·42—17·94 g. per kg. of flour and its N content was 17·40—17·65%. The isoelectric point, determined by addition of phosphate or AcOH–acetate either to a 70% EtOH solution or to an alkaline solution of gliadin, is identical for different samples (p_H 6·41—6·59). The precipitation at the isoelectric point is greater in AcOH–acetate buffer (92·03%) than in phosphate buffer (80·76—81·75%).

XII. A cryst. globulin (p_H 3·98—4·61) was isolated from rice flour, which was poorer in diamino-acids than the non-cryst. globulin also obtained (p_H 3·89). P. G. Marshall.

Urea and ureides in the higher plants. I. Occurrence of urea in the vegetable kingdom and its transformation during the vegetative period. G. Klein and K. Tauböck [with H. Linser] (Jahrb. wiss. Bot., 1930, 73, 194—225; Chem. Zentr., 1931, i, 1298—1299).—The xanthhydrol reaction has been employed for the approx. determination of free or ureide-urea in plant organs and of its variation during the vegetative period. A. A. Eldridge.

Volatile nitrogenous bases in higher plants. M. Steiner (Beitr. Biol. Pflanzen, 1929, 17, 247—258; Chem. Zentr., 1931, i, 1298).—In general, leaves contain gaseous NH_3; the occurrence of NMe_3 in *Amorphophallis Rivieri* was followed as regards stage of growth and organs. Previous observation of the occurrence of $NHMe_2$ and NMe_3 in the fruit of *Phallus impudicus* was confirmed. Nicotine was detected by means of the reaction with dinitronaphthol in various organs of *Nicotiana rustica*. *Allium ursinum* contains no amine in the flowers or leaves. A. A. Eldridge.

Nitrogenous bases in the protein synthesis of higher plants. II. Distribution and transportation of ammonia and volatile amines. M. Steiner and H. Löffler (Jahrb. Wiss. Bot., 1929, 71, 463—532; Chem. Zentr., 1931, i, 1298).—NH_3 is liberated from the tissue preferably with 5% aq. Na_2CO_3 and 5% aq. NaCl; tests for various amines were critically examined. Numerous plants were tested histochemically. Amines, particularly NMe_3, *iso*amylamine, and *iso*butylamine, were found in 48 species. A. A. Eldridge.

Total nitrogen in Bartlett pear shoots. A. S. Mulay (Plant Physiol., 1931, 6, 333—338).—Individual shoots, whether from the same or different trees, vary considerably in N content, the variations being of the same order in both cases. Bark and wood from green shoots have less total N than those from brown shoots. A sample of 35—40 shoots is necessary to obtain results with an experimental error of ±5%. A. G. Pollard.

Volatilisation of nicotine from the tobacco plant. J. Chaze (Compt. rend., 1931, 192, 1268—1269).—Nicotine is identified by means of the cryst. ppt. deposited on passing air over the leaves into aq. silicotungstic acid. C. C. N. Vass.

F.-p. determination of physiological solutions. J. M. Johlin (J. Biol. Chem., 1931, 91, 551—557).—The f. p. of a small vol. of aq. solution is determined with a min. of supercooling by seeding with small metal rings cooled in solid CO_2 and covered with frost. R. K. Callow.

Acetate–veronal buffer. L. Michaelis (Biochem. Z., 1931, 234, 139—141).—The prep. of this buffer solution is described and a table indicates the p_H range 9·64—2·62. P. W. Clutterbuck.

Oxidimetric determination of small amounts of alcohol. L. Smith (Svensk Kem. Tidskr., 1931, 43, 83—98).—A modification of Widmark's micromethod for the determination of EtOH in blood (A., 1922, ii, 789). EtOH is absorbed in 2 c.c. of conc. H_2SO_4 in a stoppered flask maintained at 60° for 30—120 min. in a thermostat. 0·1 c.c. of $0 \cdot 1N$-$K_2Cr_2O_7$ is then added, and the flask replaced in the thermostat for 30 min. Water is added, followed by a slight excess of standard arsenite solution, and the excess of the latter is titrated with $KBrO_3$. The method has been employed to determine the concentration of EtOH in human breath. H. F. Harwood.

Colorimetric determination of potassium in small amounts of biological fluids. M. Dreguss (Biochem. Z., 1931, 233, 375—380).—The K in 0·05—0·1 c.c. of biological fluid is precipitated as K Na cobaltinitrite, the ppt. is dissolved by addition of Griess–Ilosvay reagent, and the colour of the solution is compared with that of a standard. The results deviate, on the average, about 2·5% from those obtained by the method of Kramer and Tisdall (A., 1921, ii, 412). W. McCartney.

Determination of copper in biological material. J. M. Inouye and F. B. Flinn (J. Lab. Clin. Med., 1930, 16, 49—51).—An electrolytic method is described. Chemical Abstracts.

Micro-determination of tungsten. L. Pincussen and B. Minz (Biochem. Z., 1931, 234, 19—24).—A colorimetric method is described for the determination of 0·1—10 mg. of W depending on the production of a blue colour on alkalising the tungstate after reduction with quinol in acid solution. The presence of P and Fe invalidates the method. In blood and tissues the method is not as sensitive, owing to difficulties in ashing, and only detects amounts of the order of 5 mg. P. W. Clutterbuck.